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Burning Behaviour Characteristics of Toluene Diisocyanate (TDI) in Flexible Polyurethane Foam Fire Environment

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Abstract

This paper describes the burning behaviour pattern of commercially important toluene diisocyanate (TDI) stored in cylindrical stainless steel containers and exposed to fire of flexible polyurethane foam stack. The behaviour of TDI in containers was examined through ad hoc laboratory fire tests in which the containers filled partially with TDI were placed in the sand bath heated to attain temperature of 200°C and 300°C separately and also when exposed to fire of flexible polyurethane foam stack placed by the side of TDI containers. First two experiments indicate the need of energy input and temperature range for auto-ignition and subsequent mass loss of TDI in the containers. The last three experiments describe the effect of foam stack fire on TDI filled in containers for their vaporisation, burning, distortion rupturing and bursting conditions of containers. After ignition TDI starts burning in a steady manner rather than vigorous manner without leaving any residue in the containers. It was found that the behaviour of TDI in containers when exposed to fire is governed mainly by the rupture (blowing off lid) characteristics of containers as a result of pressure rise of TDI within the containers. The paper also recommends good storage practices for safe storage of TDI in containers.

Key-words

Toluene diisocyanate, isocyanate, isocyanurate, allophanate, burning behaviour, oligomerisation, flexible polyurethane foam, auto-ignition, fire resistant

Introduction

The first isocyanate was synthesized by Wurtz in 1848. However, the commercial importance of isocyanate was recognized only after 1945. About 2 million tons of toluene diisocyanate is used per annum worldwide as the amount has grown steadily to this level in last 40 years. TDI is the principal raw material for various polyurethane products and therefore modern polyurethane industry is heavily based on it. Being a non-flammable material at ambient temperature, a little attention has so far been paid about the fire hazards In the TDI storage area when stored in the close vicinity of polyurethane foam stack or other flammable materials which could be ignited easily either accidentally or could be by arson. Although some work has been reported about the burning behaviour of TDI in fire conditions [1], however not sufficient literature is available if large quantities of TDI in containers are surrounded in polyurethane foam fire. TDI is supplied in the tank cars to the end users where it is stored in drums. The storage of TDI drums should be away from the foaming, foam curing and storage areas however in practice it is not so. In many foam manufacturing industries, the TDI drums are stored either in the foaming, foam curing and storage areas or adjacent to these areas. Such type of storage of TDI drums storage poses high fire hazards when TDI is involved in the polyurethane foam stack fire. The major fire losses pertaining to polyurethane foam industries in northern part of India only were about 23 million $ in the year 1998-2001 [2]. TDI is highly toxic liquid (tolerance 0.005 ppm in air) because it is a reaction product of phosgene gas and aromatic amine precursors. Thus in general good practices are already available for safe handling and storage of TDI due to its physiological properties [3-5], but not due to fire exposure conditions. Therefore sufficient work is still required to be done so that its fire hazard potential is also taken care of in its storage and use.

Basic TDI Chemistry and Properties

TDI is derivative of isocyanic acid in which aryl group is directly linked to the N=C=O group via nitrogen atom. Structurally industrial TDI consists of a mixture of 2, 4 and 2, 6 isomers in the ratio of 80:20 respectively (Scheme 1). Commercial TDI is pale yellow liquid having pungent odour of bitter almond. Some of its important physical characteristics are given in Table 1. TDI

Functionality is highly reactive towards proton bearing nucleophiles. This reaction occurs by nucleophilic addition across the carbon nitrogen double bond. The basis for the high reactivity of TDI is the low electron density of the central carbon atom as indicated by the resonance structure in Scheme 2. The presence of electron withdrawing substituents on the aromatic ring of TDI also tends to increase its reactivity.

