

10-3

Tom 132

821

Item 25

Report and Several Drawings Concerning the Removal of Carbon Oxysulfide (COS) from gases

Contains items:

- 25a) The removal of carbon oxysulfide (COS) from gases
- 25b) Drawing supposed to represent installation for the removal of carbon oxysulfide (COS) from gases
- 25c) Ditto
- 25d) Ditto

25a

Report Concerning the Removal of Carbon Oxysulfide (COS) from Gases

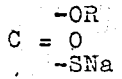
The ethane which is furnished by the Saargas-liquefaction plant contains variable amounts of sulfur. During a period of 8 days the following quantities were determined:

1.	8.7	mg/m <sup>5</sup>	S	corrected
2.	80.9	" "	"	"
3.	5.8	" "	"	"
4.	75.0	" "	"	"
5.	13.6	" "	"	"
6.	236.9	" "	"	"
7.	43.7	" "	"	"
8.	69.7	" "	"	"

In the average the gas contains 67.4 mg/m<sup>3</sup> S.

Beside extremely low amounts of H<sub>2</sub>S and CH<sub>3</sub>SH the sulfur content of the gas is due to COS.

Resulting from its very weak acid properties COS is substantially more difficult to extract from gases than H<sub>2</sub>S, SO<sub>2</sub> and CO<sub>2</sub>. Aqueous solutions of alkalis and solid alkalis as well as the alkaline earth metals are inefficient. Soda lime will show a fairly good absorptive-ness in the beginning but after a short period of time it is coated with a layer resulting in an absolute inefficiency. The most efficient absorbents were alkali-alcoholates which form alkali-alkyl-thiocarbonat



with the extracted COS.

Due to the high vapor pressure of the respective alcohols the alcoholates of the lower alcohols cannot be employed. Alcohol vapors which form CO in the ethane splitting installation, must be avoided if the ethylene is to be polymerized. The higher alcohols dissolve but too small amounts of alkali and their high per cent alcoholates which are obtained from the reaction with alkali-metals are too viscous.

In the early days of 1942 a process was developed by Drs. Mayber and Winter to utilize the alcoholates of semisters of the glycols, especially of the ethyl glycol. The glycolethers are distinguished by a good solubility for alkalis and by a low viscosity of the obtained solutions. By the application of a vacuum distillation process the waterfree alcoholates can be easily obtained.

Solubility of Caustic Soda in Various Glycol Ethers

150 g of methyl-ethyl-propyl-butyl-glycol resp. were shaken for three hours at normal temperature with an addition of 30 g caustic sod. A shaking machine was employed. The solutions were decanted from the

undissolved residue. The obtained solution contained:

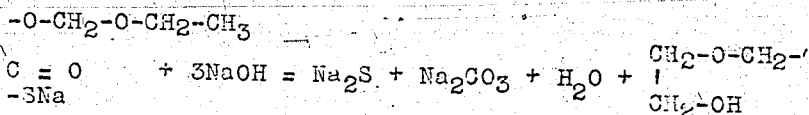
Methyl-glycol-solution	16.9%	NaOH
Ethyl-glycol-solution	14.4%	"
Propyl-glycol-solution	12.4%	"
Butyl-glycol-solution	10.08%	"

Due to the low boiling point of the methyl glycol a commercial application of the methyl-glycol-solution was not contemplated. The butyl-glycol-solution was not employed because the product of reaction between COS and the sodium salt of butyl-glycol is insoluble and precipitates instantaneously causing a clogging of the scrubber.

From May until December 1942 a solution which contained 5 parts caustic soda in 100 parts ethyl-glycol was utilized for commercial operation, later on a 10% solution was used. It was possible to extract approx. 6,000-6,500 m<sup>3</sup> ethane which was under a pressure of 4-6 atm. by means of 70 liter of the 5% solution; the 10% solution was able to treat almost twice as much. From time to time it was necessary to make up the losses which are due to the vaporized ethyl-glycol. With a daily output of 330-340 m<sup>3</sup> gas a following with paraffin oil operated scrubber extracted 25 cm<sup>3</sup> (The original shows 25 m<sup>3</sup> which is certainly wrong--translator's note).

