Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions for Coating Applications

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Anionic blocked isocyanate-containing urethane prepolymer dispersions were synthesized from poly(oxypropylene) glycol, polyarylpolyiso-cyanate (PAPI 2094), dimethylolpropionic acid (DMPA), and methyl-ethyl ketoxime (MEKO). A stoichiometric amount of tetraethylenepentamine (TEPA) was added as a crosslinker to the blocked polyisocyanate dispersions resulting in one-package crosslinkable, waterborne urethane coatings. The samples were characterized by means of mechanical properties, chemical resistance, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The deblocking kinetics of the blocked polyisocyanates at different baking temperatures were studied.

INTRODUCTION

Development of high-quality, one-package coatings with zero or low VOCs is one of the most difficult challenges that the coating industry faces today. Research on waterborne coatings has been carried out to find a new alternative to address this challenge. The interest in waterborne coating technologies in coating industries has been stimulated by economic and ecological pressures. The increasing cost of solvents as well as the federal regulations on solvent emission are forcing several industries to use waterborne polymer coating systems. Waterborne polyurethane coating systems are probably one of the fastest growing areas in the coating industry at present. Due to their unique properties, they have found widespread usage in fabrics, wood, plastics, metal, and the like. However, many waterborne polyurethane coating systems cannot meet some of the performance requirements compared to the corresponding solvent-based coatings. This is presumably due to the lack of coating systems which have appropriate crosslinking.

In industrial practice, there are different methods available for the preparation of waterborne polyurethanes such as the acetone process, prepolymer-ionomer process, and melt dispersion process, among others.[1,2] The critical step in which the various processes differ is the high molecular weight built-up (chain extension). In acetone process, acetone is used as an intermediate aid to control the viscosity during the critical chain extension step. In the prepolymer-ionomer process, a hydrophilically modified prepolymer with terminated NCO groups is dispersed with water and chain extension is accomplished by addition of diamine to the dispersion. The melt dispersion process uses urea to cap NCO-terminated prepolymer. The capped prepolymer is dispersed in water and then chain extension is accomplished by methylolation of the biuret groups with formaldehyde and subsequent polycondensation reaction. A suitable crosslinkable polyurethane coating requires a rapid crosslinking reaction between polyurethane and the crosslinker and a suitable temperature for film formation. Different techniques have been reported for the preparation of crosslinkable or crosslinked coatings from polyurethane dispersions.[1,2] For example, the pre-crosslinked polyurethane dispersions are usually produced in the prepolymer-ionomer and melt dispersion processes and are used for the preparation of crosslinked coatings. However, some of these crosslinked polyurethane dispersions frequently do not reach efficient crosslinking. The disadvantages of some crosslinking methods and the requirements of one-package systems in various applications have led to the development of blocked isocyanate-containing urethane prepolymers as precursors for waterborne urethane coatings.

Blocked polyisocyanates have been employed in the coating industry for many years and have formed an integral part of polyurethane coating technologies.[3] They have been used extensively in waterborne,[4,5] solvent-based,[6] and powder coatings.[7,8] The blocked isocyanate groups are stable at ambient temperatures and will deblock to generate isocyanate groups at an elevated temperature. The isocyanate groups subse-

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Table 1—Raw Materials

Designation	Chemical Description	Suppliers
Poly-G 20-112	Poly(oxypropylene) glycol (OH functionality=2.0, MW=1000)	Olin Chemical Co.
Poly-G 20-56	Poly(oxypropylene) glycol (OH functionality=2.0, MW=2000)	Olin Chemical Co.
DMPA	Dimethylolpropionic acid	TRIMET Tech. Product, Inc.
PAPI 2094	Polyarylpolyisocyanate (NCO functionality=2.3, Eq. wt=132)	Dow Chemical Co.
MEKO	Methylethyl ketoxime	Allied Signal
TEA	Triethylamine	Air Products & Chemical Co.
NMP	N-methylpyrrolidone	BASF Corp.
BD	1,4-Butanediol	E.I. DuPont de Nemours & Co.
TEPA	Tetraethylenepentamine	Dow Chemical Co.
T12	Dibutyltin dilaurate	Air Products & Chemical Co.
DMF	N,N-Dimethylformamide	Fisher

quently react with other active hydrogen-containing components to form urethane or urea linkages, as shown in *Scheme* 1. The reaction proceeds through two possible mechanisms: elimination-addition and substitution. Several techniques such as thermogravimetric analysis (TGA),[9] differential scanning calorimetry (DSC),[10] dynamic mechanical analysis (DMA),[11] and FTIR,[12] were employed to study the deblocking kinetics as well as the crosslinking reactions.