TDI generally undergoes two types of chemical reactions i.e. addition and oligomerisation (self-addition) reactions. TDI addition reaction normally proceeds by addition to the carbon nitrogen double bond. The hydrogen atom of compound containing replaceable active hydrogen becomes attached to the isocyanate nitrogen, and reminder of the group becomes covalently attached to the carbonyl carbon. The self-addition reactions do not involve active hydrogen but usually involve breaking the susceptible carbon nitrogen bond. These reactions are catalysed by acids and bases of both Bronsted and Lewis character. Some of these reactions are highly exothermic particularly the TDI and water reaction. Some of the chemical reactions [6] of industrially important TDI are shown in Scheme 3-10. When TDI is heated above 250°C rapid thermal decomposition occurs. During TDI heating, vapours evolved are ignited and the decomposition products consist mainly carbon monoxide, water vapours, carbon dioxide and small amount of hydrogen cyanide and nitrogen oxides. The range and extent of thermal decomposition of the resulting products depend upon temperature attained and available humidity [7].

Experiments

A series of ad hoc fire tests were devised and carried out at the Laboratory for assessing the effect of heat exposure by burning flexible PU foam adjacent to commercial grade TDI (80/20) stored in cylindrical stainless steel containers by adopting different fire scenarios. The different fire scenarios were (i) exposing the TDI filled cylindrical container kept partially in sand bath which was heated for limited duration to attain the sand temperature at 200°C, (ii) by keeping the same placement conditions and Increasing the duration of heating to achieve higher temperature 300°C and (iii) by placing the Cylindrical stainless steel containers partially filled with TDI in the close proximity of flexible polyurethane foam stack which was ignited from the side opposite and away of the containers. Under this set of experiments the different combinations such as the quantity of TDI, number of cylindrical stainless steel containers, quantity of flexible polyurethane foam stack and sealing (tightness of lids) conditions of the containers were studied.

The experiments resulted in getting information on fire hazard from TDI in containers by studying different variables like temperature attained, mass loss, condition of lids of TDI filled containers, residue left, smoke generation, failure and bursting of TDI cylindrical containers lids as a result of their exposure to flexible polyurethane foam stack fire.

Experiment Set-I

This experiment set was designed to observe the behaviour of TDI (80/20) filled container when placed in sand bath medium which was heated by indirect heat source up to 200°C. The experiments were conducted using 65-ml capacity cylindrical stainless steel container filled with 50-ml TDI (80/20) liquid. Sand bath was the medium used for indirect heating of TDI container which was placed in the sand bath up to its half height i.e. 25mm. One thermocouple connected to the digital temperature indicator was placed on the surface of the sand bath to measure its temperature during heating. LPG burner of 10-mm diameter was used as heat source for sand bath. The temperature of the sand bath was noted and recorded continuously. After heating the sand bath up to 200°C, the heating source was removed and the TDI (80/20) in the container was allowed to cool at the ambient conditions to attain room temperature. The weight of the TDI (80/20) in container was measured after cooling it at ambient temperature to determine the mass loss of TDI (80/20) during heating.

Experiment Set-II

In this experiment the temperature of the sand bath was increased from 200°C to 300°C by using the same heat source. The container was placed in the sand bath in such a way so that its two third height covered in the sand for observing the behaviour of TDI (80/20) in the container. Stainless steel cylindrical container of 65-ml capacity was filled with 50-ml TDI (80/20) liquid. Two thermocouples

Were mounted one on the outer surface of TDI (80/20) container and the other on the sand bath to measure the temperature of the TDI filled container and the sand bath respectively. The sand bath was heated by exposing it to 10-mm diameter LPG burner. The temperatures of the sand bath and container were measured continuously. During heating, observations were made for evolution of TDI vapours, flame and smoke etc. After heating the sand bath up to 300°C, and inturn the TDI (80/20) filled container to a temperature of 270°C, LPG burner was removed and the TDI (80/20) container was allowed to cool to room temperature. Finally the observations were made for TDI (80/20) residue left in the container as in the experiment set-I.

