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STUDIES ON FEASIBILITY OF WATER AND SODIUM CARBONATE SOLUTION AS DECONTAMINANT FOR DISPOSAL OF TOLUENE DIISOCYANATE WASTE

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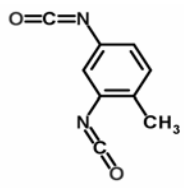
ABSTRACT

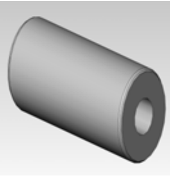
Toluene diisocyanate (TDI) is used as curative in solid propellant system due to its immense experience in the process. This chemical is regulated under the clean air act as a hazardous air pollutant and has been documented to cause asthma, lung damage, in severe cases, fatal reactions. It is procured in 250 Kg barrel from Industry for solid propellant plant's regular activities. The used TDI drums, waste generated on cleansing operation of Toluene Diisocyanate master hopper with dioctyladipate, come under hazardous waste. Such wastes need proper disposal methodology. A systematic study was done using water and sodium carbonate aqueous solution with toluenediisocyanate of known quantity. The presence of free isocyanates was confirmed through chromatography and spectroscopic technique (FT-IR). The results demonstrate that water, sodium carbonate aqueous solution are not effective neutralizing agents for Toluenediisocyanate and is reported in the article.

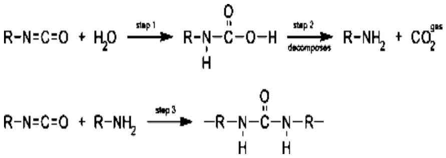
Key words: Hazardous waste, Propellant, Polyurethane, Spectrum, Toluenediisocyanate, Threshold limit.

INTRODUCTION

Environmental performance is a key part in modern philosophy[1-7]. There is a constant work for improving the environmental burdens arising from the emissions of many chemicals. Realizing the significant damage to the environment and limitation of natural resources since 1970s has lead to an increased awareness of environment issues in our society.







$$R{-}N{=}C{=}O + H_2O \xrightarrow{\text{step 1}} R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H \xrightarrow[\text{decomposes}]{\text{step 2}} R{-}NH_2 + CO_2^{\text{gas}}$$

$$R{-}N{=}C{=}O + R{-}NH_2 \xrightarrow{\text{step 3}} {-}R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R{-}$$

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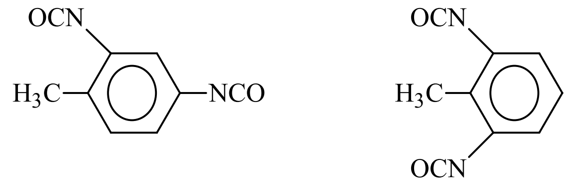
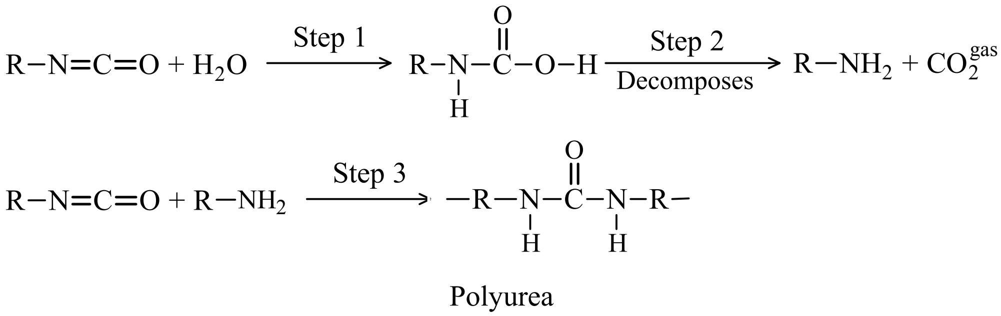
Our main focus is on handling of toluenediisocyanate[8] which is toxic, colorless to pale yellow liquid and for most it is recognized that there is some threshold level above which the material becomes harmful, if inhaled ingested or it makes skin contact with a sensitive area of the body[1,2]. According to Environmental Protection Agency, TDI is having threshed hold limit value of 0.005 ppm. Thus accumulation and then disposal of waste containing TDI causes great concerned from the environmental protection point of view. The commercial TDI has two isomers-2,4 and 2,6 diisocyanato methyl benzene exists in the ratio of 80/20 or 65/35 % and structure as shown in Fig. 1. Ultimate disposal is not the only challenge associated with current and future generation of hazardous waste, environmental releases of this chemical have become a common place of occurrence during transportation and storage. The used TDI drums/wastes containing TDI, come under Resource conservation and Recovery Act as 'toxic hazardous waste due to the presence of considerable amount of TDI which demand its neutralization for disposal'[9,10].



