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Development of Eco-friendly Neutralizing Agents for Toluene Diisocyanate

Das Bakul[1]*, T.V. Ramana Reddy[1], MTK Balaji[1] and T. Veera Reddy[2]
[1]Satish Dhawan Space Centre, Sriharikota, Nellore, AP, INDIA
[2]Vikrama Simhapuri University, Nellore, AP, INDIA

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Abstract

The present communication provides an effective methodology which is simple, time saving and economical in order to have a safe, healthy and friendly process environment in plant. The toxicology and environmental effects of Toluene Diisocyanate (TDI) is exposed during process operations and is highly concerned from the environmental protection point of view. In almost every-scenario, the threat of environmental exposure is contingent upon the proper handling of this chemical. This chemical is colorless to pale yellow liquid, found responsible for asthma, lung damage, and severe cases fatal reactions. Ordinary discharge of waste containing TDI in the environment leads to imbalance of the ecosystem due to the presence of considerable amount of free Isocyanates. The paper deals with suitable formulation of isopropyl alcohol, rectified spirit (95%ethanol), dilute ammonia and soap solution to neutralize free TDI and then its presence was confirmed through spectroscopic technique. The formulations are promising eco-friendly neutralizing agent which neutralizes the available TDI within 24 hours only.

Keywords: Propellant, isocyanate, polyurethane, urea, spectra etc. Abbreviations: TDI- Toluene Diisocyanate; IPA- Isopropyl alcohol; FTIR- Fourier transforms infrared spectrophotometer.,

Introduction

The application of TDI in the field of solid propellant[1,2] processing or manufacturing of paint, primer or polyurethane polymer is continued over the world in the last 4-5 decades. In fact it is now found to be a mature curator for solid propellant. A typical solid propellant contains approximately 86% solid consisting ammonium per chlorate as inorganic oxidizer, aluminum as metallic fuel that are filled in 14% liquid of Hydroxyterminated polybutadiene, Dioctyladipate, ambilink. The measure amount of TDI as curator[3,4] which is added in propellant formulation reacts with hydroxyl group of the liquid ingredients to form polyurethane linkage. The urethane linkage[5,6] exerts three dimensional structures to propellant and provides the necessary mechanical and interfacial properties to have a robust structure as shown below.

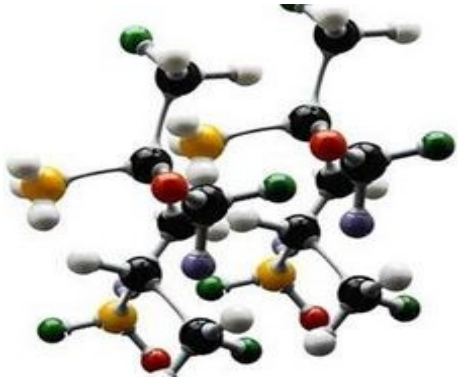


Figure-1
Polyurethane 3D linkage

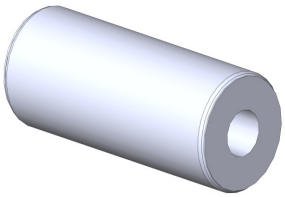


Figure-2
Propellant Grain 3D structure

TDI is a toxic chemical, known as diisocyanato methylbenzene, colorless to pale yellow liquid, regulated under clean air act as hazardous air pollutant[7-10] and documented to cause for asthma, lung damage, and severe fatal reaction. It is having two isomers 2, 4 and 2, 6 TDI as shown below (figure 3) and commercial % composition ratio is 80/20% or 65/35. Environmental Protection Agency restricted its threshold[11] concentration limits to 0.005ppm in the working place without any health disorder.

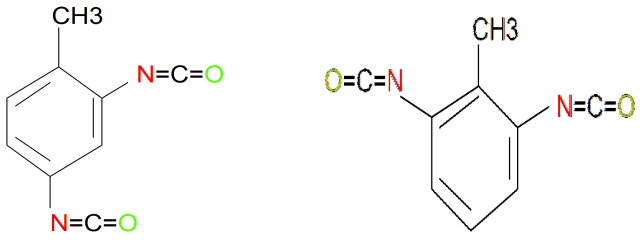
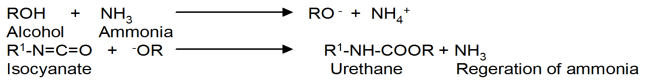


