

# Diethyl Ketone-Based Imine as Efficient Latent Hardener for Epoxy Resin

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**ABSTRACT:** Several imines were synthesized and evaluated as water-initiated hardener for epoxy resin. Imines with a lower electron density on the C=N carbon showed a faster hydrolysis rate. Diethyl ketone-based imines were the most efficiently hydrolyzed among the imines examined, and the adhesive properties of epoxy resin with diimines used as the hardeners were evaluated. A novel diethyl ketone-based diimine, *N,N'*-di(1-ethylpropylidene)-*m*-xylylenediamine (10), served as an efficient latent hardener of epoxy resin. Epikote 828 containing 10, filler, and dryer increased the adhesive strength faster than Epikote 828 containing filler and dryer with methyl isobutyl ketone-based imine. The mixed system of epoxy resin and 10 showed good storage stability at room temperature. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1744–1749, 2002

**Key words:** diethyl ketone; imine; adhesive; one-component epoxy resin

## INTRODUCTION

Epoxy resin is widely used in coatings, paintings, and adhesives because of its good mechanical strength and chemical resistance.<sup>1</sup> Epoxy resin is commonly cured by mixing two components: reactive resin and hardeners (catalysts). It is desirable to develop one-component systems using “latent hardeners,” which show no activity under normal conditions but do with external stimulation such as heat and photo irradiation. We have developed several onium salts, aminimides, car-

boxylates, sulfonates, phosphonates, and phosphonium ylides as latent thermal initiators and photoinitiators.<sup>2–4</sup> Although heat and photoirradiation are the external stimulations most commonly used, there are some cases where using atmospheric water as the stimulation is necessary to achieve one-component epoxy resin. The candidates for water-stimulated latent hardeners are imines,<sup>5</sup> oxazolidines,<sup>6</sup> enamines,<sup>7</sup> and silylamines,<sup>8</sup> all of which release amines as the initiating species. Among these compounds, imines that can be easily synthesized attract much attention, but only a few imines have been industrialized as hardeners so far. The main reason for this is the slow hydrolysis rate, which is inappropriate for practical use. The application of one-component imine-curing epoxy resin to adhesives

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may be especially difficult because of the small area that comes in contact with the atmospheric water. This article deals with novel imines showing a fast hydrolysis rate and with the adhesive property and storage stability of epoxy resin that contains imines as hardeners.

## EXPERIMENTAL

### Measurements

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded on a JEOL EX-400 at 27°C, using tetramethylsilane as an internal standard in  $\text{CDCl}_3$ . Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One (Yokohama, Japan). Mass spectra were recorded on a Shimadzu GCMS-QP5050A (Kyoto, Japan). Hydrolysis rates of imines were evaluated by gas chromatography (GC) on a GL Science GC-390B (Tokyo, Japan). Adhesive strength was measured with a Shimadzu Autograph AG-50kNG. Viscosity was measured with a Toki Sangyo RB-80-H (Tokyo, Japan).

### Materials

Benzene was dried and distilled by the usual method and stored over molecular sieves (4A) before use. All the monoamines, the ketones, and phenylisocyanate were obtained from Tokyo Kasei Kogyo, Tokyo, and used without further purification. Bisphenol-A-type epoxide oligomer (Epikote 828) was obtained from Yuka Shell Epoxy (Tokyo, Japan). *m*-Xylylenediamine was obtained from Mitsubishi Gas Chemical (Tokyo, Japan). Fillers NS100, MS700, and RY200S were obtained from Shiraishi Calcium (Amagasaki, Japan), Maruo Calcium (Akashi, Japan), and Nihon Aerogel (Tokyo, Japan), respectively. A dryer KBM403 was obtained from Shin-etsu Chemical (Tokyo, Japan).

### Synthesis of Imines

#### Typical Procedure

A solution of an amine (30 mmol) and a ketone (20 mmol) in hexane (100 mL) was refluxed for a day, removing water by azeotropic distillation with a Dean-Stark trap.<sup>9</sup> After that, hexane and an excess amount of amine were removed by rotary evaporation. The residue was distilled under a reduced pressure to obtain the corresponding

imine. Diimines were prepared by refluxing *m*-xylylenediamine (1 mol) and a ketone (4 mol) for 3 days. After that, phenylisocyanate was added to the reaction mixture and the resulting mixture was heated at 40°C for 2 h to block the residual amino groups of the product. To the residual amino group, which was determined by gas chromatography (GC), 1.5 equivalent of phenylisocyanate was used.

