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(54) PRODUCTION OF CYANOGEN

(71) We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of cyanogen.

Cyanogen can be obtained by reacting hydrocyanic acid with nitrogen dioxide and water in the presence of a cupric salt (German Auslegeschrift 1,297,589). Although a satisfactory yield is obtained by this process, the cyanogen formed contains an equimolar quantity of nitrogen monoxide.

This gas mixture is difficult to handle on an industrial scale in so far as explosive mixtures can be formed and isolation of the pure cyanogen involves considerable technical outlay.

Cyanogen is formed by reacting hydrocyanic acid with gaseous oxygen in the presence of cupric salts and oxygen activators at pH values finely adjusted in the strongly acid range (German Patent Specification 1,163,302). This process is difficult to carry out on a large scale on account of the large excess of oxygen in relation to hydrocyanic acid which has to be subsequently separated off from the cyanogen, and on account of the very strict control of the pH value which is required. In addition, the cupric salt solution has to be heated to around 80°C. before the reaction in order to increase the velocity of the reaction.

In spite of this, the throughput of hydrocyanic acid is extremely low as demonstrated by Example 1 of German Patent Specification 1,163,302, and is not accelerated to any appreciable extent even by the addition of oxygen (carriers or activators).

In addition it has been found during comparison tests that where anthrahydroquinone is used as an oxygen activator, a special peak in the gas chromatogram appears, which does not appear where H_2O_2 is used instead of oxygen and anthraquinone, indicating a different reaction mechanism. The yield of cyanogen only amounts to 10 to 20% and hence is equivalent to the cyanogen yield obtained where oxygen alone is used. Neither does the addition of anthraquinone produce any change in the cyanogen yield.

Cyanogen is formed from hydrocyanic acid in the presence of cupric salts in accordance with the following equation:

$$\text{I)} \quad 2\ Cu^{2+} + 4HCN \rightarrow 2\ Cu\ CN + (CN)_2 + 4\ H^+$$

After the cupric ions have been consumed, this reaction comes to a standstill unless the cuprous cyanide formed can be oxidised quickly enough into cupric ions in accordance with the following equation:

[*Price 25p*]

$$\text{II)} \quad 2\ CuCN + 4\ HCl + O \xrightarrow{-2\ \ominus} 2\ Cu^{2+}Cl_2 + 2\ HCN + H_2O$$

The cupric chloride hydrate used as catalyst in Example 1 of German Patent Specification 1,163,302 has to be employed in a quantity 4.75 times greater than that required in accordance with equation I in order to convert the hydrocyanic acid into cyanogen over a period of 1 hour. This factor illustrates the difficulties that are involved in reoxidising the cuprous ion by the process disclosed in the aforementioned German Patent Specification.

The present invention provides a process for the production of cyanogen by the catalytic oxidation of hydrogen cyanide with hydrogen peroxide in the presence of cupric bromide, cupric chloride, cupric cyanide, cupric nitrate or cupric sulphate. Preferably reoxidation of cuprous ions formed during the reaction into cupric ions, which determines the throughput rate of the entire process is accelerated by the presence of ferric ions in the reaction mixture. It has also been found that any tendency which the hydrogen peroxide has to uncontrolled decomposition may be inhibited by the presence of certain organic solvents.

It is surprising that the relatively rapid decomposition of hydrogen peroxide into water and oxygen in the presence of cupric and ferric ions may be almost completely avoided and that the oxidation potential of the hydrogen peroxide can be utilised in favour of the reoxidation of the cuprous ions into cupric ions required in accordance with equation II, optionally through the coupled reaction of the ferrous ions into ferric ions in accordance with equation III:

$$\text{III)} \quad \text{a)} \quad Cu^{+} + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+}$$

$$\text{b)} \quad 2\ Fe^{2+} + 2\ H^{+} + O \longrightarrow Fe^{3+} + H_2O$$

This reaction is promoted by the addition of organic solvents. The addition of water-miscible solvents has a favourable effect upon the reaction of the hydrogen peroxide above all at temperatures in excess of 20°C. because it inhibits for example decomposition into water and molecular oxygen. Water-immiscible organic solvents have a similar effect. It is possible by using these solvents to react hydrogen peroxide which is present in organic solvents in the aqueous catalyst solution and thereafter to remove the solvent without any need for further dilution with water.