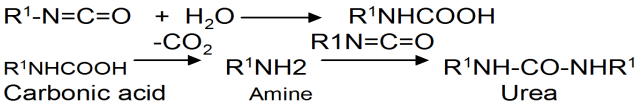
Figure-3
Structure of 2, 4 and 2, 6 TDI

The waste[12] generated while working with TDI are used drums or container, spills, master hopper cleansing mixture, unused TDI etc. These wastes need proper disposal methodology in the light of Resource conservation and recovery act[13]. Now let us focus on the reaction of Isocyanate with compounds that contain active hydrogen group such as hydroxyl, water amine.

Reactions with Alcohol: Isocyanate reacts with alcohol to form carbamate (urethane). This is exothermic reversible in nature aliphatic primary alcohols are more reactive and react much faster than the secondary. The presence of base like ammonia fasten the reaction

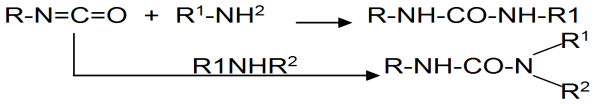


Reaction with water: The reaction of Isocyanates and water to produce carbonic acid which breaks into carbon dioxide and primary amine, the amine will then react with another Isocyanate to form symmetrical urea.



Das et al[13] demonstrated that Water, Sodium carbonate solutions are not able to neutralize TDI completely, for a period of time 72 hours.

Reaction with Amine: Isocyanates react with 1°, 2°, amine to produce di and trisubstituted urea respectively. These conversions are exothermic in nature and diamines are used as chain extending and curing agents in Polyurethane (PU) manufacturing.



Methodology

An attempt was made to decontaminate TDI utilizing the behavior of Isocyanates towards alcohol in presence of dilute ammonia and soap solution in eco-friendly manner. The idea lies in the fact that alkoxy group is generated in situ with the abstraction of hydrogen by ammonia from alcohol and alkoxy group attacks more electrophilic carbon of isocyanate group to form carbamate with the regeration of ammonia. Soap solution being surfactant; accomplish the good mixing of the components and help to complete the reaction. FT-IR spectral signature of the reaction product will confirm whether TDI is completely neutralized or not.

Scope of the study: i. All the experimental results are based on 24 hours study only, ii. Easy availability and handling of these chemicals, iii. Minimum plant utility requirement, iv. Application of diluted solution of inexpensive almost non toxic chemicals, v. Neutralization of TDI completely from the waste and its safe disposal, vi. Regenerated ammonia can be further use avoiding environmental discharge, till exhausted.

Chemicals used: i. Distill water (pH =6-7, conductivity < 10µs) obtained from simple distillation of water. ii. isopropyl alcohol, 99.5%, excelar, qualigens; iii. Ammonia 30% GR, Merck; Diluted with water; ammonia solution (1:2), iv. Rectified spirit, 95% ethanol; v. Soap solution 10%.

Apparatus used: Measuring jar, Beakers, Plastic container (500ml capacity) made of polyethylene.

FT-IR spectrometer: FTLA 2000, ABB Bomem Inc; was used for recording spectral signature.

Experimental: TDI sample (Purity 99.6%; source: Bayer Industry) was taken for studies.

Study-1: 1.1-(TDI with Isopropyl alcohol together with dilute ammonia and surfactant): 500ml container having little TDI (~ 6.1g), was filled with a solution of 85 parts water, 5 parts IPA, 5 parts dilute ammonia (1:2) and 5 parts soap solution; left for 24 hours leaving to stand with bungs removed so that carbon dioxide gas evolved without making any pressure buildup. **Observations**: i. white material found to deposited at bottom and adhere of the wall of the container. FT-IR spectral signature of the white material (KBr pellet):

1.2-A solution having 80 parts water, 10parts IPA, 5 parts dilute ammonia (1:2) and 5 parts soap solution was used for further study.

1.3-Solution containing 75 parts water, 15 parts IPA, 5 parts dilute ammonia (1:2) and 5 parts soap solution was employed for further study.

1.4 - Solution containing 70 parts water, 20 parts IPA, 5 parts dilute ammonia (1:2) and 5 parts soap solution was employed for further study. Observation: Cream white material found to deposit at bottom with adheres inside of the container.

