

IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Of the methods evaluated for analysis of ammonia in air, several offer acceptable sensitivity, specificity, precision, and accuracy. The method of choice for sampling and analysis is detailed in Appendices I and II. It entails the scrubbing of air with a midget impinger containing dilute sulfuric acid and color development with Folin-Nessler's Reagent.

Several adaptations of chemiluminescence based upon the oxidation of ammonia to nitric oxide have been reported to have varying degrees of efficiency. [59,60] Lasers have been utilized by Shimizu, [61] Kreuzer et al, [62] and Hinkley and Kelley [63] for spectrophotometric determination of ammonia. Greatly increased sensitivity is possible, but the availability, expense, and operator expertise requirements of these instrumental procedures place their practical application out of reach for most industrial hygiene laboratories.

The selective ion electrode apparently will obviate, upon documentation of its specificity, accuracy, and precision, the need for chemical analysis of impinger samples. Sensitivities seem to be adequate. [64,65] The interferences from volatile amines will also have to be taken into consideration.

Some additional analytical techniques include enzymatic assays, [66,67] pyridine-pyrazole, [68,69] indophenol color development, [70-73] gas chromatography, [74,75] ninhydrin color development, [76] coulometry, [77] and conductometric diffusion, [78] These methods have a combination of shortcomings including incompatible sampling requirements and lack of

sensitivity and accuracy. They do have the potential for adaptation to workable air monitoring techniques.

The colorimetric determination of ammonia using an alkaline solution of mercuric iodide and potassium iodide was first proposed by Nessler in 1856. [79] The ammonia reacts with Nessler's reagent to form a colored colloid that is subject to flocculation on standing, [68,80,81] but the control of alkalinity and the appropriate potassium iodide excess help to reduce this problem. [68,81] Volatile amines, aldehydes, acetone, alcohols, and ammonium salts interfere with the Nessler method. [68] Formaldehyde has been reported [69] to interfere quite strongly.

Sampling frequency should be adequate to describe the fluctuations of every operation, particularly maximum concentrations of ammonia. Samples can be collected with bubblers [82] or impingers [69] containing 0.02 N sulfuric acid. Okita and Kanamori [69] reported that 7 ppm ammonia was collected in impingers with an efficiency of 94.8-99.5% when sampled for 3-16 minutes at flow rates of 0.5-3.0 liters a minute. In contrast, 0.03 ppm ammonia was collected with an efficiency of only 58% when sampled for 95 minutes at a flowrate of 1.5 liter a minute, and 62% when sampled for 120 minutes. A glass fiber filter impregnated with 5 N sulfuric acid collected 95.3-98.0% of the ammonia in 3 1-hour tests at a flowrate of 15 liters a minute. Because of the potential health hazards associated with the improper use of mercury compounds, the Nessler's reagent must be handled and disposed of with care.

Ammonia detector tubes provide a quick, relatively simple, and reasonably accurate method for spot checking potential exposure areas. If the limits in accuracy are recognized, detector tubes may be useful for

determining areas which require compliance with various sections of the recommended standard or which require more detailed industrial hygiene surveys. A number of ammonia detector tubes have been tested and certified by NIOSH [83] in accordance with the provisions of 42 CFR 84, as amended. Basically, in order to be certified detector tubes must exhibit 1) accuracy within $\pm 35\%$ at half of the NIOSH Test Concentration (NTC) and $\pm 25\%$ at 1, 2, and 5 times the NTC (for ammonia, the NTC is 50 ppm); 2) channeling (beveled stained-unstained interface) of less than 20%; and 3) tube reader deviation (standard deviation estimate of 3 or more independent readers) of less than 10% of the average of the readers. Detector tubes are subject to positive errors (high readings) in the presence of amines and negative errors (low readings) in the presence of acid gases. Another device for making "on the spot" evaluations and instructions for its fabrication was reported by Gisclard et al. [84] This device consisted of a 100 cc syringe used to draw air through 0.0001 N sulfuric acid containing methyl purple indicator. Although the device actually indicates only total alkalinity, the ammonia concentration could be estimated based on the air volume necessary to cause a color change.

