

# Novel Phthalocyanine/Polyol High-Solids Coatings: Structure–Property Relationships

BERT J. EXSTED and MAREK W. URBAN\*

Department of Polymers and Coatings, North Dakota State University, Fargo, North Dakota 58105

## SYNOPSIS

A convenient synthetic procedure for preparing nickel carboxylated phthalocyanine is reported. Upon further hydroxylation, such metal phthalocyanine moieties are incorporated into several melamine-based polyester high-solids systems and the structure–property correlations are examined. Molecular level spectroscopic FTIR analysis and mechanical testing are correlated in an effort to establish structure–property relations in these coatings. It is found that the presence of metal phthalocyanine macrocycle as a cross-linking agent enhances such properties as adhesion, hardness, and impact resistance. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

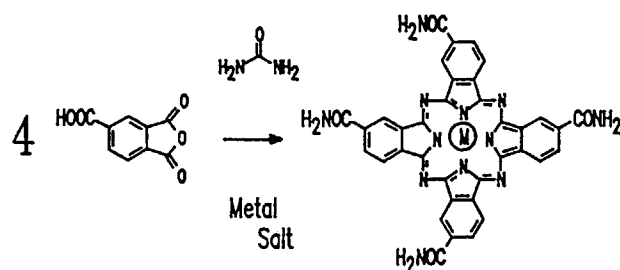
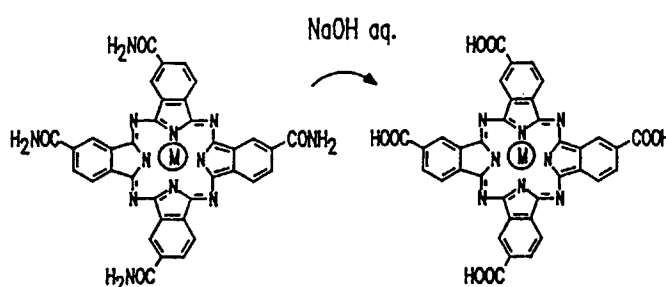
Although existing literature on the use of phthalocyanines in various polymeric applications is plentiful, reported research on these macrocyclic molecules has primarily been limited to their role as a pigmentation component.<sup>1,2</sup> Relatively little research, however, has been reported on their potential use as a reactant within coating systems. This has primarily been attributed to the nonfunctionality of the phthalocyanine's ring structure. Hence, the traditional phthalocyanine moiety has been embedded into a coating system, rather than being covalently bonded.<sup>3,4</sup> Incorporating peripheral functionality off phthalocyanine's aromatic rings, however, presents itself with the interesting prospect of rendering this macrocyclic colorant reactive toward various cross-linking agents, which, in turn, should influence macroscopic properties.

Previously reported attempts of peripherally functionalizing phthalocyanines have often used costly starting materials and involved numerous synthetic steps.<sup>5,6</sup> In an effort to elude these obstacles, a new synthetic pathway for the preparation of a tetrahydroxy-functional phthalocyanine, which uses relatively inexpensive starting reagents and can

be carried out in one step, has been developed.<sup>7</sup> In this new synthetic scheme for the preparation of a hydroxy-functionalized phthalocyanine, a tetracarboxylated phthalocyanine is first prepared by substituting trimellitic anhydride in the place of customary phthalic anhydride, as schematically depicted in Figure 1, Steps 1a and 1b. Hydroxylation of the phthalocyanine monomer, illustrated in Figure 2, is achieved by reacting the acid end groups of the tetracarboxylated phthalocyanine monomer with a commercially available, monofunctional epoxide (Glydex N-10; Exxon). A similar epoxy/carboxylic acid hydroxylation reaction scheme has recently been demonstrated for acrylic acid containing resins by Buter.<sup>8</sup>

Once hydroxylated, the phthalocyanine moiety can be further reacted/cured with an etherified, melamine formaldehyde cross-linking agent. Because of its wide commercial acceptance as a polyol cross-linker, hexamethoxymethyl melamine (HMMM) was selected as the curing agent of choice. Previously reported melamine/polyol coating properties have commonly been cited as exhibiting adequate physical and mechanical properties for many industrial applications.<sup>9,10</sup> Despite this, melamine-based coatings are still considered unsatisfactory with respect to their chip-resistant behavior. In addition, environmental concerns have confined many of these melamine-based systems to high-solid coating formulations. As a consequence, an industrial

\* To whom correspondence should be addressed.

Step 1a: PolycyclotetramerizationStep 1b: Saponification

**Figure 1** Synthesis of  $\text{Ni}(\text{Pc})(\text{COOH})_4$  by (Step 1a) polycyclotetramerization and (Step 1b) saponification.

use of melamine cross-linking agents is limited and new and better ways of improving current melamine-based coating film properties are sought, while still maintaining satisfactory low levels of volatile organic emissions imposed by the Environmental Protection Agency (EPA).<sup>11,12</sup>

This study reports on a convenient synthetic procedure for the preparation of a tetrahydroxy-functional, nickel phthalocyanine monomer that can be formulated into a high-solids, melamine-based (HMMM) system and cross-linked to influence various coating performance behavior. Several polyol/melamine coating formulations are investigated and their resulting structure-property relationships obtained in physical and mechanical film testing are reported herein.

