Doc. No.: CHD 07 (23932) WC March 2023

BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

NITRIC ACID- CODE OF SAFETY

(First Revision)

भारतीय मानक मसौदा

नाइट्रिक एसिड - सुरक्षा संहिता

(पहला पुनरीक्षण)

ICS 71.060.30

Chemical Hazards Sectional Committee, CHD 07	Last date for Comments: 22 December 2023
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FOREWORD

(Formal clause may be added later)

Nitric acid is an important industrial chemical mainly used in the manufacture of fertilizers, dyes, drugs, explosives, celluloid and nitrates. It is also used in organic synthesis, metallurgy, medicine, photo-engraving, ore floatation, etching of steel tools and the like. In spite of its long range of uses, it is also one of the most corrosive and hazardous chemical. Handling of nitric acid, therefore, presents various hazards which are better prevented than cured. A sound code of practice will reduce the frequency of hazards and also in many cases the amount of damage caused by an accident.

This standard attempts to guide the users in the recognition of the hazards and recommended handling procedures. This standard describes properties nitric acid, the nature of hazards associated with it and essential information on storage, handling, packing, labelling, waste disposal, cleaning and repair of tanks, selection and training of personnel, personal protective equipment and first-aid. The elimination of accidents is vital to public interest. Accidents produce economic and social loss, impair individual and group productivity. Realization of this loss has led the authorities to devote a good deal of attention to safety education.

The properties of nitric acid listed in **4** have been taken from literature and have been included for information only. Moreover, these properties pertain to pure nitric acid. BIS has published a separate standard IS 264: 2005 on the requirements, methods of sampling, and test for nitric acid of technical, explosive, analytical grades.

This standard was first published in 1968. With a view to update the standard based on the experience of last five decades and on the currently available data the committee felt a need to revise the standard. In this revision general properties, safety measures for controlling hazards, and essential information on symptoms of asphyxiation, first-aid, medical treatment, storage, handling, labelling and employee safety have been incorporated. In this revision the title of standard has also been modified.

The various clauses of the standard have been aligned with the format being applied for all Indian Standards on code of safety of chemicals.

1 SCOPE

1.1 This standard prescribes a code of safety concerning the hazards related to nitric acid. It describes the properties and essential information for safe handling and use of nitric acid.

1.2 It does not, however, deal with hazards relating to manufacture of nitric acid or to the raw materials used in its manufacture.

2 REFERENCE

The standards listed below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	Title
IS 1260 (Part 1): 1973	Pictorial marking for handling and labelling of goods: Part 1 dangerous goods
IS 2925 : 1984	Specification for industrial safety helmets (second revision)
IS 4155: 2023	Glossary of Terms Relating to Chemical and Radiation Hazards and Hazardous Chemicals (<i>first revision</i>)
IS 8519 : 1977	Guide for selection of industrial safety equipment for body protection
IS 8520: 2023/ISO 19734:2021	Eye and face protection guidance on selection, use, and maintenance (first revision)
IS 10667 : 1983	Guide for selection of industrial safety equipment for protection of foot and leg

IS 15 : 202	8	Industrial emergency showers, eye and face fountains and combination units - Specification (<i>first revision</i>)
IS 158 2008	03:	Respiratory protective devices -self contained closed circuit breathing apparatus chemical oxygen (ko ₂) type, self generating, self rescuers - specification

3 TERMINOLOGY

For the purpose of this standard, the definition of terms given in IS 4155 shall apply.

4 PROPERTIES OF NITRIC ACID

4.1 General Information

Nitric acid is mineral acid, with high corrosivity and toxicity. In it is purest form it is colourless but with time due to decomposition of nitric acid to oxides of nitrates its colour changes to yellow cast. Nitric acid has strong oxidising properties. Commercially it is manufactured by catalytic oxidation of ammonia. Commonly it is used in laboratories for testing, and manufacturing of explosives and fertilizers.

4.1.1 *Chemical Name* – Nitric acid

4.1.2 *Common Name & Synonyms* – Nitric acid, aqua fortis and hydrogen nitrate.

4.1.3 Uses

Nitric acid is used for the production of ammonium nitrate, a major component of fertilizers. It is also used for producing explosives like nitroglycerin and trinitrotoluene (TNT) and for oxidizing metals. It is also used in preparation of nitrocellulose. Due it strong oxidizing property it is used in oxidation of metals to the corresponding oxides or nitrates.

4.2 Identification

4.2.1 *Formula* – HNO₃.

4.2.2 *CAS Number* – 7697-37-2.

4.2.3 UN Number – 2031

4.2.4 UN Class – 8

4.3 Physical Properties

4.3.1 General

Nitric acid, in its pure form it is colorless but colour changes to yellow with time due to decomposition of nitric acid to oxides of nitrates. Nitric acid has choking odour and bitter taste due its strong oxidizing properties.

4.3.2 *Molecular Mass* – 63.01 g/mol.

4.3.3 *Physical State* – colorless liquid that solidifies at –42 °C (–44 °F) to form white crystals.

4.3.4 *Colour* – Colorless to light brown.

4.3.5 *Odour* – Characteristic choking.

4.3.6 Boiling Point

Pure acid starts boiling at 86 °C at atmospheric pressure. The boiling point thereafter rises due to decomposition of the acid. Aqueous solutions from a constant boiling mixture at 68 per cent nitric acid boiling at 121.6 °C.

4.3.7 *Melting Point* – 42 °C.

4.3.8 *Vapour Density* (Air = 1) - 2.5.

4.3.9 *Specific Gravity* – 1.408 (Water = 1).

4.3.10 *Viscosity at* 30 °C – No data available.

4.3.11 *Vapour Pressure at* 20 °C – 6 kPa (20 °C).

4.3.12 *Heat of Combustion* – No data available.

4.3.13 *Refractive Index at* 25°C – No data available.

