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TOM 132 859

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Item 30

Drawing 240-248 on layout plan for a claus unit

Item 31

A New Process for Separation of NH₃-CO₂-H₂S Mixture

- I. Separation of Ammonia Sulfide and Ammonium Carbonate or Bicarbonate Mixtures
- II. Application of the Process on Gaswork or Coke Oven Waste Liquor

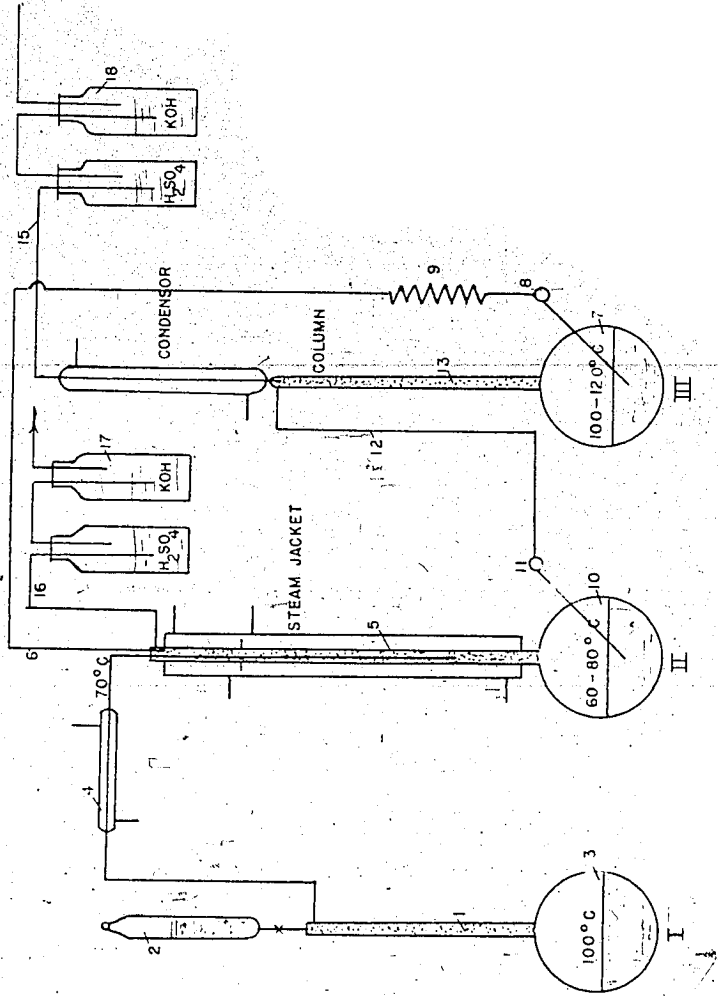
I. Separation of ammonium sulfide and ammonium carbonate or bicarbonate mixtures

Waste liquors are often obtained, especially when gases must be purified, which simultaneously contain ammonia, carbon dioxide or hydrogen sulfide or their mixtures. Such type of waste liquors can be liberated from the dissolved ammonia by means of injected steam. Cooling the obtained vapors an ammonia containing condensate is obtain. Since however besides ammonia also carbon dioxide and hydrogen sulfide are vaporized by the stripping procedure, the obtained liquor contains the ammonia in the form of ammonium carbonate or ammonium sulfide. With respect to the ammonia, it is very often desirable to recover the latter as a pure substance and to separate CO₂ and H₂S. Hitherto known separation methods used a step-by-step heating procedure which however resulted in only a partial separation of NH₃, CO₂ and H₂S.

A solution of the problem, as I realized it, would be to recover either of the constituents-ammonia as a weak base or H₂S or CO₂ as a weak acid- as a chemical constituent while the other is separated. In a subsequent system the combined constituent is stripped by means of heat and recovered separately. Weak acids, such as alanine, phenol, amino acids will combine with the ammonia whereafter the compound is decomposed at elevated temperatures, for instance 100°C., releasing the pure ammonia. Should, however, the weak acids be separated, alkaline acting substances have to be used which at normal or slightly elevated temperatures combine with CO₂ or H₂S while the ammonia remains untouched. Such substances are organic bases, as ethanol amines, alkal salts of amine acids etc.

Preliminary investigations of various solutions with respect to their suitability to separate ammonium sulfide into NH₃ and H₂S were performed using the apparatus which is represented by picture 1. The (NH₄)₂S solution to be stripped was fed to the column I (1) by means of a separatory funnel (2) and brought to a boil in the flask (3) where by NH₃ and H₂S are liberated. The vapors which have a temperature of 70°C. are introduced into the middle part of the column II (5) by means of pipe (4). The respective solution to be tested was injected into column II (5) using pipe (6). The solution was drawn off from the reboiler of column III (7) by means of pump (8) and passed through condenser (9) and pipe (6) to the column II (5). One of the gaseous constituents depending on the character of the separating liquid was absorbed and combining with the separating liquid reached flask (10), the latter being kept at temperatures of 60 to 80°C. The solution

PICTURE 1: APPARATUS FOR TESTING THE SUITABILITY OF SOLUTIONS TOWARDS THE DECOMPOSITION OF $(\text{NH}_4)_2\text{S}$ INTO NH_3 AND H_2S OR OF $(\text{NH}_4)_2\text{CO}_3$ INTO NH_3 AND CO_2 — PICTURE 1