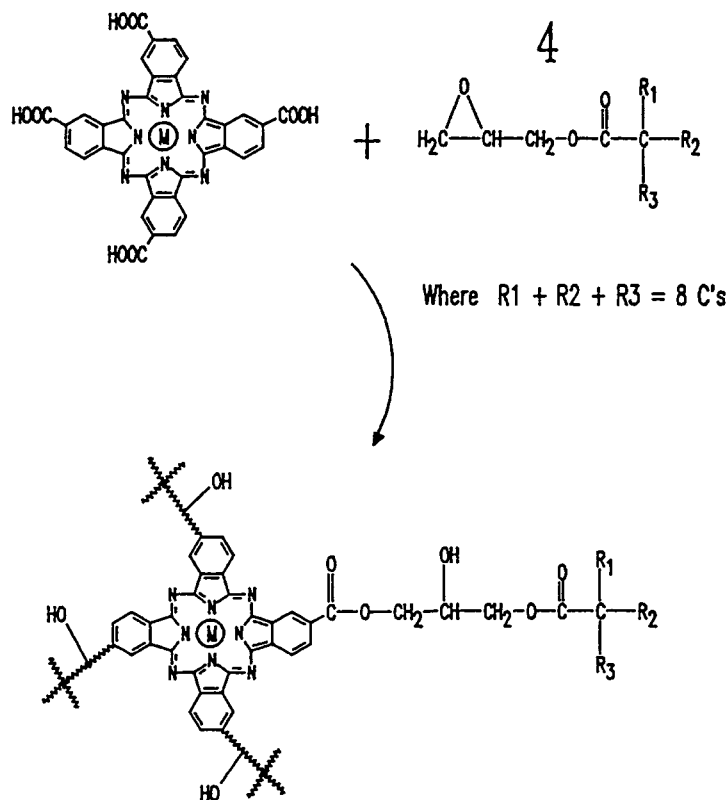
## EXPERIMENTAL

### Synthetic and Formulation Procedures

#### Synthesis of $\text{Ni}(\text{Pc})(\text{COOH})_4$

Into a breakaway 1 L flask equipped with a condenser, mechanical stirrer, thermometer, and a ni-

trogen inlet were added the following: 192.130 g (1.000 mol, Aldrich) trimellitic anhydride; 10.975 g (0.270 mol, Matheson, Coleman & Bell) nickel sulfate hexahydrate; 300.000 g (5 mol, Aldrich) urea; 1.960 g (0.01 mol, Aldrich) ammonium molybdate; 0.535 g (0.01 mol; Alfa) ammonium chloride; and 100 mL nitrobenzene (J. T. Baker Chemical). The resulting mixture was heated to 185°C and maintained at this temperature for a period of 4 h. After cooling, the solidified product was pulverized with a mortar and pestle into a fine powder and repeatedly Büchner-filtered with acetone (3 L) in an effort to remove any residual solvent. Excess metal salts were removed by transferring the phthalocyanine product into a 1 L flask and boiling the crude product for 12 h in 500 mL of 2 M hydrochloric acid, saturated with sodium chloride. After filtration, the peripherally functional phthalocyanine was saponified for 12 h in 750 mL of refluxing 2 M aqueous sodium hydroxide solution that was saturated with sodium chloride. It was then filtered, neutralized with 2 M hydrochloric acid, filtered again, and washed several times with distilled, deionized water and acetone, respectively. The resulting violet-blue, tetracarboxylated nickel phthalocyanine powder was stored in a vac-

*Step 2: Hydroxylation*

**Figure 2** Synthesis of  $\text{Ni}(\text{Pc})(\text{ROH})_4$  by a hydroxylation reaction of  $\text{Ni}(\text{Pc})(\text{COOH})_4$  with glycidyl decanoate.

uum oven ( $120^\circ\text{C}$ ) under vacuum ( $10^{-3}$  Torr). Yield: 79.831 g (42.8%).

ANAL: calcd for  $\text{C}_{36}\text{H}_{16}\text{N}_8\text{O}_8\text{Ni}$ : C, 57.86%; H, 2.16%; N, 15.00%.

Found: C, 54.03%; H, 2.40%; N, 16.57%.

### Synthesis of $\text{Ni}(\text{Pc})(\text{ROH})_4$

Into a breakaway 1 L reaction vessel equipped with a mechanical stirrer, thermometer, condenser, and a nitrogen inlet were added the following: 30.000 g (0.040 mol)  $\text{Ni}(\text{Pc})(\text{COOH})_4$ ; 40.150 g (0.176 mol,  $\text{CH}_2\text{OCHCH}_2\text{OCCCR}_3$ , where  $R_3 = 8 \text{ C's}$ : Glydex N-10, Exxon) glycidyl decanoate; 0.088 g (0.5 g/mol epoxide, Aldrich) benzyltriphenylphosphonium chloride catalyst; and 300 mL phenyl ether (Aldrich). The reaction vessel was slowly heated to  $175^\circ\text{C}$  and maintained at this constant temperature for a period of 3 h. The resulting violet-blue-colored, hydroxylated phthalocyanine was Büchner-filtered, precipitated out of solution with approximately 3 L hexane, centrifuged at 3000 rpm (International

Centrifuge, Model V) for 20 min, washed repeatedly with hexane, and oven-dried ( $120^\circ\text{C}$ ) under vacuum ( $10^{-3}$  Torr). For reasons of convenience, the resulting  $\text{Ni}(\text{Pc})[\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCCCR}_3]_4$  product will be abbreviated as  $\text{Ni}(\text{Pc})(\text{ROH})_4$  throughout the rest of this paper. Yield: 15.913 g (23.9%).

ANAL: calcd for  $\text{C}_{88}\text{H}_{112}\text{N}_8\text{O}_{20}\text{Ni}$ : C, 63.67%; H, 6.80%; N, 6.75%.

Found: C, 63.74%; H, 6.62%; N, 7.42%.

