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Kiev, USSR, 21 September - 1 October 1971

New Delhi, India, 2 - 13 October 1971

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THE MONTEDISON UREA PROCESS FOR LARGE CAPACITY PLANTS<sup>1/</sup>

by

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SUMMARY

THE MONTECATINI UREA PROCESS FOR LARGE CAPACITY PLANTS<sup>1/</sup>

by

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The industrial synthesis of urea is obtained by modern processes intended to solve in the most economic and rational way the fundamental problem of how to recycle to the reactor the ammonia and carbon dioxide resulting from the decomposition of ammonium carbamate not converted into urea. In the stripping processes with  $\text{NH}_3$  or  $\text{CO}_2$ , carbamate is decomposed at the same pressure as that of the synthesis reactor and the gases are sent back to the reactor prior to condensation. In the ME process, decomposition is obtained by heating at a pressure of about 60 atm., followed by condensation at the same pressure. Due to the high temperature at which condensation takes place, the heat is recovered as steam and used in the same plant both directly and after turbo-compression.

Such a process was successfully implemented for the first time in a urea plant of capacity 700 mt/d, which started operating in 1968, in another plant of 1,000 t/d prilled urea, and in five additional large-capacity plants.

It is a high efficiency cycle, owing to the high reaction pressure (200 kg/cm<sup>2</sup> g.) and high  $\text{NH}_3/\text{CO}_2$  ratio to the reactor, with low recycle (low  $\text{H}_2\text{O}/\text{CO}_2$  ratio), without requiring the addition of water in the condensation phase. The total consumption of steam at 20 kg/cm<sup>2</sup> g. is 850 kg/t urea, which ranges among the lowest quantities needed

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by the various modern processes. The process is also characterized by the admission of about  $\frac{1}{7}$  of  $\text{CO}_2$  into the carbamate condenser at about  $80 \text{ kg/cm}^2 \text{ g.}$  this allows condensation of all recycle ammonia without additional equipment thus there is also an increase in the quantity of heat recovered in the carbamate condenser corresponding to the quantity of carbamate formed by the primary  $\text{CO}_2$  fraction introduced into it.

Three solutions are considered:

- 1) all the machines are motor-driven and steam exported.
- 2) turbo-compression from 2 to  $4 \text{ kg/cm}^2 \text{ g.}$  of the steam produced and its complete consumption in the plant
- 3) main machines driven by steam turbines, with a large reduction of electric power consumption.

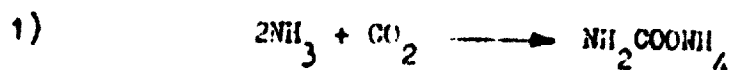
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We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

## I. INTRODUCTION

In all processes, the industrial synthesis of urea is obtained by reacting liquid ammonia and gaseous carbon dioxide at high pressure and temperature. There is formed ammonium carbamate by means of highly exothermic reaction (1) :



After an adequate residence time in the reactor, within a temperature range between 160 and 200 °C and a pressure range between 100 and 250 atm., reaction 1) practically complete, is followed by endothermic reaction 2) in the liquid phase:



Reaction 2) is not complete and has a urea conversion efficiency of 50 to 70% according to the operating conditions. The key factors for obtaining a high urea efficiency per pass and as a consequence a low recycle of unreacted to the reactor are : temperature, pressure and molar ratios of  $\text{NH}_3$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to  $\text{CO}_2$ .

In modern total-recycle plants all ammonia and  $\text{CO}_2$  must be converted into urea and water; therefore the not converted reagents have always to be separated from the urea solution and to be recycled to the reactor. Recently, the properly called stripping processes have solved the above fundamental recycle problem by decomposing most of the carbamate not transformed into urea at the same reaction pressure, stripping off with primary gaseous  $\text{NH}_3$  or  $\text{CO}_2$  the solution effluent from the reactor. The carbamate dissociation tension in heterogeneous equilibrium 1) is in fact function of the vapour phase temperature and composition. If any of the two vapour phase components ( $\text{NH}_3$  or  $\text{CO}_2$ ) is in excess, carbamate may also dissociate at a high pressure.