The presence of ferric salts in a purely aqueous reaction solution accelerates reoxidation of the cuprous ions into cupric ions in accordance with equations III a) and III b) to such an extent that in this case, too, the hydrogen peroxide cannot decompose into water and molecular oxygen. If the reaction in the organic solvent is carried out with ferric and cupric ions, the best result is obtained with these optimal reaction conditions. Under these conditions, the reaction of the hydrocyanic acid with hydrogen peroxide is so fast that the throughput rate of the hydrocyanic acid is determined solely by the rate at which the heat of reaction can be dissipated. In other words, the more quickly the heat of reaction is dissipated, the greater the throughput of hydrocyanic acid can be.

The hydrogen cyanide may be used in gaseous or liquid form. It is also possible to use aqueous solutions which generally contain at least 5% by weight of hydrocyanic acid, and also spent acid.

The cupric salts used in accordance with the invention and the corresponding ferric salts are preferably present in the reaction mixture in concentrations of up to 20% by weight (total quantity of both salts), the cupric and ferric ions preferably being present in equivalent quantities. The preferred total quantity of salts, amounts to about 10% by weight. The cupric and ferric salts can be used in the form of commercial-grade salts.

The reaction is generally carried out at a temperature of from 0 to 100°C. and preferably at a temperature of from 15 to 50°C. The pressure level can be varied as desired. Thus, the reaction can be carried out at normal pressure, at slightly reduced pressure or at a slight excess pressure. Naturally the reduced pressure should not be so low that the boiling point of the hydrocyanic acid is exceeded. A pressure of 1 to 5 atms. absolute is preferred.

Hydrogen peroxide may be used in the form of 3 to 90% by weight, preferably 15 to 50% by weight aqueous solutions. It is also possible to use solutions of hydrogen peroxide in organic solvents of the kind formed in accordance with our co-pending Applications Nos. 43515/69 (Serial No. 1,279,302) and 47583/70 (Serial No. 1,320,200).

Hydrocyanic acid and hydrogen peroxide (100%) are generally reacted together in equivalent quantities.

Suitable water-miscible or water-immiscible solvents include particularly alkyl esters of low molecular weight fatty acids, such as alkyl acetates. Ethyl acetate or *n*-propyl acetate is particularly suitable. Saturated alkyl or alkylene sulphones, especially tetramethylene sulphone, are also eminently suitable. The organic solvents can be present in the reaction mixture in a quantity of up to 80% by weight and preferably in a quantity of from 30 to 50% by weight.

The reactants and the salt solutions may be mixed for example in a drum mixer or a screw mixer. In cases where organic hydrogen peroxide solutions are used, it is of particular advantage to introduce the hydrogen peroxide solution into a mixture of hydrocyanic acid and aqueous salt solutions.

Ferric chloride may be used as the ferric salt for reoxidising the cuprous ions formed. This is of particular advantage when oxidation of the hydrogen cyanide is carried out in the presence of cupric chloride.

Cupric sulphate is particularly suitable for use as the catalytically active copper salt, above all for carrying out the reaction in a continuous cycle. In addition, it is of particular advantage to use ferric sulphate as the source of ferric ions. Ferric sulphate is preferably used in combination with cupric sulphate. Ferric sulphate can also be formed *in situ* during the reaction from ferrous sulphate and hydrogen peroxide. Accordingly, there is no need for the ferric sulphate to be present as such from the outset during the reaction, instead it is sufficient to add ferrous sulphate.

If it is desired to recover the cupric and ferric ions, they can be recovered following removal of the cyanogen from the reaction mixture by precipitation with alkali metal or alkaline-earth metal carbonates in the form of basic copper or iron corbonates. Calcium carbonate is particularly suitable for precipitation. In the case when the sulphates are used the carbonates are then converted back with sulphuric acid into the corresponding cupric and ferric sulphates and re-added to the catalyst solutions to be used.

It is also possible, however, to distil off the water introduced with the hydrogen peroxide and the water of reaction from the recycled catalyst solution and hence to restore the concentration of the catalyst solution to its original level.

