

Note

RAPID METHOD FOR ISOCYANATE PREPOLYMER EXAMINATION

KASEMSUKSAKUL Leck^{*}, SEKIKAWA Yoshiaki^{**}, KASIMURA Hideaki^{**}
YAGASAKI Kunihide^{**} and SHIMADA Masaru^{**}

^{*}Customs Laboratory Division, Thai Customs Department,
BKK 10900, THAILAND

^{**}Central Customs Laboratory, Ministry of Finance
531, Iwase, Matsudo - shi, Chiba - ken, 271, JAPAN

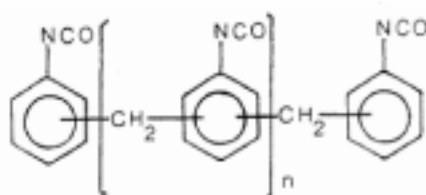
An appropriate analytical method for Customs purpose has been applied to analyze isocyanate prepolymer, by means of the Harmonized System. Thin layer chromatographic (TLC) - technique has been developed to separate the compositions of isocyanate prepolymer after being derivatized by 1 - (2 - pyridyl) piperazine. The suitable developing solvent is of a mixture of dichloromethane : acetone (1 : 1) as well as methyl acetate. The results showed good separation with six spots on TLC - plate. Study on gel - permeation chromatographic technique, using JAIGEL - 1H 600 X 200 mm. I.D. (2 pcs) pore size 10Å and chloroform as an eluent, also showed six peaks but gave poor resolution.

1 INTRODUCTION

The prepolymers by means of the Harmonized System are the products which are characterized by some repetition of monomer units although they may contain unreacted monomers. Prepolymers are not normally used as such but intended to be transformed into higher molecular weight polymers by further polymerization ⁽¹⁾.

Isocyanate prepolymers are extensively used in the manufacture of polyurethane. The most widely used is crude 4, 4' - diphenylmethane diisocyanate (MDI) or polymeric MDI which contains about 50% diisocyanate, usually largely the 4, 4 - isom -

er ; the remainder consists of the tri - , tetra - , penta - and hexa - polyisocyanates together with a small amount (10 - 20 %) of higher molecular weight polyisocyanates ⁽²⁾. The crude MDI or polymeric isocyanate is classified in subheading 3909. 50 of polyurethanes on the Harmonized Commodity Description and Coding System ⁽³⁾. The general



formular of polymeric MDI is ;

According to a new classification of the prepolymers on the Harmonized System, the suitable analytical method has necessary to be studied for the Customs purpose. The objective of this study is to investigate a simple and appropriate method to examine the isocyanate prepolymer by means of the Harmonized System. In this study, thin - layer chromatographic method has to be considered to separate the mixture of MDI, tri - , and their oligomers after being derivatized by 1 - (2 - pyridyl) piperazine. Besides, the other isocyanates such as tolylene diisocyanate (TDI) , hexamethylene diisocyanate (HMDI) , etc. can be determined. The reaction is as follows ⁽⁴⁾;



2 EXPERIMENT

2.1 Apparatus

1. Sprayer
2. Thin layer plates were of MERCK 10×20cm, 0.2mm highperformance thin - layer silica gel 60 (HP - TLC) and MERCK 10×20cm, 0.25mm silica gel 60 F 254, and activated by drying at 110 for 2h.
3. UV - lamp
4. One - microliter disposable micropipette was used throughout this study.
5. Developing chamber

2.2 Chemicals

All reagents, solvents and standard 4,4' - di,phenylmethane diisocyanate were of analytical grade, unless otherwise indicated. Isocyanate samples were provided from Nippon Urethane Service Company. All chemicals were used without further purification.

2.3 Procedures

1. Absorbing solution

1 - (2 -pyridyl) piperazine 0.28ml (1.8mmol) was pipetted into 3ml dichloromethane.

2. Iodoplatinate reagent

One hundred milliliters of 6 % m/v potassium iodide aqueous solution was added into 100ml 0.3% m/v chloroplatinic acid aqueous solution.

3. Standard isocyanate solution

4, 4' - Diphenylmethane diisocyanate 50mg (0.2 mmol) was dissolved in 5ml dichloromethane. The solution should be freshly prepared in order to avoid the polymerization reaction.

4. Isocyanate derivatives

The solution of 4, 4' - diphenylmethane diisocyanate 0.5ml was added into 0.5ml 1 - (2 - pyridyl) piperazine solution. The mixture was kept at 60 about 15min.

