# BACKGROUND INFORMATION ON AMMONIA

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# INTRODUCTION

It appears that Doberman was the first to synthesize ammonia directly from its elements as he reported in 1823. Haber was probably the first to appreciate the importance of a suitable catalyst as the key to commercial development of the direct synthesis of ammonia.[1] Starting in 1908, Haber (et al) carried out detailed experimental investigations for many years in the search for a suitable catalyst and practical operating conditions. After many thousands of individual experiments a satisfactory catalyst was found, which consists of iron promoted with metallic oxides. As to operating conditions, Haber (et al) also developed the apparatus for the synthesis of ammonia. This principal is used in all present day converters with some modifications (Figure 1).

The converter developed by Haber consists of a thin-walled iron tube wrapped with asbestos paper around which is a nickel heating element. Inside the tube is a glass or quartz catalyst tube constricted on one end to form a cappillary tube which continues inside of the steel inlet gas tube to a point outside of the converter. Gas is circulated through the system as the arrows indicate. Ammonia contained in the gas is removed either by cooling or by an absorption agent such as water or acid.

Commercial synthetic ammonia production started in 1913 and subsequent rapid growth of the industry developed.

## Process[1]

Current synthesis of ammonia consists essentially of producing a gas mixture containing hydrogen and nitrogen in the proportion of 3 parts hydrogen to 1 of nitrogen, purifying this mixture, and synthesizing to ammonia under pressure in the presence of a suitable catalyst. In practically all modern plants, modification of the original Haber Bosch process are used. (Figure 2)

A modified water gas is produced in water gas generators. Coke from bituminous coal or lignite is first blasted to incandescent heat with air, most of the products of combustion going to the atmosphere. Water gas containing carbon dioxide, carbon monoxide, and hydrogen is obtained by passing steam through the fuel bed. The nitrogen required for ammonia synthesis is usually furnished by adding a sufficient quantity of the products of combustion from the blasting step to the gas stream. This mixed gas passes through a scrubber-cooler, where dust particles and undecomposed steam are removed with water, and the gas is then stored in a gas holder.

Gas from the holder is mixed with steam and passed through a carbon monoxide converter containing a catalyst, where most of the carbon monoxide is converted to carbon dioxide and hydrogen, and is then stored in a converter gas holder. Converted gas is compressed to 25

Figure 1.

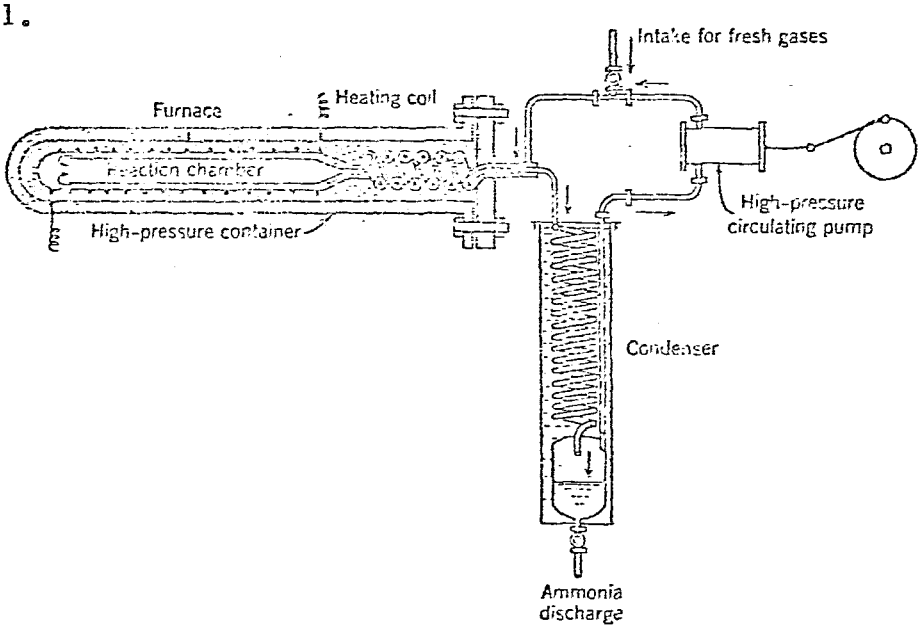
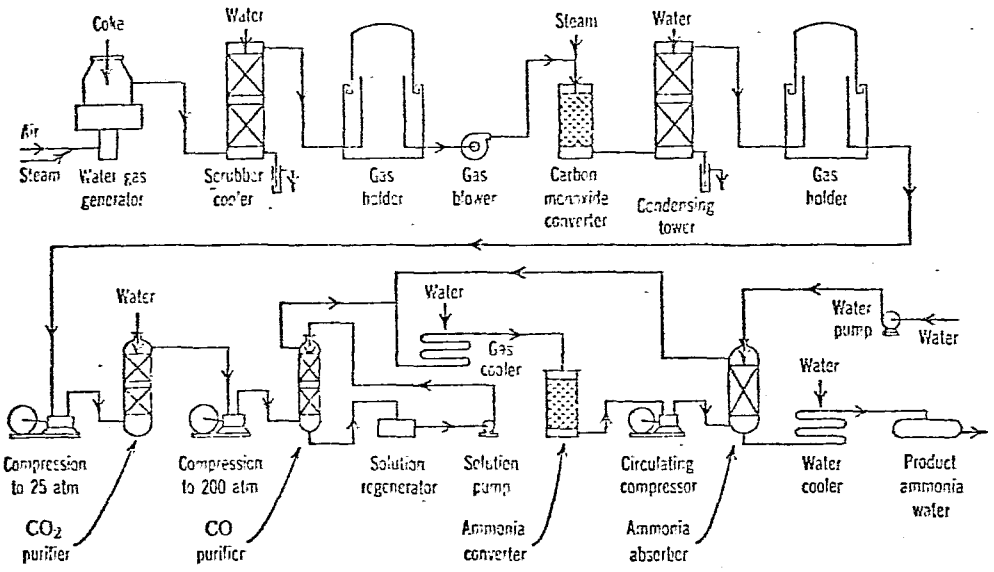

