Polyorthoesters for Low-VOC Coatings

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A series of new oligomeric polyorthoesters for low-VOC coatings was prepared by protecting OH groups with orthoester compounds to achieve both low viscosity and excellent compatibility with crosslinking agents. These new oligomeric polyorthoesters were synthesized through a co-condensation reaction among polyol, orthoester, and a- or b-glycol compounds under an acidic condition. Here, the a- or b-glycol compounds were used as stoppers to prevent excessive polymerization. The polyorthoesters can easily be hydrolyzed with atmospheric moisture, and the produced OH groups can react with appropriate crosslinking agents. It is unique in this system that even the stoppers, a- or b-glycol compounds, can react with the crosslinking agents to achieve an extremely low VOC emission. The polyorthoesters cured with polyisocyanate compounds proved to be highly crosslinked polymers showing excellent mechanical properties, chemical resistance, etc.

INTRODUCTION

How to Achieve Low VOC Emission

While many types of coatings have been proposed to reduce VOC in organic coatings, including the high-solids, waterborne, and powder types, the high-solid type is presumed to be easier to use than the others in practical applications. Two important steps must be taken to develop a successful high-solids coating. One is to minimize the viscosity of the binder resin, and the other is to avoid generation of volatile materials during the crosslinking reaction. Lowering the molecular weight and polarity are both effective to reduce the viscosity of the binder resin, and the addition reaction and ring-opening reaction are both suitable to avoid volatile compounds from being generated during the crosslinking process. However, it becomes necessary to introduce more functional groups into the binder resin to compensate for reductions in the performance of the coating due to the lower molecular weight. These additionally introduced functional groups indisputably lead to a higher polarity of the binder resin, and this compromises the compatibility between the binder and the other materials. To surmount this dilemma (to achieve both low viscosity and polarity without spoiling the good compatibility), studies have investigated the protection of the functional groups. In this work, the OH group was chosen as the functional group in the binder resin since it is the most easily available. Polyisocyanate was chosen as the crosslinking agent since it crosslinks with the OH group by an addition reaction. Finally, orthoester was chosen as an OH protector.

Orthoesters

Orthoesters are well known dehydrators and OH protectors (see *Schemes* 1 and 2).

These OH protectors are used under mild acidic conditions in the field of biochemistry. The orthoesters easily react with alcohol compounds by ester-exchange reaction, and they are easily hydrolyzed to produce two OH groups and one ester moiety. Attempts have already been made to apply these types of reaction industrially in photoresist[2] and drug delivery[3] technologies. It has been known that bicyclo-orthoester compounds[4] and spiro-orthoester compounds[5,6] are used as crosslinkable groups in coating technology. In these crosslinking reactions, cationic ring-opening polymerization occurs with the use of a Lewis-acid catalyst.[7] Utilization of hydroly-

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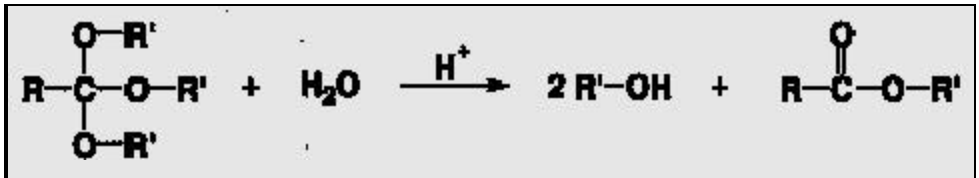

Scheme 1—Reaction of orthoester as a popular dehydrator.

Scheme 2—Utilization in the field of biochemistry.[1]

sis of these orthoesters in crosslinking reaction is also known.[8]

New Design in OH Protection

Orthoesters are promising for OH protection because of their smooth transformation between protection and deprotection. Secondly, all three OR groups of the orthoesters are able to react with alcohol compounds by the ester-exchange reaction. Further, 1,2- or 1,3-diols and orthoesters readily form cyclic structures by the ester-exchange reaction. Utilizing these features, we designed a new system of OH group protection with α– or β-glycol compounds as stoppers, as shown in *Figure* 1.

This protection system offers the following advantages:

(a) it can protect any type of OH group;

(b) it can control the molecular weight of the protected compounds;

(c) it can produce 2 moles of the OH groups from each OR group by hydrolysis;

(d) it can minimize volatile emission because of the reaction between the produced OH and the polyisocyanate.

