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C.R.D.D REPORT No. 307/R/47

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A REVIEW OF THE LITERATURE AND OF WORK DONE IN  
A.R.D. AND C.R.D.D. ON PICRITE AND ITS INTERMEDIATES  
WITH A VIEW TO FINDING A CHEAP AND ECONOMICAL  
PROCESS.

BY

A. W. H. PRYDE.

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A.W.H. PRYDE

This report contains information of overseas origin.

SUBMITTED BY: A. FORSTER

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SUMMARY

Objects of Investigation.

To investigate the various methods of preparing Calcium Cyanamide and guanidine salts with a view to evolving an economic process for picrite manufacture using indigenous <sup>new</sup> materials, the process to be simple and require inexpensive plant by which capacity for 100,000 tons of picrite per annum could be provided cheaply for emergency purposes.

Scope of Investigation.

The literature has been surveyed and some experimental work done on alternative methods with a view to assisting in their assessment. The methods assessed are:-

- (1) The action of gaseous ammonia, with or without carbon monoxide, carbon dioxide or diluent gases, on calcium carbonate, lime etc. to give calcium cyanamide.
- (2) The heating of ammonium thiocyanate to give guanidine salts.
- (3) The action of hydrogen cyanide on heated lime to form calcium cyanamide.
- (4) The reaction of urea and thionyl and sulphuryl chloride to give cyanamide.
- (5) The reaction between lime and urea or related products to give calcium cyanamide.
- (6) The reaction between cyanogen chloride and ammonia at 100°C to give guanidine hydrochloride.
- (7) The reaction between urea and liquid ammonia at 300°C in the presence of aluminium powder.

Conclusions

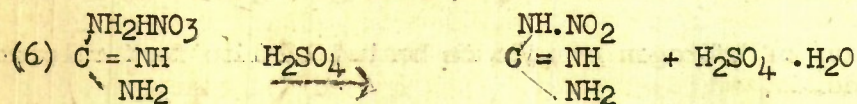
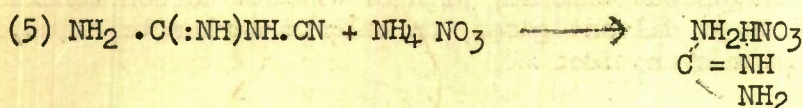
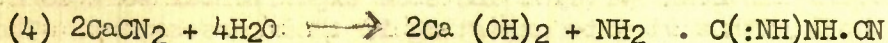
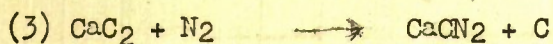
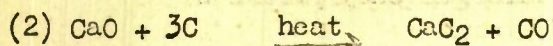
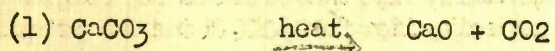
Costing data is lacking to make really reliable assessments but there is evidence to indicate that methods (1) and (7) are the only methods that give any reasonable hope of meeting the requirements.

Recommendations.

Should it still be considered essential to find an alternative method of manufacturing picrite other than through carbide then the methods most worthy of further study and detailed costing are methods (1) and (7) namely the reaction between ammonia and lime or calcium carbonate at 600°C and the reaction between urea, liquid ammonia and aluminium powder.

## INTRODUCTION

The accepted method of picrite manufacture is via calcium cyanamide which is made from calcium carbide and nitrogen. The calcium cyanamide is treated with hot water with or without the addition of carbon dioxide when dicyan-diamide is formed and is isolated and fused with ammonium nitrate to form guanidine nitrate which is then dehydrated to nitroguanidine, the equation being as follows:-



Picrite is used as an ingredient of flashless, smokeless, low temperature propellant which have obvious advantages from a military viewpoint. It has been estimated by Professor W.E. Garner that no better propellant is likely to be found in the next ten years<sup>(1)</sup>. During the last war most of the picrite used by the Services was shipped from Canada where 33,800 tons/annum were manufactured at Welland, using the above calcium carbide method. It has been estimated that in a future war picrite would be put to greater use, the estimated requirements being 100,000 tons/annum<sup>(2)</sup>. To meet future requirements there are thus the following possibilities:-

- Increase the Canadian capacity for picrite to 100,000 tons/annum. This would be quite a strain on shipping which is already overloaded in wartime.
- Use existing Canadian capacity of 33,000 tons annually and erect capacity in this country for some 66,000 tons annually.
- Erect capacity for 100,000 tons picrite in the United Kingdom and thus become independent of shipping.

Of these three alternatives, the latter has been deemed preferable but unfortunately the existing process requires a very costly plant and abundant cheap electrical power which is not available in this country at the moment. Capacity for 200,000 tons of calcium cyanamide would have to be laid down. Such a plant would have to remain idle as the most likely method of using it would be to supply fertiliser for agriculture which has already standardised on ammonium salts. The small quantity of carbide and cyanamide required in this country in peace time can be imported from Norway at £12 per ton whereas home produced is £15 per ton<sup>(3)</sup>. 3600

It therefore seems obvious that a process is required for manufacturing picrite in which the capital cost of plant is low so that it could be erected and stand idle without locking up too much capital. At the same time the process should use less power and it seems desirable that the cost of picrite should not be greatly in excess of that produced by the carbide process. In view of the very considerable amount of research which has been done in the

/last

last thirty years or more, in particular by Frank and Carr on alternative methods for cyanamide manufacture and on guanidine and its salts with so little success, it does not seem likely that the above requirements will be easily met. It is, however, the aim of this review to cover the alternative methods given in the literature, work done in A.R.D. in the past and work being done in C.R.D.D. at present, to see if there are any possible processes to meet the above requirements.

There are two possible lines of approach:-

- (A) Possible new methods of manufacture of calcium cyanamide, free cyanamide, dicyandiamide or related products.
- (B) Possible new methods of manufacture of guanidine or guanidine salts other than through cyanamide.

The literature has been explored and the following references are given:-

(A) 1. From Sodamide.

- (a) Alkali salts of cyanamide are formed by the reaction between alkali amides and carbon or by the action of ammonia gas on a mixture of alkali metals and carbon at a temperature which is suitable for the formation of the corresponding alkali cyanamides.<sup>(4)</sup>
- (b) Likewise sodium cyanamide is obtained from heated sodamide by passing carbon dioxide over it<sup>(5)</sup>.
- (c) Sodium amide when fused, reacts with carbonic nitride<sup>(6)</sup>.
- (d) Also by heating together sodium amide and sodium cyanide or cyanate.<sup>(7 & 8)</sup>

2. From Ammonia and carbonates of Alkaline Earths etc.

- (a) When the carbonates of calcium, magnesium, barium, lead, sodium, potassium or lithium are heated in a current of ammonia the respective cyanamides are formed.<sup>(9-13)</sup>
- (b) Calcium carbonate with gaseous ammonia at 700-850°C gives calcium cyanamide.<sup>(14)</sup>
- (c) Oxides, formates and carbonates of the alkaline earths, treated with a mixture of ammonia and carbon monoxide under pressure at a temperature of 400-850°C give cyanamide. The presence of water increases the yield of cyanamide. Iron is avoided as it causes decomposition but hydrogen sulphide or carbon disulphide inhibits this decomposition. Ceramic materials or zinc are recommended as materials of construction.<sup>(15)</sup>
- (d) Calcium carbonate heated with the passage of ammonia, in the presence of small quantities of oxides of metals or metals such as iron, gives calcium cyanamide. The iron is claimed to increase cyanamide formation.<sup>(16)</sup>
- (e) Calcium carbonate is reacted with ammonia at a suitable temperature to form calcium cyanamide. The water of the reaction can be removed with carbon in which case lime can be used in place of carbonate.<sup>(17)</sup>
- (f) Cyanamides are produced continuously from carbonates of the alkali metals or magnesium heated with ammonia and gases containing carbon such as carbon monoxide or dioxide. Copper free from cuprous oxide, or phosphor bronze may be used to make the plant.<sup>(18)</sup>

- (g) Calcium cyanamide is formed when ammonia gas is passed over calcium carbonate heated to its dissociation temperature. (19)
- (h) Calcium cyanamide is continuously produced by the reaction of  $\text{NH}_3$  and  $\text{CO}$  mixtures on lime heated to  $650-800^\circ\text{C}$ . (20)
- (i) Calcium cyanamide is produced by treating calcium compounds with mixtures of  $\text{NH}_3$  and  $\text{CO}$  or  $\text{NH}_3$  and  $\text{CO}_2$ . (21)
- (j)  $\text{NH}_3$  or mixtures of  $\text{NH}_3$  and  $\text{CO}_2$  reacted with alkali hydroxides, carbonates or compounds which yield oxides, in presence of a halide of calcium or magnesium at temperatures above  $400^\circ\text{C}$  under conditions preventing a reducing atmosphere e.g.  $\text{K}_2\text{CO}_3$  mixed with  $\text{CaCl}_2$  and heated to  $670^\circ\text{C}$  in a current of  $\text{NH}_3$  and  $\text{CO}_2$  gives 99% yield of  $\text{CaCN}_2$ . (22)
- (k) Synthetic ammonia and carbon monoxide are passed into reactive contact with heated calcium carbonate.  $\text{NH}_3$  and  $\text{CO}_2$  are removed from the resulting gases. The remaining gas, along with the initial gas for the ammonia synthesis containing  $\text{CO}$  and  $\text{N}_2$  is conducted into a hydrogen contact furnace in reactive contact with steam.  $\text{CO}_2$  is separated from the emerging gases. The resulting gas, containing  $\text{CO}$ ,  $\text{H}_2$  and  $\text{N}_2$  are freed from  $\text{CO}$  and used for the ammonia synthesis and the separated  $\text{CO}$  is used for the manufacture of calcium cyanamide by the initial reaction. (23)

### 3. From ammonia and various other compounds.

- (a) Dialkali cyanamides are formed by passing gaseous ammonia over a mixture of molten alkali and alkali cyanide or over alkali amides and cyanides at a temperature of over  $400^\circ\text{C}$ . (24)
- (b) Dialkali cyanamides are obtained by passing ammonia gas over molten alkali and carbon at a temperature which is below that for the formation of the corresponding cyanides. Alkali amide and carbon can be used in place of alkali metal at a temperature of  $350-400^\circ\text{C}$ . Instead of carbon easily volatile carbonaceous gases such as benzene, benzol, alcohol, acetylene, etc., can be used. (25)
- (c) Dialkali cyanamides are formed by passing ammonia gas into a molten mixture of alkali cyanide and alkali metal. (26)
- (d) Calcium carbamate heated to  $650-900^\circ\text{C}$  under conditions which enable the gases and vapours formed to be removed gives calcium cyanamide e.g. reduced pressure, inert gas or carbon monoxide, ammonia or nitrogen. The gases may be cyclically circulated and the water and carbon dioxide formed by the reaction removed outside the reaction vessel. The presence of  $\text{H}_2\text{S}$  helps to reduce the adverse effects of any iron present. (27)
- (e) High percentage calcium cyanamide is produced by passing ammonia and carbon monoxide over calcium carbamate at  $600-800^\circ\text{C}$ . The waste gases can be used to produce ammonium carbamate for further production of calcium carbamate. (28)
- (f) Calcium carbamate is heated to convert it as far as possible to calcium cyanamide and is then treated with ammonia at  $600-800^\circ\text{C}$  to further enrich it. (29)

#### 4. From Urea and Related Compounds.

- (a) Cyanamide is formed by the reaction of thionyl chloride on urea. (30)
- (b) Alkali or alkaline earth cyanamides are formed by heating urea, ammonium carbonate or ammonium carbamate with metallic sodium, (31) or with anhydrous lime. (32)
- \* (c) Ca Cyanamide is obtained by heating melam with lime. (34)
- (d) Calcium cyanamide is produced by heating oxides or carbonates of calcium or other alkaline earths with cyanic acid or substances which give rise to it. (35)
- (e) Cyanamide is obtained by the desulphurisation of thiourea with mercuric oxide or lead salts such as lead acetate in caustic soda, lead hydroxide and alkali or with hypochlorous acid. (36)