Intake for fresh gases
Furnace
Heating coil
Reaction chamber
High-pressure container
High-pressure
circulating pump
Condenser
Ammonia
discharge

Figure 2.


Coke
Water
Steam
Water
Air
Steam
Water gas generator
Scrubber cooler
Gas holder
Gas blower
Carbon monoxide converter
Condensing tower
Gas holder
Water
Water
Gas cooler
Water pump
Water
Water
Compression to 25 atm
Compression to 200 atm
Solution regenerator
Solution pump
Circulating compressor
Water cooler
Product ammonia water
$CO_2$ purifier
CO purifier
Ammonia converter
Ammonia absorber

atm. and passed, counter current to water, through a carbon dioxide purifier. The gas, now free of carbon dioxide, is compressed to 200 atm. and passed counter current to an ammoniacal cupreous solution in a carbon monoxide purifier. Here the residual carbon monoxide, unconverted in the carbon monoxide converter, is removed. The resultant relatively pure gas mixture, consisting of 3 parts hydrogen and 1 part nitrogen, is injected as makeup gas into the synthesis loop.

Circulating gas in the synthesis loop passes over a catalyst in the high-pressure ammonia converter where part of the gases unite to form ammonia. The exit gas from the converter is boosted in pressure by the circulating compressor in order to overcome pressure drop in the synthesis loop, and then passes through the ammonia absorber where the ammonia formed, is removed by water washing. The unconverted gas then joins with incoming makeup gas, and after passing through a water cooler, in order to condense out excess moisture, recirculates through the converter and the synthesis loop. The makeup gas contains a small percentage of argon, and sometimes methane, which also acts as an inert. In any process using recirculation these inerts tend to build up; their concentrations is therefore controlled to the desired extent by bleeding a protion of the circulating gas from the synthesis loop. Ammonia solution from the ammonia absorber is sold as such or sent to a distillation unit where the ammonia is recovered in the anhydrous state.

Separation of the ammonia from the circulating gases in the synthesis loops of all of the processes is done by condensation by cooling or by absorption in water. Since ammonia is now marketed to a great extent in the anhydrous state, and some hydrous ammonia is obtained as a by-product by scrubbing purge gases, most plants use the condensation method. The temperatures required to condense ammonia from a mixture of hydrogen and nitrogen gas at various pressures are in a range of $-20^{\circ}C$ to $+15^{\circ}C$. Pressures range from 50 to 1000 atm. When higher pressures are used, condensation can be accomplished by mere water cooling. When lower pressures are used, refrigeration is required.

Production and Use

Tables 1 and 2 reveal producers for 1961 and 1974 as indicated.[1,2] A cross reference of these tables may be helpful in determing well established firms in the field of ammonia production. It is evident that the ammonia industry has grown considerably in the past 15 years (10-12% annually). There were 12,602,000 more tons of ammonia produced in 1974 than in 1961.

Approximately 2/3 of the ammonia produced in the United States is consumed by agriculture in the form of fertilizers. Some of the principal fertilizers and fertilizer manufacturing process which utilize ammonia are anhydrous ammonia, ammonia liquor, ammonia nitrate, sodium nitrate, urea, urea ammonia nitrate solutions, amonium sulfate and amonium nitrate-limestone.

Of the remaining quantity produced, there are many uses.

1. Acids and Alkalies

   Most of the nitric acid consumed in the United States is made by the oxidation of anhydrous ammonia. The nitric acid can be further processed to produce nitrates and numerous other chemicals including dyes, insecticides and detergents.

2. Cleaning Agents

   Household ammonia, frequently used in homes and factories as a cleaning agent, is a weak solution of ammonia and water. Ammonia is also used in the compounding of certain dry cleaning and specialty soaps. Ammonia is used effectively as a stain remover for marble.

3. Explosives

   Most industrial and military explosives contain nitrogen, the basic source for which is ammonia. At the explosive plant ammonia is converted to nitric acid, which is used to produce the basic ingredients of explosives.

4. Food and Beverage Industries

   Ammonia is used in the fermintation industry as a source of nitrogen which is required for the growth of microorganisms. Ammonia is used in the beverage industry as an ammoniating agent for glycyrrhizin and as an extract for bitterness. Ammonia is also used as a fumigant and as a refrigerant in many food and beverage concerns.

5. Leather

   Ammonia is used as a slime and mold preventive in tanning liquors, and as a curing agent in making leather. The manufacture of mothproofing agents and other protectives for furs and hides involves the use of ammonia.

6. Dissociated ("Cracked") Ammonia

   Anhydrous ammonia has the ability to be shipped in the liquid form and thus serves as a convenient source of hydrogen or of an inert atmosphere. Dissociated ammonia is used as reducing atmosphere for bright annealing of stainless steels, nickel and its alloys, bronze, beryllium-copper, and other copper alloys, and high-low carbon steel.

