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VINYL CHLORIDE MONOMER[1]

by

[illegible]
[illegible]-St. Gobain
[illegible]

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United Nations Industrial Development Organization

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Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries
in Developing Countries

Baku, USSR, 20 - 31 October 1969

SUMMARY

VINYL CHLORIDE MONOMER [1]

by

M. Antonini
Pechiney-St.-Gobain
Paris, France

Vinyl chloride monomer is today an industrial raw material of great importance. World production capacity was over 3 million tons per annum in 1967 and has been expanded at an average rate of 15% per annum, which shows that the consumption has by no means reached finality.

Vinyl chloride has been known since the early days of organic chemistry. It was first prepared in 1835. Its industrial development however is comparatively recent as more than a century elapsed between the discovery of the product and the beginning of its technical use (1835-1945). While its industrial manufacture from acetylene was worked out in 1912 and the first polymers of vinyl chloride had been

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[illegible] at W[illegible] [illegible] however [illegible] in 1933. [illegible] 1935-1945 [illegible] the [illegible] develop[illegible] in Germany [illegible] after the war [illegible] manufacture of [illegible] result of which [illegible] wide diversification [illegible] its [illegible].

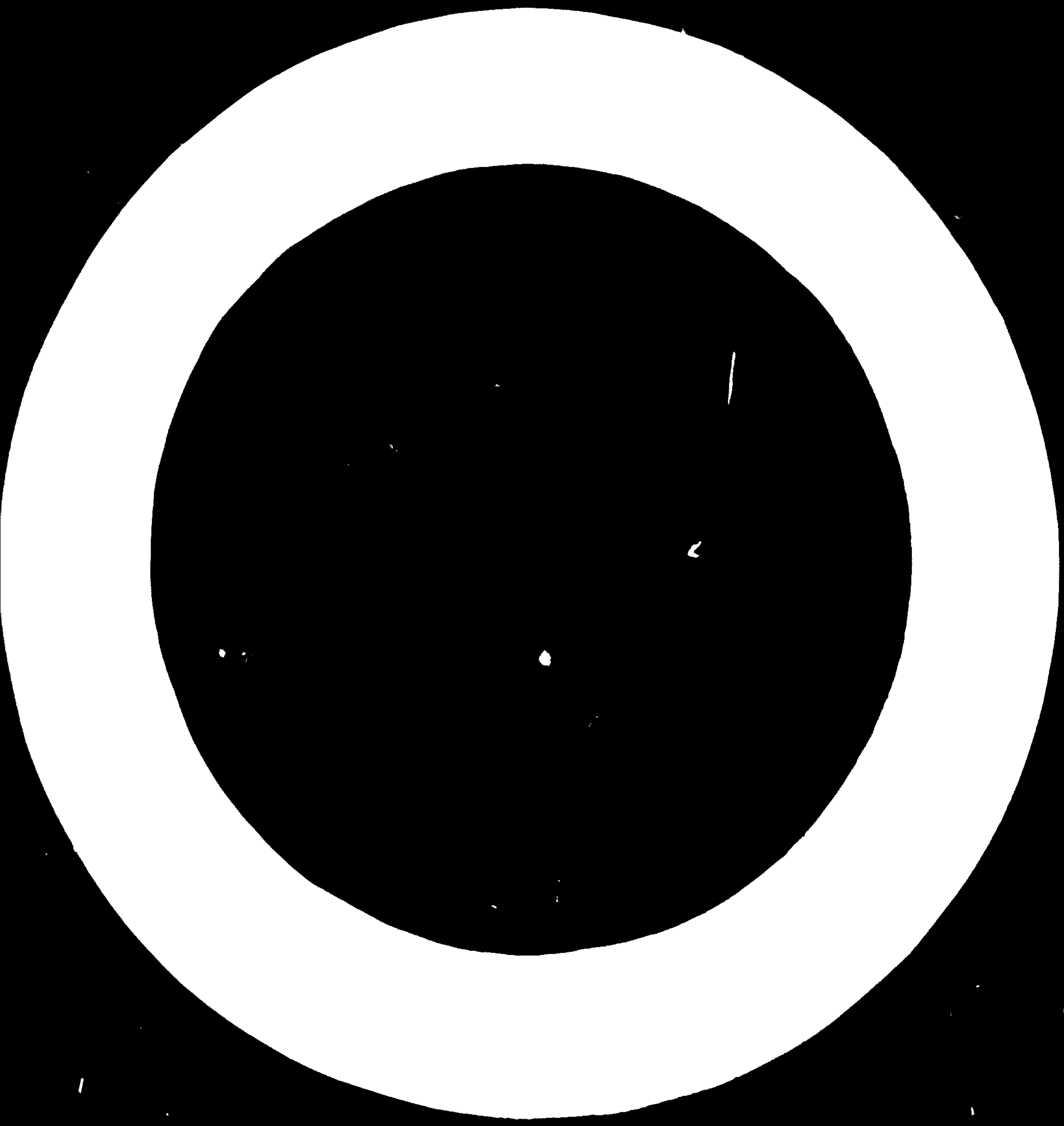
The [illegible] of [illegible] and [illegible] is one of the most striking [illegible] the competition between raw [illegible] of various origins. [illegible] first [illegible] acetylene [illegible], [illegible] acetylene of petroleum origin (by [illegible], [illegible] cracking, partial combustion of hydrocarbons) and then from ethylene [illegible]. Today, the ethylene of petroleum origin is [illegible] replacing acetylene. This has been [illegible] very quickly in Europe where [illegible] to 1960 acetylene had remained [illegible] the [illegible].

The [illegible] of vinyl chloride [illegible] process from acetylene and hydrochloric acid [illegible] chlorination of ethylene in the [illegible] followed by the pyrolysis of dichloroethane [illegible] with the problem of [illegible] of hydrochloric acid. [illegible] hydrochloric acid [illegible] producing vinyl chloride [illegible] led to the creation of so-called "integrated processes" which, for example, [illegible] acetylene [illegible] ethylene [illegible] both [illegible] either [illegible] where [illegible] nature of the [illegible] is [illegible] by the particular [illegible] hydrochloric [illegible] or chlorine.

More recently however, techniques have been developed [illegible] utilization of integrated processes [illegible] ethylene. This is carried out [illegible] an oxychlorination process [illegible] modern version of the ancient process [illegible] the transformation of hydrochloric acid into chlorine ([illegible] process) which has been improved by the use of catalysts in a fluidized bed.

Since 1954, these processes have developed rapidly and even faster since 1960. More than 10 original processes are at present available and their [illegible] have been generally shown by the licensing [illegible]. They [illegible] the nature of the catalyst used, a fixed or fluidized bed, by the temperature and pressure of the reaction and by the quantities of the [illegible] reacting which may differ according to the importance given to the yield on ethylene or on hydrochloric acid.

This sort of reaction moreover, allows us to integrate the production of vinyl chloride with those of chlorinated solvents. The [illegible] process is an example of this type of integration as it allows to produce practically all the group of the chlorinated products from ethylene.