The previously described oligomers and/or polymers containing OH groups protected with the orthoesters are hereinafter referred to as "polyorthoesters."

EXPERIMENTAL

Materials

All of the materials used were of commercial grade and were not purified further. The abbreviations used for materials are given in *Table* 1.

Sumidur N 3300 (polyisocyanate: hexamethylenediisocyanate type isocyanurate) was supplied by Sumitomo Bayer Urethane Co., Ltd.; Nacure 5543 (methanol solution of dodecylbenzenesulfonic acid neutralized with amine; effective constituent approximately 25%) was supplied by King Industries Inc.; and PLACCEL 303 and 305 (polycaprolactone polyol) were purchased from Daicel Chemical Industries, Ltd.

Preparation

SYNTHESIS OF POLYORTHOESTERS: The following methods are known for the synthesis of polyorthoesters or their precursors.

(a) ester-exchange reaction between the orthoesters and alcohol compounds;

(b) reaction between diketene acetal and polyol compounds;

(c) reaction between epoxide and lactone compounds[7];

(d) rearrangement of oxetane compounds with ester bonds.[9]

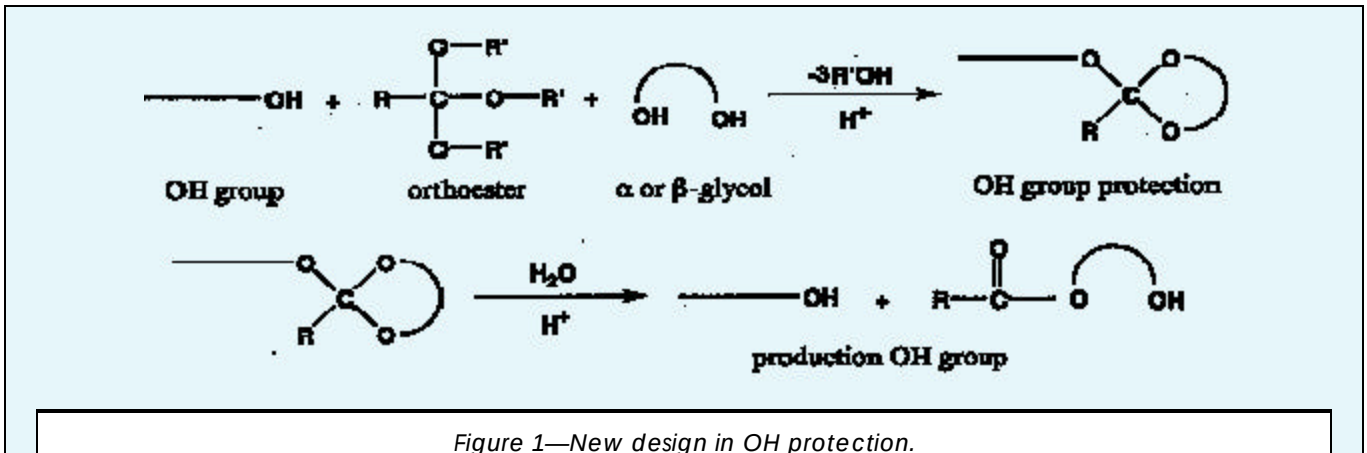

Figure 1—New design in OH protection.

Table 1—Abbreviations Used

PE	Pentaerythritol
DPE	Dipentaerythritol
MOF	Methyl orthoformate
MOA	Methyl orthoacetate
BEPD	2-Butyl-2-ethyl-1,3-propanediol
1,6HD	1,6-Hexanediol
N 3300	Sumidur N 3300
PMA	Propyleneglycol methyl ether acetate
DIW	Deionized water

We selected method (a) because it can easily be scaled up to practical and industrial production. PE and DPE were used as polyol compounds to protect the orthoesters and glycol compounds. PE was considered favorable since it is an inexpensive material. MOF and MOA were used as the orthoester compounds, and BEPD was used as glycol as the stopper. 1,6HD was used as reference. The compositions of the polyorthoesters are shown in *Table* 2.

