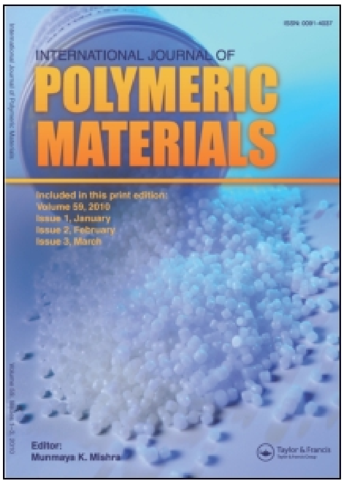

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Synthesis, characterization, and coating application of novel polyamines

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SYNTHESIS, CHARACTERIZATION, AND COATING APPLICATION OF NOVEL POLYAMINES

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A series of novel polyamine resins were synthesized by the preparation of ketimine terminated resins from ketimine blocked diethylene triamine (I) and bisester derivative (II) of epoxy resin and subsequent hydrolysis. ***I*** *was synthesized by the condensation reaction of diethylene triamine with methyl isobutyl ketone.* ***II*** *was synthesized by the reaction of epoxy resin (DGEBA) with amino ethyl benzoate (AEB). The hydrolysis of ketimine containing resin was evaluated by the change in pH value of the reaction mixture, and by infrared spectroscopy and Gel Permeation Chromatography of the resulting product. The thermal stability and coating properties of the synthesized polyamines were studied in some detail. The hydrolytic rate of ketimine increased with increase temperature or the amount of added acid.*

Keywords: epoxy resin, polyamine, thermal stability, infrared spectroscopy

INTRODUCTION

Epoxy resins are widely used because of their excellent adhesion and chemical and atmospheric corrosion resistance. Generally, the crosslinking agents for epoxy resin can be divided into two types. The first cures through the secondary hydroxy groups in the epoxy resin backbone, such as melamine/formaldehyde [1], benzoquamine/formaldehyde [2] and urea/formaldehyde [3] resins. The second type cures the epoxy groups of epoxy resin by an addition reaction, such as with diamines or polyamines. The diamines typically used include *m*-phenylene diamine, 4,4′-diaminodiphenylsulfone and 4,4′-diaminodiphenyl methane [4–6].

The reaction of the epoxy ring with amines and alcohols is well established [7] and hence the reaction of epoxy resin with aminoethyl

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benzoate may yield the bisester derivatives which are then reacted with ketimine blocked diethylene triamine to give ketimine terminated resin which can be easily hydrolyzed to give polyamine resin.

In this paper, the hydrolysis of ketimine terminated resin and coating properties of polyamines were studied in some detail.

EXPERIMENTAL

Materials

Amino ethyl benzoate was obtained from SDS chemicals, Boisar, India. All other chemicals used were of laboratory grade. Commercial epoxy diglycidyl ether of bisphenol-A (DGEBA) and Triglycidyl *p*-amino phenol (TGPAP) were obtained from Synpol Products Pvt. Ltd., Ahmedabad, India.

The specifications of DGEBA are as follows:

(1) Epoxy equivalent weight: 190
(2) Viscosity at 25°C: 40–10 poise
(3) Density at 25°C: $1.16-1.17\,\mathrm{g\,cm^{-3}}$

The specifications of TGPAP are as follows:

(1) Epoxy equivalent weight: 210
(2) Viscosity at 25°C: 40–10 poise
(3) Density at 25°C: $1.16-1.17\,\mathrm{g\,cm^{-3}}$

(A) Ketimine Blocked Diethylene Triamine (I)

0.463 mole diethylene triamine (DETA) (47.7 gm), 1.12 mole methyl isobutyl ketone (MIBK) (112 gm) and 250 ml benzene were heated at 60°C in a 500 ml three-necked flask equipped with an electric stirrer and reflux condenser. After cooling, the benzene was distilled under reduced pressure. The obtained di(2-methylisobutyketiminoethyl) amine was purified by distillation at 118–120°C. The product was a colorless liquid at room temperature.