The gases thus stripped are condensed and recycled to the reactor.

The most important advantage those processes offer as compared to the former ones is the possibility to condense the gases obtained from stripping at the same reaction pressure without adding process water, with the recovery moreover of the

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condensation heat to produce low pressure steam. High pressure stripping actually allows carbonate distillation (even if not complete) at the reactor pressure, by merely reducing the usual reaction pressure from 200 + 250 atm. to 130 + 150 atm.; in this way the reaction efficiency lowers considerably because, at such a reduced pressure, in order to maintain the reagents in the liquid stage as required by reaction 2), also temperature must be lowered. Besides this negative factor regarding the conversion efficiency, there is another one which affects the stripping processes: the ammonia quantity too is to be reduced, unless the amount of process water is increased, in order to maintain the reagents in the liquid phase.

Moreover, like former processes, the stripping ones require various recycle stages at decreasing pressures in order to recover all ammonia; such recovery by stages is obtained in the form of an aqueous solution, which practically means a water flow back to condenser and consequently to the reactor.

Also the processes without stripping with aqueous solution recycle can be considerably improved once the obstacle of the condensation heat recovery is overcome; that implies the need of condensing after distillation at a suitably high pressure, even if considerably lower than the synthesis pressure, so as to increase temperature and allow heat recovery by steam production to be used in the same plants. This difficulty has been overcome by the Montecatini Edison process on which are based many large urea units in operation.

Thus the purpose of reducing steam consumption to about 850 kg/t of urea has been attained as done in the stripping processes, while respecting at the same time the conditions for high efficiency and low recycle, that is high  $\text{NH}_3/\text{CO}_2$  ratio, low water content in recycle carbonate and high reaction temperature.

The main characteristic of all the modern processes is low steam consumption, this being one of the fundamental plant savings. Now in fact in all processes,  $\text{NH}_3$  and  $\text{CO}_2$  requirements reach values that are not far from the stoichiometric one. In the various modern processes heat recovery is obtained by means of steam produced at a temperature allowing it to be used for the process, and not by means of direct



heat exchange between process streams.

Before examining the new Montecatini Edison process, it may be added that the modern stripping processes have been substantially intended to reduce heat consumption for carbamate decomposition. In fact, when in former processes improvements were gradually made meant to reduce the quantity of unreacted carbamate by a high conversion efficiency (obtained by increasing the  $\text{NH}_3$  to  $\text{CO}_2$  ratio and decreasing the  $\text{H}_2\text{O}$  to  $\text{CO}_2$  ratio) and meant to recover the condensation heat (by raising temperature), they always inevitably resulted in a rise of the reaction temperature (due to the smaller recycle to which the reaction heat was to be yielded) and a higher enthalpy entering the reactor (due to the higher carbamate temperature). It was therefore indispensable to remove considerable heat quantities from the reactor; in fact the two parallel effects of high efficiency and bigger thermal recovery practically brought the first condenser pressure to coincide with that of the reactor and it was consequently impossible in the first distillation unit to conduct as usual decomposition of the carbamate in equilibrium with its own gases at the same pressure as in the 1st condenser.

The various methods followed during these last years to overcome the above difficulty are substantially the only feature which differentiates the various processes; they are :

Pressure lowering in the first distiller to normal values (30 atm.)

↓  
adiabatic thermocompression of the gases up to the reactor pressure (Chemico)

Modification of the carbamate dissociation equilibrium

↓  
stripping with primary  $\text{CO}_2$  (DSM and Horsk hydro)

↓  
stripping with primary  $\text{NH}_3$  (SIAL and Weatherly) ( $\text{NH}_3$ , inert gases)

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In all the three processes, heat is recovered in the form of steam, to be used in the plant itself for thermal uses (DSM and SNAM) or as power (for compressor running) and subsequently for thermal uses (Chemico).