The formation of one-package crosslinkable urethane coatings is one of the inherent advantages associated with the use of blocked polyisocyanates. Merging the technologies of aqueous polyurethane dispersions and blocked polyisocyanate could result in high quality, one-package and low VOCs, coatings with long pot-life and low film-formation temperature. In waterborne blocked polyisocyanate systems, factors such as dispersion stability, film formation temperature, and compatibility with water dispersible additives play an important role.

Research work on structure-properties relationship of waterborne polyurethane-urea systems has been carried out in our laboratories.[13-19] The preparation and characterization of the waterborne blocked anionic urethane dispersions are described in this paper. The deblocking and crosslinking reactions of the blocked urethanes were also studied.

Table 2—Composition of Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions

Samples	P-1	P-2	P-3
Composition:			
PPG-100	50.0	—	50.0
PPG-2000	—	70.0	—
DMPA	20.1	9.4	10.1
1,4-DB	—	6.3	—
PAPI 2094	95.0	83.1	60.0
TEA	15.0	7.1	7.6
MEKO	29.0	25.6	17.6
NMP	20.0	20.0	—
Water	607	504	436
Total	836.1	806.5	581.3
DMPA/PPG/1,4-DB (mole)	3/1/0	2/1/2	1.5/1/0
COOH content (wt.)	3.23	1.57	2.33
Soft segment content (%)	23.9	34.7	34.4

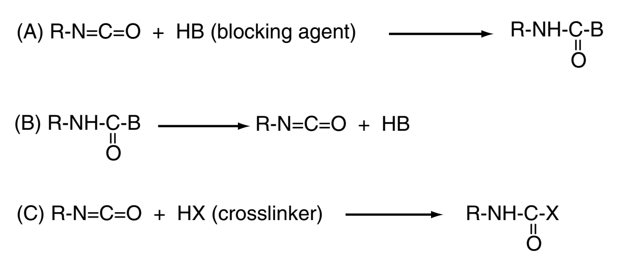
EXPERIMENTAL

Raw Materials

The raw materials used in this study are listed in *Table* 1. The poly(oxypropylene) glycols (Poly-G 20-112 and 20-56) were dehydrated under vacuum for 24 hr at 70-80°C before use. PAPI 2094 and dimethylolpropionic acid (DMPA) were used as received. Tetraethylenepentamine (TEPA), triethylamine (TEA), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), 1,4-butanediol (BD), and methylethyl ketoxime (MEKO) were dried over Linde 4Å molecular sieves before use.

Preparation of Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions

The preparation of these dispersions is shown in *Scheme* 2. The preparation was carried out in a reaction kettle, equipped with a thermometer, stirrer, inlet, and outlet of dry nitrogen, and a heating jacket. The kettle was purged with dry nitrogen to maintain a dry atmosphere during the progress of the reaction. The completion of the reaction was monitored by



$$\text{(A) R-N=C=O + HB (blocking agent)} \longrightarrow \text{R-NH-}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-B}$$

$$\text{(B) R-NH-}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-B} \longrightarrow \text{R-N=C=O + HB}$$

$$\text{(C) R-N=C=O + HX (crosslinker)} \longrightarrow \text{R-NH-}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-X}$$

Scheme 1—The isocyanate group in blocked isocyanate. (A) Blocking reaction; (B) deblocking reaction; and (C) crosslinking reaction.