(B) Bisester Derivative of Epoxy Resin (IIa–c)

A mixture of amino ethyl benzoate (2 mol), DGEBA (1 mol) and triethyl amine (0.5 ml) was heated at 60–65°C, for 8 hours. The resulting mixture was poured into a large amount (250 ml) of dry ether. The ether was decanted and the viscous liquid was again washed with dry ether (2 × 100 ml) to remove unreacted amino ethyl benzoate and DGEBA. The dark brown viscous liquid was then vacuum distilled to remove remaining solvent species.

Polymerization

(A) Ketimine Terminated Resin (IIIa – c)

100 gm (IIa – c) and 150 gm toluene were heated at 90 – 95°C in a five necked flask equipped with an electric stirrer, dropping funnel and an inert nitrogen blanket. The water was removed by toluene azeotropic distillation. The azeotropic distillation was continued until no further evolution of water was observed. After cooling at 60°C, a calculated amount of I was added into the flask. The whole reaction mixture was heated at 80 – 85°C for 3 hours. Finally, toluene was distilled under vacuum (0.5 mm) to obtained resin IIIa – c.

(B) Polyamine (IVa – c)

20 gm water were added to 100 gm of 50 wt% toluene solution of resin IIIa – c. The mixture was stirred at room temperature for 1 hour. Then toluene, water and MIBK were distilled under reduced pressure. At room temperature compound IVa – c are viscous liquids.

Measurements

The C, H and N contents of sample were estimated by means of Carlo Erba elemental analyzer (Italy). The IR spectra were taken on Nicolet Impact 400D spectrophotometer. Thermogravimetry (TG) of all polymer samples was carried out on Dupont 951-thermogravimetric analyzer in air, at heating rate of 10 K min^{-1}.

Coating on Mild Steel Panels

Coating compositions were prepared by combination of epoxy resin (DGEBA and TGPAP) and three polyamines in three different ratio *viz.* 60 : 40, 70 : 30 and 80 : 20. The compositions were then thinned with methanol methyl cellosolve mixture (1 : 3) to the required viscosity for application and were freed from coarse skin by passing through 150 μm sieve (IS: 460-1960). All resin systems were then coated on the mild steel panel (confirming to deep drawing quality as per IS: 384-1964). The coated mild steel panels were placed in vertical position for drying immediately; then examined after specific time intervals for the tack-free test and cured thermally.

Characterization of Mild Steel Panels

The film was applied on mild steel panels (6″ × 4″) and mechanical properties were studied as per Indian Standard Specification [8], in which mechanically operated "Sheen" scratch hardness tester was employed where the hardened needle loaded with weight moves over the dried film applied on a panel. In this method, panels were prepared by application of resin mixture on mild steel panel which were allowed to dry for a specific period (48 hours) and was fixed on a sliding base. A counter-balanced pivoted arm is fixed over the slide and on one end of this arm a needle is attached which has hemispherical shaped end. This arm is lowered in such a manner that the needle-end touches the resin film surface vertically. A known weight was put over the needle and the sliding base is moved so that the needle moves on the surface of dried resin film. The weight on the needle was incrementally increased and the process repeated until a stage is reached where the movement of the needle cuts a groove in the resin film and the mild steel panel is exposed. The minimum weight that causes this was referred to as scratch hardness of the resin film. The values in impact strength were arrived by multiplying weight of indenter in lb. (6.25 lb.) with maximum height in inches from where the indenter falls without any visible damage to the films.

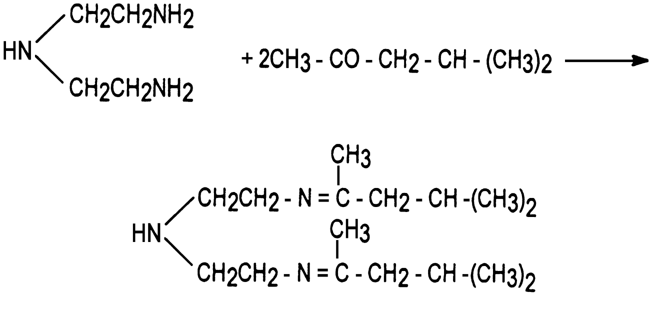
The flexibility was measured using 1/4″ and 1/8″ conical mandrel. Here, the test sample was applied on a mild steel panel and allowed to dry for 48 hours. The panel was then put under a mandrel of a specific diameter with the resinous side of the panel touching the mandrel. The panel was then given a bend 180°C in one second and removed. The resin film is examined at the place of bend and if any cracks appear it is concluded that the resin film has poor flexibility.