2,4-Toluene diisocyanate 2,6-Toluene diisocyanate

Fig. 1: TDI structure

The very high reactivity of Isocyanates, especially with nucleophilic reactants has always been of intriguing interest to the organic chemist[11,12]. The isocyanates react with water to form polyurea which can be nutrient for plant. The rate of reaction is slow but presence of base makes the reaction faster. Sodium carbonate is weak base and is suitable to use in the reaction at small concentration level from environmental protection point of view.



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Polyurea

Scheme 1: Water with isocyanate

Similarly, Toluenediisocyanate on reaction with water produces an amine and carbon dioxide and is exothermic in nature. The generated amine further reacts with TDI to form carbanilide (urea derivative).

The scope of this study is to realize water and sodium carbonate as decontaminant for disposal of TDI waste and further development work on the line. Water is easily available, non-hazardous solvent and sodium carbonate has soil value. The final reaction product can be dispose after evaluation for free isocyanate by taking its spectral signature and isocyanate content.

Chemicals used

1. Distill water (pH = 6-7, Conductivity < 10 μs) obtained from simple distillation of water.
2. Sodium carbonate, AR grade; 5% and 10% (by wt.) solution was prepared with distill water.

Apparatus used

Measuring jar, beakers, plastic container (500 mL capacity) made of HDPE.

FT-IR spectrometer

FTLA 2000, Make: ABB; was used for recording spectral signature.

Spectroscopy is study of the interaction of electronic wave with matter wave. Molecular vibrations result either by stretching along its chemical bonds or bending its bond angle through absorption of vibration energy (infrared). The bond between two atoms (point mass) may be considered as spring having force constant obeying Hooke's Law. On simple approximation, the stretching vibrational frequency (ν) of two atoms of masses m_1 and m_2 linked by a bond can be calculated as, $\nu = ½ \pi c \sqrt{k/\mu}$

Where μ, reduced mass $= m_1 m_2 / m_1 + m_2$ and c is the velocity of light.

A molecule, whose vibration can cause a change in its dipole moment, absorbs energy in the infrared region. Such a molecule is called infrared active. The most useful infrared region lies between 4000 – 650 cm^{-1}.

IR spectrum is displayed as a plot of energy of the infrared radiation versus the percent of transmittance light by the compound.

Thin layer chromatography (TLC)

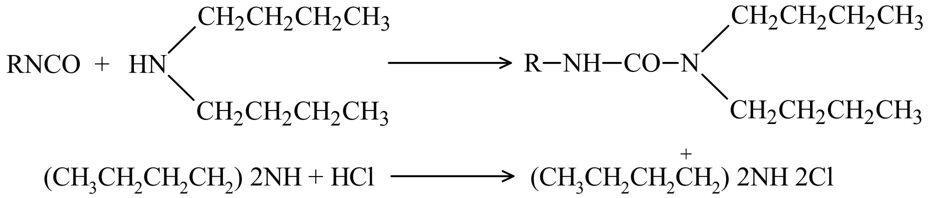
TLC silica gel 60F254, Merck; was used for study.