Cracked ammonia serves in powder metallurgy as a medium for the reduction of metal oxides and for the sintering of pressed, powdered metal parts. It can be a source of hydrogen for atomic hydrogen welding and for the electronics industry.

7. Metallurgy

Ammonia can be used as a process agent in the detinning of scrap metals.

8. Petroleum Refining

Ammonia is used as an acid neutralizating agent to protect refinery equipment from the acids contained in the petroleum. It can also be used as a color stabilizer and desulfurizer for naptha, gasoline and kerosene.

9. Pharmaceuticals

Ammonia is utilized in the production of sulfa drugs and pharmaceuticals containing amino acids.

10. Pulp and Paper

Ammonia can be substituted for calcium in the bisulfite pulping of wood with improved results. It can also be used as a solvent for caseine in the coating of paper.

11. Textiles

Ammonia is used in the production of cuprammonium rayon and nylon. It is also incorporated in the dying and scouring of cotton, wool, rayon and silk. Acetate rayons are delustered by immersing the fabric in a 2% ammonia solution.

12. Refrigeration

There is more ammonia used as a refrigerant than any other since it is best suited for large industrial installations. Certain characteristics of ammonia, such as high latent heat of vaproation, low vapor density, chemical stability, and low corrosion to iron parts make it widely acceptable.

13. Rubber

Ammonia is employed by the rubber industry to keep synthetic and natural latex from coagulating during shipment. It is also used as an atmosphere during the curing of rubber.

14. Synthetic Resins

Urea, a component of synthetic resins, is usually formed at synthetic ammonia plants by reacting ammonia and carbon dioxide under pressure.

15. Water Purification

Industrial and municipal water supplies are often purified with a combination of chlorine and ammonia. Four parts chlorine are added to one part anhydrous ammonia to form a mixture of mono and dichloramines, which has a greater sterilization potential than does chlorine alone.

## Exposure

There is an estimated 500,000 persons in the United States exposed to ammonia. A list of potential exposures has been tabulated in Tabel 3.

## Toxicity

The recommended 8 hour time weighted average exposure ceiling level for ammonia is 50 ppm. Exposure to ammonia creates uncomfortable and at times dangerous conditions. Contact with liquid ammonia or liquid solutions can cause injury to the eyes, skin and respiratory tract. Ammonia gas, with only moderate exposure can cause headache, salvation, burning of the throat, anosmia, perspiration, nausea, vomiting and substernal pain. Higher concentrations may cause pulmonary edema or respiratory arrest.[3]

Gerhard Bittersohl[4] has suggested that ammonia may be carcinogenic or syncarcinogenic. This paper has been included as Appendix I.

## Sampling Analysis[5]

The sampling and analysis procedures that were recommended in the criteria document are given in Appendix II.

## REFERENCES


1. Kirk - Othmer: Encyclopedia of Chemical Technology. John Wiley and Sons, Inc., New York, Vol. 2, p. 265-296, 1963.

2. Director of Chemical Producers. Chemical Information Services, Stanford Research Institute, California, p. 416-417.

3. W.M. Gafafer, D.Sc.: Occupational Diseases, A Disease to Their Recognition. U.S. Dept. of HEW, p. 76-78, 1964.

4. Bittersohl, G.: Epidemiologic Study on Cancer of Workers in a Chemical Plant. Presented at the XVI International Congress on Occupational Health, Tokyo, 1969. Tokyo, Japanese Industrial Safety Association, p. 250-252, 1971.

5. Occupational Exposure to Ammonia. U.S. Department of HEW, PHS, Center for Disease Control, NIOSH. Cincinnati, Ohio. Pub. # 74-136, p. 89-96.

Table 1

AMMONIA PRODUCERS

| Corporation | Location | Annual Capacity Nitrogen, Thousand Short Tons |
|---|---|---|
| Allied Chemical Corp. | Hopewell, Va. | 330 |
| | Omaha, Neb. | 66 |
| | South Point, Ohio | 260 |
| American Cyanamid Co. | Avondale, La. | 43 |
| Apache Powder Co. | Benson, Ariz. | 8 |
| Armour and Co. | Selma, Mo. | 58 |
| Atlantic Refining Co. | Pt. Breeze, Pa. | 50 |
| California Ammonia Co. | Lathrop, Calif. | 34 |
| Calumet Nitrogen Products Co. | Hammond, Ind. | 86 |
| Commercial Solvents Corp. | Sterlington, La. | 110 |
| Cooperative Farm Chemicals Assn. | Lawrence, Kan. | 115 |
| Deere & Co., Grand River Chemical Div. | Pryor, Okla. | 52 |
| Dow Chemical Co. | Freeport, Tex. | 95 |
| | Midland, Mich. | 29 |
| | Pittsburg, Calif. | 8 |
| E.I. du Pont de Nemours & Co., Inc. | Belle, W. Va. | 185 |
| | Niagara Falls, N.Y. | 7 |
| | Gibbstown, N.J. | 86 |
| Escambia Chemical Corp. | Pensacola, Fla. | 58 |
| Food Machinery & Chemical Corp., Westvaco Div. | Charleston, W. Va. | 21 |
| W.R. Grace & Co., Grace Chemical Div. | Woodstock, Tenn. | 130 |
| Hercules Powder Co. | Louisiana, Mo. | 33 |
| | Pinole, Calif. | 49 |
| Hooker Chemical Corp. | Tacoma, Wash. | 17 |
| Ketona Chemical Corp. | Ketona, Ala. | 41 |
| Mississippi Chemical Corp. | Yazoo City, Miss. | 90 |
| Coastal Chemical Corp. | Pascagoula, Miss. | 43 |
| Monsanto Chemical Co., Lion Oil Co. Div. | El Dorado, Ark. | 185 |
| | Luling, La. | 145 |
| National Distillers and Chemical Corp. | Tuscola, Ill. | 58 |