### $\text{Ni}(\text{Pc})$

Nickel phthalocyanine was synthesized and characterized, as previously described.<sup>13</sup>

### Synthesis of a Polyester Diol or $\text{PE}(\text{OH})_2$

Into a 500 mL round-bottom flask equipped with a nitrogen inlet, mechanical stirrer, thermometer, Dean-Stark trap, and condenser were added the following: 156.225 g (1.500 mol, Aldrich) neopentyl

glycol; 73.075 g (0.5 mol, Aldrich) adipic acid; 74.060 g (0.5 mol, Aldrich) phthalic anhydride; 0.303 g (0.1 wt % solids: FastCat 4100, M & T Chemicals) hydrated monobutyl tin oxide; and 30.000 g *p*-xylene (Baker analyzed). The reaction was carried out in two stages: In the first stage, the reaction vessel was heated to approximately 155°C and maintained at this temperature in an effort to open the anhydride ring and react the low molecular weight neopentyl glycol, thereby preventing it from escaping. After 1 h, the reaction was carried to its second stage where it was heated to a constant temperature of 220°C for approximately 4 h until a final acid number of 0.84 mg KOH/g polyester was reached, resulting in a 99.8% calculated conversion value. Using a series of calibrated polystyrene standards and tetrahydrofuran as the eluting solvent, the number-average molecular weight of the resulting linear polyester diol was determined by size-exclusion chromatography (Millipore Waters Associates GPC Model 730 data module) to be approximately 775 g/mol, with a polydispersity index of 2.05.

### Solubility Properties

The room-temperature solubilities of individual coating formulation components were determined in a series of organic solvents, listed in Table I. Approximately 0.010 g of each component was added to a scintillation vial containing 3 mL of solvent and the resulting mixture was sonicated for 5 min. The solutions/mixtures were permitted to stand undisturbed for a period of 24 h before each was visually rated as soluble (s), partially soluble (p), or insoluble (i).

### Polyol/Melamine Formulations

Hexamethoxymethyl melamine (HMMM, Resimene 746, Monsanto), *p*-toluene sulfonic acid catalyst (Aldrich), tetrahydroxy-functionalized nickel phthalocyanine, Ni(Pc)(ROH)<sub>4</sub>, and a polyester diol, PE(OH)<sub>2</sub>, were incorporated into high-solid, coating formulations at various weight ratios, as outline in Table II. Methylisobutyl ketone (MIBK, Aldrich) was chosen as the solvent medium.

### Polyol/Melamine Coatings

Each coating formulation, listed in Table II, was drawn down with a #36 Gardco Applicator Rod ( $\frac{1}{4}$  in. stainless-steel bar wrapped with a 0.036 in. stainless-steel wire) onto 3 × 9 in., cold-rolled, 24-gauge steel panels (Bonderite-1000, Parker Chemical Co.) and cured in a forced-air convection oven at 150°C for 30 min. Curing conditions were in accordance to optimized cure window temperature studies performed by Bauer and Dicke<sup>14</sup> Attempts to prepare similar Ni(Pc) coatings were unsuccessful, due to excessive flocculation of the nonfunctional pigment at concentration levels listed for Ni(Pc)(ROH)<sub>4</sub> in Table II. Consequently, further characterization of these defected coatings was abandoned.<sup>15</sup>

### Analytical Methods

#### Elemental Analysis

Elemental analyses (C, H, and N) were performed by Desert Analytics Organic Microanalysis of Tucson, Arizona.

Table I Coating Component Solubility Data at 25°C

Solvent	Glycidyl Decanoate	Ni(Pc)(COOH) <sub>4</sub>	Ni(Pc)(ROH) <sub>4</sub>	PE(OH) <sub>2</sub>	HMMM
<i>n</i> -Hexane	s	i	i	i	i
Benzene	s	i	p	p	s
Toluene	s	i	p	p	s
<i>p</i> -Xylene	s	i	p	p	s
Methyl isobutyl ketone <sup>a</sup>	s	i	s	s	s
Pyridine <sup>a</sup>	s	i	s	s	s
Acetone	s	i	p	s	s
<i>n</i> -Butanol <sup>a</sup>	s	i	s	s	s
Dimethyl-formamide <sup>a</sup>	s	p	s	s	s
Dimethyl sulfoxide <sup>a</sup>	s	p	p	s	s
Methanol	s	i	i	s	s
(Water)	i	i	i	i	i

s = soluble, p = partially soluble, and i = insoluble.

<sup>a</sup> Potential coating formulation solvents.

**Table II** Coating Formulation Systems and Properties

System	Formulated Weight % Solids <sup>a</sup>			Total Wt % Solids (ASTM D 2369)	Viscosity at 10,000 s <sup>-1</sup> (Pa s)
	PE(OH) <sub>2</sub>	Ni(Pc)(ROH) <sub>4</sub>	HMMM		
<b>1a</b>	70	0	30	70.2	0.08
<b>2b</b>	0	70	30	70.5	0.08
<b>2c</b>	0	50	50	71.1	0.08
<b>2d</b>	0	30	70	70.3	0.08
<b>3e</b>	0	0	100	69.8	0.08
<b>4f</b>	65	5	30	70.5	0.08
<b>4g</b>	60	10	30	70.8	0.08
<b>4h</b>	55	15	30	70.3	0.08
<b>4i</b>	50	20	30	71.2	0.10
<b>4j</b>	45	25	30	70.5	0.08
<b>4k</b>	40	30	30	70.4	0.08

<sup>a</sup> The wt % solids was converted to a gram scale and an equivalent of 42.00 g of methyl isobutyl ketone (MIBK) with 0.30 g of *p*-toluene sulfonic acid catalyst was added to each formulation.

### Infrared Spectroscopy

Photoacoustic Fourier transform infrared (PA FTIR) spectra were collected on a Digilab FTS-10M spectrometer continuously purged with purified air (free of hydrocarbons, carbon dioxide, and water, Balston Filter Products). The phthalocyanine samples and their respective coatings were enclosed in a helium-purged photoacoustic cell. Resulting single-beam spectra were recorded at a resolution of 4 cm<sup>-1</sup> and ratioed against a carbon black reference. All spectra were transferred to an AT compatible computer and analyzed with the aid of Spectra Calc software (Galactic Inc.).

### Formulation Properties

Resulting coating formulations were evaluated with respect to their application-viscosities at high shear rates (10,000 s<sup>-1</sup>) using a standardized I.C.I. cone and plate viscometer (Model License #6489) at 25°C. In an effort to mimic actual application cure temperatures and times, the nonvolatile organic content of each formulation was performed by a modified procedure (150°C, 30 min.) of ASTM method D 2369.