Environmental Levels and Engineering Controls

Little information has been published concerning workroom levels of ammonia encountered in industry, or the control measures used and their effectiveness. The workroom levels that have been reported are not high, suggesting that adequate control may be readily obtained by use of local exhaust ventilation. In 1971 Carlsson [85] found 5-50 ppm ammonia in chicken houses as a result of decomposing floor litter and bedding

material. The lower concentrations were found at the beginning of the growing period for broiler production, and the higher concentrations at the end when the chickens were caught and the chicken houses were cleaned. Ventilation intakes near the ceiling of chicken production buildings did not control the ammonia which was produced near the floor. Recommended remedial measures included complete redesign of chicken production facilities, with interim relocation of ventilation intakes to floor level.

Mangold [44] investigated complaints originating in a reproduction department using diazo-type machines. The ammonia concentration in 2 2-hour samples was 8 ppm with room windows closed and machine ventilation operating. In 2 similar samples taken the next day levels were 10 and 17 ppm. Mangold felt that peak concentrations of ammonia were probably responsible for the complaints since concentrations determined up to that time had been low. Sequential samples were then taken over 2 working days, representative of the breathing zone air for workers receiving treated paper from the machine onto a cutting table. Fifteen-minute samples with 30-minute periods intervening showed a range of 4-29 ppm. Highest concentrations occurred when the machines were stopped for the noon break and ventilation was shut off. Mangold concluded that the existing machine ventilation was effective for control of ammonia emitted by the machinery, but that it did not control the ammonia escaping from the processed paper extruded from the machines onto the cutting table. Other levels measured for a variety of processes are listed in Table XI-4. [42,86,87]

Although over 80% of the ammonia manufactured is used as fertilizer or for fertilizer manufacture, [5] investigations of low level exposures in agricultural operations have not been found. Reports of accidental acute

exposures in agricultural operations indicate the serious nature of such occurrences. [25,88] All of the papers surveyed underscored the need for care and safe work practices any time ammonia is used, but this is especially true in agricultural operations.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standard

In 1943 the US Public Health Service [89] published toxic limits for various substances. The maximum allowable concentration (MAC) for ammonia was given as 100 ppm. No basis for this value was given except to state that it was the most widely accepted value.

In 1945, Cook [90] reviewed the MACs of industrial atmospheric contaminants as promulgated by a number of states (California, Connecticut, Massachusetts, New York, Oregon, and Utah) and the US Public Health Service. Connecticut had no MAC for ammonia, but for the other 5 states and for the USPHS the MAC was 100 ppm. Cook cited Lehmann [91] as the original source published in 1886. Lehmann [91] concluded that 300-500 ppm, following a period of adaptation, could be tolerated for a prolonged period without harm, and further, that concentrations of 1,000-2,000 ppm were safe for short periods. Lehmann recommended that prolonged exposure to concentrations over 500 ppm should definitely not be allowed. Ammonia concentrations of 70-110 ppm in a gas works were said to be at the threshold of irritation.

In 1946, the American Conference of Governmental Industrial Hygienists (ACGIH) established a MAC for ammonia of 100 ppm, [92] which in 1948 became a Threshold Limit Value (TLV), [93] still at 100 ppm. The documentation [94] published in 1962 cited Smyth, [14] Vigliani and Zurlo, [43] Cook, [90] Elkins, [95] and others in support of the 100 ppm TLV. The following year, however, the TLV was reduced to 50 ppm. [96] The 1966 documentation [97] of the 50 ppm TLV cited the reports by Weatherby [49] and Dalhamn [55] in addition to the literature previously cited [94] in

support of the 100 ppm TLV. The 50 ppm TLV was said [97] to have been selected to protect against respiratory irritation and was expected to eliminate most complaints of discomfort. In 1969, the ACGIH issued a notice of intent to change the recommended limit of 50 ppm from a time-weighted average (TWA) to a ceiling value. [98] However, the actual change never occurred because the ACGIH recommended in 1970 [99] and adopted in 1973 [100] a TLV of 25 ppm as a TWA. The 1971 documentation [101] stated that experience indicated a "maximum acceptable concentration without severe complaints of 20-25 ppm." This apparently was based on results of unpublished plant surveys conducted by the Detroit Department of Health. The limit of 25 ppm was said to have been selected to protect against eye and respiratory irritation and to "minimize widespread complaints of discomfort among office workers and similar uninured individuals." [101]

The US Navy in 1962 [102] established 25 ppm as the maximum limit for continuous exposure during a 60-day dive in a submarine, and 400 ppm as the maximum allowable concentration permissible for 1 hour under operational conditions.