Ordinary laboratory equipment equipped with a temperature controller, a stirrer, a condenser, and a fractionating column was used for synthesis of the polyorthoesters. All the materials were initially charged into the flask, then the temperature was raised to 80°C and kept at the temperature for a few hours while removing the methanol produced. Next, the temperature was raised to 190°C to complete the reaction. The reaction was considered complete when 96% of the theoretical amount of methanol was removed.

PREPARATION OF CROSSLINKED COATING FILMS: A clear coating (unpigmented) sample, here called S-1, was prepared by mixing the polyorthoester with Sumidur N 3300 and Nacure 5543. The composition of the clear coating was: A-1 / N 3300 / Nacure 5543 = 10.0 / 19.1 / 1.2 (wt). The amount of N 3300 was determined stoichiometrically to the OH groups in the polyorthoesters produced by the hydrolysis. Nacure 5543 was added as a catalyst for the hydrolysis of the polyorthoesters. An adequate amount of propyleneglycol methyl ether acetate (PMA) was added if it was required in application onto tinplate surfaces. The samples were applied with an applicator so that the dry thickness was approximately 40 µm. The coated plates were dried at specified temperatures for 30 min in an oven.

Measurements

CHARACTERIZATION OF POLYORTHOESTERS: IR spectra were measured on a Fourier transform infrared spectroscope (Model FTIR-420, Japan Spectroscopic Co., Ltd.). The viscosity of the oligomers and polymers was measured with a Gardner-Holdt viscometer (ASTM D 1545). Measurement of the molecular weights was carried out with a gel permeation chromatograph (Model HLC-8020, Toyo-Soda Co., Ltd., calibrated with polystyrene standards). Degassed tetrahydrofuran was used as an eluent in conjunction with an RI detector. The solubility parameter (SP) was derived from the turbidimetric titration result as follows.[10] The solution, 0.5 g of each sample was dissolved in 10 ml of acetone, was titrated with n-hexane and DIW, respectively to a certain cloud point. The solubility parameters used were acetone, 9.75; n-hexane, 7.24; and DIW, 23.43.

$$SP = (V_H^{0.5}\delta_H + V_D^{0.5}\delta_D) / (V_H^{0.5} + V_D^{0.5}) \quad (1)$$

$$V_H = H / (10 + H) \quad (2)$$

$$V_D = D / (10 + D) \quad (3)$$

$$\delta_H = 9.75 \times 10 / (10 + H) + 7.24H / (10 + H) \quad (4)$$

$$\delta_D = 9.75 \times 10 / (10 + D) + 23.43D / (10 + D) \quad (5)$$

V_H : the volume fraction of n-hexane
V_D : the volume fraction of DIW
δ_H : the solubility parameter of the mixture of n-hexane / acetone
δ_D : the solubility parameter of the mixture of DIW / acetone
H : the titer of n-hexane (ml)
D : the titer of DIW (ml)

FOLLOW-UP OF CURING PROCESS: Progress of the reaction was determined by comparison between two charts of IR spectra taken before and after the reaction. Changes in gravity during the curing process were measured using thermal analysis equipment: thermogravimetry / differential thermal analysis (TG / DTA, Model TG / DTA 320U, Seiko Instruments Inc.).

MEASUREMENTS OF CROSSLINKED FILM PROPERTIES: The degree of crosslinking was evaluated from gel fraction ratios. The gel fraction was obtained as weight ratio (in %) of residue to the original film after six hours extraction by refluxing acetone. The film hardness (KHN) was measured by indentation hardness (Tukon hardness, ASTM D 1474). Stress-strain behaviors were determined with an automatic tensile testing machine (Tensilon Model UTM-II, Toyo Measuring Instruments Co,. Ltd.) while applying a fixed elongation rate of 10 mm / min at 20°C. Dynamic viscoelasticity was measured by a dynamic viscoelastometer (DDV-II, Toyo-Baldwin Co., Ltd.) with a deformation frequency of 110 Hz and an elevation rate of 4°C / min. A value of intercrosslinkage molecular weights (Mc) was obtained by the following equation.[11]

$$Mc = 3dRT / E \quad (6)$$

R : the gas constant (kg cm / deg)
d : the density of film (g / cm^3)
E : the minimum dynamic modulus at rubbery state (kg / cm^2)
T : the absolute temperature (K)