Table 1 (Continued)

| Corporation | Location | Annual Capacity Nitrogen, Thousand Short Tons |
|---|---|---|
| Northern Chemical Industries, Inc. | Searsport, Me. | 36 |
| Olin Mathieson Chemical Corp. | Lake Charles, La. | 86 |
| | Niagara Falls, N.Y. | 7 |
| Pennsalt Chemicals Corp. | Wyandotte, Mich. | 30 |
| | Portland, Ore. | 12 |
| Petroleum Chemicals, Inc. | Lake Charles, La. | 110 |
| Phillips Petroleum Co., Chemical Div. | Etter, Tex. | 165 |
| | Houston, Tex. | 220 |
| Phillips Pacific Chemical Co. | Finley, Wash. | 58 |
| Pittsburgh Plate Glass Co. | Natrium, W. Va. | 25 |
| Rohm & Haas Co. | Deer Park, Tex. | 39 |
| St. Paul Ammonia Products, Inc. | St. Paul, Minn. | 90 |
| Shell Chemical Co. | Shell Pt., Calif. | 89 |
| | Ventura, Calif. | 66 |
| Smith-Douglass Co., Inc. | San Jacinto, Tex. | 36 |
| Solar Nitrogen Chemicals, Inc. | Lima, Ohio | 105 |
| | Joplin, Mo. | 86 |
| Southern Nitrogen Co., Inc. | Savannah, Ga. | 82 |
| Southwest Nitrochemical Corp. | Chandler, Ariz. | 23 |
| Spencer Chemical Co. | Military, Kan. | 145 |
| | West Henderson, Ky. | 63 |
| | Vicksburg, Miss. | 58 |
| California Chemical Co. | Richmond, Calif. | 95 |
| Sun Oil Co. | Marcus Hook, Pa. | 86 |
| Tennessee Corp. | East Tampa, Fla. | 100 |
| Tennessee Valley Authority | Sheffield, Ala. | 74 |
| Texas Corp. | Lockport, Ill. | 63 |
| Union Oil, Collier | Brea, Calif. | 95 |
| United States Steel Corp. | Geneva, Utah | 58 |
| Valley Nitrogen Producers, Inc. | Helm, Calif. | 49 |
| Total | | 4,743 |

Table 2

AMMONIA PRODUCERS, 1974

| | | Annual Capacity (Thousands of Tons) | Remarks |
|---|---|---|---|
| Air Products and Chems, Inc. | New Orleans, La. | 210 | |
| | Pensacola, Fla. | 75 | |
| Allied Chem. Corp. | | 340 | |
| Specialty Chems. Div. | Hopewell, Va. | 340 | |
| | South Point | | |
| Union Texas Petroleum Div. | | | |
| Agricultural Dept. | Geismar, La. | 340 | |
| | Omaha, Neb. | 200 | |
| American Cyanamid Co. | | | |
| Agricultural Div. | New Orleans, La. | 340 | |
| Apache Powder Co. | Benosn, Ariz. | 15 | |
| Beker Indust. Corp. | | | |
| Agricultural Products Corp., subsid. | Conda, Idaho | 100 | |
| Borden Chem. Div. | | | |
| Petrochems. | Geismar, La. | 285 | By-product $H_2$ and natural gas |
| CF Indust., Inc. | | | |
| Chattanooga Nitrogen Complex | Tyner, Tenn. | 165 | |
| Donaldsonville Nitrogen Complex | Donaldsonville, La. | 720 | |
| Fremont Nitrogen Complex | Fremont, Neb. | 50 | |
| North Carolina Nitrogen Complex | Tunis, N.C. | 210 | |
| Terre Haute Nitrogen Complex | Terre Haute, Ind. | 135 | |
| Coastal States Gas Corp. | | | |
| Colorado Interstate Corp., subsid. | | | |
| Wycon Chem. Co., subsid. | Cheyenne, Wyo. | 145 | |
| Columbus Nitrogen Corp. | Augusta, Ga. | 130 | |
| Cominco American Inc. | | | |
| Camex, Inc., subsid. | Borger, Tex. | 400 | |
| Commercial Solvents Corp. | Sterlington, La. | 340 | |
| Cooperative Farm Chems. Association | Lawrence, Kans. | 340 | |
| Diamond Shamrock Corp. | | | |
| Diamond Shamrock Oil and Gas Co. | Dumas, Tex. | 160 | |