#### 5. Miscellaneous Reactions.

- (a) Metallic cyanamides are obtained by heating barium cyanide\* in a stream of nitrogen, by passing sodium vapour and nitrogen over heated potassium cyanide or by heating potassium cyanide and sodium hydroxide in a stream of nitrogen. (37)
- ≠ (b) Alkali cyanamide is obtained by melting together potassium cyanate or cyanide and caustic soda. (38)
- (c) Cyanamide is formed by the reaction between cyanogen chloride and an aqueous or ethereal solution of ammonia. (39)
- \* (d) Cyanamide is obtained by heating nitrosoguanidine with water (40) or by heating  $\text{CH}_2\text{N}_4\text{S}$  with water. (41)
- \* (e) Alkaline earth cyanamides are obtained by heating or melting titanium nitrides with oxides, carbonates, sulphates or other salts of alkaline earths in the presence of carbon. In this way lime gives almost entirely calcium cyanamide and baryta gives a mixture of barium cyanide and barium cyanamide. (42)
- 0 (f) Calcium cyanamide is formed when nitrogen compounds of silica and aluminium e.g. aluminium nitrate, is heated with lime and carbon at the lowest temperature necessary for homogenous fusion. (43)
- (g) Calcium cyanamide is formed along with sulphur and carbon bisulphide when calcium sulphate is mixed with carbon and a catalyst of halides, oxides, carbamates or oxy salts of alkaline earths or earth metals and is heated to  $1000-1200^\circ\text{C}$  with nitrogen or gases containing nitrogen. (44)
- \* (h) Cyanamide is prepared by the electrolysis of potassium acetamide in liquid ammonia solution. (45)
- \* (i) Disodium cyanamide is obtained when sodium azide is carefully added to fused sodium cyanide. (46)
- (j) Calcium cyanamide is formed when calcium cyanate is heated. (47)
- \* (k) Cyanamide is formed by the action of bromine on potassium cyanide dissolved in liquid ammonia. (48)
- \* (l) Cyanamide and carbon dioxide are formed by the reaction of dilute mineral acids on cyanocarbamic acid. (49)

- ✓
- \* (m) Cyanamide is formed by the oxidation of formaldehyde with calcium permanganate solution. (50)
- \* (n) Cyanamide is formed when sugars such as glucose, fructose, arabinose, mannitol, glycerol etc. are oxidised with ammoniacal potassium permanganate. (51)
- (o) Calcium Cyanamide is formed by the action of hydrocyanic acid on lime at 600-800°C. (52)

(B) Methods of Preparation of Guanidine and Guanidine Salts.

1. Guanidine salts from Cyanamide.

- e (a) Guanidine chloride is formed by heating cyanamide and ammonium chloride in alcoholic solution at 100°C under pressure. (53)
- e (b) By heating cyanamide with ammonium nitrate in aqueous solution at 150°C under pressure. (54)
- e (c) From cyanamide and ammonium picrate in the cold. (55)
- e (d) From calcium cyanamide and ammonium nitrate by heating together at 100°C. (56)
- e (e) By heating cyanamide with ammonium thiocyanate in aqueous solution to 100°C for 10 hours.
- e (f) From cyanamide and thio-urea. (57)
- \* (g) Sodium cyanamide solution, neutralised with nitric acid, evaporated and heated to 155°C with ammonium nitrate gives a 43.1% yield of guanidine nitrate. (58)
- e (h) Guanidine nitrate is formed in excellent yield by treating calcium cyanamide with mixtures of ammonium nitrate and urea. (59)

2. Guanidine or its salts from Dicyandiamide.

1. By hydrolysis in which case only one of the carbon atoms is converted to guanidine.

- / (a) By treating dicyandiamide with aqua regia. (60)
- / (b) By treating dicyandiamide with aqueous ammonia under pressure at 150°C. (61)
- / (c) By treating dicyandiamide with water under pressure. (62)
- / (d) By treating dicyandiamide with sulphuric acid or phosphoric acid at 140°C. (63)
- / (e) By treating dicyandiamide hydrochloride with potassium chlorate in weak hydrochloric acid at 100°C. (64)

2. By ammoniation of dicyandiamide. - In this case both carbon atoms are converted to guanidine.

- / (a) By fusing together dicyandiamide and ammonium salts e.g. chloride, nitrate, sulphate and thiocyanate. (65)
- / (b) By heating dicyandiamide with alcoholic ammonium chloride. (66)
- / (c) By heating dicyandiamide with aqueous ammonium chloride at 150°C. (67)

### 3. Guanidine or its salts from Urea or substituted Ureas.

- o (a) Guanidine is formed when urea is heated along with ammonium chloride in liquid ammonia under pressure or from all aquo-ammono-carbamic acids under similar conditions. (68)
- (b) Guanidine is prepared by treating urea with ammonia under dehydrating conditions.  $\text{NH}_3$  and  $\text{CO}_2$  can be used in place of urea. Suitable dehydrating agents are finely divided nickel aluminium or phosphorous pentoxide.  $\text{Al}_2\text{O}_3$  or  $\text{MnO}_2$  may be present. (69)
- \* (c) By the hydrolysis of cyanurea with warm dilute sulphuric acid. (70)
- (d) By heating thiourea (71). This is an intermediate stage in the ammonium thiocyanate reaction.

### 4. Guanidine and its salts from Derivatives of Methane.

- (a) By treating carbon tetrachloride with ammonia under high pressure at  $140^\circ\text{C}$ . (72)
- \* (b) By treating methylamine with iodine in liquid ammonia solution. (73)
- \* (c) By heating methylamine and ammonium azide in liquid ammonia solution at  $100^\circ\text{C}$ . (74)
- \* (d) By heating chloropicrin with alcoholic ammonia under pressure at  $100^\circ\text{C}$  (75)
- o (e) By the action of ammonia on phosgene. (76)
- o (f) By treating ethyl-O-carbonic ester with aqueous ammonia at  $150^\circ\text{C}$ . (77)
- \* (g) By treating hydrocyanic acid with iodine in liquid ammonia solution. (78)
- (h) From cyanogen halides and alcoholic ammonia at  $100^\circ\text{C}$ . (79)

### 5. Guanidine and its salts from Ammonium Thiocyanate.

- (a) By heating ammonium thiocyanate with zinc oxide in a current of ammonia. (80)
- (b) By heating ammonium thiocyanate with lead nitrate in a current of ammonia. (81)
- (c) By heating ammonium thiocyanate to  $180-200^\circ\text{C}$ . (82)
- (d) By heating a heavy metal thiocyanate in an atmosphere of ammonia or a double ammonium salt of a heavy metal thiocyanate in an autoclave. (83)
- (e) Molten ammonium thiocyanate treated with gaseous ammonia and nitrate or carbonate of Pb., Zn, or Cu. in a closed vessel gives a quantitative yield of guanidine salt. (84)

### 6. Miscellaneous Methods.

- \* (a) By treating biguanide or its salts with ammonia or ammonium salts. (85)
- / (b) By evaporating a solution of decyandiamidine carbonate. (86)
- / (c) By the hydrolysis of decyandiamide with boiling water in the presence of carbon dioxide. (87)
- o (d) By heating buiret in a current of hydrogen chloride. (88)

- ⌘ (e) By the reduction of nitromethane. (89)
- o (f) By the electrolysis of concentrated aqueous ammonia using gas carbon electrodes. (90)
- ⌘ (g) From mercury fulminate and aqueous ammonia at 60 - 70°C. (91)
- ⌘ (h) By the action of barium permanganate on arganine in aqueous solution at 30-60°C. (92)
- ⌘ (i) By treating guanine with potassium chlorate and hydrochloric acid. (93)
- ⌘ (j) By prolonged heating of hippomelamine with 3% hydrogen peroxide solution. (94)
- ⌘ (k) Along with urea by the oxidation of Thymonucleic acid with calcium permanganate in alcoholic solution. (95)
- ⌘ (l) By the oxidation of gelatine in boiling water with barium or calcium permanganate. (96)
- x (m) By the oxidation of egg albumin with alkaline potassium permanganate. (97)
- ⌘ (n) By bacteriological decomposition of guanine. (98)

#### Discussion of the Methods given in the literature.

On studying the above list of possible methods one finds that the papers given in the literature rarely give sufficient information to assess the absolute worth as practical large scale manufacturing processes. Fortunately many of the methods given in the literature are obviously of only academic interest since the compounds used in the reactions are difficultly prepared or costly to obtain. These reactions have been marked thus ⌘

Other reactions which at first sight look possible have to be rejected as the yields quoted are too low to make any manufacturing process a practical proposition. These have been marked o.

Other of these reactions such as the reactions of dicyandiamide on ammoniation and hydrolysis to give guanidine salts must be eliminated as competitors since dicyandiamide can only be economically prepared from calcium cyanamide. These have been indicated thus /.

Other reactions given for guanidine preparation which start from calcium cyanamide are eliminated since part of the problem is the preparation of calcium cyanamide. These have been marked e.

Any possible method through sodium cyanamide has been rejected owing to the difficulty of its separation from the sodium and subsequent recovery of the sodium which would make the process uneconomic. These have been marked 7.

Any possible process through sodamide has been rejected as sodamide, which is prepared from metallic sodium, would be too costly to be considered for making cyanamide and in addition there would be the complication of the recovery of the sodium from the cyanamide.

We are thus left with the following methods which are worthy of further consideration.

/1.

1. The action of gaseous ammonia, with or without the addition of carbon monoxide, carbon dioxide or diluent gases, on calcium carbonate, calcium carbamate, lime or the corresponding magnesium salts to give calcium cyanamide.
2. The heating of ammonium thiocyanate with or without the presence of lead, mercury or other salts to give guanidine salts.
3. The action of hydrogen cyanide on heated lime to form calcium cyanamide.
4. The reaction between urea and thionyl chloride to give cyanamide.
5. The action between lime and urea or related products.
6. The reaction between cyanogen chloride and ammonia at 100°C.
7. The reaction between urea and liquid ammonia at 300°C in the presence of aluminium powder nickel or phosphorous pentoxide.

Further Discussion of the above methods and a Summary of work done on these.

1. The Action of NH<sub>3</sub> and CaCO<sub>3</sub> etc.

Much work has been done on the reaction between ammonia gas on heated calcium carbonate or lime particularly by Frank and Caro who patented a process for the manufacture of calcium cyanamide by passing ammonia and carbon monoxide from producer gas over heated calcium carbonate. (23) The waste gases contain NH<sub>3</sub>, CO, H<sub>2</sub>, Ne and CO<sub>2</sub>. The ammonia and the CO<sub>2</sub> are removed by cooling them out and are recovered for reuse. As the gases are cycled round the system, carbon monoxide and hydrogen must be bled off. This is converted to carbon dioxide and hydrogen in a steam contact furnace, the carbon dioxide is removed, and the hydrogen is used in the ammonia synthesis. The complete flow diagram is given in Diagram I.

In the A.R.D. Holden and Freshwater have investigated this process, passing NH<sub>3</sub>, NH<sub>3</sub> + CO<sub>2</sub> and NH<sub>3</sub> + CO over heated calcium carbonate. (99) Using ammonia alone they conclude that at 650-700°C products containing up to 60% CaCN<sub>2</sub> can be obtained but that only 5% of the NH<sub>3</sub> would be converted in one passage. Using ammonia and CO<sub>2</sub> at 800-850°C a product containing 70% CaCN<sub>2</sub> can be obtained with 10% conversion. Using ammonia and CO at 800-850°C a product containing 85-90% CaCN<sub>2</sub> can be obtained, the conversion of ammonia varying from 10% at 2:1 ratio of gases to 20% at 1:2 ratio.

Holden and Freshwater give details of a small scale continuous plant which they made and operated on a countercurrent system using chalk and carbon monoxide-ammonia mixtures at a 2:1 ratio. They obtained a maximum purity of 84.5% CaCN<sub>2</sub> at 20% conversion of NH<sub>3</sub> and 70% CaCN<sub>2</sub> at 26% conversion of NH<sub>3</sub>. Unfortunately Holden and Freshwater did not say in their report whether the issuing gases contained ammonia that could be recycled and did not measure ammonia losses in their actual experiments. For this reason no assessment of the process as indicated can be made.

The reaction between lime and mixtures of ammonia and carbon monoxide has been studied by Chard in C.R.D.D. He has found that at 800°C much of the ammonia is decomposed by cracking but that at 600°C with any ratio of CO/NH<sub>3</sub> the ammonia loss is practically nil when using silica apparatus but at 650°C approximately 5% of the ammonia was lost. It was found that the gaseous phase reaches an equilibrium at which no further reaction occurs. The best run obtained to date using 1/1 ratio of CO/NH<sub>3</sub> at 600°C is 15% conversion of ammonia, ammonia loss by cracking being negligible and average purity of calcium cyanamide as 50%. Owing to the very low conversions and to the low purity of the cyanamide obtained it is doubtful whether a full scale process

/developed

developed from the above information would be an economic proposition. This work, however, is not completed and a possible process may develop from it. No report on the above work has so far been issued.