The glass transition temperatures (T_g) used the peak in tan delta measured by the previously mentioned dynamic viscoelastometer. The chemical resistance was evaluated by the gel fractions obtained from the extraction process carried out in either alkaline or acidic condition. These conditions used the following mixed

Table 2—Compositions of the Polyorthoesters (mole wt)

	(MW)	A-1	A-2	A-3	A-4
PE	(136)	1 (136)	1 (136)		1 (136)
DPE	(250)			1 (250)	
MOF	(106)	4 (424)		4 (424)	4 (424)
MOA	(120)		4 (480)		
BEPD	(160)	4 (640)	4 (640)	4 (640)	
1,6HD	(118)				4 (472)
Formic acid	trace	trace	trace	trace	
–MeOH	(32)	–12 (-384)	–12 (-384)	–12 (384)	–12 (–384)

Table 3—Properties of the Synthesized Polyorthoesters

No.	Polyols	Orthoesters	Glycols	Visocisity	OHV (calc.)	Notes
A-1	PE	MOF	BEPD	X+	550	Transparent
A-2	PE	MOA	BEPD	M	515	Precipitation
A-3	DPE	MOF	BEPD	Z4	528	Transparent
A-4	PE	MOF	1,6HD	—	—	Gelation

solutions: alkaline condition, acetone/H_2O/NaOH = 90/9.5/0.5 wt%; acidic condition, acetone/H_2O/H_2SO_4 = 90/9.5 / 0.5 wt%.

MEASUREMENTS OF VOC: The volatile organic compounds (VOC) were obtained by the following equation.

$$VOC\ (lb/gal) = (1 - NV/100) \times \rho \times 8.33 \quad (7)$$

NV : nonvolatile of diluted clear coating sample with PMA by ASTM D 2369 (%) (preparation viscosity: FC#4, 60"or 150" at 20°C)

ρ : density of diluted clear coating sample (g/cm^3)

RESULTS AND DISCUSSION

Properties of Synthesized Polyorthoesters

Table 3 shows properties of the synthesized polyorthoesters. The reference sample synthesized with 1,6HD showed gelation during the synthesis. 1,2- and 1,3-diols readily formed cyclic structure. 1,6HD did not have these diols, so it is likely that the intermolecular reaction preceded the intramolecular reaction. Although PE and DPE have high melting points, poor solubility, and strong crystalline properties, the synthesized polyorthoesters with PE or DPE were viscous liquids that had lost these original characteristics. Another polyorthoester synthesized with MOA had shown slight crystalline precipitate after several months of storage. Although the crystalline precipitate has not been analyzed yet, we presume that the use of MOA produced more crystalline compositions than found in the others.

Among all these polyorthoesters, A-1 synthesized from PE, MOF, and BEPD was thought to be the most successful material for the high-solid coating. Therefore, we mainly investigated A-1 as a representative polyorthoester.

Figure 2 shows the idealized structure of A-1. Although it was not quantitatively proved, it is believed that the majority of the mixture derived from the orthoester functional groups is shown in *Figure* 2. An IR spectrum chart of A-1 is shown in *Figure* 3. This spectrum demonstrates that esterification due to side reactions was almost negligible. The GPC profile of A-1 is shown in *Figure* 4. This profile appears to be that of a mixture. No high molecular component is observed since the BEPD worked as a stopper preventing excessive polymerization. It was extremely difficult to identify each fraction in the GPC profile with GPC-MS and LC-MS.

Table 4 shows the results of a comparison between the characteristics of A-1 and two polycaprolactones regarded as typical OH oligomers. A-1 has two obvious advantages. One is the lower viscosity and the other is better compatibility with the crosslinking agent. Despite much higher OH values, A-1 showed a much lower viscosity due to elimination of hydrogen bonds by the OH protection. The OH protection provides another advantage, namely, reduction of the polarity. The solubility parameter was derived from turbidity titration results. Besides the effect of the OH protection, relatively hydrophobic glycols such as BEPD can help bring the