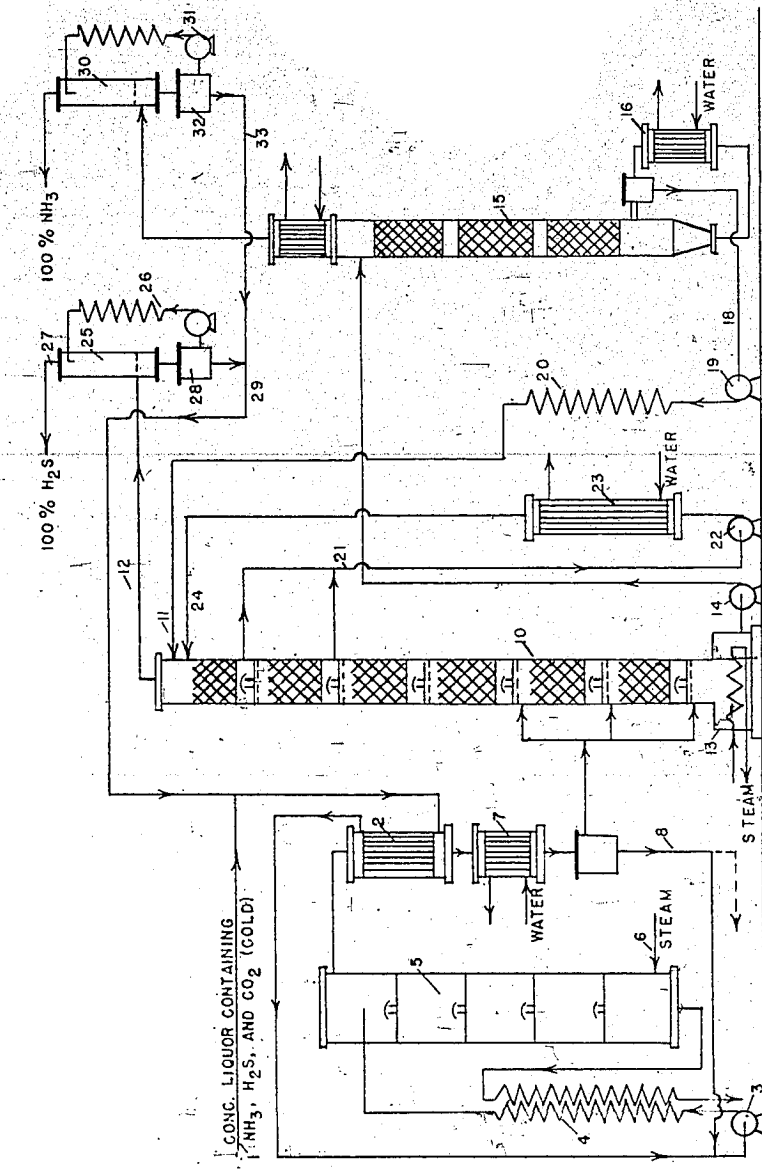
saturated with the respective constituent was pumped to the upper end (13) of the column III by means of pump (11) and pipe (12). By heating the solution to 100-120°C., the solution was stripped from the absorbent gaseous constituent by flowing through column III and flask (7). The vapors escaped by passing through column (13), condenser (14), and pipe (15). The stripped and refreshed solution is returned to column II (5) by means of pump (8) and condenser (9). The separated gaseous constituents flow through the pipes (15) or (16) respectively. They can be analyzed by passing through the washing bottles (17) or (18) respectively.

When carrying out the experiments 100-500 cc. of the ammonium sulfide solution containing about 20 g NH_3 and 20 g H_2S were stripped. Such a volume of separating liquid was recirculated between the column II and III so that the ratio of NH_3 to separating liquid varied from 1:0.5 to 1:1.5. Table I contains the results of the experiments. By comparing the results it can be easily seen that the phenol compounds and their homologues show especially favorable properties with respect to their separating capability. Since the waste liquors to be treated besides $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{S}$ often contain phenols in addition, which are vaporized together with the NH_3 - CO_2 - H_2S vapors and are simultaneously absorbed by the separating liquids, the application of phenols is of considerable advantage. If however the separating liquid itself consists of phenols or their homologues, no deterioration of the separating liquid is to be expected but on the contrary the vaporized phenols are recovered.

With corrosion tests concerning the durability of metals complete an iron apparatus was designed and constructed because iron seemed to offer satisfactory resistance against the applied phenol solution. Sketch 2 represents the principle of the apparatus.

The concentrated waste liquor, containing NH_3 , H_2S , and CO_2 flowing through pipe (1) is preheated in the condenser (2) is fed to the still (5) by means of pump (3) passing through heat exchanger (4). Live steam is injected into the lower part of the still (6) in order to strip the water from NH_3 , H_2S , and CO_2 . The escaping vapors, passing through condensers (2) and (7) are cooled to about 80°C. The condensate which originates from the cooling process is returned into the crude liquor to be treated by means of pipe (8) and introduced just before pump (3). The stripped vapors at a temperature of 80°C. are injected into the lower part of the separating column (10) by means of pipe (9). The separating liquor is sprayed into column (10) flowing through pipe (11). The phenols descending through column (10) combine with the ammonia vapors while H_2S and CO_2 escape by means of pipe (12). The ammonium phenolate solution is collected in the receiver (13) which by means of a steam coil is kept at 60-70°C. By means of pump (14) the solution is transferred to column (15). The ammonium phenolate solution is heated to approx. 100°C. in the reboiler (16). The liberated ammonium vapors escape by means of pipe (17). The stripped solution by means of pipe (18) pump (19) passing through condenser (20) is returned to column (10) by means of pipe (11). It has been considered advisable to recirculate a part of the solution by means of pipe (21), pump (22), condenser (23), and pipe (24), whereby the liquid is cooled during its passage through cooler (23). The H_2S - CO_2 mixture escaping through pipe (12) is washed by water in the scrubber (25) whereby ammonia vapors still present in the gas are absorbed, simultaneously the gas mixture is cooled by condenser (27). The pure gaseous H_2S and

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PICTURE 2 - PILOT PLANT FOR THE SEPARATION OF NH₃ FROM H₂S AND CO₂

G.C.E. 6/25/47

CO₂ or the mixture of both leave the condenser through pipe (27). The extracted NH₃ is accumulated in the water. From time to time the fouled solution is drawn off from the container (28) and returned to the crude liquor by means of pipe (29). The ammonia vapors which have been liberated in the column (15) by means of pipe (17) are transferred to the scrubber (30). A recirculating water solution of ammonia, which is cooled by the condenser (31), extracts the last traces of H₂S and CO₂. The solution containing H₂S and CO₂ is collected in the container (32) and returned to the crude liquor by means of pipe (33). It was possible to treat 10 liter per hour concentrated ammonia-liquor. The separating effect of H₂S and CO₂ was as high as 99%.