SNAM stripping process has been recently (1) modified so as to reduce some of the above disadvantages. More precisely, the reactor pressure has been rendered independent of pressure in the stripper-condenser group. As done in the Montecatini Edison process patented in 1967 (2), a carbon dioxide portion is admitted into the carbamate condenser; the condensation heat is recovered as always by the production of low pressure steam. The carbamate solution effluent from the condenser is brought again to the reactor pressure by an ejector using a portion of primary ammonia as power (while the balance is sent to the stripper). Evidently a limitation is caused by the portion of the ammonia to be used as power which is not such as to permit a reaction pressure much higher than that of the stripper.

## II. NEW MONTECATINI EDISON PROCESS

Unlike what necessarily occurred in the stripping processes with inert gases or with  $\text{NH}_3$  or  $\text{CO}_2$ , in the new Montecatini Edison process there is no need of lowering the reaction pressure and temperature with all the entailed negative aspects deriving from the decreased conversion efficiency of carbamate into urea. Temperature and pressure (200°C and 200 atm.) have been even slightly increased without repercussions in connection with the danger of stainless steel corrosion in the reactor lining. In fact it has also been possible to maintain the  $\text{NH}_3/\text{CO}_2$  ratio high (it is known that the solution corrosiveness decreases as excess ammonia increases).

No changes therefore with regard to high pressure synthesis - exception made for an improved efficiency - and no need of experimenting. The new concept of the process concerns the operating conditions for the apparatuses immediately downstream of the reactor, mainly the carbamate decomposer and the carbamate condensers. Briefly, there has been optimized the carbamate decomposition pressure; the solu-

tion effluent from the reactor is decomposed in a distiller at 80 atm. and 190°C into  $\text{CO}_2$  and  $\text{NH}_3$  and most of excess  $\text{NH}_3$  is evaporated by means of the steam line heat.

A complete solution of this key point could not be found in a theoretical way only; a modest experimentation has been required. It has been necessary to ascertain whether at a relatively high pressure the carbamate dissociation would occur almost completely without modifying equilibrium 1) by adding  $\text{CO}_2$  or  $\text{NH}_3$ , as done in the stripping processes. Theoretically, mechanisms have been expected to conduct dissociation of carbamate in solution. They have been subsequently verified by means of dynamic determinations of vapour tensions of various composition carbamates.

That is actually the only experimentation required prior to the design of an industrial plant capacity 700 t/d, which started operating in June 1968 in the G.M.A. Factory at Sluiskil, Netherlands. The decomposition gases, separated from the urea solution, always at the same pressure of 80 atm., are mostly condensed in an apparatus described elsewhere (3) of special design, in the form of ammonia aqueous solution and carbamate at relatively high temperatures : 145 °C at the upper inlet and 135°C at the lower inlet.

Gas condensation occurs at the decomposition pressure (80 atm.) and under conditions suitable to produce steam at 3 kg/cm<sup>2</sup> abs. to be used for the process or available for export. In this apparatus, about 875 kg of steam per metric ton of urea are produced with enormous advantage for the whole process savings. In the mentioned plant, a portion of this steam is also turbocompressed to raise pressure up to 5 kg/cm<sup>2</sup> abs. and is used in the plant itself. The selection of the cycle with or without steam turbocompression is conditioned by the actual distribution of the factory steam lines. In any case, the production plant requires a max. steam consumption of 850 kg per ton of urea considering steam at 20 kg/cm<sup>2</sup> abs. A characteristic of the new process is also the admitting of a portion of primary  $\text{CO}_2$  (about 1/4 of the total) into the condenser instead of the reactor; that offers the following advantages :

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- a modest reduction - not to be however neglected - of power consumption for  $\text{CO}_2$  compression, as  $1/4$  of it is compressed only up to 80 atm. instead of 200 atm.;
- possibility to condense at 80 atm. almost all recycle ammonia without separate equipment for rectification, condensation and recycle;
- increase in the quantity of heat recovered in the first condenser corresponding to the carbamate formed from the fraction of primary  $\text{CO}_2$  admitted into it;
- pressure reduction in the 1st condenser (in spite of the low  $\text{H}_2\text{O}$  content and of the high ammonia content in the recycle composition).

It is definitely a high efficiency process (low  $\text{H}_2\text{O}/\text{CO}_2$  ratio and high  $\text{NH}_3/\text{CO}_2$  ratio) with a high heat recovery.