Study-2: Repeat study, using a solution of 10 parts, 15 parts, 20 parts and 25parts of rectified spirit keeping the same proportion of dilute ammonia (1:2) and soap solution for 24 hrs observations

2.1 Rectified spirit-95% ethanol, together with dilute ammonia and surfactant. 500ml container having little TDI(~6.1g), was filled with a solution of 80 parts water,10 parts rectified spirit, 5 parts dilute ammonia(1:2) and 5 parts soap solution; left for 24 hours to stand removing the lid so that carbon dioxide gas evolved without making any pressure buildup. Observations: i. white material found to deposited at bottom and adhere of the wall of the container, ii. The whole solution was remained colorless.

2.2 Study with 80 parts water +15 parts rectified alcohol + 5 parts dilute ammonia + 5 parts soap solution.

2.3-Study with 70 parts water + 20 parts rectified spirit + 5 parts dilute ammonia (1:2) + 5 parts soap solution.

2.4-Study with 65 parts water + 25 parts rectified spirit + 5 parts dilute ammonia + 5 parts soap solution.

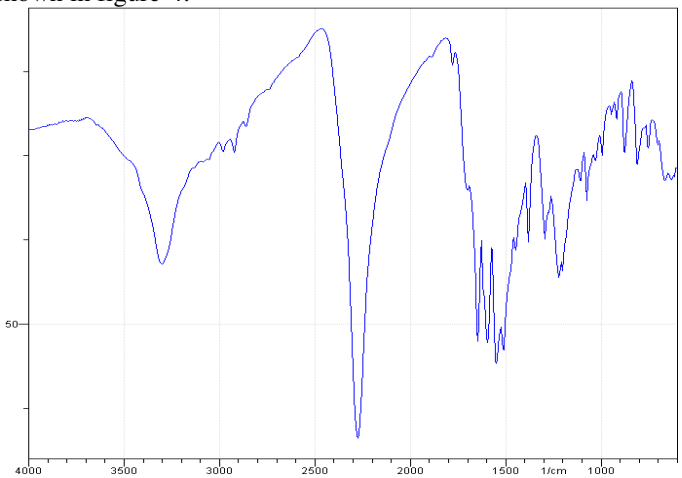
Results and Discussion

FT-IR analysis for Study-1: Strong sharp peak @ 2275cm^{-1} and weak band @ 1720cm^{-1} was noticed for study 1.1 which are due to stretching of –N=C=O and –NHCO group respectively.

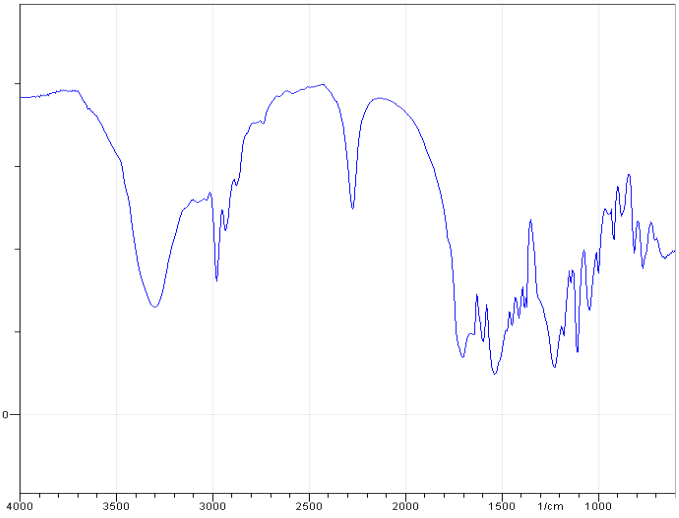
IPA reacts with Isocyanates to form carbamate (urethane) and ammonia facile the reaction faster. Soap solution being surfactant; accomplish good mixing of all the reaction partners. But the used solution with the above concentration of the components is not able to destroy isocyanates completely after 24hrs.

FT-IR spectra remain unaltered for study 1.2; spectrum of study1.3 as shown in Fig.4 shows the presence of Isocyanates group@ 2275 cm^{-1} with less intensity. Spectral signature (KBr pellet) of study 1.4 shows no peak @ 2275-2240 cm^{-1} band; which implies the absence of free Isocyanates i.e. TDI became converted into allophonate, polyurea, polyurethane upon action with water, IPA, ammonia .The peak @ 1690, 1640, 3300 cm^{-1} confirmed that as shown in figure-4.