Applicability of the process:

- 1) Separation of NH₃ from H₂S and CO₂ which are present in waste liquors. Such type of waste liquors are a by-product of hydrogenation-coke oven plants and gas works.
- 2) The ammonia vapors, liberated from CO₂ and H₂S, can be returned to the gas to be stripped from CO₂ and H₂S. Both of the constituents are extracted, whereby solutions of ammonium carbonate and ammonium sulfide are obtained. Separating the NH₃ from H₂S and CO₂ and recirculating the purified ammonia-solution a gas purification process can be performed.
- 3) Ammonia containing gases to be liberated from H₂S and CO₂ are scrubbed with water. Ammonia and CO₂ or H₂S respectively can be recovered by subjecting the obtained liquor to the separating process.

The recovery of NH₃ and CO₂ or H₂S respectively from concentrated ammonia-liquors

The described apparatus was employed for the separate recovery of NH₃ and CO₂ or H₂S respectively from concentrated ammonia liquors. In the beginning ammonia liquor containing 10-20 g NH₃ was employed but later on strong liquors with an ammonia content as high as 150-200 g/l were treated. The plant was operated with such an output that always 5-6 cu. m. gaseous NH₃ per hour had to be treated. When concentrated liquor was employed, approx. 15-25 liters per hour could be separated.

By means of steam the liquor is completely stripped from ammonia. By cooling to 80°C. the vapors containing NH₃, H₂S, and CO₂, the entrained water vapors are partly condensed. The condensate which besides water consists of NH₃, H₂S, and CO₂ is returned to the crude liquor and treated anew.

The vapors are transferred to that column which separated NH₃ from H₂S and CO₂; 40 liters per hour phenol-solution were fed to the column. The phenol solution is fed to the top of the column with a temperature of 25°C. The ammonia combines with the phenols and the obtained phenolate solution is collected in the lower part of the column, where a temperature of 70°C. is maintained. A proper temperature control is necessary in order to prevent any dissolution of H₂S and CO₂ in the phenol solution followed by the formation of (NH₄)₂S and (NH₄)₂CO₃. Should (NH₄)₂S and (NH₄)₂CO₃ happen to be present in the ammonium phenolate solution, the ammonia vapors which are stripped in the following column would contain CO₂ and H₂S as impurities. A temperature increase from the top to the bottom of the column from 25-70°C. must be maintained. Should there be an increase in temperature in the middle part of the column, the phenolate solution is cooled by a condenser; 75 liters per hour of the phenolate solution had to be

recycled in order to maintain the proper temperatures. The H_2S-CO_2 mixture leaving the column contains but 1-3% ammonia vapors, sometimes not more than 0.1-0.2%. The ammonia leaving the ammonia-separating column contained 2-5% H_2S and CO_2 . During its passage through the final scrubber the recovery of a 98-99% pure ammonia was achieved. Since it is mostly possible to draw off from the ammonia separating column almost pure ammonia vapors, the scrubber has to be operated but occasionally. The spent solution is returned to the crude liquor. By the application of the described procedure, losses are eliminated resulting in a complete recovery of ammonia, H_2S and CO_2 from the liquor fed to the separating unit. The prepared table contains the results of numerous test runs.

As shown, the separating effect of the unit was as high as 98-99%. Approximately 100-150 cu. m. NH_3 are stripped from 1 cu. m. of the separating liquid. The steam consumption and consequently the economy of the process depend on the volume of ammonia vapors which are absorbed per 1 cu. m. of the acting liquid.

During the test runs metal samples were put into the inside of the apparatus in order to determine the resistance of various metals against the phenol solution. Table 2 contains the obtained results. According to the table iron is most resistant; for heating coils and parts which are supposed to come into contact with the heated solution V_2A or Sicromal should be employed; while all parts which are subjected to the influence of ammonia or H_2S -containing vapors should be made of aluminum.

Separation of ammonium carbonate solutions into ammonia and carbon dioxide

Summary

In connection with gas purification processes waste liquors are obtained which contain ammonia as well as hydrogen sulfide and carbon dioxide. There exists a demand to recover from such liquors separated ammonia, hydrogen sulfide and carbon dioxide.

A new process has been developed which works as follows: by means of weak acids the ammonia, which is present in the vapors originating from stripping the liquor, is selectively extracted whereby H_2S and CO_2 are drawn off and can be recovered separately from the ammonia. In a following apparatus the ammonia is stripped from the absorbing liquid consisting of weak acids.

Suitable weak acids are phenols and their homologues. A small scale plant was designed and constructed having an output of 20 liters per hour of concentrated ammonia liquor. When operating the plant it was possible to recover separately ammonia and H_2S and CO_2 whereby the separated constituents are 97-98% pure.

The following report contains the results which have been obtained when the ammonia liquor of the Huls coke-oven-plant was used.

Part II

Application of the process to the separation of waste liquors originating from gaswork-or-coke-oven operation. Separation of the stripped vapors, containing $(NH_4)_2S$ and/or $(NH_4)_2CO_3$ into NH_3 , H_2S and CO_2 .
Combustion of the recovered ammonia to nitrogen oxide.