I.7 [illegible].34/5[illegible]
[illegible]

Background ([illegible] I)

Vinyl chloride is not a new product, [illegible], chronologically, traces the development of that compound, however, [illegible] found, not only information concerning vinyl chloride itself, but also concerning acetylene, for the development of vinyl chloride is closely bound up with that of acetylene. Vinyl chloride [illegible], [illegible] industrial development [illegible] about 193[illegible] [illegible] later thirties. This [illegible] several factors [illegible], [illegible] available-ble, nor was the method of preparation sufficiently advanced to give rise to [illegible] industry, vinyl chloride, moreover, had little application [illegible], whilst its development has taken place solely in the domain of plastic materials, and it [illegible] for [illegible] vinyl chloride [illegible], [illegible], finally, [illegible] all, the polymer [illegible] and [illegible] of this compound [illegible] commercially.

The first synthesis of vinyl chloride was carried out by REGNAULT in 1835, [illegible] dichloroethane-1,[illegible] alcoholic potash [illegible] solution in alcohol, [illegible] the [illegible] ethylene; indeed, [illegible] dichloroethane-1,2 (Dutch [illegible] liquid) was obtained then by treating ethylene ([illegible]) with chlorine.

In [illegible], [illegible] history of vinyl chloride was for [illegible], [illegible] competition between acetylene and ethylene [illegible].

The only industrial [illegible] leading to vinyl chloride, up to about 1950, was acetylene, the synthesis of which, by BERTHELOT, goes back to 1860. The [illegible] industrial process of production of acetylene [illegible], [illegible] calcium carbide was obtained in the laboratory by [illegible] 1862.

[illegible] acid [illegible] acetylene have been known since 18[illegible], [illegible] REBOUL effected the synthesis of vinyl bromide by acetylene plus hydrocyanic acid.

The first [illegible] expensive [illegible]

The [illegible] produced [illegible] centre [illegible] chloride, [illegible] the G.I. [illegible] They had [illegible] chloride [illegible].

The investigations of the [illegible], however, were directing their attention [illegible] ([illegible] - [illegible]) [illegible] discovered. [illegible] during the [illegible] tons/year.

After the war, [illegible] countries [illegible] largest [illegible].

The development [illegible] by the search for [illegible] ethylene [illegible] acetylene.

A recent [illegible] after 195[illegible] ([illegible] – 1956) which [illegible] processes in which the [illegible] production of hydrocyanic acid.

[illegible] vinylchloride [illegible] integrated with [illegible]. [illegible] process secures an [illegible].

4. [illegible]

[illegible] useful [illegible] of [illegible]. [illegible] current [illegible] process [illegible].

[illegible] chloride [illegible]. The [illegible] of the [illegible] hydrochloric [illegible] is effected [illegible], [illegible] 150 and 200°C, [illegible]. The reaction generally takes [illegible] develops which gradually [illegible] of the catalyst [illegible].

[illegible] carbide [illegible], [illegible] progressively [illegible] in them [illegible].

[illegible] (chloride [illegible] purity, and [illegible], [illegible] considerable [illegible] the [illegible] produce [illegible] industrial [illegible] (which [illegible], [illegible] litres [illegible] acetylene [illegible], [illegible].

[illegible] acetylene [illegible] from [illegible], when [illegible] furn[illegible] the [illegible] preceding [illegible] furnace operating

di[illegible] continu[illegible]. [illegible]
[illegible] rapid[illegible] [illegible], [illegible] synthe[illegible].

[illegible] with [illegible], [illegible] [illegible]—[illegible] [illegible], [illegible] synthe[illegible] [illegible] [illegible], [illegible] [illegible], [illegible] the [illegible] [illegible]—[illegible], [illegible] [illegible].

[illegible] the [illegible], [illegible] towards [illegible] of [illegible]. [illegible], [illegible] first [illegible] the [illegible], [illegible], [illegible] especially [illegible]; [illegible] in acetylene, [illegible]—[illegible], such as [illegible], [illegible] oil. [illegible] put into [illegible]. [illegible] was with [illegible]. [illegible] [illegible]. [illegible] are very specific [illegible], [illegible] and [illegible]. [illegible], [illegible] acetylene, [illegible], [illegible] products of [illegible] treatment, the [illegible], [illegible] carbon and hydrogen. [illegible] the [illegible] 1.0[illegible] to 1.5[illegible] according to the [illegible]) with [illegible] order of several tens milli-second, [illegible] very suddenly, so that the decomposition of the [illegible] acetylene cannot [illegible]. Still, [illegible] process, [illegible] do not lead to [illegible] products [illegible], mainly: hydrogen, [illegible] monoxide, [illegible], ethylene.

These processes [illegible] which

which is not [illegible] and eventually [illegible] of vinyl chloride [illegible] the [illegible] still [illegible] high temperature and [illegible] process, [illegible]. In this type of process, a furnace is heated [illegible], and the temperature [illegible] then introduced into this furnace [illegible] cracking, followed by very rapid cooling [illegible]. When the furnace has cooled as [illegible] is resumed and the cycle [illegible] industrially.

[illegible] partial combustion [illegible] temperature is [illegible] by [illegible]. Industrially, [illegible] their name [illegible]. [illegible] (which [illegible]), in which [illegible] and bring [illegible] of gas containing [illegible].

[illegible] these processes [illegible] obtain a mixture of acetylene and ethylene in variable proportions, then the concentration of the [illegible] in practical conditions, which [illegible] of the [illegible]. On the basis of [illegible] (Nippon Nitrogen Company) and the Japanese [illegible] ([illegible]) have established a process of synthesis of vinyl chloride in which [illegible] gases containing acetylene and ethylene are, after preliminary purification, [illegible] hydrochloric acid on a mercury chloride catalyst [illegible] [illegible]ence [illegible] [illegible]ected [illegible] pressure [illegible] acetylene.

The [illegible] the II [illegible]

[illegible]

[illegible] is still [illegible]

[illegible]

[illegible] which [illegible]

[illegible]

[illegible] hydro[illegible] chlor[illegible] this [illegible] the indu[illegible] in the United States. [illegible] investi[illegible] the direct chlorination of [illegible] ethyl chloride [illegible] the [illegible]

[illegible].36/59

[illegible] and other [illegible] vinyl chloride.

[illegible] development of the vinyl chloride industry

[illegible] vinyl chloride [illegible] (proportion) [illegible] hand [illegible] the United States.

[illegible] thousands of tons [illegible] greater than in th [illegible] Western Europe and [illegible] production capacity of [illegible] of the order of [illegible], [illegible] of vinyl chloride [illegible] of its [illegible]

[illegible] material ethylene [illegible] for the synthesis [illegible] than of vinyl chloride, [illegible] of [illegible] ethylene [illegible] developed [illegible] whole, [illegible] material for [illegible] where the price [illegible]

[illegible] processes

[illegible] long time in the domain of the [illegible] between the productions of [illegible] acid. [illegible], in order to effect the synthesis [illegible] the basis of acetylene it was [illegible] hydrochloric [illegible] the rapid development of the [illegible], with production of of hydrochloric acid, a by-product, and even [illegible] the synthesis of vinyl chloride has [illegible] utilizing the HCl produced, for example, in the synthesis of chloro-prene. [illegible] however, finding [illegible] in the form of aqueous solution, it is necessary to [illegible] a balance between the production and the utilization of hydrochloric acid, [illegible] resulting from the synthesis of chloro-ethylene [illegible] and, in particular, from the synthesis of vinyl chloride [illegible] process.