*N*-(1-ethylpropylidene)benzylamine (**1**): yield, 2.92 g (83.5%); boiling point (b.p.), 81°C/2 mmHg; IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.94–1.15 (m, 6H), 2.26–2.38 (m, 4H), 4.55 (s, 2H), 7.18–7.32 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.71, 24.15, 32.23, 53.88, 126.20, 127.34, 128.33, 140.73, 175.92. Mass spectrum: *m/e* 175 ( $\text{M}^+$ ).

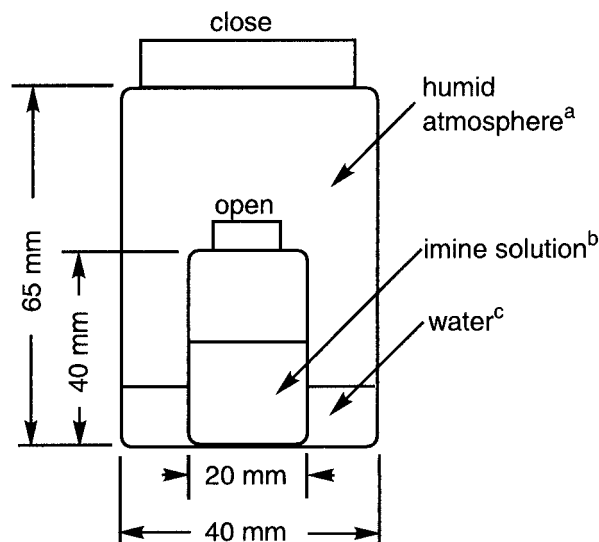
*N*-(1-ethylpropylidene)butylamine (**2**): yield, 2.24 g (79.6%); b.p., 73°C/27 mmHg; IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm), 0.93 (*t*,  $J = 7.2$  Hz, 3H), 1.05–1.10 (m, 6H), 1.32–1.41 (m, 2H), 1.56–1.63 (m, 2H), 2.19–2.28 (m, 4H), 3.29 (*t*,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 11.03, 13.87, 20.60, 23.47, 32.58, 33.29, 50.19, 174.49. Mass spectrum: *m/e* 141 ( $\text{M}^+$ ).

*N*-(1-ethylpropylidene)-2-methylpropylamine (**3**): yield, 2.07 g (73.4%); b.p., 65°C/28 mmHg; IR (KBr), 1664  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.92 (*t*,  $J = 3.4$  Hz, 6H), 1.02–1.10 (m, 6H), 1.90–1.94 (m, 1H), 2.18–2.27 (m, 4H), 3.10 (*d*,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.62, 20.56, 23.64, 29.78, 32.47, 58.29, 174.15. Mass spectrum: *m/e* 141 ( $\text{M}^+$ ).

*N*-(1-propylbutylidene)butylamine (**4**): yield, 2.76 g (81.6%); b.p., 83°C/12 mmHg; IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.90–0.97 (m, 9H), 1.33–1.60 (m, 8H), 2.15–2.19 (m, 4H), 3.29 (*t*,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 13.88, 14.27, 19.81, 20.22, 32.74, 33.33, 42.22, 50.41, 172.57. Mass spectrum: *m/e* 169 ( $\text{M}^+$ ).

*N*-(1-methylpropylidene)butylamine (**5**): yield, 1.81 g (71.2%); b.p., 63°C/34 mmHg; IR (KBr), 1660  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.98 (*t*,  $J = 8.0$  Hz, 3H), 1.11 (*t*,  $J = 8.2$  Hz, 3H), 1.32–1.41 (m, 2H), 1.56–1.1.63 (m, 2H), 1.80 and 1.98 (s, 3H), 2.19–2.27 (m, 2H), 3.22 (*t*,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.87, 13.83, 16.38, 20.58, 32.89, 35.58, 50.25, 170.27. Mass spectrum: *m/e* 127 ( $\text{M}^+$ ).

*N*-(1,3-dimethylbutylidene)butylamine (**6**): yield, 2.50 g (80.6%); b.p. 63°C/11 mmHg; IR (KBr), 1659  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.88–0.93 (m, 9H), 1.32–1.38 (m, 2H), 1.55–1.65 (m, 2H), 1.77 and 1.96



**Figure 1** Hydrolysis condition of imine. (a) >99%RH; (b) 0.5 mol/L solution in benzene, 5.0 mL; (c) 5.0 mL.

(s, 4H), 2.10 (*d*,  $J = 6.8$  Hz, 2H), 3.23 (*t*,  $J = 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 13.82, 16.98, 20.62, 22.28, 26.05, 32.87, 40.86, 50.98, 51.74, 168.73. Mass spectrum:  $m/e$  155 ( $\text{M}^+$ ).