The waste liquor which originates from the carbonization of coal contains, besides free ammonia, considerable amounts of ammonia combined with H_2S and CO_2 . By stripping the liquor and condensing the vapors,

Table I
Separation of NH₃ and H₂S originating from ammoniumsulfide solution

date	Type of the empl. separating sol.	Ratio NH ₃ : mol./mol.	50%	Column I		Column II		Column III	
				NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S
1/3/38	Phenol	1 : 1.8	50%	100	100	51.3	97.2	48.7	2.8
1/5/38	"	1 : 2.7	"	100	100	4.6	79.5	95.4	20.5
1/5/38	"	1 : 3.4	"	100	100	6.6	93.6	93.4	6.4
1/4/38	"	1 : 3.4	"	100	100	20.3	93.9	79.7	6.1
1/6/38	"	1 : 3.4	"	100	100	8.3	69.8	91.7	30.2
1/22/38	"	1 : 4.8	"	100	100	14.0	96.9	86.0	3.1
1/12/38	"	1 : 4.9	"	100	100	32.2	97.0	67.8	3.0
1/17/38	"	1 : 5.1	"	100	100	3.0	93.8	97.0	6.2
1/18/38	"	1 : 5.2	"	100	100	0.1	96.3	99.9	3.7
1/18/38	"	1 : 5.2	"	100	100	0.1	96.7	99.9	3.3
1/13/38	"	1 : 5.3	"	100	100	0.0	88.5	100.0	11.5
1/19/38	"	1 : 5.4	"	100	100	23.7	89.9	76.3	10.1
1/15/38	"	1 : 5.5	"	100	100	10.5	92.5	89.5	7.5
1/7/38	"	1 : 5.7	"	100	100	3.0	85.0	97.0	15.0
1/20/38	"	1 : 6.1	"	100	100	0.1	79.0	99.9	21.0
1/11/38	"	1 : 6.5	"	100	100	2.1	82.2	97.9	17.8
12/31/37	"	1 : 7.0	"	100	100	8.5	82.6	91.5	17.4
12/31/37	"	1 : 10.0	"	100	100	5.3	97.2	94.7	2.7
12/30/37	"	1 : 10.0	"	100	100	4.3	87.6	95.7	12.4
12/28/37	"	1 : 10.0	"	100	100	3.0	77.4	97.0	22.6
12/28/37	"	1 : 50.0	"	100	100	2.6	69.8	97.4	30.2
12/28/37	"	1 : 74.0	"	100	100	62.2	94.4	37.8	5.6

(Continued on next page)

Table 1 (Cont.)

Date	Type of empl. sol.	Ratio NH ₃ : sep. sol. sol./ml.	Initial NH ₃ column I	% NH ₃ + H ₂ S		Column III NH ₃ H ₂ S	
				Column II NH ₃ H ₂ S	Column III NH ₃ H ₂ S		
12/22/37	Triethylenetetramine 50%	1 : 0.20	100	100	42.5	26.5	73.5
12/22/37	"	1 : 0.55	100	100	50.4	18.6	81.4
1/24/38	"	1 : 2.1	100	100	99.4	21.1	0.6
2/20/38	85% Triethylenetetramine	1 : 2.3	100	100	97.9	49.5	2.1
12/21/37	100% + 30% Xylolol	1 : 0.54	100	100	22.7	23.9	77.3
12/20/37	Diethanolamine 50%	1 : 0.56	100	100	39.5	38.9	60.5
12/21/37	Dioethanolamine 80%	1 : 0.60	100	100	34.0	34.0	66.0
12/30/37	Monocethanolamine 30%	1 : 1.9	100	100	34.7	77.0	15.3
12/29/37	" 100%	1 : 2.8	100	100	82.2	33.3	17.8
12/27/37	Diaminopropanol 24.5%	1 : 1.0	100	100	57.5	29.9	42.5
1/3/38	" 98%	1 : 1.0	100	100	97.2	44.0	2.8
12/7/37	Dik-Lauzo D = 1.160 30%	1 : 0.72	100	100	55.3	31.0	44.7
5/17/38	Methylalanine 45%	1 : 9.3	100	100	0.0	80.0	100.0
5/19/38	" 45%	1 : 9.4	100	100	1.0	78.9	99.0
5/17/38	" 45%	1 : 10.4	100	100	2.4	79.5	97.6
1/24/38	Methylglycocol 50%	1 : 2.1	100	100	53.2	89.6	46.8
12/13/37	" 50%	1 : 2.5	100	100	19.4	74.3	80.6
5/20/38	Glycocol 17%	1 : 3.4	100	100	3.0	61.5	97.0
5/20/38	" 17%	1 : 5.8	100	100	2.5	55.8	97.5
12/22/37	Hydroquinone 50%	1 : 0.5	100	100	31.4	72.6	68.6
12/22/37	" 50%	1 : 1.0	100	100	19.0	73.5	81.0
12/7/37	Sodium phosphate (Mono-H) 45%	1 : 0.68	100	100	96.8	99.8	0.2
12/6/37	Sodium phosphate (DI-H) 45%	1 : 2.78	100	100	100.0	95.6	0.0

Table 2

Designation of metals	Type of solution	Flask reflux- condenser	H ₂ S-CO ₂ separating col.		NH ₃ -separating column	
			mm/year	mm/year	mm/yr.	mm/yr.
Aluminum	Phenol-sol. 50%	0.1395	-	-	-	-
Cast iron		0.4815	-	-	-	-
Wrought iron		0.2580	-	-	-	-
V ₂ A		0.0706	-	-	-	-
Sicromal		0.0544	-	-	-	-
N ₅		0.0808	-	-	-	-
N ₆		0.0762	-	-	-	-
Boiler plate	Crude phenol 100%	-	2.330	0.033	0.055	0.316
Cast iron		-	1.670	0.001	0.080	0.575
N ₆		-	0.675	0.013	0.015	0.027
V ₂ A Supra		-	0.019	+0.10	0.001	+0.02 +mg/c
Sicromal 10		-	0.022	+0.17	0.000	+0.01 +mg/c
Aluminum		-	+0.03	0.085	0.118	0.119+mg/c

concentrated liquor containing 20% NH_3 can be obtained. The liquor however contains the simultaneously liberated H_2S and CO_2 -gases which seriously hinder the application of the liquor for the manufacturing of nitric acid.

