

RESEARCH ARTICLE

STUDIES ON NEUTRALIZATION OF TOLUENE DIISOCYANATE AND DIOCTYL ADIPATE MIXTURE GENERATED FROM CLEANING OPERATION OF TDI CONTAINER

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ABSTRACT

Toluene Diisocyanate (TDI) and Dioctyladipate (DOA) are the two important liquid ingredients for formulation of Solid Propellant. The former is used as curative and the latter as plasticizer for processability in propellant manufacturing. Toluene Diisocyanate is procured in 250 kg drums for solid propellant plant's regular activity. Then it is transferred from Drum to small container fitted with valve for batching by nitrogen pressure pumping system. After process utilization, these containers need proper cleaning for further use. For this Dioctyl adipate being ester, inactive towards TDI and is used to clean the containers. The resultant mixture which contains both TDI and DOA comes under Hazardous Waste due to the presence of considerable amount of TDI. In order to dispose the mixture, a common treatment methodology is reviewed for the mixture before and after treatment with suitable eco-friendly decontaminant composed of 65 parts water, 25 parts rectified spirit, 5 parts ammonia (1:2) and 5 parts (10%) soap solution. FT-IR spectrophotometer, Single point Monitor meter was used for the study. The results are summarized in the article.

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INTRODUCTION

The role of TDI in the manufacturing of solid propellant Sutton G.P 1992 is as curative agent that basically forms urethane linkages with hydroxyl functional group of the pre polymer resin, hydroxyl terminated polybutadiene through curing. It is this linkage which actually firmly held all the solid ingredients (86%) used in the Propellant and is responsible for structural integrity of the grain. It is chemically known as diisocyanato-1-methyl benzene and having two isomers 2, 4 and 2, 6 TDI as shown in Fig.1 these two isomers remain in the ratio of 80/20 or 65/35 % depending on the process preparation of the chemical.

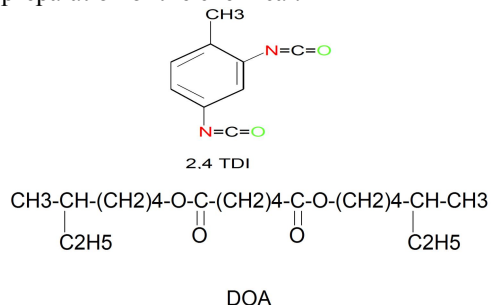


Fig. 1 Structure of TDI & DOA

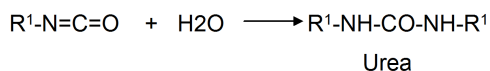
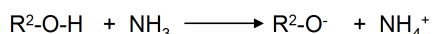
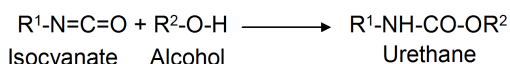
On the other hand, DOA which is ester based organic compound, structure as in Fig.1 is used as plasticizer to improve the process ability David Randall *et al.*, 2002 ; Gum Wilson *et al.*, 1991 2, 3 of the propellant slurry and mechanical properties such as flexibility, low temperature properties of the cured propellant etc. It also acts as a high energy fuel due to

hydrocarbon back bone of the molecule.

The most suitable cleaning solvent for TDI container to make ready for further use is DOA. The generated mixture of DOA and TDI is toxic hazards due to presence of considerable amount of TDI. There is generation of approximately 100 kg of this mixture in the processing of approximately 80 tons of propellant. There is no reaction between TDI and DOA from chemical point of view. The mixture on keeping is settling into lower fraction of TDI and DOA on the upper layer due to variation of density. But the mixture is toxic hazards owing to presence of TDI above 0.5% which can migrate even though DOA has no harmful effect on environment. Inhalation of TDI in significant quantities Anderson *et al.*, 1980; Baur *et al.*, 1994; OSHG for TDI 1988 produces serious respiratory health effect, including asthma, lung damage, irritation to eye, nose, throat choking, waves of productive cough, chest pains, abnormal distress nausea and vomiting. Skin contact may cause redness, swelling and painful blistering. This substance is possibly human carcinogen. Hence, before discharging to environment, it is essential to make a treatment the mixture so that concentration of TDI becomes zero or below the threshold limit ACGIH 1986.

The idea put forward with the study is that TDI reacts with water to form symmetrical urea with the evolution of carbon dioxide but DOA has no effect on that. The neutralization of TDI couldn't achieve cent percent, only with water and sodium carbonate solution within a span of 72 hrs Das Bakul, Veera Reddy *et al.*, 2012. The rectified spirit reacts with TDI to form polyurethane. The presences of ammonia fasten the

reaction and at the end regenerated ammonia can be reused with the minimal discharge in the environment.



Reactions Scheme 1: With alcohol, ammonia and water
The formulation Das Bakul, Reddy *et al.*, 2013 of 65 parts water, 25 parts rectified spirit, 5 parts (1:2) ammonia and 5 parts soap solution serve the purpose. The present study is to extend the formulation for the said mixture and to see the feasibility of neutralization of TDI with the course of time.