Resistance towards water, acid, alkali and organic solvents were determined as per a standard method described in the literature [9]: coated panels were dipped separately at room temperature in distilled water, 5% sulfuric acid solution, 5% sodium hydroxide solution and in acetone. The samples were taken out at regular intervals, washed with distilled water (except the panels dipped in solvent), air-dried and checked for appearance.

RESULTS AND DISCUSSION

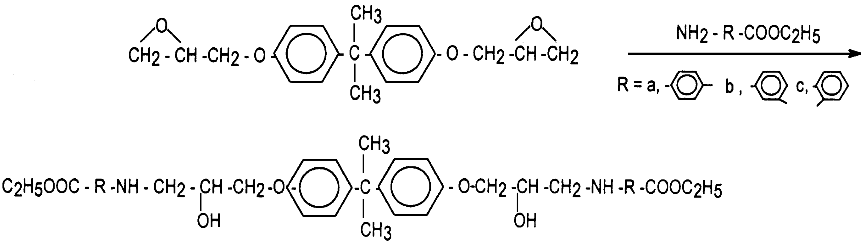
Polyamine resins were synthesized by the reaction of the ketimine blocked diethylene triamine I with bisester derivative of epoxy resin IIa–c and subsequent hydrolysis of the resulting resin. As shown in Scheme 1, diethylene triamine first reacted with MIBK to form the primary amine protected triamine I. As shown in Scheme 2, amino ethyl benzoate (AEB) reacted with epoxy resin (DGEBA) to form bisester derivative of epoxy resin IIa–c which subsequently reacted with I to give ketimine terminated resin IIIa–c as shown in Scheme 3. IIIa–c can be easily hydrolyzed to give polyamine resin IVa–c as shown in Scheme 4.

The hydrolysis reaction of compounds of I and IIIa–c were evaluated by IR spectra, GPC curves and changes of pH value of the reaction mixture. Figure 1 shows; the IR spectra of IIIa and its hydrolysis products IVa. It can



(I)

SCHEME 1

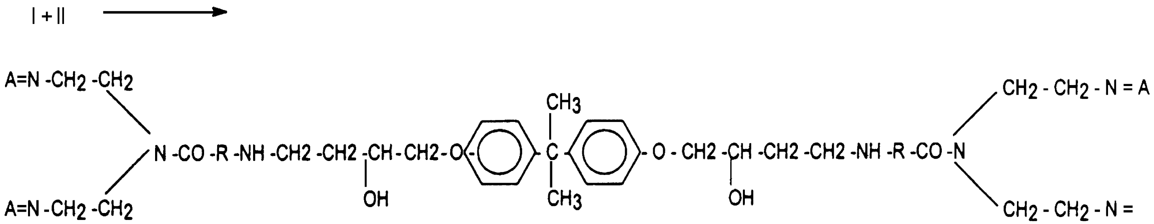


(IIa-c)

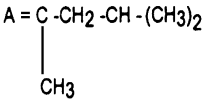
SCHEME 2

be seen that the spectrum of IIIa shows stronger N—H stretching absorption at 3400 cm^{-1} without absorption band at 1680 cm^{-1} of C=N. MIBK will be liberated during the hydrolysis of ketimine, so infrared spectra can be used to follow the changes of absorption of C=O at 1700 cm^{-1} and C=N at 1680 cm^{-1}. The changes of absorption ratios of [C=O]/[alkyl] and [C=N]/[alkyl] with the hydrolytic time during the hydrolysis of IIIa are shown in Figure 2. The ratio of [C=O]/[alkyl] gradually increases with the hydrolytic time and levels off after about 1 h. On the contrary, the ratio of [C=N]/[alkyl] decreases with hydrolysis time and also reaches a limiting value. The absorption peak of C=N might not disappear completely. This is due to the fact that ketimine hydrolysis is a reversible process when the water content is low and the generating MIBK has not been removed from the solution, where it reacts with primary amine again.

Figure 3 illustrates the GPC curves of IIIa and the hydrolysis product of IIIa. The hydrolysis of IIIa liberates MIBK, which causes an additional absorption peak at 25.5 min of elution time.