This is why there [illegible] general procedures, which [illegible] possible [illegible] "integrated processes", where [illegible] vinyl chloride without having by-products, [illegible] without having to provide hydrochloric acid.

Table 5 shows four types of general processes. In the first, pure ethylene and pure acetylene [illegible] the conventional methods [illegible]. [illegible] chlorination of ethylene [illegible] dichloroethane 1-2 which is purified, then pyrolyzed, [illegible] which, after purification, is ready for polymerization [illegible] hydrochloric acid, used [illegible] the catalytic hydrochlorination of acetylene. [illegible] vinyl chloride thus obtained are sent for purification, then [illegible] polymerization. This process is [illegible].

In the second process, [illegible] ethylene and acetylene, produced [illegible] of thermal cracking of hydrocarbons. I have already given some details of this. The mixture containing dilute acetylene and ethylene is first subjected to hydrochlorination with HCl produced in the factory itself. First part of the vinyl chloride formed is separated out, the remaining mixture, containing ethylene, is subjected to chlorination to obtain the dichloroethane 1-2 which is purified, pyrolyzed and converted to vinyl chloride. The hydrochloric acid generated in the pyrolysis stage is used in the hydrochlorination stage.

In the third type of integrated process, chlorine is the only raw [illegible] used, and the utilization of the HCl is effected by converting it into chlorine by the conventional process of [illegible], which goes back to [illegible]5, but which has been [illegible] by the electro-chemical [illegible] involved. With the [illegible] chloride [illegible] to the [illegible] installation [illegible] liquid phase to [illegible] process of [illegible], and the [illegible] ethylene.

Similarly, in the [illegible] presented here, [illegible] inorganic [illegible] (ether) [illegible] that is to say [illegible] in liquid phase, while [illegible] which likewise [illegible] purification, is involved, the [illegible] sufficient purity, [illegible].

The [illegible] process, but it goes further [illegible] synthesis of [illegible] perchloroethylene, [illegible],

[illegible]. Different present-day processes [illegible] chlorination [illegible]

The process of [illegible] which consists in chlorinating an ethylenic [illegible], especially ethylene, with [illegible] oxygen [illegible] - in mixture have long been known. The first patents [illegible] to 1921, but the practical [illegible] towards 1955, the first being [illegible], which built an installation for oxychlorination of ethylene to dichloroethane 1-2 in a tubular reactor in which [illegible], this [illegible] being diluted [illegible] substance, silicon [illegible], for the reaction of or chlorination [illegible] and when the reaction [illegible] sed it gives rise [illegible], which is difficult to control. [illegible] example, [illegible] and to [illegible]. [illegible] either [illegible] solidification [illegible], [illegible] it possible to [illegible] compressed [illegible] the zone. That is why [illegible] the [illegible], which [illegible] fairly numerous ([illegible]) [illegible] on the millimeter [illegible]. [illegible] reactors [illegible], [illegible], [illegible] cheap. With [illegible], [illegible] either diluted [illegible], [illegible] Company [illegible], [illegible], that is to say that, in the zone [illegible], [illegible] by the non-active [illegible], [illegible] ([illegible] diluted) [illegible] in [illegible], [illegible] moderate enough [illegible].

In this type of process [illegible] point of view of raw [illegible], [illegible]. [illegible] that the Japanese [illegible] installing [illegible] which were [illegible]. The [illegible] Company [illegible] used oxygen [illegible]; but [illegible] not know whether it [illegible] whether it [illegible] to air. All the other [illegible] air, [illegible] a very cheap raw material, but which [illegible] nitrogen and [illegible] a separation between the [illegible] products and the [illegible] of nitrogen leaving the reactor. [illegible] less low pressure. [illegible] information on the pressures used in these different processes, [illegible] the pressure is [illegible] of 7 [illegible], [illegible], [illegible], in respect of the [illegible]-[illegible] process. [illegible]

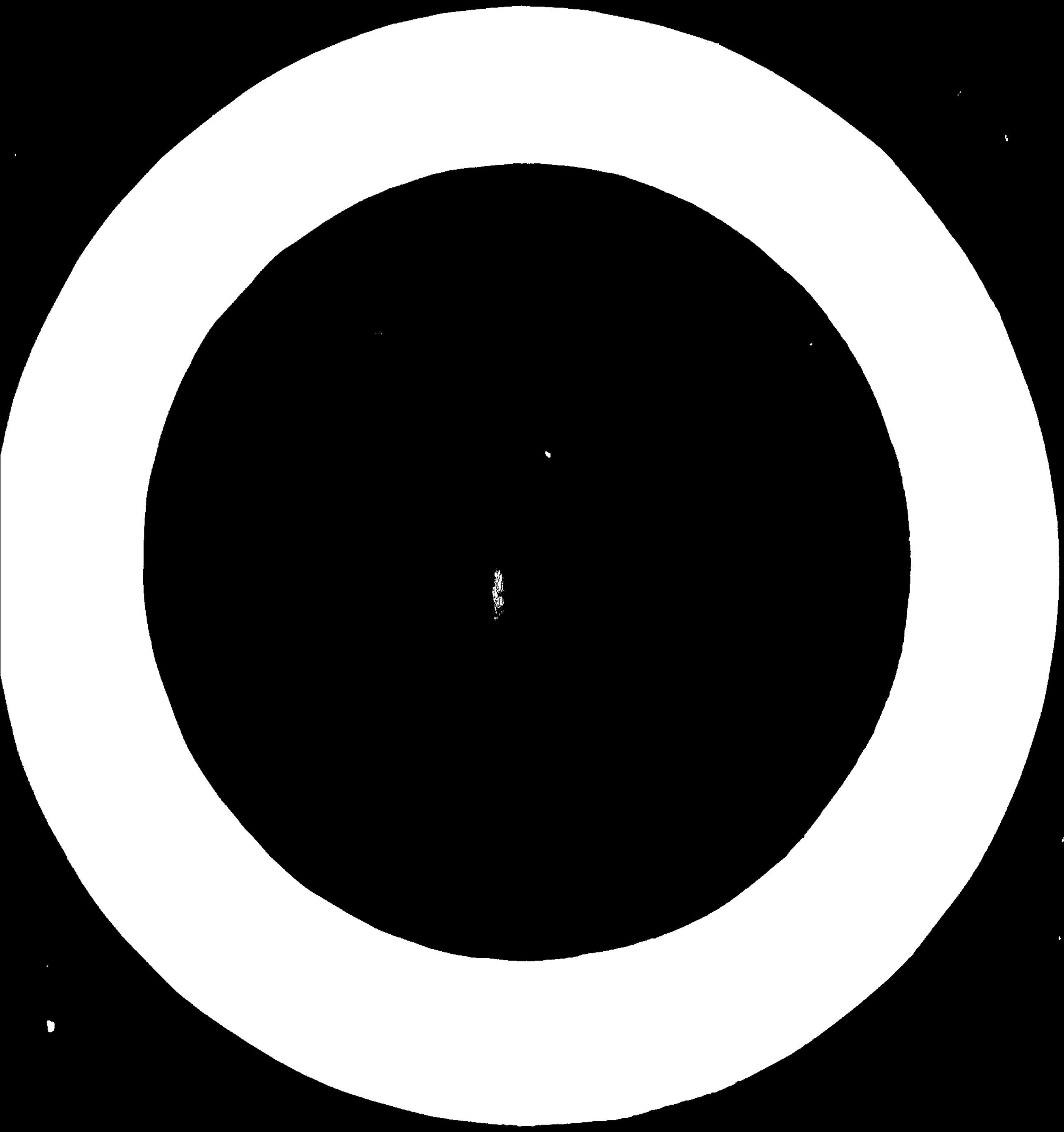
[illegible] 25 [illegible]