Table 2
(Continued)

| | | Annual Capacity (Thousands of Tons) | Remarks |
|---|---|---|---|
| Dow Chem. U.S.A. | Freeport, Tex. | 115 | Chlorine Cells |
| E.I. du Pont de Nemours & Co., Inc. | | | |
| Biochems. Dept. | Belle, W. Va. | 340 | |
| Elastomer Chems. Dept. | Beaumont, Tex. | 340 | |
| Plastics Dept. | Victoria, Tex. | 100 | |
| El Paso Natural Gas Co. | | | |
| El Paso Products Co., subsid. | Odessa, Tex. | 115 | |
| Farmland Indust., Inc. | Dodge City, Kans. | 210 | |
| | Enid, Okla. | 400 | |
| | Fort Dodge, Iowa | 190 | |
| | Hastings, Neb. | 140 | |
| Felmont Oil Corp. | Olean, N.Y. | 85 | |
| First Mississippi Corp. | | | |
| FIRSTMISS INC., subsid. | Fort Madison, Iowa | 340 | |
| FMC Corp. | | | |
| Chem. Group | | | |
| Indust. Chem. Div. | South Charleston, W. Va. | 25 | Chlorine Cells |
| Gardinier, Inc. | | | |
| U.S. Phosphoric Products | Tampa, Fla. | 130 | |
| Goodpasture, Inc. | Dimmitt, Tex. | 85 | |
| W.R. Grace & Co. | | | |
| Agricultural Chems. Group | Big Spring, Tex. | 125 | |
| | Memphis, Tenn. | 330 | |
| Green Valley Chem. Corp. | Creston, Iowa | 35 | |
| Gulf + Western Indust., Inc. | | | |
| The New Jersey Zinc Co., subsid. | Palmerton, Pa. | 40 | |
| Hercules Inc. | | | |
| Synthetics Dept. | Hercules, Calif. | 70 | |
| | Louisiana, Mo. | 70 | |

Table 2
(Continued)

| | | Annual Capacity (Thousands of Tons) | Remarks |
|---|---|---|---|
| Kaiser Aluminum & Chem. Corp. | | | |
| Kaiser Agricultural Chems. Div. | Savannah, Ga. | 160 | |
| Lone Star Gas Co. | | | |
| Nipak, Inc. subsid. | Kerenes, Tex. | 125 | |
| | Pryor, Okla. | 105 | |
| Mississippi Chem. Corp. | Pasxagoula, Miss. | 175 | |
| | Yazoo City, Miss. | 395 | |
| Mobil Oil Corp. | | | |
| Mobil Chem. Co., div. | | | |
| Petrochems. Div. | Beaumont, Tex. | 260 | |
| Monsanto Co. | | | |
| Monsanto Agricultural Products Co. | Luling, La. | 420 | |
| N-Ren Corp. | | | |
| Cherokee Nitrogen Div. | Pryor, Okla. | 55 | |
| High Plains Div. | Plainview, Tex. | 25 | |
| Occidental Petroleum Corp. | | | |
| Hooker Chem. Corp., subsid. | | | |
| Hooker Chems. and Plastics Corp., subsid. | | | |
| Electrochemical and Specialty Chems. Div. | Tacoma, Wash. | 25 | Chlorine Cells |
| Occidental Chem. Co., subsid. | | | |
| Southern Region | Plainview, Tex. | 55 | |
| Western Div. | Hanford, Calif. | 25 | Leased from Pennzoil |
| | Lathrop, Calif. | 95 | |

Table 2
(Continued)

| | | Annual Capacity (Thousands of Tons) | Remarks |
|---|---|---|---|
| Olin Corp. | | | |
| Agricultural Chems. Div. | Lake Charles, La. | 485 | |
| Pennwalt Corp. | | | |
| Chem. Div. | Portland, Ore. | 10 | Chlorine Cells |
| Phillips Pacific Chem. Co. | Kennewick, Wash. | 155 | |
| Phillips Petroleum Co. | | | |
| Fertilizer Div. | Beatrice, Neb. | 210 | |
| Plastics Div. | Pasadena, Tex. | 230 | |
| PPG Indust., Inc. | | | |
| Chem. Div. | | | |
| Indust. Chem. Div. | | 50 | Chlorine Cells and natural gas |
| Reichhold Chems., Inc. | St. Helens, Ore. | 90 | |
| Rohm & Haas Co. | | | |
| Rohm & Haas Texas Inc., subsid. | Deer Park, Tex. | 50 | |
| St. Paul Ammonia Products, Inc. | East Dubuque, Ill. | 210 | |
| J.R. Simplot Co. | | | |
| Minerals and Chem. Div. | Pocatello, Idaho | 110 | |
| Skelly Oil Co. | | | |
| Hawkeye Chem. Co., subsid. | Clinton, Iowa | 140 | |
| Standard Oil Co. of California | El Sagundo, Calif. | 20 | Refinery waste water |
| | Richmond, Calif. | 135 | Natural Gas and refinery waste water |
| Chevron Chem. Co., subsid. | | | |
| Ortho Div. | Fort Madison, Iowa | 105 | |
| Standard Oil Co. (Kentucky), subsid. | Pastagoula, Miss. | 500 | |
| Standard Oil Co. (Indiana) | | | |
| Amoco Oil Co., subsid. | Texas City, Tex. | 700 | |
| The Standard Oil Co. (Ohio) | | | |
| Visitron Corp., subsid. | | | |
| Chems. Dept. | Lima, Ohio | 500 | |
| Tenneco Inc. | | | |
| Tenneco Chems, Inc. | | | |
| Organics and Polymers Div. | Houston, Tex. | 210 | |
| Tennessee Valley Authority | Muscle Shoals, Ala. | 65 | |