4.3.14 Solubility in Water – Freely soluble in water.

4.3.15 *pH*−<1 at 20 °C

4.3.16 *Odor Threshold* – 0.29 ppm

4.3.17 *Relative Density* – 1.4.13 g/cm³ at 20 °C (68 °F)

4.4 Chemical Properties

4.4.1 Reactivity

4.4.1.1 The acid is a strong oxidizing agent and attacks many organic and inorganic materials with evolution of heat and may cause fire.

4.4.1.2 The dangerous oxides of nitrogen are very insidious and exposure to low concentrations may not be recognizable. Heavy evolution of oxides are easily recognized by the light of deep reddish-brown fumes. The vapours of nitric acid may be detected by their acid odour.

4.4.1.3 Nitric acid react violently with water releasing ample amount of heat energy. It decomposes as temperature rises with release toxic and corrosive fumes of nitric acid. It also react vigorously with metal powders releasing highly flammable gases or vapours.

4.4.1.4 Reacts explosively with metallic powders, carbides, cyanides, sulfides, alkalies and turpentine. Can react explosively with many reducing agents. Arsine, phosphine, tetraborane all oxidized explosively in presence of nitric acid. Cesium and rubidium acetylides explode in contact with nitric acid. Explosive reaction with Nitric Acid + Nitrobenzene + water. Detonation with Nitric Acid + 4-Methylcyclohexane.

4.4.2 *Polymerisation* – No data available.

4.4.3 *Allotrope Formation* – No data available.

4.4.4 *Corrosion Properties* – Nitric acid is highly corrosive in nature.

4.5 Fire and Explosion Hazard Properties

4.5.1 *Ignition Temperature* – No data available.

4.5.2 Auto Ignition Temperature – No data available.

4.5.3 *Flash Point* – Not flammable.

4.5.4 Upper Explosive Limit - No data available.

4.5.5 *Lower Explosive Limit* - No data availablele.

4.5.6 *Fire Risk* – No data available.**4.5.7** Generally Nitric acid is a Non-Flammable, but under certain condition or certain other chemicals becomes vigorous and flammable.

4.5.8 Nitric acid will vigorously attack most metals. Strong nitric acid may cause spontaneous ignition when in contact with organic materials, such as sawdust, excelsior, wood scraps and shavings, paper, cotton waste and hessian bags. If fire starts, it will burn vigorously.

4.5.9 Nitric acid may cause explosion when in contact with hydrogen sulphide and certain other chemicals.

4.5.10 Nitric acid or its vapour will, under certain conditions, nitric acid wood, cotton, starch and similar organic materials, lowering their ignition temperature and greatly increasing their flammability.

4.5.11 Flammable in presence of cellulose or other combustible materials. Phosphine, hydrogen sulfide, selenide all ignite when fuming nitric acid is dripped into gas. (Nitric Acid, fuming)

5 HEALTH HAZARDS & TOXICITY INFORMATION

5.1 General Information

5.1.1 Nitric acid is a highly corrosive and toxic chemical. If not handled carefully, it may lead to severe health hazards. On contact with the skin or eyes, nitric acid causes irritation and produces several burns. Inhalation of the vapour as well as inhalation of most of the oxides are injurious to the lungs. Nitric acid mists are particularly hazardous when inhaled as they can cause corrosion of mucous membranes, delayed pulmonary edema, and even death. Ingestion of nitric acid can produce severe, rapid corrosive burns of the mouth, throat, and gastrointestinal tract. The onset of symptoms following inhalation of the vapours may be delayed for several hours.

5.1.2 A threshold limit value of 10 ppm for nitric acid fumes and 5 ppm for nitrogen dioxide fumes has been suggested as the safe concentration in air for an 8 h exposure. In addition, even short time exposures to higher concentration (100 ppm to 500 ppm) should be avoided.

5.2 Routes of entry

5.2.1 Skin

Mixture of nitric acid causes irritation, and on prolonged exposure may produce severe pain and chemical burns. It may also lead to permanent scarring depending upon the concentration of the acid and the duration of exposure.

5.2.2 Eyes

Direct contact with eye can cause severe eye burns, pain and redness which may lead to permanent injury and possibly blindness.

5.2.3 Ingestion

If ingested, severe burns of the mouth and throat, as well as a danger of perforation of the esophagus and the stomach.

5.2.4 Inhalation

Inhalation of nitric acid can cause delayed pulmonary edema, pneumonitis, and dental erosion. The severity of the symptoms depends on the dose, duration, and work being done.

5.3 Toxicity information

a) Threshold limit value – time-weighted average (TLV-TWA) — 4 ppm.

b) Short term exposure limit (STEL) — 4 ppm.

c) Immediately dangerous to life or health (IDLH) - 25 ppm.

d) Lethal dose (LD₅₀) (human oral), (median dose) — 430 mg/Kg.

e) Lethal concentration (LC_{Lo}) (human, oral) — not available.

f) Inhalation (rat) $LC_{50} - 2500$ ppm for 1 h.

5.4 Antidote

There is no antidote for nitric acid poisoning.

5.5 Health Effects

5.5.1 Signs and Symptoms

Nitric acid causes severe irritation or burns to the eyes, skin, gastrointestinal tract, and respiratory system.

5.5.2 Acute Toxicity

5.5.2.1 Systemic effects

5.5.2.1.1 The toxic effects of nitric acid and of the oxides differ somewhat. It is a combination of these compounds which is commonly encountered in industry since the oxides may be formed wherever nitric acid is used and these may be mixed with nitric acid vapour. Gaseous oxides of nitrogen consist of nitric oxide (NO), nitrous oxide (N₂O), nitrogen trioxide (N₂O₃), and nitrogen dioxide (NO₂ and N₂O₄). The chemical relationship of these compounds is so close that they seldom occur separately in industry. Toxicologically the most important are the two forms of nitrogen dioxide, N₂O₄ (colourless) and NO₂ (dark brown), both of which are highly toxic. The colour of the gaseous oxides varies from colourless to chocolate brown, depending upon the

percentage composition of the mixture, which is largely a function of temperature. At toxic concentrations the gaseous oxides may, therefore, be dark brown or colourless. The intensity of colour is not an indicator of the degree of danger.