Experiment Set-III

The experiment set consists of five TDI (80/20) cylindrical containers each filled with 50 ml TDI (80/20) placed by the side of the flexible polyurethane foam stack of 450mmx450mmx200mm size and 40kg/m^3 density. The total weight of flexible polyurethane foam stack used as the heat source was 1620-gm. The PU foam stack was placed adjacent to five numbers of TDI (80/20) filled (50ml each) containers to simulate the conditions if TDI containers stored near the flexible foam stack and fire takes place accidentally in foam stack. The lids of the containers were loosely held. The placement and positions of TDI containers and flexible polyurethane foam stack are illustrated in Figure 1. The fire was initiated from one side of the flexible foam. The PU foam stack was easily ignitable and the flame spread was very fast along its surface. Subsequently TDI vapours were found evolving from the containers at 7 minutes. After 8 minutes of ignition, the whole area including TDI (80/20) filled containers were engulfed in fire. Immediately the vapours from TDI (80/20) containers caught fire and were observed to be burning with smoky flame. The water was sprayed after 10 minutes on fire of the TDI (80/20) containers. There was an instantaneous reaction of water with minor quantity of remaining TDI (80/20). After 12 minutes of initiation of fire the whole PU foam and TDI (80/20) liquid were consumed in fire.

Experiment Set-IV

These experiments were planned and carried out on the similar pattern as of experiment setIII. The only difference is that the TDI filled container lids were made airtight and exposed to 2430 gm. polyurethane foam against 1620 gm stack fire. After 9 minutes of initiation of fire, the whole area including TDI (80/20) filled cylindrical containers were in the grip of fire. TDI (80/20) liquid started generating vapours resulting in leakage from lid and burning around the container-rim. Subsequently, when the fire exposure was continued few lids of the containers blown off into the air. Immediately TDI (80/20) containers caught fire and started burning with partially smoky flame. The remaining lids of the containers were also blown off. The water was sprayed on TDI containers after 12 minutes of initiation of fire. There was an instantaneous reaction of water with TDI liberating gasses. After 14 minutes of fire the whole PU foam and TDI (80/20) liquid were consumed in fire.

Experiment Set-V

After carrying out III and IV sets of experiments, wherein it was established that TDI (80/20) liquid in cylindrical containers when exposed to fire of flexible polyurethane foam, evaporates and generates vapours resulting in pressure build up within the containers, causing opening the lids and burning of TDI (80/20). The experimental set V was planned keeping in mind the blown off of lids of the closed cylindrical containers resulting in burning of released TDI content at high temperatures which was attained due to burning of flexible polyurethane foam stack by addition of more vapours of TDI (80/20). This set-up consists of twelve TDI (80/20) containers with TDI (80/20) contents of 50 ml each and the flexible polyurethane foam stack of 450mmx450mmx500mm of 40 kg/m^3 density with total mass of 4050 gm as shown in Figure 2. The flexible polyurethane foam stack was placed adjacent to twelve numbers of TDI (80/20) filled (50ml each) containers to simulate the actual fire incidence. Two thermocouples were mounted on the outer surface of the two TDI (80/20) cylindrical containers one in the first row adjacent to flexible polyurethane foam stack while other in the farthest fourth row. The containers were placed in four rows to determine the effect of fire on TDI filled containers placed at different distances. Thus, One thermocouple was mounted on the outer surface of the TDI (80/20) filled container placed close to flexible polyurethane foam stack while other on the outer surface of TDI filled container placed in the fourth row to measure the temperature difference across the first and fourth rows. The lids of the containers were specially made airtight. The fire was initiated from one side of the flexible foam stack. The PU foam stack was easily ignitable and the flame started spreading very fast along its surface. After 14 minutes of fire, the whole area including TDI (80/20) containers was in the grip of fire. TDI (80/20) liquid started evolving vapours due to which pressure was built up inside the TDI (80/20) containers resulting lids to fly into the air. Immediately TDI (80/20) in containers caught fire and started burning with partially smoky flame. After 24 minutes of fire, the whole PU foam and TDI (80/20) liquid were consumed in fire. The TDI in containers burning and blowing off of TDI containers lid are shown in Figure 3.

Results & Discussion

The fire experiments conducted on flexible polyurethane foam stack along with TDI filled containers generated the considerable amount of data which are useful to understand the behaviour of TDI in different fire scenarios. The indirect heating of TDI up to 200°C (below the temperature of its boiling point) shows no mass loss after cooling. When TDI was heated to the temperature in the range of its boiling point (251°C), small amount of vapours started coming out through the edges of the lid. These vapours got ignited and burnt with self-sustaining combustion in a steady manner when temperature reached in the range of auto ignition temperature (270°C) of TDI. The flame was self-extinguished after TDI liquid was consumed completely and no residue was left in the container.