reaction is generally of 250 to 300°C.

The first four processes mentioned in this table saw the light before 1954. The others have come out between 1954 and the present time or are in process of being launched. Some of them are already under licence to other companies. Table 5 also shows apart from the [illegible] process which works at temperatures of 400°C in fluid bed, a [illegible] process of oxychlorination developed on the pilot scale by the [illegible] company KELLOGG which counts on [illegible] the [illegible] liquid phase, that is to say, that the ethylene is treated with an aqueous solution containing cupric chloride and is converted [illegible] under these conditions, while the reduced solution, containing cuprous chloride is reoxidized to cupric chloride by HCl and air in another phase of the process.

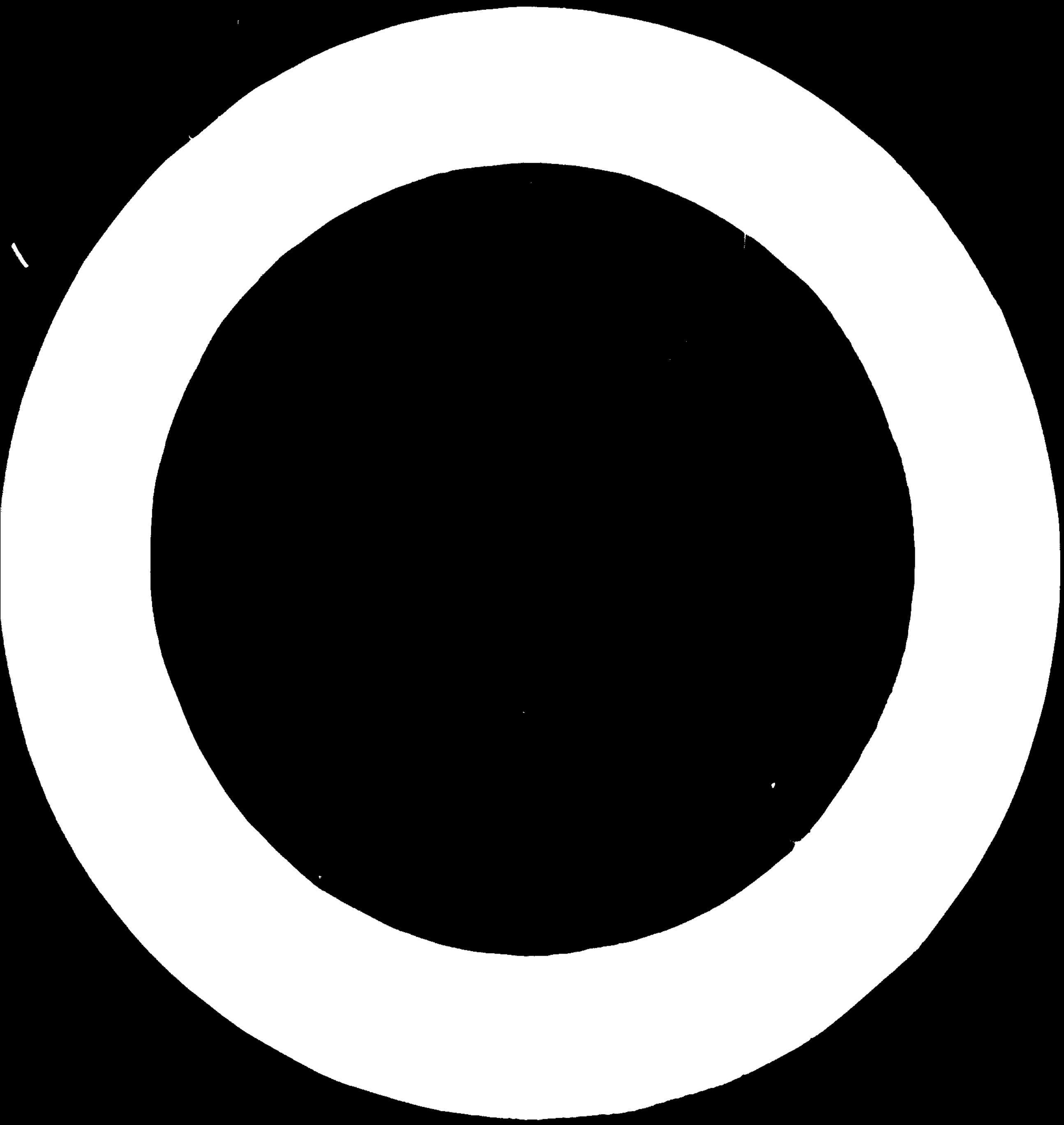
PROCEDES D'OXYCHLORATION

PROCEDE	Réacteur	Catalyseur	Air ou O2	Pression	Température	Licences
DOW	Lit fixe	Dilué		non (?)		•
MONSANTO	" fluide		O2 (?)	probable		+
[illegible]	" fixe	Homog		oui		+
GOODRICH	" fluide			2-3 bars	250°C	+
[illegible] I [illegible] - [illegible]	Lit fluide			7 bars		+
P.P.G.	" "			probable		+
VULCAN	" fixe	Dilué prog.		oui		+
[illegible]	" "					+
[illegible]	?					•
[illegible]	Lit fluide		O2	probable		•
[illegible]	" "			7-8 [illegible]	21[illegible]°C	•
[illegible] ([illegible])	Lit fluide					•
[illegible]	Phase liquide			[illegible]		