5.5.2.1.2 Gaseous oxides are formed when nitric acid comes in contact with certain metals, such as copper, brass and zinc, or with any organic material, such as wood, sawdust, cloth and paper. Gaseous oxides are also present in hazardous concentrations during various operations, such as burning of certain explosives, nitration processes, processes involving the use of nitric acid, electric arc-welding, soldering, the operation of diesel engines, and many other operations.

5.5.2.1.3 Evidences of damage to the lungs following exposure to the oxides of nitrogen characteristically appear after a delay of 4 h to 30 h. This, in the form of edema, may be severe and sometimes fatal.

5.5.2.1.4 The breathing of an atmosphere containing 25 ppm, through 8 h period may cause pulmonary signs and symptoms. Pulmonary edema may follow exposure for only 4 h to 1 h to higher concentrations (100 ppm to 150 ppm). A few breaths of the gaseous oxides in a concentration of 200 ppm to 700 ppm will cause severe pulmonary damage which may prove fatal within 5 h to 8 h.

5.5.2.2 Local effects

Nitric acid or its concentrated vapours will produce immediate severe and penetrating burns to the skin and membranes. Contact with the eyes will produce very severe, immediate damage and may result in permanent damage with visual impairment.

5.5.3 Chronic Toxicity

5.5.3.1 Systemic effects

The nature of nitric acid precludes the ingestion of sufficient quantities to produce any systemic effects except those which might be secondary to irritation to the tissues of the eyes, nose, or upper respiratory tract.

5.5.3.2 Local effects

Repeated exposure of the skin or of the eyes, nose, throat and upper respiratory tract may cause chronic irritation.

6 6 PERSONAL PROTECTIVE EQUIPMENT

6.1 Availability and Use

6.1.1 While personal protective equipment is not an adequate substitute for good, safe working conditions, adequate ventilation, and intelligent conduct on the part of employees working with caustic soda, it is, in many instances, the only practical means of protecting the worker, particularly in emergency situations. One should keep firmly in mind that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area maybe exposed to danger.

6.1.2 The correct usage of personal protective equipment requires the education of the workers in proper employment of the equipment available to him. Under conditions which are sufficiently hazardous to require personal protective equipment, its use should be supervised and the type of protective equipment selected should be capable of control over any potential hazards.

6.2 Non-Respiratory Protection

6.2.1 Eye Protection

6.2.1.1 Chemical safety goggles

Cup-type or rubber framed goggles, equipped with the approved impact resistant glass or plastic lenses, should be worn whenever there is danger of nitric acid coming in contact with the eyes. Goggles should be carefully fitted to ensure maximum protection and comfort *see* IS 8250.

6.2.1.2 Spectacle-Type Safety Goggles

Metal or plastic rim safety spectacles with unperforated side shields which may be obtained with prescription safety lenses or suitable all-plastic safety goggles may be used where continuous eye protection is desirable, as in laboratories. These types, however, should not be used where complete eye protection against nitric acid is needed *see* IS 8250.

6.2.1.3 Face Shields

Plastic shields (full length, 20 cm *Min*) with forehead protection may be worn in addition to chemical safety goggles where greater face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of material striking the eyes from underneath or around the sides of the face-shield *see* IS 8250.

6.2.2 Head Protection

Suitable industrial safety helmets *see* IS 2925 should be worn where there is danger from falling objects. If hard hats are not considered necessary, brimmed felt or treated fibre hats may be worn to give protection against liquid leaks and splashes.

6.2.3 Foot Protection

Rubber safety shoes with built-in steel toe caps are recommended for workers handling drums and carboys of nitric acid. Rubbers should be thoroughly cleaned after contamination *see* 10667.

6.2.4 Body, Skin and Hand Protection

6.2.4.1 Sustained or intermittent skin contact with liquid nitric acid will produce burns at the site of contact. Rubber gloves and aprons should be worn when there is possibility of body contact. Protective clothing contaminated by nitric acid should be bushed with flowing water promptly and cleaned inside and out each time it is used. Affected areas of the body should be flushed thoroughly with water. As a general hygienic measure, facilities for personal cleanliness should be provided and washing before lunch and at the end of the work day should be encouraged *see* IS 8519.

6.2.4.2 Wearing of wool clothing (shirt, pants, socks) is recommended for work in acid areas since cotton clothing is attacked more rapidly.

6.2.4.3 Personal hygiene

Emergency showers and eye baths *see* IS 10592 should be placed in convenient locations wherever phenol is being used. Employees should be instructed that direct contact with the chemical requires the immediate application of large amounts of water to the contaminated area.

6.3 Respiratory Protection

Severe exposure to nitric acid may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection and trained in its use and care. Available types are described briefly below.

NOTE- Respiratory protective equipment shall be carefully maintained, inspected, cleaned and sterilized at regular intervals, and always before and after use by another person.

6.3.1 Self Contained Breathing Apparatus

This permits the wearer to carry a supply of oxygen or air compressed in the cylinder, and the selfgenerating type which produces oxygen chemically, allows considerable mobility *see* IS 15803. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air, oxygen or regenerating material carried. Compressed oxygen should not be used where there is danger of contact with flammable liquids or vapours, especially in confined spaces, such as tanks or pits. A special type of self-contained breathing apparatus may be used which is provided with a small cylinder of compressed air for escape but is supplied with air through an airline for normal work purposes.

6.3.2 Positive Pressure Hose Masks

These are supplied by blowers and require no internal lubrication. The wearer shall be able to use the same route for exit as for entrance, and shall take precautions to keep the hose line free of entanglement. The air blower shall be placed in an area free of contaminants.

6.3.3 *Air-Fine Masks* These are supplied with clean compressed air and are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air piped to the area from a compressor. It is extremely important that the air supply is taken from a safe source, and that it is not contaminated by oil decomposition from inadequate cooling at the compressor. The safer method is to use a separate compressor of the type not requiring internal lubrication. Pressure reducing and relief valves, as well as suitable traps and filters, shall be installed at all mask stations.