The reason for carrying out the described experiments was to investigate the process, which was developed by Dr. Baehr with respect to its applicability to the separation of such liquors which originate from the carbonization of coal.

Principle of the process

The principle of the process is as follows: The NH_3 , CO_2 and H_2S containing vapors are passed through a tower packed with Raschig rings to which xylol or xylol-phenol-mixtures are fed. The ammonia vapors combine with the absorbent while CO_2 and H_2S remain untouched and leave the tower at its top, ready for further utilization. The xylol enriched with NH_3 is pumped to a following tower in the lower part of which the liquid is heated to such a temperature, that the previously absorbed ammonia vapors are liberated. The described procedure achieves the separation of NH_3 from CO_2 and H_2S .

The design of the employed apparatus is represented by sketch I. The waste liquor containing NH_3 , H_2S and CO_2 flows from container (a) into the stripper I which is heated by indirect steam. The liberated vapors are cooled to about 60°C . by means of the condenser (b) and are introduced into the lower ring (c) of tower II. The tower is composed of various rings which are equipped with suitable distributors for the liquor. The receiver (d) situated underneath the tower can be heated by steam. In order to prevent H_2S and CO_2 from being carried over into the NH_3 -separating tower, a temperature of 65 - 75°C . is maintained in the receiver. The H_2S - CO_2 -gases leave the upper rings of the tower by passing through pipe (h).

The absorbent withdrawn from tower II by means of pump (f) and transferred to the ammonia-separating tower III, which being lower, is heated by steam in its lower part (e). By maintaining a temperature of about 100°C . the ammonia is almost completely stripped. The ammonia vapors, after having passed through the condenser (g) are discharged. The stripped absorbent is returned to the tower II by means of pump (h) flowing through condenser (i). The absorbent describes a cycle between the towers II and III.

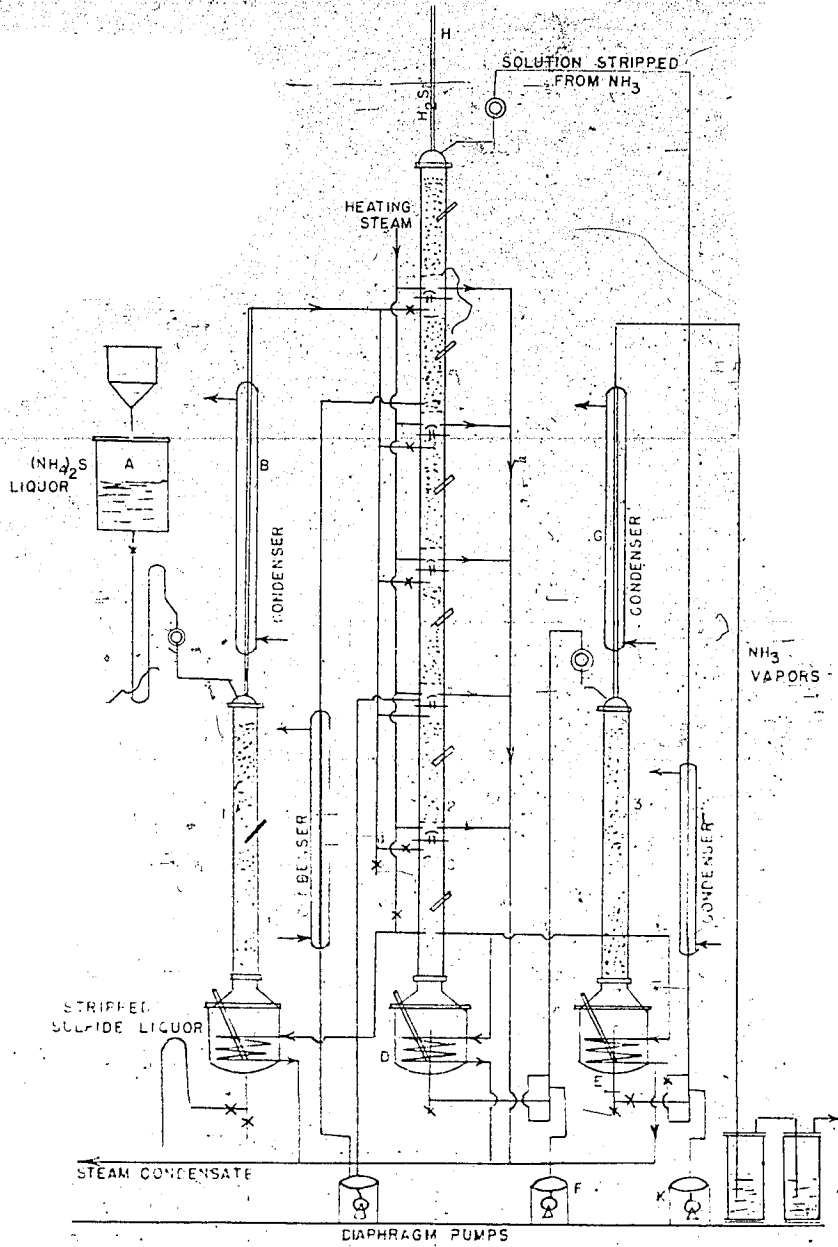
The small scale plant supplied by the Leuna works had an output of 20 liters per hour of 20% ammonia liquor. The plant has been operated from March 25 to June 13, 1938. Up to May 17, 1938 the employed ammonia liquor originated from the alkazid plant which was operated with coke oven gas. The liquor to be treated contained but small amounts of CO_2 . Applying temperature of 98°C . the liquor was almost completely stripped from NH_3 and H_2S . From May 17, 1938, besides H_2S , the ammonia liquor contained considerable amounts of CO_2 . Applying equal temperatures as before it was now impossible to strip the liquor from the ammonia, H_2S and CO_2 vapors. Due to mechanical difficulties it was impossible to raise the temperature.