The technical advantage of the process according to the invention is embodied in the production in high yields of a substantially pure cyanogen which is free from oxygen and nitrogen dioxide. In addition, the volume/time yield is considerably increased and, depending upon the rate at which the heat of reaction is dissipated, is between 10 and 100 times greater than the volume/time yields hitherto obtained by the direct oxidation of hydrocyanic acid in the presence of cupric salts.

The invention is illustrated by the following Examples.

EXAMPLE 1.

11.2 g of $CuBr_2$ are dissolved in 50 ml of tetramethylene sulphone in a 250 ml-capacity spherical flask equipped with stirring mechanism, thermometer, reflux condenser and inlet tube (dipping beneath the surface of the solution), and a mixture of 10.8 g of liquid hydrocyanic acid and 43 ml of an aqueous hydrogen peroxide solution (15%) added dropwise over a period of 50 minutes. The heat of reaction is dissipated by cooling with ice water and vigorous stirring, and the temperature kept at 23°C. Cyanogen is obtained in a yield of approximately 80% of the theoretical, based on the hydrogen peroxide used, by condensing the gas formed. According to analysis by gas chromatography, the cyanogen contains only traces of oxygen, hydrocyanic acid and water.

EXAMPLE 2

11.2 g of $CuBr_2$ and 14.8 g of $FeBr_3$ are dissolved in 50 ml of water in an apparatus of the kind described in Example 1, and the resulting solution cooled with ice water while stirring vigorously. A mixture of 16.2 g of liquid hydrocyanic acid and 64.5 ml of 15% aqueous hydrogen peroxide is added dropwise over a period of 60 minutes and the temperature kept between 10 and 14°C. The gas formed contains between 85 and 90% of the theoretical of cyanogen, based on the hydrogen peroxide, and according to analysis by gas chromatography contains only traces of oxygen, hydrocyanic acid and water.

EXAMPLE 3

11.2 g of $CuBr_2$ and 40.8 g of $FeBr_3$ in 50 ml of tetramethylene sulphone are cooled with ice water in the apparatus described in Example 1. A mixture of 27 g of liquid hydrocyanic acid and 107.5 ml of 15% aqueous hydrogen peroxide is added dropwise over a period of 75 minutes and the temperature kept between 10 and 14°C. The gas formed is condensed and 26.4 g of a condensate which, according to analysis by gas chromatography, contains 95% of pure cyanogen, is obtained. For confirmation, the condensate is heated to 0°C. and the corresponding gas investigated once again by gas chromatography. It is pure cyanogen in a quantity of 23.2 g, i.e. 89.2% of the theoretical, based on hydrogen peroxide. The residue of 3.2 g consists only of hydrocyanic acid and water

After the reaction solution is left standing for two days, 2.5 g of oxamide is isolated which can be converted into gaseous cyanogen by heating the solution. The total yield then amounts to 95.4% of the theoretical, based on hydrogen peroxide.

If the above mentioned yield of 89.2% of the theoretical is expressed at 1 kg of cyanogen, obtained per hour, a reaction volume of 8.5 litres is required for this quantity, in other words the volume/time yield amounts to 8.5 $l/kg.h^{-1}$. This volume/time yield can be increased several times by using concentrated hydrogen peroxide solutions.

EXAMPLE 4

Figure 1 of the accompanying drawings shows a continuously operating industrial apparatus. In this apparatus a solution of 1.74 kg of cupric bromide and 2.3 kg of ferric bromide in 20.0 kg of water is initially delivered through pipe 1*c* into reactor 1 and thereafter cycled from the reactor 1 which is equipped with heat exchanger 1*d* and stirring mechanism 1*e*, in the direction of distillation retorts 2 and 2 and back into the reactor 1 by means of a pump 7. Equivalent quantities of hydrocyanic acid and hydrogen peroxide (2 moles of $HCN + 1$ mol of H_2O_2) are continuously introduced into the reaction solution in reactor 1 through the pipes 1*a* and 1*b*. The cyanogen gas formed is removed for further use from the head of the reactor 1 through pipe 1*f* and a condenser 1*g* which is intended to condense any hydrocyanic acid vapours entrained, and pipe 1*h*.