## 2. By heating Ammonium Thiocyanate.

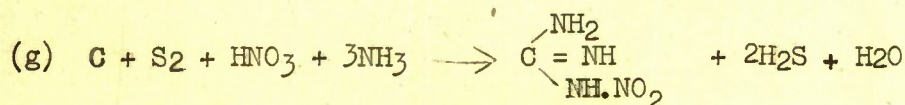
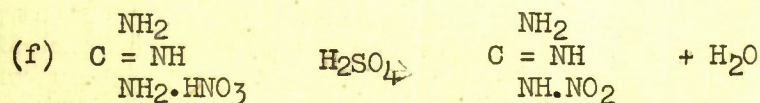
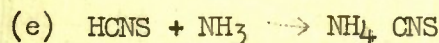
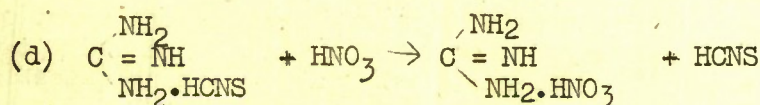
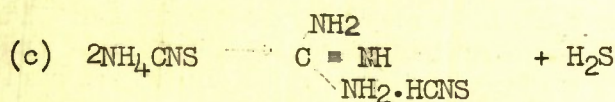
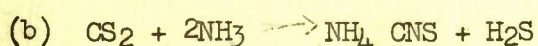
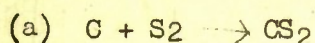
A method for this process has been given by Coulson<sup>(100)</sup>. Ammonium Thiocyanate is heated in enamelled iron-jacketed pan, closed, and fitted with inlet and outlet pipes and heated to a temperature of 210-220°C. Hydrogen sulphide is evolved during the reaction. Ammonia gas is passed into the atmosphere above the melt and the exit gases are cooled and collected in cold water. The ammonia input is regulated so as to remove the products of decomposition soon after they are formed. The ammonia used is recovered as ammonium thiocyanate which can be reused. Heating is for 3-4 hours when 30-40% of the original charge has distilled off and the product contains about 70% Guanidine thiocyanate, the rest being unchanged ammonium thiocyanate.

The crude guanidine thiocyanate is dissolved in water to give an 80% solution and nitric acid (Sp.Gr.1.4) is slowly added with cooling. Sufficient nitric acid is added to convert 75% of the crude into nitrate. The solution is allowed to stand for one hour and is then filtered on a vacuum filter. The crude guanidine nitrate is dissolved in a small quantity of hot water and brought to the boil. Whilst boiling vigorously nitric acid is added in small quantities to oxidise the remaining thiocyanate. When this is completed the solution is hot filtered, neutralised with ammonia and guanidine crystallises out on cooling, is dried at 100°C and finally crushed and dehydrated with sulphuric acid.

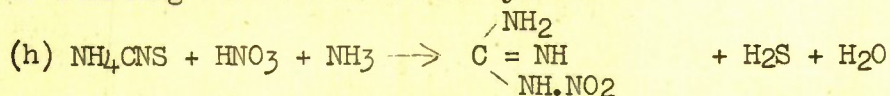
The liquors from the crude Guanidine nitrate crystals are neutralised with ammonia and evaporated to dryness yielding a product containing about 90% ammonium thiocyanate, some ammonium nitrate and some cyanate. This recovered thiocyanate can be used again.

c A flow diagram of the process as outlined by Coulson in his report is given in Fig.6. Unfortunately data is not available to show all the quantities involved.

The equations for the reaction are:-



or starting from ammonium thiocyanate



/Coulson

Coulson quotes that 1000 lbs ammonium thiocyanate after processing gives 269 lbs of finished nitroguanidine and that 535 lbs of this are recovered for reuse which means that 465 lbs of ammonium thiocyanate give 269 lbs of picrite. Theoretically 465 lbs of ammonium thiocyanate ought to give 636 lbs of picrite.

• Efficiency from  $\text{NH}_4\text{CNS}$  = 42.3%.

Efficiency from Carbon.

It is quoted in the literature that the efficiency from carbon to  $\text{CS}_2$  is 66%. The efficiency of carbon usage from  $\text{NH}_4\text{CNS}$  to picrite is 42.3% which gives an overall efficiency from carbon to picrite of 28.2%.

100,000 tons picrite theoretically require 11,540 tons of carbon.

• Carbon usage =  $11540 \times \frac{100}{28.2} = 40,900$  tons per annum.

Efficiency from Nitrogen (Exclusive of  $\text{NH}_3$  process).

The reaction between  $\text{CS}_2$  and ammonia to form ammonium thiocyanate is quoted as quantitative so 98% efficiency can be taken as a fair figure for large scale industrial manufacture.

The efficiency from  $\text{NH}_4\text{CNS}$  to picrite is 42.3%. Three of the nitrogens in the picrite molecule come from  $\text{NH}_4\text{CNS}$  through ammonia at this efficiency. The fourth comes from nitric acid which is introduced towards the end of the process. No figures are available for the losses of  $\text{HNO}_3$  during the subsequent processing but 25% loss should be a fair figure to use. The efficiency from  $\text{NH}_3$  to  $\text{HNO}_3$  is 85%.

• Overall efficiency on the fourth nitrogen is 64%.

The total  $\text{NH}_3$  requirements for 100,000 tons of picrite per annum is therefore  $\frac{51}{104} \times \frac{100}{42.3} \times 100,000 + \frac{17}{104} \times \frac{100}{64} \times 100,000 = 115,000 + 25,000 = 140,000$  tons per annum.

Efficiency from Sulphur.

269 lbs nitroguanidine require 465 lbs of ammonium thiocyanate. 100,000 tons require 173,000 tons of ammonium thiocyanate. Now all of the sulphur is evolved as  $\text{H}_2\text{S}$

• Weight of  $\text{H}_2\text{S}$  evolved =  $\frac{34}{76} \times 173,000 = 77,400$  tons

It is stated in the literature that  $\text{CS}_2$  can be made from  $\text{H}_2\text{S}$  by passing it over heated carbon and that there is a 70% conversion at 900°C. (101)

Thus 77,400 tons of  $\text{H}_2\text{S}$  will make  $77,400 \times \frac{76}{68} \times \frac{70}{100} = 62,000$  tons of  $\text{CS}_2$   
 Allowing 98% efficiency from  $\text{CS}_2$  to  $\text{NH}_4\text{CNS}$  this will make  $62,000 \times \frac{98}{100} \times \frac{152}{76} = 121,600$  tons of  $\text{NH}_4\text{CNS}$

This leaves 51,400 tons ammonium thiocyanate to be made from fresh sulphur at an efficiency from sulphur of 88%.

• Weight of fresh sulphur required =  $\frac{32}{76} \times 51,400 \times \frac{100}{98} \times \frac{100}{88} = 25,100$  tons/annum.

Thus for the manufacture of 100,000 tons of picrite per annum we require:-

- (1) 140,000 tons  $\text{NH}_3$ /annum.
- (2) 40,900 tons carbon/annum.
- (3) 21,500 tons sulphur/annum.

The ammonia would be supplied from this country but it must be regarded as doubtful whether this quantity could be found in wartime without an increase in the countries ammonia capacity.

The literature on carbon bisulphide manufacture makes it clear that activated charcoal is the only form of carbon that is used and much of the 40,900 tons would have to be imported. Owing to its low bulk density this might take up as much shipping space as 100,000 tons of picrite. It is believed, however, that  $\text{CS}_2$  is made from ordinary coke in Australia but it can be expected that the efficiency will be much lower using coke. Information on this process is expected soon.

Sulphur, not being an indigenous raw material would have to be imported.

It would seem, therefore, that the ammonium thiocyanate method would not save much shipping space.

Cost of Basic Raw Materials.

	<u>cost d/lb.</u>	<u>lbs per lb.product</u>	<u>cost/lb.produced</u>
$\text{NH}_3$	1.5	1.4	2.1
Carbon (as coke)	.5	409	.2045
Sulphur	.9	.215	.1935
			<u>2.508</u>
		Total	<u>2.508</u>

Plant

On safety grounds one can assume that at least four factories would be built. Each would have an output of 25,000 tons/annum or 500 tons/week of picrite.

143,000 tons  $\text{CS}_2$  are required per annum therefore each factory must make 43,250 tons  $\text{CS}_2$ /annum or 865 tons/week.  $\text{CS}_2$  is usually made in fairly small units with an output of about half a ton a day which would be out of the question for large scale manufacture. A plant using electrical heating is described in Thorpe's Dictionary of Applied Chemistry which has furnaces some 16 feet in diameter and 40 feet high with an output of 7 tons/day which have a life of 8 months to a year before requiring renewal. If these were used owing to the short life, at least twenty five would be required in each factory.

Each factory would use 35,000 tons of  $\text{NH}_3$ /annum or 700 tons/week. On the assumption that  $\text{NH}_3$  would not be imported at intervals of less than a week some twenty ammonia storage tanks of about 40 tons capacity would be required in each factory.

The ammonium thiocyanate reaction is carried out in autoclaves and a pressure of 200 lbs sq.inch is developed. The reaction is carried out in aqueous solution and the water is evaporated off in the autoclave. Quantities are not known but it seems reasonable to assume that an autoclave some ten feet in diameter by ten feet in depth with coil or jacket heating would only

/produce

produce about five tons of ammonium thiocyanate per shift. As described in Coulson's report conc. ammonia liquor was used so that there was about 50% water to be evaporated. It may, however, be possible to use less water when a greater pressure would be expected in the autoclaves which would have to be more substantial. Ten such autoclaves would be required in each factory on this basis.

The heating of the ammonium thiocyanate is done in retorts fitted with wide gas exit pipes. For 25,000 tons of picrite it is necessary to treat 94,300 tons ammonium thiocyanate/year, or 89 tons/shift. Allowing one shift for charging and processing the autoclave and allowing retorts of ten ft. diameter and ten feet depth to process ten tons a shift ten to twelve vessels would be required.

For the recovery of  $\text{NH}_4\text{CNS}$  from the waste liquors five or six similar autoclaves, similar to the ones used for the original  $\text{NH}_4\text{CNS}$  reaction, will be required.

In addition to the above, crystallisers, filters, centrifuges, boilers, dehydrators, driers, crushers, diluters, evaporators etc. as laid out in Fig. 5. will be required as well as a plant for reconcentrating 20%  $\text{H}_2\text{SO}_4$  to 96%, the quantities involved being of the order of 7,000 tons of 20%  $\text{H}_2\text{SO}_4$  per week. Using pot stills, one could expect an output of not more than 10 tons/day per still. Allowing for maintenance some 30 stills per factory would be required.

It is obvious therefore, that each of the four factories involves much plant, at least twice that involved in erecting a TNT factory for an equivalent output which, during the last war cost about £2,500,000. The cost of the ammonium thiocyanate factories for £100,000 tons/annum could therefore not be much less than £20,000,000 and probably considerably greater. With so much plant involved and the amount of recovery and recycling and the large number of stages and very high maintenance on the  $\text{CS}_2$  plant labour requirements would be large, at a rough estimate, on an analogy with a TNT factory, 2000 men in each factory, including supervision. The total fuel usage would be more than that of the carbide process.

It would seem, therefore, that the ammonium thiocyanate process as an alternative to the carbide process has little to commend it. In fairness, however, it must be stated that the nitrogen and carbon losses as given by Coulson in his report seem abnormally high and further investigations on the process might put it in a more favourable light, e.g. it has been suggested by Dr. A. Forster that a direct fusion of the ammonium thiocyanate with an ammonium salt such as the sulphate or the nitrate might result in all of the thiocyanate being changed to guanidine salts in one reaction and avoid much of the recycling necessary in the process as given by Coulson. Experiments show, however, that ammonium nitrate and ammonium thiocyanate when heated to  $200^\circ\text{C}$  react violently without the evolution of  $\text{H}_2\text{S}$  and the reactants are violently ejected, presumably due to decomposition of the ammonium nitrate. At temperatures lower than this and below the decomposition temperature for ammonium nitrate there was no apparent reaction. With ammonium sulphate ammonia is first evolved, followed by decomposition of the ammonium thiocyanate with the liberation of free sulphur, presumably due to the ammonium hydrogen sulphate formed attacking the thiocyanate due to its acid nature. Other ammonium salts could hardly be used in the process as the acid radical would be liberated in the dehydration process and would give a spent acid which would be very difficult to recover. It seems therefore, that this suggested modification could not be of any value.