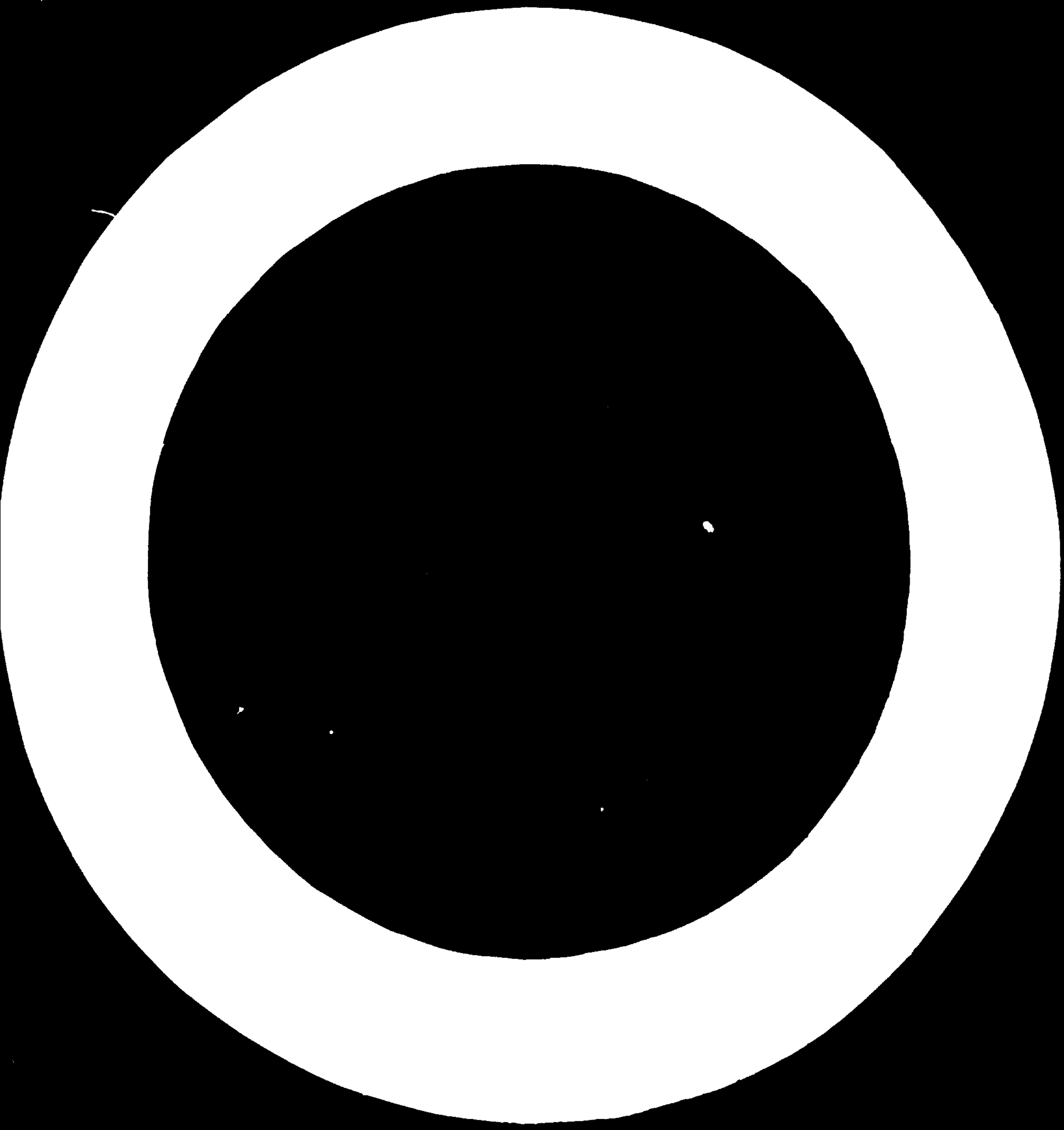
[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	1906		[illegible]
[illegible]	[illegible]	[illegible]	1912	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]			[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
	[illegible]				[illegible]
	[illegible]		[illegible]	[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]	[illegible]
	[illegible]		[illegible]		