*N*-(1,2-dimethylpropylidene)benzylamine (**7**): yield, 2.96 g (84.7%); b.p., 95°C/4 mmHg; IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.15 (*d*,  $J = 6.8$  Hz, 6H), 1.86 (s, 3H), 2.55–2.62 (m, 1H), 4.50 (s, 2H), 7.23–7.34 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 14.97, 19.49, 40.11, 54.60, 126.29, 127.46, 128.44, 140.70, 175.04. Mass spectrum:  $m/e$  175 ( $\text{M}^+$ ).

*N*-(1,2-dimethylpropylidene)butylamine (**8**): yield, 1.83 g (64.8%); bp, 65°C/26 mmHg; IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.91–0.96 (m, 3H), 1.03–1.08 (m, 6H), 1.31–1.41 (m, 2H), 1.55–1.63 (m, 2H), 1.74 and 1.90 (s, 3H), 2.43–2.50 (m, 1H), 3.23 (*t*,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 13.89, 19.72, 20.60, 32.89, 40.04, 50.79, 173.32. Mass spectrum:  $m/e$  141 ( $\text{M}^+$ ).

*N*-(1-ethylpropylidene)-1-methylpropylamine (**9**): yield, 2.29 g (65.4%); bp, 64°C/35 mmHg; IR (KBr), 1662  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.91 (*t*,  $J = 8.4$  Hz, 3H), 1.03–1.11 (m, 9H), 1.44–1.52 (m, 2H), 2.16–2.27 (m, 4H), 3.39 (*t*,  $J = 6.6$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.89, 11.40, 21.62, 23.11, 30.90, 32.69, 55.46, 172.41. Mass spectrum:  $m/e$  141 ( $\text{M}^+$ ).

*N,N'*-di(1-ethylpropylidene)-*m*-xylylenediamine (**10**): yield, 255.1 g (93.8%); IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.03–1.15 (m, 12H), 2.33 (m, 8H), 4.56 (s, 4H), 7.16–7.28 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.76, 24.11,

32.58, 53.94, 125.46, 126.60, 128.12, 140.59, 175.94. Mass spectrum:  $m/e$  272 ( $\text{M}^+$ ).

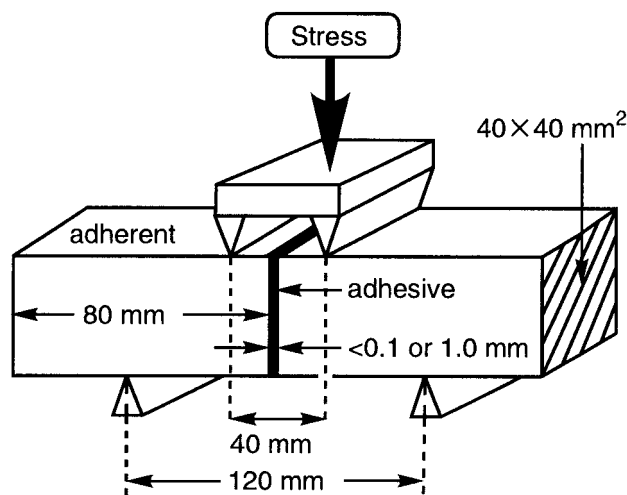
*N,N'*-di(1,3-dimethylbutylidene)-*m*-xylylenediamine (**11**): yield, 287.1 g (95.7%); IR (KBr), 1663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.91–0.97 (m, 12H), 1.86–2.10 (m, 8H), 2.20 (m, 4H), 4.48 (s, 4H), 7.21–7.31 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 17.75, 22.47, 26.51, 50.67, 55.05, 126.32, 127.64, 128.23, 140.51, 170.65. Mass spectrum:  $m/e$  300 ( $\text{M}^+$ ).

### Formulated One-Component Epoxy Resin with Fillers and Imines

One-component epoxy resin was compounded as follows: Epikote 828 (100 g), calcium carbonate (NS100 [120 g] and MS700 [60 g]), and silica (RY200S, 7.5 g), as fillers, were mixed at 100°C under reduced pressure for 2 hours by an Inoue Seisakusho PML-5L (Yokohama, Japan). After cooling to room temperature, an imine and KBM-403 ( $\gamma$ -glycidoxypolytrimethoxysilane, 40 g), as a dryer, were added to the mixture, and the resulting resin was further kneaded for 1 hour under  $\text{N}_2$  atmosphere.