The solution had to be replaced as soon as 10 cm<sup>3</sup> did not absorb more than 80 cm<sup>3</sup> COS because COS began to appear in the finished gas. The COS-determination was made by means of cadmium acetate solution (yellow color).

As long as no COS has been absorbed the ethyl-glycol solution remains unchanged for a long period of time. With COS absorbed the absorptiveness of the solution decreased very rapidly in the beginning but very slowly afterwards. This is probably due to a hydrolysis of the formed thiocarbonate according to the following equation:



In order to determine the influence of the water content on the absorptiveness and durability of the glycol-ether-solutions, three solutions were prepared from each ether which contained 0, 4.5, and 9% respectively. The same volume of COS (11.017 liter) was introduced into each of the solutions, whereafter in intervals of 24 hours the total absorptiveness of the solution against COS was determined using the apparatus which has been described in memorandum 102 (Memorandum 102, October 20, 1942, Drs. Rackz and Hauber: Determination of the absorptiveness of an ethyl-glycol-ether-solution against COS).

By plotting the cm. of COS, which have been absorbed by 10 cm. the respective solutions against the age of the solution measured in hours, the curves of diagram 1 are obtained.

The strong influence of the water content on the absorptiveness and durability of the solutions can be easily observed. But the COS containing waterfree solutions show different durability. The ethyl-glycol-solution is much more durable than the propyl-glycol-solution.

#### Higher Ether-alcohols

Besides the rapid decrease of the absorptiveness additional disadvantage of the respective glycol-ethers are their high volatility as well as the formation of insoluble thiocarbonates which may result in clogged scrubbers. Some higher boiling ethers of glycerol were therefore investigated. We synthesized the -dimethyl-ethyl-propyl-ethers

of glycerol from -di-chloro-hydrin and the respective sodium alcoholates.

-di-methyl glycerol	b.p. 165-175°C.
-di-ethyl glycerol	b.p. 180-185°C.
-di-propyl glycerol	b.p. 215-225°C.

In addition the tetrahydro furfuryl alcohol (b.p. 174°C.), which can be obtained by high pressure hydrogenation of the furfural, was investigated. By dissolving 4.15 g of sodium metal in 100 g of alcohol the alcoholates of the respective alcohols were produced. All 4 ether alcoholates were by far superior to the glycol-ether-solutions. The obtained sodium thiocarbonate-esters are much more durable and are soluble in an excess of the respective ether alcohols. Due to the high price of the compounds their commercial applicability is out of question for the time being.

#### Regeneration of the Spent Solution

The regeneration of the spent solution was carried out by rapid distillation applying vacuum followed by a rectification of the obtained distillate. It was possible to recover 88% ethyl-glycol from the commercially spent solution. The produced ethyl-glycol solution had an equal absorptiveness as such a solution which had been prepared from pure ethyl glycol provided that the alkali content was the same.

#### Alcanol-amines as absorbents for COS

The Girdler process which applies aqueous 30-50% mono-di- and tri-ethanolamine solutions is capable of extracting  $H_2S$ ,  $CO_2$  and  $SO_2$  from gases. The process works very well if the above mentioned acids must be removed, but the diluted solutions are inefficient against COS. Experiments however which were carried out applying high percent aqueous as well as water-free alcanolamines, especially with mono-alcanol-amines, were especially successful. The absorptiveness of mono-di-, and tri-ethanolamine against COS is as follows:

	1 mol. will absorb	1 g will absorb
Mono-ethanol-amine	11,580 ccm. corr.	190 ccm. corr.
Di-ethanol-amine	5,280 " "	50 " "
Tri-ethanol-amine	1,440 " "	9.6 ccm. corr.