### 3. The Action of Hydrogen Cyanide on heated lime.

Frank and Heimann<sup>(102)</sup> have obtained calcium cyanamide by the action of a mixture of nitrogen and gaseous hydrogen cyanide on lime heated to about  $600^\circ\text{C}$ . Data on yields etc. is, however, inadequate so the author of this

/report

report has investigated the reaction from the process angle (103). Whereas Frank and Heimann used hydrogen cyanide and nitrogen the author used only hydrogen cyanide vapours. Thus gaseous hydrogen cyanide was passed over finely powdered lime at various temperatures and at various rates in tubes of silica, steel, stainless steel and copper. Of these, only copper and silica were found to be suitable. Yields of cyanamide, based on HCN usage, varied from 80 - 98% in silica tubes and 94.2% has been achieved in a copper tube. Steel was found to be unsuitable as the water formed in the reaction reacted with the steel. Calcium carbonate instead of lime gave lower yields and the formation of ammonia in a side reaction.

The above process seems promising but obviously hinges on the cost of manufacture of hydrogen cyanide. Messrs I.C.I. Limited have supplied some information on this point. (10). Their process for the manufacture of HCN is to pass a mixture of methane, air and ammonia over a platinum-rhodium catalyst, followed by absorption and distillation of the HCN. They could give no costs of manufacture of HCN but stated that the market price of HCN was over £100 per ton. Since 1 ton of picrite requires 1.5 tons HCN the cost of picrite by this method must be prohibitive even allowing that HCN might be produced considerably cheaper than the market value. The manufacture of HCN by this method would mean setting up a plant for manufacturing 200,000 tons methane per annum as well as the plant for HCN. As there is 50% less of ammonia in the HCN reaction it seems probable that this country would find it difficult to supply the necessary 190,000 tons of ammonia which would be required without some increase in its ammonia capacity. A plant would also be necessary for the manufacture of 160,000 tons of lime per annum. The capital cost of the HCN plant alone has been given by I.C.I. as £77.4/ton year exclusive of site development, general offices, electric substation, stores, boiler plant and repair workshops etc. For 200,000 tons  $\text{CaCN}_2$ /annum the capital cost of the HCN plant alone would be £11.4 millions which is much greater than the £7.4 million required for 200,000 calcium cyanamide by the carbide process. On every basis, therefore, there can be no hope of using the process with the I.C.I. method of manufacture of HCN.

There are, of course, other methods of making HCN. The literature has been explored and the following are given:-

- (1) From alkyl formate vapour and ammonia at 200-300°C in presence of a dehydrating catalyst. (105)
- (2)  $\text{NH}_2$  and CO at 550°C in presence of vanadium oxide. (106)
- (3) Formamide and inert gases at 500°C with a catalyst of Cerium or Thorium oxide and pumice. (107)
- (4) From ammonium thiocyanate and oxygen at 350-700°.
- (5) From CO and  $\text{NH}_3$  at 400-800°C using dry porous charcoal as catalyst. (108)
- (6) From CO and  $\text{NH}_3$  at high temperatures using metallic oxides of 4th, 5th or 6th groups in the presence of more than 1 volume of hydrogen to each volume of  $\text{NH}_3$ . (109)
- (7) Formamide or HCN or both are made by passing vapours of alkyl formates with  $\text{NH}_3$  over a dehydrating contact mass such as  $\text{Al}_2\text{O}_3$ , thoria, aluminium phosphates, zeolites or  $\text{SiO}_2$  gel. If  $\text{NH}_3$  is present in excess  $\text{NH}_4\text{CN}$  is formed. High gas speeds give formamide and low speeds HCN. (110)
- (8) HCN is made by rapidly heating formamide or ammonium formate to 400-900°C. Catalysts can be  $\text{Al}_2\text{O}_3$ , bauxite,  $\text{TiO}_2$ , thorium oxides, iron oxides, silica gel, aluminium silicates and phosphates and alkali silicates, borates and aluminates alone or together or on

/supports

supports such as pumice, asbestos or activated carbon. The catalyst chamber can be made of silica, nickel or copper or alloys of iron with nickel or chromium. (111)

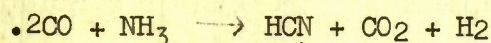
- (9) HCN is made by passing vapours of formamide and/or ammonium formate in a highly diluted state and at high velocity over metals such as Fe, Mn, Ni, Al or Cu which may be as granules, turnings or wire gauze. (112)
- (10) HCN is made by passing a gaseous mixture of  $N_2$  and hydrocarbons through the electric arc at  $400-600^\circ C$ . The gases are cooled in a steam generator, absorbed on alkali and the gases recirculated. (113)
- (11)  $NH_3$  and CO are passed over a catalyst of carbide of iron nickel or cobalt, which may be mixed with Mo, Mn, W, Ce, Fe, or Cu or their compounds at  $450^\circ C$ . The resultant gases may be cooled to separate ammonium cyanide or may be absorbed in caustic alkali. (114)
- (12) A mixture of kerosene or fuel oil vapours and nitrogen is passed through an electric arc. (115)
- (13) From coke oven gas and ammonia. (116)
- (14) From ammonia gas and benzene or toluene. (117)
- (15) From  $NH_3$  and CO using as catalyst a mixture of MgO and  $UO_2$ . (118)
- (16) From  $NH_3$ , a hydrocarbon and just enough oxygen to make the reaction exothermic when the mixture is passed over a Pt-Rh catalyst. (119)
- (17) From  $NH_3$ , water vapour and a gaseous hydrocarbon such as coal gas at  $1150-1500^\circ C$ . (120)
- (18) From  $NH_3$ , 1 volume, hydrocarbon gas equivalent to 2 to 5 volumes of  $CH_4$  and 5-15 volumes of air, preheated to  $400-1000^\circ C$  and passed over finely divided wood charcoal at 1100 to  $1500^\circ C$ . (121)
- (19) A gaseous mixture of  $NH_3$ , MeOH, Et OH, or  $C_2H_4Cl_2$  etc. is passed over a hot oxidation catalyst such as Pt, Ir, Rh, Os, Au or Ag with the addition of a volatile hydrocarbon derivative free from nitrogen but containing at least one hydrogen atom and at least one hydrogen atom substituted by an atom other than hydrogen or nitrogen. (122)
- (20)  $NH_3$  and CO over a mixture of MgO and  $CuSO_4$ . (123)
- (21) Hydrocarbon, carbon or other carbonaceous material is burned in air to give a flue gas at a temperature of  $400-1000^\circ C$  and a mixture of  $NH_3$  with excess hydrocarbon and sufficient air or oxygen to burn a part of this excess, is introduced into the hot flue gas. (124)
- (22) By passing a mixture of CO and  $NH_3$  over a specially prepared sintered form of alumina activated with Zr or Ce oxide. (125)
- (23) HCN has been made on quite a large scale in Germany by bubbling CO into Methyl alcohol under pressure to form methyl formate which is reacted with ammonia under pressure to formamide which is dehydrated using a catalyst.

Of these methods only the latter and the reaction between CO and  $NH_3$  seem of much value as possible economic methods of making HCN.

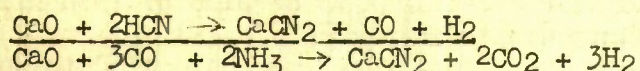
The reaction between CO and  $NH_3$  has recently been studied by Mr. Chard in this Department. Using the method given in ref. (125) it has been found

that using a 10:1 ratio of CO:NH<sub>3</sub> 35% 50% conversion is possible in one passage of the gases at temperatures between 500 and 600°C with practically no loss of ammonia. (126) Chard has gone on from this and has suggested possible processes for using this method by linking it up with the ammonia synthesis to give the possibility of an economic process. (127) The advantages of using the CO, NH<sub>3</sub> process and linking up with the ammonia synthesis are:-

- (1) The water gas plant needed for HCN manufacture is already present in the NH<sub>3</sub> plant. The HCN reaction is as follows:-



and  
or



- (2) We see therefore, that the hydrogen evolved can be passed back to the ammonia plant after removal of CO<sub>2</sub>.

From the above basic idea three possible cycles are given. These are:-

A. Using the ordinary NH<sub>3</sub> process water gas plant. The water gas would be reacted with ammonia to make HCN which would be absorbed, distilled and fractionated to liquid HCN for use and then reacted with lime. The end gases containing a high percentage of H<sub>2</sub> would be partially separated by absorption of CO by nickel or in a diffusion plant to give water gas for recycling and a 5:1 mixture of H<sub>2</sub> and CO for passing on to the ammonia process. The flow sheet is given in figure 2.

B. This scheme involves making practically pure CO by passing CO<sub>2</sub>, which is a byproduct of the ammonia synthesis, over coke heated to 1000°C. A flow sheet is given in fig.3 which shows no recycling of CO but the end mixture of CO and H<sub>2</sub> could be recycled and the amount adjusted to give the desired ammonia output. With no recycling, approximately 1¼ lb of NH<sub>3</sub> per lb CaCN<sub>2</sub> made would be available for export. By recycling the end gases with approximately ½ bled off to the NH<sub>3</sub> plant a completely closed cycle is achieved, all the NH<sub>3</sub> made being used up to make cyanamide e.g. the Doulais ammonia plant if converted in this way could produce 70,000 tons CaCN<sub>2</sub> per annum.

C. This method would use a Linde plant to separate the gaseous mixture but in all other respects is similar to A and B.

An estimate of the fuel and power usage by the above methods has been made (assuming 100% yield of CaCN<sub>2</sub> from NH<sub>3</sub>) and compared with the fuel and power required for CaCN<sub>2</sub> from carbide. They are found to be almost the same.

A labour comparison would almost certainly favour the carbide process.

The probable higher purity of the product is in favour of the HCN method.

A comparison of the necessary plant has also been made and it has been concluded that method B. would give a plant probably slightly cheaper than that of the plant for cyanamide via carbide. However, subsequent information on the cost of the I.C.I. HCN plant makes this conclusion doubtful. The plant for manufacturing HCN from CO and NH<sub>3</sub> cannot be very different from that of the I.C.I. plant using methane, air and ammonia though only about half the size since 100% yield of HCN is expected from ammonia. This plant alone would therefore cost about £6 million which is nearly as much as the cost of the plant for making cyanamide via carbide. The whole plant would therefore cost much more.

/The

The cost of  $\text{CaCN}_2$  made by the above method could not be much cheaper than that from the carbide process. It would seem therefore, that there is little prospect of this method superceding the carbide process.

The German process for making HCN from CO and  $\text{NH}_3$  via methyl alcohol, methyl formate, and formamide involves pressure vessels, a three stage reaction, fractionations and the loss of fairly expensive solvents and could hardly be a cheaper method than the above or require a cheaper plant and would not appear to solve the problem.

One must therefore conclude that the manufacture of calcium cyanamide from lime and hydrocyanic acid is not likely to be advantageous or to give an inexpensive plant which could be erected as a stand by for emergencies.

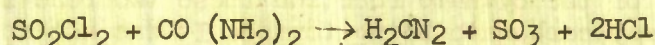
#### 4. From Thionyl or Sulphuryl Chloride and Urea.

According to rather scanty information given in Bulletin de La Societe Chimique de France (3) 11 1069, thionyl chloride and urea react at ordinary temperatures, giving off hydrogen chloride and forming cyanamide. No yields are quoted. The author of this report in attempting to obtain more information on this reaction was quite unable to duplicate the above results. (128) Even on warming the mixture to the boiling point of the thionyl chloride no reaction was noted and no cyanamide was found.