The process is in fact characterized by the following basic parameters :

- molar ratio of  $\text{NH}_3$  to  $\text{CO}_2$  : (3.6)
- molar ratio of  $\text{H}_2\text{O}$  to  $\text{CO}_2$  : (0.50)
- conversion efficiency : (0.63)

A successful implementation of the process design for the first industrial plant was expected. Such plant was started up as safely and rapidly as other plants based on the previous widely experimented processes; that was actually the consequence of the use of techniques and apparatuses already satisfactorily applied, thus avoiding for instance new-design apparatuses such as  $\text{CO}_2$  or  $\text{NH}_3$  stripper or recycle gas thermocompressor or reactor with incorporated exchangers and relevant problems. Also the new carbamate condenser natural circulation type was actually similar to the previous ones, having to operate as vertical water tube boiler instead of working by cooling water, with the advantages of a small tube/shell  $\Delta t$  (expansion problems) and of a constant temperature on the steam side.

### III. DESCRIPTION OF THE PROCESS

The process which is outlined below has been followed in a plant capacity 1,000 t/d prilled urea already in operation on an industrial scale. The key concepts

mentioned above (Fig. 1) are applied in this process. Since recovered steam could be used for external use, the steam turbocompressor is not employed and therefore the consumption of fresh steam at 25 kg/cm<sup>2</sup> abs. is 1,100 kg/mt urea with a recovery of 250 kg steam at 3 kg/cm<sup>2</sup> abs., which corresponds to a net specific consumption of 850 kg; all the machines are electric motor driven. Raw materials requirements and recoveries as well as utilities are reported in Case I Table 1.

Liquid ammonia and CO<sub>2</sub> are both compressed in PA1 and CA1 up to the synthesis pressure (200 kg/cm<sup>2</sup> abs.); (ammonia is preheated by steam). They are sent to reactor A1 (which is a column without internals). A CO<sub>2</sub> portion (about 1/4) is drawn from the last but one stage of CA1 at 80 atm. and is sent to condenser F2. The mixture effluent from the reactor at 200 atm. and 200°C is expanded and sent to distiller F1 where most carbamate is decomposed at 80 atm. and 190°C. The mixture effluent from F1 enters separator SD1 where vapours are separated from the urea solution; vapours flow to first condenser F2 where they are mostly condensed in aqueous NH<sub>3</sub> solution and ammonium carbamate at a temperature ranging between 145 and 135 °C and at 80 kg/cm<sup>2</sup> abs. The condensation heat allows the production of steam at 3 kg/cm<sup>2</sup> abs. The gases not condensed in F2, mainly consisting of NH<sub>3</sub>, are fed to condenser F2 bis which operates at the same pressure as F2 but at a temperature of 115 °C, that is lower; also the carbamate discharged from F2 is sent to F2 bis.

Owing to the lower operating temperature in F2 bis, the gases are completely condensed. The inerts discharged from F2 bis are washed in column C1 in order to recover the ammonia balance and are subsequently vented to the atmosphere.

Steam produced in F2 (875 kg/t) is used in the plant, more precisely in F7, in reboiler F12, in ammonia preheater F12 bis and in vacuum ejectors. It is made partially available at battery limits, as recovery steam.

The condensed solution is recycled to the reactor by carbamate piston pumps PA2 (centrifugal pumps instead of reciprocating ones are being installed) which pump the solution from 80 atm. to the reactor pressure of 200 atm.

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The urea solution is sent to the two stages at decreasing pressure (12 and 3 kg/cm<sup>2</sup> abs.), each stage comprising a distillation, a separation of the distilled vapours and a condensation of the separate vapours. The condensate obtained from the 3rd stage is recycled to the 2nd from where the 2nd stage condensate is recycled to the first and from this, together with the 1st stage condensate, is recycled to the reactor. The urea solution at 75% is subsequently concentrated in 2 stages under vacuum at 0.3 and 0.03 kg/cm<sup>2</sup> abs. respectively.