6.3.4 Chemical Cartridge Respirators

These may be used to avoid inhalation of disagreeable but relatively harmless concentrations of nitrous vapour. These respirators, however, are not recommended for protection where toxic quantities may be encountered.

CAUTION Filter type respirators do not offer protection against gases and are unsuitable for use when working with nitric acid or nitrogen oxides.

7 STORAGE, HANDLING, LABELLING AND TRANSORT

7.1 Storage

7.1.1 Drums

Stainless steel drums are normally used for nitric acid up to 99 percent in strength. Aluminium drums are used for strengths 80 percent or above. Aluminium drums should be checked frequently for leakage at the bung, as corrosion will take place at this point if 'breathing' occurs. Store drums with body plugs up, on skids, on a properly drained site. They should be stored out of the direct rays of the sun in order to minimize temperature changes of the contents and resulting tendency to breathe.

7.1.2 Carboys

Carboys should be stored preferably under cover on floors of acid resistant brick or concrete treated with sodium silicate. Suitable drainage facilities should be provided. If necessary to store outdoors, keep out of direct rays of the sun and provide suitable dunnage for bottom tier to rest on, in a properly drained site Store where contents will not freeze.

7.1.3 Tank

Nitric acid up to and including 99 percent strength is stored in stainless steel equipment. Aluminum equipment is used for the higher concentrations. However, nitric acid may be stored as mixed acid (a mixture of concentrated nitric and sulphuric acid) in steel tanks. Each storage tank should be provided with a vent of sufficient size and discharging at a safe location.

NOTE — All the containers shall be stored in an isolated place away from turpentine, carbides, metallic powders and combustible materials.**7.2 Handling**

7.2.1 General

Nitric acid is a corrosive liquid which will burn the skin and attack most metals. It will also react violently with many chemicals and all cellulosic materials. Extreme care is, therefore, important in all phases of handling and storage of nitric acid.

7.2.2 Small containers

7.2.2.1 Glass bottles

Employees handling glass bottles should be equipped with proper personal protective equipment. Handle the bottles carefully to avoid breakage. Do not breathe vapour.

7.2.2.2 *Carboys*

The following instructions for handling carboys should be followed:

- a) Carefully inspect all carboys on receipt and set aside any damaged ones for special handling.
- b) Be sure closures are securely fastened before moving either filled or empty carboys.

c) Place a cap or boot over the neck of the carboy before moving it.

d) Use specially designed hand-trucks for transporting individually boxed carboys around the plant. Do not use hooks.

e) Never handle carboys by the closure or neck of bottle.

f) Never 'walk' a carboy on the edge of the box.

g) When removing full or empty boxed carboys from storage tiers, trucks or cars, and when stacking full or empty carboys, the neck of the bottle should never be tilted toward the workman.

h) Filled boxed carboys of nitric acid should not be tiered more than two carboys high. Empty boxed carboys should be stored on their side, not over four tiers high, in such a manner that the necks may not protrude into aisles or passageways.

j) When opening carboys, always keep the hands and face to the side and never over its neck. The recommended method of removing the wire holding the stopper in place is to use a wire cutter (preferably the face type). Never attempt to remove the wire by twisting or prying; to do so may break the neck of the bottle and injure the workman. The screw cap closures on carboys should be turned only slightly to relieve any accumulated pressure before they are completely removed.

k) Never use air pressure to empty carboys. Use a tilter especially designed for the purpose, or a safety siphon fabricated, of material resistant to nitric acid.

m) It is mandatory that empty carboys be completely drained before presentation to the transportation company.

n) The white ACID labels shall be removed, obliterated, destroyed, or completely covered by the white EMPTY label. Make sure that all carboy parts, such as box tops, caps, and stoppers, are returned to the supplier. Screw caps, ground-glass stoppers, and box tops should be affixed in place on their respective bottles and boxes. Other parts should be returned in a suitable container marked clearly with description of contents.

7.2.3 Drums

The following instructions should be followed for handling drums:

a) Inspect drums for loose plugs and signs of leakage or damage before moving. Set aside for special handling if damage is found. Tighten loose plugs.

b) In case of concentrated acid stored in aluminium drums, severe corrosion may be induced at bung opening from dilution with atmospheric moisture if there is any leakage at this point. Inspect at frequent intervals.

c) AVOID ROUGH HANDLING OF DRUMS. Do not drop. Drums should be handled carefully to and from their place of storage. Before emptying contents, substantially support the drums and block them to prevent movement.

d) To remove the body plug, place bung up, and use a pipe wrench or plug wrench with a long handle. Stand to one side and ace away during the operation. After plug starts, give one full turn.

If accumulated internal pressure vents, allow it to reduce to atmospheric pressure; then only should the plug be loosened further or removed.

e) Loosen plugs of stored drums weekly, especially in hot weather, to release pressure that may build up in drums.

f) Drums should be emptied by gravity only, with the use of a faucet or safety siphon fabricated of material resistant to nitric acid. Application of pressure to the drum for this purpose is extremely dangerous and should never be attempted.

g) Before drums are returned to the supplier, they should be completely drained, and all openings shall be properly closed. The white ACID labels shall be removed, obliterated, destroyed, or completely covered by the white EMPTY label. Under no circumstances should drums be used for any other liquid.

7.2.4Tank trucks

7.2.4.1 General

Protective equipment consisting of an acid hood, (acid-resistant apron and gloves and long-sleeved shirt and trousers prefer ably of wool or other acid-resistant material) should be worn while venting or connecting and disconnecting pipelines. Acid goggles and a brimmed hat should be worn under all conditions except when an acid hood is being used. If necessary to work on connections beneath the tank, a full acid suit should be worn. Such work should not be performed while transfer of acid is in progress.

