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Review Paper

Methods of Decontamination of Toluene Di-Isocyanate (TDI) spills and leftovers

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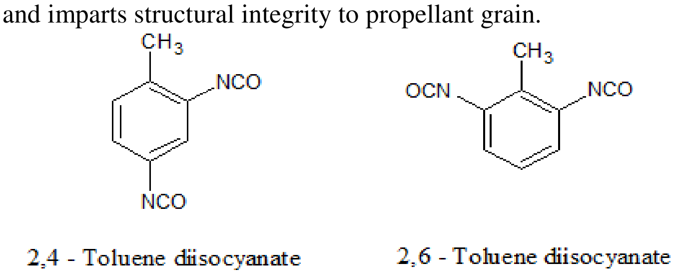
Abstract

TDI (Toluene Di-Isocyanate) is widely used in the production of polyurethanes and it is to be handled carefully due to its toxic effects on the human health and environment. TDI spills and leftovers are to be treated with extreme care in order to avoid human exposure to the toxic gases and wastes. It is necessary to neutralize or convert the reactive isocyanate groups of the spills or leftover of TDI into harmless compounds. This report elaborately describes the effects of TDI on human health and also the reactions of TDI with important functional groups and chemicals like amines, alcohols and water. This report also brings out the neutralization methods available for treatment of the minor spills and leftover of TDI.

Keywords: Toluene diisocyanate, TDI, isocyanate, polyurethane, solid propellant, neutralization, disposal.

Introduction

Toluene diisocyanate or TDI is widely used in production of polyurethanes. Polyurethanes are produced by the condensation / addition reaction of an isocyanate and a material with hydroxyl functionality, such as a polyol. The polyurethanes have found wide applications as solid elastomers, flexible foaming materials etc. Mostly used commercial grade TDI is a mixture of 2,4–toluene diisocyante and 2,6–toluene diisocyanate isomers in 80:20 ratio respectively[1]. TDI is used in rocket propellant formulation along with polyol to form polyurethane which binds and imparts structural integrity to propellant grain.



Scheme–1
Structure of Toluene diisocyanate

The handling of TDI is an hazardous job and must be done with experience in hands. The following sectinons deal with the effects of TDI on the health and decontamination of TDI spills and leftovers at work place.

Effect of TDI exposure on health of personnel

TDI is less volatile and gives off less vapours at ambient temperature. But, TDI reacts rapidly with water, ammonia, alcohols and amines and the reactions are exothermic. During these reactions, it will result in higher amount of vapours.

TDI exposure causes irritation and damage to skin, mucous membrane and eyes. TDI contact with skin may shows symptoms of rashes, itching and swelling of contact area. The most reported adverse effect of TDI exposure is sensitization, which may cause asthma. Acute exposure may also cause sensitization. The symptoms of asthma sensitization include breathlessness, coughing, wheezing and nocturnal awakening[1,2]. For some people, the exposure may lead to death.

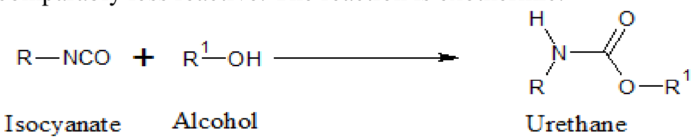
The Occupational Safety and Health Act (OSHA) Permissible Exposure Limit (PEL) of TDI is 0.005 ppm. This OSHA PEL is for 8 – hours averaged permissible exposure[3]. For the short term exposure the limit is 0.02 ppm, while the odor threshold i.e., the minimum amount required to sense the odor of TDI is 2 ppm only.

Hence, sufficient care must be taken while handling TDI to prevent adverse health effects. The personnel should wear impervious clothing, gloves, goggles and suitable respiratory devices. Further the handling of TDI must be done in moisture free, dry atmosphere. In order to understand the possible decontamination techniques for TDI, it is essential to have a knowledge of chemical reactivity of isocyanates towards various reagents.