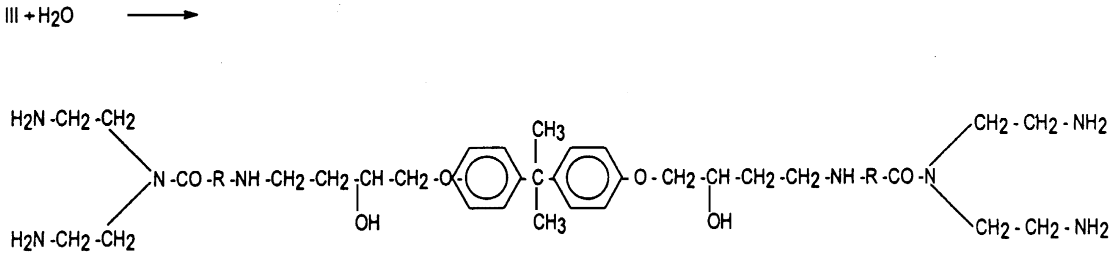


(IIIa-c)



$A = C(CH_3)-CH_2-CH-(CH_3)_2$

SCHEME 3



(IVa-c)

SCHEME 4

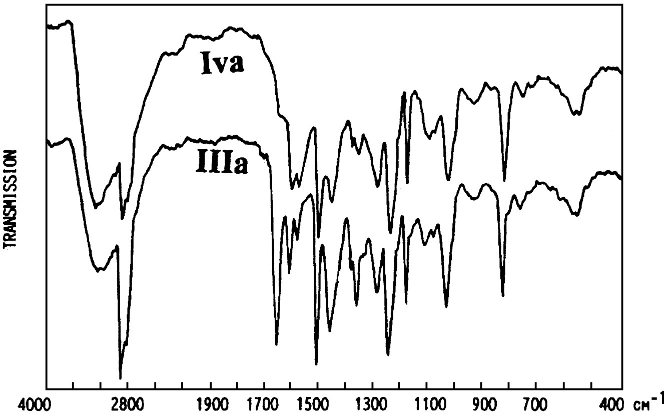


FIGURE 1 IR spectra of IIIa and IVa.

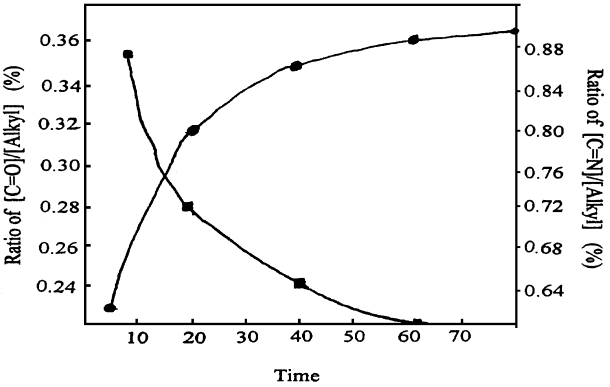


FIGURE 2 IR absorption ratios of [C=O]/[alkyl] and [C=N]/[alkyl] versus hydrolytic time during the hydrolysis of IIIa.

The negative absorption is due to the presence of water. The molecular weight of IVa is lower than that of IIIa so the curve peaks of IV shift to higher elution time.

The changes of pH value during the hydrolysis of I and IIIa are shown in Figure 4. The pH value of the reaction solution increased with time and then reached a constant value. The increase of pH value is due to the formation of primary amine groups. For high water content (95 wt%), the hydrolysis was completed within brief time at room temperature. A higher hydrolytic temperature gives a faster hydrolytic rate and hence higher increased rate of pH value as shown in Figure 5. The addition of acetic acid enhanced the

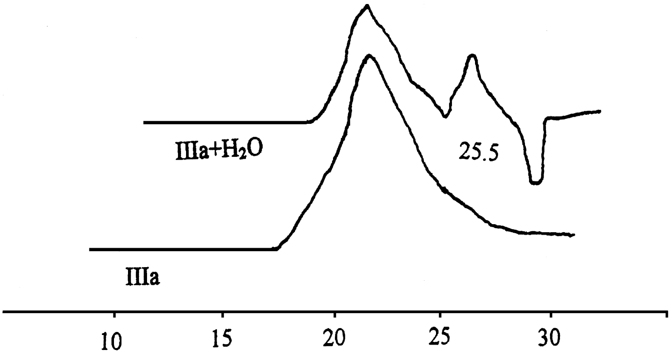


FIGURE 3 GPC curves of IIIa and its hydrolytic product.