7.2.4.2 Fittings

The packing and lubricant for pumps, glands, etc, shall be of a material recommended for nitric acid handling. The pump, glands, flanged fittings, gaskets, and valve stems should be provided with splash shields or collars in cases where personnel would be exposed to acid leaks or sprays if acid should escape. Where access to the top of the tank truck is needed, the spot should be provided with stairs and platform. Non-combustible construction is preferred. Overhead loading lines should be counterweighted with a pulley and weight system.

7.2.4.3 Damage en route

In case a tank truck becomes damaged en route so that it cannot proceed safely to destination, every effort should be made to park it where it will not endanger traffic or property. The police and fire departments should be notified and public warned to stay away. The truck should be parked if possible, in a vacant lot and away from an area in which there is a concentration of people. If leaking, the acid should be trapped in a depression or pit and if possible, neutralized with soda ash or lime and the neutralized material subsequently thoroughly washed away. Litmus paper should be used to determine that the spill has been adequately neutralized. If available, another authorized tank truck should be brought to the disabled vehicle to pump off the leaking acid.

7.2.4.4 Unloading

Tank trucks should be visually inspected for leaks before they are allowed to enter the plant and the necessary precautions taken for prompt and safe unloading of any vehicles found leaking.

7.2.4.4.1 Unloading should preferably be performed during daylight hours. If vehicles are unloaded at night, proper and adequate lighting should be provided around the truck and the working areas involved in the operation.

7.2.4.4.2 Tt is preferable that the truck pad be so arranged that liquid spillage will drain away from the truck and exposed structures. The pad should be of sufficient length to allow the truck and trailer a minimum of a 90 cm clearance at each end and 45 cm clearance on each side. Because of the hazard of backing equipment into roadways and the possible need to move a truck quickly from the unloading spot, it should be so arranged that the truck may be driven away in a forward direction. Where a drive through arrangement is used, a chain, gravity-swing guard gate, or equivalent, should be provided across the truck entrance to the driveway, when the same is not in use.

7.2.4.4.3 Only qualified and properly instructed employees should operate the truck and make the hook-up of the unloading line from the tank truck to the receiving tank.

7.2.4.4. Contents of the tank truck should be checked before they are transferred. If a sample is required for testing purposes, the truck driver should open the man-hole. The person taking the sample should wear the prescribed protective equipment.

7.2.4.4.5 An authorized and qualified representative of the buyer should give approval to unload into the storage tank. This representative should designate the specific unloading connection to be used.

7.2.4.4.6 Before connecting for unloading, the truck engine should be stopped and not started again during the entire unloading operation unless it is necessary to operate the pump by power take-off or to use the truck engine to operate compressors as a source of air for air pressure unloading.

7.2.4.4.7 Truck parking brakes should be set and, where necessary, the wheels blocked. A sign should be placed near truck stating in effect 'DANGER-UNLOADING ACID' to caution others to stay away from the operation.

7.2.4.4.8 Whether unloading by pump or air, the piping should be so arranged that the acid will drain toward the storage tank when the pump is shut down or when the discharge valve is closed.

7.2.4.4.9 It should be ascertained that all valves are properly set and that the overflow line on the storage tank will discharge to a safe location. It should also be determined that there is room in .it for the amount of acid to be transferred.

7.2.4.4.10 When unloading line shall be run across a walkway, suitable warning signs should be provided to denote the hazard.

7.2.4.4.11 Before starting to vent or connect, a water hose should be connected and ready for emergency use and the emergency shower should be tested.

7.2.4.4.12 The acid flow should not be started until the truck driver is so instructed by the buyer's authorized representative.

7.2.4.4.13 Wherever, practical, cargo tanks should be unloaded by pumping. When unloading by pumping, the following procedure should be followed:

a) Operate relief valve to vent the cargo tank. If the cargo tank is not equipped with relief valves, the venting should be accomplished with care through the valve on the air inlet line.

b) Carefully open valve or remove blind flange (whichever may be applicable) on the air inlet line. Leave this line open during pumping.

c) After ascertaining that there is no pressure in the tank, carefully remove the blind flange from the standpipe (starting with bottom bolts) and connect unloading line to the standpipe.

7.2.4.4.14 If unloading is to be done by means of air pressure, the following procedure should be adopted:

a) First of all, make sure valve on standpipe is closed.

b) Make connection from cargo tank to storage tank.

c) Open air inlet valve and slowly apply unloading pressure (the air pressure shall never exceed the safe working pressure of the tank).

d) Open the valve on the standpipe slowly until there is a normal flow of acid into the storage tank.

e) When the truck is empty, shut off the air and vent off the pressure.

f) After pressure has been vented, disconnect air-line.

g) Do not disconnect the acid unloading line until the cargo tank is at atmospheric pressure and the standpipe is drained.

h) After disconnecting the acid unloading line, close valves (or replace blind flanges) on the standpipe and air-line.

7.2.4.4.15 If a spill or overflow should occur during a transferring operation, the pump or supply of air should be stopped, valves shut off and spill cleaned up before other actions are taken.

7.2.5 Tank cars

7.2.5.1 Unloading

Unloading operations should be conducted by carefully instructed reliable employees under adequate supervision.

7.2.5.2 See that train or engine crew accurately spots the car at the unloading line. The unloading track should be level.

7.2.5.3 It is considered good practice to place derails at one or both ends of the unloading track approximately one car-length from the car being unloaded, unless the car is protected by a closed and locked switch or gate.

7.2.5.4 The hand-brake shall be set and wheels blocked at the time car is placed for unloading. Metal 'CAUTION' signs should be placed before and after the car, fastened to the track, preferably near the entering switch, as a warning to persons and switching crews approaching the car. These

signs shall not be removed until the car has been unloaded and all fittings disconnected. Signs should be of size not less than 30 cm x 40 cm painted light blue and should bear the legend in

white 'STOP ! TANK CAR CONNECTED', letters in the word 'STOP' being 10 cm high and the others 5 cm high. Enamelled signs with stand are standard equipment, available from safety equipment dealers.

7.2.5.5 Supplier's instructions for unloading should always be followed, and all caution markings on both sides of tank or dome should be read and observed. In the event of a leak in tank car or fitting, immediately contact the supplier for instructions.