In order to continuously separate off the water introduced with the hydrogen peroxide solution and the water formed by the reaction, the reaction solution is delivered through pipe 1*i* into the distillation retort 2 (de-alcoholisation) in which it is freed from dissolved cyanogen gas and unreacted residues of hydrocyanic acid (waste gas delivered through pipe 1*l* into the reactor 1), regenerated in the distillation retort 3 (water distillation) and returned through pipes 1*m* and 1*l* to the reactor 1. The water distilled off from the distillation retort 3 is delivered through pipe 1n, heat exchanger 3*a* and the pipe 1*o* into water receiver 4 where it is separated off. 13.42 Kg of hydrocyanic acid and 24.00 kg of 35% by weight aqueous hydrogen peroxide solution are reacted in this apparatus over a period of 9 hours at a reaction temperature of 35°C. (kept constant by a cooling coil 1*d* in the reactor 1) and under a pressure of 0.03 atms. gauge. The yield comprises 5950 l or 12.62 kg of crude cyanogen gas which, according to analysis by gas chromatography, has the following composition:

98.08% cyanogen
0.20% nitrogen
1.10% oxygen.

The yield corresponds to 97.6% of the theoretical.

If desired, the reaction mixture can be kept circulating through pipe 1*i*, heat exchanger 6 and pipe 1*p* by means of pump 7 in order to keep the temperature constant.

The references 5*a* to 5*p* denote valves in the system, valves 5*c* to 5*k* being part of the exhaust-gas section of the apparatus and being intended for equalising pressure.

EXAMPLE 5

Using the industrial apparatus described in Example 4, 8.50 kg of hydrocyanic acid and 15.92 kg of 35% by weight aqueous hydrogen peroxide solution, are reacted over a period of 6 hours as described in Example 4 in a solution of 1.74 kg of cupric bromide and 2.30 kg of ferric bromide in 15.00 kg of water and 6.00 kg of tetramethylene sulphone. The reaction temperature is kept at 35°C. Under a slight excess pressure of 0.03 atms. gauge, cyanogen gas (containing 98.5% of cyanogen) is obtained in a quantity of 3770 litres of 8.20 kg. The yield comprises 98.0% of the theoretical.

EXAMPLE 6

17.1 g of $CuCl_2 \cdot 2H_2O$ (0.1 mole) and 27.0 g of $FeCl_3 \cdot 6H_2O$ (0.1 mole) are dissolved in 100 g of water in a 250 cc capacity spherical flask equipped with stirring mechanism, thermometer, reflux condenser and inlet pipe (dipping beneath the surface of the solution), followed by the addition over a period of 60 minutes at 30°C. of 16.2 g (0.6 mol) of hydrocyanic acid and 10.2 cc of 30% hydrogen peroxide solution (0.3 mol).

The gas formed is analysed by gas chromatography and is found to have a constant content of 55% of cyanogen and approximately 15% of cyanogen chloride. Oxygen and hydrocyanic acid can also be detected as residual gases.

EXAMPLE 7

17.1 g of $CuCl_2 \cdot 2H_2O$ (0.1 mol) and 27.0 g of $FeCl_3 \cdot 6H_2O$ (0.1 mol) are dissolved in 100 g of tetramethylene sulphone in the apparatus described in Example 6, followed by the addition with stirring over a period of 60 minutes at 45°C of 16.2 g (0.6 mol) of hydrocyanic acid and 10.2 cc of 30% (0.3 mols) of hydrogen peroxide solution.

The gas formed is analysed by gas chromatography and is found to have a constant content of 62% of cyanogen and approximately 5% of cyanogen chloride. The residual gas consists of oxygen and hydrocyanic acid.

EXAMPLE 8

25 g of $CuSo_4 \cdot 5H_2O$ (0.1 mol) and 20 g $Fe_2(SO_4)_3$ (0.05 mol) are dissolved in 50 g of H_2O in a 250 ml. spherical flask equipped with stirring mechanism, thermometer, reflux condenser and inlet tube dipping beneath the surface of the solution, followed by the addition with stirring over a period of 100 minutes of 27 g of hydrocyanic acid and the equivalent quantity of 30% hydrogen peroxide solution (50 ml.=17.0 g 100%). The temperature is kept at 45 to 60°C accompanied by the evolution of gas. The gas investigated by gas chromatography contained 97% of pure dicyanogen.

