The Manufacture of Hydrocyanic Acid by the Andrussow Process

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The manufacture of hydrocyanic acid by the catalytic combination of methane, ammonia and air has increased remarkably in recent years. Some of the features of this process, particularly the variety of platinum metal catalysts employed in it, are surveyed in this article.

Cyanogen compounds have in the past been employed chiefly in the extractive metallurgy of silver and gold, in electroplating and for the surface hardening of metals. Manufacture was chiefly through the Landis and Castner processes, neither of which however yielded hydrocyanic acid directly.

The development since the thirties of extremely useful polymeric acrylic compounds has created a demand for very considerable quantities of hydrocyanic acid, and several methods of direct synthesis have been intensively studied. A synthesis from carbon monoxide, methane and ammonia through an intermediate formate-formamide stage has been employed by the Koppers Company. A large plant for the production of hydrocyanic acid direct from carbon monoxide and ammonia was built in Germany during the war, but was never put into operation.

The method which has, in a variety of modifications, proved generally successful, is based on that first described by Andrussow in 1930 (1) which employs methane, ammonia and air.

The Uses of Hydrocyanic Acid

The greater part of the hydrocyanic acid manufactured in this way is consumed in the manufacture of acrylonitrile, either by condensation with ethylene oxide to form ethylene cyanhydrin, or directly by liquid-phase catalytic combination with acetylene.

Acrylonitrile is polymerised with butadiene to form special-purpose synthetic rubbers (G.R.'N'). These nitrile rubbers are used for mechanical rubber pads, textile and paper sizings, and for petrol and oil resistant goods. They are marketed in the United States under brand names Hycar, Paracril, Butaprene and Chemigum. Hycar will shortly be manufactured in this country by British Geon Ltd. Acrylonitrile polymers are also capable of being spun into textile fibres, and its employment in such materials as Vinyon, Dynel, Acrilan, Orlon and Creslan is now the largest single use.

Smaller proportions of hydrocyanic acid are required for the manufacture of acrylates and methacrylates, which can be polymerised to form plastics, such as Perspex, with very high optical transmission, and in the preparation of adiponitrile, a necessary intermediate in the manufacture of Nylon. Small quantities are also used in the production of acrylic acid, which forms polymers exhibiting strong hydrophilic properties.

The Principles of the Process

The endothermic conversion of methane and ammonia into hydrocyanic acid and hydrogen according to the reaction

$$CH_4 + NH_3 \rightarrow HCN + 3H_2 - 60K \text{ Cal.}$$

is theoretically possible, but the practical difficulties of supplying heat to maintain the required reaction temperature of 1000 to 1200°C make it unattractive. The strongly exothermic reaction obtained by the catalytic

combination of methane, ammonia and air

$$CH_4 + NH_3 + 1\tfrac{1}{2}O_2 \rightarrow HCN + 3H_2O + 115K \text{ Cal.}$$

is better suited to large-scale manufacture, since after it is initiated, at a temperature of about 1000°C, it becomes self-sustaining. Although other hydrocarbons could be substituted for methane, this does not appear to have been done in any of the successful processes.

To obtain an optimum yield a very short contact time, of the order of 0.0003 second, is desirable and consequently a high operating temperature is necessary to reach equilibrium. In practice, some carbon monoxide and nitrogen are formed by direct combustion and some ammonia is decomposed at the high operating temperature, so that the product gases contain hydrogen cyanide, nitrogen, carbon monoxide, carbon dioxide, hydrogen and water vapour, as well as unconverted ammonia that must be recovered. Apart from the greater complexity of the recovery arrangements, the operating characteristics of the process are closely similar to those of the old established ammonia oxidation process.

Low-cost anhydrous ammonia can easily be obtained in any major centre of chemical industry. At present natural gas forms the principal source of cheap methane, and is used by the Montecatini Company in Lombardy and by manufacturers in the United States. Where natural gas is not available, town's gas or coke-oven gas must be methanised over a nickel catalyst. Petroleum refinery gases may also be employed.