Theother isocyanate derivatives were prepared by mixing 0.5ml of isocyanate sample solutions (100 mg isocyanate sample in 0.5ml dichloromethane) and 0.5ml 1 - (2 - pyridyl) piperazine solution.

5. Separation of isocyanate derivatives on TLC
One microliter of the isocyanate derivatives or standard solutions to be analyzed were spotted by using disposable micropipette onto the TLC - plate. The spotted TLC plate was dried and kept in the developing chamber. The solvent front was run to a height of approximately 8 cm. The plate was then dried with a hot - air blowre. The spots were examined under UV - lamp and by forming the colour of iodoplatinate derivatives, by spraying the iodoplatinate solution onto the spotted TLC - plate. The derivatives and blank appear as dark purple and blue - green spots on a pink background.

3 RESULTS AND DISCUSSION

By TLC - technique, the mixture of MDI and their oligomers could not be directly separated because of the high polarity of isocyanate group, which strongly reacts with the silica gel. Therefore, the urea derivatives are suggested to improve the separation

technique. In this study, 1 - (2 - pyridyl) piperazine was appreciably considered to be a derivatizing agent since its reaction with both aliphatic and aromatic isocyanate is rapid and exothermic. In addition, the substituted ureas formed posses significantly high molar absorptivity in the UV wavelength region which is suitable to be analyzed

by UV - detector⁽⁵⁾. Table1 shows the samples list examined in this study.

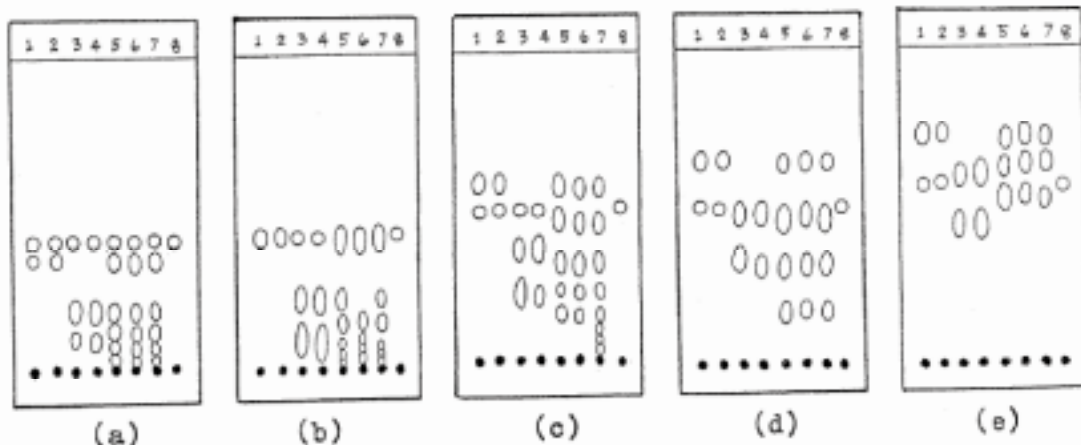
3.1 Separation of 1 - (2 - pyridyl) piperazine derivatives of isocyanates by TLC

The eluting solvent systems were studied for TLC - separation as shown in Table2. According

Table1 Samples list of isocyanates and polyisocyanates

symbol	chemical compositions		
T-80	TDI-mixture (tolylene diisocyanate)	2,4-TDI	80%
		2,6-TDI	20%
T-100		2,4-TDI	>95%
		2,6-TDI	< 5%
MT	MDI (4,4'-diphenylmethane diisocyanate)		
MR-200	crude-MDI		
	polymethylene polyphenyl polyisocyanate		
		n=0,	35-40%
		n=1,	-30%
		n=2,3,4,... poly,	remainder
C-1021	MR-200,T-80 mixture	MR-200	20%
		T-80	80%