Table 2
(Continued)

| | | Annual Capacity (Thousands of Tons) | Remarks |
|---|---|---|---|
| Terra Chems. Internat'l, Inc. | Port | 210 | |
| Tipperary Corp. | Lovington, N.M. | 35 | |
| Triad Chem. | Donaldsonville, La. | 370 | |
| Tyler Corp. | | | |
| Atlas Powder Co., subsid. | Joplin, Mo. | 135 | |
| Union Oil Co. of California | | | |
| Collier Carbon and Chem. Corp., subsid. | Brea, Calif. | 270 | |
| | Kenai, Alas. | 520 | |
| United States Steel Corp. | | | |
| USS Agri-Chemicals, Div. | Cherokee, Ala. | 175 | |
| | | 325 | Coke-oven gas |
| | Geneva, Utah | 70 | Coke-oven gas |
| Valley Nitrogen Producers, Inc. | El Centro, Calif. | 210 | |
| | Helm, Calif. | 175 | |
| Arizona Agrochemical Co., subsid. | Chandler, Ariz. | 35 | |
| Vulcan Materials Co. | | | |
| Chems. Div. | Wichita, Kans. | 25 | Chlorine Cells |
| The Williams Companies | | | |
| Agrico Chem. Co., subsid. | Blytheville, Ark. | 340 | |
| | Donaldsonville, La. | 340 | |
| | Total | 17,445 | |

Source: Compiled in association with the Chemical Economics Handbook.

Table 3

OCCUPATIONS WITH POTENTIAL EXPOSURE TO AMMONIA

Acetylene Workers
Aluminum Workers
Amine Workers
Ammonia Workers
Ammonium Salt Makers
Amiline Makers
Annealers
Boneblack Makers
Braziers
Bronzers
Calcium Carbide Makers
Case Hardeners
Coal Tar Makers
Coke Makers
Corn Growers
Cyanide Makers
Decorators
Diagotypy Machine Operators
Drug Makers
Dye Intermediate Makers
Electroplaters
Explosive Makers
Farmers
Fertilizer Workers
Galvanizers
Gas Purifiers
Gas Workers, Illuminating
Glass Cleaners
Glue Makers
Ice Cream Makers
Ice Makers
Ink Makers
Laboratory Workers, Chemical
Laquer Makers
Latex Makers
Manure Handlers
Metal Extractors
Metal Powder Processors
Mirror Silverers
Nitric Acid Makers
Organic Chemical Synthesizers
Paper Makers
Perfume Makers
Pesticide Makers
Petroleum Refinery Workers
Photoengravers
Photographic Film Makers
Plastic Cement Makers
Pulp Makers
Rayon Makers
Resin Makers
Rocket Fuel Makers
Rubber Cement Mixers
Rubber Workers
Salt Extractors
Seier Workers
Shellac Makers
Shoe Finishers
Soda Ash Makers
Soluay Process Workers
Stablemen
Steel Workers
Sugar Refiners
Sulfuric Acid Workers
Synthetic Fiber Makers
Tanners
Tannery Workers
Urea Makers
Varnish Makers
Vulcanizers
Water Base Paint Workers
Water Trenters
Wool Scourers

SOURCE: Occupational Diseases, A Guide to Their Recognition. U.S. Dept. of HEW 1964.

APPENDIX I

Bittersohl, G: Epidemiologic Study on Cancer of Workers in a Chemical Plant

# EPIDEMIOLOGIC STUDY ON CANCER OF WORKERS IN A CHEMICAL PLANT

Gerhard BITTERSOHL, *Germany (DDR)*

In a chemical factory with about 30,000 employees an epidemiologic study on the occurrence of malignant neoplasms was carried out. In this factory mainly mineral oil is manufactured to petrol, plastics, solvents and some other organic substances.

Since the establishment of the plant a permanent increase of neoplasms – in relation to 10,000 employees – was observed as is shown in the first figure. This progress corresponds to the general statistical evaluation in our country.

The analysis of all cancers – carried out in the period from 1958 to 1967 – shows that as to the male patients the neoplasms of the digestive system and the respiratory system amount to 50% of all malignant growths. With reference to the women the cancer of the mamma and the genitals take place on the top with about 64%. Figure 2 shows the distribution of cancers in the different organs in comparison with the inquiries in our republic. According to that with reference to the male employees of the chemical factory distinct prevalence of the cancers of the respiratory system and a little predominance of the cancers of the digestive tract, of the urinary organs and of the lymphatic and hematopoetic system is to be seen. In women the malignant tumors of the genitals and the lymphatic and hematopoetic system stand out remarkably with regard to the statistical evaluation of the GDR.

It was impossible to set up relations between an attacked organ and professional groups. As a matter of experience an organic specificity as proof of a possible or sure etiological coherence is no doubt supposed or desired as supposition for several carcinogenic substances. This does not lock out, however, the possibility that primary tumors in spite of the same pathogenic causality can increasingly be observed in other organic systems too. This is shown by recent observations of Reml. Johnson, Sato and others.

A connection between profession or place of employment and localization of malignant neoplasms was only to be stated at the malignant tumors of the skin. In 94% of all cases workers were attacked who permanently had to do with tar or mineral oil and who were exposed on influence of heat or sunlight at the same time. Exclusively unprotected parts of the body as the head and the upper extremities were attacked. A special accumulation was observed in this part of the hydrogenation unit where tar and distilling residues of the mineral oil were manufactured.