The mono-ethanol-amine will absorb four times as much COS as the di-ethanol-amine and 20 times as much as the tri-ethanol-amine. In addition the following liquid, water-free amines were investigated:

	1 gram will absorb
Cyclohexylamine	202 ccm. corr.
Benzylamine	75 " "
Ethylene diamine	136 " "
Dutanolamine	127 " "
Ortho-toluidine	0 " "

It is evident that the cyclohexylamine absorbs more COS than the mono-ethanolamine, but due to its greater volatility it was not applicable.

The mono-alcohol amines will absorb almost exactly  $\frac{1}{2}$  mol. COS as represented by the following table:

	Determined	Computed for $\frac{1}{2}$ mol. COS
1 gram mono-ethanol amine	190 ccm. corr.	183 ccm. corr.
1 " mono-butanol amine	127 " "	125 " "

Furthermore the properties of alcohol amines, which were absorbed by supporters, were investigated. Investigated were active charcoal, pumice and kieselguhr which had been impregnated with 10% mono-di- or tri-ethanol amine. In all cases a substantial decrease of the absorptiveness was observed.

The application of solid organic bases was likewise a failure. The following bases were investigated:

Hexamethylene-tetramine, cyanoguanidine, guanidine, tri-sodium- tri-ethanol amine (which is precipitated if tri-ethanol amine is mixed with strong sodium hydroxide solution), furthermore mono-sodium-tri-ethanol amine.

Under commercial conditions the gaseous ethane is led through 2 bubble cap scrubbers which are 3,500 mm high and 150 mm wide. They contain 10 plates, each of which is charged with 12 liter ethanolamine. Approx. 450 m<sup>3</sup> gaseous ethane are desulphurized per day. During the summer the pure ethanolamine should be employed whereas it should be diluted with 10% water during the winter in order to prevent freezing.

Freezing point of the pure ethanolamine	
" " " 95%	+10.3°C.
" " " 90%	+1°C.
	± 7°C.

The application of mono-butanol amine was considered practicable because its vapor pressure is but 1/3 as high as that of the ethanolamine (See sketch 2). The very low freezing point of mono-butanol amine (-40°C.) is another advantage. But a test run under commercial conditions showed that the butanol amine absorbed smaller volumes of COS than the mono-ethanol amine. By an extended contact time it will be possible to employ the butanol amine should there arise difficulties with the ethanol amine due to low outside temperatures.

The process works without any difficulties since December 1942. In a test run which is just running 9,330 m<sup>3</sup> gaseous ethane were completely desulphurized during 470 operating hours by means of 24 liters of ethanol amine. No decrease of its absorptiveness could be observed and no additional ethanol amine had to be refilled in order to make up losses.