### Coating Properties

Resulting dry-film thicknesses were recorded by a General Electric Film Gauge (Type B, Model 8D041ADM131) and were found to be approximately 1.5 mil thick in accordance to ASTM method D 1186. Solvent resistance values of the cured coatings were obtained by saturating a Kim-Wipe

(Kimberly Clark) with acetone and rubbing the surface of the coated panels back and forth. The number of rubs required to mar or dissolve the film was reported. Other coating properties were determined by standardized ASTM methods: e.g., conical flexibilities (ASTM D 522), crosshatch adhesion (ASTM D 3359), reverse impact resistance (ASTM D 2794), and Tukon hardness (ASTM D 1474).

### Dynamic Mechanical Thermal Analysis (DMTA)

Free films of a traditional 70 : 30 weight ratio of PE(OH)<sub>2</sub> to HMMM, described in Table II, system **1a**, along with an optimized 40 : 30 : 30 weight ratio of PE(OH)<sub>2</sub>/Ni(Pc)(ROH)<sub>4</sub>/HMMM, system **4k**, were obtained by mercury amalgamation of tin-plated panels. Each film was cut into a 10 × 30 mm rectangular sample and subjected to DMTA analysis (Polymer Labs) at a scanning frequency of 10 Hz, with a set heating rate of 2°C/min.

## RESULTS AND DISCUSSION

In an effort to modify the performance properties of a traditional, melamine-based, polyol coating system, a hydroxy-functionalized phthalocyanine was synthesized and incorporated into a high-solids, melamine-based coating formulation.

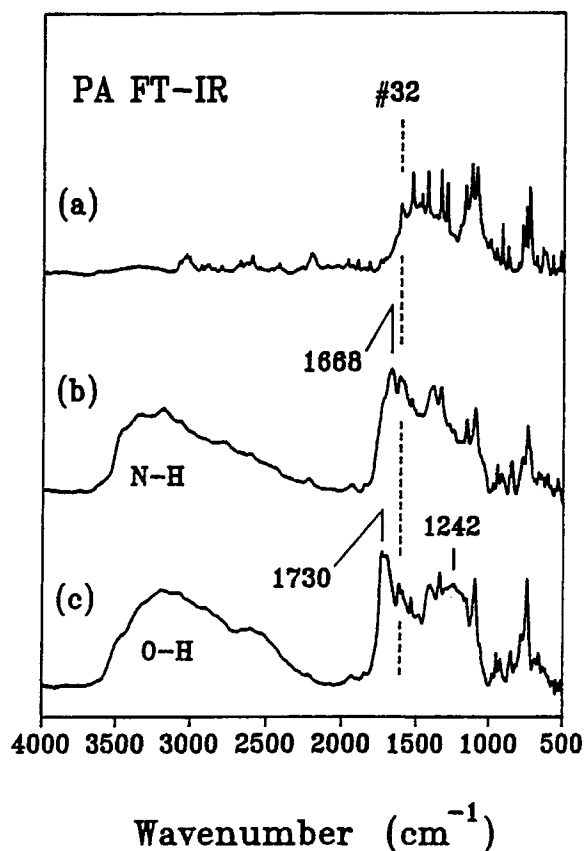
Traditional polyol coreactants for melamine-based systems, such as linear polyacrylate and polyester diols, are generally solvated by industrial organic solvents and are usually considered to be melt processable. The phthalocyanine moiety, however,

being highly aromatic in nature, is characterized by its inherent insolubility in virtually all organic solvents. Additionally, the inability of the phthalocyanine macrocycle to undergo a melting transition often presents difficulties in the characterization and processing of this material. As a consequence, alternative synthetic and characterization techniques, e.g., PA FTIR spectroscopy and elemental analysis, were needed.

#### Synthesis and Spectroscopic Analysis of $\text{Ni}(\text{Pc})(\text{ROH})_4$

Enhancement of the phthalocyanine's solubility and processing nature was attempted by peripherally functionalizing the aromatic rings of the phthalocyanine moiety through a polycyclotetramerization reaction of trimellitic anhydride with urea and a metal sulfate. The PA FTIR spectra displayed in Figure 3, traces b and c, spectroscopically illustrate the peripheral functionality of the nickel phthalocyanine moiety, upon comparison with its nonfunctional  $\text{Ni}(\text{Pc})$  analog, trace a. In accordance to Sidorov and Kotlyar's vibrational band numbering scheme, the phthalocyanine  $\text{C}=\text{C}$  stretching frequency (band 32), which is observed at approximately  $1610\text{ cm}^{-1}$  in traces a–c, are labeled as an inherent reference mode.<sup>16</sup> Substitution of trimellitic anhydride for phthalic anhydride in the polycyclotetramerization reaction, schematically depicted in Figure 1, was observed to result in the formation of several new vibrational modes. As discussed by Bellamy,<sup>17</sup> the sharp new band at  $1668\text{ cm}^{-1}$  and the overlapping bands around  $3400\text{--}3000\text{ cm}^{-1}$  in Figure 3, trace b, can be assigned to an amide carbonyl ( $\text{C}=\text{O}$ ) and various  $\text{N}-\text{H}$  stretching modes of the peripherally amide-functionalized phthalocyanine product, respectively. Upon alkaline saponification, the  $\text{Ni}(\text{Pc})(\text{CONH}_2)_4$  amide vibrational bands disappear and vibrational modes characteristic of a carboxylated nickel phthalocyanine moiety,  $\text{Ni}(\text{Pc})(\text{COOH})_4$ , are detected. This is shown in Figure 3, traces b and c. A distinct upfield shift of the amide to the carboxylic acid  $\text{C}=\text{O}$  carbonyl infrared absorption band is observed to occur from  $1668$  to  $1730\text{ cm}^{-1}$ , respectively. Additionally, trace c displays broad absorption bands at  $1242$  and  $3300\text{ cm}^{-1}$ , which are characteristic of the respective  $\text{C}-\text{O}$  and  $\text{O}-\text{H}$  stretching vibrational modes of carboxylic acid end groups, as discussed elsewhere.<sup>18</sup>