() HP - TLC



() Ordinary TLC

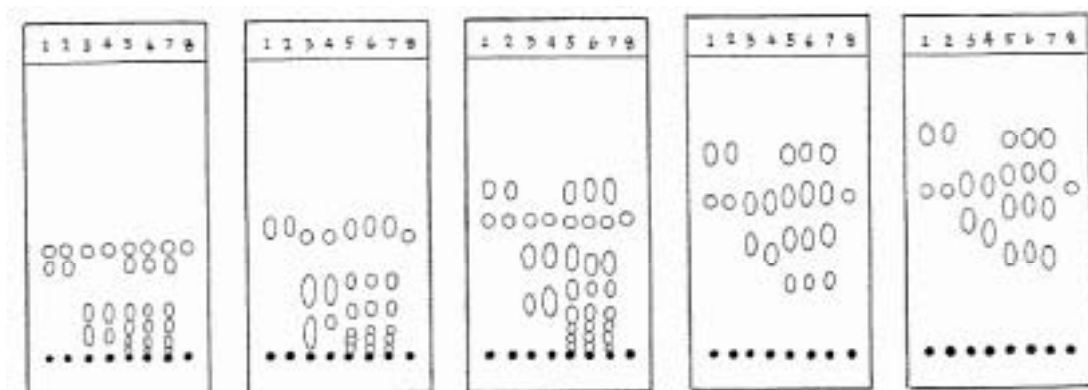


Fig. 1 Chromatograms of isocyanate urea derivatives on()HP - TLC and()ordinary TLC plates developed with dichloromethane : acetone solvent ;

(a)2 : 1 (b)1. 5 : 1 (c)1 : 1 (d)1 : 2 (e)1 : 3 ;

1 = standard, 4' - diphenylmethane diisocyanate, 2 = MT, 3 = T - 100, 4 = T - 80, 5 = C - 1021, 6 = MR - 200, 7 = PAPI (polymethylene polyphenylisocyanate), 8 = absorbing solution.

to the high polarity of the urea derivatives, the R_f values increase with an increase in the polarity of

the eluting solvent. In addition, the more higher polarity of eluting solvent, the more difficult to

Table 2 Eluting solvent systems examined

	solvent
1	dichloromethane-acetone
2	hexane-acetone
3	ethyl acetate-toluene
4	diethyl ether-dichloromethane
5	diethyl ether-propane-2-ol
6	toluene-ethyl methyl ketone
7	toluene-acetone-25%NH ₃
8	ethyl acetate
9	ethyl acetate-hexane
10	n-propyl alcohol
11	ethyl methyl ketone
12	methyl-isobutyl ketone
13	acetone
14	ethyl acetate-acetone
15	methyl formate
16	methyl acetate

separate the urea derivatives, are as shown by Fig. 1. moreover, the increasing in polarity of the eluting solvent, showed the streal of the sample spots.

Table3 and 4 showed the R_f values of crude MDI urea derivatives on HP - TLC and ordinary TLC using the eluting solvent of dichloromethane : ace - tone. The R_f values of the isocyanate urea derivatives on ordinary TLC is virtually equal to on HP - TLC so that polyisocyanate is possibly analyzed by ordinary TLC. According to the proportions of the mixture solvent to be studied in the experiment, dichloromethane : acetone ; 1 ; 1 gave the best separation with six spots, whereas the others gave the separation less than six spots and poor resolution. The isocyanates would not be removed from the starting point by

using the lower polarity of eluting solvent. In contrary, the isocyanates would not be separated even though those isocyanates were removed from the starting point by using higher polarity of eluting solvent. In Table4 also showed the separation of polyisocyanate by using a single solvent of methyl acetate which gave a good separation as mixture solvent.

The infrared spectrum of urea derivative is shown by Fig.2. The isocyanate functional group at wavenumber 2230cm^{-1} is disappeared whereas the urea functional group at 1600cm^{-1} is presence after being derivatized by piperazine. The resulting suggests that the reaction between isocyanate and 1 - (2 - pyridyl) piperazine is complete.

Table3 R_f values of crude MDI urea derivatives on HP - TLC

developing solvent proportion		R_f value					
dichloromethane : acetone							
2:1	0.33	0.17	0.11	0.11	0.05		
1.5:1	0.44	0.26	0.17	0.10	0.06		
1:1	0.56	0.41	0.32	0.23	0.15	0.10	
1:2	0.69	0.53	0.40	0.25			
1:3	0.71	0.60	0.46	0.31			

Table4 R_f values of crude MDI urea derivatives on ordinary TLC

developing solvent proportion		R_f value					
dichloromethane : acetone							
2:1	0.34	0.19	0.12	0.06			
1.5:1	0.43	0.22	0.15	0.09	0.05		
1:1	0.55	0.42	0.31	0.21	0.14	0.10	
1:2	0.65	0.47	0.33	0.17			
1:3	0.71	0.64	0.52				
methyl acetate	0.56	0.42	0.30	0.22	0.14	0.10	