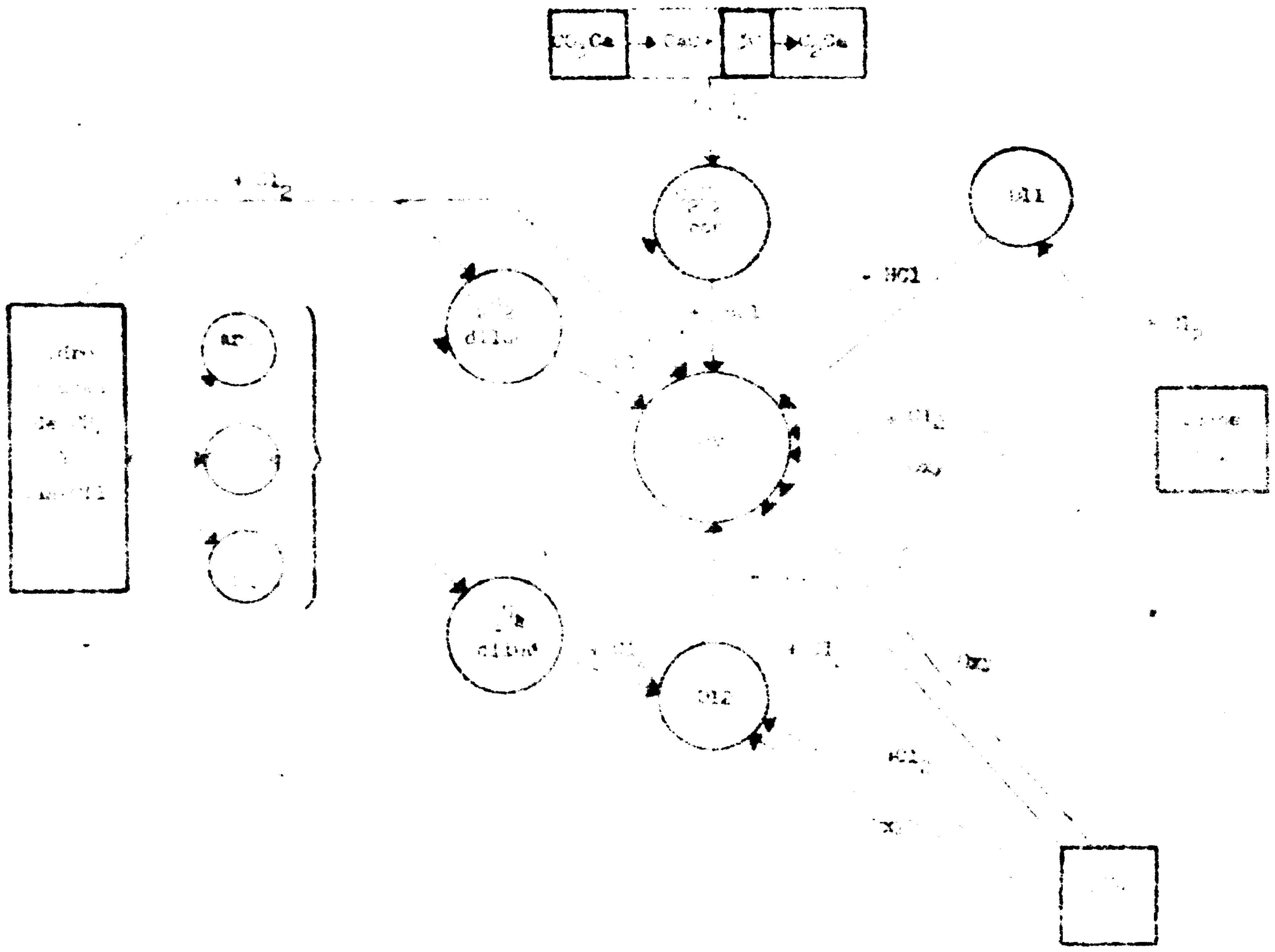


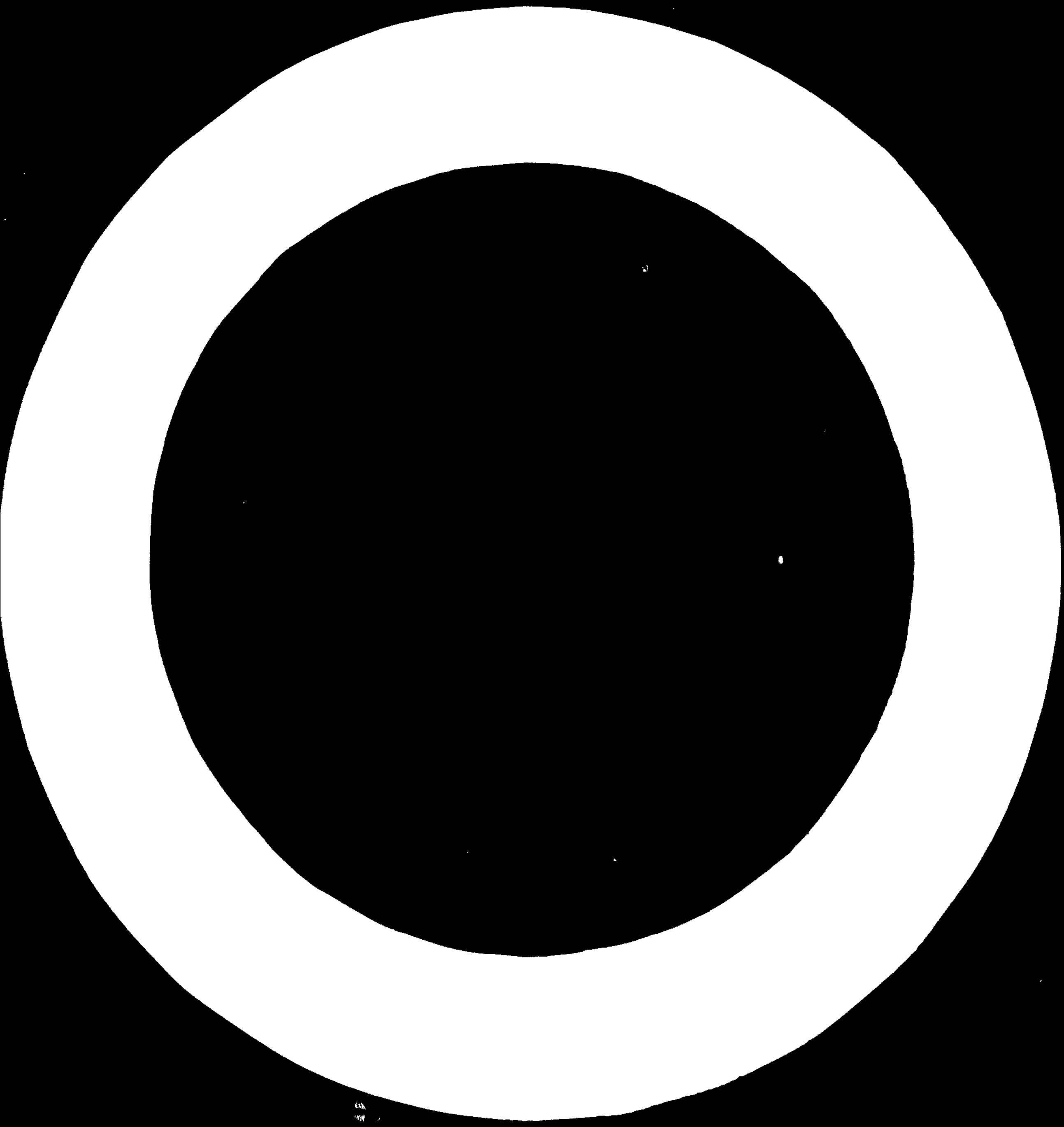
[illegible]

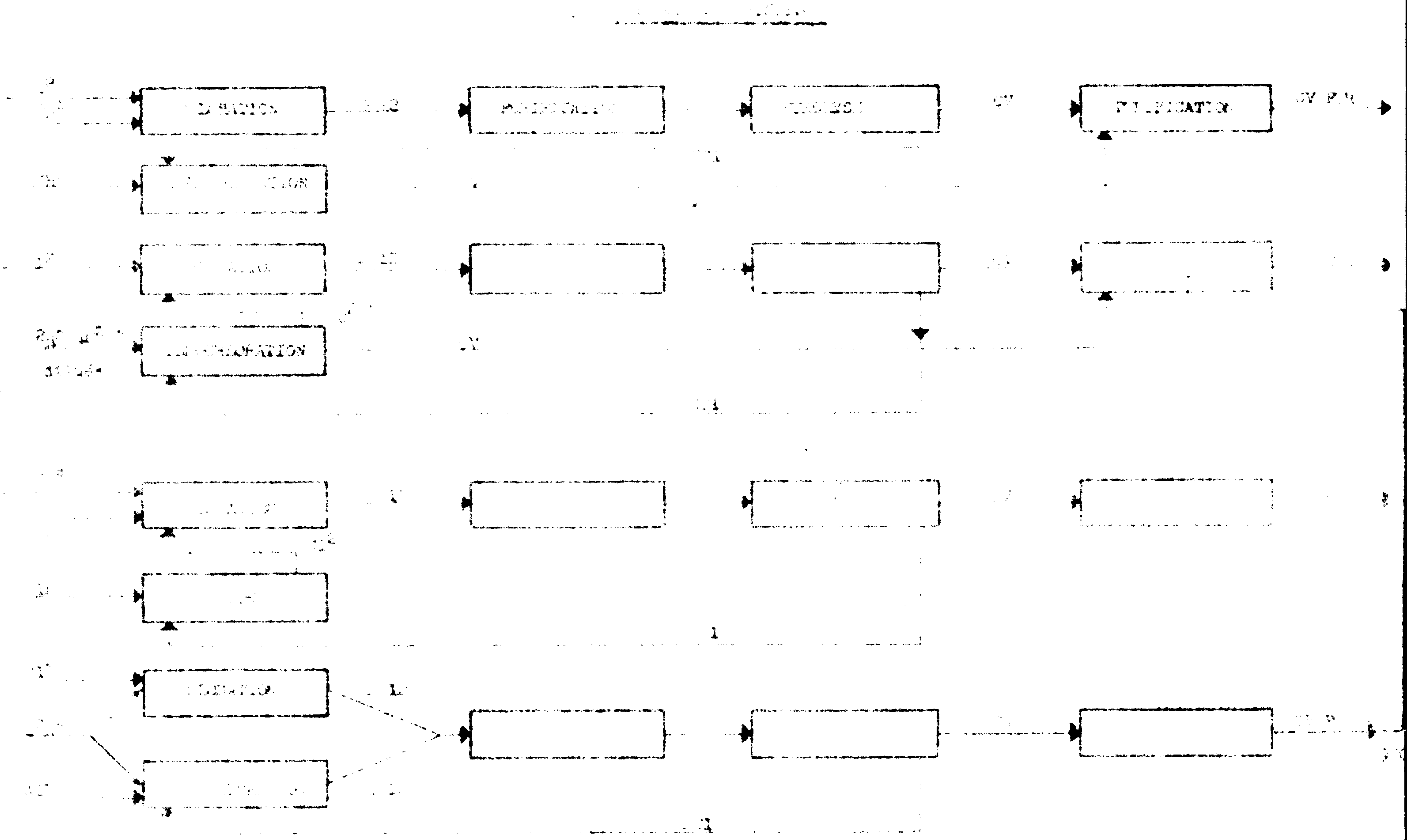
	C20 1.0 00[illegible] t/[illegible]	C2T2 [illegible] – T20 50 000 t/[illegible]	[illegible] – 212 [illegible] t/an	[illegible] – [illegible]12 35 000 t/[illegible]
[illegible] premières	38.5	53.7	[illegible]	7[illegible].5
[illegible] production	37.[illegible]			
[illegible]	1,8	[illegible],4	I,[illegible]	[illegible].3
[illegible]	[illegible],5	1,5	[illegible]	3,4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible] 35[illegible]	7[illegible]	