A technique for rapid separation and qualitative analysis of small amounts of materials is a form of solid-liquid adsorption chromatography. The technique is restricted to the use of a single solvent system with the solvent ascending the adsorbent plate, carrying with it the components of the mixture at different rates rather than descending the column of adsorbent. The stationary phase consists of a thin layer of sorbent (e.g., silica gel, cellulose powder or alumina) coated on an inert, rigid backing material such as glass plate, aluminum foil or plastic foil. As a result, the separation process takes place on a flat and essentially two dimensional surfaces.

Assay of isocyanates

Isocyanates content was estimated on the principle that n-dibutyl amine reacts with isocyanate in nonaqueous solvent (1,4-dioxane) and unreacted amine was back titrated with standard hydrochloric acid and is shown in reaction Scheme 2.

Chemicals/Reagents used: n-Dibutylamine + 1, 4-Dioxane mixture (1.5 : 100) ratio; Bromophenol blue indicator; Std. Hydrochloric acid (0.05 N).



$$RNCO + HN\begin{matrix}\diagup CH_2CH_2CH_2CH_3\\ \diagdown CH_2CH_2CH_2CH_3\end{matrix} \longrightarrow R{-}NH{-}CO{-}N\begin{matrix}\diagup CH_2CH_2CH_2CH_3\\ \diagdown CH_2CH_2CH_2CH_3\end{matrix}$$

$$(CH_3CH_2CH_2CH_2)\ 2NH + HCl \longrightarrow (CH_3CH_2CH_2\overset{+}{C}H_2)\ 2NH\ 2Cl$$

Scheme 2: Isocyanate with n-dibutylamine

EXPERIMENTAL

TDI sample (Purity 99.6% source: Bayer Industry) was taken for studies. Following studies were carried out in simulation with used TDI drums, propellant waste containing TDI etc.

Study-1 (TDI with water)

500 mL plastic container having little TDI (~6.1 g) was filled with distill water, leaving to stand with bungs removed to allow carbon dioxide to expels.

Observations

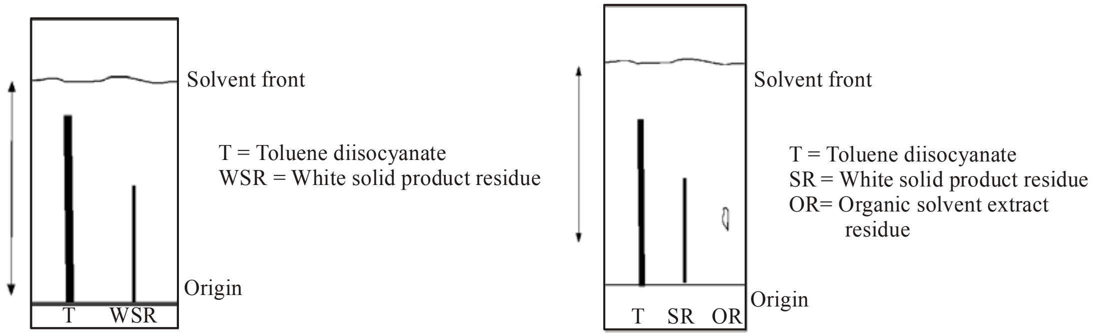
After 24 hrs.: Oily substances seen on water surface with deposition of white mass at the bottom adhere with the container.

After 48 hrs.: Semisolid mass with deposition of white material.

After 72 hrs.: White solid material was found to deposit inside the container.

The white material was washed with hot water and then dried on sunlight. Then TLC as well as FT-IR spectrum was recorded for this material.

Thin layer chromatography diagram of TDI and reaction product is shown in Fig. 2.



TLC Diagram of study-1 **TLC Diagram of study-2**

Fig. 2: Thin layer chromatograms

TLC

The chromatogram pattern of both TDI as well as reaction product with water is same, no separation of solute was found. It does not give any firm conclusion about the reaction products.

FTIR spectrum analysis

The spectrum was recorded in ABB FTLA 2000 spectrophotometer with dry KBr pellet of the product.

