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Development of a new method for the determination of purity of N-phenyl-β-naphthylamine(Nonox-D) using toluene diisocyanate(TDI)

Mehilal*, K.I.Dhabbe, B.Bhattacharya

High Energy Materials Research Laboratory, Pune-21, (INDIA)

Tel : 020-25869104 ; Fax : 020-25869091

E-mail : info@hemrl.org

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ABSTRACT

N-Phenyl-β-naphthylamine (Nonox-D) is used as an antioxidant in rubber industry as well as in composite propellant formulations based on hydroxyl terminated polybutadiene (HTPB). A new method has been developed to determine the purity of Nonox D using TDI. The secondary amine of Nonox D reacts with excess of TDI. The quantity of remaining TDI was determined by reacting with excess of dibutylamine which was further determined by titrating against standard hydrochloric acid. The data obtained by analyzing different sources of Nonox-D indicate that the developed method is much reliable, fast and accuracy tolerance is in the range of ±0.5%.

INTRODUCTION

Hydroxyl terminated polybutadiene(HTPB) based solid rocket propellants are currently being used in space as well as on going missile programme[1]. However, due to presence of one double bond(-C=C-) in the chain segment of every repeating unit of HTPB, it is prone to degrade due to atmospheric oxygen, moisture and temperature. The oxidative degradation usually leads to hardening, discolourization as well as surface changes of polymer matrix which ultimately affects the shelf life and mechanical properties of the polymer. The polymers are protected against oxidative degradation by incorporating certain chemical compounds called antioxidants. Antioxidants are significantly effective even in small amounts in preserving the original properties of the polymer. They oppose oxidation and in a good number of cases suppress undesirable reactions, promoted by oxygen or peroxides. The common antioxidants fall in the class of phenols, aromatic amines and salt and condensation products of amines and amino phenols with aldehydes, ketones and thio compounds. Also, it is well recognized that presence of phenol/amine stabilizers in solid propellants such as double base[2] and composites[3] are of primary importance for long term chemical/mechanical durability of rocket motors. A number of antioxidants, like butylated hydroxyl toluene (BHT), diphenyl amine(Accinox-B), N-phenyl-β-naphthylamine (Nonox-D), 2,2-methylene bis-(4-methyl-6-tertiarybutylphenol) (Vulcanox-BKF) and polymerized 1,2-dihydro-2,2,4-trimethylquinoline (Accinox-TQ) have been reported and used for HTPB systems[4]. However, commonly used antioxidants in composite propellants based on HTPB are Nonox D[5] and to be effective even at 0.1% level. Further more, the service performance over a long storage period depends on the nature, effective concentration and purity of the antioxidants added.

In view of better performance and commercial interest in different grades of Nonox-D, there is a need for rapid and simple method for the estimation of the purity of Nonox-D. The most commonly used method to determine purity of organic nitrogen is Kjeldahl method[6]. However, this method is highly laborious and time consuming as it requires several hours of digestion, distillation followed by titration. This method is non reproducible and non specific for Nonox-D as nitrogen in any form also contributes and thus producing erratic results. Further, gas/liquid chromatography has also been reported as a powerful analytical technique for the quantitative estimation of purity of Nonox-D. However, this technique always needs a reference sample of the purity of more than 99.99%. To avoid the need of reference sample, a new method for the determination of purity of Nonox-D using toluene diisocyanate have been developed and used for the estimation of purity of Nonox-D.

In the following section, we report the determination of purity by reacting secondary amine of Nonox-D with -NCO group of TDI. The unconsumed TDI is further treated with excess of dibutyl amine which is back titrated with standard hydrochloric acid.

EXPERIMENTAL

Material

N-Phenyl-β-naphthylamine(Nonox-D), procured from Aldrich, ABR organics Hyderabad and Surbhi chemicals industries, Pune, were used as such for the determination of purity. Toluene diisocyanate(TDI) procured from Bayer, Germany, having purity >99.5% was used as received. Dibutylamine and toluene, AR grade, were procured from Merck-India. Bromothymol blue AR grade was used as indicator and 0.5N HCl of MERCK-India was used as titrating reagent.