Platinum Gauze Catalysts

Although the use of base metal oxides, or iron, bismuth and cobalt have been described in patents, all the reported processes employ platinum-group metal catalysts. A pad of gauzes woven from platinum or platinum alloy wire, similar to the catalyst pads used for ammonia oxidation, enables a short contact time to be obtained and offers little
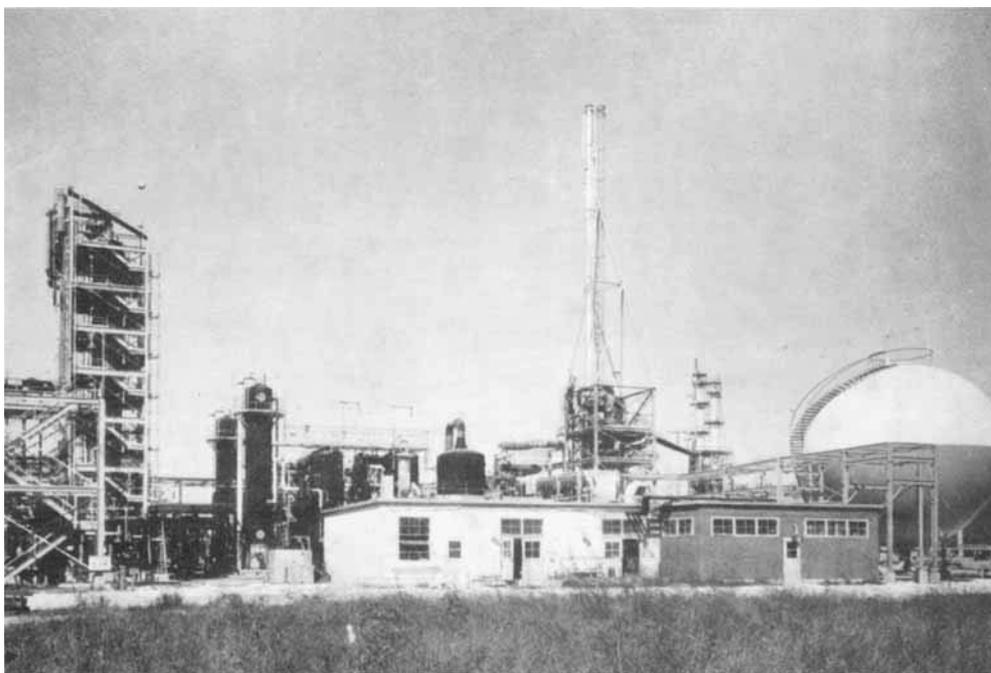
A general view of the hydrogen cyanide unit in the Fortier Plant of the American Cyanamid Company at New Orleans

Rhodium-platinum alloy wire gauze before use (left) and after about 1,000 hours exposure to catalytic reaction
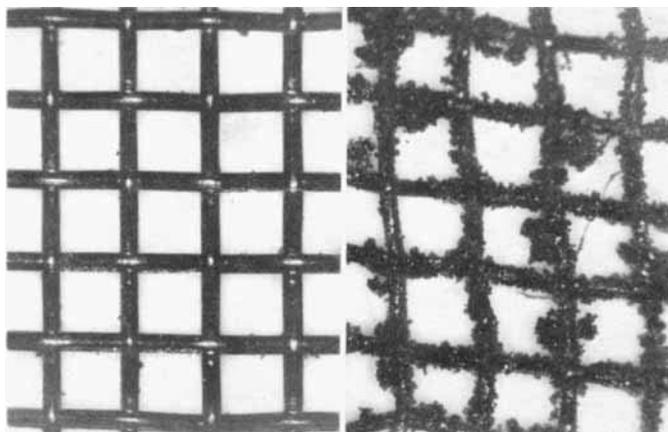
resistance to the high velocity gas flow. It can also be preheated with little difficulty to initiate the reaction. Catalysts of this sort were in fact proposed by Andrussow. Their use has however been accompanied by some difficulty.

Chretien and Thomas (2) and Maffezzoni (3) found that after a short period of use, embrittlement of the wires and deposition of carbon occur. The trouble is particularly pronounced at the periphery, and it was proposed in United States Patent 1,957,749 (assigned to B. F. Goodrich & Co.) to clamp the gauze pad between ceramic or refractory rings and to flush the catalyst edges with carbon-free gas.