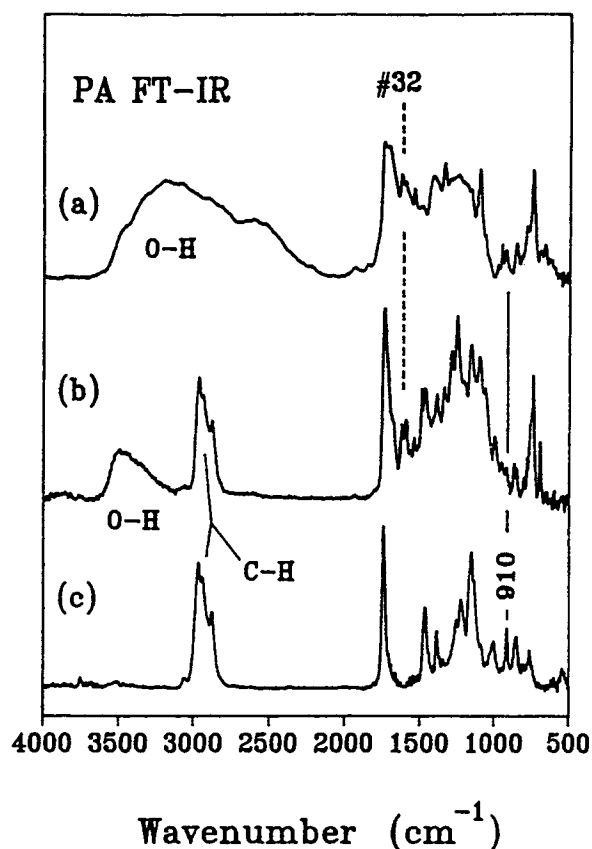
Although the resulting carboxylated phthalocyanine moiety,  $\text{Ni}(\text{Pc})(\text{COOH})_4$ , contains functional groups that are capable of cross-linking with a hexamethoxymethyl melamine curing agent, as previously reported in the literature,<sup>19</sup> it was not found



**Figure 3** PA FTIR spectra of (a)  $\text{Ni}(\text{Pc})$ , (b)  $\text{Ni}(\text{Pc})(\text{CONH}_2)_4$ , and (c)  $\text{Ni}(\text{Pc})(\text{COOH})_4$ .

to be soluble in a series of commercially available solvents that readily dissolve other melamine-based coating components. Consequently, it could not be dispersed into a high-solids coating system. Again, a list of each component's respective solubilities is provided in Table I.

In an effort to alter its solubility, the tetracarboxylated metal phthalocyanine,  $\text{Ni}(\text{Pc})(\text{COOH})_4$ , was further reacted by a hydroxylation reaction with a commercially available monofunctional epoxide, glycidyl decanoate. In this reaction, previously illustrated in Figure 2, the carboxylic acid functions as a nucleophile and opens the oxirane ring of the alkylated epoxide to form an ester linkage and a secondary alcohol. The PA FTIR spectrum shown in Figure 4, trace b, verifies the formation of hydroxylated  $\text{Ni}(\text{Pc})(\text{ROH})_4$  by displaying a new secondary  $\text{O}-\text{H}$  stretching band at approximately  $3500\text{ cm}^{-1}$ . Although this new vibrational band remains broad, it is noticeably less intense and less hydrogen-bonded than is the  $\text{O}-\text{H}$  stretching frequency of its carboxylated precursor,  $\text{Ni}(\text{Pc})(\text{COOH})_4$ , as shown in trace a. Resolved antisymmetric and symmetric  $\text{C}-\text{H}$  stretching vibrational



**Figure 4** PA FTIR spectra of (a)  $\text{Ni(Pc)(COOH)}_4$ , (b)  $\text{Ni(Pc)(ROH)}_4$ , and (c) a monofunctional epoxide, glycidyl decanoate.

modes, characteristic of the alkyl-terminated, tetrahydroxylated phthalocyanine (trace b), are also observed at 2963, 2934, and 2874  $\text{cm}^{-1}$ , respectively. Figure 4, trace c, suggests that the source of these C—H vibrational modes originates from the alkyl-terminated epoxide starting reagent,  $\text{CH}_2\text{OCHCH}_2\text{OOCCH}_2\text{R}$ . Additional supporting evidence for the ring-opening hydroxylation reaction is provided by the diminishment of the absorption band at 910  $\text{cm}^{-1}$  in Figure 4, trace b. This is a vibrational frequency inherently characteristic of an epoxide ring deformation, as shown in trace c.<sup>20</sup> Lastly, elemental analysis data, provided in the Experimental section, support the formation of  $\text{Ni(Pc)(ROH)}_4$ , since theoretically calculated elemental percentage values of C, H, and N match experimental values.

#### Spectroscopy and Properties of $\text{Ni(Pc)(ROH)}_4$ Coatings

Upon hydroxylation, the phthalocyanine polyol became soluble in a given series of commercially avail-

able organic media, which are listed in Table I. Of the five organic media slated as potential coating formulation solvents, three were disregarded due to potential health risks, e.g., pyridine, dimethylformamide, and dimethyl sulfoxide. The final selection for a melamine-based, hydroxylated phthalocyanine coating formulation solvent remained between an alcohol (e.g., *n*-butanol) and a ketone (e.g., methylisobutyl ketone, MIBK). Based upon a review of the coatings literature, however, MIBK was ultimately chosen as the best potential solvent medium.<sup>21</sup> It has been reported that MIBK, being a ketone, is known to serve as an effective hydrogen-bond acceptor, thereby contributing to the solvation of the hydroxylated formulation components. However, alcohols (e.g., *n*-butanol), unlike ketones, are known to serve as both hydrogen-bond donors and acceptors. Consequently, alcohols can form intermolecular associations between the hydroxylated resin components within the coating's formulation, building elaborate networks, which result in a viscosity increase of a high-solids coating system above its applicational limit of 0.1 Pas. A ketone solvent, however, functions only as a hydrogen-bond acceptor and overcomes this problem of interassociated network formations.<sup>22</sup>