A number of occupational limits have been set by foreign countries and international groups. The USSR [103,104] established 0.02 mg/liter (approximately 30 ppm) as the workroom air standard. A Spanish standard [105] specified 100 ppm as the "maximum tolerable concentration." After comparison of the ACGIH and USSR recommendations current at the time, the Joint ILO/WHO Committee on Occupational Health [106] in 1968 recommended a safe concentration zone of 20-35 mg/cu m (approximately 30-50 ppm). Included in the ILO/WHO report were MAC recommendations from 12 countries

and from 5 states in the United States, with values ranging from 20-70 mg/cu m (30-100 ppm).

The present federal standard (29 CFR 1910.93) for ammonia is an 8-hour time-weighted average of 50 ppm based on the ACGIH recommendation in 1968.

Basis for Recommended Environmental Standard

Exposure to high concentrations of ammonia gas can be fatal, the LC50 for mice, rabbits, and cats having been reported as approximately 10,000 ppm. [46,47] Humans have been killed after accidental exposures to high ammonia concentrations. [17,18,21,27] Because these were accidental exposures ammonia in air was not measured, but in one case [21] a rough estimate of 10,000 ppm was made. Chronic lung disease has been reported after accidental exposure to high concentrations of ammonia gas, [17,19,24,26] and after workers were sprayed or splashed with anhydrous or aqua ammonia. [20,27] As a result of ammonia splashes in the face, permanent eye damage with visual impairment was described in 7 individuals. [20,23,25,28,29] Ammonia gas produced blindness in some guinea pigs exposed for 30-120 minutes at a concentration of 5,000-6,000 ppm. [45]

Guinea pigs exposed at 170 ppm for 6 hours daily, 5 days a week for 18 weeks reportedly developed mild degenerative and congestive changes in the spleens, livers, kidneys, and suprarenal glands. [48] These findings were not duplicated when guinea pigs, rabbits, dogs, and monkeys were exposed at approximately 1,100 ppm for 8 hours daily, 5 days a week for 6 weeks, [50] but nonspecific inflammatory changes were seen in the lungs. There were no abnormal pathological findings [50] in a similar group of

animals exposed for the same duration at 220 ppm, at 60 ppm continuously for 114 days, or in rats continuously exposed at 180 ppm for 90 days. Autopsy findings were normal in pigs continuously exposed at concentrations up to 145 ppm for 5 weeks, [51] but Doig and Willoughby [52] reported thickened tracheal epithelium and a decreased number of goblet cells in weanling pigs continuously exposed at approximately 100 ppm for up to 6 weeks. Ammonia has been reported to arrest ciliary activity in rats and rabbits, [54-58] but recovery took place soon after exposure ended. [55] Approximately 100 ppm in the trachea was the lowest concentration that affected the ciliary activity of rabbits. [56,57] The air concentration necessary to reach such a level in the human trachea apparently would be considerably higher, since Landahl and Hermann [36] reported approximately 83% nasal retention in 4 subjects tested. Humans exposed at 500 ppm for 30 minutes [35] and for 4 hours [32] experienced no apparent adverse effects, such as coughing or irritation of the lower respiratory tract, but there was severe upper respiratory irritation and a marked increase in respiratory minute volume. [35] However, particulates might potentiate the effect of ammonia on the lower respiratory tract, since Dalhamn and Reid [58] reported significantly more tracheal damage in rats inhaling ammonia plus activated carbon particles than in rats inhaling either alone.