Some important Chemical Reactions of isocyanates

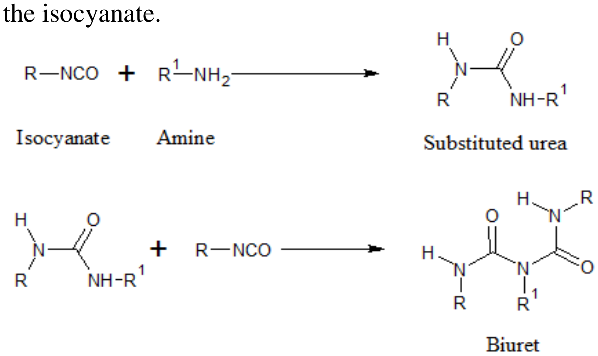
As mentioned earlier isocyanate reacts vigorously with water, ammonia, alcohols and amines. The different reactions of isocyanate with alcohols, amines and water are discussed here. The presence of active hydrogen on a molecule makes it reactive towards isocyanates.

Reaction of Isocyanate with Alcohols: The reaction of primary alcohols with isocyanates is vigorous with the formation of urethanes[4,5]. The reactivity of secondary alcohols towards isocyanates is less than primary alcohols, but urethanes formation is noticed in that case also. Tertiary alcohols are comparably less reactive. The reaction is exothermic.



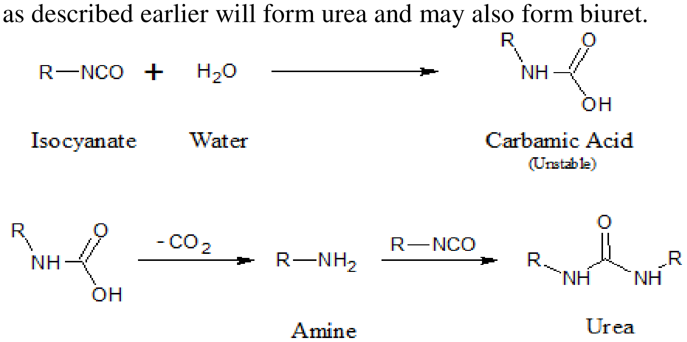
Scheme–2
Reaction of isocyanate with alcohol to yield urethane

Reaction of Isocyanate with Amines: Primary and secondary amines react readily with isocyanate resulting in ureas and its derivatives[4,5]. The vigorous reaction of primary aliphatic amines with isocyanates is attributed to their strong nucleophilic and autocatalytic nature of primary aliphatic amines. In some cases the second active hydrogen of primary amines may react with another molecule of isocyanate forming a structure called biuret of the isocyanate.



Scheme–3
Reaction of primary amines with isocyanates giving urea and biuret

Reaction of Isocyanate with Water: Isocyanates form urea rapidly upon reaction with water. The reaction of isocyanates with water is reported to be a complex one, involving an unstable intermediate. The unstable intermediate decomposes into amine with the evolution of carbon dioxide[4,5]. The amine, as described earlier will form urea and may also form biuret.

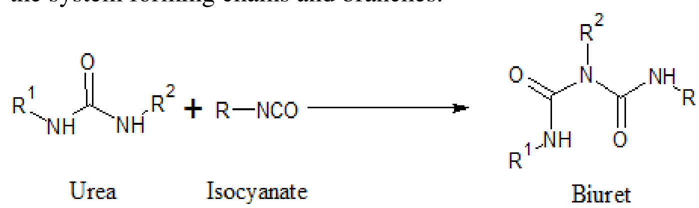


Scheme–4
Reaction of isocyanate with water resulting in unstable carbamic acid, amine and urea with evolution of carbon dioxide

Considering the reaction up to the formation of Biuret, a water molecule consumes 3 molecules of isocyante with the evolution of carbon dioxide. This reaction may also result in the formation of chains and branches. Thus, even a small amount of water or moisture in isocyanate shows the drastic effects and this aspect is to be taken into account while dealing with isocyanates.