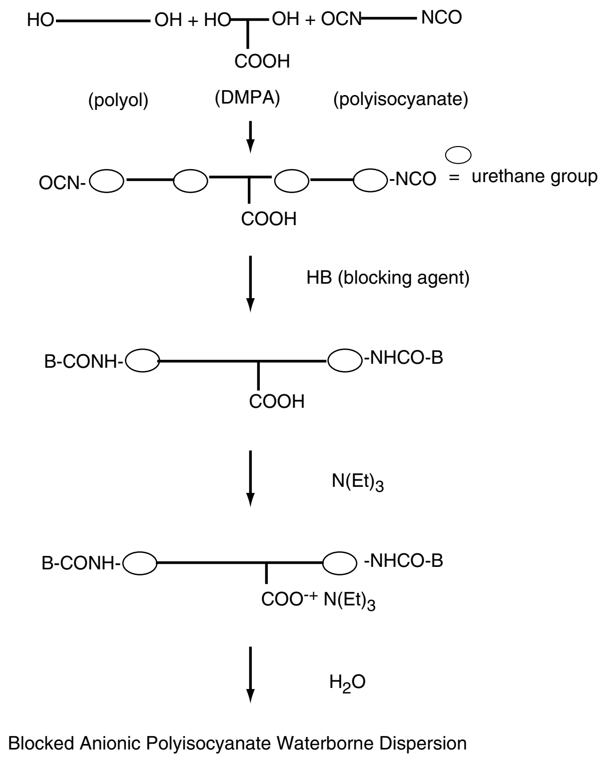
Table 3—Properties of Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions

	P-1	P-2	P-3
Viscosity (cps)[a]	30	28	36
Solids content (%)	25	25	25
pH	7.7	7.6	7.8
Storage stability (RT)[b]	> 6 month	> 6 month	> 6 month

(a) At shear rate of $50s^{-1}$.
(b) With crosslinker TEPA.

measuring the NCO content using the di-n-butylamine titration method. The preparation procedures are described in the following and the compositions are presented in *Table* 2.

Preparation of Dispersion P-1: 20.1 parts of DMPA were weighed into the reaction kettle and 20 parts of NMP were added to dissolve the DMPA. Fifty parts of PPG1000 and 95 parts of PAPI 2094 were then placed in the kettle while stirring. The reaction was carried out at 70-75°C until the theoretical NCO value was reached (7.3%). Eighty parts of acetone were added to dilute the system. The reaction mixture was then cooled down to 50°C and 20 parts of MEKO were added dropwise over 50 min. The reaction was carried out until no NCO peak could be found in the FTIR. The blocked isocyanate-containing urethane with pendant COOH groups was then neutralized with 15 parts of triethylamine (TEA) at 50°C for 20 min. Also, 607 parts of water were added to accomplish the dispersion under vigorous stirring. After a uniform dispersion was obtained, the acetone was distilled off under vacuum.



Scheme 2—Preparation of anionic blocked isocyanate-containing urethane prepolymer dispersion.

Preparation of Dispersion P-2: 9.4 parts of DMPA were placed into the reaction kettle and 20 parts of NMP were used to dissolve the DMPA. Seventy parts of PPG2000, 6.3 parts of 1,4-BD and 83.1 parts of PAPI2094 were then placed in the kettle while stirring. The reaction was carried out at 70-75°C until the theoretical NCO value was reached (6.2%). Eighty parts of acetone were added to dilute the system. Then the reaction mixture was cooled down to 50°C and 25.6 parts of MEKO were added dropwise over 50 min. The reaction was carried out until no NCO peak could be found in the FTIR. The blocked isocyanate-containing urethane was then neutralized with 7.1 parts of triethylamine (TEA) at 50°C for 20 min. Then, 584 parts of water were added to carry out the dispersion under vigorous stirring. After a uniform dispersion was obtained, the acetone was distilled off under vacuum.

Preparation of Dispersion P-3: The preparation procedure of P-3 was the same as that described for P-1, except without adding NMP.

In these anionic blocked isocyanate-containing urethane dispersions, tetraethylenepentamine (TEPA) was added in

Table 4—Mechanical Properties of Coatings Based on Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions

	P-1			P-2			P-3		
Baking temperature, °C	110	125	140	110	125	140	110	125	140
Baking time, min	30	30	30	30	30	30	30	30	30
Tensile at break, Psi	5650	6040	6800	6100	6480	8300	7020	7270	8000
MPa	38.93	41.62	48.86	42.03	44.65	57.19	48.37	50.10	55.13
Tensile at yield, Psi	—	—	—	5500	5405	8400	6400	7050	7800
MPa	—	—	—	37.90	37.25	57.88	44.10	45.58	53.75
Elongation at break, %	10	10	10	76	65	40	55	35	30
Pencil hardness	F	F	H	F	F	F	F	F	F
Crosshatch adhesion[a]	5	5	5	5	5	5	5	5	5
Impact resistance, lb/in.									
Direct	>160	>160	>160	>160	>160	>160	>160	>160	>160
Reverse	20	20	20	>160	>160	>160	>160	>160	>160

(a) Crosshatch evaluation is classified as #5 indicating that there is no flaking on the test panel.