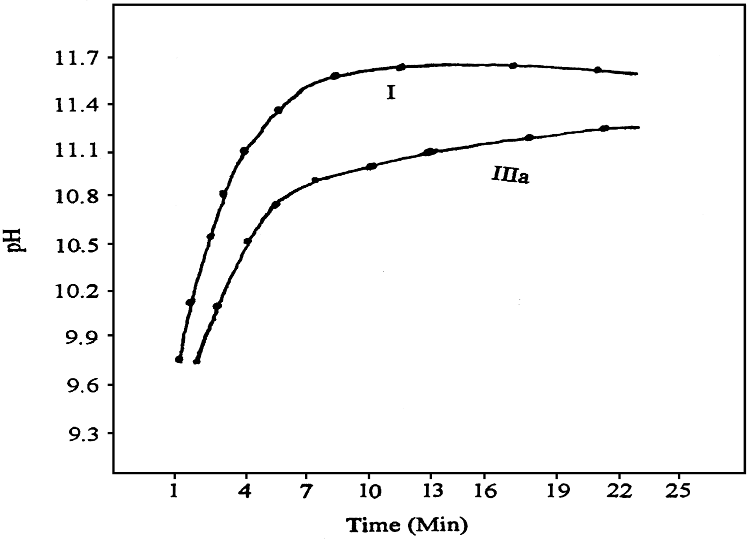


FIGURE 4 pH value of solution versus hydrolytic time during the hydrolysis of I and IIIa at room temperature.

hydrolysis rate as shown in Figure 6 as more acid is added the rate of pH changes increased and pH values of final hydrolyzed solution decreased.

The thermogravimetric data of polyamines are listed in Table 1. The thermogravimetric data reveal on examination that the polyamine samples start their decomposition between 250–300°C depending upon the polyamine formation. The rate of weight loss is high around 450–500°C and is completed at about 650°C.

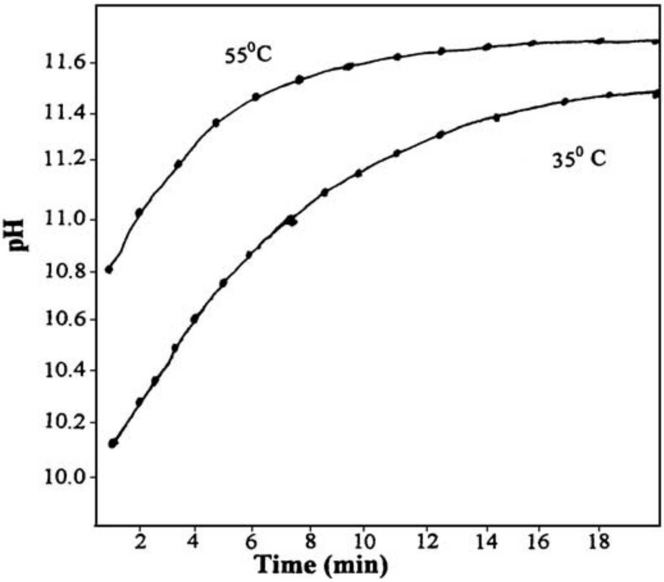


FIGURE 5 pH value of solution versus time at different temperature.

Data furnished in Table 2 are for scratch hardness; impact strength and flexibility test of the coated panel using various systems in different ratios has been prepared for the study.

All samples passed flexibility test of 1/4″ and 1/8″ conical mandrel, which confirm the good flexibility of the coated film. All the panels passed stripping test for adhesion. This is expected due to free hydroxyl group present in the resin system, which contribute to strong bond formation with the surface of the mild steel panels. The good adhesion of the film may also be due to the possibility that polyamide characteristics of the curing agents displaces the water from the surface of the substrate, allowing the film to adhere and cure to a dense impermeable barrier [10].