The sharp strong peak @ 2275 cm^{-1} is assigned to –N=C=O stretching of Isocyanate and peak @ 1640 cm^{-1} due to the >C=O stretching of urea derivative (3, 3 diisocyanato 4, 4 dimethylcarbanilide) (Fig. 4).

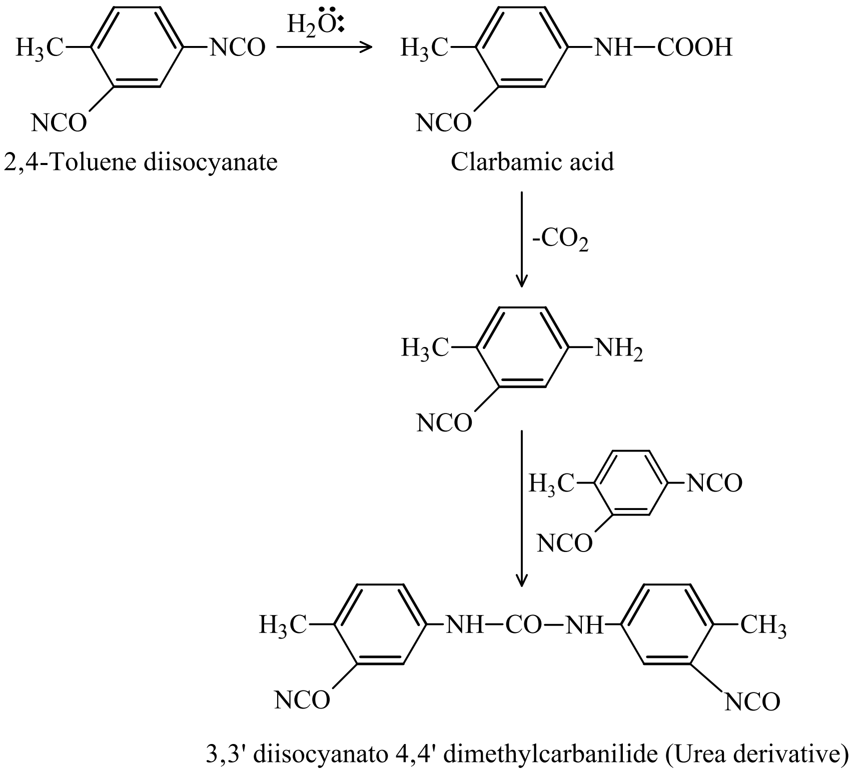
Explanation

Toluenediisocyanate converted into amine with the evolution of carbon dioxide by the nucleophilic attack of water. The amine which turns to urea by the reaction of free Isocyanates. This conversion process continues and ultimate product is polyurea, having isocyanate group in the aromatic sextet. The TLC and FT-IR spectrum tells us that.

Reactions involved are shown as below:

Study-2 (TDI with 5% Sodium carbonate solution)

500 mL container having little TDI (~ 6.1 g) was filled with 5% sodium carbonate solution and left for 72 hrs. leaving to stand with bungs removed so that carbon dioxide gas evolved during the process, can easily come out and there won't be any chances of pressure buildup.



Scheme 3: TDI with water

Observation:

(i) White polymeric substance found to settle in the container.

(ii) Solution became light pink in color.

The white polymeric substance was washed with hot water, dried and its spectra (KBr pellet) and TLC was recorded.

TLC

The chromatogram obtained was found to identical with Study-1.

FT-IR analysis

The peak @ 3309 cm^{-1} and multiple bands in the region 3400-3000 cm^{-1} are assigned to amide association to form dimmer/polymer which is an indication of formation of polyurea. The strong broad band in the region 2275-2240 cm^{-1} is due to –NCO stretching vibration (Fig. 4).

Study-3 (TDI with 10% Sodium carbonate solution)

On treatment with 10% sodium carbonate solution, almost same results were obtained.

TLC, FT-IR spectrum was recorded after 72 hrs.