Upon using MIBK as a solvent, the prepared melamine-based, tetrahydroxylated phthalocyanine coating formulations were observed to display high-shear viscosity levels at/or below 0.1 Pas, as shown in Table II, systems **2b–2d**. These levels are considered adequate for room temperature brushing, spraying, and/or rolling applications.<sup>23</sup> Additionally, the ASTM nonvolatile solid percentages of the hydroxy-functional phthalocyanine-coating formulations were experimentally found to be around 70 wt %, which readily classifies them as high-solids coating formulations according to EPA standards.<sup>21</sup>

A polyester diol was also incorporated into several high-solids formulations as listed in Table II, systems **1a** and **4f–k**, at concentration levels ranging from 40 to 70 wt % total solids. To maintain a low applicational viscosity level, the polyester diol resin was synthesized to a number-average molecular weight window for a low viscosity, high-solids coating formulation, as established by Belote and Blount.<sup>24</sup>

Once the polyester molecular weight was optimized and an appropriate ketone solvent was chosen, several high-solids, melamine-based coating systems were formulated. The first polyester-containing system, **1a** of Table II, was formulated to serve as a control coating, since it represented a traditional, high-solids, polyester coating system that is typically used by the coatings industry today.<sup>25</sup> Melamine-

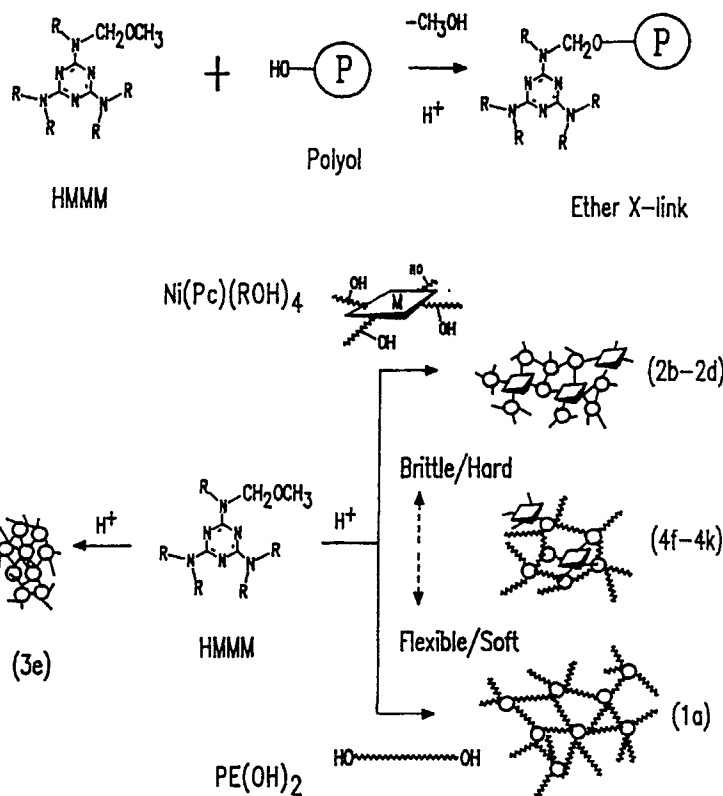
based coating systems **2b–2d** were formulated with the newly synthesized tetrahydroxylated nickel phthalocyanine, in place of the traditional polyester diol. A pure hexamethoxymethyl melamine (HMMM) coating without any hydroxylated phthalocyanine in 5 wt % increments, ranging from 5 to 30 wt % total solids. As shown in Table II, all these coating systems achieved high shear viscosities (at  $10,000\text{ s}^{-1}$ ) of 0.1 Pas or less, thereby meeting rheological requirements for application, while still maintaining a high-solids concentration of 70 st % total nonvolatile organic content.

Melamine-based coating formulations were drawn-down onto Bonderite steel panels and cured at  $150^\circ\text{C}$  for 30 min to obtain an average coating film thickness of 1.5 mil. Upon baking, the hexamethoxymethyl melamine (HMMM) curing agent was observed to undergo an acid-catalyzed transesterification reaction with the hydroxyl groups of the polyester and phthalocyanine polyol resins, as illustrated schematically in Figure 5.<sup>26,27</sup> Melamine-curing of the polyol reagents was monitored by in-

frared spectroscopy, which has previously been reported in numerous studies of transparent melamine-based coatings.<sup>28–30</sup> Photoacoustic Fourier transform infrared (PA FTIR) spectroscopy was used in this study to monitor the transesterification reaction. The PA FTIR spectra in Figure 6, traces c and d, show the diminishment of HMMM's C—H stretching and C—O—C deformation vibrations at  $2828$  and  $915\text{ cm}^{-1}$ , respectively, as methanol from the methoxymethyl ( $-\text{CH}_2\text{OCH}_3$ ) groups leaves the system and new alkoxy ( $-\text{CH}_2\text{OR}$ ) linkages are formed. These spectral changes have previously been attributed to the transesterification cross-linking reaction, as described by Meijer.<sup>31</sup> The hydroxy-functionality of both the tetrahydroxylated phthalocyanine and polyester diols, at around  $3500\text{ cm}^{-1}$ , are also observed to diminish upon the formation of new ether linkages, which are shown in Figure 6, traces a, b, and c, respectively.