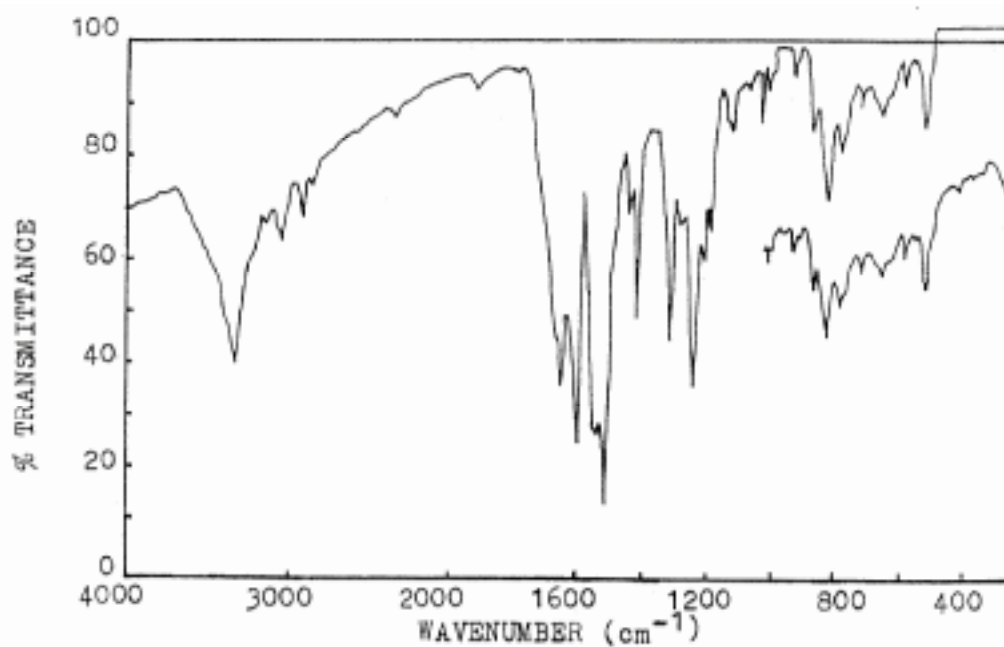


Fig.2 Infrared spectrum of MDI - 1 - (2 - pyridyl) piperazine urea derivative.

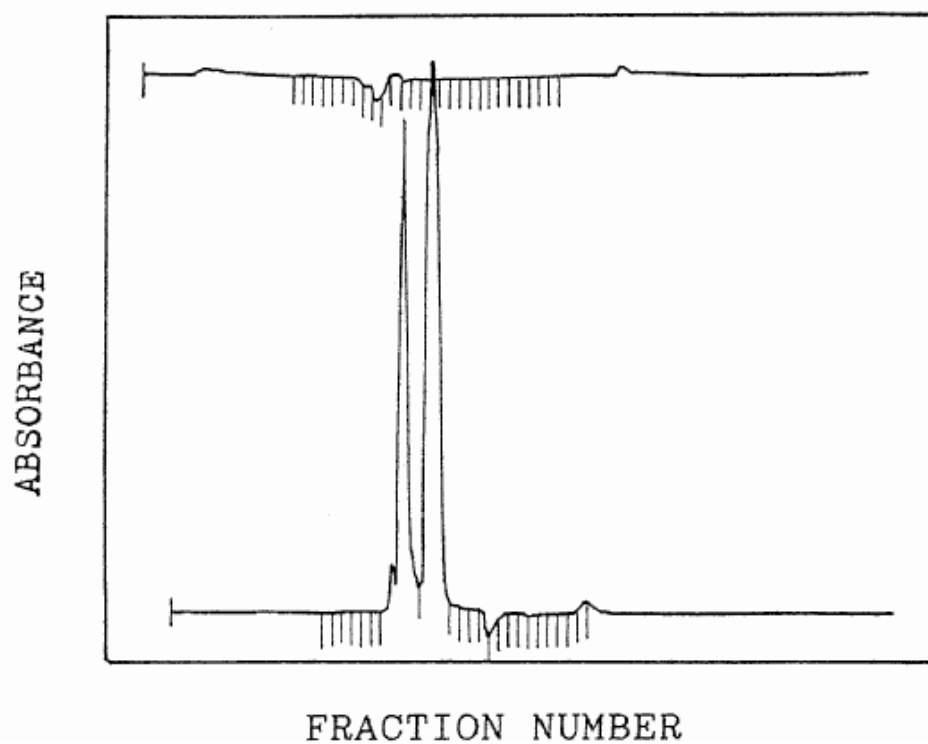


Fig.3 Gel permeation chromatogram of crude MDI.