Procedure

To a dry iodine flask(capacity 250mL) accurately weighed 2.175g of TDI and 25mL of AR grade toluene followed by 0.5g of Nonox D. The stopcock was tightly closed and kept for 45 minutes at room temperature. In the mean time, 50mL of already prepared dibutyl amine reagent(17.5ml of dibutylamine and 82.5ml of toluene) was added to the flask. After addition of dibutylamine reagent, the flask was again kept for half an hour. After half an hour, 2.0ml of 0.04wt % solution of bromothymol blue indicator, prepared in distilled water, was added to the flask followed by 65mL of isopropanol. It was titrated against 0.5 N HCl which gave end point blue to yellow. A blank titration was also carried out without Nonox-D.

RESULTS AND DISCUSSION

It is well known that -NCO group reacts with active hydrogen possessed by an electronegative element. The order of reactivity[7] of -NCO group with active hydrogen is as follows.

Aliphatic amine>aromatic amine>primary alcohol>water> secondary alcohol>tertiary alcohol>carboxylic group>urea> amide>urethane

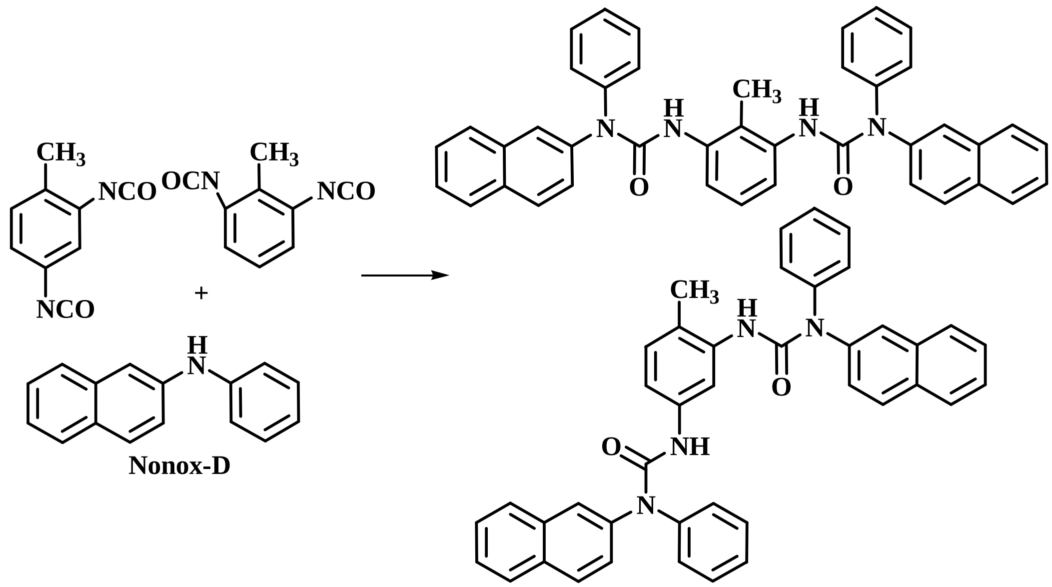
It is clear from the above reactivity that aliphatic/ aromatic amine reacts with -NCO group readily. This reaction is utilized to determine the purity of toluene diisocyanate (TDI) by reacting with excess of dibutylamin[8]. The product of this reaction is urea derivative of aromatic and aliphatic moieties. The excess dibutylamine is titrated against standard hydrochloric acid. Further, a blank titration is also carried out without using TDI to get exact volume of acid consumed. The percent purity of TDI is calculated by using following equation.

$$\%\text{purity of TDI} = \frac{(\text{Blank} - \text{sample}) \times N_{HCl} \times 8.7 \times 100}{W_{TDI}}$$