It is probable that the difficulties are mostly associated with impurities in the feed, or with imperfect control of feed composition, since in the Rohm and Haas plant at Darmstadt, described by Kautter and Leitenberger (4), a gauze life of 4,000 hours was being obtained, and a life of 8,000 hours—approximately a year—was expected with more experience. In this plant, 10 per cent rhodium platinum alloy gauzes are employed, several being placed together in a pad and supported so as to minimise mechanical stress. No volatilisation of the platinum occurs, and the operational conditions are controlled so as to avoid deposition or over-heating.

A catalyst loss rate of 0.6 gm per ton of hydrogen cyanide produced was reported in a pilot unit operated by the Freeport Sulphur Company.

Catalyst operating temperatures are higher than in ammonia oxidation, ranging from 900 to 1200°C, so that the use of rhodium alloys which have much greater mechanical strength and lower recrystallisation rates than pure platinum at these temperatures is evidently desirable. No differences in conversion efficiency between pure platinum, rhodium-platinum or iridium-platinum have been reported. Although Andrussow (5) has recommended the use of gauze with thicker wire and larger meshes than normal, only conventional ammonia-oxidation gauze has generally been used.

Either 5 per cent and 10 per cent rhodium-platinum, 0.06 mm or 0.076 mm $\times$ 1024 mesh are typical specifications. The growth of dendritic crystals on the surface of the catalyst wires, which is always observed during the oxidation of ammonia, is evidently characteristic of this process also. Heavy metals, as well as arsenic and sulphur compounds, are acute poisons to the platinum and platinum alloy catalysts.

Supported Platinum Catalysts

The high operating temperatures and gas velocities essential to this process impose relatively severe stresses on gauze catalysts, and a great deal of attention to supporting the pads has been necessary. Ceramic rod
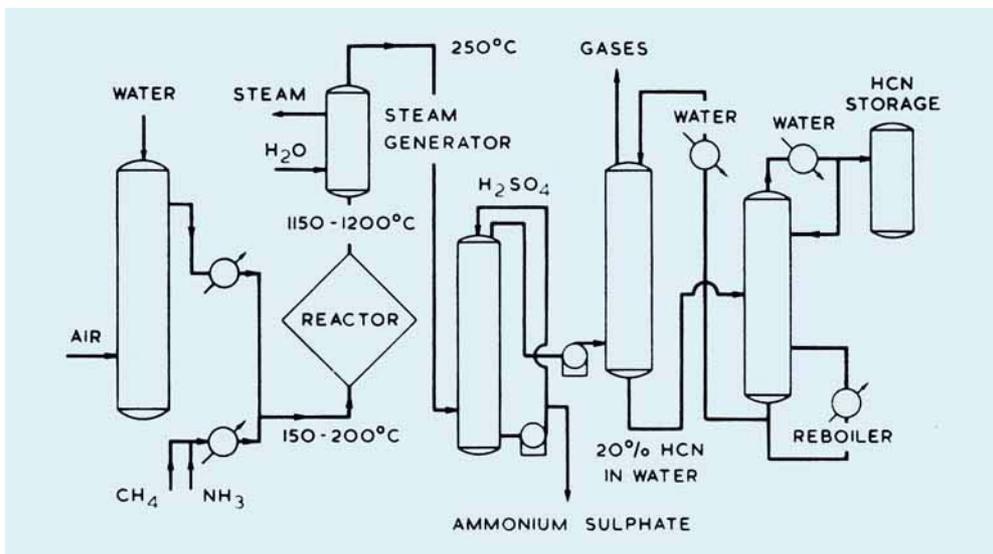
*Flow diagram of the Montecatini process for the catalytic synthesis
of hydrogen cyanide from methane, ammonia and air*

supports were used at Darmstadt. Metal supports made of heat-resisting materials which are not catalyst poisons are described by B. F. Goodrich in British Patent 739,277.

There has consequently been considerable interest in the development of supported catalysts capable of withstanding the high operating temperatures, and a number of proposals have been made, some of which have been satisfactorily put into operation. In this, the process is notably different from that of ammonia oxidation.