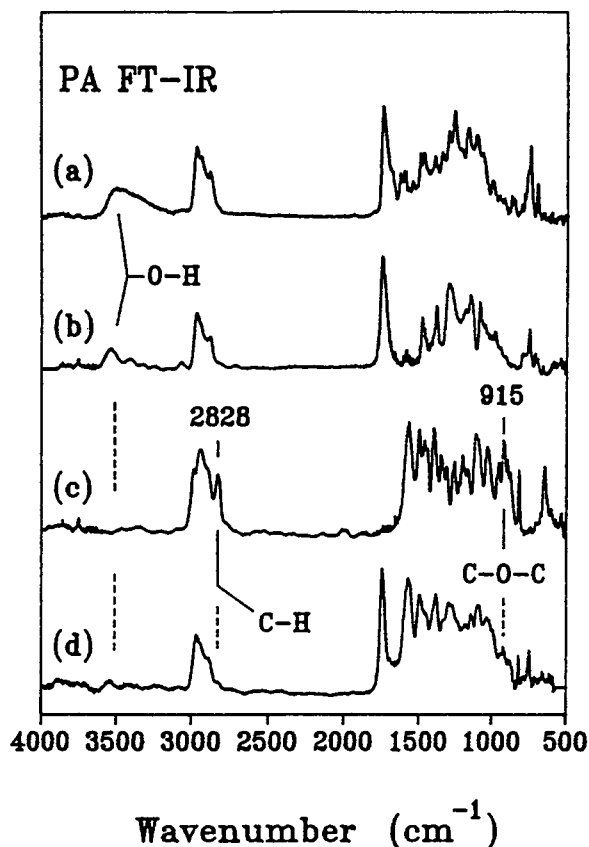
At this point, it becomes appropriate to correlate some of the recently discussed molecular level changes with the macroscopic behavior of the cured

### Step 3: Transesterification



**Figure 5** A transesterification reaction of HMMM cross-linking tetrahydroxylated nickel phthalocyanine and a polyester diol.





**Figure 6** PA FTIR spectra of (a) Ni(Pc)(ROH)<sub>4</sub>, diol, PE(OH)<sub>2</sub>, (c) HMMA hydroxylated phthalocyanine/polyester melamine system (4k).

coating systems. Cross-linking of the hydroxylated polyols with a melamine curing agent, which was observed spectroscopically, can also be monitored by a solvent resistance test, as graphically displayed in Figure 7. Although acetone rub resistance is not yet classified as a standardized ASTM testing method, it is generally accepted as a measure of the degree of cross-linking within a given coating system. A value greater than 200 double rubs is typically associated with a highly cross-linked film, whereas a low number of double rubs (e.g.,  $\leq 25$ ) suggests that the film is not fully cured. As shown in Figure 7, all of the melamine-based coating formulations (1a–4k) display solvent resistance values greater than 200, indicating that the resulting films are highly cross-linked. Evidence of cross-link formation in the nonhydroxylated, melamine-based control formulation (3e) is also noted. This, however, is not surprising since HMMM has previously been reported in the literature to undergo self-condensation thermosetting behavior.<sup>18,32</sup>

Being highly functionalized and aromatic in na-

ture, however, the self-condensed melamine coating (3e) becomes less flexible (more brittle) in comparison to its traditional, melamine-cured, polyester counterpart (1a). This behavior was observed by bending the coated metal substrate 180° over a conical mandrel and recording its conical flexibility, which is given in Figure 8. All the nonpolyester-formulated systems (2b–3e) readily displayed coating stress cracks that were observable with the unaided eye. Upon correlating the length of these cracks to an ASTM calibration scale, the elongations of these failed coating specimens were determined to be within the range of 20–25%. The traditional and hydroxylated phthalocyanine/polyester coating formulation (1a and 4f–4k), however, were observed to readily withstand the maximum tensional force applied across the plane of the cured film, yielding elongation values of  $\geq 33\%$ . In these systems (1a and 4f–4k), as in other reported melamine-cross-linking studies,<sup>24,33</sup> the linear polyester diol resin can be envisioned to serve as a flexible chain spacer between the melamine-cured cross-links or network junction points, which is schematically illustrated in Figure 5.

Absence of a flexible spacer in the cured coating samples 2b–3e may have played an additional role in the resulting coating adhesion data, as evidenced by adhesion values displayed in Figure 9. In this ASTM D 3359 test, an adhesion rating of 5 corresponds to no observable coating removal from the metal substrate, whereas a value of 1 or less corresponds to a film detachment of approximately 65%. Although numerous other factors, e.g., film/substrate compatibility, surface cleanliness, humidity, etc., may adversely affect the adhesion of a coating to a metal substrate, all these experimental variables were held constant during this study. Consequently, the discrepancy between coating samples 2b–3d, which lack the polyester resin, and coating samples 1a and 4f–4k, which were formulated with the polyester, are believed to be influenced by the presence of the flexible spacer. Since phthalocyanines are brittle and notoriously known for their inability to undergo a melting transition,<sup>2</sup> cross-linking of this macrocyclic tetrol with a highly functionalized, aromatic melamine resin resulted in a very rigid polymer network system, which is evidenced by the conical mandrel elongation data in Figure 8.

Based upon these circumstances, the most probable explanation for the loss of adhesion in the nonpolyester-containing coatings, 2b–3e, is believed to be related to the potential buildup of internal stresses within the coatings system upon film curing. During the curing stage of an HMMA cross-linking

Coating Component Weight Percentages											
System:	1a	2b	2c	2d	3e	4f	4g	4h	4i	4j	4k
PE(OH) <sub>2</sub>	70	0	0	0	0	65	60	55	50	45	40
NI(Pc)(ROH) <sub>4</sub>	0	70	50	30	0	5	10	15	20	25	30
IDMH	30	30	50	70	100	30	30	30	30	30	30