The gases effluent from the 1st under-vacuum concentration stage are condensed in C3 and NH<sub>3</sub> is recovered from the solution thus obtained in rectification column C4 where water practically free from ammonia is discharged from the bottom. The gases which flow from C4 are condensed in C3 and the ammonia solution thus obtained is sent to the 3rd recycle.

Molten urea effluent from the last concentration stage is sprayed from the top of natural draught tower B1. The atomizers and the tower are so designed as to obtain at the bottom a prilled product having an excellent particle size, powder-free, completely cooled and solidified and not subject to caking, that is ready to be sent to storage without cooling and screening.

Figure 2 is picture showing a general view of the plant capacity 1,000 t/d based on such process.

#### IV. ALTERNATIVES TO THE PREVIOUS CYCLE

In Table 1, requirements refer also to Cases II and III.

Case II - It differs from Case I in steam using, which is complete. In fact, steam produced at 3 kg/cm<sup>2</sup> abs. is compressed in a turbocompressor operated by a turbine supplied with the line steam.

Compressor and turbine both discharge into a common header at an intermediate pressure of 5 to 7 kg/cm<sup>2</sup> abs. Steam is used in the same urea plant. The power necessary to bring this recovery steam fraction to a temperature sufficient for its using in the plant is obtained freely, by expanding the steam from the line

in a turbine instead of an expansion valve. The turbine-steam compressor group is compact and economic; its incidence on the investment cost is negligible. This alternate is suitable for plants having a capacity of 600 to 1,500 t/d. The first plant implementation according to this cycle was obtained in the above 700 t/d plant, ordered in January 1967, started up in June 1968 at full load and since then satisfactorily in operation. Following this cycle are now under construction two plants, each having a capacity of 1,500 t/d (on 2 lines) and a plant having a capacity of 500 t/d.

Case III - The difference mainly lies in the machines operating by steam turbines. It is particularly suitable for big capacity plants (between 800 and 1,500 t/d).  $\text{CO}_2$  is compressed up to 200 kg/cm<sup>2</sup> abs. by centrifugal compressors (such machines with a high revolution number are constructed by Nuovo Pignone firm, Firenze, Italy) (Ref. 4). Also the ammonia and carbonate reciprocating pumps are driven by back-pressure turbines. A considerable reduction of electric power consumption is thus obtained (10 kWh/t urea) while the consumption of steam at 40 kg/cm<sup>2</sup> g. is of course increased (1,250 kg).

#### V. INDUSTRIAL ACHIEVEMENTS

According to the process described above in its main alternates, Montecatini Edison have up to now designed and constructed 6 urea plants having a capacity ranging between 500 and 1,500 t/d. The first two plants having a capacity of 700 and 1,000 t/d respectively, have been running at full load for 3 years and 1 year respectively. The process, being a gradual evolution of the former ones, which were based on total recycle, is extremely simple and ensures the highest safety due to the long-dated and wide experience acquired by Montecatini Edison, who have implemented and operated all over the world 65 plants for urea production (both prilled and crystalline) for a total capacity of  $5 \times 10^6$  t/y.

In the long story of the urea process evolution, Montecatini Edison have been the first urea producer on an industrial scale according to the Hauser-Montecatini process since 1959. The implemented plants have been characterized by the

most various features which may be resumed as follows :

- open cycle, with partial recycle;
- carbamate recycle in gaseous phase (selective recycle, in aqueous solution, or under the form of crystals in suspension);
- two, three or four carbamate recycle stages;
- with or without separate ammonia recycle;
- with or without stripping of recycle carbamate;
- without heat recovery or with recovery of direct heat (that is yielded to a process fluid) or with indirect heat recovery (that is with steam production);
- capacities for single units ranging between 50 and 1,000 t/d (units having a capacity of 1,500 t/d are being designed);
- supply of raw materials ( $\text{NH}_3$  and  $\text{CO}_2$ ) in the liquid or gaseous state, or in a mixture (tail gases from other productions : for instance from melamine plants)
- producing granular and crystalline urea, urea in solution and prilled.

It may therefore be affirmed for certain that the whole range of the now feasible conditions for urea production has been accurately explored by Montecatini Edison.