Data listed in Table 2 indicates that TGPAP resin systems show better coating properties than the systems where DGEBA was used. This difference may be caused by the higher functionality of the TGPAP resin. This may be responsible for the formation of highly crosslinked network structure. It is also observed that the strength increases with a decrease in the proportion of curing agent. The corresponding increase in the epoxy content is also responsible for the improvement in the flexibility of the coated film. It is also observed that the coating properties are slightly higher for the system in which IVc being used than the system in which IVa and IVb being used. This may be due to steric effect: in para position there is less

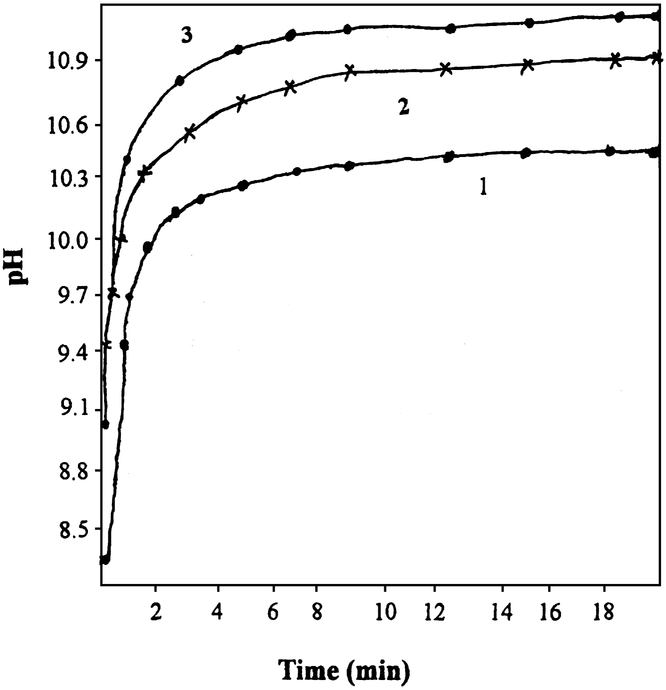


FIGURE 6 pH value of solution versus time at various additive amounts of acid. Acid content: (1) 3 wt% (2) 2 wt%, and (3) 1 wt%.

TABLE 1 Thermogravimetric analysis of materials

System		*% Weight loss from TGA at °C*					
Resin: *Polyamine*	*Ratio* (*in wt%*)	250	300	400	500	600	650
DGEBA: IVa	60:40	3.7	4.0	30	47	90	95
DGEBA: IVb	60:40	3.5	4.2	28	46	91	94
DGEBA: IVc	60:40	3.0	3.8	29	43	87	92

steric hinderance such that the molecular weight of the polymer is slightly higher than *meta* and *ortho* position polymer.

The coated films were tested for water and solvent resistance. In case of water resistance, coating based on all the resin systems show no color change or blistering. The coated panels were immersed for 48 hours in water and solvent but no cracking or loss in gloss were observed, which indicates that the systems have excellent solvent and water resistance. 2% alkali solution tested for 48 hours shows that all the panels remained unaffected. The observation reveals that on exposing the coated panels to two %

TABLE 2 Impact strength and scratch hardness of the coated panels

System *Resin*: *polyamine*	*Ratio* (*in wt%*)	*Impact strength* (*gm*)	*Scratch hardness* (*gm*)
DGEBA: IVa	60 : 40	162	1300
DGEBA: IVa	70 : 30	175	1325
DGEBA: IVa	80 : 20	192	1360
DGEBA: IVb	60 : 40	165	1307
DGEBA: IVb	70 : 30	177	1330
DGEBA: IVb	80 : 20	190	1370
DGEBA: IVc	60 : 40	166	1320
DGEBA: IVc	70 : 30	179	1332
DGEBA: IVc	80 : 20	193	1371
TGPAP: IVa	60 : 40	186	1350
TGPAP: IVa	70 : 30	198	1390
TGPAP: IVa	80 : 20	210	1400
TGPAP: IVb	60 : 40	188	1365
TGPAP: IVb	70 : 30	199	1397
TGPAP: IVb	80 : 20	221	1415
TGPAP: IVc	60 : 40	191	1370
TGPAP: IVc	70 : 30	203	1400
TGPAP: IVc	80 : 20	223	1430

Sulfuric Acid for 48 hours no substantial loss in gloss or change in appearance were observed. The above indicates excellent adhesion as well as good resistance to acid, alkali, water, and organic solvent.

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