On the average the gases leaving the H_2S - CO_2 -separating tower still contained 0.3% NH_3 . Nothing but the H_2S - CO_2 ratio was determined. Since the CO_2 -content was not taken into account, based on CC_2 - H_2S the NH_3 -concentration would have been a little lower.

The most favorable temperatures were 75°C . in the receiver and 30°C . at the gas exit, whereby the temperature should continuously decrease from ring to ring from top to bottom.

SMALL SCALE APPARATUS FOR THE SEPARATION OF $(NH_4)_2S$

SKETCH I



Applying a temperature of 98°C. in the receiver of the NH₃-separating column secured an almost complete stripping of NH₃-containing absorbent. The escaping gas besides 98.6% NH₃ still contained 1.4 NH₃.

The NH₃-content of the xylenol before the NH₃-separating column was 58.17 g/l, whereas the stripped xylenol still contained 9.5 g/l NH₃. Due to the small size of the apparatus it was impossible to determine any xylenol losses due to entrainment because the losses, which were caused by slightly leaking pumps, were considerably higher.

Furthermore it was impossible to measure the steam consumption because the steam had to be withdrawn from the end of a very long pipe which carried large volumes of steam condensate, which were separated just before the plant.

The plant could be operated fairly satisfactorily and the proper temperatures could be easily maintained. Choking of the discharge pipes which carried NH₃ and H₂S respectively was sometimes observed because heating facilities had not been provided for.

Reaction of the xylenol upon repeated heating

In order to make sure whether the properties of the xylenol were changed by the repeated heating, distillation analyses were carried out at intervals of several days. As indicated by the following table no alterations could be observed.

Date	Distillate to				Residue g	Remarks
	ccm. used	100°C. ccm.	190°C. ccm.	190-220°C. ccm.		
April 4	100	1.0	7.8	89.0	2.2	Original xylenol
"	6 100	1.5	4.4	92.0	2.1	
May 18	100	2.0	4.8	91.0	2.2	
April 6	100	4.0	7.3	86.0	2.7	Samples drawn from
"	12 100	2.0	6.5	89.0	2.5	the pilot plant. No
"	22 100	1.5	5.5	91.0	2.0	xylenol refilled
May 18	100	2.0	4.8	91.0	2.2	Samples drawn from the
June 8	100	1.8	6.2	90.0	2.0	pilot plant. Small volumes of xylenol refilled.

The fresh xylenol was of a yellow color, whereas the xylenol which had been in operation was of a dark brown color.

Material

The apparatus was entirely made of iron. After a three month operation the heating coil of column I (ammonia still) was considerably corroded. The inlet feed pipe as well as the walls were more or less corroded. Such corrossions were to be expected, because iron is attacked by hot ammonia liquors.

The walls of column II (CO₂-H₂S-separating column) were not affected. The heating coil inside the receiver was slightly corroded. After a two month operation the steam coil of column III (NH₃-separating column) showed pinhole corrosion, especially at the welded joints. The coil was replaced by one made of aluminum which however after a one month operation showed pinhole corrosion. The iron walls were not affected. In order to obtain more detailed information about the influence of the absorbent, as well as of the respective gases upon various metals, samples had been fixed to various sections of the plant.

Table 4 represents the obtained results. The most suitable metals are 99.5% aluminum and sicromal for column I (ammonia still)
 V₂A-supra, sicromal 10, aluminum 99.5% for column II (H₂S-CO₂-separation)
 V₂A-supra, aluminum 99.5% for column III (NH₃-separation)
 Boiler plate, cast iron and N₆ show small losses too if employed in the boiler construction.

Experiments concerning the combustion of the recovered NH₃ to nitric acid

In order to determine whether any deterioration of the platinum catalyst occurs if waste-liquor-ammonia is burned, the following 2 experiments were performed: NH₃ which had been liberated from waste liquor was purified from H₂S by means of bog iron ore and burned to nitrogen oxide. Subsequently the NH₃ withdrawn from the separation unit was subjected to the same test.

The usually employed laboratory apparatus was used for the experiments and the routine analyses were made. Concentrated crude ammonia liquor (14-20%) was poured into a distilling flask equipped with a distilling head and stripped. The liberated vapors were led through two drying towers filled with bog iron ore in order to extract the hydrogen sulfide. In a subsequent mixing flask, packed with Raschig rings, air was added to 80 liter ammonia, whereafter the mixture was passed over the catalyst. The attached diagram represents the obtained yields which were as high as 98% (July 14, 1937-March 13, 1938

Beginning with March 27, 1938 gaseous NH₃ was withdrawn from the pilot plant and used for the oxidation. The NH₃-gases were passed through a small scrubber into which ammonia liquor was injected (15 liters per hour). A small volume of the saturated solution was continuously withdrawn and returned to the ammonia still. Approximately 3-4 liters per day of fresh water were added in order to keep constant the volume of the scrubbing solution. By the scrubbing process the ammonia gases were partly liberated from H₂S and entrained phenols.

The purified NH₃-gas was transferred to a small gas holder (capacity 400 liters) from which by means of small blower it was passed through a container packed with bog iron ore and finally to the combustion chamber.

Two slightly different test runs were made simultaneously:

- 1) Without further additional purification the ammonia gas was directly passed over the catalyst.
- 2) Before entering the furnace the gas was led through 2 washing bottles filled with NaOH-solution. The ammonia-air mixture consisted of 80 liters NH₃ per hour and 720 liters air per hour. The furnace temperatures, the average of which was 700°C., varied between 640-720°C.

The platinum gauze which had been used for carrying out the experiments between December 14, 1937 and June 13, 1938 was used for the NaOH treated gas. A new platinum gauze had been used for the gas which had not been passed through sodium hydroxide solution. In both cases the yield averaged 98%.