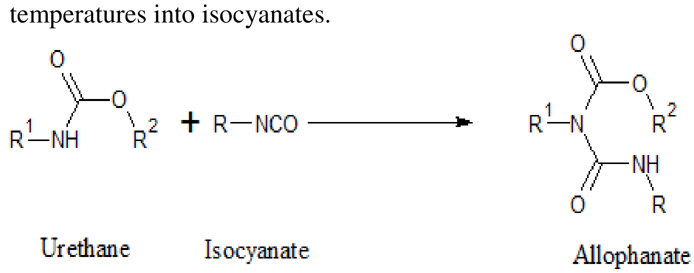
Summarizing, the reaction of isocyanate with water gives water insoluble polyureas and carbon dioxide. The reaction rate of TDI with water at temperatures less than 50^0C is very low. As the temperature increases the reaction becomes more vigorous, but the vapours increases. Addition of base to water increase the rate of reaction with TDI, since the base abstracts the proton forming hydroxyl.

Reaction of Isocyanate with Urea: Urea may form from the reaction of isocyanate with amines. The presence of active hydrogen on the urea makes it further reactive towards isocyanate. The reaction of isocyanate to urea forms biuret[4]. The reaction may further proceed utilizing other active hydrogens in the system forming chains and branches.



Scheme–5
Reaction of isocyanate with urea forming biuret

Reaction of Isocyanate with Urethane: Urethane also contains active hydrogen like urea and hence reactive towards isocyanate. Urethanes may form from the reaction of isocyanate with alcohols. The reaction of isocyanate with urethane results in allophanate[4]. The allophanate dissociates at higher temperatures into isocyanates.



Scheme–6
Reaction of isocyanate with urethane forming Allophanate

Neutralization of TDI

As explained earlier the TDI spills and left overs are potentially hazardous. The disposal of them as such may result in drastic effects to human beings and environment. Hence there is a need to dispose them only after neutralizing the isocyanate groups using suitable methods. Neutralization of isocyanate indicates that treating isocyanate group using a suitable method so as to convert all the isocyanate into harmless compounds like urea, urethane for disposal. The following sections describe various methods in practice for the neutralization of TDI.

The neutralization of TDI can be done using chemicals and also using natural products. Those methods which are reported are discussed in the following sections.

Chemical Methods of TDI neutralization

As mentioned earlier, there are various reactions in which isocyanate can react and form harmless compounds. A solution used for the neutralization of TDI is called TDI neutralization solution and it should be made available during the handling operations of TDI.

Neutralization using water: TDI can be neutralized using water, which react with isocyanates to form urea. These ureas can be safely disposed without any problem. But this reaction is exothermic and very slow at temperatures less than 50^0C[6]. It is advisable not to increase the temperature for neutralization, because it may result in voltalization of TDI and causes further problem.Also, reversible formation of TDI from the unstable intermediates in the neutralization reaction with water observed. Hence, TDI neutralization using water, basic medium is suggested to ensure an effective neutralization to occur.

Neutralization using water and ammonia: As discussed above, TDI neutralization using water is slow and hence usually ammonia is added to enhance its efficiency. The availability of hydroxyl ion will enhance neutralization reaction. The reaction rates of TDI with hydroxyl and water are given in table 1[1].

3 – 8% ammonia aqueous solution is generally used for the neutralization. Also, ammonia neutralizes the vapours of TDI effectively.

Table-1
TDI reaction rates with water and hydroxyl

Isomer	Rate constant x 10^4 (litre/mol.sec)		Activation Energy (kJ/mol)	
	Hydroxyl	Water	Hydroxyl	Water
2, 4 TDI	21.0	5.8	33.0	41.8
2, 6 TDI	7.4	4.2	41.8	50.2

Neutralization using water, ammonia and surfactant: Since water is immiscible with TDI, the aqueous solution of ammonia is added with surfactants. The addition of surfactants generally facilitate the reaction to a higher extent and hence increases the neutralization.

