SAFETY ASPECTS OF HANDLING *ISO*CYANATES IN URETHANE FOAM PRODUCTION

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SUMMARY

The handling and storage of the group of chemicals known as poly*iso*cyanates are discussed. together with the questions of fire hazards, materials of construction, extraction and ventilation. Employee safety, protective equipment and medical aids are also considered.

Introduction

Chemicals in any form can be safely stored, handled or used if the physical, chemical, and hazardous properties are fully understood, and if proper precautions, including the use of adequate safeguards and personal protection equipment, are taken. In this paper, the chemicals to be considered are the group of chemicals known as poly*iso*cyanates, and the methods of every-day handling of them is important and involves a number of safety precautions.

The word "*iso*cyanates", as used today, covers a small group of polyfunctional organic chemicals which are being used in increasing quantities in widely varying industries. The most common *iso*cyanate (see Table I) is toluene di*iso*cyanate, which is a mixed isomer of 2:4 and 2:6 toluene di*iso*cyanate used in the production of rigid and flexible urethanes and urethane coatings. Other common *iso*cyanates are methylene bis (4 phenyl *iso*cyanate), which is being used in increasing quantities in the production of rigid urethanes, and as a bonding agent for elastomers and textile fibres, and naphthalene 1:5 di*iso*cyanate, used quite extensively in the production of solid urethane elastomers.

Poly*iso*cyanates have assumed importance as the building units of high molecular weight polymers having properties of adhesives, plastics, rigid or elastic foams, and synthetic rubbers.

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These *iso*cyanates react with compounds containing active hydrogens, and the reaction rate depends upon the nature of the active hydrogen compound. In some cases the reaction can be violent, and to ensure that this can always be properly controlled is one of the reasons for the safety precautions we shall be considering.

Another reason is toxicity. Although polyurethanes have proved to be physiologically inert, the *iso*cyanate monomers which are used as starting materials in the polymerisation are not physiologically inert. The level of the "acute toxicity" of the *iso*cyanate monomers is generally low, but the monomers or their vapours are irritating to the skin, eyes, and respiratory tracts. They may cause allergic asthmatic reaction.

Special Safety Precautions

*Iso*cyanates react readily with moisture and should therefore be kept dry. The physical state of the toluene di*iso*cyanates and methylene bis (4 phenyl *iso*cyanate) at normal temperatures can create a hazard. TDI 80/20 should be stored and used at temperatures above 16°C to prevent crystallisation which could create hazards in the processing equipment by plugging feed lines and relief valves. Pure MDI will dimerise at normal temperature and should be stored at 0°C or lower in the solid state or 40–50°C in the liquid state. Provided moisture is rigorously excluded from *iso*cyanate storage vessels and containers, no undue hazard will exist.

TABLE I.—*Properties of Some Common* Iso*cyanates*

Chemical	Toluene di*iso*cyanate	Methylene bis (4 Phenyl *Iso*cyanate)	Naphthalane 1:5 di*iso*cyanate
Structure	2·4 2·6		
Common forms	80/20 2·4 2·6 Isomer ratios 65/35 2·4 2·6 Isomer ratios 80/20 2·4 2·6 undistilled	Pure MDI undistilled MDI	Pure NDI
Boiling point	250°C.		
Melting point	4–14°C.	42°C	121–125°C
Vapour pressure	0·003 mm at 20°C 11·0 mm at 120°C	0·5 mm at 156°C 5·0 mm at 140°C	5·0 mm at 169°C
Flash point	135°C		
Toxicity level (H.M. Factory Inspectorate)	0·02 ppm	Not stated	Not stated

The corrosiveness of *iso*cyanates is low and the hazards here are more concerned with external factors which can create a situation in which a toxic hazard exists. *Iso*cyanates do not constitute a severe fire hazard in themselves, but the presence of *iso*cyanates in a fire, which could lead to free *iso*cyanates from burst drums or leaking pipes and vessels, constitutes a severe hazard from the toxic aspect.