In a series [38] of 5-minute exposures, 1 of 10 subjects complained of "chest irritation" during exposure at 134 ppm, 5 experienced lacrimation and/or eye irritation, 7 had nasal irritation, and 8 had throat irritation. At 72 ppm, 3 subjects reported eye and throat irritation and 2 experienced nasal irritation. At 50 ppm, 2 of the people reported dryness of the nose, and 1 reported the nasal dryness at 32 ppm. [38] In a second experimental

exposure study (Table XI-3), [37] 4 of 6 volunteers exposed at 50 ppm for 10 minutes rated the irritation, on a scale of 0-4, as 2 ("moderate irritation") with the other 2 subjects rating the irritation as 0 ("not detectable") and 1 ("just perceptible"). The irritation at 30 ppm was rated as "not detectable" by 3 of 5 and "just perceptible" by 2 of 5.

No data were found on concentrations that are irritating to workers who are regularly exposed to ammonia and who therefore presumably have a higher irritation threshold. In several of the plant surveys reviewed by Pagnotto, [written communication, September 1973] ammonia concentrations of 9-45 ppm were detected in areas where the industrial hygienist commented that ammonia was initially irritating to the eyes or nose, but that one quickly became accustomed to the ammonia. This phenomenon of acclimatization or inurement was also observed in several experimental exposures, wherein animals appeared to become accustomed to concentrations which initially had been irritating. [50-52]

Other than sensory effects--either irritation or annoyance--there is no evidence of acute or chronic adverse effects of ammonia exposure except after accidental exposure at extremely high concentrations, estimated in one fatal exposure to have been 10,000 ppm. [21] Subjects have been experimentally exposed [32,35] at a concentration of 500 ppm for up to 4 hours. The most serious effect reported, after a 30-minute exposure, was upper respiratory irritation which in 2 of 7 subjects was severe and persisted for 24 hours. [35] At more reasonable concentrations, 100 ppm or less, some individuals report irritation of the eyes and upper respiratory system, and some persons apparently can feel irritation or annoyance even

at concentrations below 30 ppm. [37,38,44, and LD Pagnotto, written communication, September 1973]

It is difficult to interpret these subjective reports of irritation at relatively low concentrations of ammonia, since the sensation considered irritating by one individual might be considered merely annoying or disagreeable by another. The term "irritation" obviously is not well defined, as illustrated by the fact that in one experimental exposure, [37] 4 of 6 subjects exposed for 10 minutes considered 50 ppm disagreeable (termed "moderately irritating," Table XI-3), while in another study [38] in which 10 subjects were exposed for 5 minutes, none reported irritation at 50 ppm (2 reported dryness of the nose). At 72 ppm, only 3 reported eye irritation and only 2 reported nasal irritation. [38] This report suggests that most uninured workers might find concentrations as high as 75 ppm not to be irritating in 5 minutes, while the other study [37] suggests that after 10 minutes 50 ppm may become irritating to some. However, other reports of animal [50-52] and human [LD Pagnotto, written communication, September 1973] exposures suggest that one can quickly become accustomed to concentrations of ammonia that at first had been disagreeable.

Although the nasal dryness reported at 50 ppm during a 5-minute exposure [38] might become irritating after extended exposure, the concentration of ammonia inhaled appears to be the more important factor, the irritating or annoying effects being more dependent upon concentration than length of exposure. For this reason, a standard expressed as a time-weighted average is inappropriate since it would permit fluctuations to concentrations considerably higher than 50 ppm. Therefore, in order to minimize the discomfort felt by some unacclimatized individuals, to

restrict the potential for fluctuations to more irritating concentrations, and to ensure that such possibly irritating exposures are brief, NIOSH recommends 50 ppm as the environmental standard, expressed as a ceiling not to be exceeded during the workday.

