

## CYANIDE FORMATION IN OXIME BLOCKED ISOCYANATES OF CATION ELECTRO- DEPOSITED PAINTS

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This paper describes the formation of hydrogen cyanide (HCN) in cation electro-deposited (CED) paints. Larger amounts of HCN were formed from all of the oxime blocked isocyanates. In order to elucidate the formation mechanism of HCN, labeled IPDI-AO (<sup>13</sup>C and <sup>15</sup>N) were synthesized, and then the presence of labeled cyanogen chloride (CNCl) was examined by GC-MS.

**KEY WORDS:** Isocyanates, oxime, electrodeposited paints, HCN formation.

### INTRODUCTION

Recently, cyanide ion was detected in wastewater and waste from various factories that do not handle any cyanide compounds<sup>1-4</sup>. Here we report the formation of hydrogen cyanide (HCN) in oxime blocked isocyanates which are used for cation electro-deposited paints. Various kinds of oximes such as methylethylketone oxime (MEKO), acetone

oxime (AO) and cyclohexanone oxime (CyHO) are used as blocking agents of isocyanate instead of alcohols and amines, because oximes are deblocked at low temperature. Although a cyanide compound is not incorporated into the oxime blocked isocyanate, HCN is often detected during the determination of total cyanide. Therefore, various kinds of isocyanates, oximes, blocked isocyanate with oximes, alcohols and amines, were examined as to their effect on the formation of HCN during the analytical distillation process. In order to elucidate the formation mechanism of HCN, labeled acetone oximes ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) were synthesized, and reacted with isophoronediiisocyanate (IPDI). After distillation, the presence of  $^{13}\text{CNCl}$  and  $\text{C}^{15}\text{NCl}$  was examined using GC-MS.

## EXPERIMENTAL METHODS

### *Apparatus and Reagents*

The same distillation equipment and reagents required by International Standard Organization (ISO) methods<sup>5</sup>, Standard Methods (SM) of the United State of America<sup>6</sup> and Japanese Industrial Standard (JIS)<sup>7</sup> were employed for the separation of total cyanide. All chemicals used were of the highest grade commercially available. The samples of isocyanates, oximes and oxime blocked isocyanates were obtained from Mitsubishi Kasei Corp. and Nippon Oil and Fat Co., Ltd., which were used without further purification.

### PROCEDURE

The total cyanide determination procedure is based on the ISO, SM and JIS methods. In order to investigate the formation of HCN, 1g of sample was added to the solution (ca. 250 ml) for distillation together with the agents and acid described in the three standardized reference methods. Distillation was carried out at a rather high temperature (higher than 100°C) and in highly acidic solution (lower than pH 2). The cyanide ion in the distillate was determined by the 4-pyridine carboxylic acid-pyrazolone method<sup>7</sup>. In order to confirm cyanide formation, distilled vapour was directed into a silver nitrate solution. The resulting precipitate was filtered and dried under reduced pressure. An X-ray diffraction pattern of the precipitate could confirm the presence of cyanide. AO( $^{13}\text{C}$ ) was reacted with labeled acetone ( $\text{CH}_3^{13}\text{COCH}_3$ ) and hydroxylamine, and also AO( $^{15}\text{N}$ ) was reacted with labeled hydroxylamine ( $^{15}\text{NH}_2\text{OH}$ ) and acetone. Labeled AOs ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) were reacted with IPDI. One-half gram of labeled IPDI-AO was distilled according to the JIS method. One ml of 1% chloramine-T solution was added to the 5 ml of distillate and 20 ml of citric buffer solution (pH 3), and then cyanogen chloride (CNCl) was determined by GC-MS.

## RESULTS AND DISCUSSION

### 1. Formation of HCN in paint related substances

The effects of isocyanate, oximes and oxime blocked isocyanates, alcohols and amines were examined using the three standardized reference methods such as the ISO, SM and JIS methods. The results are presented in Table 1.