Ignition and burning of flexible polyurethane foam was carried out separately. It was found that flexible polyurethane foam is easily ignitable, highly flammable and flame spread is very fast along its surface in all the directions. During burning flexible polyurethane foam melted and spread on the floor with flame.

During experiment-III TDI (80/20) filled containers with loose lids were kept by the side of flexible polyurethane foam stack and ignition was initiated On one side of the foam stack. It was found that the TDI (80/20) filled container's temperature increased which was due to the combined effect of heat transfer by radiation, direct flame-contact and hot convective currents of flame gases along with the spread of molten and burning PU foam. When temperature reached in the range of boiling point and auto-ignition temperature of the TDI, vapours coming out from the containers caught fire.

For the experiments carried out under IV the lids of TDI containers were made air tight and exposed to the foam stack fire. It was found that after 9 minutes of initiation of fire whole area including TDI (80/20) filled containers were in the grip of fire and TDI 980/20) liquid started generating vapours and the fraction of vapours started burning around the containers rim. Subsequently, when the fire exposure was continued up to 10-11 minutes sufficient pressure was built up inside the TDI (80/20) filled containers which resulted in blowing off three lids of the containers. The temperature reached during this period was from 316 to 340°C. After the blowing off the lids the containers caught fire and started burning with partially smoky flame. While in experiment V after 14-15 minutes of initiation of fire the rupture of all four TDI containers was observed in the first row i.e. adjacent to flexible polyurethane foam stack. The temperature during that period in that row was in the range of 326-338°C. After 17-18 minutes of fire the similar rupture of six TDI containers was recorded in the subsequent rows i.e. second, third and fourth row placed at a distance of 40mm, 80mm and 120mm respectively from burning foam stack. The temperature in these rows varied form 326 to 338°C. The time differences for the rupture of TDI containers in the first and last three rows occur due to the fact that last three rows have a fair distance from burning foam stack which takes little more time to attain the temperature which had resulted in blowing off of the lids. Therefore, it may be concluded that rupture of containers (blowing off lids) from second and third rows could have been taken place when the temperature of these 2nd and 3rd rows was in the range of 320°C 340°C. TDI liquid was also released from the ruptured containers, which continued to burn until whole TDI content had been consumed. After cease of burning there

Was no residue left inside the TDI containers. It was observed during experiment IV and V that the lids of some containers i.e. one in experiment IV and two in experiment V were not blown up in the air because of leakage of vapours through the lids. However their lids were found in open condition when observed after the total TDI and foam stack was consumed. During fire, the maximum temperature attained in the TDI containers close to foam stack was 530°C while the temperature in the fourth row of TDI containers from the flexible foam was 326°C. The experiments carried out on flexible polyurethane foam and TDI in containers under the conditions as described earlier can be of great value in understanding the sequence of events involved in burning of TDI in flexible PU foam fire. Flexible PU foam, if ignited starts fast burning, melting, dripping, spread of melt portion on the floor and spread of fire through molten foam. TDI content after ignition burns easily with self-sustaining flame. However, these experiments have not been designed for finding out the actual burning rates of flexible polyurethane foam and TDI liquid. The variation of temperatures with time in first and fourth rows along with the details of rupture and bursting of the containers (blown of the lids) have been shown in Figure 4.

During fire the rupture of the weakest points (lids) of the TDI containers could have been avoided if their lids were either loosely held or have some special device due to which sufficient pressure of TDI vapours could not be built inside the containers to blow off their lids. The important risk events occurred when the TDI containers built up sufficient internal stress resulting in the failure of their weakest points. Rupture led to spillages also however, vapour evolution and flaming depended upon the temperature, pressure and fire development. The results are summarised in Table 2.