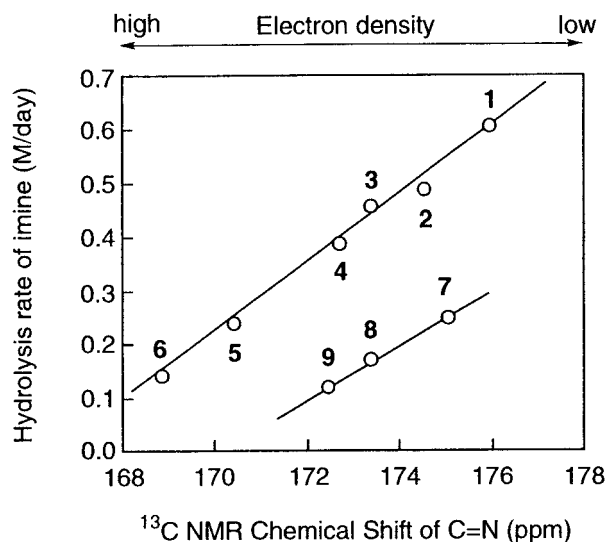
### Measurement of Hydrolysis Rate of Imines

An imine solution in benzene (0.5 mol/L) was placed under conditions of high humidity (>99%RH) at 20°C (Fig. 1), where the amount of water in the imine solution was <0.08 mol/L (16 mol% for imine), which was measured by a Hiranuma AQ-6 aquacounter (Mito, Japan) (Karl Fischer's method). The hydrolysis of imine was monitored by GC analysis, using naphthalene as



**Figure 2** Schematic diagram of bending test.





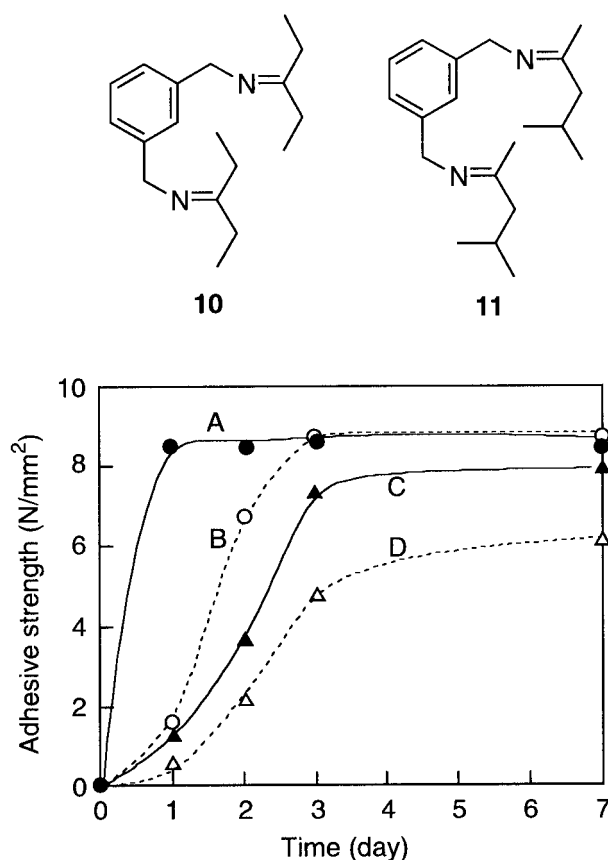
**Figure 4** Relationship between hydrolysis rates at 20°C and  $^{13}\text{C}$  NMR chemical shifts of C=N of imines. 1–9 are accorded with Table I.

conversion plots, along with the  $^{13}\text{C}$  NMR chemical shifts of the imine carbon atoms. Imines 1, 2, 3, and 4 prepared from diethyl and dipropyl ketones were hydrolyzed faster than industrially used imines 5 and 6.