Directly before the addition of air 0.023 and 0.015 g phenol per cu. m. was determined in the gas. No deterioration of the platinum gauzes could be observed. As soon as the experiments had been finished the platinum gauzes were shipped to the Leuna works for further inspection. The report reads as follows:

Not very much can be reported about the forwarded platinum gauzes

They are uniformly activated but considerably worn out. In commercial operation such a loss of weight is not permissible. The loss of weight of the acting surface proper could not be determined because:

1. The gauzes are heavily damaged.
2. The ratio of the reaction weight to the total one is unfavorable.

Summary

The process developed by Dr. Baehr which is supposed to separate NH_3 - H_2S - CO_2 -mixtures into NH_3 and H_2S - CO_2 has been employed for the separation of concentrated ammonia liquor. The experiments were carried out at the Huls-coke-oven-plant employing a small scale apparatus.

The mixtures could be separated into a NH_3 -gas with an ammonia content of 96% and in a CO_2 - H_2S -gas which still contained 0.8% NH_3 . The crude ammonia liquor contained 73.5% NH_3 , 22.6% H_2S and 3.9% CO_2 . The recovered ammonia was burned to nitric acid using a platinum catalyst. The output was 80 liters per hour of ammonia. The yields were 98%.

TABLE I (PART 2)

COLUMN II - H ₂ S-CO ₂ -SEPARATION				COLUMN III - NH ₃ -SEPARATION				Gas comp. Exit III							
Temperatures: column II		After stripping		Gas-comp. Exit II.		RO-boiler		Temperatures		Cond.		Exit III			
5	6	col. II- NH ₃	col. I, II, NH ₃	H ₂ S	H ₂ S	NH ₃	col. exit	col. exit	Column exit	OC.	OC.	H ₂ S	NH ₃		
°C.	°C.	E/l	E/l	%	%	%	°C.	°C.	°C.	°C.	°C.	g	g		
												%	%		
22	20	-	-	13.6	99.3	0.10	0.7	20	86	35	35	0.07	1.95	3.5	93.6
25	25	-	-	20.0	98.8	0.24	1.2	20	100	42	42	-	-	-	-
22	22	-	-	16.1	99.6	0.054	0.4	20	99	61	61	0.098	1.35	7.19	99.6
30	30	-	-	13.1	99.3	0.085	0.65	20	98	75	75	0.076	1.10	6.8	99.1
28	25	-	-	-	-	-	-	20	90	86	86	-	-	-	-
26	24	-	-	-	-	-	-	20	97	65	65	0.160	2.50	6.15	97.5
34	25	-	-	-	-	-	-	20	97	94	94	0.209	1.30	15.7	90.7
62	27	-	-	13.9	99.4	0.005	0.60	20	95	48	48	0.051	1.00	4.2	99.0
44	31	-	-	5.54	98.8	0.005	1.2	20	99	78	78	-	-	-	-
55	25	-	-	17.17	99.5	0.985	0.47	20	96	80	80	0.095	1.51	6.4	98.19
55	48	-	-	17.03	99.5	0.085	0.50	20	93	68	68	0.161	2.96	5.2	97.04
18	18	-	-	13.1	99.4	0.071	0.54	20	99	82	82	-	-	-	-
20	20	-	-	14.4	99.6	0.05	0.36	20	98	80	80	0.016	0.19	8.68	99.0
39	32	-	-	7.7	99.9	0.008	0.11	20	99	65	65	0.059	2.30	2.51	97.7
50	42	-	-	0.35	99.4	0.001	0.6	20	94	64	64	0.34	4.00	4.00	96.0
39	21	-	-	16.80	99.8	0.025	0.13	20	96	68	68	-	-	-	-
48	32	-	-	9.75	99.2	0.005	0.80	20	95	60	60	0.017	0.20	12.7	99.8
50	44	-	-	5.90	98.5	0.005	1.42	20	95	52	52	0.015	0.30	1.3	99.8
37	25	-	-	7.0	99.7	0.021	0.30	20	90	52	52	0.012	0.1	17.85	93.9
42	30	-	-	7.25	98.87	0.035	1.13	20	95	52	52	0.091	0.29	31.3	99.7
25	18	-	-	15.65	99.47	0.082	0.53	20	94	63	63	0.096	0.80	12.45	99.2
34	27	-	-	5.35	98.43	0.085	1.57	20	98	63	63	0.141	1.50	10.00	98.5
38	25	-	-	15.30	99.40	0.085	0.60	20	97	70	70	0.150	1.20	4.25	98.8
35	28	-	-	5.00	98.30	0.085	1.70	20	97	52	52	-	-	-	-
38	27	-	-	13.60	99.20	0.085	0.80	20	95	83	83	0.102	0.90	22.35	99.1
35	28	-	-	-	-	-	-	20	95	52	52	0.430	2.40	18.00	97.6