Almost no HCN was formed from the isocyanates (HMDI, IPDI, TDI) using the three standardized reference methods. Small amounts of HCN were formed from the oximes such as MEKO, AO and CyHO, when tested using the SM and JIS methods. On the other hand, significant levels of HCN were formed from the oximes when tested by the ISO method. It is attributed to the cuprous ion, which is used as a reagent in the ISO method. We, therefore, considered that HCN formation is not observed from isocyanates and oximes, except when tested by the ISO method. Larger amounts of HCN were formed from all of the oxime blocked isocyanates using the three standardized reference methods. The difference in HCN amount between the different isocyanates might be due to their molecular weight and specific solubility in water. The formation of HCN in oxime blocked isocyanate was confirmed by the X-ray diffraction method. On the other hand, almost no HCN was formed from blocked isocyanate with butyl alcohol and diisobutyl amine moieties.

**Table 1** Formation of hydrogen cyanide in paint materials and oxime blocked isocyanates

Samples Isocyanate	Oxime	Taken (g)	Total cyanide (HCN) ( $\mu\text{g}$ )			X-ray Diffrac. AgCN
			JIS <sup>1)</sup>	Stand Methods <sup>1)</sup>	ISO <sup>2)</sup>	
(paint materials)						
HMDI		1.0	<0.5	1.0	<0.5	—
IPDI		1.0	0.9	<0.5	<0.5	—
TDI		1.0	<0.5	0.7	<0.5	—
	MEKO	1.0 <sup>3)</sup>	0.6	2.6	39.1	—
	AO	1.0 <sup>3)</sup>	0.9	3.0	81.9	—
	CyHO	1.0 <sup>3)</sup>	1.0	2.7	27.0	—
(oxime blocked isocyanates)						
HMDI-MEKO		1.0 <sup>3)</sup>	301.	267.	272.	Detected
IPDI-MEKO		1.0 <sup>3)</sup>	294.	280.	306.	Detected
IPDI-AO		1.0 <sup>3)</sup>	124.	171.	137.	Detected
IPDI-CyHO		1.0 <sup>3)</sup>	129.	43.6	57.4	—
TDI-MEKO		1.0 <sup>3)</sup>	78.3	48.2	233.	—
IPDI-BA		1.0 <sup>3)</sup>	1.1	3.5	0.5	Not Detected
IPDI-DIBA		1.0 <sup>3)</sup>	0.6	3.7	0.8	Not Detected

1) in 100 ml distillate;

2) in 25 ml distillate

3) dissolved in methyl alcohol

HMDI : Hexamethylenediisocyanate; IPDI : Isophoronediiisocyanate;

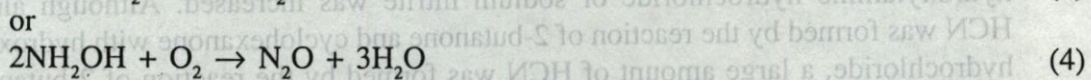
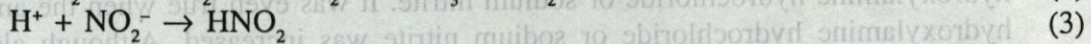
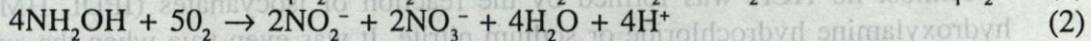
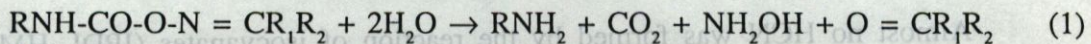
TDI : Tolylenediisocyanate;

MEKO : Methyleneethylketone oxime (2-Butanone oxime); AO : Acetone oxime;

CyHO : Cyclohexanone oxime; BA : Butyl alcohol; DIBA : Diisobutylamine

## 2. Reaction of paint related substances with $\text{NH}_2\text{OH}$ or $\text{NaNO}_2$

We assumed that oxime blocked isocyanate decomposed to isocyanate and ketone oxime during distillation, and subsequently isocyanate changed to an amine and carbon dioxide, and then the ketone oxime changed to hydroxylamine and a ketone. In addition, it was theorized that hydroxylamine was oxidized to nitrogen oxide such as nitrous acid or nitrous oxide. These reactions are shown as follows:



Therefore, we have investigated the reaction of isocyanates, ketones and amines with hydroxylamine hydrochloride or sodium nitrite according to the JIS method. The results are presented in Table 2.