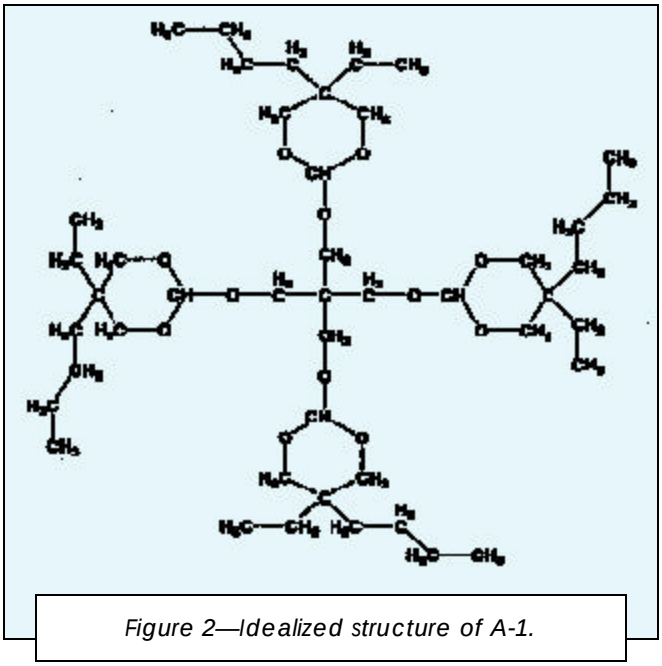

Figure 2—Idealized structure of A-1.

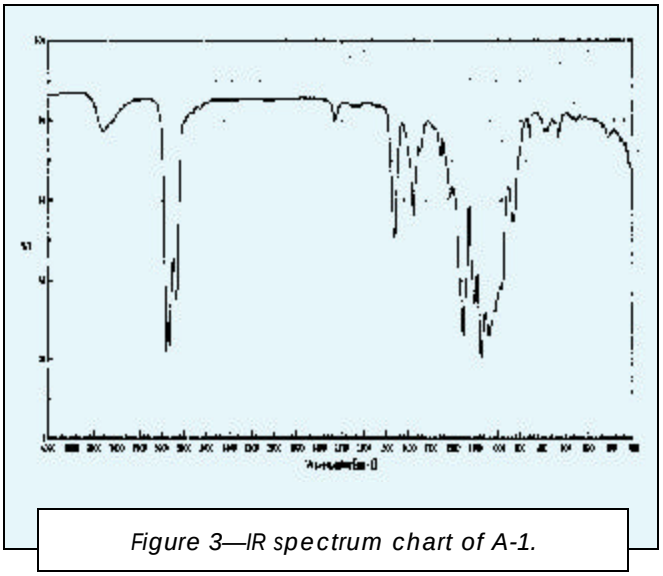

Figure 3—IR spectrum chart of A-1.

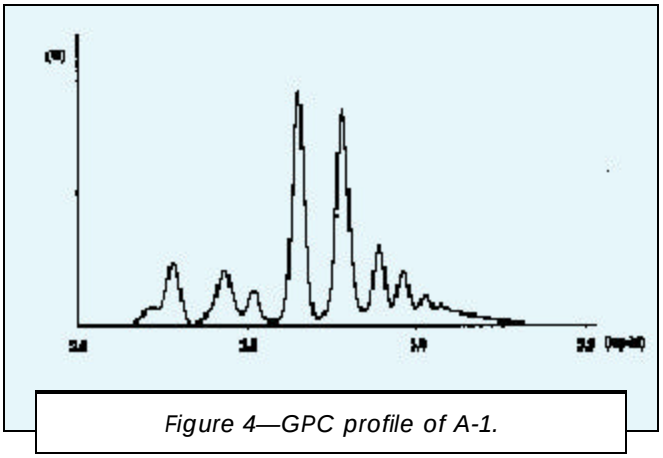

Figure 4—GPC profile of A-1.

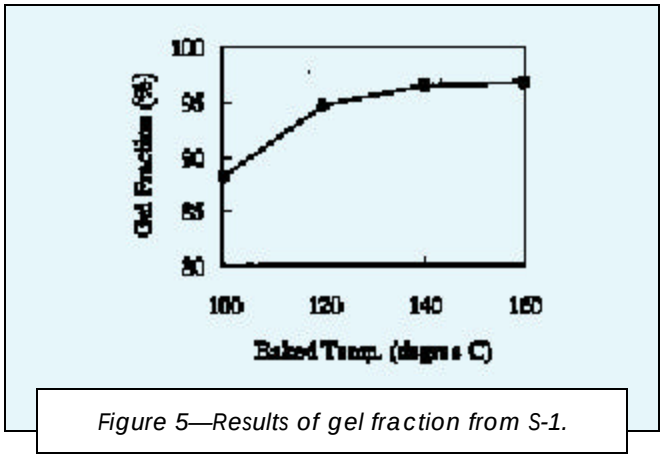

Figure 5—Results of gel fraction from S-1.

solubility parameter close to that of the crosslinking agent by lowering the polarity. As a result, A-1 showed excellent compatibility with the crosslinking agent.