7.2.5.6 Under no circumstances should the acid connection be removed until all pressure in the car tank has been released through the safety valve. Should the operator fail to release all pressure before disconnecting the acid line, he may be seriously injured from spurting acid.

7.2.5.7 Pump discharge of lading

The safer method of unloading nitric acid is by pump, with suction connected to the eduction pipe at the dome. The procedure is essentially as given below, except that the tank car shall be vented to atmosphere while pumping. If air pressure on the tank is required to prime and start pumping, it shall be limited up to 2.10 kg/cm^2 .

7.2.5.8 Compressed air used for discharge of lading

Under no circumstances should air pressure in excess of 2.10 kg/cm^2 be used for unloading tank cars. Use of air beyond this pressure constitutes a hazard and may result in tank damage or possible bursting. If 2.10 kg/cm^2 air pressure is not adequate for unloading, a centrifugal type acid pump should be used.

7.2.5.9 Compressed air shall be free as far as possible from oil, excess moisture and foreign matter. To insure this, the air supply should be taken from the 'TOP' of the air receiver (reservoir) preferably located near the unloading spot. This receiver should be drained at regular intervals. If the receiver is located farther than 1 m from the car spot, an oil and water separator should be installed in the air-line adjacent to the tank car.

7.2.5.10 Discharge connections shall be detached immediately after tank is unloaded. Unloader shall stay with the car throughout the unloading operation and until all discharge fittings are disconnected and car fittings replaced.

7.2.5.11 Should any hazardous conditions arise, immediately close air supply, consult the foreman, and do not reopen until repairs or adjustments have been completed.

7.2.5.12 Unloading operations

Unloading operations should be carried out strictly in the following sequence:

a) Relieve any internal pressure in the tank car through the safety valve, using care to avoid breathing any vapour released, and gradually releasing the pressure that may be accumulated so as not to carry acid spray with the air and vapour.

b) Carefully remove the air inlet nozzle cover. (If the blow leg cover is removed first, internal pressure may cause acid to flow). Be prepared to release pressure gradually during this operation, in case the safety valve has failed to operate for some reason. Samples should be taken through the air inlet opening by means of a stainless steel rod with a dipping device built into the bottom end.

c) Remove acid pipe cap or plug and connect plant acid line.

d) Make pipe connection from plant air-line to the air connection on the tank car dome. The airline shall have a pressure reducing or safety valve set at not over 2.10 kg/cm: also an air gauge and valve to release car tank pressure when emptied. The valve for releasing pressure should be so located that it may be reached in an emergency, such as discharge line failure.

d) Apply air pressure slowly until there is normal flow of acid into the storage tank; then adjust air pressure and maintain until the car tank is completely empty. A drop in pressure and the sound of air rushing through the discharge pipe indicates that car tank is empty. Continue the flow of air until the discharge line is completely empty, then shut off the air, open the relief valve, and allow the acid pipe to drain.

e) Disconnect plant air fittings from the air inlet on the car and replace nozzle cover.

f) Do not disconnect the acid line from the tank car until the car tank is at atmospheric pressure and sufficient time given to permit complete drainage of line to the car tank or storage tank.

g) Carefully disconnect plant acid line from the discharge pipe fitting and tightly replace blind flange.

7.2.5.13 Return precautions

As soon as a tank car is completely unloaded, the unloading connections shall be removed and all closures made tight. The placards on sides and ends of the tank car shall be removed, or reversed (if in metal placard holders), by the party discharging the tank car. The empty tank car shall be offered to the receiving carrier either without placards, or preferably with 'DANGEROUS - EMPTY' placard.

7.3 Packing

7.3.1 Nitric acid may be packed in glass carboys (capacity 25 to 30 kg) which should be sound construction and be individually provided with strong wooden crates.

7.3.2 For rail transport each nitric acid carboy should be provided with a well luted stopper and should be put in a wooden or iron case, the interspace being packed with whiting, kieselguhr or other non-combustible absorbent material.

7.3.3 Drums made of stainless steel or aluminium or tanks made of stainless steel should be used for packing bigger quantities of acid.

7.4 Labelling

7.4.1 Each container shall be securely closed and shall bear legibly and indelibly the following information:

a) Name and grade of the material;

b) Lot or batch number and date of manufacture;

c) Tare, gross and net mass; and

d) Indication of the source of manufacture.

e) Physical, chemical and toxicological data as per the criteria given in the relevant schedule of the Manufacture, Storage and Import of Hazardous Chemicals Rules, 1989. While referring to the statutes, the stipulations given in the subsequent amendments of those statutes shall be taken into account.

Manufacturers name with label warnings required by regulations or ordinances form part of the label or placard.

7.3.2.2 Each container shall also be marked with Fig. 1 of IS 1260 (Part 1) along with the following information printed in the space provided. The lower half of the label shall have the following text printed in addition to or in combination with any other statements required by statutes, regulations or ordinances

NITRIC ACID

DANGER! CAUSES SEVERE BURNS

Do not get liquid or vapors in eyes, on skin, on clothing.

Keep away from heat and open flame. In case of contact immediately remove all contaminated clothing involving shoes, and flush skin or eyes with plenty of water at least 15 min, for eyes get medical attention.

7.4 Transport

Only driver trained in phenol handling should be employed for transportation of phenol. Driver should carry TREM card when vehicle is on road.

NOTE — If transport of the hazardous chemical is involved it shall be carried out in accordance with the Central Motor Vehicles Rules, 1989. While referring to the statutes, the stipulations given in the subsequent amendments of those statutes shall be taken into account.