Table 5—Chemical Resistance of Coatings Based on Anionic Blocked Isocyanate-Containing Urethane Prepolymer Dispersions

	P-1			P-2			P-3		
Baking temperature, °C	110	125	140	110	125	140	110	125	140
Baking time, min	30	30	30	30	30	30	30	30	30
MEK double rub resistance, times	>200	>200	>200	>200	>200	>200	>200	>200	>200
Coating thickness, um									
Before 200 times of double rub	201	193	184	151	170	166	201	183	194
After 200 times of double rub	201	193	185	153	171	166	202	184	194
Pencil hardness									
Before 200 times of double rub	F	F	H	F	F	F	F	F	F
After 200 times of double rub	F	F	F	B	HB	HB	B	B	B
Xylene double rub resistance, times	>200	>200	>200	>200	>200	>200	>200	>200	>200
Coating thickness, um									
Before 200 times of double rub	195	188	191	162	166	181	205	176	174
After 200 times of double rub	195	188	191	162	165	182	204	176	176
Pencil hardness									
Before 200 times of double rub	F	F	H	F	F	F	F	F	F
After 200 times of double rub	F	F	H	HB	F	F	HB	F	F
Weight loss, %[a]	9.1	7.7	3.7	6.1	4.3	1.6	11.7	3.7	1.5

(a) The weight loss of the samples which were immersed in THF at room temperature for 10 days.

stoichiometric amounts as crosslinker to produce one-package, crosslinkable waterborne coatings.

Preparation of Blocked PAPI 2094

In a round bottom flask equipped with a stirrer, reflux condenser, thermometer, and a heating mantle, 26.2 parts of PAPI 2094 were mixed with 500 parts of DMF. Also, 17.6 parts of MEKO in 150 parts of DMF were added dropwise over 30 min. The reaction system was kept at 40-50°C for 2-3 hr until no NCO peak could be found in the FTIR. The reaction product was then precipitated in water. The precipitate, separated by filtration, was dissolved in NMP, reprecipitated in water, and washed three times with acetone to obtain a pure product.

Measurements

The viscosity of the dispersions was measured using a Rheometrics RFS-2 viscometer at room temperature. The free polyurethane-urea films were made by casting the one-package crosslinkable waterborne coatings in a silicone coated mold and dried at room temperature. The mechanical properties (tensile strength and elongation) of these coatings were measured on an Instron-Tensile Tester at 5 in./min crosshead speed, according to ASTM Test Method D 2370.

The crosslinkable waterborne coatings were applied to phosphate treated steel panels (Q-Panel, Type QD-smooth finish, thickness 0.020 in., acetone cleaned) by a Gardner universal blade applicator and baked at a given temperature (110, 125, or 140°C) to deblock and cure the coatings. The thickness of the dry coatings was about 6-8 mil. The chemical resistance of these coatings was measured according to ASTM Test Method D 5402. The impact resistance of these coatings was measured according to ASTM Test Method D 2794 by means of a Gardner impact tester 5510 (punch diameter 5/8 in.). The pencil hardness was determined by Gardner pencil hardness test kit, according to ASTM Test Method D 3363. The crosshatch adhesion was tested using a Gardner paint adhesion test kit (ASTM D 3359).

The glass transition temperatures (T_gs) of these blocked anionic polyisocyanates and the waterborne coatings were determined on a DuPont 910 differential scanning calorimeter in a DuPont 9900 thermal analyzer system at a temperature range from –100°C to 100°C at a heating rate of 20°C/min. Indium was used to calibrate the instrument. Thermogravimetric analysis (TGA) was carried out on a DuPont 951 thermal analyzer at a heating rate of 5°C/min in air. The measurement was carried out in two distinct types: dynamic and isothermal. The samples were kept in a vacuum oven at room temperature for at least 72 hr before measurement.