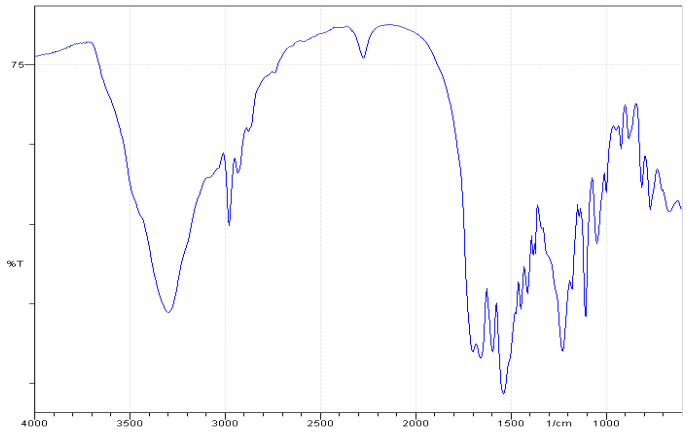
FT-IR analysis for study-2: The strong sharp peak @ 2275cm^{-1} shows (for study 2.1) the presence of free Isocyanates. The peak @ 2275 cm-1 for study 2.2, shows the presence of free Isocyanates but the intensity of the peak was found to reduce. The weak peak as found for 2.3 @ 2275 cm^{-1} confirms the gradual neutralization of Isocyanates from the container. For study 2.4, there is no peak at 2275-2240cm^{-1} band; hence it can be concluded that no Isocyanate left over in the container and Peak at 1720cm^{-1}, 1640cm^{-1}, 3300cm^{-1}(N-H stretching) are because of urethane and allophonate compound formation as shown in figure-4.



