FIRE SERVICES EXAMINATIONS BOARD

STUDY NOTE

EXAMINATION	STATION OFFICERS' EXAMINATION
PAPER	OPERATIONS
SUBJECT	FIREFIGHTING AND RESCUE INCIDENTS
ITEM	ISOCYANATES INVOLVED IN FIRE
STUDY NOTE No.	3103

INTRODUCTION TO THE STUDY NOTE

This study note has been prepared as the basis of study in connection with the qualifying examinations for promotion.

Candidates will be expected to demonstrate knowledge of the information contained in the study note and understand how it should be applied:

The 'References' made at the end of the Study Note are included for information only and candidates will not be expected to study these as part of the bibliography.

FIRES AND OTHER OCCURRENCES INVOLVING ISOCYANATES

1. Introduction

Special hazards present themselves to firefighters when attending incidents involving highly toxic substances.

Although there are many such substances, this Study Note is confined to isocyanates because they are quite widely used in manufacturing processes.

2. Properties

Isocyanates may be divided into 2 main classes:

(a) Those, which, at normal summer ambient temperatures, have a relatively high vapour pressure. They are used extensively for flexible urethane foams, and

(b) Those with a relatively low vapour pressure and are used for semi-rigid and rigid foams.

Isocyanates are used in certain adhesive processes, in certain specific varnishes and more widely as ingredients in the manufacture of synthetic rubbers, polyurethane foams, lacquers and solid products etc.

Semi-rigid foams are also used as packaging materials. They are generated "in situ" and require the use of diphenylmethane di-isocyanates (MDI) solution and polyol in portable equipment.

Most isocyanates are liquid, a few are solid and they are sold under a variety of trade names.

3. Common isocyanates

(a) Toluene di-isocyanates (TDI)

Toluene di-isocyanates are colourless to pale yellow liquids with a specific gravity of 1.22 at 25^{o}C (77^{o}F) but they may solidify if stored at temperature below 8^{o}C to 15^{o}C.

Vapour is readily given off at normal ambient temperatures and a comparatively small rise in temperature increases the volatility considerably.

(b) Diphenylmethane di-isocyanates (MDI)

These isocyanates are generally in liquid form. They are of low volatility at ambient temperatures. Compositions based on MDI have been developed for use with in situ foam production. The volatility of MDI increases of course with increased temperature.

(c) Other di-isocyanates also used industrially are:

(i) Naphthalene di-isocyanate (NDI) and

(ii) Hexamethylene di-isocyanate (HDI).

(iii) MDI, NDI and HDI may also be found in crystalline or dust forms.

By virtue of the elevated temperatures in a fire, MDI, NDI and HDI may be as volatile as TDI.

4. Hazards

The hazards to firefighters from isocyanates arise from the toxic vapours given off in their raw state, particularly when they are involved in fire.

It is important therefore that brigades maintain an up-to-date list of premises where these substances are stored and where they are used in manufacturing processes.

Special problems can also arise at disposal dump fires if containers of isocyanates are involved.

Isocyanates will react with water with the evolution of carbon dioxide and the formation of solid polymers. This however is a very slow process, since isocyanates are not soluble in water and reaction takes place at the interface only. Complete reaction would be measured in days rather than hours.

They are not particularly flammable (TDI Flash Point 132^{o}C (270^{o}F)) but all will burn if involved in fire giving rise to irritating vapours.

5. Medical Considerations

Isocyanate vapours are not absorbed through the skin, but even at quite low concentrations they may cause irritation of the eyes, nose and throat and cause difficulty in breathing. They have a pungent odour, but are detectable by sense of smell only at much higher concentrations than those which affect the eyes, nose and throat. Symptoms caused by exposure to vapours may be immediate or may be delayed for several hours.

Much concern is frequently expressed about the dangers of isocyanates by virtue of their low Threshold Limit Value (TLV) of 0.02 parts per million. This very low TLV has been found necessary only because of their sensitising properties for those whose work brings them into daily contact.