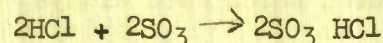
The reaction was quoted to be as follows:-



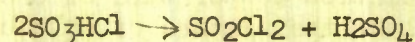
The author of this report thought that possibly, as the above report is a very old one, not thionyl but sulphuryl chloride might have been intended. If so and a good yield of cyanamide was obtained, there was the prospect of a simple and possibly cheap process thus:-



It was hoped that the  $\text{SO}_3$  and the HCl would be evolved as gases to which could be added another molecule of  $\text{SO}_3$ . On condensing this mixture chlor-sulphuric acid would be formed thus:-



On heating with 1% mercuric sulphate as catalyst the original sulphuryl chloride could be recovered thus:-



There would, therefore, be no need to make fresh sulphuryl chloride for each batch, indeed the reaction boils down to the dehydration of urea by converting  $\text{SO}_3$  to  $\text{H}_2\text{SO}_4$  which could either be exported for use in industry or reconverted to  $\text{SO}_3$  using the new German process.

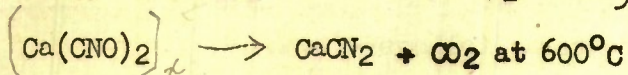
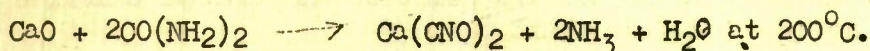
Experiment showed that there is a reaction between urea and sulphuryl chloride and cyanamide is formed.

Experiments were made with varying amounts of the reactants under a number of different conditions and with the addition of aluminium chloride in small quantity but yields were always very poor, being only of the order of 5% of theory, possibly due to the fact that the HCl and  $\text{SO}_3$  formed were not evolved but must form chlorosulphonic acid in solution in the sulphuryl chloride and this chlorosulphonic acid reacts with the urea. Separate experiments with urea and chlorosulphonic acid gave a violent reaction but no cyanamide was formed. A few experiments were tried with the addition of lime to the urea - sulphuryl chloride mixture without great success. Since further elaboration would have made any possible process cumbersome no further work was done on this reaction.

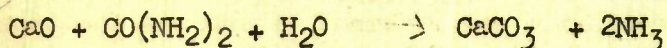
## 5. The Reaction between Lime and Urea.

Very little information of any great value is given in the literature concerning this reaction. The author of this report has done numerous experiments under various conditions which have been reported on ref. 128 and others which have not yet been reported.

- (a) A number of experiments were done with mixtures of urea and lime dropped into a tube at 600-700°C. This gave poor yields of cyanamide, the best achieved being 18.9% of the urea converted to cyanamide.
- (b) A number of experiments were done with urea and lime mixtures heated to 200°C till no more ammonia was evolved followed by heating to 600°C. It was found that to achieve a high purity of CaCN<sub>2</sub> a very large excess of urea had to be used when yields were poor. Better yields were obtained with nearer the theoretical quantities but the purity of the product was too low to be any use e.g. 12 gms urea and 11.2 gms lime gave a yield of 28.74% on the urea and a purity of 31.28% CaCN<sub>2</sub>. It was thought that the mechanism of the reaction was:-



That this is the mechanism of the reaction has been proved by experiment. These experiments also showed however, that lime reacts with urea according to the following reaction:-



Since H<sub>2</sub>O is a product of the cyanate reaction these two reactions proceed at the same time, carbonate being formed. It was not found possible to isolate the mixtures of calcium carbonate and calcium cyanate from the unchanged urea when excess urea was used nor was it found possible to react the theoretical amounts of lime and urea to leave no free urea. Attempted analysis of the mixtures of calcium cyanate, calcium carbonate and urea which were always obtained all failed.

One possible method of obtaining the theoretical yield of cyanamide from urea seemed to be to react lime with a large excess of urea at a temperature of 140°C, which is below the dissociation temperature of urea, and to collect all the ammonia evolved, hot filter the mixture of calcium cyanate and calcium carbonate from the excess urea and heat it to 600°C when one could hope for the theoretical yield of calcium cyanamide, allowing for the recovered ammonia which could be converted to urea and used again. Owing to the formation of carbonate the purity of the cyanamide would not be very high, perhaps only 50% but this strength could be used to form dicyandiamide by hot water extraction and the lime could be recovered. Unfortunately all efforts to separate the cyanate-carbonate mixture from the large excess of liquid urea failed, filters all choked and no solvent for urea could be found which did not also dissolve calcium cyanate. It is hardly possible, therefore, that this method could ever be applied on a large scale production.

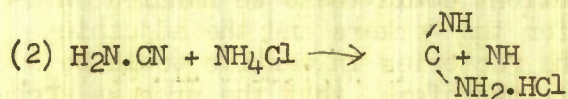
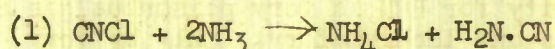
- (c) Since yields are low when there is a large excess of urea present and the mixture is heated to 600-700°C efforts were made to use up all the urea by prolonged heating of nearly the theoretical quantities of lime and urea. Actually a slight excess of lime was used. 82 gms of lime and 66 gms of urea were ground together to pass through 150 B.S.S. mesh and heated together at 140°C till no more ammonia was evolved, the mixture was reground and reheated repeatedly till no more ammonia was evolved (the total heating time

time was about twelve hours). The mixture was heated to 600-700°C and the ammonia evolved measured at both stages of the reaction. The yield of CaCN<sub>2</sub> was 20.1% of the original urea and 74.2% allowing for recoverable ammonia and the purity of the product was 14.89%. This method is, therefore, of little value as the cyanamide purity is much too low.

Allowing a value of 60% Calcium Cyanamide as the minimum purity, we have found it necessary to use a large excess of urea in any process which we have so far been able to devise, which must make this process for the manufacture of cyanamide very uneconomical. A flowsheet of a possible process is given in figure 4. This is based on the reaction between 12 gms urea and 5.6 gms of lime, heated first to 200°C and then to 600-700 C when 7 gms of calcium cyanamide were produced at 56% purity and 4.01 gms of recoverable ammonia were evolved. The yield from the original urea is only 23.3% of theory. allowing for recoverable ammonia being reconverted to urea for use again the yield is 59% of theoretical. No information is available as to the cost of making urea but ammonia costs £12.5 per ton to produce (ex Doulais), CO<sub>2</sub> as a byproduct of the ammonia process can be obtained at the cost of compression which will be negligible. Allowing for a possible yield of only 80% of urea, 42.5 tons ammonia will produce 60 tons of urea, i.e. the ammonia cost per ton of urea is £8.85 per ton. allowing for manufacturing costs £15 per ton should be a possible figure for urea if manufactured in conjunction with the ammonia process though this is doubtful in view of the fact that urea has a market value of nearly £40 per ton. allowing £15 ton for urea, £6.15 per ton for conversion of ammonia to urea, and £3 per ton for lime, the cost of manufacturing Calcium Cyanamide by the above method, neglecting processing costs and depreciation on plant, would be £34 per ton. It is obvious therefore, that the process would be very uneconomical. As no figures are available for the cost of the urea plant no estimate can be made of the capital cost of plant. It is unlikely however, that it would be much cheaper than the plant for the carbide process. Imperial Chemical Industries Ltd. have been asked for information on the urea process but so far nothing has been received.

#### 6. The Reaction between Cyanogen Chloride and Alcoholic Ammonia.

It is stated in the literature<sup>(82)</sup> that cyanogen chloride reacts with ammonia in alcoholic solution to give a quantitative yield of guanidine hydrochloride, the mechanism of the reaction being through cyanamide thus:-



The feasibility of the methods must depend largely on the ease with which guanidine hydrochloride can be converted to nitroguanidine and the yield obtained. Experiments in this department have shown that guanidine hydrochloride can be very readily converted to nitroguanidine by dissolving the dry salts in a 2.5/1 ratio by weight of sulphuric acid and warming to drive off HCl gas followed by the addition of just over the theoretical amount of conc. nitric acid, leaving the mixture at room temperature for about two hours and diluting to 20% acid, followed by filtration and washing till free of acid. In this way a 90% yield of nitroguanidine was obtained and the HCl recovered in a suitable form for reversion to chlorine. This part of the reaction is thus very simple and presents no difficulties on a large scale, the plant being simple and capable of continuous operation.

The reaction between cyanogen chloride and ammonia is carried out in autoclaves at 100°C and should present little difficulty on a large scale although the plant involved would be very considerable.

Cyanogen chloride can be made from hydrogen cyanide and chlorine, two methods being given in the literature.<sup>(129)</sup> In the first of these a 12-15% /solution

solution of HCN in water has chlorine bubbled through it in very fine bubbles. The cyanogen chloride distills off along with 10-20% HCN and is purified by retreatment with chlorine. The HCl remaining behind in solution will be approximately 20% strength. The other method is a pressure method and uses 4% HCN solution which would give only 5-6% HCl. A further weight of HCl equal to that in the above solutions can be recovered from the guanidine hydrochloride. If this was passed into the weak HCl then an acid of some 35% strength could be obtained using the above method which, of course, would have to be reconverted to chlorine. For the Deacon process where gaseous HCl is required, very large quantities of concentrated sulphuric acid, with its consequent concentration would be necessary and probably uneconomical. If the old  $MnO_2$  process was used less than 30% of the HCl would be recovered as chlorine. It would probably be best therefore, not to mix the weak HCl and the gaseous HCl. The gaseous HCl, which accounts for 50% of chlorine used, could be reconverted to chlorine, using the Deacon process at an efficiency of 60-70% giving 30-35% of the original chlorine for reuse. 65-70% fresh chlorine would, therefore, be required for each batch of nitroguanidine. The disposal of the weak HCl would present quite a problem on the huge scale envisaged and might have to be neutralised with lime or soda before going to drain.

For the manufacture of HCN there are three alternative methods, only one of which is in general use in this country, namely the reaction between methane, ammonia and air. This is a very inefficient process as the efficiency from methane and ammonia is only about 50% and the plant is costly. This method of manufacture of HCN could hardly be considered for this application.

In Germany HCN has been made on a large scale quite successfully from carbon monoxide and ammonia via methyl alcohol, methyl formate and formamide at reasonable efficiencies but involves a three stage reaction in pressure vessels, fractionations and solvent losses and the plant would inevitably be costly.

A mixture of  $NH_3$  and CO, passed over a catalyst at  $600^\circ C$  gives HCN quite successfully on a small scale but there is reason to believe that it is not feasible on a large scale.

Apart from any other considerations any factory making picrite by the above method would require storage capacity for HCN, a very poisonous gas and cyanogen chloride which is both poisonous and lachrymatory. Only by very careful design and extreme safety precautions could these be handled on a large scale and the question of safety for the workers and the adjoining population in the event of bombing of the factories in wartime would be a very grave difficulty. Despite the fact, therefore, that the process probably involves less plant than any of the others it cannot be recommended.

The plant required would be:-

- (1) A plant for 32,000 tons HCN per annum.
- (2) A plant to make 69,100 tons cyanogen chloride per annum.
- (3) A plant to make 102,000 tons guanidine hydrochloride per annum.
- (4) A plant to convert the guanidine chloride to nitroguanidine.
- (5) A plant to make 84,000 tons of chlorine per annum.
- (6) A plant to concentrate approx. 1,500,000 tons of 20%  $H_2SO_4$  per annum to 96% sulphuric acid.

Approximately two thirds of the chlorine made would be lost so that 56,000 tons per annum of fresh chlorine would be consumed in the process.

#### Raw Material Costs.

1. lb. of picrite requires:-

/(a)

- |  |         |
|--|---------|
| (a) 0.391 lb HN <sub>3</sub> at 1.5d per lb. | = 0.587 |
| (b) 0.56 lb Cl <sub>2</sub> at 2.5d per lb.  | = 1.4   |
| (c) 0.32 HCN at 6.0d per lb.                 | = 1.92  |

3.907d

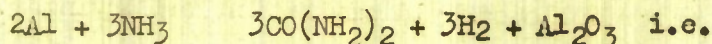
On the data available no estimate can be made of processing costs but these would probably be less in this process than in any of the others. The process might, therefore, be reasonably economical.

#### 7. The reaction between Urea, liquid Ammonia and Aluminium.

D.R.P. 527, 237 gives a method of preparing guanidine salts by the reaction between urea, liquid ammonia and dehydrating agents such as aluminium powder, nickel powder, aluminium chloride and phosphorus pentoxide. Examples quoted are:-

- (1) 300 gms urea, 150 gms Aluminium powder and 100 gms liquid ammonia heated to 300°C in an autoclave for 8 hours. Yield = 270 gms guanidine.
- (2) 300 gms urea, 670 gms AlCl<sub>3</sub> and 100 gms liquid ammonia heated to 300°C for 5 hours. Yield = 800 gms guanidine hydrochloride.
- (3) 300 gms urea, 180 gms P<sub>2</sub>O<sub>5</sub> and 100 gms liquid ammonia heated to 300°C for 6 hours. Yield = 490 gms of mixture of approx. equal parts of guanidine and guanidine phosphate.