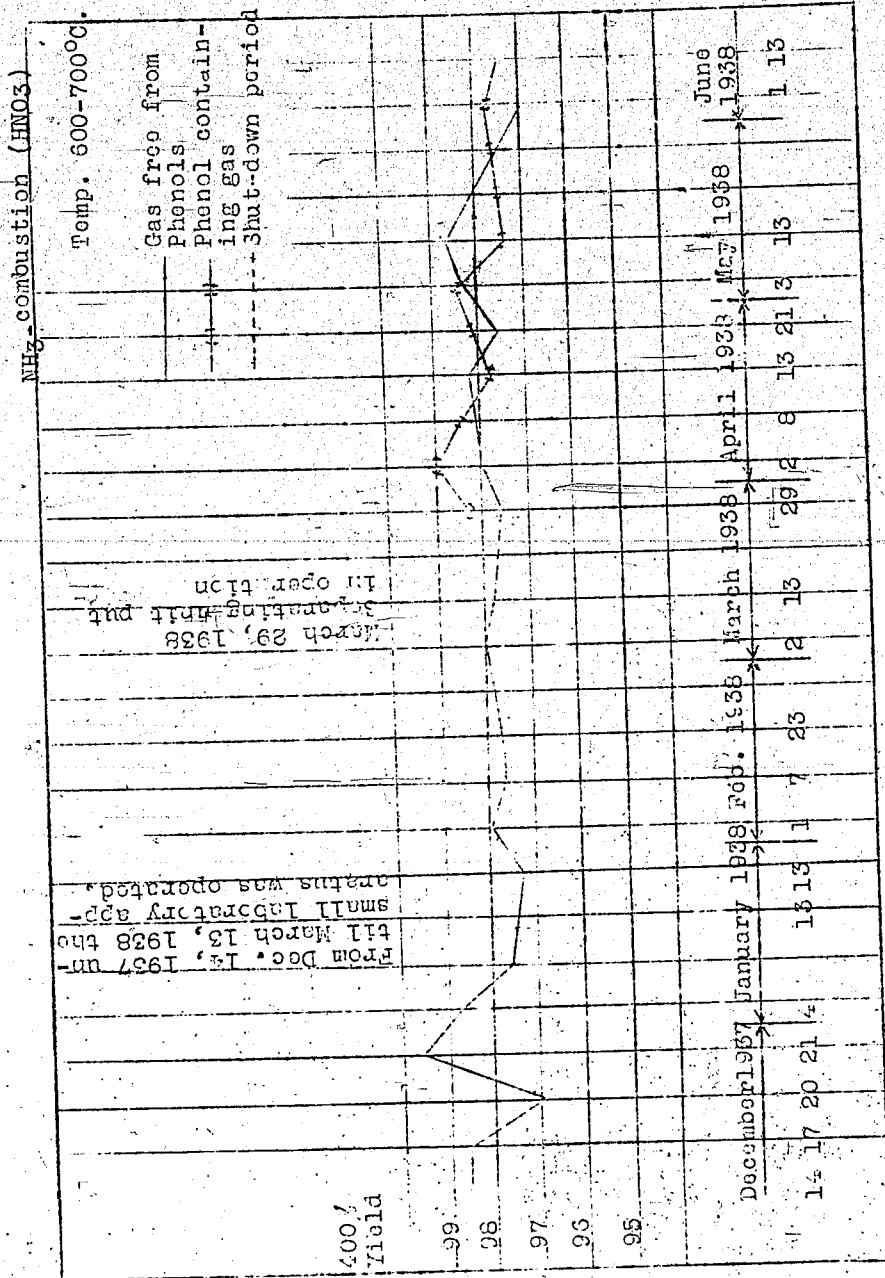


TABLE III
SEPARATION OF ANILINE CARBONATE SOLUTIONS INTO ANILINE AND CARBON DIOXIDE
SMALL SCALE PLANT

Test run no.	Aniline liquor lit/hr.	Employed NH ₃ Cu. m.	Content H ₂ S cu. m. Air. cu. m.	CO ₂ exit cu. m.	Stripping still Still condenser exit oc.	H ₂ S-CO ₂ -column		Analysis		NH ₃ column		Phenol soln sprayed in					
						Still lower upper oc.	ring C. ring C.	H ₂ S CO ₂ %	H ₂ S CO ₂ %	Still exit oc.	Still exit oc.		H ₂ S CO ₂ %	H ₂ S CO ₂ %			
1	3.0	1.0	-	1.0	92	100	91	23	-	99.3	0.2	100	21	-	1.3	98.7	20
2	4.0	1.0	-	1.0	93	100	83	24	-	99.7	0.3	106	56	-	0.4	99.6	20
3	4.0	1.0	-	1.0	100	100	66	48	-	99.7	0.3	112	60	-	-	-	20
4	4.0	1.0	-	1.0	100	100	87	32	-	-	-	103	78	-	1.1	98.9	20
5	2.0	1.0	-	1.0	98	100	73	30	-	99.7	0.3	106	57	-	1.6	98.4	20
6	2.0	1.0	-	1.0	98	100	65	29	-	99.9	0.1	111	49	-	0.6	99.4	20
7	2.0	1.0	0.32	1.0	51	102	63	28	-	99.9	0.1	107	34	-	10.02	99.98	20
8	1.0	0.95	0.32	0.95	51	102	68	34	18.97	81.0	0.03	102	62	0.0	1.6	98.4	20
9	1.0	0.95	0.21	0.95	55	102	66	31	-	-	-	102	64	0.0	-	100.0	29

SEPARATION OF CONCENTRATED ANILINE LIQUOR INTO ANILINE, H ₂ S AND CO ₂																	
10	20	5.93	0.31	2.1	92	53	66	52	15.0	84.3	0.7	95	93	0.2	6.2	95.6	40
11	22	5.93	0.31	2.1	99	62	81	32	23.9	75.9	0.2	102	90	0.2	4.2	95.6	40
12	22	5.03	0.31	2.1	100	63	72	34	23.4	76.4	0.2	100	60	0.7	2.2	97.1	40
13	22	5.03	0.31	2.18	98	44	70	24	9.9	90.0	0.1	104	74	0.2	0.0	99.9	40
14	19.5	4.86	0.31	2.18	198	53	67	24	15.6	84.0	0.2	102	76	0.3	0.0	99.7	40
15	20.5	5.38	0.35	2.46	96	66	65	-	-	99.6	0.4	102	71	0.0	0.4	97.6	40
16	20.5	5.48	0.35	2.46	97	58	72	24	9.3	90.4	0.3	104	85	0.2	2.2	97.6	40
17	20.5	5.49	0.33	2.38	99	60	60	29	99.7	94.3	98	80	0.9	2.7	96.4	40	
18	22.0	5.49	0.33	2.38	97	62	68	21	12.6	87.2	0.2	102	84	0.4	4.3	95.3	40