EXAMPLE 9

A solution of 0.75 kg of copper sulphate and 0.60 kg of iron-(III) sulphate in 30 kg water is delivered through pipe 1c into the reactor 1 of the continuous-cycle apparatus shown in Fig. 2. The solution is circulated by means of the pump 3 through the heat exchanger 1d and the pipe 1a to obtain rapid intermixing. Equimolar quantities of hydrogen peroxide and hydrocyanic acid (1 mol of H_2O_2+2 mols HCN) are introduced into the reaction solution through the pipes 1a and 1b. The dicyanogen gas formed is removed for further use from the head of the reactor 1 through the pipe 1f. In order continuously to separate the water introduced with the hydrogen peroxide solution and the water formed during the reaction, the reaction solution is delivered through the pipe 1i into the distillation column 2 in which it is freed from dissolved dicyanogen gas and unreacted residues of hydrocyanic acid (waste gas off through pipe 1g) and reconcentrated by distilling off water. The solution then flows back to the reactor 1 through the pipe 1k. In the event of prolonged operation, the limited hydrolysis of the hydrocyanic acid by oxidation into CO_2 and ammonia is reflected in the consumption of acid. Accordingly, a quantity of acid equivavalent to that consumed has to be periodically added to the catalyst solution.

In this apparatus, 1.4 kg/hour of hydrocyanic acid and 2.26 kg/hour of 35% by weight aqueous hydrogen peroxide solution were continuously reacted over a period of 400 hours at a reaction temperature of 22 to 25°C to give 1.325 kg/hour of dicyanogen gas, a yield which corresponds to 98.0% of the theoretical, based on hydrocyanic acid. The dicyanogen gas still contains 0.2% of CO_2 and 1.8% of oxygen.

EXAMPLE 10

A continuous apparatus is shown in Figure 3 in which the function of reactor 1 and the corresponding lines are the same as described in Example 9. The reaction solution is in this case subjected to continuous reaction with hydrogen peroxide and the water produced during the reaction is passed by way of line 1(i) to distillation column 2 where it is freed from dissolved cyanogen and unreacted hydrocyanic acid. This gas is removed through line 1(g) and returned to the reactor 1. Spent catalyst then passed by way of line 1(k) to a vessel 4, where it is mixed hot with a corresponding quantity of $CaCO_3$. In this way the copper and iron ions are precipitated as basic carbonates and the sulphate ions are precipitated as $CaSO_4$. The precipitated material is removed through line 1(l), water is removed in centrifuge 5 and then the precipitate is passed by way of line 1(m) to a vessel 6. In vessel 6 the basic carbonates are dissolved with the corresponding quantity of dilute sulphuric acid and passed by way of line 1(n) to centrifuge 5 where the $CaSO_4$ is separated. The solution of copper and iron sulphates is passed by way of line 1(h) back into reactor 1. The products produced by this process correspond in properties to those of Example 9.

WHAT WE CLAIM IS:—

1. A process for the production of cyanogen, by the catalytic oxidation of hydrogen cyanide with hydrogen peroxide in the presence of cupric bromide, cupric chloride, cupric cyanide, cupric nitrate or cupric sulphate.

2. A process for the production of cyanogen by the catalytic oxidation of hydrogen cyanide with hydrogen peroxide in the presence of cupric bromide, cupric cyanide or cupric nitrate.

3. A process as claimed in claim 2 wherein reoxidation of cuprous ions formed during the reaction is accelerated by the presence of ferric ions.

4. A process as claimed in claim 2 or 3 wherein uncontrolled decomposition of the hydrogen peroxide is inhibited by the presence of an organic solvent.

5. A process as claimed in claim 4 wherein the organic solvent is tetramethylenesulphone.

6. A process as claimed in any of claims 2 to 5 wherein the hydrogen cyanide is used in gaseous form, in liquid form or in the form of an aqueous solution.

7. A process as claimed in any of claims 2 to 6 wherein the hydrogen peroxide is used in the form of a 15 to 50% by weight aqueous solution.

8. A process as claimed in any of claims 2 to 7 wherein the reaction is carried out at a temperature of from 15 to 50°C.

9. A process as claimed in any of claims 2 to 8 wherein the reaction is carried out at a pressure of from 1 to 5 atms. absolute.