Of the dehydrating agents, aluminium is obviously the cheapest and most convenient. This reaction between urea, liquid ammonia and aluminium must follow the equation:-



54 parts aluminium + 51 parts ammonia + 180 parts urea give 173 parts guanidine, 6 parts hydrogen and 102 parts aluminium oxide.

300 gms urea would require 85 parts ammonia and 90 parts of aluminium to give 288.3 parts of guanidine and 170 parts aluminium oxide.

The author of this report has made several attempts to duplicate the above work but has been unable so far to study the reaction due to limitations in apparatus. It is hoped to study the reaction to see if better yield can be obtained with a smaller excess of ammonia and of aluminium. Till this can be done it is necessary to draw up a possible process from the figures supplied in the patent.

Allowing for losses in extractions of the guanidine, the conversion to nitrate and the dehydration to picrite, approximately 100,000 tons of guanidine must be made per annum.

A flowsheet for the process is given in fig.5.

On the basis of the above flowsheet, assuming that the excess ammonia and aluminium are both recoverable for reuse, 110,000 tons of urea, 31450 tons of ammonia and 33,300 tons of aluminium are required for 100,000 tons of guanidine. A.M.M.P. (X) give a cost of £70 per ton for secondary blown aluminium powder size 36/dust and about £10 per ton as the probable value

of the recovered alumina. With urea at an estimated £15 per ton and ammonia at £12.5 per ton, the material cost of guanidine amounts to approx. £38 per ton. The cost of Canadian picrite is of the order of £70 per ton. To convert guanidine to picrite 1 molecule of  $\text{HNO}_3$  is required per molecule of guanidine. 100,000 tons guanidine theoretically requires approx. 107,000 tons  $\text{HNO}_3$  at a cost of approx. £10 per ton. This brings the cost of the raw materials required for picrite manufacture to £48 per ton based on the assumption that 100,000 tons guanidine will give only 100,000 tons of picrite. Theoretically of course, 100,000 tons of guanidine should give 187,000 tons of picrite. On the theoretical basis the cost of raw materials i.e. urea, ammonia, aluminium and nitric acid is £25.7 per ton.

With the data available the manufacturing costs cannot be estimated but it seems probable that there is a distinct possibility that this process would give an economical method of manufacturing picrite in this country especially if linked up with the ammonia synthesis plant when the  $\text{CO}_2$  for the urea can be obtained for nothing since large quantities are at the moment blown to atmosphere. In addition, the hydrogen evolved in the guanidine process could probably be used in the ammonia synthesis and thus cheapen the ammonia process and slightly reduce the cost of picrite by this method.

The plant unfortunately involves the following:-

- (1) A urea plant to manufacture 111,000 tons urea per annum. This is a pressure plant.
- (2) A plant rather similar to the urea plant for the reaction between the urea, liquid ammonia and aluminium. Since this reaction is at  $300^\circ\text{C}$  and  $\text{H}_2$  is evolved to replace the ammonia used, to keep to a pressure of 50 ats, the volume of the vessels must be large in comparison with the weight of reactants. Since the time of the reaction is 8 hours it is obvious that this plant will be large and costly.
- (3) A plant for recovery of 5,550 tons  $\text{NH}_3$  per annum. This could be by absorption in the water followed by distillation and drying.
- (4) A flotation plant for recovery of 22,200 tons of aluminium per annum.
- (5) A drier for the recovered aluminium and aluminium oxide.
- (6) The guanidine would be in solution in water when recovered. This would be neutralised with nitric acid when guanidine nitrate would separate out and would have to be filtered from the mother liquor on a continuous classifier. The mother liquor would be used for the next extraction of guanidine.
- (7) A dehydration plant in which the guanidine nitrate is treated with sulphuric acid or a mixed acid of sulphuric and nitric.
- (8) A plant to concentrate the spent acid.

It must be considered very doubtful that such a plant, along with its offices and services, could be erected at a cost of less than £23.7 million, which is the estimated cost of the plant for 100,000 tons picrite per annum from carbide.

#### Some General Notes.

Going to basic fundamentals, to form one molecule of picrite, four molecules of nitrogen are required. In any of the possible processes two of these must come from ammonia, one directly and the other indirectly through

nitric acid. There are only two methods of obtaining fixed nitrogen which are of any practical value.

(1) fixation to Calcium cyanamide;

(2) fixation to ammonia.

(1) Comparing the basic energy requirements for the two methods from figures based on Kenfig and Doulais respectively, we find that the energy (as standard fuel) requirements per ton of nitrogen fixed as cyanamide and as ammonia are respectively 5.13 and 3.23 tons/ton of  $N_2$ . The carbide process uses more than half of its energy as power whereas that of the ammonia process is split up in the ratio of 5:1 in favour of coal. Since the cyanamide process has also fixed the necessary carbon molecule an extra 0.43 tons of carbon will be required making the total from ammonia to 3.66 tons of  $N_2$  fixed.

Nearly all electricity in this country is made from coal/<sup>so</sup> we see that there is an appreciable saving in coal possible by using a process in which all of the nitrogens of the pierite molecule are fixed as ammonia.

Since cyanamide would cost approximately £15 per ton to manufacture in this country while ammonia costs £12.5 per ton the relative costs per ton of fixed nitrogen are £43 and £15.2 respectively. It should, therefore, be possible theoretically to make pierite cheaper using only ammonia as a source of fixed nitrogen. Owing to poor yields, difficulties in manufacturing processes, costly plant etc. this has not yet been realised up to the time of writing this report.

#### Conclusions.

It must be realised that due to lack of costing data it has been found impossible to make very accurate comparisons of costs of manufacture and of plant. The conclusions stated below are therefore largely opinion. Before any really reliable comparisons can be made much information must be obtained by experiment and from private industry.

The general conclusions are:-

- (1) It seems unlikely that any simple means of making pierite, which will give a plant of low cost, can be developed unless some new and very simple method is discovered for fixing nitrogen and combining it with carbon.
- (2) By passing mixtures of CO and  $NH_3$  over lime at  $600^\circ C$  and combining the process with the ammonia synthesis it may be possible to make calcium cyanamide cheaper than by the carbide method. Since the cost of the cyanamide is only a small part of the cost of pierite, the overall saving would be small. The total fuel usage by this method might be less than for the carbide process.
- (3) By the reaction of urea, liquid ammonia and aluminium powder it may be possible to make pierite at an appreciably lower cost than by the existing method. The cost of plant is likely to be heavy but the total fuel usage might be appreciably less than by the carbide process.

#### Recommendations.

While the prospect of being able to build a plant for the manufacture of 100,000 tons of pierite per annum in this country at a low cost seems remote, if it is still considered necessary to do so then the author of this report recommends that further work should be done on the reactions between:-

(1)

- (1) lime and mixtures of CO and NH<sub>3</sub> at 600°C;
- (2) urea, aluminium and liquid ammonia at 300°C, since these seem to be the methods most likely to give picrite at an economical cost.

Acknowledgements.

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- C.S.T. = Trans. of the Chemical Society
- C. = Chemische Zentralblatt
- Z.Ang. = Zeitschrift für Angewandte Chemie
- Z.El.Ch. = Zeitschrift für Elektrochemie
- B. = Berichte der Deutschen Chemischen Gesellschaft
- Z.a.Ch. = Zeitschrift für Anorganische Chemie
- C.r. = Comptes rendus de l'Académie des Sciences
- Ch.Z. = Chemiker - Zeitung
- D.R.P. = German Patent
- G. = Gazzetta Chimica Italiana
- A. = Liebigs Annalen der Chemie
- J.Pr. = Journal für Praktische Chemie
- Bl. = Bulletin de la Société Chimique de France
- J.C.S. = Journal of the Chemical Society
- M. = Monatshefte für Chemie
- H. = Zeitschrift für Physiologische Chemie
- B.Ph.P. = Beiträge zur Chemischen Physiologie und Pathologie
- R.A.L. = Atti della Reale Accademia dei Lincei (Rendiconti)
- B.P. = British Patent
- F.P. = French Patent
- J.S.C.I. = Journal of the Society of Chemical Industry
- F.N.S.C. = Franklins Nitrogen System of Compounds
- J.A.C.S. = Journal of the American Chemical Society
- W.D. = Watts Dictionary
- Ind.Eng.C. = Industrial and Engineering Chemistry
- R.P. = Russian Patent
- N.P. = Norwegian Patent
- J.Ph.C. = Journal of Physical Chemistry
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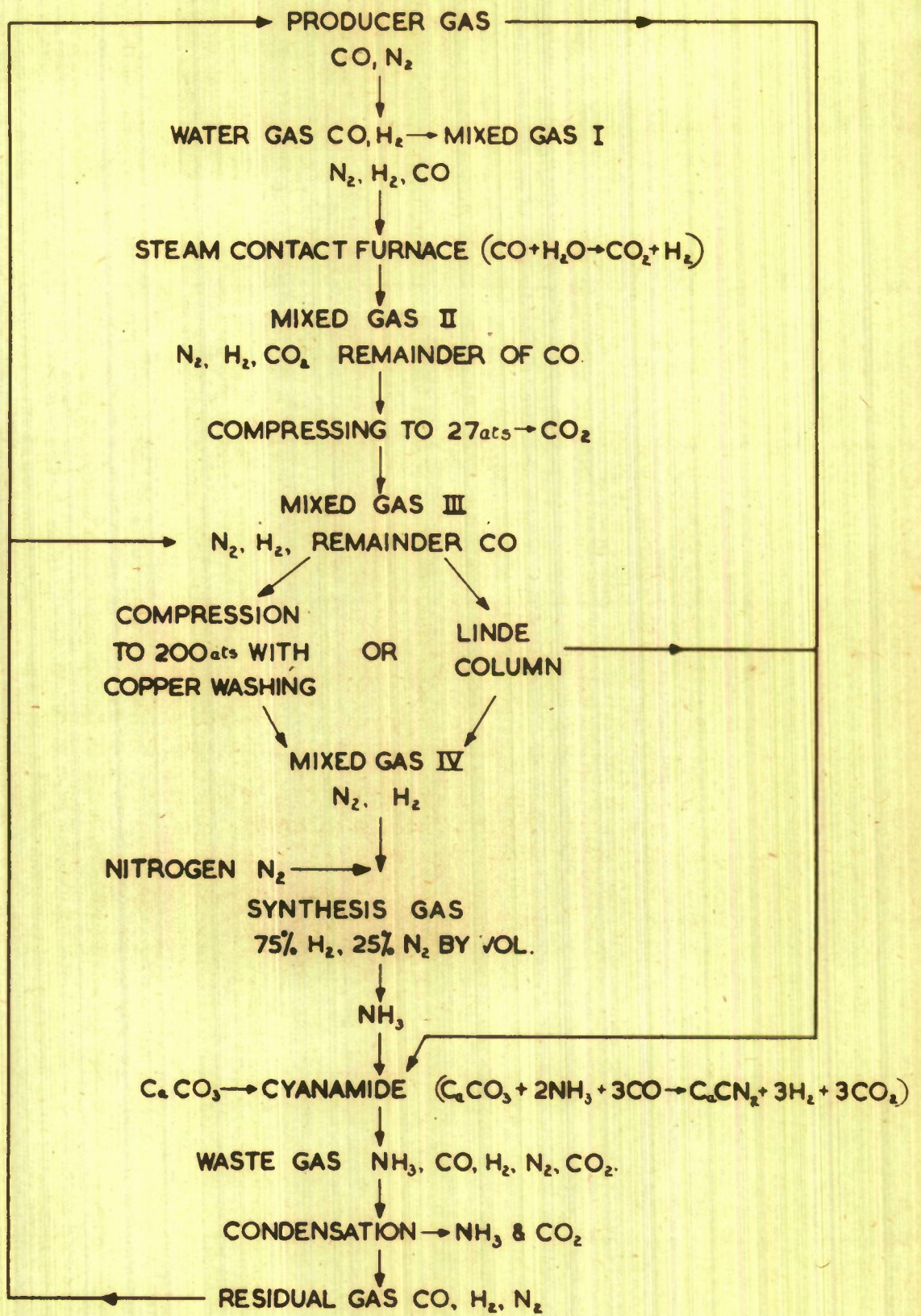