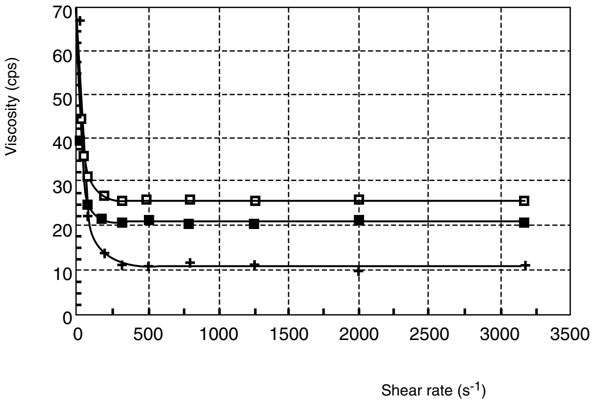


Figure 1—Rheological profiles of anionic blocked isocyanate-containing urethane prepolymer dispersions: (+) P-1; (■) P-2; and (□) P-3.

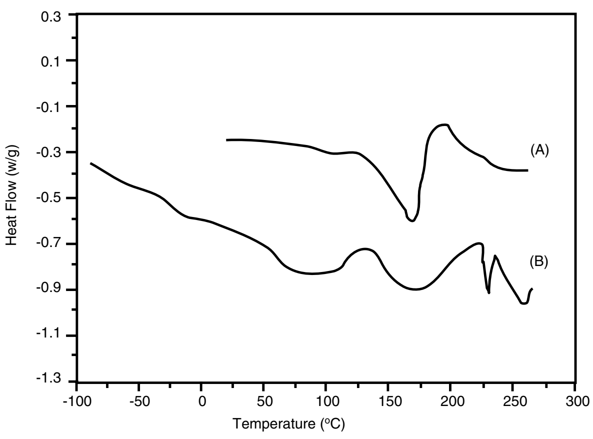


Figure 2—DSC curves of blocked PAPI 2094 and anionic blocked isocyanate-containing urethane prepolymer. (A) Blocked PAPI 2094; (B) Anionic blocked isocyanate-containing urethane prepolymer sample P-3.

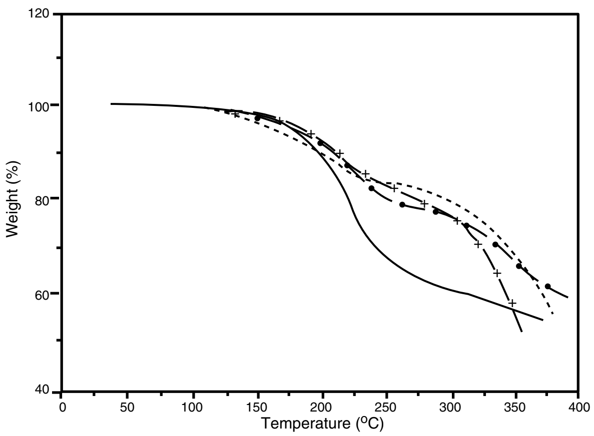


Figure 3—Thermogravimetric curves of anionic blocked isocyanate-containing urethane prepolymers and blocked PAPI 2094. (________) Blocked PAPI 2094; (—●—●—) P-1; (- - - - -) P-2; and (—X—X—) P-3.

RESULTS AND DISCUSSIONS

Physical Properties of Dispersions

The anionic blocked isocyanate-containing urethane prepolymer dispersions were characterized by means of pH values, viscosities, and solids content. The results are listed in *Table* 3. All measurements were based on 25% solids content. The pH value of the dispersions indicated weak basicity. This is due to the fact that the internal salt groups of the dispersion were formed by the relatively strong base TEA and the weakly acidic pendant COOH groups. The viscosity of these dispersions was essentially the same, as shown in *Table* 3.

The rheological measurements of anionic blocked isocyanate-containing urethane prepolymer dispersions P-1, P-2, and P-3 exhibited Newtonian behavior at a shear rate of 100-3200s^{-1} (*Figure* 1). The blocked anionic polyisocyanate dispersions with the crosslinker TEPA showed similar rheological profiles. The Newtonian behavior of the rheology profile is of considerable value in coating applications, such as high-speed reverse-roll coil coatings, direct gravure printing, etc.

The storage stability of these anionic blocked isocyanate-containing urethane prepolymer dispersions with different crosslinkers was determined by means of viscosity measurement. The dispersions with TEPA were stable (no viscosity change) at room temperature for at least six months due to the low solids content. The storage stability was found to be affected by the type of crosslinkers and the solids content. For example, the storage stability was less than one week when hexylenediamine was used to replace TEPA as crosslinker.