10. A modification of the process claimed in any of claims 2 to 9 wherein catalytic oxidation is carried out in the presence of cupric chloride in place of the cupric bromide, cupric cyanide or cupric nitrate.

11. A process as claimed in Claim 10 wherein reoxidation of cuprous ions formed during the reaction is accelerated by the presence of ferric chloride.

12. A process as claimed in any of claims 2 to 9 wherein reoxidation of cuprous ions formed during the reaction is accelerated by the presence of ferric chloride.

13. A process for the production of cyanogen by the catalytic oxidation of hydrogen cyanide with hydrogen peroxide in the presence of cupric sulphate.

14. A modification of the process claimed in any of claims 2 to 9 wherein catalytic oxidation is carried out in the presence of cupric sulphate in place of the cupric bromide, cupric cyanide or cupric nitrate.

15. A process as claimed in Claim 14 wherein reoxidation of cuprous ions formed during the reaction is accelerated by the presence of ferric sulphate.

16. A process as claimed in any of claims 2 to 9 wherein reoxidation of cuprous ions formed during the reaction is accelerated by the presence of ferric sulphate.

17. A process as claimed in claim 15 or 16 wherein the ferric sulphate is formed *in situ* during the reaction from hydrogen peroxide and ferrous sulphate.

18. A process as claimed in any of Claims 3 to 9, 11, 12 and 15 to 17 wherein cupric and ferric ions are recovered from the reaction solution freed from cyanogen by precipitation with an alkali metal or an alkaline-earth metal carbonate.

19. A process as claimed in any of claims 1 to 17 wherein following removal of cyanogen the catalyst solution is freed, by distillation, of water introduced with hydrogen peroxide and water of reaction and is recycled.

20. A process for the production of cyanogen substantially as hereinbefore described with reference to any of Examples 1 to 3.

21. A process for the production of cyanogen substantially as hereinbefore described with reference to Examples 4, 5, 8 or 9 and the accompanying drawings.

22. A process for the production of cyanogen substantially as hereinbefore described with reference to Example 6 or 7.

23. Cyanogen when produced by a process as claimed in any of claims 1, 14 to 19 and 21.

24. Cyanogen when produced by a process as claimed in any of claims 2 to 9 and 20.

25. Cyanogen when produced by a process as claimed in any of claims 10, 11 or 22.

26. Cyanogen when produced by a process as claimed in claim 12.

27. Cyanogen when produced by a process as claimed in claim 13.

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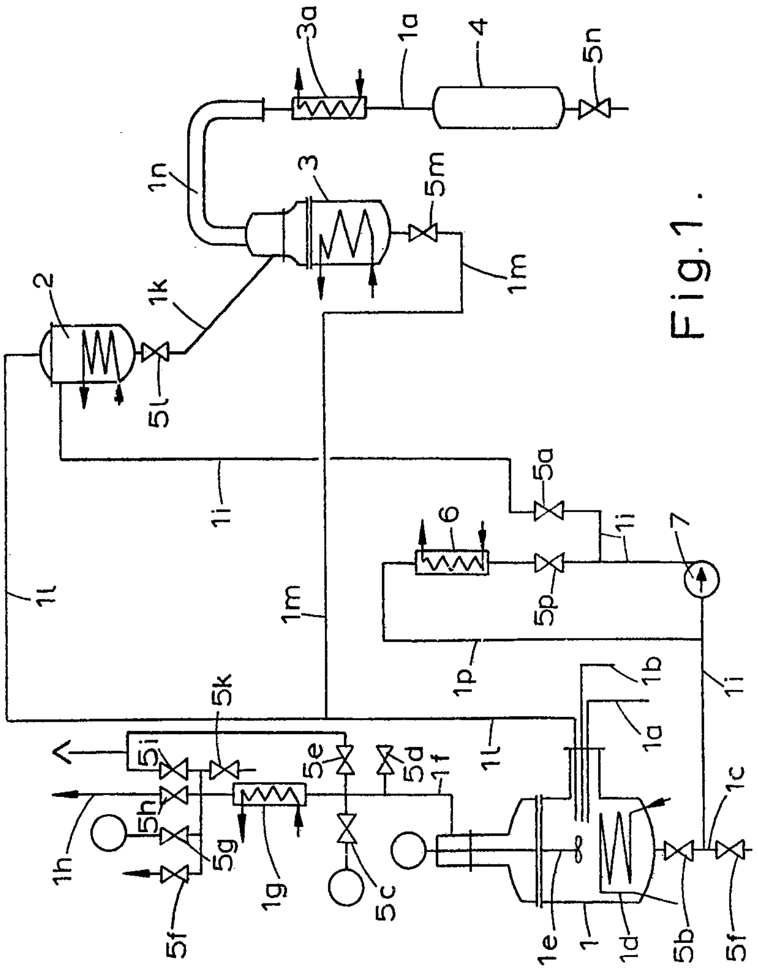
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Fig. 1.