Conclusions

Flexible polyurethane foam, which was used as fuel to assess the burning behaviour of TDI liquid, is easily ignitable and flammable. The burning rate of flexible polyurethane foam is very high. After ignition, TDI burns with self-sustaining combustion in a steady rather than vigorous Manner. No residue occurs unless the fire is extinguished mid-term. Smoke is produced when TDI burns, and smoke vision obscuration can be anticipated. This study concludes that in common with other materials, which do not readily catch fire, TDI should be stored separately from easily ignited materials. Thus following protection measures in addition to other active and passive fire protection measures should be adopted in polyurethane foam manufacturing industries.

- Toluene diisocyanate used as principal raw material in polyurethane foam manufacturing industry should be stored in a separate fire resistant compartment of adequate fire resistance rating away from foam manufacturing, curing and storage areas.
- TDI stored in containers, the pressure release valves should be designed and provided on the container according to the capacity of the container.
- Provisions should be made for the exhaust of hot gases/vapours from the compartment where TDI and flexible polyurethane foam is stored.
- Special precautions should be taken for electrical connections and lights. No fittings should touch the PUF cake and should not be on the storage area of the flexible polyurethane foam cake.
- Adequate slope should be provided on the floor with proper drainage system where TDI containers and polyurethane foam cakes are stored for the escape of unburnt material flowing out from storage containers during unfortunate incident of fire and fire fighting operations.
- Natural ventilation conditions in the occupancy should be taken care while selecting the storage of raw materials, process manufacturing, packing, storage of finished product and delivery of the final product.

The authors feel that more work is required to devise fire prevention and fire protection to mitigate fire hazards as a result of storage of flexible polyurethane foam and TDI in containers by simulating the behaviour of real fires with large quantity of PUF and TDI in confined spaces as these fires are going to be more severe than fires in open spaces.

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Table 1. Some important physical characteristics of TDI

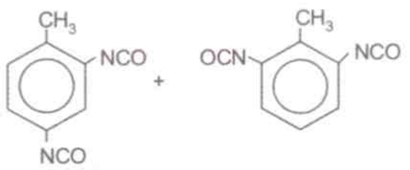
•Physical state	Liquid, pale yellow
Molecular formula	$C_9H_6O_2N_2$
•Molecular weight	174.16
•Equivalent weight	87.08
•Melting point	19°C
•Boiling point	251°C at atmospheric pressure
•Freezing point	14°C
•Flash point	132°C
•Ignition temperature	135°C
•Fire point	143°C
•Auto-ignition temperature	270°C
•Specific gravity	1.22 Gram/Cm^3 at 25°C
•Vapour density	6 (air:1)
•Vapour pressure	3x10^{-2} mm Hg (25°C)
•Tolerance	0.005 ppm in air

Table 2. TDI containers behaviour in indirect heating and flexible PU foam stack fire

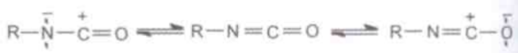
Fire tests number	I	II	III	IV	V
Number of containers	1	1	5	5	12
Capacity of containers, (ml)	65	65	65	65	65
Total quantity of TDI, (ml)	50	50	250	250	600
Fuel-Flexible PU foam, (gm.)	NA*	NA*	1620	2430	4050
TDI vapours first observed, (min.)	NA*	15	7	8	13
Burning first observed, (min.)	-	20	8	9	14
Containers lid conditions	Loose	Loose	Loose	Air-tight	Air-tight
Containers rupture, (min.)	Nil	Nil	Nil	10-11**	14-18**
Number of ruptured containers	Nil	Nil	Nil	4	10
Rupture temperature range, (0C)	NA*	NA*	NA*	316-340**	326-338**

***Not Applicable**
****Limits showing rupture time and temperature of first and last rows**

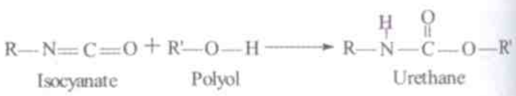
Scheme 1



Scheme 2



Scheme 3



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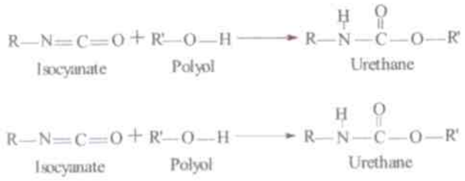
Scheme 4