Item 25 b

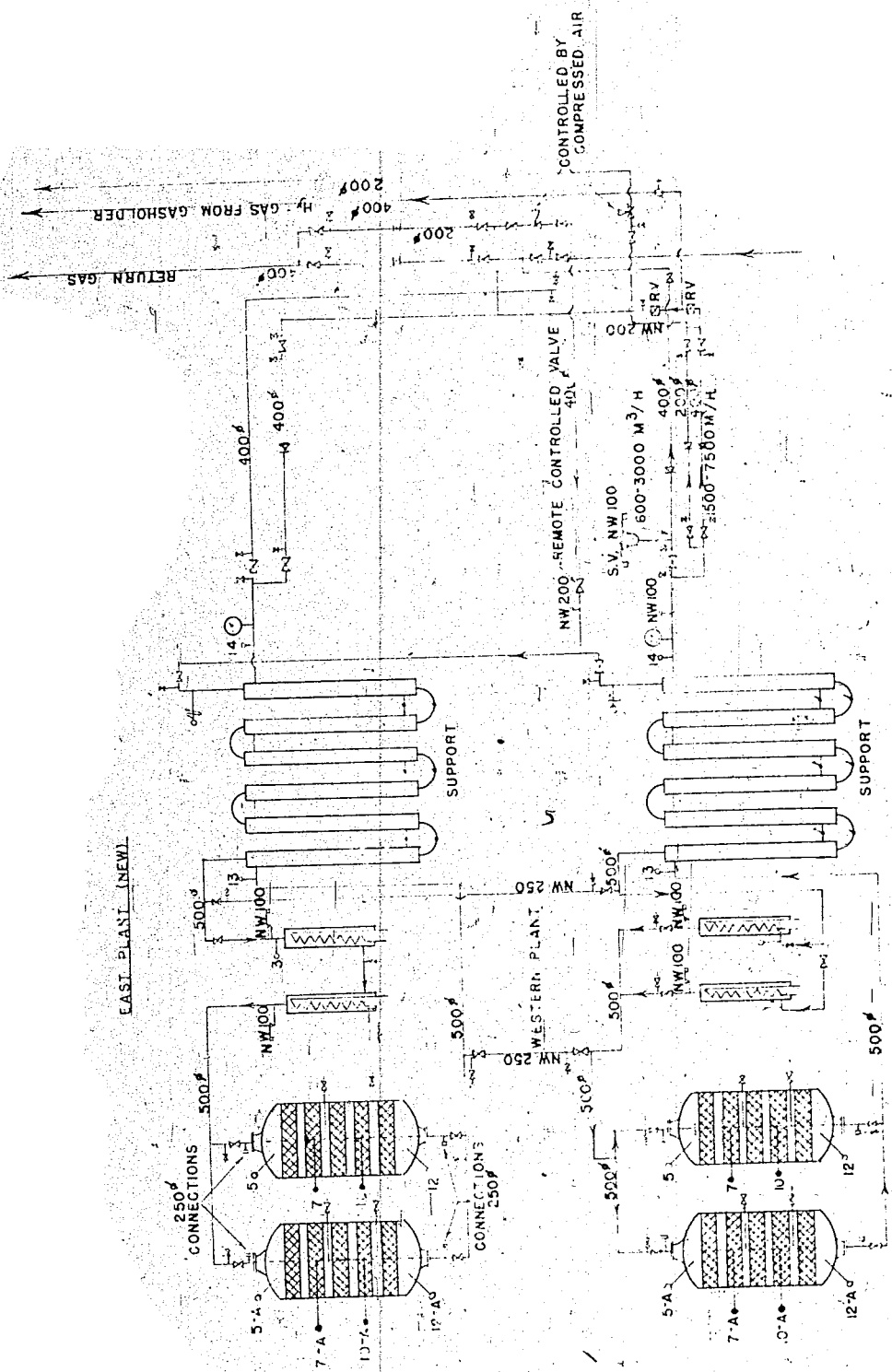
Drawing supposed to represent installation for the removal of COS from gases