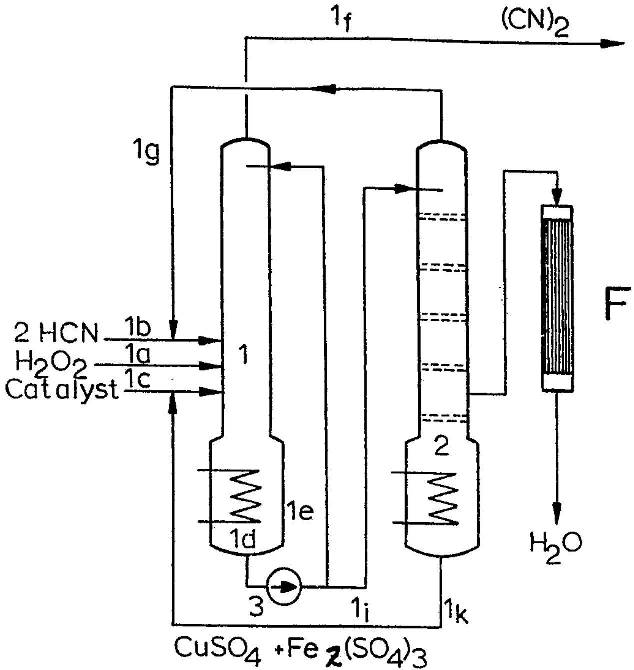
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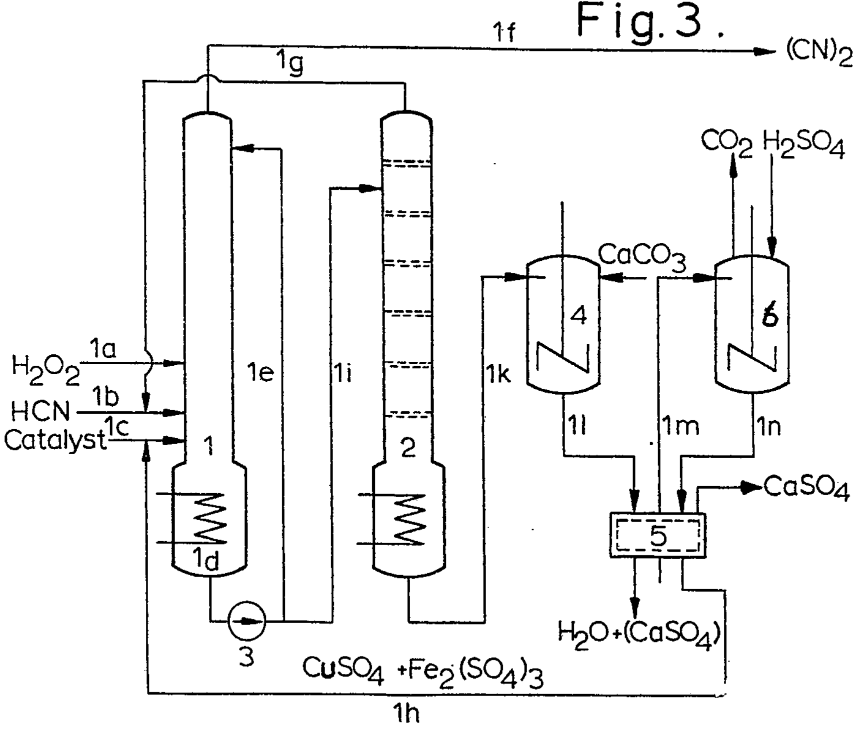
Fig. 2.

Fig. 3.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