Column, JAIGEL - 1H600X20 mm. I. D. (2 pcs), pore size 10A ; Eluent, CHCl₃ ; Sample, 5% 5 ml.

Detector, UV254 nm. and RI.

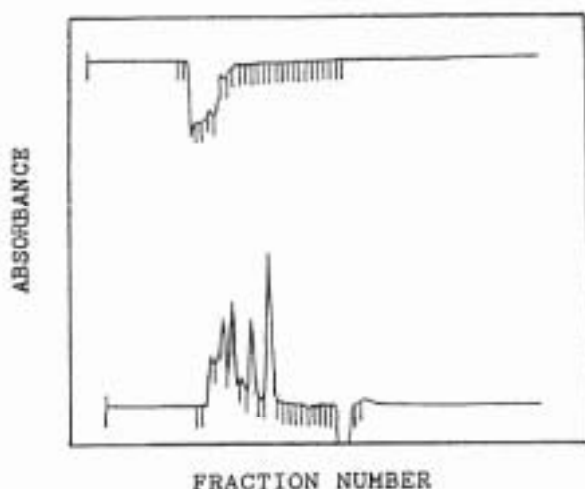


Fig.4 Gel permeation chromatogram of crude MDI - 1 - (2 - pyridyl) piperazine urea derivative.
Column, JAIGEL - 1H600X20mm. I.D.(2pcs), pore size 10Å ; Eluent, CHCl₃ ; Sample, 5%5 ml.
Detector, UV254nm.and RI.

3 , 2 Separation of isocyanates and polyisocyanates by gel permeation chromatography

For gel permeation chromatographic separation, it was found that underivatized isocyanates could not be separated because the chromatogram showed only two peaks as in Fig.3. However, after being derivatized, the polyisocyanates were separated to six peaks with poor resolution as shown by Fig. 4. It can be concluded that the pore size of the packing column is not suitable for those isocyanates. For improving the resolution, the recycle technique is suggested to be studied.

4 CONCLUSION

The TLC - technique has been developed to analyze the compositions of the isocyanate prepolymer, by means of the Harmonized system. Owing to the high polarity of isocyanate group, the mixture of MDI and their oligomeric could not be directly separated on TLC - plate. Therefore, the derivatization by 1 - (2 - pyridyl)piperazine is considerably applied to improve the separation.

1. The results showed good separation with six spots on TLC - plate, by using a suitable developing solvent of dichloromethane : acetone(1 : 1) as well as methyl acetate.
2. The R_f values of the compositions of MDI urea derivatives on ordinary TLC are virtually equal to HP - TLC so that the mixture of isocyanate prepolymer can be analyzed by ordinary TLC.
3. Separation on gel - permeation chromatography, using 600X200 mm. pore size 10 Å and chloroform as an eluent, also showed six peaks but gave poor resolution, whereas underivatized isocyanate prepolymer gave only two peaks. It would be concluded that the column was not suitable to separate the isocyanate prepolymer. The recycle technique is suggested to be studied to improve the resolution.

ACKNOWLEDGEMENT

The authors would like to express deeply gratitude to Mr. ISHIHARA Takuji and Mr. KUWATA

Shin - ichiro for access to laboratory facilities and encouragement during the course of the work. Greatful

acknowledgements also go to Central Customs Laboratory and Thai Customs Department.

REFERENCES

1. Harmonized Commodity Description and Coding System, Explanatory Notes.(1986). V2. Customs Co - poeration Council.
2. WOODS, G. Flexible Polyurethane Foams, Chemistry and Technology.(1982). Applied Science Publishers, London and New Jursey, 334p.
3. Letter of CCC. Reference 90. N. 453 - Fu/Fl. (1990) June, 5. Brussels.
4. ELLWOOD, P. A., H. L. HARDY and R. F. WALKER. (1981). Determination of Atmospheric Isocyanate Concentrations by High Performance Thin Layer Chromatograph Using 1 - (2 - pyridyl) piperazine Reagent. Analyst. Jan. V 106. 85 - 93.
5. GOLDBERG, P. A., R. F. WALKER, P. A. ELLWOOD and H. L. HARDY. (1981). Determination of Trace Atmospheric Isocyanate Concentrations by Reversed - Phase High performance Liquid Chromatograph Using 1 - (2 - pyridyl) piperazine Reagent. J. of Chromatogr. 212. 93 - 104.