The turning-point outlined above may be considered important but not final; in any case for the time being, as compared to the best known commercial processes, it offers the following advantages :

- high conversion efficiency in the reactor and therefore smaller sizes and lower costs of the apparatuses;
- the apparatuses for heat recovery operate at less severe conditions : considerably lower pressures and temperatures; less heavy corrosion conditions, thus contributing to reduce the operating costs;
- steam consumption equal or even lower than in any other process.

Such process, however, which has already been widely followed on a commercial scale, does not represent a point of arrival. Further studies and researches on pilot plants are under way for the development of still more interesting cycles



which we hope to be soon in a position to submit to the urea plant technologists.

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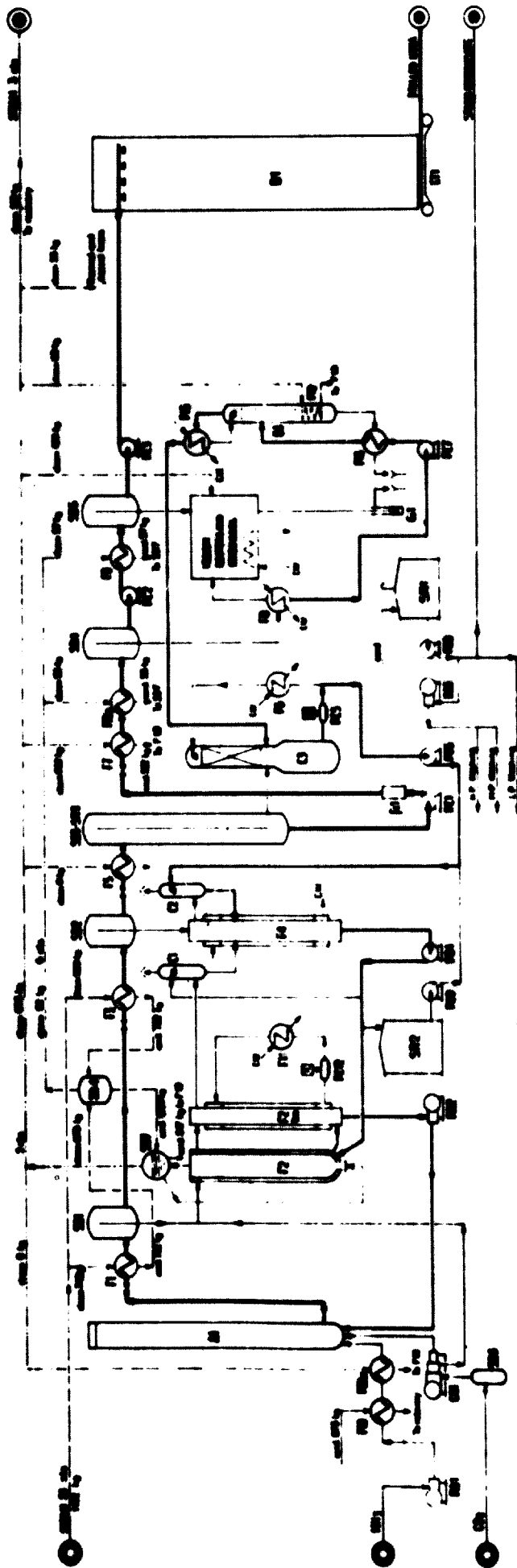
TABLE I

	Liq. NH <sub>3</sub> (100%) kg	Gas. CO <sub>2</sub> (100%) kg	Steam kg	El. Power kWh	Cool. H <sub>2</sub> O m <sup>3</sup> at 30°C	Recovered Steam kg
<u>Case I</u> - recovery steam partially exported	575	760	1,100 (at 20 atm)	140	100	250
<u>Case II</u> - recovery steam employed in the plant for thermal uses	575	760	850 (at 20 atm)	140	100	-
<u>Case III</u> - recovery steam employed in the plant for thermal uses and as power	575	760	1,250 (at 40 atm and 400°C)	10	130	-