Mechanical Properties

Frisch and co-workers have studied the structure-properties relationships of various polyurethane anionomer dispersions.[13-19] It was reported that the modulus and hardness of waterborne polyurethane coatings increased with increasing DMPA and BD contents in the polyurethanes. A similar behavior was reported by other researchers.[20] The mechanical properties of the anionic blocked isocyanate-containing urethane prepolymer based coatings were studied in terms of tensile strength, elongation at break, pencil hardness, adhesion, and impact resistance. The properties of these coatings are shown in *Table* 4. The mechanical properties of the samples P-1, P-2, and P-3 were studied at different deblocking temperatures (110, 125, and 140°C) at a constant baking time (30 min). It was observed that with increasing deblocking temperature, the tensile strength increased and the elongation at break decreased in all of these samples. This may be due to the

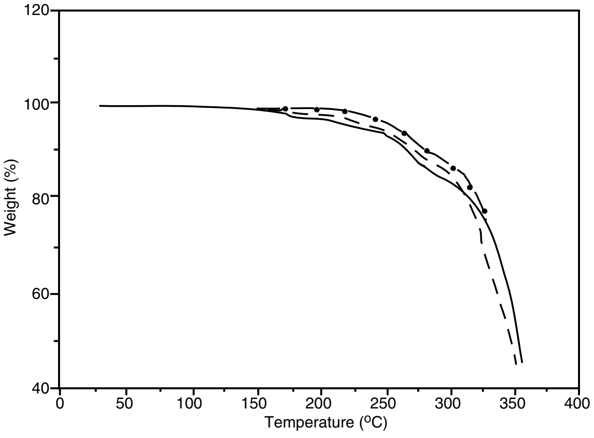


Figure 4—Thermogravimetric curves of coatings based on anionic blocked isocyanate-containing urethane prepolymer sample P-3 containing TEPA. (————) baked at 110°C for 30 min; (– – – – –) baked at 125°C for 30 min; and (–●–● –) baked at 140°C for 30 min.

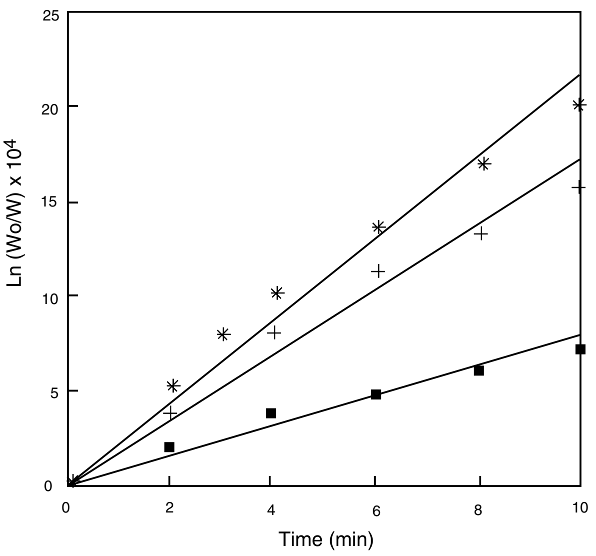


Figure 5—First-order reaction plot of the deblocking of blocked PAPI 2094. (■) 110°C; (+) 125°C; and (∗) 140°C.

fact that the degree of crosslinking was related to the deblocking reaction which increased by increasing the deblocking temperature.

The pencil hardness for all the samples was in the range of F-H. The crosshatch adhesion of these samples to steel panels was excellent. The Gardner impact resistance was measured in both direct and reverse direction. For all samples, the impact resistance was greater than 160 lb/in., except for sample P-1, which had a very low impact strength in the reverse direction, presumably due to the higher hard segment content resulting in brittleness of the coatings.

Chemical Resistance

The chemical resistance of these anionic blocked isocyanate-containing urethane prepolymer based coatings was tested by methylethylketone (MEK) and xylene double rub tests. As shown in *Table* 5, it was observed that all samples showed good resistance to MEK and xylene. Both the appearance and thickness of the coatings did not change after 200 double rubs with MEK and xylene. The pencil hardness of these coatings decreased after 200 MEK double rubs. These coatings were immersed in tetrahydrofuran (THF) at room temperature for 10 days. It was observed that the coatings made from the higher deblocking temperature exhibited lower weight loss (*Table* 5). One explanation for this is that the coatings were more crosslinked and more stable at higher deblocking temperatures.