It is recognized that many workers handle small amounts of ammonia or work in situations where, regardless of the amounts used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with all of the provisions of this recommended standard. However, concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. Therefore, environmental monitoring and recordkeeping is recommended for those work situations which involve exposure above half the recommended limit, to delineate work areas that do not require the expenditure of health resources for control of inhalation hazards. Half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard definitely exists. Because possibly disabling eye, skin, or respiratory tract injuries may result from accidental exposures, it is recommended that appropriate work practices, training, and other protective measures be required regardless of air concentrations in workplaces with reasonable potential for emergencies. For the same reasons, it is recommended that medical surveillance be made available to anyone adversely affected by ammonia exposure.

It appears that a standard of 50 ppm, expressed as a ceiling, will protect the worker from all adverse effects of long-term ammonia exposure, but epidemiological and experimental studies are needed for verification.

Apparently because of the excellent warning properties of ammonia and the general belief that workers will not remain in acutely hazardous concentrations, there has been little attention to the possibility of effects due to chronic low-level exposure. One study [40] of a small worker population, for whom no exposure data were given, reported no adverse effects on ventilatory function or respiratory symptomatology as a result of exposure to ammonia in an Egyptian ice plant. Another report [41] implicated ammonia as an occupational carcinogen in a group of chemical workers. However, the paper presents insufficient information on the work population, on the exposures involved, and on methods used in the study. The conclusions are therefore unconvincing in the absence of confirmation. These 2 reports [40,41] apparently are the only published attempts to identify chronic effects, if any, of long-term exposure to ammonia. The lack of data on the subject is sufficient to warrant new studies, but the need is made more pressing by the suggestion, despite the weaknesses of the report, that ammonia may be an occupational carcinogen.

VI. WORK PRACTICES

Work practices with regard to the safety precautions for handling anhydrous ammonia are the subject of a considerable body of literature. [2,8,9,88,107-113] Less has been written concerning the use of aqueous solutions of ammonia, [1,114-116] although the problems and effects are essentially similar to those of anhydrous ammonia gas. [1,114] All of these references are concerned largely with prevention and control of hazards arising from emergency situations involving escape of anhydrous ammonia in liquid or gaseous form, or spills of aqua ammonia. The use of natural and/or local exhaust ventilation for control of ammonia gas has had limited review. [2,107,110] Reports of work practices specifically for the prevention of low level exposure are not available. In general, good engineering practices should be used to control continuous low-level exposures and to minimize excursions. For example, good ventilation practices are recommended in the current edition of Industrial Ventilation-A Manual of Recommended Practice published by the American Conference of Governmental Industrial Hygienists.

A. Warning Properties

Fieldner et al [13] reported that the lowest concentration of ammonia detectable by odor was about 50 ppm. Leonardos et al [15] reported 47 ppm as the lowest concentration consistently identified by all 4 subjects exposed to ammonia. If some subjects identified ammonia at lower concentrations, this was not reported. Saifutdinov [16] reported a threshold for olfactory perception of ammonia of 0.7-0.8 ppm, using unspecified methods recommended by the Committee for Sanitary Protection of the Atmosphere (USSR). The American Industrial Hygiene Association's

Hygenic Guide for ammonia [112] reported that the odor of ammonia is detectable at 1-5 ppm, but no supporting evidence was given. These discrepancies in the reported odor threshold need to be resolved, but it does appear that earlier estimates in the 50 ppm range were too high. Despite uncertainty about the odor threshold, the concept that the annoying properties of ammonia will prevent voluntary exposure to acutely hazardous concentrations is frequently encountered. [1,2,9,107-117]

B. Eye Protection

Ammonia is a severe eye hazard, causing serious injury with extreme rapidity. [25,118] On the basis of all available evidence, eye injuries constitute the most serious hazard from ammonia in terms of possible permanent disability. [25] According to Grant, [118] ammonia penetrates the eye more rapidly than other alkalis. For these reasons, it is of extreme importance that water suitable for flushing ammonia from eyes be readily available whenever the possibility exists of eye contact with ammonia. When ammonia is splashed or sprayed into the eyes, time is the most important consideration [118,119] and the first 10 seconds are critical if blindness is to be prevented. [108] Nothing is better than pure water for irrigation of the eyes [118] and no time should be lost searching for a specific antidote other than water. [119] Eyes affected by ammonia should be flushed with water for at least 15 minutes, forcibly holding open the lids if necessary. Medical attention should be obtained without delay, but not at the expense of thoroughly flushing the eyes. Contact lenses prevent effective eye irrigation and should not be worn around ammonia. Chemical goggles with hooded ventilation openings should

be used in addition to face shields if eyes and face are not protected by fullface respiratory protection.