Scheme 1 illustrates a proposed mechanism of imine hydrolysis.<sup>10</sup> The rate-determining step is step 1, where water attacks the C=N group to form an N, O-hemiacetal. Step 1 is a nucleophilic reaction, so this step would preferably take place as the electron density of C=N decreases.  $^{13}\text{C}$  NMR chemical shifts commonly increase as the electron densities decrease in a series of analogous compounds. Figure 4 depicts the relationship between the  $^{13}\text{C}$  NMR chemical shifts of C=N and the hydrolysis rates of imines 1–9. Imines 1–6 and 7–9 showed good linear relationships, indicating clearly the increase of hydrolysis rate as the chemical shift. It was suggested that an imine with a lower electron density on the C=N carbon would show a faster hydrolysis rate. The smaller hydrolysis rates of imines 7–9 compared with those of 1–6 would be responsible for the presence of bulky isopropyl or sec-butyl group adjacent to the C=N group, which may hinder the  $\text{H}_2\text{O}$  attack on the C=N group.

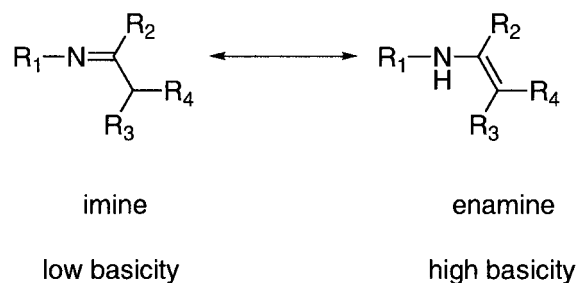
#### Adhesive Properties of One-Component Epoxy Resin

A diamine can give cured epoxy resin with mechanical strength better than a mono-amine as a



**Figure 5** Adhesive strength of Epikote 828 containing 50 mol% 10 or 11, filler (NS100: 120 g, MS700: 60 g, RY200S: 7.5 g were contained in Epikote 828: 100 g.) and dryer (KBM403: 40 g was contained in Epikote 828: 100 g) at 25°C and 50%RH [(A) 10 with an adhesive thickness of  $<0.1\text{ mm}$ , (B) 10 with an adhesive thickness of 1.0 mm, (C) 11 with an adhesive thickness of  $<0.1\text{ mm}$ , (D) 11 with an adhesive thickness of 1.0 mm).

hardener because the former provides a crosslinked structure. We examined the adhesive strength of epoxy resin cured with diimines derived from diethyl and methyl isobutyl ketone. The resin containing diethyl ketone-based imine



**Scheme 2**



**Table II Storage Stability of Epikote 828 Containing 50 mol% of 10 or 11, Filler<sup>a</sup> and Dryer<sup>b</sup>**

Adhesive	Viscosity (mPa/s)	
	Before Storage	After Storage <sup>c</sup>
With10	12,000	13,000 (108%)
With11	11,800	13,200 (112%)

<sup>a</sup> NS100: 120 g, MS700: 60 g, RY200S: 7.5 g were contained in Epikote 828: 100 g.

<sup>b</sup> KBM403: 40 g was contained in Epikote 828: 100 g.

<sup>c</sup> Storage at 25 °C for 1 month.

10 increased the adhesive strength faster than that with methyl isobutyl ketone-based imine 11 (Fig. 5), which result agreed with the hydrolysis experiment of the corresponding monofunctional imines. The lower adhesive strength of samples C and D, compared with that of samples A and B, may be because of incomplete epoxy conversion caused by the lower activity of imine 11 compared with that of iminie 10. It was confirmed that diethyl ketone-based imine 10 served as an efficient latent hardener of epoxy resin. The amount of applied adhesive was larger in the sample with an adhesive thickness of 1.0 mm than in that with a thickness of <0.1 mm. Consequently, its being permeated by water required more time, resulting in the slower increase of the adhesive strength of the sample with an adhesive thickness of 1.0 mm than that with a thickness of <0.1 mm.

#### Storage Stability of One-Component Epoxy Resin

Although an imine exhibits basicity much lower than an amine, it also exists as an enamine, the

tautomer with basicity larger than an imine (Scheme 2).<sup>11</sup> Therefore a one-component epoxy resin using imine as a hardener has the possibility of curing or increasing the viscosity during storage. Epikote 828 containing 50 mol% of 10 or 11, filler, and dryer was kept at 25°C for 1 month to examine the storage stability. The viscosity slightly increased during this period (Table II), causing no problem for practical usage.

In summary, we developed novel diethyl ketone-based imines efficiently undergoing hydrolysis, as compared with methyl isobutyl-based ones, commercially utilized as water-initiated hardener for epoxy resin. One-component epoxy resin containing a bifunctional diethyl ketone-based imine showed good adhesive property and storage stability.

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