The toxicity of *iso*cyanates is the major hazard and stringent precautions are necessary to reduce and maintain the maximum allowable concentration (MAC) of free *iso*cyanate below 0·02 ppm.

Physiological Effects

With the increasing use of *iso*cyanates in industry, much more attention is being given to the study of their physiological effects. The major studies have been concerned with the physiological effects of toluene di*iso*cyanate, which is the commonest *iso*cyanate in the polyurethane industry today. For the purpose of this discussion therefore toluene di*iso*cyanate will be used as the reference *iso*cyanate and what is regarded as good practice for this chemical may be taken as applying equally well to all other *iso*cyanates.

Toluene di*iso*cyanate is a colourless-to-pale yellow liquid with a pungent odour. This characteristic odour, and its strong irritating effect on the eyes and upper respiratory passages are warnings of the presence of TDI in the atmosphere and no one will voluntarily stay in a high concentration of this vapour. However, smaller concentrations which cannot be detected either by their odour or by their other effects on the senses can also be harmful if exposure is prolonged.

Several authors have published reports on the physiological effects of *iso*cyanates. Fuchs and Valades[1] described a chemical study of toxic reactions of a group of workers exposed to TDI. After 8–60 days of exposure, workers complained of irritation of eyes and throat, bronchial irritation; and then asthmatic attacks. The symptoms cleared up on rest away from the job but reappeared if the men returned to work.

Reinl[2] in 1953 mentioned the strong physiological activity of *iso*cyanates of high vapour pressure. He noted that *iso*cyanates in vapour form have a strong irritating effect on all mucous membranes, particularly respiratory organs and eyes. He mentioned the possible occurrence of asthmatic or bronchial difficulties relating to what he termed "*iso*cyanate allergy".

Zapp[3] in 1957 reported on clinical studies of the toxicity of toluene 2.4 di*iso*cyanate. Acute oral toxicity was investigated by administering graded doses of undiluted material by stomach tube to rats.

A lethal dose of 5800 mg/kg of body weight with 95% confidence limits of 7200 and 4600 mg/kg was established. Pathological examination revealed corrosive action on the stomach and possible toxic effects on the liver. Further tests suggested the possibility of cumulative effects.

Skin absorption toxicity was found to be low on rabbits, but severe local skin irritation did result. Tests on guinea pigs confirmed this result and, in addition, it was possible to produce allergic skin sensitisation. Application of TDI to the eyes of rabbits resulted in marked irritation of the eyelid and minor damage to the corneal epithelum.

Acute inhalation studies on rats showed that 660 ppm (estimated) of *iso*cyanate vapour for six hours was lethal, whereas 60 ppm for six hours was not. Animals which died showed acute pulmonary congestion and edema.

Sub-acute inhalation tests at low concentrations, 1–2 ppm, on animals confirmed the reports of Fuchs and Valades[1] and Reinl[2] that the *iso*cyanates are strong irritants of the eyes and respiratory tracts. Zapp[3] did not, however, observe in animals the asthmatic type of reaction which has been reported occurring in human beings. Published and unpublished reports have confirmed asthmatic reactions do occur in men exposed to TDI and other *iso*cyanates.

Zapp,[3] from the experimental and clinical observations carried out, considered it safe to conclude 2:4 TDI is a material of low acute toxicity which, nevertheless, possesses a potential for producing considerable industrial morbidity. Exposure to TDI and other di*iso*cyanates must be held to an absolute minimum if this morbidity is to be avoided.

Recently, Trenchard and Harris[4] have described an outbreak of winter respiratory illness which proved to be the result of exposure and sensitisation to toluene di*iso*cyanate.