At a differentiation upon single departments it was stated that the threefold number of malignant tumors is to be found in the production plants in comparison with the offices of the chemical factory. The cases of the workshops and other plants are between these values. This may give us the idea that beside the general present conditions in several plants of production there must be further carcinogenic or syncarcinogenic causalities.

At a further differentiation of the production plants it was stated that during the period of observation no malignant neoplasms appeared at all. On the other hand some plants were evident by a great many of cancers. Figure 3 shows that especially the gas plants, the plant for the manufacture of chromium catalysts and the tar-handling parts of the hydrogenation unit are attacked. By this former observations of other authors are confirmed.

The high rate of cancers in all plants producing or manufacturing ammonia, however, is evident. In these plants a five to six times higher rate of malignant tumors than in the other ranges of the production plants was observed as the figure shows. This corresponds to a fifteen times higher frequency of cancers with regard to the whole chemical factory. The ammonia is produced by the process of HABER and BOSCH and in the amine plant it is converted to mono-,

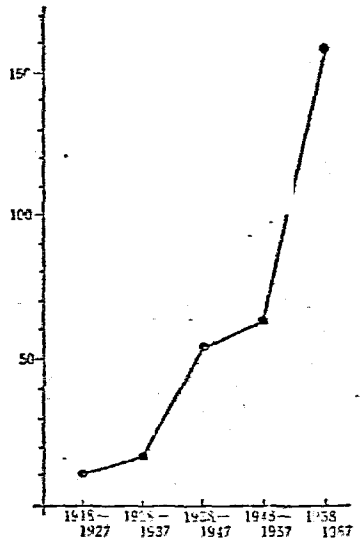



*Fig. 1. Cancer on 10,000 employees*

di- and trimethylamine with gaseous methanol. In these plants the MAK-Values obligatory for the GDR for ammonia of 25 $mg/m^3$ are exceeded by the two- to threefold. Maximum values appearing for a short time even amount to a multiple of these quantities. As to 80% of the employees the time of exposure is more than 10 years. Owing to their direct employment in the production the men are more exposed than the women.

The cancers as cause of death are very high in these plants too. It amounts to 40% of all dead in the ammonia plant and to 60% in the amine plant.

As to the organs exclusively lungs, stomachs, lymphytic tissue and urinary organs are attacked.

Till now nothing became known about the importance of ammonia as a cancerogenic or syncancerogenic causality. There are only a few and uncertain conceptions about a possible mechanism of action. It is possible that ammonia as a syncarcinogenic substance is of effect together with the polycyclic hydrocarbons coming from the hydrogenation unit and provable in the air of the factory. On the other hand ammonia possesses two free electrons at the N-atom and therefore has the tendency to change to an ammonium-ion by absorption of a proton. For that reason one may also comprehend ammonia as a radical. Hence there are connections with the conception of Wirtschafter, Cronin and others about the importance of free radicals as for instance at the effect of some solvents, at the development of carbonium-radicals at the effect of nitrosamins and so on.

We considered these observations worth to be informed though our researches about this problem are not yet finished.

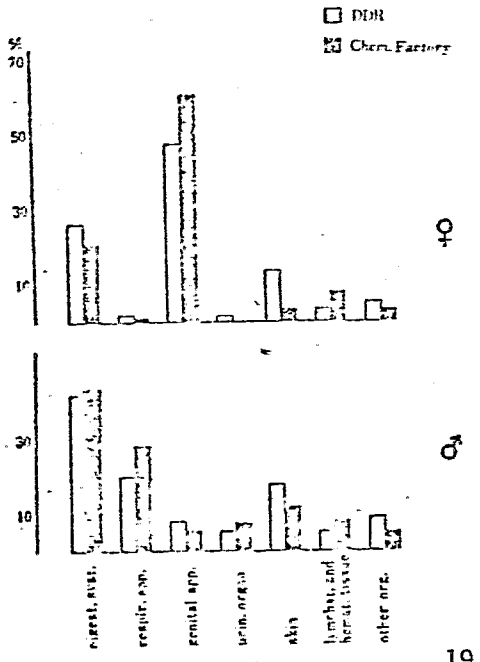



Fig. 2 Distribution of cancers on organs

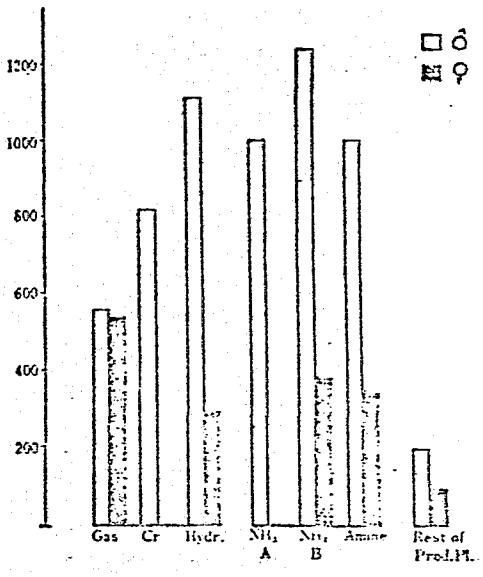



Fig. 3. Frequency of cancer on 10,000 employees

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# APPENDIX II

## Sampling & Analytical Methodologies For Ammonia

## VIII. APPENDIX I

## METHOD FOR SAMPLING AMMONIA IN AIR

### General Requirements

Ammonia concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the recommended standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include a log of

(1) The date and time of sample collection

(2) Sampling duration

(3) Volumetric flowrate of sampling

(4) A description of the sampling location

(5) Other pertinent information

### Equipment for Air Sampling

(a) Stopwatch

(b) Vacuum pumps with calibrated rotameter

(c) Midget impingers

(d) Solid Standard Taper 24/40 stoppers

(e) Polyvinyl tubing

(f) Dispensing glassware and supporting equipment as may be deemed necessary. Glassware should be borosilicate quality, washed thoroughly with detergent, and followed by rinses with tap water and distilled water.