Thermal Behavior

The T_gs of the blocked PAPI 2094 and the anionic blocked isocyanate-containing urethane prepolymer based coatings were determined by DSC measurements. As shown in *Table* 6, the T_g values of the polyether soft segments in these coatings were found to be in the temperature range of –10 to –20°C.

Table 6—Glass Transition Temperature of Anionic Blocked Isocyanate-Containing Prepolymer Based Coatings

Sample	Baking Condition	T_g, °C
P-1/TEPA	Blocked	-19
	Deblocked, 110°C/30min	-20
	Deblocked, 125°C/30 min	-20
	Deblocked, 140°C/30 min	-19
P-2/TEPA	Blocked	-17
	Deblocked, 110°C/30 min	-16
	Deblocked, 125°C/30 min	-18
	Deblocked, 140°C/30 min	-19
P-3/TEPA	Blocked	-9
	Deblocked, 110°C/30 min	-11
	Deblocked, 125°C/30 min	-10
	Deblocked, 140°C/30 min	-11

The T_g values of the soft segments in these samples were much higher than those of pure poly(oxypropylene) glycol which was reported as –69°C.[21] The baking conditions did not show any significant effect on the T_g values of these coatings.

The DSC technique was used to determine the deblocking temperature range of the blocked isocyanates.[10] As shown in *Figure* 2, the DSC measurements indicated that the deblocking of the blocked PAPI 2094 occurred at a temperature range of 130-180°C. The DSC curve of the anionic blocked isocyanate-containing urethane prepolymer sample P-3 showed a very broad peak from 50-180°C. The similar behavior in DSC curves of anionic blocked urethane samples P-1 and P-2 was also observed. We believe that, for anionic blocked urethane samples, the melting of the short- and long-range order in hand segment domains of urethanes[22] might take place at these temperature ranges where deblocking might occur. This may result in the broadening of the DSC curves and affect the

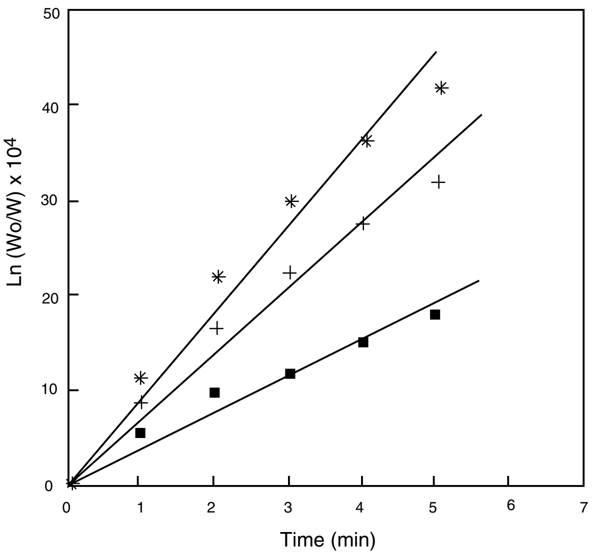


Figure 6—First-order reaction plot of the deblocking of anionic blocked isocyanate-containing urethane prepolymer sample. P-3 (■) 110°C; (+) 125°C; and (∗) 140°C.

determination of the deblocking temperature range by DSC measurement.

The dynamic TGA curves (*Figure* 3) showed that the deblocking of the three anionic blocked urethanes and blocked PAPI 2094 occurred over the temperature range of 110-150°C. The thermogravimetric curves of the coatings based on sample P-3 containing TEPA are shown in *Figure* 4. The thermal stability was assessed from the TGA curves. It was found that the thermal stability patterns of the samples with different baking history were similar. The samples, baked at higher temperatures, had higher retention in weight percent. It indicated that the deblocking was more complete at higher baking temperature leading to higher crosslinking and, thereby, higher thermal stability. The coating samples based on P-1/TEPA and P-2/TEPA exhibited a similar behavior.