Table 2 Formation of hydrogen cyanide by the reaction of paint materials and hydroxylamine or sodium nitrite

Sample	Taken amount (g)	(NH <sub>2</sub> OH)Cl (g)	NaNO <sub>2</sub> (g)	Total cyanide (HCN) (μg) <sup>1,2)</sup>
IPDI	1.0	0.1	-	1.4
		0.5	-	1.7
		1.0	-	1.9
IPDI	1.0	-	0.1	<0.5
		-	0.5	0.7
		-	1.0	0.8
HMDI	1.0	0.1	-	1.9
		0.5	-	2.3
		1.0	-	2.2
HMDI	1.0	-	0.1	2.9
		-	0.5	2.3
		-	1.0	4.8
2-Butanone (MEK)	1.0	0.1	-	<0.5
		0.5	-	<0.5
		1.0	-	<0.5
2-Butanone (MEK)	1.0	-	0.05	245.
		-	0.2	3720.
		-	0.5	5140.
Cyclohexanone	1.0	0.1	-	<0.5
		0.5	-	<0.5
		1.0	-	<0.5
Cyclohexanone	1.0	-	0.05	19.7
		-	0.2	69.6
		-	0.5	139.
IPDA	1.0	0.1	-	<0.5
		0.5	-	<0.5
		1.0	-	<0.5
IPDA	1.0	-	0.1	3.7
		-	0.5	21.0
		-	1.0	28.7
HMDA	1.0	0.1	-	<0.5
		0.5	-	<0.5
		1.0	-	<0.5
HMDA	1.0	-	0.1	<0.5
		-	0.5	12.7
		-	1.0	17.7

1) in 100 ml distillate

2) When precipitate is present in distillate, filter before determination

IPDI : Isophoronediiisocyanate; HMDI : Hexamethylenediisocyanate;

MEK : Methyl ethyl ketone;

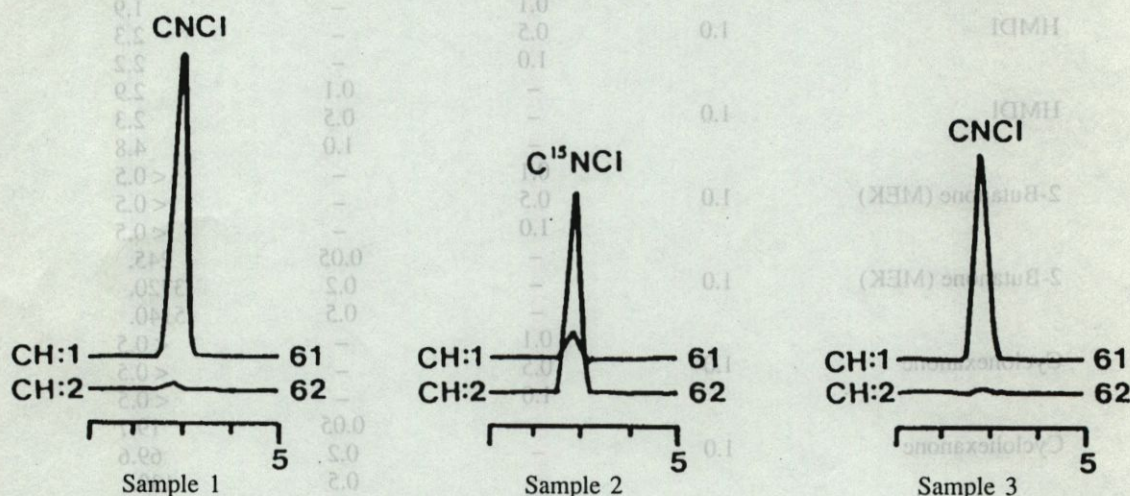
IPDA : Isophoronediamine; HMDA : Hexamethylenediamine;