Curing with Polyisocyanate

The composition of the clear coating sample (S-1) has already been described. The viscosity of the sample (S-1) from A-1, N 3300, and Nacure 5543 was V, which was low enough to enable handling of the sample as a liquid material. *Figure* 5 demonstrates the curability at each temperature as a function of the gel fraction %. The sample was baked at each specified temperature for 30 min. A considerably high gel fraction % was obtained at each temperature even though the formulation contained only low molecular weight compounds.

In order to identify the types of crosslinking reactions, IR spectra were measured before and after baking (see *Figure* 6). The loss of the NCO groups was proven by the decrease of the peak at 2270 cm^{-1} (NCO), the loss of the orthoesters was proven by the decrease of the peak at 1070 cm^{-1}, the formation of urethane bonds was proven by the appearance of the peaks at 3360 and 1530 cm^{-1}, and the formation of ester bonds was proven by the appearance of the peaks at 1720 and 1250 cm^{-1}. The results of the TG/DTA analysis are shown in *Figure* 7. The observed weight loss was only 3% during the temperature increase to 200°C, and the maximum exothermic peak was approximately at 110°C.

Based on these results, we suppose the crosslinking reaction proceeds in the following way. First, portions of the orthoester groups in the polyorthoester are hydrolyzed by atmospheric moisture under acidic conditions. Then, 2 moles of the OH groups and 1 mole of ester-bond-containing compound are produced from 1 mole of the orthoester group. Finally, the produced OH groups react with polyisocyanate to initiate the crosslinking (see *Figure* 8).

In the chemical scheme demonstrated in *Figure* 8 the orthoester hydrolyzing forms five molecules. In this case, one is a triol, one is a diol, and three are mono-ols. Thus, the average functionality of the mixture is 1.6 hydroxyl groups per molecule. Since the average functionality of the polyisocyanate is about three, this combination is supposed to be unsatisfactory in terms of a well balanced crosslinking formation. Excellent performances, however, were achieved with this combination as described later. These excellent performances can be explained by the extremely high OHV of the hydrolyzed molecules. Then, a great number of urethane bonds can be formed by the crosslinking. It was determined that the urethane bonds densely contained in the crosslinking film can improve performances with hydrogen bonds.

Pot Life

It was expected that the reaction between the polyorthoester and the polyisocyanate could be inhibited in a closed condition. The viscosity changes of A-1, N 3300, Nacure 5543, and mixtures thereof were investigated under the closed condition (see *Tables* 5 and 6).

The three components were very stable when stored separately, but the mixture containing all three very quickly increased. Although Nacure 5543 played a very significant role in this viscosity increase, the mixture of A-1 and N 3300 also contributed substantially to the increase just after the mixing. It is more than likely that the unprotected OH groups remaining in small amounts in the polyorthoester reacted with the polyiso-

Table 4—Comparison Between the Characteristics of Polyorthoester and Polycaprolactones

	MW (theoretical)	OHV (theoretical)	Viscosity (Gardner)	Viscosity (type B, cP)[a]	SP[b]	Compatibility[c]
A-1	816	550	X+	1350	9.1	Good
PLACCEL-303	300	540	Y-	1800	13.2	Very Poor
PLACCEL-305	550	305	X	1300	11.9	Poor