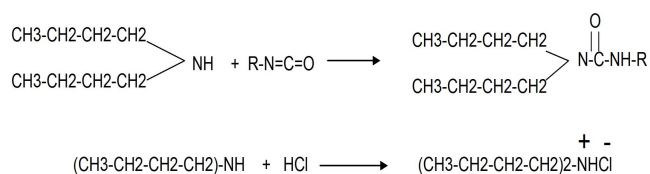
MATERIAL AND METHODS

Chemicals used

- Distill water (pH =6-7, Conductivity < 10µs) obtained from simple distillation of water.
- Ammonia 30% GR, Merck; Diluted with water to make solution (1:2).
- Rectified spirit, 95% ethanol;
- Soap solution 10 %

TDI estimation

TDI was estimated on the principle that dibutyl amine reacts with isocyanate in nonaqueous solvent (1,4-dioxane) and unreacted amine was back titrated with standard hydrochloric acid solution. n-Dibutylamine and 1,4-Dioxane was taken in (1.5:100) ratio; Bromophenol blue as indicator, std hydrochloric acid(0.05N) was used.



Reactions Scheme 2: Di-n-butylamine and Isocyanate

Apparatus used

Measuring Jar, Plastic Beaker, Glass rod, Balance;
FT-IR Spectrometer- FTLA-2000 was used to take spectral signature; Single Point Monitoring System for TDI (0 to 100 ppb)

Table 1 TDI concentration before treatment

Test	S1	S2	S3
Appearance	Orange Yellow liquid with white material	Light yellow liquid with deposition of white material	Light yellow thick liquid with deposition of white material
TDI content (%)	12.7	65.8	1.1
Total TDI quantity	12.3 g	64.9 g	0.892 g

Table 2 TDI concentration after treatment

Time	S1	S2	S3
	TDI (%)		
24 hrs of treatment	0.20	0.53	NIL
48 hrs of treatment	NIL	0.32	NIL
72 hrs of treatment	NIL	0.21	NIL

Experimental

The three TDI container cleaned with DOA mixture was collected for experiment. The mixture was marked as S1, S2 and S3.

The original mixtures before treatment were estimated for TDI content and FT-IR spectra were also taken as shown in Fig.2.

Table 3 Response of SPM

Time	S1	S2	S3
24 hrs of treatment	No response	3.4 ppb	No response
48 hrs of treatment	No response	No response	No response
72 hrs of treatment	No response	No response	No response

Treatment of the Mixture

The total quantity of material of S1 (96.85 g), S2 (98.63 g), S3 (81.1 g), was transferred to three different 500 ml beaker and then 100 ml composite neutralizing agent formulation of 65 parts water, 25 parts rectified spirit, 5 parts 1:2 ammonia and 5 parts 10% soap solution was added in each beaker; then stirred for 5 minutes and kept as such.

Observation for S1

White product (poly urea) found to deposit in the beaker after 24 hrs; then the product was tested for TDI after 24 hrs, 48 hrs respectively.

FT-IR Spectra: Main peaks are 1485 cm-1, 1730 cm-1, 2274 cm-1, 2885 cm-1, 2932 cm-1, 2951 cm-1 (before treatment)

FT-IR Spectra: Main peaks are 3340 cm-1, 2958 cm-1, 2934 cm-1, 1730 cm-1, 2272 cm-1(weak broad peak) after 24 hrs of treatment

Peaks after 48 hrs of treatment: 3400 cm-1, 2958 cm-1, 2935 cm-1, 1725cm-1 but no peak at 2240-2275 cm-1

TDI content: 0.20% after 24 hrs of treatment

Observation for S2

The product so formed found at bottom and adhere of the beaker within 24 hrs. The FT-IR spectra were recorded for the product after 24 hrs, 48 hrs and 72 hrs.

Main Peaks:

3350 cm-1, 2958 cm-1, 2935 cm-1, 1720cm-1, 1480 cm-1 and very weak peak at 2274 cm-1 (72 hrs of study)

TDI content: 0.21%

Observation for S3

The product identified as poly urea, urethane and DOA remains intact, chemically it has no change. The spectrum reveals that there is no peak at 2240-2275 cm-1 after 24 hrs of treatment.

DISCUSSION OF THE RESULTS

The spectrum before treatment of all the three mixture suggests that there is no change of main peak values of DOA and TDI; both the chemical exist distinctly in the mixture.