At the same time, Jennings and Gower[5] reported on two specific cases of exposure to TDI. In the first patient, who had been subjected to an unusually heavy exposure of TDI, purpura developed. Both men were found to have thrombocytopenia. The authors suggested the possibility of an immunological mechanism for TDI induced thrombocytopenia but further work is required before this theory can be substantiated.

These studies carried out over the past ten years illustrate the hazards associated with *iso*cyanates.

Sensitisation occurs rapidly in many cases and subsequent exposure after sensitisation can lead to respiratory attacks of undue severity. Operatives who become sensitised should be barred from exposure to *iso*cyanates.

In the case reported by Jennings and Gower,[5] recovery was effected in both cases and no abnormality was recorded. Both cases were subsequently barred from exposure to *iso*cyanates.

The safety aspects to be discussed are those which the author's company have found to be most suitable for the work done in our plants or in our laboratories. They are based on our experience with *iso*cyanates and polyurethanes over a number of years and have proved to be most effective.

Storage and Supply

Toluene di*iso*cyanate monomer shows no tendency to polymerise or decompose in the pure state. Inhibitors are not necessary to maintain stability and this holds true for most common *iso*cyanates. The exception to this is pure methylene *bis* 4 phenyl *iso*cyanate for which the problem of storage (because of its tendency to dimerise at low temperature) is complex.

For processes where toluene di*iso*cyanate is a raw material, totally enclosed supply systems should be used. This is important because the escape of TDI vapours could lead to total evacuation of the working or storage areas.

In a urethane foam plant, it is desirable that the storage facilities for TDI should be constructed in such a way that complete isolation is achieved, and the only contact of TDI with the other reactive ingredients—the polyols, catalyst and

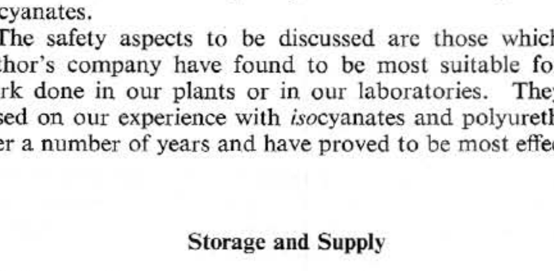

Fig. 1.—*Storage tank to machine and recirculating system*

water—should not take place until the reactants are all mixed in the mixing head. Pressurisation of TDI vessels should be carried out with dry air or nitrogen to avoid reaction with water vapour in the air which produces solid substituted ureas. These ureas can block feed lines, valves, filters, and pumps in the circuit and create undue hazard. Cleaning of equipment (after a blockage) can be costly, often necessitating complete replacement.

The filling of TDI storage tanks from bulk delivery vehicles should be engineered in such a way that again a completely closed circuit is formed between the storage tank and the delivery tank. Transfer is usually carried out by pumping, and the dry air in the storage tank should be displaced into the delivery tank, thus maintaining the exclusion of moisture throughout the system.

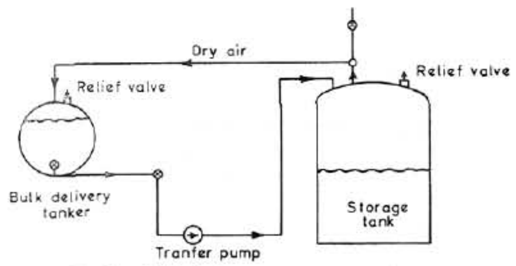

Fig. 2.—*Bulk delivery to storage tank system*

Treatment of Spillages

In the treatment of spillages of TDI, rapid and effective neutralisation can be achieved by the use of a mixture of *iso*propanol, water, and ammonia, either in the liquid form or absorbed in kieselguhr and sawdust. If the TDI is in the solidified state, and this is often the case when the ambient temperature is below 15°C, this type of neutraliser is less effective and reacts very slowly. When solid TDI requires neutralising, a 50/50 mixture of *iso*propanol-perchlorethylene gives a more effective result. It should be noted that perchlorethylene itself constitutes a hazard and suitable respiratory equipment should be worn.