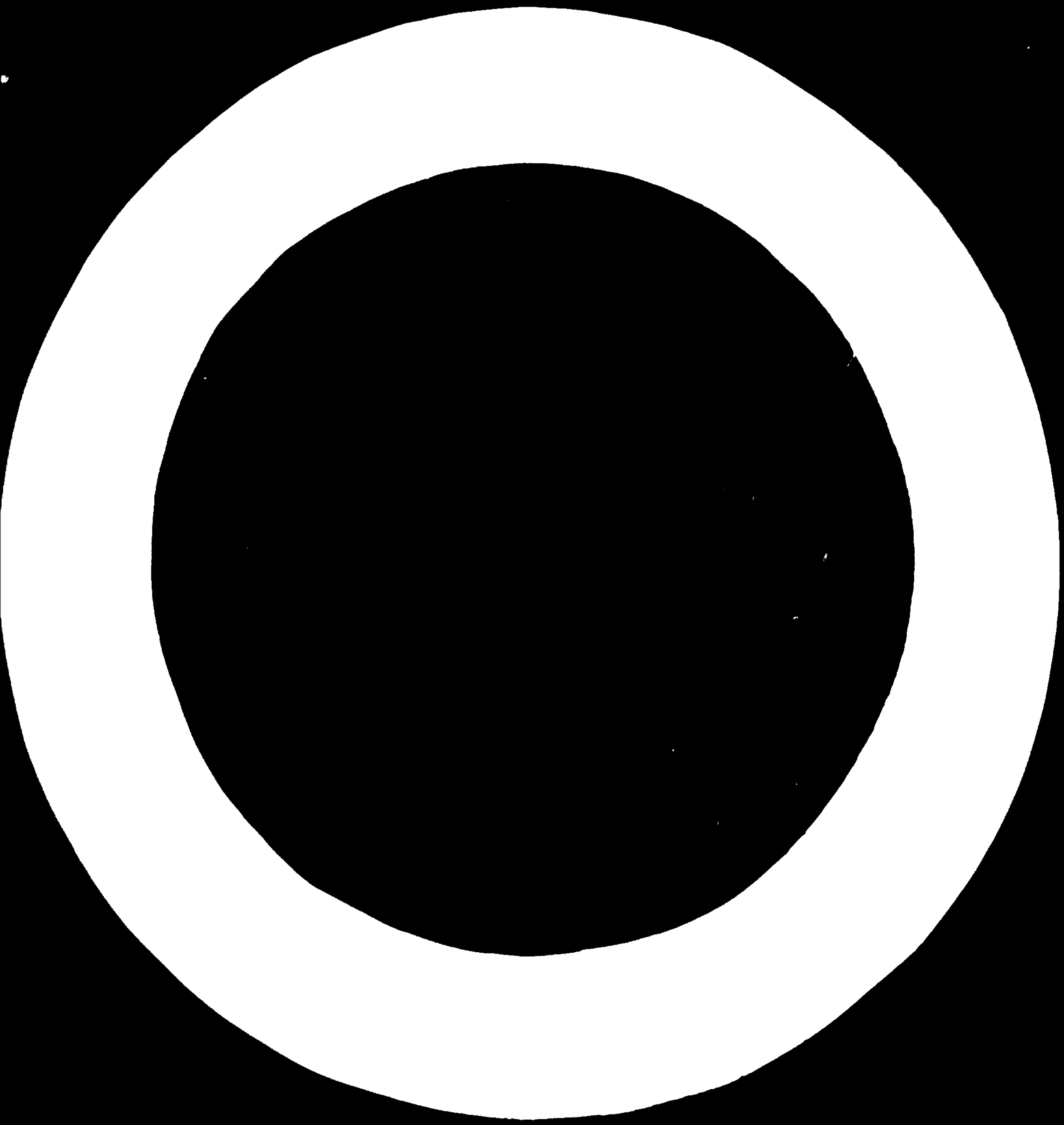


IV - SCHEMA GENERAL DES PROCEDES

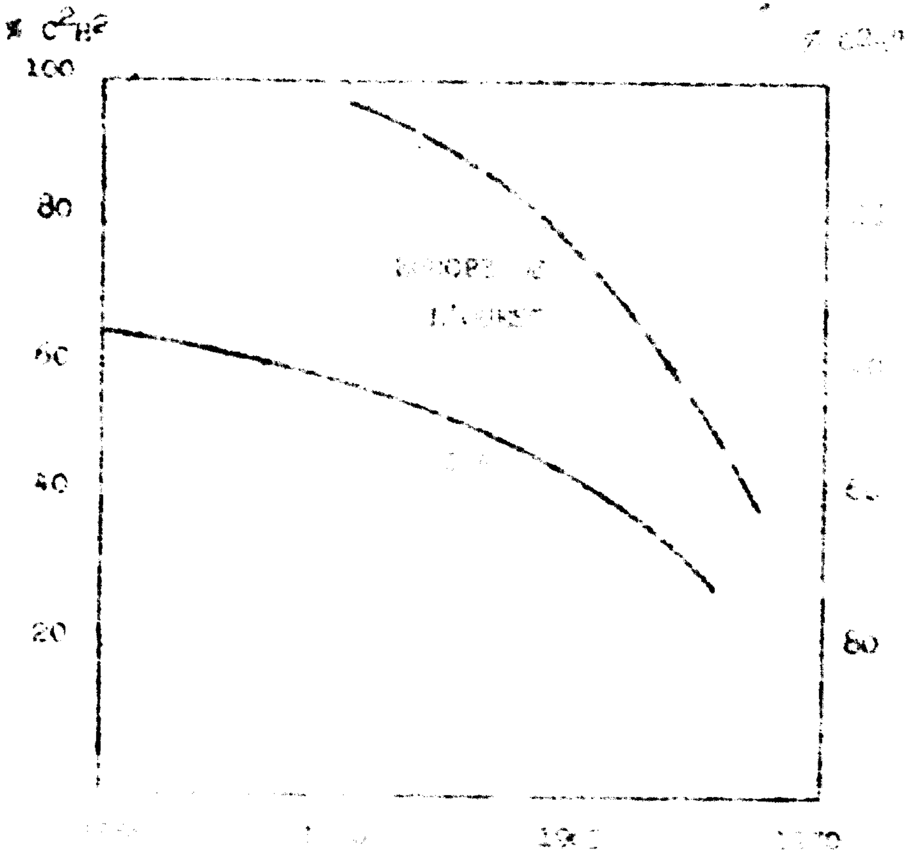