Deblocking Kinetics

The macrokinetic measurements of thermal deblocking of the blocked PAPI 2094 and the anionic blocked isocyanate-containing urethane prepolymer P-3 with and without crosslinker TEPA were determined by isothermal TGA, and the results are shown in *Figures* 4-6. The experimental data showed that the deblocking reaction of these samples followed first order reaction.

The effect of temperature on the deblocking of these samples was investigated and the results are summarized in *Table* 7. The rate constant (k) and activation energies (Ea) of the deblocking reaction were calculated by using the following equations:

$$k=\ln(w_o/w)/t$$

$$k=A^*\exp(-Ea/RT)$$

where w_o is the weight of sample, w is the weight retention of the sample of time t, T is the temperature, A is a constant, and R is the gas constant. As shown in *Table* 7, the reaction rates were in the order of P-3/TEPA > P-3 > blocked PAPI. The percentage loss of MEKO during the baking process for these samples was also summarized in *Table* 7. Thames and Boyer[23] have reported that the dissociation temperature of blocked polyisocyanates was related to polymer structure. In this study, the results indicated that deblocking rate was much higher in anionic blocked urethane prepolymers than that observed in the blocked PAPI 2094, although the deblocking of these samples occurred over the same temperature range. It was reported that the addition of polyols can accelerate the deblocking process in blocked polyisocyanate.[23] Isothermal TGA measurements showed that the deblocking rate increased by adding TEPA in the blocked anionic polyisocyanate samples P-3 (*Table* 7). The activation energies of deblocking of these samples were in the range of 9.9-10.8 Kcal/mole.

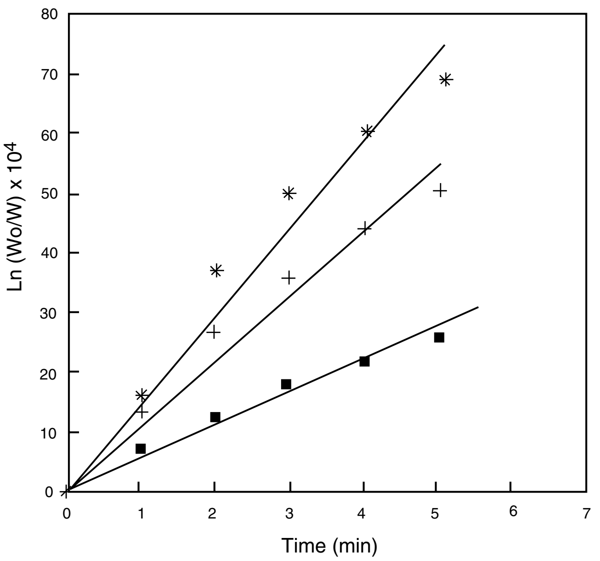


Figure 7—First-order reaction plot of the deblocking of anionic blocked isocyanate-containing urethane prepolymer sample P-3 containing TEPA. (■) 110°C; (+) 125°C; and (*) 140°C.

CONCLUSIONS

One-package crosslinkable waterborne coatings were prepared from anionic blocked isocyanate-containing urethane prepolymers. The anionic blocked urethane dispersions were prepared from poly(oxypropylene) glycol, polyarylpolyisocyanate (PAPI 2094), dimethylolpropionic acid (DMPA), and methylethyl ketoxime (MEKO). The dispersions containing crosslinker TEPA exhibited good storage stability at room temperature, presumably due to the structure of TEPA and the low solids content (25%) in these dispersions. The coatings based on these anionic blocked urethane dispersions showed good mechanical properties and chemical resistance. It was found that the anionic blocked isocyanate-containing urethane prepolymers had a faster deblocking rate than that of blocked PAPI 2094.

Table 7—Kinetic Parameters of Anionic Blocked Isocyanate-Containing Urethane Prepolymers and Blocked PAPI 2094 at Various Deblocking Temperatures

	Blocked PAPI 2094			P-3			P-3/TEPA		
Deblocking temperature (°C)	110	125	140	110	125	140	110	125	140
Deblocking time (min)	30	30	30	30	30	30	30	30	30
k^*10^3, min^{-1}[a]	0.73	1.6	1.9	4.2	6.8	9.2	5.6	10.8	15.8
Ea, Kcal/mole[b]		9.9			10.6			10.8	

(a) The reaction rate of the deblocking reaction.
(b) The activation energy of the deblocking reaction.

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