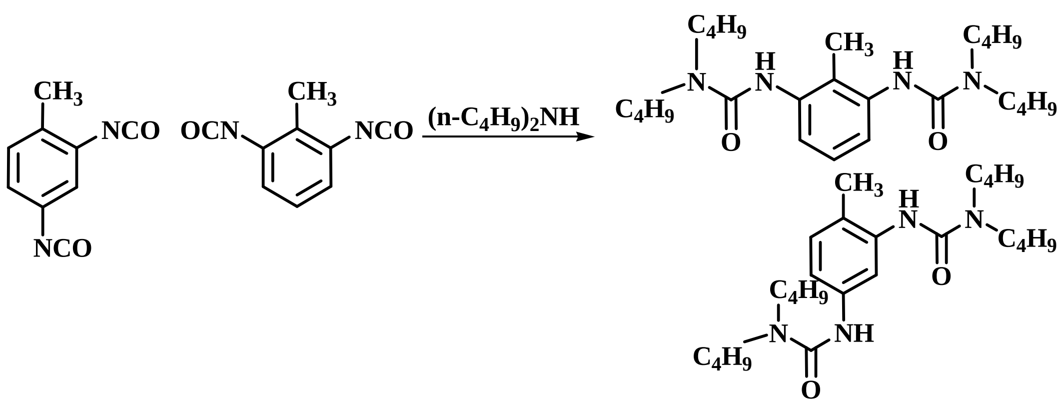
Where N_{HCl} is normality of HCl, W_{TDI} is weight of TDI

Keeping in mind the reactivity of active hydrogen of electronegative elements with NCO group, 2-phenylnaphthyl amine (Nonox D) was also tried as it contains one active hydrogen atom attached to nitrogen. The reactivity of aromatic amine with NCO group has also been studied by NMR technique[9] which elaborates the competitive reactivity of –NCO group with active hydrogen of different antioxidants by varying the NCO/OH ratio. Based on the above reactivity and NMR supported data, we have successfully estimated the purity of Nonox D using TDI.

In this method, first of all percentage purity of TDI was determined by reacting excess of dibutylamine followed by titration against standard hydrochloric acid using bromothymol blue as indicator. After confirming the percentage purity of TDI, the same TDI was used for the determination of purity of Nonox D. The excess of TDI first reacted with active hydrogen of Nonox D. The remaining TDI was then treated with excess of dibutylamine. It was further titrated against standard hydrochloric acid using bromothymol blue as indicator along with blank. The reaction scheme of TDI with Nonox-D as well as dibutylamine is as follows



SCHEME 1 : TDI reacts with Nonox-D



SCHEME 2 : TDI is further treated with dibutylamine

$$n\text{-}C_4H_9NH \xrightarrow{HCl} n\text{-}C_4H_9)_2NH^+{}_2Cl^-$$

SCHEME 3 : Dibutylamine is titrated against standard HCl

Based on the obtained data, the calculation of purity of Nonox- D is carried out as

1000mL of 1M Nonox D ≡ 87g of TDI or 174g of TDI ≡ 438g of Nonox-D or

1000mL of 1M TDI ≡ 438g of Nonox-D or 1mL of 1M TDI ≡ 0.438 g of Nonox-D

$$\%\ \text{purity of Nonox-D} \equiv \frac{(\text{Blank-Sample})*N\ HCl*0.438*100}{W\ \text{Nonox D}}$$

Where, N_{HCl} is normality of HCl, $W_{Nonox\ D}$ is weight of Nonox-D taken.

Further, the purity of Nonox-D was ascertained by using Aldrich make Nonox-D of known purity(>99.5%). The developed method was employed to determine the purity of Nonox D of Aldrich make along with ABR Organics and Surbhi make. The results obtained are presented in TABLE 1. It is clear from the TABLE 1 that purity of Aldrich is >99.5%. The sample of ABR Organics and Surbhi show the purity of Nonox-D is

TABLE 1 : Data on purity of Nonox-D of different source

Sl.No	Aldrich(%)	ABR organics(%)	Surbhi(%)
1	99.50	96.28	94.25
2	99.60	96.22	94.48
3	99.45	95.98	94.02
4	99.70	95.88	94.57
5	99.5	95.78	94.06

96% ±0.5% and 94%±0.5%, respectively, indicting better purity of ABR organics in comparison to Surbhi chemicals. The purity determination value of developed method was also cross checked by using gas chromatography for the same samples and data obtained are in the agreement of developed method. Furthermore, the developed method has already been included in the text of quality improvement and this method is being used as routine analysis of Nonox D to estimate its purity before use in propellant compositions.

CONCLUSION

A new method for the determination of purity of Nonox-D has been developed using TDI. The developed method is accurate and reliable. The tolerance limit of this method is ±0.5%. Moreover, the developed method does not need reference sample as advanced instrumental methods need. The developed method has also been included in the text of routine quality check of Nonox-D for the determination of its purity before use in propellant formulations

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