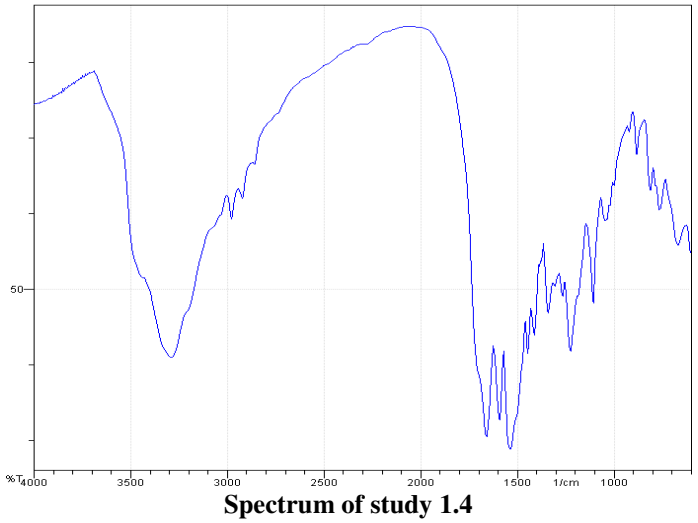
Spectrum of study 1.1



Spectrum of study 1.2

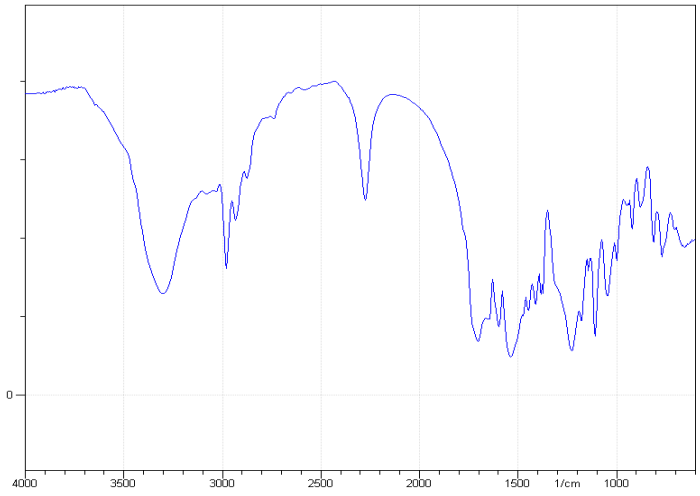


Spectrum of study 1.3

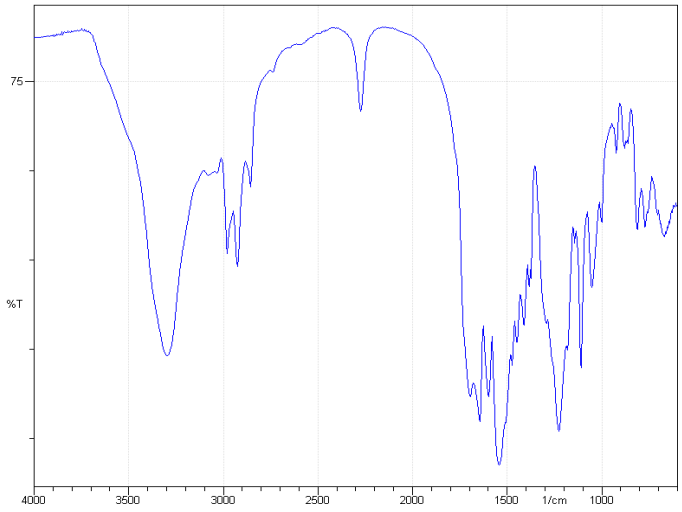


Spectrum of study 1.4

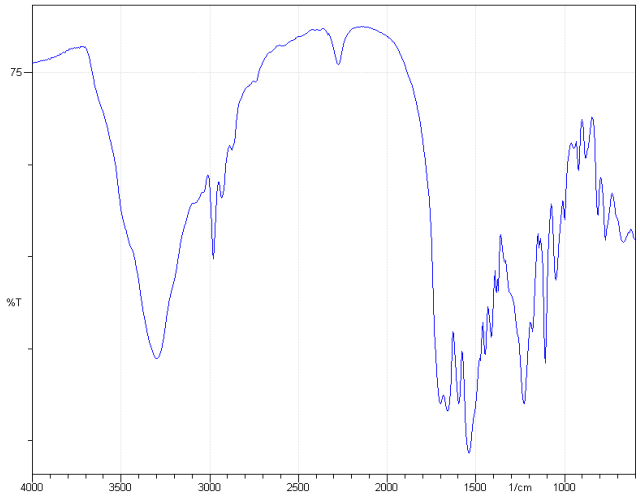
Figure-4
Spectral signatures of Study-1



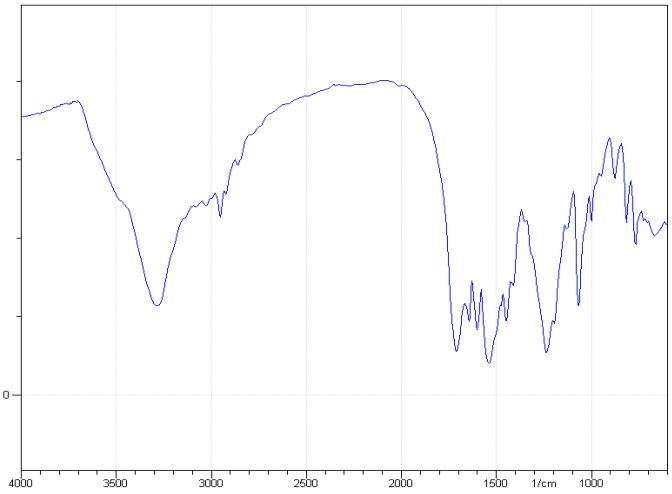
Spectrum of Study 2.1



Spectrum of Study 2.2



Spectrum of Study 2.3



Spectrum of Study 2.4

Figure-5
Spectral signatures of Study-2

The study 1.4 and 2.4 was repeated with TDI and regenerated ammonia solution and indeed it was found that Spectral signature is similar to spectrum of 1.4 and 2.4.

Conclusion

The formulations– 70parts water +20 parts IPA + 5 parts dilute ammonia (1:2) + 5 parts soap solution (10 %) and 65 parts water + 25 parts rectified spirit + 5 parts dilute ammonia (1:2) + 5 parts soap solution (10%) are suitable one and provides an effective formulation to neutralize the available TDI in the container after 24 hours only. Ammonia as such is hazardous and hence it was used in very low quantity after dilution with water and the same is regenerated after reaction. The generated aqueous solution having ammonia is also viable for further neutralization of TDI minimizing the discharge of ammonia in the environment. The suggested decontaminant solutions are eco-friendly and economical.

Acknowledgement

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