Every effort should be made to localise spillage of TDI by the use of drip trays or barriers. A major leakage of TDI into sewers or drains would require the same sort of treatment as a minor spillage but on a massive scale.

Fire Hazard

Because of its high flash point, toluene di*iso*cyanate does not constitute a severe fire hazard. However, it is important that the proper fire-fighting equipment is available in case it should be needed. Water spray is effective for extinguishing fires covering large areas. Automatic sprinkler systems are useful in certain applications. Carbon dioxide or dry chemical extinguishers are also effective.

Personnel who are engaged in fighting toluene di*iso*cyanate fires must be protected against nitrogen dioxide fumes as well as toluene di*iso*cyanate vapours. Any fire fighter close enough to be in contact with these fumes should wear self-contained breathing apparatus. The usual fireman's body protection should be worn.

Materials of Construction

In general, plain steel equipment is satisfactory as a material of construction. Tanks may be lined with heat-cured phenolic coatings to prevent discoloration during storage. Stainless steel pipe lines and tanks are perfectly satisfactory but their cost is not warranted unless, as is the case for the production of clear urethane coatings, the absolute minimum of colour must be maintained. Where flexible pipe is used for transporting *iso*cyanates, it should be capable of withstanding pressures up to 200 lb/in^2 and be chemically resistant to attack. Armoured polytetrafluor ethylene (PTFE) tubing, and polyvinyl alcohol-lined hoses give the best service life for constant exposure to TDI, providing moisture is excluded.

Relief valves should be of the totally enclosed type which feed back to the main storage vessels and all lines and valves exposed to atmospheric temperatures should be lagged and steam chased to prevent freezing.

Provision should be made to make possible the addition or removal of *iso*cyanates without opening the equipment. Whenever it is found necessary to open it, adequate ventilation should be available to remove immediately any vapour that may be present.

Extraction and Ventilation in Urethane Facilities

Good ventilation is most important in all places where toluene di*iso*cyanate is handled. A hood-type ventilation unit should be situated over equipment where TDI vapours can reach the atmosphere. The volume of air being extracted should be such that the hood-face velocities are within acceptable limits. The Manufacturing Chemists Association in their Report[6] recommends 100 ft^3/min ft^2 of hood opening. The type of hood to be used will, of course, depend upon the particular application and the ventilation system should be designed by experienced engineers. The design principles which have generally been found suitable are as follows:

(1) The exhaust hood should be located as close as possible to the source of the escaping vapour.

(2) The process should be enclosed as much as possible.

(3) Baffles and side shields should be used whenever possible.

(4) The velocity of air at the point of vapour dispersal should be sufficiently high to capture the vapour particles. This is particularly important, because toluene di*iso*cyanate vapours are six times as heavy as air and tend to flow downward.

(5) Vapours should not be drawn past the operator's face.

(6) The hood should be positioned so that it does not interfere with the operator's work.

In some cases the process equipment in which leaks of TDI might possibly occur is too extensive to be enclosed by an exhaust hood. In such cases, mechanical ventilation of the entire room may be found necessary. A down-draught type of ventilation is then most desirable because of the heaviness of the TDI vapour.

The equipment installed at the author's research laboratory adheres closely to the design principles enumerated. It is our experience that commercial foam plants in operation, both here and abroad, also follow these principles closely.

A typical slabstock machine for commercial operation would probably be enclosed for the first 20–60 ft of its length, as this is the region of maximum vapour concentration when the plant is operating, and it is in this area where the maximum extraction should be maintained.

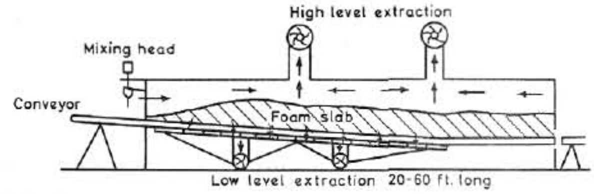

Fig. 3.—*Extraction system for urethane slabstock machine*

On the small conveyor unit which is in operation at the author's laboratory, both top and bottom extraction are employed. Of the total extraction employed, 70% operates at the low level of the conveyor on each side of the slab, and 30% is high-level extraction.