8 SPILLAGE, LEAKAGE AND WASTE DISPOSAL

8.1 Spill and Leaks

In case of accidental spilling of nitric acid, it should be washed with large quantities of water. Absorbent combustible materials, especially sawdust and other organic materials, should never be used for this purpose. Clean dry sand or other non-combustible material may freely be used only if water is not available or if its use is impossible for other reasons. After absorption, this may be removed by shovels and the area washed with water. In case of accidental formation of gaseous oxides of nitrogen, the room should be evacuated without delay. It should be entered only by specially qualified personnel familiar with the potential dangers of gaseous oxides of nitrogen and provided with proper personal protective equipment. Adequate ventilation should be provided and the source of the toxic gases removed.

8.2 Cleaning and Repairs

8.2.1 Preparation of Tanks and Equipment

8.2.1.1 Cleaning and inspecting tanks is a hazardous task and requires well trained and well supervised personnel. All precautions pertaining to education, protective equipment, and health and fire hazards should be reviewed and understood. These operations should be under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of the work.

8.2.1.2 Tanks and equipment, pumps, lines, and valves should always be drained and thoroughly flushed with water before being repaired. Workmen should never be allowed to attempt to repair equipment while it is in operation and lines full. If pipe sections are to be removed and flanges opened, the lower bolts should be loosened first and, although the lines have been flushed, care should be taken to avoid personal contact with the liquid draining or dripping from the equipment. All spillage from the lines or equipment should be removed immediately by flushing to the drain with large quantities of water.

8.2.1.3 The tank or equipment to be repaired should first be emptied of all liquid, and all pipes leading to and from the tank (except vents) after draining should be disconnected or blanked off. Wash thoroughly with running water any sludge and residues that cannot be drained; fill tank completely with water and drain out; add soda ash or lime in sufficient quantity to neutralize any residual acid. If necessary, repeat this operation.

8.2.1.4 The tank should then be purged with fresh air and the air should be tested for nitrous fumes by an approved method before permitting personnel to enter.

8.2.2 Entering Tank

8.2.2.1 No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested and found to be safe. Furthermore, no workman should enter a tank or vessel that does not have a man-hole opening large enough to admit a person wearing a safety harness, life line, and emergency respiratory equipment. It should be ascertained that the tank or vessel may be left by the original entrance.

8.2.2.2 One man on the outside of the tank should keep the men in the tank under observation and another man should be available nearby to aid in rescue if any of the men in the tank are overcome.

8.2.2.3 A supplied air respirator or a self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank.

8.2.2.4 Special ventilation is recommended for the entire time during which men are cleaning, repairing, or inspecting the tank. Ventilation may be accomplished by exhausting or removing vapours from the bottom of the tank either through its bottom openings, or by exhausting the vapours from the tank bottom by means of a large flexible duct where tanks have a top opening only. On tanks having only a top opening care shall be exercised to ensure complete removal of vapours from the entire tank. Care shall also be taken to avoid having exhaust gases recycled into the tank.

8.2.2.5 Daring the course of the work, frequent tests should be made to determine that the atmosphere in the tank is being maintained within the safe range. This precaution is necessary because residues not completely removed by washing may re-contaminate the tank atmosphere.

8.2.2.6 In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new permit issued before resumption of work.

8.2.3 Emergency Rescue

Under no circumstance should a rescuer enter a tank to remove a victim of over exposure without proper respiratory protection, a safety harness and an attached life line. The free end of the life line should be manned by an attendant located outside the tank. Another attendant should be immediately available to assist in the rescue if needed. The rescuer should be in view of the outside attendant at all times or in constant communication with him.

8.2.4 Exterior Repair Work

Exterior tank repairs, including repairs to steam coils, cutting, riveting and welding, should be permitted only after thorough cleaning and testing of the tank to make sure that it is free of vapours and after a work permit has been issued by an authorized person.

8.3 Disposal of Waste Acid and Empty Containers

8.3.1 Waste materials from nitric acid may be washed off with large quantity of water with due consideration to local, state, and central laws regulating the health and pollution. As a safeguard against corrosion of sewer lines, the waste acid first shall be neutralized with any readily available basic compounds like soda ash or lime. Nitrates are all soluble in water and are easily flushed away.

8.3.2 Before returning the empty containers, the contents should be drained completely and all openings should be tightly closed.

8.3.3 Do not use nitric acid containers for storage of any other liquid without thoroughly washing off the acid with plenty of water and without being sure that no trace of acid or vapour is left.

8.3.4 Drums should be emptied by gravity only with the use of a faucet or safety siphon fabricated of material resistant to nitric acid. Application of pressure to the drum for the purpose is extremely dangerous and should never be attempted.

9 FIRE PREVENTION AND FIRE FIGHTING

9.1 Nitric acid is not a fire hazard itself but because of its strong oxidizing action on most materials, it may cause fire to result.

9.2 Water in quantity is most effective in fighting fires involving nitric acid, and in diluting the acid as rapidly as possible. Water spray is effective for absorbing oxides of nitrogen. Water hoses and nozzles should be provided at places of storage and handling.

10 PREVENTIVE HEALTH MEASURES AND TRAINING

10.1 Preventive Health Measures

10.1.1 Nitric acid is not a serious industrial hazard if workers are adequately instructed and supervised in the proper means of handling the chemical. Contact with the skin and eyes as well as the inhalation of its vapours and oxides should be avoided. Respiratory protection should be worn when necessary to work in an atmosphere containing nitric acid fumes. If caught in an emergency without respiratory protection, the breath should be held and escape made, if possible, without breathing. If this is not possible, short shallow breaths should be taken so as not to fill lungs. Any exposure to fumes should be reported so that the individual gets immediate medical attention.

10.1.2 Personal Hygiene

Properly designed emergency showers and eyebaths should be placed in convenient locations wherever nitric acid is used. All employees should know the location and operation of such equipment. It shall be frequently inspected to make sure that it is in proper working condition.

10.1.3 Physical Examination

10.1.3.1 Preplacement examination

It may be desirable to exclude from potential exposure to nitric acid prospective employees with the following disabilities:

- a) Those with only one functioning eye;
- b) Those with uncorrected, severe, faulty vision;
- c) Those who have chronic diseases of the upper respiratory tract or lung; and
- d) Those with severe pre-existing skin lesions.