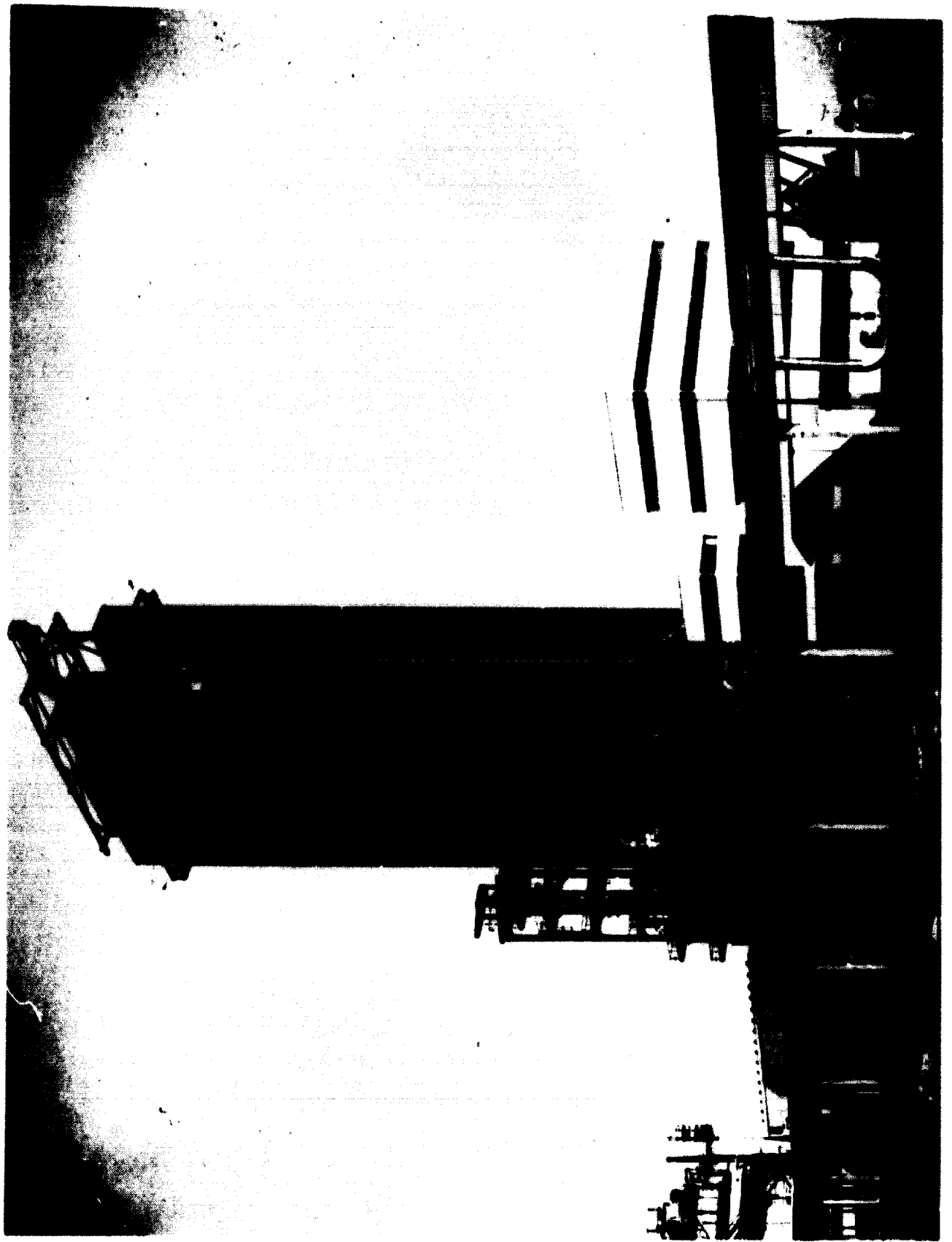
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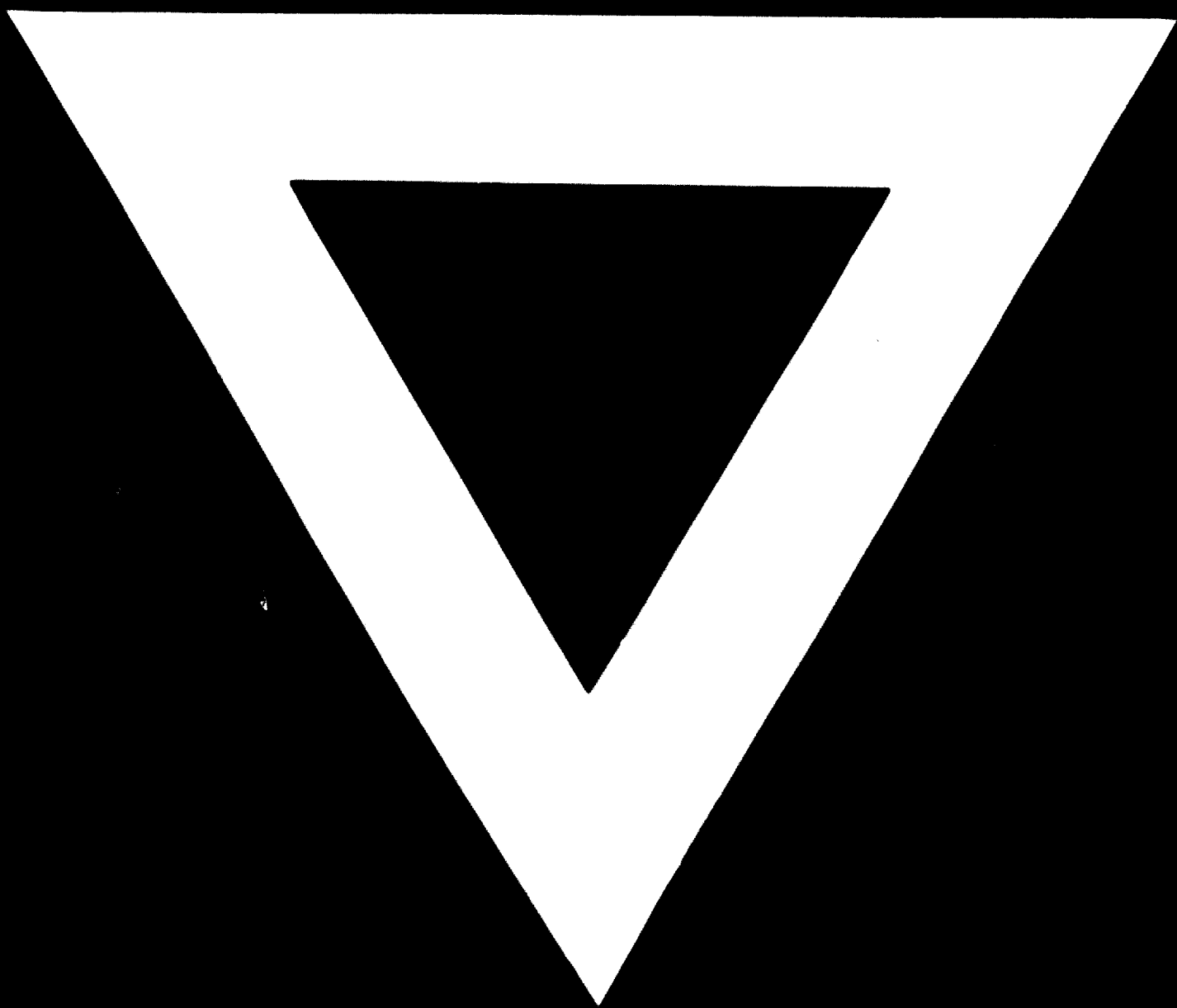
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- (2) Italian Patent No. 755.392 - 1st April 1967 - Title : "Urea Synthesis Process from Ammonia and Carbon Dioxide"
- (3) G. Nardin and T. Borelli  
Montecatini Edison Large Tonnage Urea Process  
Communication Submitted to the 38th International Congress of Industrial Chemistry - Istanbul - 8th to 12th Sept. 1969
- (4) P.L. Ferrara - Urea Synthesis Pressure Achieved by Centrifugal Compressors - Amer. Chem. Soc. - 158th - New York - Sept. 1969

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CASE I FIG. 1





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