On the rigid moulding machine, the level of extraction is 60% at floor level, and 40% at high level. In spray-booth operations, the air is continually drawn from the front of the spray-booth towards the area of spraying, and a water curtain absorbs overspray.

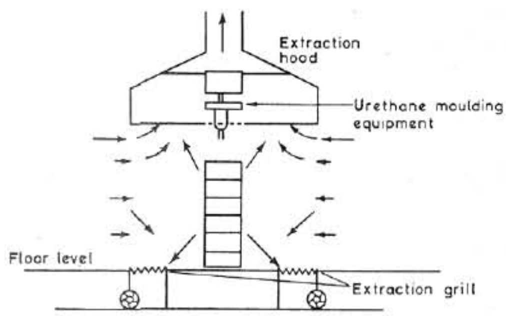

Fig. 4.—*Rigid urethane moulding extraction system*

The air in the whole working area of the laboratory is completely changed every seven minutes. The clean air is drawn in, heated and passed through grills in the ceiling of the laboratory. The extracted air from the slabstock machine, rigid foam machine or spray-booths, is collected in common trunkings, exhausted into the spray-booth where it is scrubbed by the water spray and exhausted to atmosphere. The water spray is passed through a filter-box which filters out the ureas formed.

The extraction installed is of sufficient capacity to allow all these operations to progress simultaneously without the level of TDI in the atmosphere reaching the threshold limit of 0·02 ppm. When operations are being carried out, regular checks are made on the TDI concentration in the atmosphere, using an Automatic Uni-Jet Analayzer developed by Du Pont de Nemours & Co. (Inc.), in the United States of America. This apparatus rapidly gives a reading of *iso*cyanate concentration in the atmosphere.

Employee Safety

Although a company may provide the best in the way of protective equipment and expend great effort to be sure that each process or operation is designed with safety in mind, an improperly trained or careless worker can create an undue hazard. To guard against this, employee training is probably the most important measure a company can take.

An effective employee training programme should include the following:

The operator should be thoroughly familiar with the process and its hazards, handling procedures, and the location and use of safety equipment.

One item of protective equipment which is obligatory in all the Du Pont laboratories is safety glasses or chemical safety goggles. They must be worn at all times.

Personal Protective Equipment

Personal protective equipment should not be regarded as a substitute for good, safe, working conditions, for adequate ventilation, or for intelligent conduct on the part of employees working with TDI. Certainly, in many instances, it is the only practical means of protecting the workers, particularly in emergency situations, but it is important to keep firmly in mind that personal protective equipment protects only the worker wearing it and other unprotected workers in the area may be exposed to danger.

Protective equipment is required to guard against respiratory attack in a foam plant. Severe exposure to TDI may occur in tanks during equipment repairs or when areas are being decontaminated following spills or in cases of the failure of piping or equipment. To cope with all these and, as a measure of protection in areas where exposure might otherwise occur, each worker should be assigned a gas mask or whatever type of respiratory protective device is authorised. When masks are not assigned on an individual basis, the equipment should be sterilised before use by another person.

Several types of respiratory equipment are available and the choice available in a factory depends on the facilities installed and the operations which may be carried out. Air or oxygen supplied masks, equipped with full face pieces, should be used in emergencies when the vapour concentration of the *iso*cyanate is over 2% by volume and when extended exposure to *iso*cyanate vapour is likely during equipment cleaning and repair work.

Air-line masks are used quite extensively in plants producing urethane elastomers where the operation involves hand-casting on hooded hotplates. They provide a positive air displacement across the face of the operative to supplement the hotplate extraction.