Item 25 c

Ditto

Item 25d

Steam lines of the COS-absorption-system

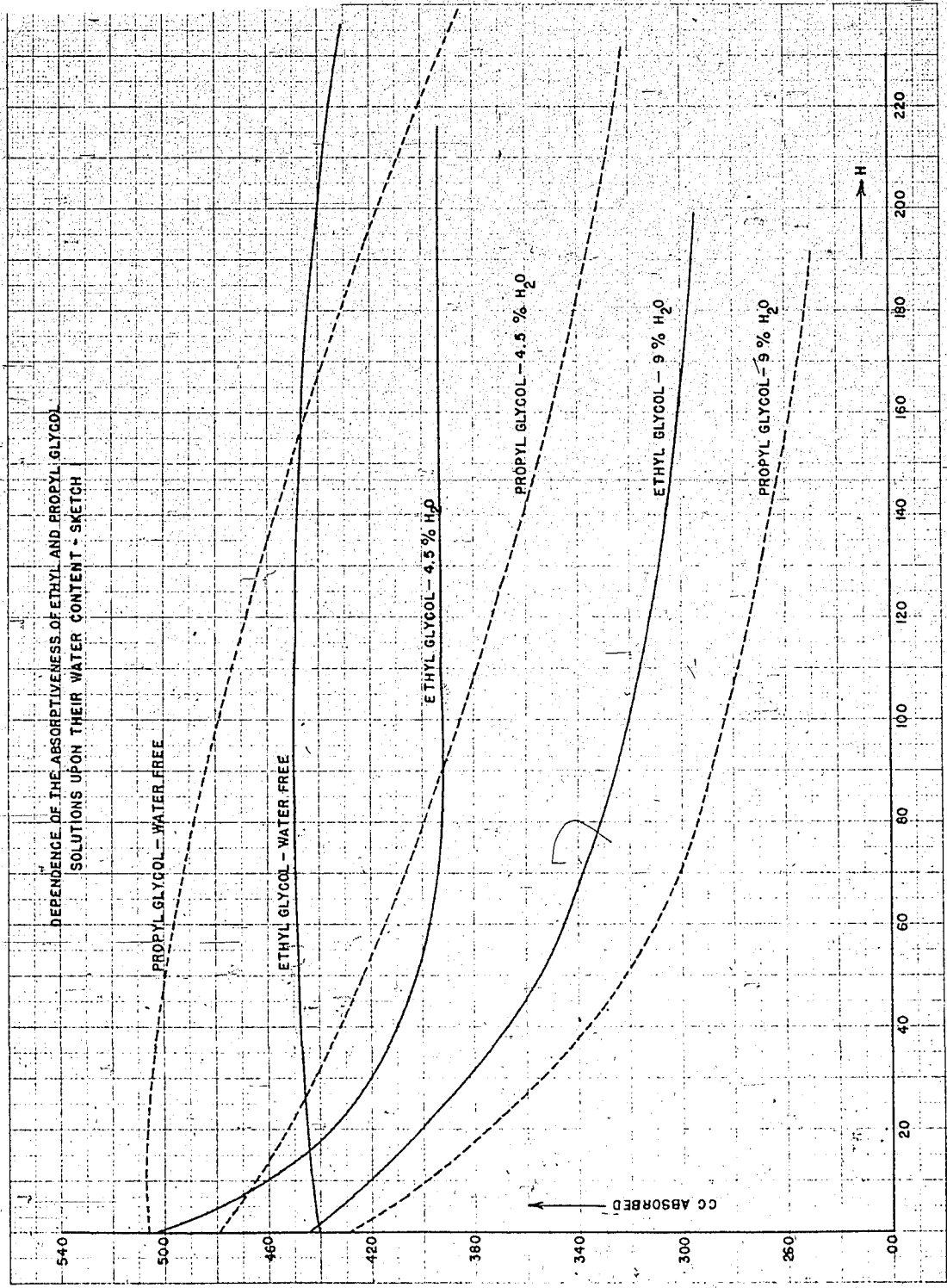


- RECORDING THERMOCOUPLE
- HAND OPERATED THERMOCOUPLE
- ⌈ THERMOMETER
- ⌈ RECORDING THERMOMETER
- ⊙ PRESSURE GAGE
- ⌈ SAFETY VALVE