(a) 60 rpm, 20°C
(b) N 3300 8.9
(c) with N 3300

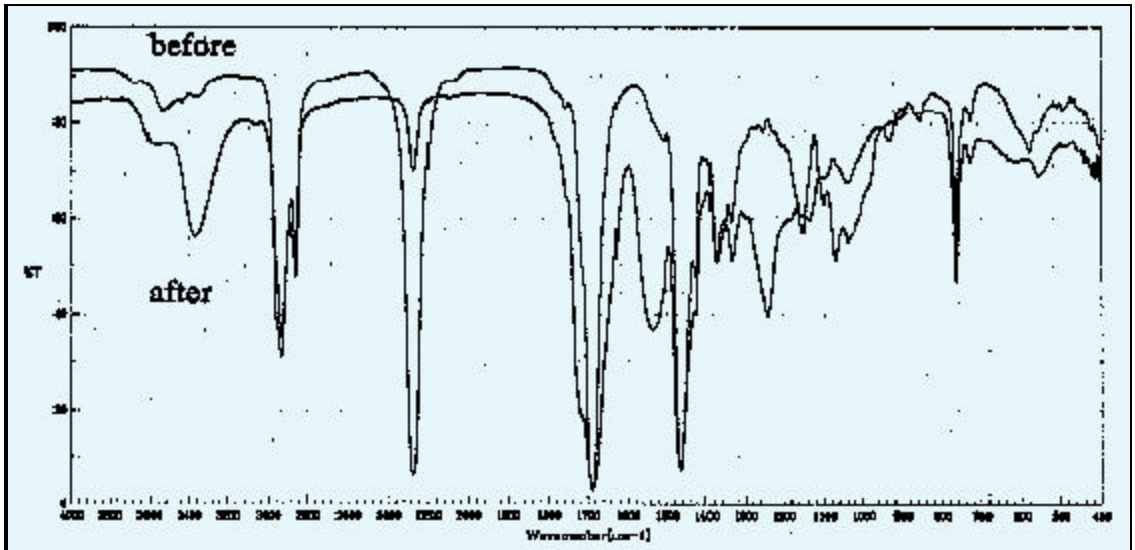

Figure 6—Comparison of IR spectra measured before and after baking.

cyanate shortly after the mixing. In most samples, the reactive groups existed at much higher concentrations than in ordinary coatings, and the dense presence of these reactive groups probably accelerated the viscosity change. Though the mixture of A-1, N 3300, and Nacure 5543 was much more stable than an ordinary polyol-polyisocyanate mixture, it was not stable enough to be kept in a single package.

Properties of Crosslinked Film

The properties of the crosslinked film baked at 140°C are shown in *Table* 7. The film was colorless and transparent, and showed a high gel fraction %, as stated before. The film was hard enough to function as a top-coat, and the Mc was small enough as an NCO crosslinking system. In spite of the use of a crosslinking system based on such low molecular weight compounds, these properties were deemed satisfactory because of the perfect compatibility among all ingredients and the very efficient crosslinking reaction.

Even after the high crosslinking was achieved, chemical resistance was a concern due to the possible generation of formate compounds by the hydrolysis. Gel fractions obtained from the extraction process carried out in either an alkaline or acidic condition were used to evaluate the chemical resistance (see *Figure* 9). The results were satisfactory and chemical bonds in the structure proved to be stable even under severe conditions. A reference prepared from a conventional acrylic polyol and a melamine-formaldehyde resin showed very poor gel fraction % under the acidic condition. This indicated that the chemical resistance test carried out in this study was rigorous enough for screening.

In summary, the properties of the coating prepared from the polyorthoester and the polyisocyanate were considered to be satisfactory for commercial applications.

VOC

Although the mixture of the polyorthoester, N 3300, and Nacure 5543 can be handled as a liquid material

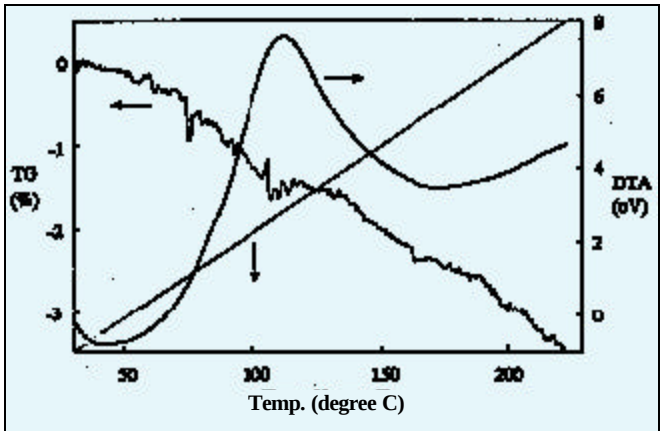

Figure 7—Results of the TG/DTA analysis of S-1.