Liquid isocyanates on the skin cause severe irritation and must be removed immediately by rinsing with copious supplies of water, followed by thorough washing with soap and water.

Solid isocyanates, if they are in the form of fine dust particles, create a risk similar to vapours if inhaled.

Medical aid should be sought immediately in all cases of personnel being contaminated with liquid isocyanate or even suspected of having been exposed to isocyanate vapour or dust.

6. Protective Measures

(a) Breathing Apparatus

The toxicity of isocyanates is such, that the use of positive pressure compressed air breathing apparatus, or airline equipment providing positive pressure, is essential

It must be borne in mind that firefighters in the open air may be exposed to fumes, all personnel therefore, engaged in firefighting operations should wear breathing apparatus unless they are well upwind.

(b) Protective Clothing

All personnel engaged in firefighting operations or in dealing with spillage's, who may be exposed to liquid isocyanates, must wear impervious protective clothing such as a Chemical Protection Suit.

Protective clothing splashed with liquid isocyanate during the course of fire fighting operations must be thoroughly washed down before being removed and be decontaminated immediately after use. Isocyanates tend to harden both rubber and PVC and increase the risk of splitting. Gloves and any protective clothing should of course not be used if they have hardened to the extent where they become clumsy or dangerous.

Should firefighting uniforms be accidentally contaminated they also must be thoroughly washed down before removal and not be worn again until they have been decontaminated and cleaned. Personnel concerned should wash thoroughly with soap and water and rinse off under a shower.

Wearers must keep on their breathing apparatus as long as practicable while their clothing is being washed down and removed so as to avoid inhaling fumes. This is particularly important with contaminated uniform as fumes in quite high concentrations may arise from the liquid trapped in the weave of tunics.

7. Operational Procedures

Firefighting

If the fire does not involve the isocyanates but is simply close to it, an extinguishing agent appropriate to the type of fire should be used.

If isocyanates are on fire, a small fire may be dealt with by using a dry powder, CO_2, BCF or foam extinguisher. The remains of the fire should then be covered with wet soil or sand. In the case of large fires copious quantities of water should be applied, preferably in the form of a spray.

Care must be taken with drums of isocyanates, which have been heated because the high rate of expansion may result in an increase in pressure which could represent a serious hazard. In such circumstances drums must be cooled.

Leakage or Spillage

In case of leakage or spillage of isocyanates without fire, no one should approach the area without full protection. If the incident occurs in the road or public place, members of the public should be kept well away from the area and to windward if possible. To prevent further leakage and more vapour being given off, drums can often be turned so that the hole is uppermost and plugged. Plugging should not be carried out if moisture has entered the drum since isocyanates react with water with the evolution of carbon dioxide; protective clothing should be worn.

Liquid isocyanates react with water to form solid polymers but this process of neutralisation takes a long time.

Washing away large spillages of isocyanates with large volumes of water, whilst reducing the immediate solution in the original area, tends to disperse the risk over a much wider area, ie through drains and sewers etc. This procedure should be avoided as the solids that result might block the drains.

Consideration should be given to containing large spillages by damming and to neutralising them by the use of wetting agents (detergents) and catalysts if available (eg soda-ash, ammonia) thus increasing the interfacial contact and speeding up chemical neutralisation.

Wetting agents are substances such as detergents which increase the wetting power of water.

Alternatively the spillage may be covered by a suitable absorbent material such as soil, sand, sawdust or vermiculite, which may then be shoveled into containers for collection and disposal.

Decontaminants

Special liquid or solid decontaminants to render the isocyanates safe may be available where the chemical is stored or used. They may also be carried on some road tankers and with drum loads, but quantities are likely to be sufficient to deal only with small spillages. These materials would be provided by the suppliers of the isocyanates and should be used as advised by a representative of the company concerned.

Small spillages can be wiped away with cotton waste and the area treated with liquid decontaminant. The cotton waste must not be left lying around, but must be decontaminated and destroyed immediately.

Personnel involved in decontamination should be provided with full protection.

References

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