Almost no HCN was formed by the reaction of isocyanates (IPDI, HMDI) and hydroxylamine hydrochloride or sodium nitrite. It was even true when the amount of hydroxylamine hydrochloride or sodium nitrite was increased. Although almost no HCN was formed by the reaction of 2-butanone and cyclohexanone with hydroxylamine hydrochloride, a large amount of HCN was formed by the reaction of 2-butanone and cyclohexanone with sodium nitrite.

In addition, almost no HCN was formed by the reaction of isophoronediamine (IPDA) and hexamethylenediamine (HMDA) with hydroxylamine hydrochloride. However, a small amount of HCN was formed by the reaction of amines (IPDA, HMDA) with sodium nitrite.

### 3. GC-MS analysis of labeled IPDI-AO

The reason why HCN is formed from oxime blocked isocyanates was further investigated. In order to elucidate the formation mechanisms of HCN from oxime blocked isocyanates, labeled IPDI-AO ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) was synthesized and then the presence of labeled CNCl was examined by GC-MS. The results are shown in Fig. 1.



**Figure 1** GC-MS analysis of labeled IPDI-AO.

Sample 1 :  $\text{RNH-CO-O-N} = ^{13}\text{C}(\text{CH}_3)_2$ ,

Sample 2 :  $\text{RNH-CO-O-}^{15}\text{N} = \text{C}(\text{CH}_3)_2$ ,

Sample 3 :  $\text{RNH-CO-O-N} = \text{C}(\text{CH}_3)_2$

Instrument : Shimadzu GC-MS QP-1000, Column : Porapak QS 80-100 mesh

3 mm $\phi$  x 1 m glass tube, Injection temp.: 200°C, Column temp.: 80°C,

Ion source temp.: 250°C, Separator temp. : 250°C, Carrier gas : 40 ml/min

Mass number : m/z 61 (CNCl), m/z 62 ( $^{13}\text{CNCl}$  or  $^{15}\text{CNCl}$ )

$^{13}\text{CNCl}$  was not produced from  $^{13}\text{C}$ -labeled IPDI-AO (sample 1), which was labeled at the carbonyl group of the acetone, therefore, it is assumed that the carbon in CNCl does not originate from acetone.  $^{15}\text{CNCl}$  was produced from  $^{15}\text{N}$ -labeled IPDI-AO (sample 2), which was labeled at the amino group of the  $\text{NH}_2\text{OH}$ , therefore, the nitrogen in  $^{15}\text{CNCl}$  originated from the hydroxylamine. Sample 3 is a IPDI-AO reference, which is not labeled.

#### 4. Formation mechanism of HCN

The formation mechanism of HCN in oxime blocked isocyanates during the analytical process is proposed as follows:

- (1) The ketone oxime, which is a blocking agent of isocyanate, is decomposed to hydroxylamine and ketone in the acidic solution during distillation. Hydroxylamine is further oxidized to nitrogen oxides such as nitrous acid or nitrous oxide by air during distillation. Therefore, nitrogen oxides react with the ketone or amine to form HCN.
- (2) It is thought that hydroxylamine, which is a decomposition product from ketone oxime, reacts with organic compounds such as ascorbic acid which is used as reducing agent<sup>7,8</sup>, to form HCN.
- (3) Oxime blocked isocyanate is rearranged in a molecule during distillation, and then cleaved to form HCN. However, the reaction mechanism has not been clarified yet. This is being further investigated.

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