FIG. I

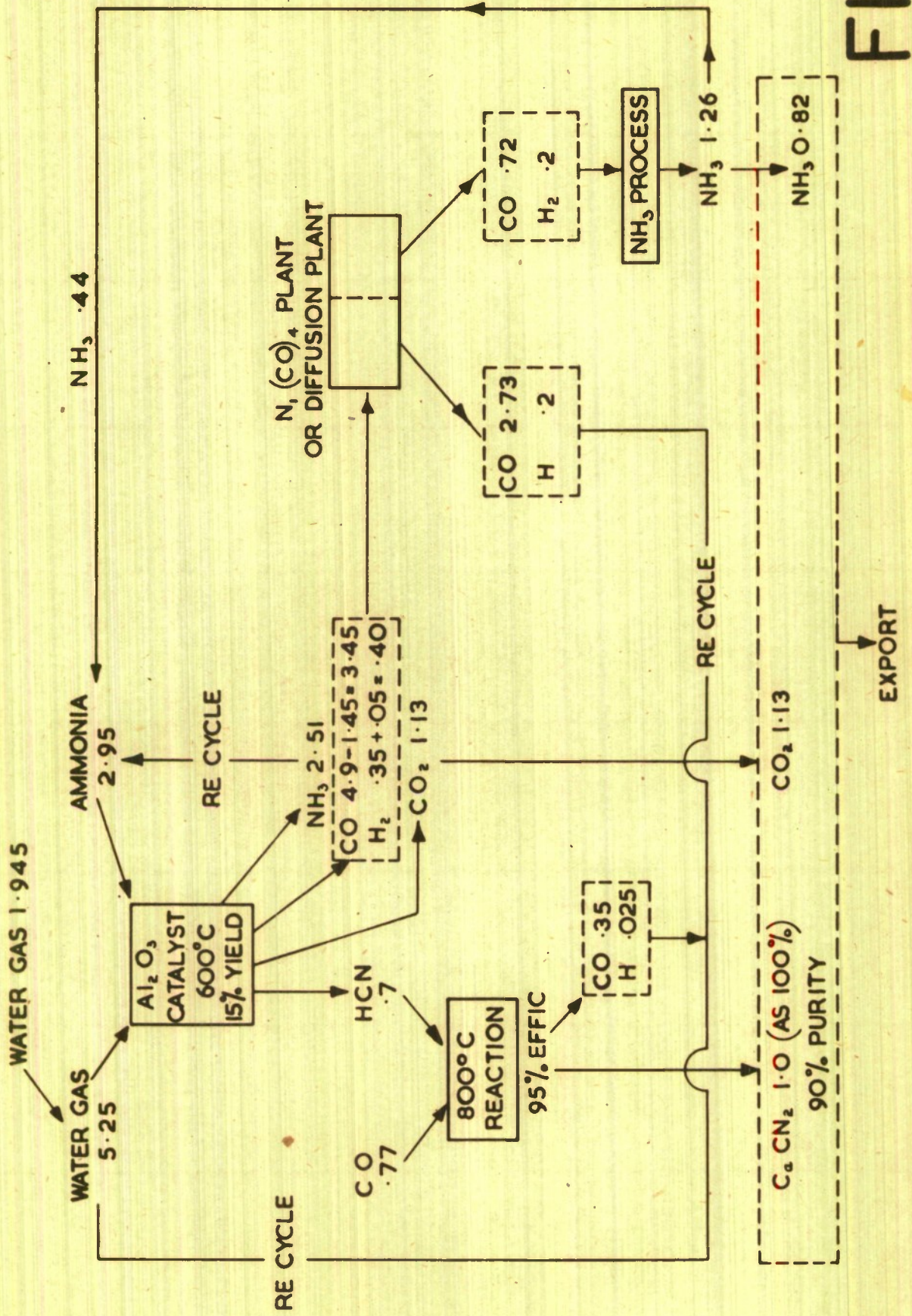


FIG. 2

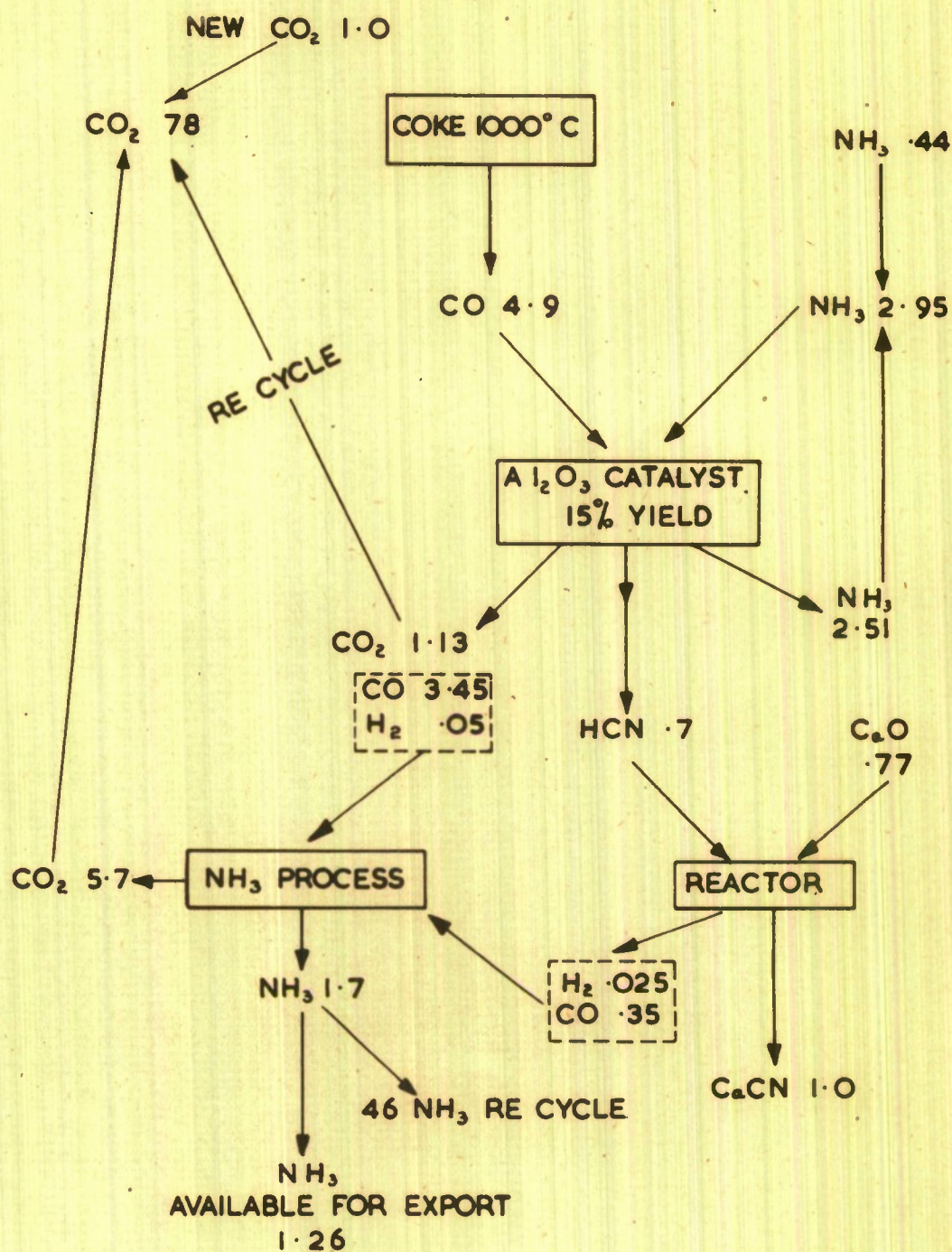


FIG. 3

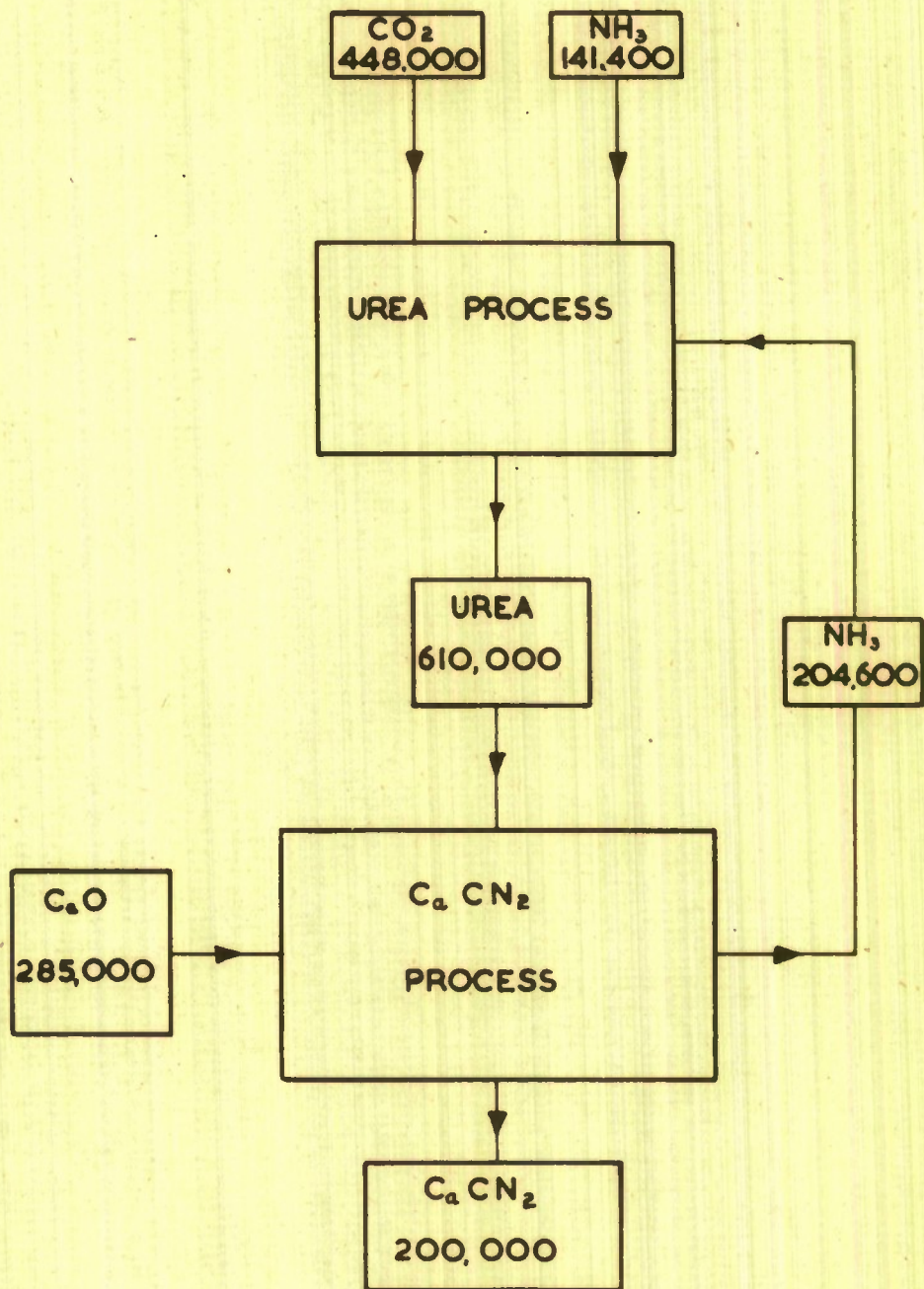


FIG. 4

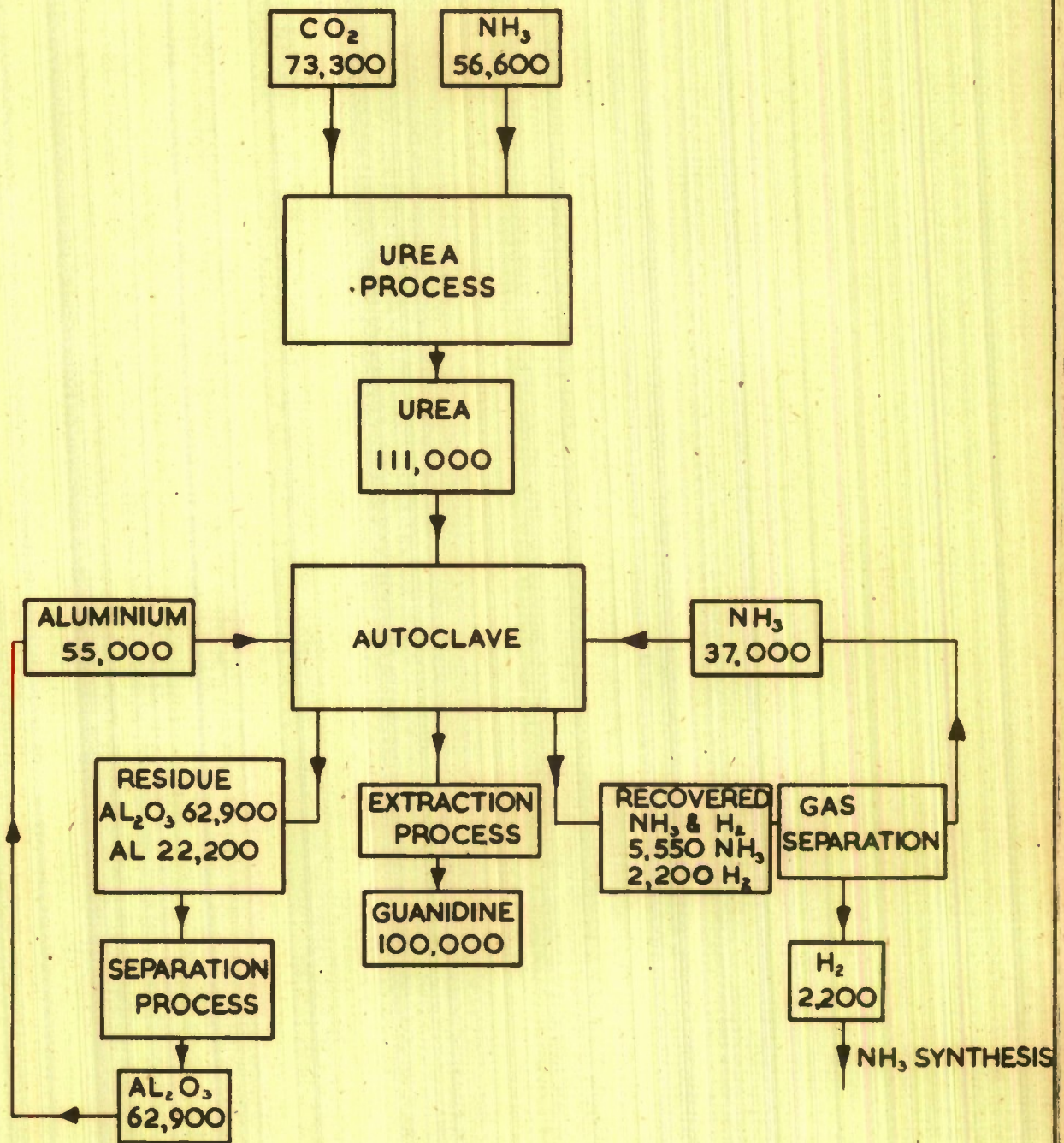


FIG. 5

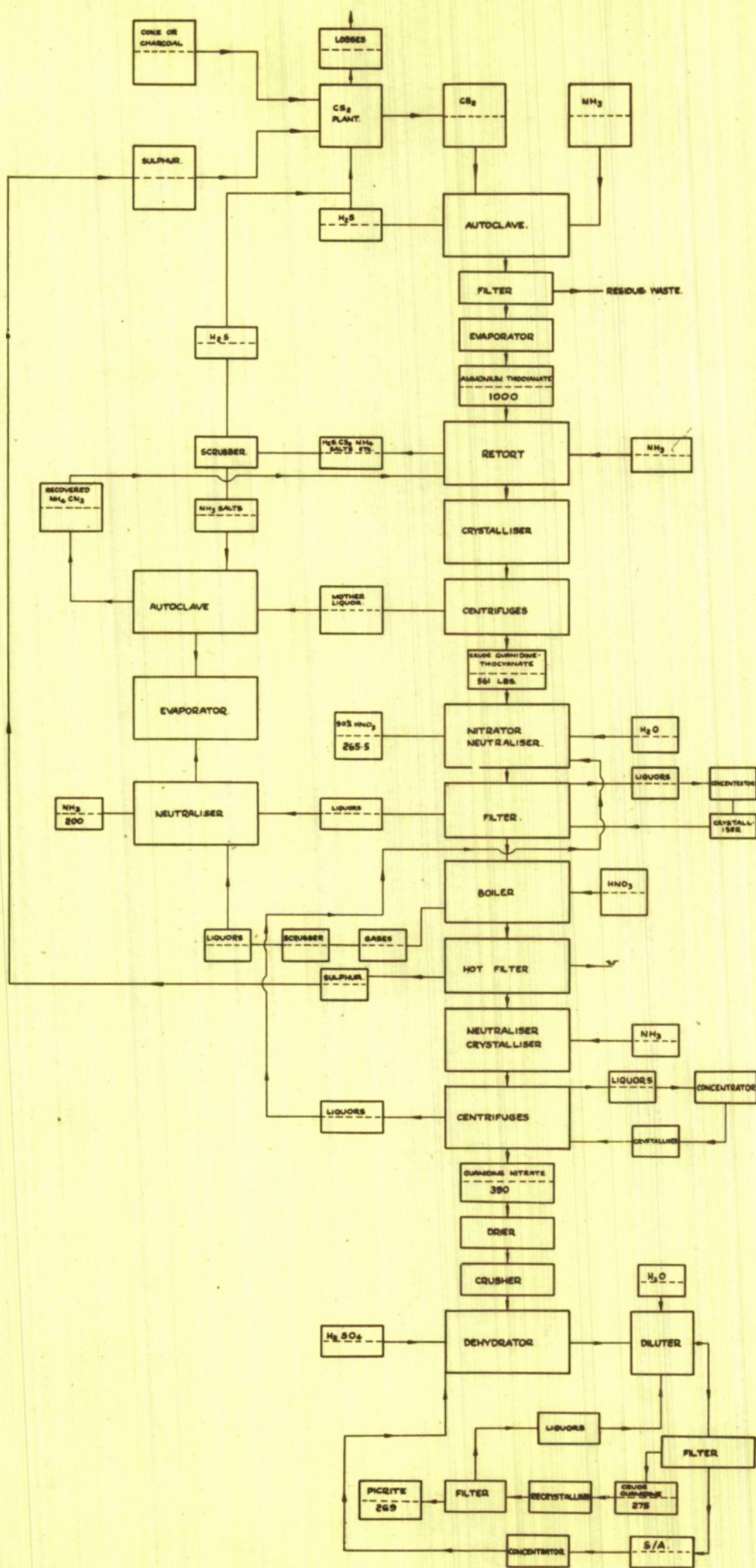


FIG. 6

4 Nov., 1947.

C.R.D.D. Report No. 307/R/47. A Review of the Literature  
and of Work done in A.R.D. and C.R.D.D. on Picric and its  
Intermediates with a View to Finding a Cheap and  
Economical Process.

Mr. Anderson:

I have read this treatise over and have  
the following comments to offer:

1. The study has been made and conclusions  
have been drawn purely from the stand-  
point of producing nitroguanidine in  
England. From that point of view,  
the reasoning and the conclusions drawn  
from it seem sound. In this country,  
however, we are in a much more fortu-  
nate position in several respects, par-  
ticularly with regard to availability of  
certain raw materials, electric power  
and chemical plant. For this reason,  
some some of the processes considered  
impracticable for use in England  
might logically be used in this country.
2. Action of  $\text{NH}_3$  Alone or Mixed with Other Bases  
on  $\text{CaCO}_3$ .

Owing to the low conversion of ammonia  
and the low purity of calcium cyanamid  
obtained, it seems doubtful that this process  
is of any practical value either here or in  
England; but this conclusion should not  
be accepted as final.

3. By Heating Ammonium Thiocyanate.

This process would be more logical for use here than in England because the materials are available here and shipping requirements are not such a factor. The yields obtained are so small, however, that it would almost seem that the process might be eliminated from further consideration on that ground alone. The cost of plant required is a further serious objection.

4. By Action of HCN on Lime at Moderately High Temperatures. (About 500-600°C).

The author points out that the availability of HCN at a reasonable price is a critical factor in this process. The same would be true in this country. It is stated that the market price of HCN in England was over £100 per ton (about 20-25 cents per pound.). 1.5 parts of HCN are required to make 1 pound of nitroguanidine. It was considered that the cost of nitroguanidine would be prohibitive on this basis.

Present price of HCN in this country is about 80 cents per pound - which would be quite out of the question. It seems probable that this could be reduced very greatly if

the material were produced in sufficient quantity.

Other disadvantages of the HCN-lime process are that HCN is a very "sticky" material to handle, being at the same time an extremely poisonous substance and a powerful high explosive.

It would seem that if ~~so~~ nitroguanidine is to be made at all through HCN, a more logical method would be to convert the HCN to cyanogen chloride (CClN) and react this with ammonia to produce cyanamid. This process will be discussed below.

5. From Thiocyl or Sulphuryl Chloride and Urea.

This reaction is not believed to have even enough merit to warrant discussion.

6. By Reaction of Lime with Urea.

Same comments as under (5).

7. From Cyanogen Chloride and Ammonia.