European Diisocyanate and Polyol Producers Association suggest the composition of TDI neutralization solution[6,7] given in the table 2.

Table-2
TDI neutralization solution (Water , Ammonia & Detergent)

Liquid Detergent	0.2 – 2 % (w/w)
Conc. Ammonia	3 – 8 % (w/w)
Water	To make 100 %

Neutralization using water, ammonia and alcohols: Alcohols react with TDI to give urethane in an exothermic reaction. The use of a base helps in abstraction of proton, hence prononunced effect in neutralization of TDI. Also, the alcohol is volatile compared to the water and hence can neutralize the vapours of TDI. But the content of the alcohol in neutralizing solution should be kept low, since it is highly flammable and increases the risk of catching fire.

Different alcohols are used in TDI neutralization solution along with ammonia and water. Some people employ surfactants to increase the miscibility. Methanol also reacts with isocyanate to form urethanes, but it is not preferred in the neutralization solution, since inhalation of methanol vapours can irritate mucous membranes, cause headache, sleeplessness, nausea, loss of consciousness, loss of eye sight and may be fatal too. In addition, reactivity of methanol towards neutralization of TDI is less[8].

Das Bakul, Ramana Reddy *et al*, prepared neutralization solution using rectified spirit (95% ethanol), ammonia, water and surfactant in different ratios and investigated the optimum composition of neutralization solution necessary for neutralizing approxmately 6.1 g of TDI in a 500ml container in 24 hours using FTIR spectroscopy. They found out that a neutralizing solution with 65% water, 25% rectified spirit, 5% dilute ammonia and 5% soap solution is optimum to neutralize the isocyanate groups in 24 hours[5]. They also made TDI neutralization solution using isopropyl alcohol, ammonia, surfactant and water in different ratios and measured the amount of isocyanate groups left after 24 hours when added to 500ml container containing approximately 6.1 g of TDI. The neutralization solution made of 70% water, 20% isopropyl alcohol, 5% dilute ammonia and 5% soap solution is found to neutralize the given TDI in 24 hours[5].

The IATSE Local 891 manual and Workers' Compensation Board of British Columbia suggests the usage of a neutralization solution made of 10% isopropyl alcohol, 1% ammonia and 89% water for decontamination of TDI spills and contaminated clothings[9,10]. They advise the use of dilute rubbing alcohol (isopropyl alcohol) for treating contaminated parts of body[9]. Hepburn suggested solution of 45% water, 50% of methylated spirits or isopropyl alcohol and 5% conc. ammonia for neutralizing isocyanates[1].

Commercially available Isocyanate Decontamination solution (Colormetric Laboratories Inc.,) is made up of approximately 10% 2–butoxy ethanol, 1% ammonia and water.

The Perstrop TDI plant in Pont de Claix, France suggest the use of neutralization solution made of 75% water, 20% soap solution and 5% n – propanol[11].

Neutralization using sodium carbonate and water: In the TDI neutralization solutions given in table 3, ammonia is used since base enhance reaction of water with TDI at ambient temperatures. In some cases sodium carbonate is used instead of ammonia in the neutralization solution.

Another study used water, 5% and 10% sodium carbonate solution for neutralization of approximately 6.1 g of TDI in 500 ml container. The left over isocyanate after 72 hours is 14.6%, 5.7% and 3.2% respectively[12]. Hepburn reported the use of 5% sodium carbonate solution for treating isocyanate disposal before draining them[1].

In addition European Diisocyanate and Polyol Producers Association (ISOPA) and The Dow Chemical Company prescribes neutralization solution made of 5-10% of sodium carbonate, 0.2-2% soap solution and water[6,7]. This method is preferrable for treatment of leftovers since, the neutralization solution is not flammable.