C. Skin Protection

During approval tests of respiratory equipment, Patty [39] observed that 1% (10,000 ppm) was mildly irritating to moist skin. Two percent (20,000 ppm) had a more pronounced action, and concentrations of 3% (30,000 ppm) or greater caused a stinging sensation. He postulated that 3% (30,000 ppm) could produce chemical burns with blistering after exposure for a few minutes. The National Safety Council [111] has carried an apparent error through several revisions. Paragraph 66 [111] states "No one can remain in an atmosphere with a concentration higher than 1.5 or 2% (15,000 or 20,000 ppm) of ammonia for more than 15 minutes without developing skin burns and blisters." Paragraph 89 of the same publication states "Atmospheric ammonia in concentrations above 2000 ppm (0.2%) will burn and blister the skin after a few seconds of exposure." No supporting data were given for either statement. In the light of Patty's observations [39] it appears that the second statement is erroneous. Other publications [1,2,9] echo Patty's figures. Therefore, skin protection should be worn in air concentrations of 10,000 ppm or more or when direct skin contact with anhydrous or strong aqua ammonia may occur.

Entry into unknown concentrations of ammonia in emergencies may cause skin injury, therefore, complete skin protection should be worn if possible. Should the emergency require entry without skin protection, stay time should be as brief as possible. Clothing should be removed and a shower taken immediately after leaving the exposure area.

D. Storage and Spills

Theoretical studies [5] and accidents [26,120] indicate that extremely hazardous concentrations of ammonia can exist for considerable distances downwind of liquid anhydrous ammonia spills. Ball [5] calculated the initial "flash," ie, immediate evaporation, from liquid to gas that would result after a spill of liquid anhydrous ammonia. In the case of a pressure-storage system under 126 pounds per square inch gauge (psig) pressure and at 75 F, about 20% of the spill would flash, while only 0.2% would flash after a spill from a refrigerated tank operating at 0.5 psig. In addition, he calculated that, under steady-state conditions of evaporation, ammonia concentrations of 1,000 ppm could exist downwind at a distance of 10 pool diameters with a wind speed of 5 miles per hour (mph). At 25 mph wind speed, 1,000 ppm would be found at a distance of about 4 pool diameters. Calculations were based on square pools of liquid anhydrous ammonia ranging from 30 ft x 30 ft-500 ft x 500 ft. With an atmospheric inversion (conditions which inhibit upward dispersion of the ammonia), these distances could increase between 2-3 times, while an atmospheric lapse state, that is, a condition which does not inhibit upward movement, would substantially reduce the downwind drift.

In a test spill, [121] 1 ton of liquid anhydrous ammonia from a refrigerated atmospheric pressure storage tank was poured into a 5 ft x 22 ft pool. With winds gusting to 15 mph, concentrations of 1,000 ppm or more were detected up to a distance of 150 feet downwind, and concentrations of 50-1,000 ppm were detected up to 500 feet downwind. Ball [5] referred to these results and considered that they correlated reasonably well with his theoretical results when extrapolated to steady-state conditions. Cato and

Dobbs [120] estimated that lethal concentrations existed 100-200 ft from the point of ammonia discharge in a tank car accident. The air temperature was 6-7 F (-17 to -14 C), a gentle breeze was blowing at 3-5 mph, and a temperature inversion existed. Storage areas and containers of ammonia should be located with due consideration of the potential for dispersion and should meet the requirements of 29 CFR 1910.111, as amended.

E. Unusual Sources

Concentrations of ammonia exceeding the recommended limit may originate from unsuspected sources, such as decomposition of organic material in chicken houses, [85] hydrolysis of cyanide emitted from electroplating solutions, [95] and the thermal decomposition of plastics. [122] Personnel should report any unaccounted for ammoniacal odor to responsible supervisory personnel for further investigation.