TLC: No change in thin layer chromatogram pattern.

FT-IR: No change in spectral signature, only intensity is reduced.

Reactions involved

The reaction path and products are similar to study with water, here basic medium facile the reaction at faster rate.

Extraction and analysis of pink colored solution of Study-2 and 3

Aqueous pink solution of study-2 and 3, was extracted with n hexane and diethyl ether; organic layer evaporated; residue (dark red) obtained was run for TLC and FTIR.

TLC: Shows separation of the material, different from TDI and white polymeric compound as shown in Fig. 2.

Fourier transforms infrared spectrophotometer (FT-IR) analysis

The peak @ 1624 cm^{-1} is due to > C=O stretching of quinone-imide (chromophore) which generally appears at 1630-1605 cm^{-1} (Fig. 3).

The spectra reveal the conversion of quinone-imides compound as shown in Fig. 3.

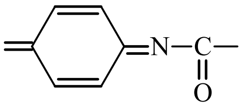
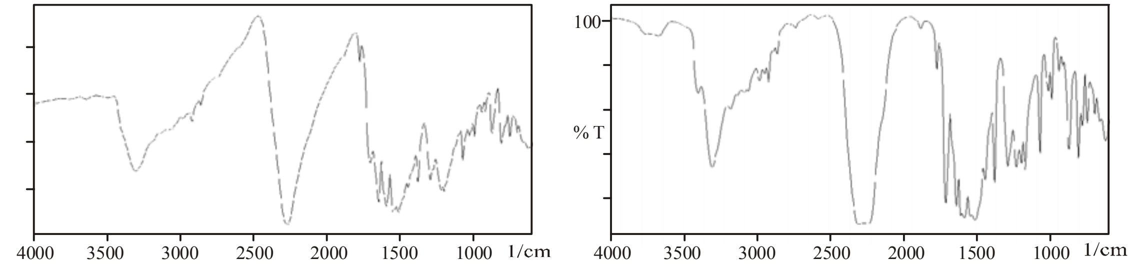
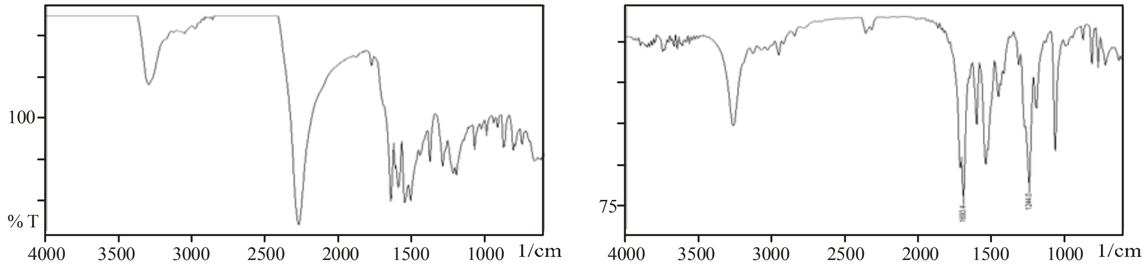


Fig. 3



Reaction product of TDI with water

Reaction product (white residue) of study-2



Reaction product (white residue) of study-3.1

Organic solvent extract residue of study 3.2

Fig. 4: FT-IR spectrum

Table 1:

Study, after 72 hrs.	Isocyanate % as TDI
Study-1 (with water)	14.6
Study-2 (with 5% Na_2CO_3 solution)	5.7
Study-3 (with 10% Na_2CO_3 solution)	3.2

Summary of the work

From the studies it is seen that after 72 hrs., practically, ordinary disposal by simply treating with water, 5%, 10% sodium carbonate solution not ensuring complete neutralization of Toluenediisocyanate even though end reaction product is polyurea and at this stage drain disposal is not permitted according to Resource Conservation Recovery Act (RCRA) as the rest free Isocyanates adds to environment leading to natural imbalance of the ecosystem.

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