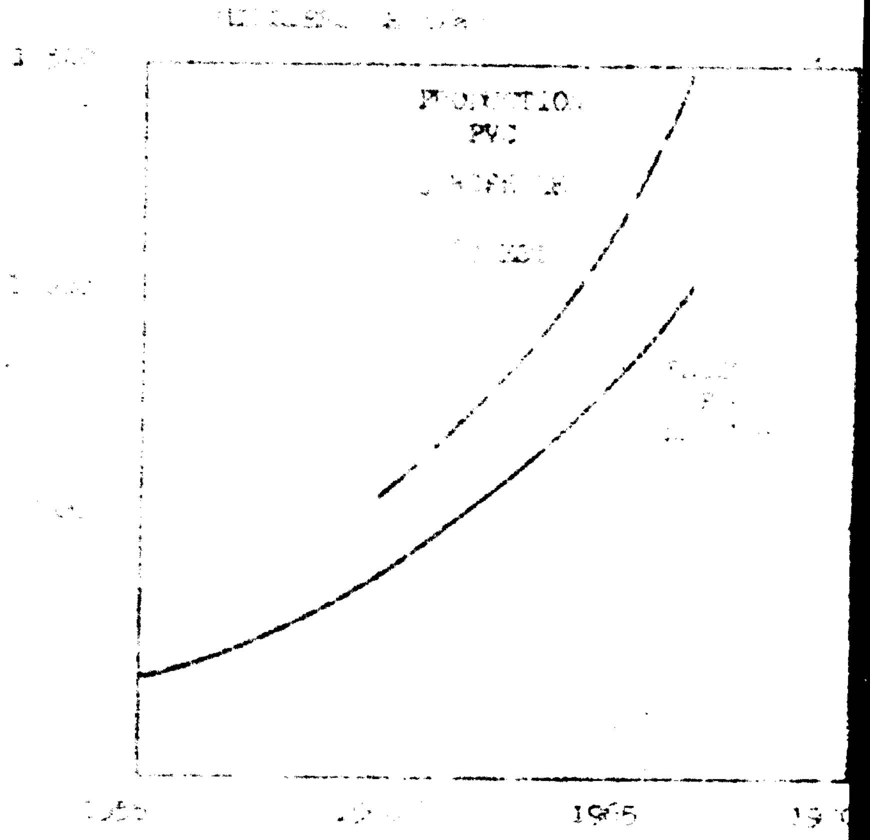


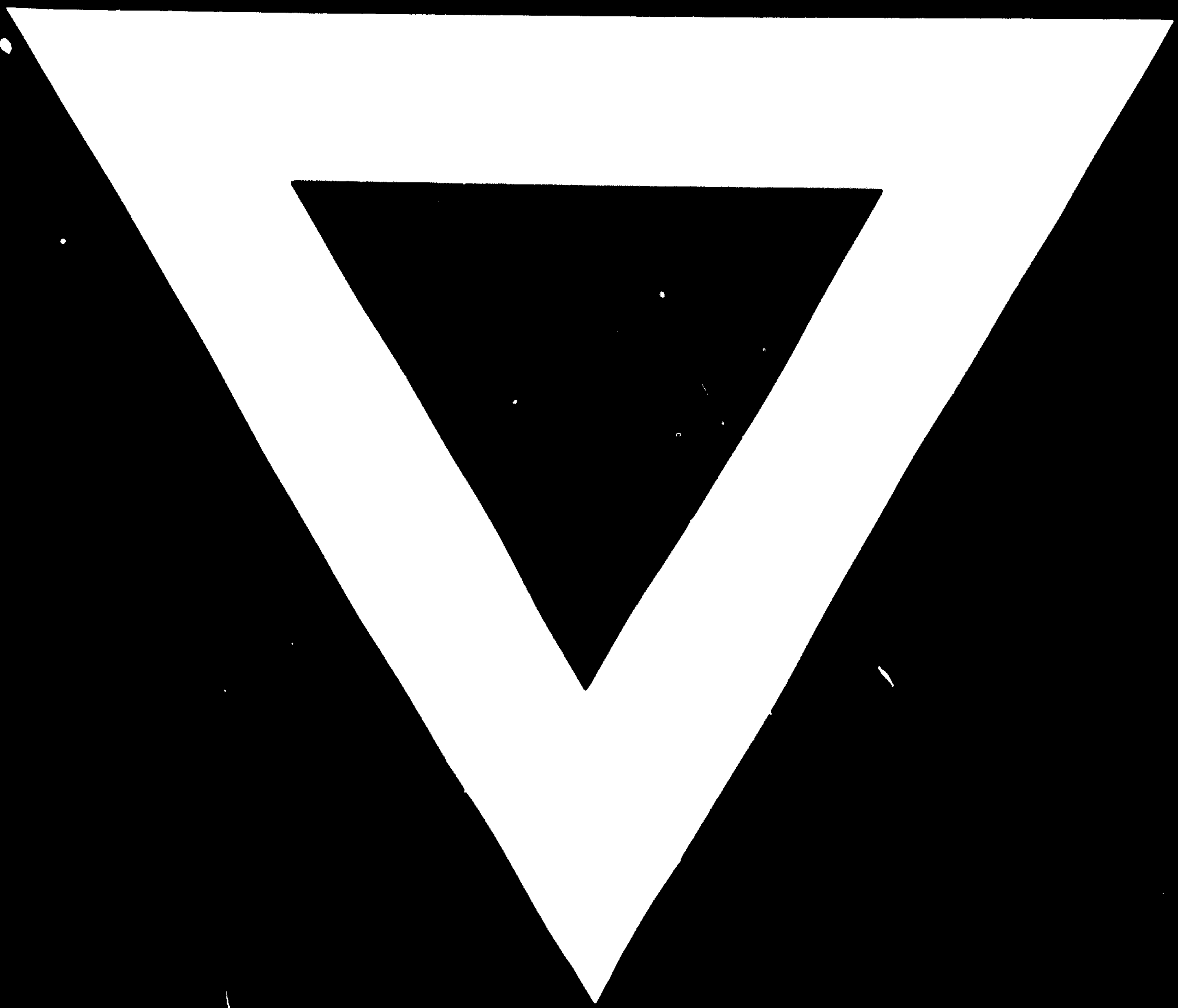




STATISTIQUES







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