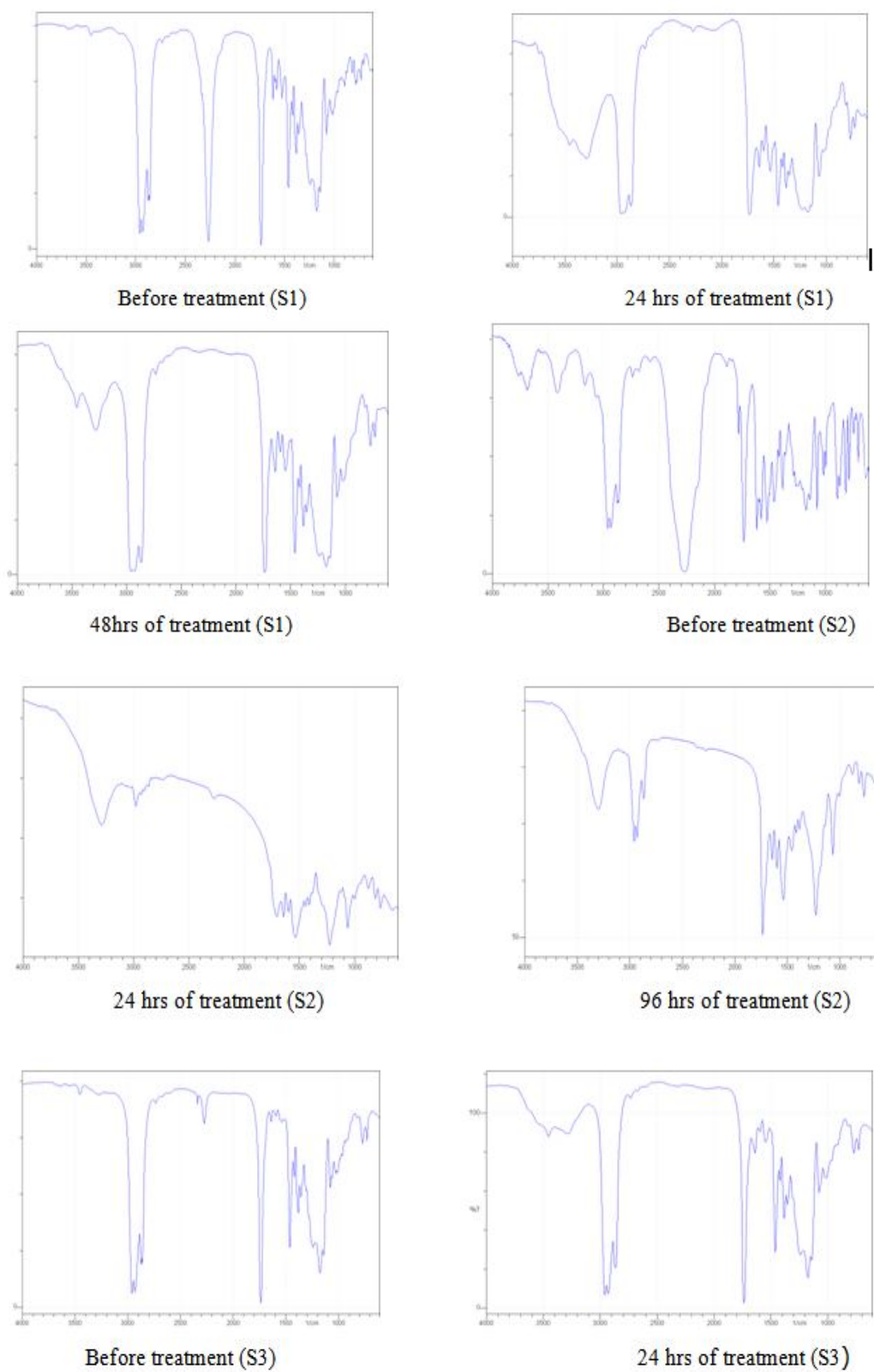


Fig. 2 FT-IR Spectrums

After treatment when the mixture is tested for TDI, it was found that the concentration of TDI gradually decreases with the conversion of polyurethane and polyurea. The sharp peak at 1720-1730 cm⁻¹ and absence of peak in the range 2240-2275 cm⁻¹ support the estimated TDI value with the course of time. TDI reacts with water and alcohol to form polyurea, urethane. Stoichiometrically it is known that 1 gm of TDI need approximately 0.61g of hydroxyl compound for its neutralization but practically it was not happened. The chemicals used more than stoichiometric amount that acts as reagent as well as solvent.

The sample S1 having TDI 12.3 g is neutralized after 48 hrs, sample S3 (TDI 0.892 g) after 24 hrs and S2 (TDI 64.9 g) after 72 hrs also left 0.21% by reaction with 100 g of neutralizing agent. The amount of TDI in the S2 mixture is less than 0.5% which does not give rise to hazardous vapor of TDI, SPM system also supports that.

CONCLUSION

The disposal of generated mixture of TDI and DOA upon cleaning of TDI container is achieved effectively by treatment with suitable formulation of water, rectified spirit, dilute ammonia and soap solution after 24 hrs, 48 hrs, and 72 hrs depending on TDI concentration in the mixture. The time is much more important for production plant and the same is also not so large for complete treatment. Once TDI concentration in the mixture is reduced to 0.5% the mixture is safe to dispose in the identified landfill as it does not generate hazardous vapor confirmed by SPM which detects TDI vapor concentration from zero to 100 ppb. The quantity of neutralizing agent used in the present study was only hundred grams for approximately same quantity of mixtures having TDI 1.1% to 65.8%. This is an elegant approach to deal with such waste for highest standard of safety, occupational health and environment.

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