10.1.3.2 Periodic health examination

No specific type of periodic health examination is needed.

10.1.3.3 Suggestions to physicians

The main feature of the clinical pattern following contact with nitric acid or its oxides is the delayed onset of pulmonary edema following sufficient vapour exposure. This may occur 4 to 30

hours after an initial contact which was virtually asymptomatic. Employees shall, therefore, be placed under observation for this period after any vapour exposures which were not patently insignificant. The occurrence of tightness in the chest, rales and an elevated white blood cell and platelet counts are important premonitory signs of impending pulmonary edema. In the treatment of vapour exposure, the use of oxygen and the corticosteroids has proved helpful. Oxygen is administered at normal or elevated pressures following exposure until the danger of pulmonary edema has passed (*see* **11.5.1.1**). The corticosteroids are administered whenever any signs of developing pulmonary damage appear and are continued until recovery occurs.

10.2 Employee Education and Training

Safety in handling nitric acid depends to a great extent upon the effectiveness of employee education, proper safety instructions, intelligent supervision, and the use of safe equipment.

10.2.1 The education and training of employees to work safely and to use the personal protective equipment or other safeguards provided for them is the responsibility of supervision. Training classes for both new and experienced employees should be conducted periodically to maintain a high degree of safety in handling procedures. Workers should be thoroughly informed of the hazards that may result from improper handling of nitric acid. They should be cautioned to prevent spills and thoroughly instructed regarding proper action to be taken in case they occur. Each employee should know what to do in an emergency and should be fully informed as to the first-aid measures.

10.2.2 In addition to the above, employee education and training should include the following:

- a) Instruction and periodic drill regarding the locations, purpose, and use of emergency fire fighting equipment, fire alarms, and emergency crash shut-down equipment, such as valves and switches.
- b) Instruction and periodic drill regarding the locations, purpose, and use of personal protective equipment.
- c) Instruction and periodic drill regarding the locations of safety showers, eye-baths, bubbler drinking fountains, or the closest source of water for use in emergencies.
- d) Instructions to avoid all unnecessary inhalation of vapours of nitric acid and nitrous oxides and all direct contact with the liquid.
- e) Instructions to report to the medical department if the employee suspects that he has been exposed to red oxide of nitrogen fumes. Reaction to this exposure may be delayed.

11 FIRST-AID

11.1 General

In case of exposure to vapours from the oxides of nitrogen (without simultaneous skin or eye burns), it is important to move the patient from the contaminated area as rapidly as possible. The patient should be carried on a stretcher or other conveyance to a spot where he can receive medical attention. Any strenuous effort after a vapour exposure may increase the chance for serious difficulty later.

11.1.1 If the patient has sustained skin or eye burns, in addition to vapour inhalation, the burns shall be treated immediately otherwise serious injury will result.

11.2 Contact with Skin and Mucous Membrane

Immediate removal by the use of large amounts of water is urgent. If the skin contact is extensive and, an emergency shower is available, the employee should get under the shower immediately. Clothes may be removed while under the shower. In other instances, flushing with large amounts of running water and washing with soap should be continued for at least 15 min. It is important to remove all clothing including shoes and socks, which may be contaminated. Subsequent medical treatment is the same as for thermal burns.

11.3 Contact with Eyes

If even small amounts of nitric acid enter the eyes, they should be irrigated immediately with large amounts of water for a minimum period of 15 min. This may be done with an eye-bath, if available, a gentle stream of water from a hose, or by pouring water from any clean container. The eyelids should be held apart during the irrigation to insure contact of water with all of the tissues of the surface of the eyes and lids. If pain is still present after the first 15 min period of irrigation, the irrigation should be continued for another 15 min. It is permissible as a first-aid measure to instill two or three drops of 0.5 percent pontocaine solution or an equally effective topical anesthetic. If this is done, cover the eye with a patch. No oils or oily ointments should be instilled. The employee should be sent to a physician, preferably an eye specialist, as promptly as possible after the irrigation has been completed.

11.4 Ingestion

If a person has swallowed any nitric acid, he should drink large amount of water immediately in order to reduce the concentration of the acid. If vomiting occurs, give more water to further dilute the acid. Medical attention should, of course, be obtained immediately.

11.5 Inhalation

11.5.1 A worker who has been exposed to the oxides of nitrogen or to nitric acid vapour shall be carried at once to an uncontaminated area, and a physician Should be called. The employee shall be kept under observation until the possibility of developing a delayed pulmonary edema is no longer present. If oxygen inhalation apparatus is available, oxygen should be administered but only by a person authorized for such duty by a physician.

11.5.1.1 Oxygen administration

Oxygen has been found useful in the treatment of inhalation exposures of many chemicals, especially those capable of causing either immediate or delayed harmful effects in the lungs.

11.5.1.2 In most exposures, administration of 100 percent oxygen at atmospheric pressures has been found to be adequate. This is best accomplished by use of a face mask having a reservoir bag of the non-rebreathing type. Inhalation of 100 percent oxygen should not exceed one hour of continuous treatment. After each hour, therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

11.5.1.3 Some believe that superior results are obtained when exposures to lung-irritants are treated with oxygen under an exhalation pressure not exceeding 40 mm H_2O . Masks providing for such exhalation pressures are obtainable. A single treatment may suffice for minor exposures to irritants. It is believed by some observers that oxygen under pressure is useful as an aid in the prevention of pulmonary edema after breathing irritants.

11.5.1.4 In the event of an exposure causing symptoms or in the case of a history of severe exposure, the patient may be treated with oxygen under 40 mm H_2O exhalation pressure for one-half hour periods out of every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruption appear.

CAUTION - It may not be advisable to administer oxygen under positive pressure in the presence of impending or existing cardiovascular failure.

11.5.2 The patient should be kept comfortably warm, but not hot.

11.5.3 Stimulants will rarely be necessary where adequate oxygenation is maintained. Any such drugs for shock treatment should be given only by the attending physician. Never attempt to give anything by mouth to an unconscious patient.