This process, like (4), depends upon the availability of HCN at a reasonable price, which is not assured at present. It has, however, the following advantages over the process discussed under (4).

a. It does not involve the preparation

of HCN in concentrated form and thereby avoids the hazard of explosion.

- b. HCN is easily converted into cyanogen chloride.
- c. Cyanogen chloride reacts with  $NH_3$  at  $100^\circ C$  in alcoholic solution to give a quantitative yield of cyanamide ( $H_2N-CN$ ), which goes on quantitatively into guanidine hydrochloride.
- d. Guanidine hydrochloride is converted easily and in good yield to nitroguanidine.

A disadvantage of this process is that it involves the handling of cyanogen chloride, which is very poisonous.

The process might be reasonably economical. All things considered, it is believed that this is among the more promising of the processes reviewed herein and that it should be studied further if a serious effort should ever be made to develop an alternative process to the one now used for making nitroguanidine.

8.

From Urea, Liquid Ammonia and Aluminum, Aluminum Chloride or  $P_2O_5$ .

This process appears plausible from

the standpoint of chemical theory and is indicated to be quite promising by the information given in the treatise being reviewed. Considerable doubt is thrown on the latter, however, by the statement on page 20, that a yield of 800 grams of guanidine hydrochloride was obtained from 300 grams of urea, 100 grams of ammonia and 670 gm of AlCl<sub>3</sub>. The maximum yield theoretically possible would have been only 475 grams.

From purely theoretical considerations it would appear that aluminum chloride would give better results than metallic aluminum powder in this reaction.

This process is probably one of the better ones among those which have been considered.

9. The data on which the above comments are based ~~are~~ <sup>are</sup> ~~messy~~ ~~in~~ ~~most~~ ~~instances~~ are in most instances and inefficient for reaching real conclusions as to the yields to be expected, cost of the finished product or the cost of plant for a given capacity. The comments must be regarded merely as opinion and probably as rather rough opinion at that. With these qualifications, however, the

following processes are believed to be worthy of serious consideration in any effort that may be made <sup>in this country</sup> to develop an alternative to the present process for manufacturing nitroguanidine:

- a. The reaction of cyanogen chloride with ammonia. (7 above).
- b. The reaction of urea, liquid ammonia and aluminum chloride. (8 above).
- c. While probably less promising than either (a) or (b), the reaction between ammonia and calcium carbonate should not be ruled out without further consideration.

D. W. S.

Note:

Under "Nitroguanidine" a publication of Division 8, NDRC entitled "Compilation of Data on Organic Explosives" states that nitroguanidine may be obtained in 92% yield by fusing  $NH_4NO_3$  with  $NH_2CONH_2$ .

$NH_2CONH_2 + NH_4NO_3 \rightarrow H_2NC(NH)NHNO_2 + 2H_2O$ . The authority cited for this statement is a Canadian Report of Aug. 15, 1943 on XR-58 (C-593). Attempt being made to secure this report.



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