Reagents

Cautiously add 56 ml of concentrated reagent grade sulfuric acid to 500 ml of distilled water; dilute to 1 liter to obtain 2 N sulfuric acid. Cool to room temperature and dilute 50 ml of the 2 N sulfuric acid to 1 liter with distilled water to obtain 0.1 N sulfuric acid absorbing solution.

Breathing Zone Sampling

Breathing zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and shall characterize the exposure from each job or specific operation in each production area.

(a) Sampling Equipment

A calibrated personal sampling pump with flowmeter (range up to 2 liters a minute), a midget impinger containing 10 ml of 0.1 N sulfuric acid absorbing solution.

(b) Sampling Procedure

The impinger outlet is connected to the personal sampling pump inlet by a piece of tubing of convenient length, but not in excess of 3 feet. The impinger assembly is attached to the worker's clothing in order to sample from the worker's breathing zone. The sample is collected at a rate of 1 liter a minute for 5 minutes.

A minimum of 3 samples shall be taken for each operation (more samples if the concentrations are close to the recommended standard). At least one blank impinger shall be provided containing sulfuric acid

absorbing solution through which no air has been sampled. One additional blank impinger shall be supplied with every 10 samples obtained.

Shipping

After sampling, remove the glass stopper and impinger stem from the impinger bottle. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount of unused absorbing solution from a wash bottle, adding the wash to the impinger to bring to a final volume of 20 ml. Stopper the impinger tightly with plastic caps (do not seal with rubber), place in an upright position, and ship the impinger samples to the analytical laboratory in a suitable container to prevent damage in transit. Special impinger shipping containers designed by NIOSH are available. Be certain that the impinger bottles are sealed very tightly to prevent leakage and loss of samples.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicated. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibrating instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a midget impinger is shown in Figure XI-1.

(a) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(b) Fill the impinger with 10 ml of the absorbing solution.

(c) Assemble the sampling train as shown in Figure XI-1.

(d) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(e) Adjust the pump rotameter to provide a flowrate of 1 liter a minute.

(f) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (approximately 1 inch of mercury).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to move from one calibration mark to another. For a 1,000-ml buret, a convenient calibration volume is 500 ml.

(h) Repeat the procedure in (g) above at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(i) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

## IX. APPENDIX II

### METHOD FOR ANALYSIS OF AIR SAMPLES

Equipment

(a) Spectrophotometer

(b) 50-ml beakers

(c) 1 each 1-, 2-, 5-, 10-, 20-ml pipets

(d) 1-cm cuvettes

(e) 1-liter volumetric flasks

Reagents

(a) Nessler Reagent

Dissolve 100 g of mercury (II) iodide and 70 g of potassium iodide in a small quantity of water, and add this mixture slowly, with stirring, to a cool solution (15-20 C) of 160 g sodium hydroxide in 500 ml water. Dilute to 1 liter. Store in rubber-stoppered borosilicate glassware and out of sunlight to maintain reagent stability for periods up to a year under normal laboratory conditions.

(b) Ammonium chloride, stock solution (1.0 ml = 1.0 mg ammonia)

Dissolve 3.141 g of ammonium chloride in water and dilute to 1 liter with distilled, ammonia-free water.

(c) Ammonium chloride, standard solution (1.0 ml = 10.0 µg ammonia)

Dilute 10.0 ml of 1.0 mg ammonia/ml stock solution to 1000 ml with distilled, ammonia-free water.

Preparation of Standard Curve

To a series of 50-ml beakers add 25.0, 23.0, 20.0, 17.0, and 13.0 ml of absorbing solution (Appendix I). To these beakers in the same order add 0.0, 2.0, 5.0, 8.0, and 12.0 ml of ammonium chloride standard solution, so that the final volume is 25 ml. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is measured spectrophotometrically in a 1-cm cell at 425 nm against the reagent blank.

Analysis of Samples

Samples should be analyzed within a week of collection. Transfer an aliquot of the blank and sample solutions to 50-ml beakers. Add absorbing solution to adjust the final volume to 25 ml in each beaker. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is determined by the same procedure as the standards.

Calculations

From the standard curve determine the micrograms of ammonia in the sample solution aliquot. Calculate the concentration of ammonia in the air as ppm:

$$\text{ppm ammonia} = \frac{1.44\ \mu l\ NH_3}{\mu g\ NH_3} \times \frac{AB}{CDE}$$

Where

$$\frac{1.44\ \mu l\ NH_3}{\mu g\ NH_3} = \frac{\mu mole}{17\ \mu g\ NH_3} \times \frac{22.4\ \mu l}{\mu mole} \times \frac{298\ K}{273\ K}$$

A = Sample solution volume in milliliters = 20 ml

(10 ml scrubber solution plus 10 ml rinse)

B = $\mu$g of ammonia in aliquot analyzed

C = Volume of aliquot in milliliters

D = Time of sampling period in minutes

E = Sampling impinger flow rate in liters/min.