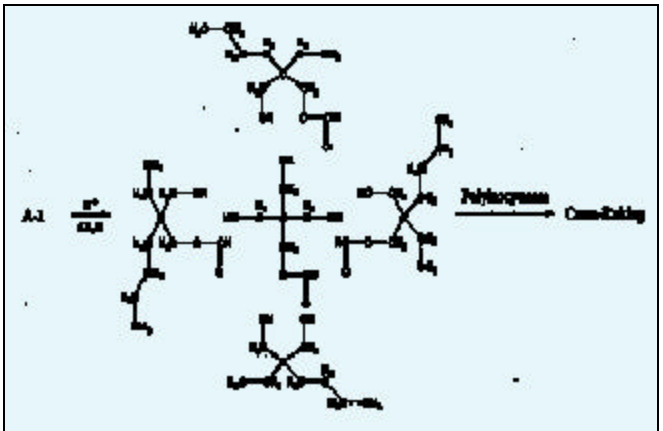

Figure 8—Image of the S-1 reaction.

Table 5—Compositions of the Samples for Pot Life Tests (g)

Sample No.	1	2	3	4	5	6	7	8
A-1	30	—	30	—	10	10	10	10
N 3300	—	30	—	30	19	19	19	19
Nacure 5543	—	—	1.2	1.2	—	—	1.2	1.2
PMA	—	—	2.4	2.4	3.2	7.3	2.3	6.4
NV% (theoretical)	100	100	90	90	90	80	90	80

Table 6—Viscosity of the Samples in the Pot Life Tests (at 30°C)

Sample No.	Initial	3 Days	6 Days	11 Days	24 Days
1	X+	X+	X+	X+	X+
2	Z	Z+	Z+	ZZ1	ZZ1
3	J–	J+	JK	L+	L+
4	TU	Z+	Z1–	Z1	Z2–
5	Q	XY	Z2	Z3	Z3Z4
6	E	LM	U+	VW	VW
7	QR	Galation	—	—	—
8	D+	Z3–	Z5–	Z6Z7	Gelation

Table 7—Properties of the Crosslinked Film Baked at 140°C

Gel fraction	97%
KHN	14
Mc	600
T_g	85°C
Breaking stress	577 kg/cm^2
Tensile modulus	17,000 kg/cm^2
Elongation	6.3%

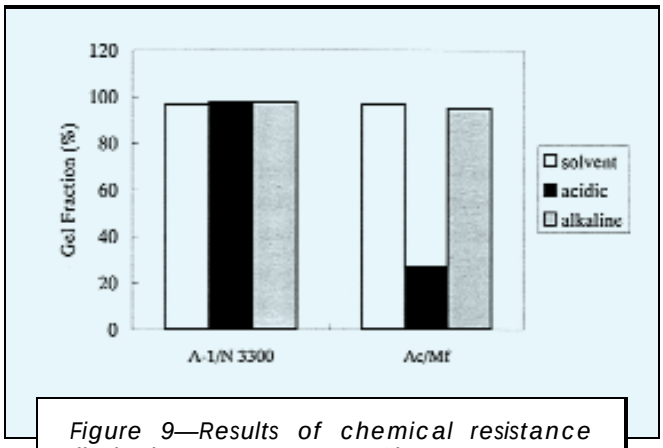

Figure 9—Results of chemical resistance (baked temperature: 140°C).

without any dilution, it was a bit too viscous for ordinary spray applications. Due to the lower molecular weight of the ingredients, the mixture could more easily be atomized than ordinary coatings. The measured VOCs at each sprayable viscosity were 1.2 lb/gal at 60" (FC#4) and 1.0 lb/gal at 150". To the best of our knowledge, 1.0 lb/gal is extremely low, especially in light of the excellent properties.

CONCLUSION

A group of polyorthoesters was successfully synthesized through a co-condensation reaction among polyols, orthoesters, and α– or β-glycol compounds under an acidic condition. The synthesized polyorthoesters were easily hydrolyzed with the atmospheric moisture and the produced OH groups reacted with the polyisocyanate. The clear coating samples showed extremely low VOC emission during the crosslinking process and the cured film showed satisfactory properties for practical applications.

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