Neutralization using Saw dust and Fullers' earth: The isocyanates are also reported to be neutralized using solids. A solid mixture of 60% saw dust and 40% Fullers' Earth – China clay can be used to neutralize the TDI spills. Fullers' Earth absorbs the TDI and also reduce its flammability. Saw dust which is source of moisture, carboxylic acid and lignin reacts with isocyanate to form ureas and urethanes. The FTIR spectrum of extract from the TDI mixed with 60% saw dust and 40% Fullers' earth gave less or no evidence of isocyanate after 96 hours[13].

Further, another multi component solid mixture consisting of 23% of saw dust, 38.5% of Fullers' earth, 19.2% of ethanol, 3.8% of triethanolamine, 3.8% of conc. ammonia solution, 11.5% of water and 0.2% water soluble dye was also reported for use of neutralization of isocyanates. The ethanol acts as solvent and triethanolamine acts as catalyst[1].

Decontamination of TDI Spills and left overs

During the handling of TDI, the spills and leftovers are common to occur. The spills and left overs must be properly neutralized and disposed immediately. As described in the earlier sections, suitable neutralization solution can be prepared and used. For the spills the neutralization solution must be sprayed and then covered with suitable absorbants like sand, saw dust. This absorbant must be collected carefully and disposed in identified disposal area[14].

For the left overs in containers, they should be added with sufficient quantity of neutralization solution and left for one or more days uncovered to let the carbondioxide escape. The residual material must be collected later and disposed in identified disposal area.

Conclusion

Since TDI is harmful, it must be handled with utmost care. The OSHA PEL of TDI is 0.005 ppm and the short-term exposure limit is 0.02ppm, whereas the odor threshold i.e., the minimum amount required to sense the odor of TDI is 2 ppm. Hence, to prevent from adverse effects of TDI, extreme care must be exercised while handling and processing. The spills and leaks must not be left unattended because they are potentially hazardous. They should be treated properly and disposed without causing any trouble to personnel and environment. The reactive isocyante groups are to be converted into harmless compounds like urea, urethane etc., by employing the neutralization solution.

Water can be used as neutralizing agent, but its reactivity at ambient temperatures less than $50^{O}C$ is not appreciable for neutralization. Addition of ammonia helps in abstraction of proton and hence enhances the reaction. The problem of immiscibility of water with TDI can be overcome using surfactants. The inclusion of alcohol into water and ammonia mixture, further enhances the amount of neutralization, due to increased hydroxyl concentration. Also, alcohol being volatile helps in preventing the TDI vapour exposure.

Table-3
TDI neutralisation solution (Alcohol, Ammonia, Water & Surfactant)

No.	Alcohol				Ammonia	Water	Surfactant	Ref
	Ethanol	IPA	n-propanol	2-butoxy ethanol				
1	25	-	-	-	5	65	5	5
2	-	10	-	-	1	89	-	8,9
3	-	20	-	-	5	70	5	5
4	-	-	-	10	1	89	-	-
5	-	-	5	-	-	75	20	10
6	0/50	50/0	-	-	5	45	-	1

[#] all numbers are percentage.

The neutralizing solution made from water 70-75%, surfactant 5%, ammonia 5% and alcohol 20-25% took 24 hours for complete neutralization of 6.1g of TDI, whereas the aqueous sodium carbonate 0-10% solution took 72 hours for maximum neutralisation of same quantity of TDI. The saw dust and fullers' clay method, took 96 hours for neutralization of TDI spill. From the study of these reports, it can be assumed that neutralizing solution composed of aqueous solution of 20-25% of alcohol with small amount of ammonia and surfactants, possess advantage of faster decontaimination. The similar composition solution is being used at SHAR centre for neutarlisation of TDI spills while processing the Solid Rocket Motor. The neutralization solution made of aqueous solution of sodium carbonate is preferred for treatment of leftovers, since absence of alcohol eliminate the chances of flamability. The saw dust and fullers' clay method, even though a slow one, it is a greener method utilizing natural products rather than chemicals. However, the neutralization solution must be chosen in view of availability of reagents, nature and size of spill and work place atmosphere. The neutralization solution must be kept handy, at the places where TDI is handled or stored.

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