Maffezzoni made experiments with platinum dispersed on a considerable variety of carriers, and the Montecatini plants now employ supported catalysts of this sort in their operations with natural gas. Supported catalysts containing mixtures of platinum metals—for example, rhodium and platinum —have been employed.

In the United States Patent 2,726,931 assigned to du Pont, a supported catalyst comprising 20 per cent rhodium and 80 per cent platinum on an alumina-zirconia porcelain base is described. The platinum metals are applied to the base by successive depositions and firings. The catalyst is

intended for use at 1000 to 1200°C. In British Patent 737,995, in the name of Lonza Elektrizitatswerke, the use of tubular reactors with the active material dispersed on the tube walls is proposed. United States Patent 2,666,689 assigned to Monsanto Chemical Company claims the use of a novel catalyst, a bed of electrodeposited rhodium crystals $\frac{1}{4}$ inch thick supported on non-reactive material. The reaction is to be conducted at 1200°C with a contact time of only 0.0002 second.

Processes and Plants

Although they all adhere to the same fundamental catalytic method, the various modifications of the Andrussow process differ in their sources of methane, in the proportions of reacting gases, in the nature of the platinum metal catalyst, and in the means of collecting and purifying the product, and recovering or recycling the excess ammonia. The technical and commercial developments of the various modifications up to the beginning of 1954 have been reviewed by Sherwood (6).

Although natural gas is the preferred

source of methane, there are of course few areas where it is readily available and in the German plant of Rohm and Haas, methane is obtained from Ruhr grid gas (town's gas) by reacting the carbon monoxide and carbon dioxide with hydrogen over nickel catalysts. Other synthetic sources of methane are also employed.

B. F. Goodrich & Company, in various patents, claim the advantages of a high methane to ammonia ratio and are able to employ unpurified natural gas in a gauze catalyst process at an operating temperature of 1100 to 1260°C. The advantages of employing a high air to gas ratio in the feed are claimed in United States Patent 2,706,675, assigned to Freeport Sulphur Company.

Rapid cooling of the reacted gases is necessary to minimise decomposition, and it is usual to have a waste heat boiler immediately following the converter. There are numerous variations in the methods of recovery, but most of them comprise the two basic steps of ammonia recovery by washing with acidified ammonia sulphate solution, followed by absorption of the hydrogen cyanide in water, sometimes under pressure, from which it is subsequently recovered by distillation and condensation. The hydrogen cyanide can be recovered from the still overhead at a concentration of 98.5 per cent or better, and it must be continuously stabilised since hydrogen cyanide has a pronounced tendency to polymerise and explode, particularly under alkaline conditions. For this reason, it is essential in all recovery processes that uncombined ammonia is removed from the product stream before the hydrocyanic acid is condensed. It is usual to add small quantities of sulphuric or phosphoric acids to act as polymerisation inhibitors.

In the novel recovery process developed by the Freeport Sulphur Company (United States Patent 2,590,146) both hydrogen cyanide and ammonia are simultaneously absorbed. The absorption medium is based on a polyhydroxy boric acid complex—an aqueous solution of pentaerythritol and boric acid—in which the hydrogen cyanide dissolves, but with which the ammonia combines. The hydrogen cyanide can be recovered by vacuum distillation at moderate temperature; the cyanide-free solution is subsequently stripped at a higher temperature at which the ammonium salt is dissociated.

The manufacture of hydrogen cyanide obviously involves great toxic and explosive hazards and a significant part of the cost of all modern plants results from the elaborate safety precautions necessary to protect operating personnel. Great care must also be devoted to the effective treatment of plant effluents because of the toxicity of cyanide to aquatic life.

Among European chemical manufacturers interested in this process are Imperial Chemical Industries, Montecatini (3), Rohm and Haas (4), Ugilot and Lonza. In the United States similar processes have been developed by B. F. Goodrich & Company, Rohm and Haas (7), Freeport Sulphur Company (8), Monsanto Chemical Company, du Pont, American Cyanamid Company, Carbide and Carbon Chemical Company and The Girdler Company.

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