F. Training

Federal Occupational Safety and Health Standards, 29 CFR 1910.111, state that personnel required to handle ammonia should be trained in safe operating practices and in the proper action to take in the event of emergencies. It further states that employers shall ensure that ammonia unloading operations are performed by properly instructed persons. 29 CFR 1910.134 requires training in the use of respiratory protection. Other references [1,2,107,111,120] stress the importance of training and drills for emergency situations. Accordingly, a requirement for training and drills is recommended.

G. Respirators

Canisters used with respirators have limitations. In ammonia concentrations of 3% by volume (30,000 ppm), an ammonia canister will last for

approximately 15 minutes. [107] Canister respirators do not protect in atmospheres deficient in oxygen. Because emergencies involve exposures to unknown concentrations of ammonia, canister type respirators are suitable for outdoor emergency use only. Self-contained breathing apparatus should be used in all other cases. If the odor of ammonia is noticeable while wearing a canister type gas mask, the ammonia concentration is too high for safety, or the canister is not effective. Shelf life of unopened canisters is limited, and unless the manufacturer recommends a shorter period, they should be replaced after 3 years. Used canisters should be promptly replaced.

H. Fire and explosion hazards

While not considered to be a serious fire or explosion hazard, [9] ammonia will burn or explode under some conditions, such as a large and intense source of ignition and a high concentration of ammonia gas. [111] In one experiment, [121] 10 tons of liquid anhydrous ammonia from a refrigerated atmospheric pressure storage tank were pumped into a pit 1 foot deep and 22 feet square. Winds were gusting to 15 mph and the air temperature was 67-70 F. Ammonia gas could not be ignited with small propane torches or with a spark igniter. Oil soaked torches thrown into the pool and into the gas downwind also failed to ignite the ammonia. However, when water was sprayed into the pool of ammonia, the gas ignited and burned on the surface of the pool, moving back and forth with the water streams. The flames died immediately when the water flow was discontinued.

The presence of iron appreciably decreases the ignition temperature, [111] and the presence of oil [2,111], or a mixture of ammonia with other flammable substances increases the fire hazard. [2] Increasing the oxygen

content of the air, or increasing the temperature and pressure of the ammonia broadens the flammable (explosive) range. [2] Contact with other chemicals such as mercury, silver oxide, halogens, calcium, and hypochlorite can cause spontaneous explosions due to chemical reactions. [2] Storage areas should be free of oil, oxidizers, or other flammable material. [110] Welding in or on confined spaces such as tanks should only be performed by qualified welders after the space has been thoroughly purged of ammonia. [111]

I. Materials

Moist ammonia corrodes copper, tin, zinc, and many alloys, particularly copper alloys. [2,9,110,111] Therefore, only iron or steel, despite the fact they decrease the ignition temperature, or other nonreactive material should be used in contact with ammonia.

J. Agricultural Uses

With over 80% of the ammonia manufactured being used as fertilizer or in fertilizer manufacture, [5] the potential for accidents involving use of ammonia in agricultural operations is evident. Most reported accidents involve ammonia transfer operations or connecting or disconnecting transfer systems. [25,88] Organizations such as the Fertilizer Institute [123] and the National Society for the Prevention of Blindness Inc [124] publish and distribute material for education and training of personnel in agricultural handling of ammonia. The use of eye, skin, and respiratory protection, and a source of water for immediate washing of skin and eyes are stressed, [108,123] as is training in the handling of ammonia equipment. Water carried on farm vehicles should be protected from freezing by insulation or by an external source of heat. Antifreeze chemicals must not be used. A

means of applying the water to the skin and/or eyes in large quantities must be available. The container should have an opening large enough for easy access, should be covered to prevent entry of dirt, and should hold at least 5 gallons. A plastic squeeze bottle containing at least 8 ounces of water should be carried by each individual to allow immediate irrigation of the eyes. This may provide a few additional seconds in which to reach the larger container of water before irreversible eye damage results.

VII. REFERENCES

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