Industrial canister-type gas masks, fitted with the proper canister for absorbing *iso*cyanate vapours, afford protection against concentrations of TDI vapour not exceeding 2% by volume. These masks should be used for relatively short exposure periods only, *e.g.* connecting drums of *iso*cyanate to machine feed-lines, neutralising small spillages.

These canister-type masks incorporate a particulate filter which is of great importance in giving maximum protection against TDI and other *iso*cyanate vapours. The particulate filter, which is a merino wool/asbestos/activated charcoal combination filter, absorbs any *iso*cyanates which, as fine droplets, would pass through a standard filter unabsorbed.

Medical Management and First Aid

Personnel selected for work in areas where TDI is used should be subjected to a careful medical examination and should be re-examined periodically. Normally the physician carrying out the examination would exclude from these working areas people who had chronic diseases of the nose, throat, or lungs, and those with, or having a history of, asthma or asthmatic bronchitis.

Employees working with TDI should not develop any chronic condition so long as reasonable and generally acceptable measures of industrial hygiene are consistently enforced. But there is a small proportion of people who are allergic to TDI vapours and who may be affected by even minute exposure; the effect takes the form of an acute spasm of the bronchial tubes whenever the individual comes in contact with the vapour. There is no known remedy for this condition, and those who have it do not become accustomed to the vapour or lose their sensitivity to it. In all such cases, the individual should be removed from all further contact with the chemical.

These bronchial spasms, and also irritation of the lungs, should be given the standard medical treatment. In most cases of exposure, administration of 100% oxygen at atmospheric pressure has been found to be an adequate remedy. This is best accomplished by the use of a face mask fitted with a reservoir bag of the non-rebreathing type. Inhalation of

100% oxygen should not exceed one hour of continuous treatment but may be reinstituted as a clinical condition indicates.

Some schools of thought have it that superior results can be obtained when exposures to lung irritants are treated with oxygen under an exhalation pressure not exceeding 4 cm of water. It is also believed by some observers that oxygen under pressure is useful as an aid in the prevention of pulmonary oedema after breathing irritants.

It may not be advisable to administer it under positive pressure in the presence of impending or existing cardiovascular failure. Medical advice should be sought immediately.

In cases of skin or eye exposure to TDI, it is important to move the patient to a spot where he can receive medical attention. The chemical must be removed immediately, or severe injury will result. This should be done by the use of large amounts of water as quickly as possible after the accident has occurred.

If the skin has been exposed and contact has been extensive, the employee should immediately get under an emergency shower, if one is available, otherwise water flushing, together with soap and water washing, should be continued for at least five minutes. Subsequent medical treatment is the same as for thermal burns.

If the eyes have been exposed, they should be irrigated immediately with large amounts of water for a minimum of 15 minutes. The eyelid should be held apart during the irrigation to ensure contact of water with all of the tissues of the surface of the eyes and lids. After the first 15-minute period of irrigation, if the pain is still present, it is permissible as a first-aid measure to instil two or three drops of 0·5% pantocaine solution or an equally effective aqueous topical anaesthetic. The employee should then be sent to a physician, preferably an eye specialist, as rapidly as possible.

If a person has accidentally swallowed some TDI, the harm that occurs will be due to the corrosive action on the oesophagus and stomach rather than any systemic toxicity. The person should instantly drink large amounts of water in order to reduce the concentration of the chemical. It is important that this be done as rapidly as possible, rather than attempt to hunt for an antidote or a neutraliser which may not be available. Medical attention should be obtained immediately.

Conclusion

We have now considered all the more important aspects of safety in handling of *iso*cyanates. It should be emphasised, however, that what has been said is based on the experience of the Du Pont Company in its plant and laboratory activities. What has been found suitable in Du Pont's operating conditions may require modification in the operating conditions of a foam-producing unit. So these measures are suggested as a guide only and should be found of value.

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