REMOVAL OF CO<sub>2</sub> FROM GASES

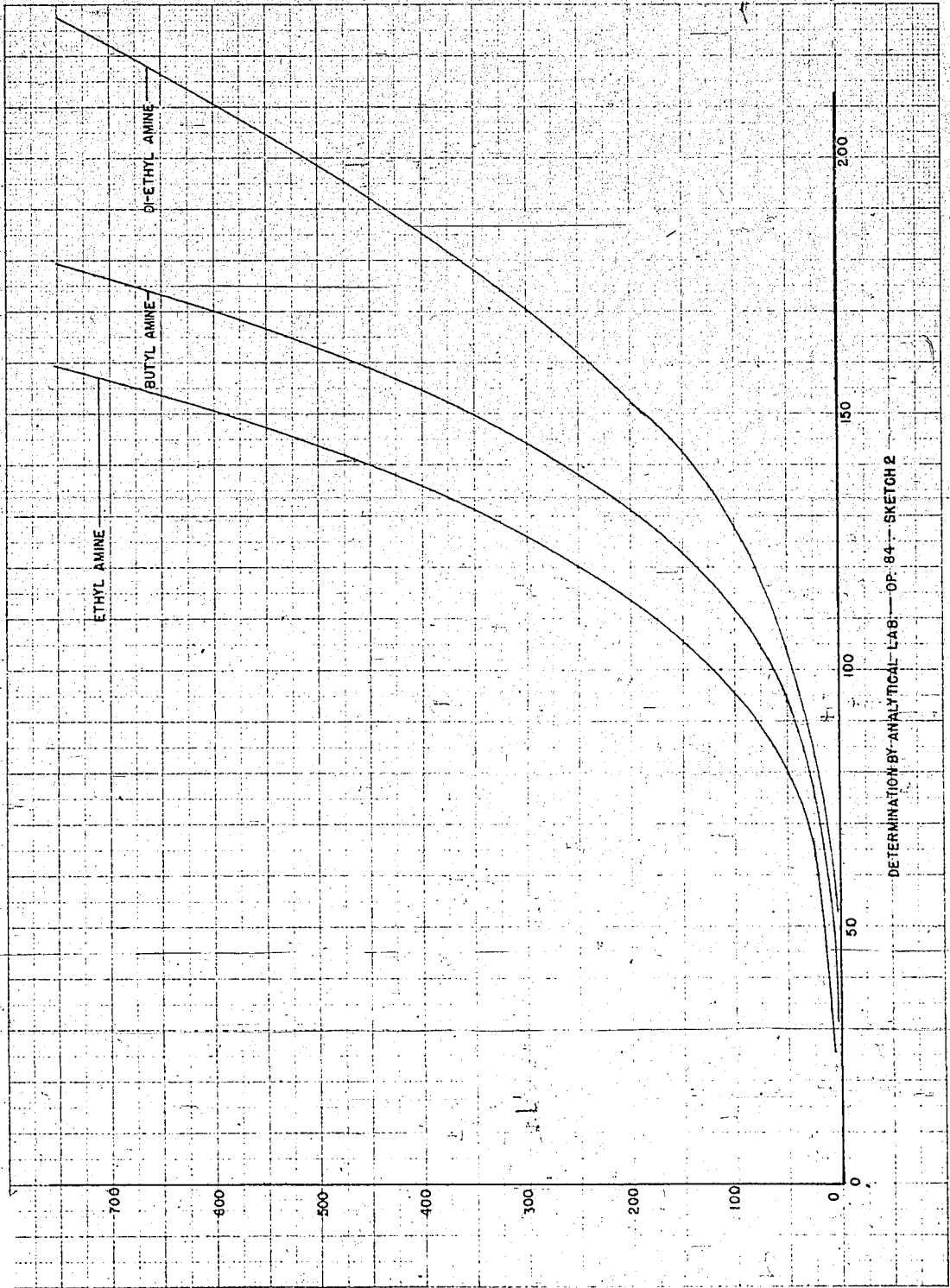
ITEM 25 b

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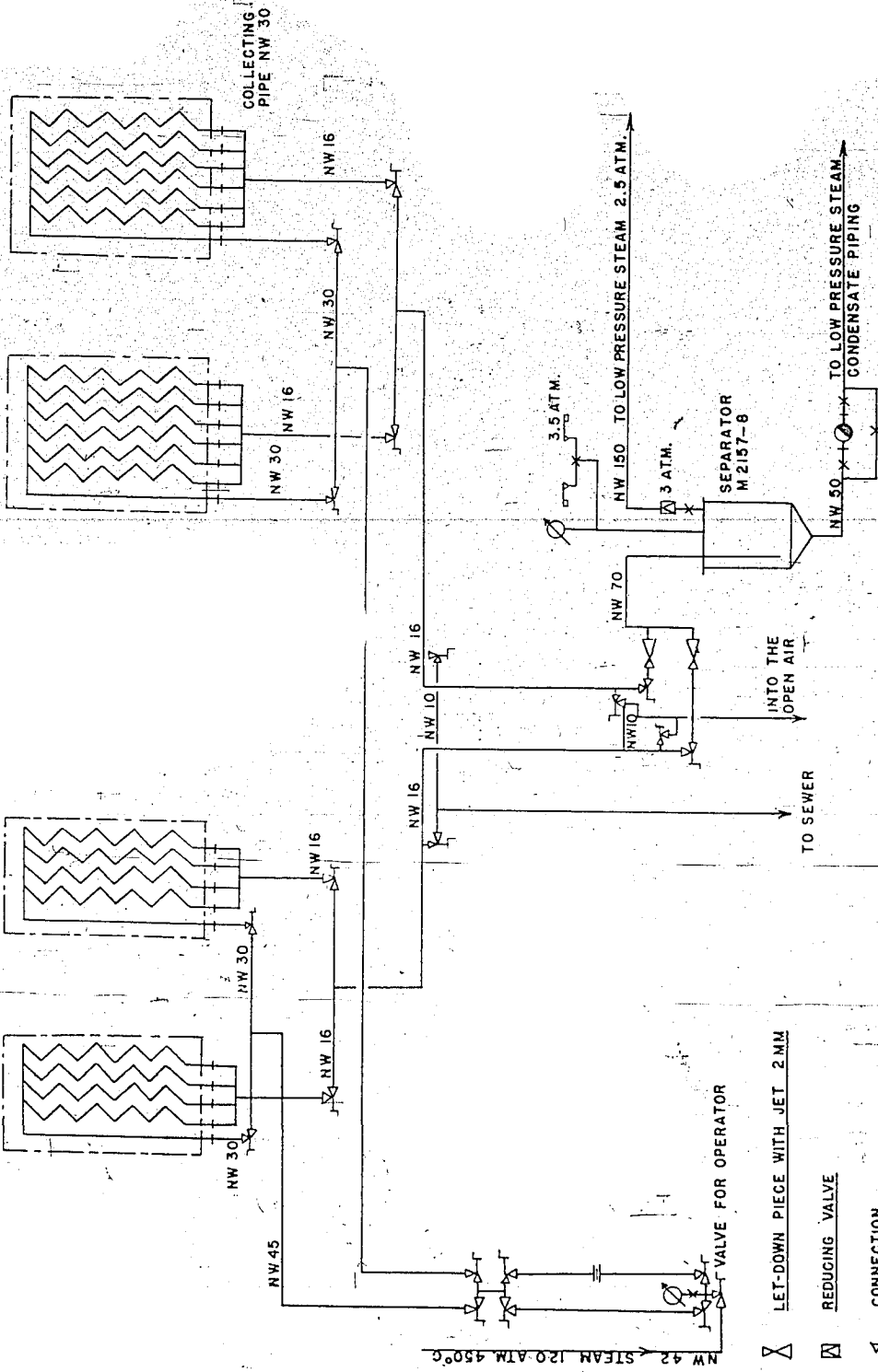




827



DETERMINATION BY ANALYTICAL LAB.—OP. 84.—SKETCH 2



- ▽ LET-DOWN PIECE WITH JET 2 MM
- ◻ REDUCING VALVE
- ◁ CONNECTION
- ⊕ BUCKET TRAP

STEAM LINES OF THE COS ABSORPTION SYSTEM

ITEM 25 d