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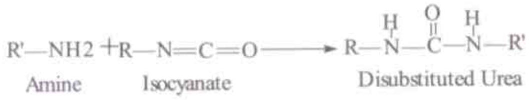
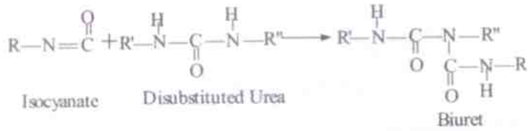
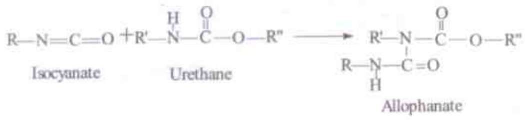


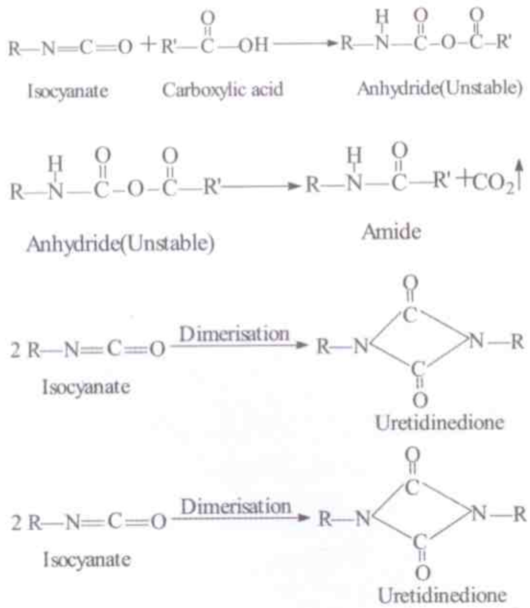
Scheme 6



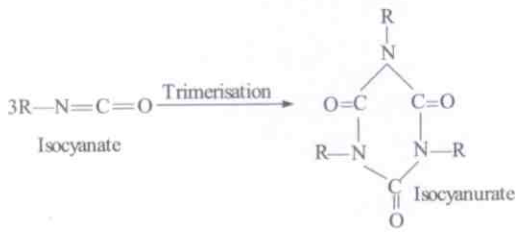
Scheme 7



Scheme 8



Scheme 10



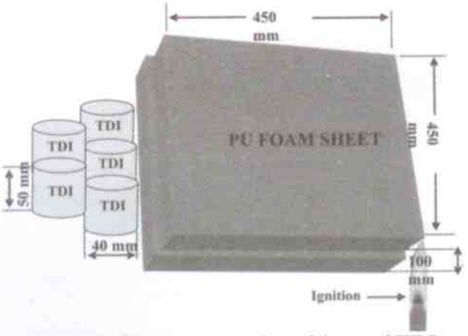


Figure 1. Placement and positions of TDI filled containers, ignition source and flexible polyurethane foam stack

Figure 2. Photograph showing placement, positions and exposure of flexible polyurethane foam stack and TDI containers

Figure 3. Photograph showing burning and blowing off lids of TDI filled containers in flexible polyurethane foam stack fire

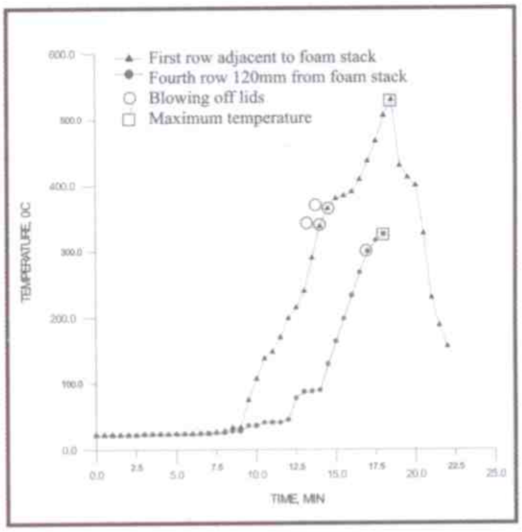


Figure 4. Performance characteristics TDI filled containers fire tests