### Solvent Resistance

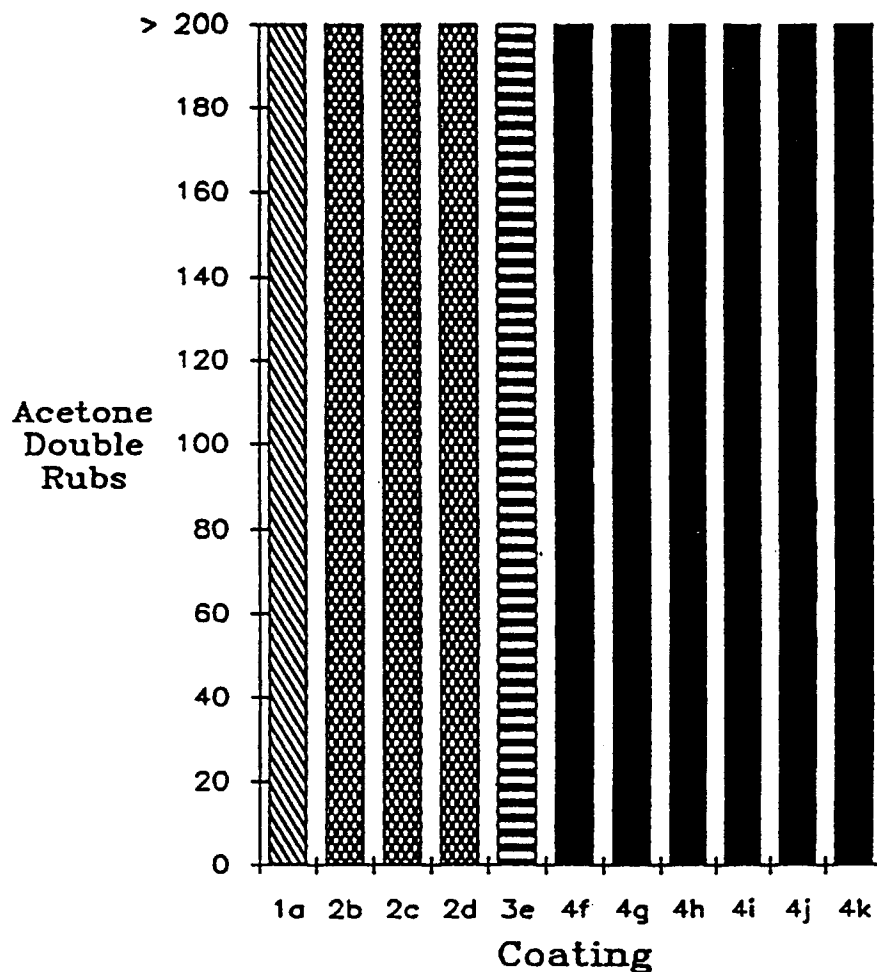


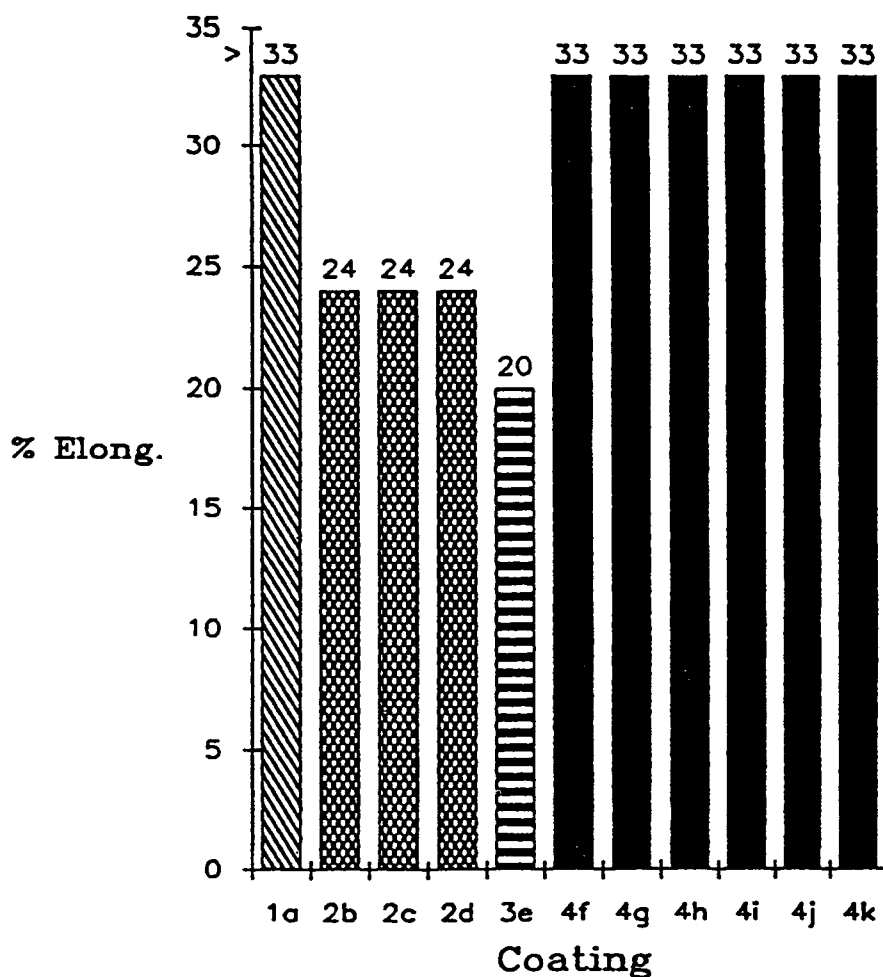
Figure 7 Solvent resistance data of various high-solids, melamine-based coating systems (1a-4k).

agent with a polyol, film shrinkage of the coating system typically occurs.<sup>34</sup> Because the flexible polyester diol, in 1a and 4f-4g, is capable of offsetting

internal stresses that result upon film curing, as displayed in Figure 9, it is postulated that the inflexible phthalocyanine moiety, with its limited ability to

Coating Component Weight Percentages											
System:	1a	2b	2c	2d	3e	4f	4g	4h	4i	4j	4k
PE(OH) <sub>2</sub>	70	0	0	0	0	65	60	55	50	45	40
NI(Pc)(ROH) <sub>4</sub>	0	70	50	30	0	5	10	15	20	25	30
MEM	30	30	50	70	100	30	30	30	30	30	30

*Conical Flexibility*



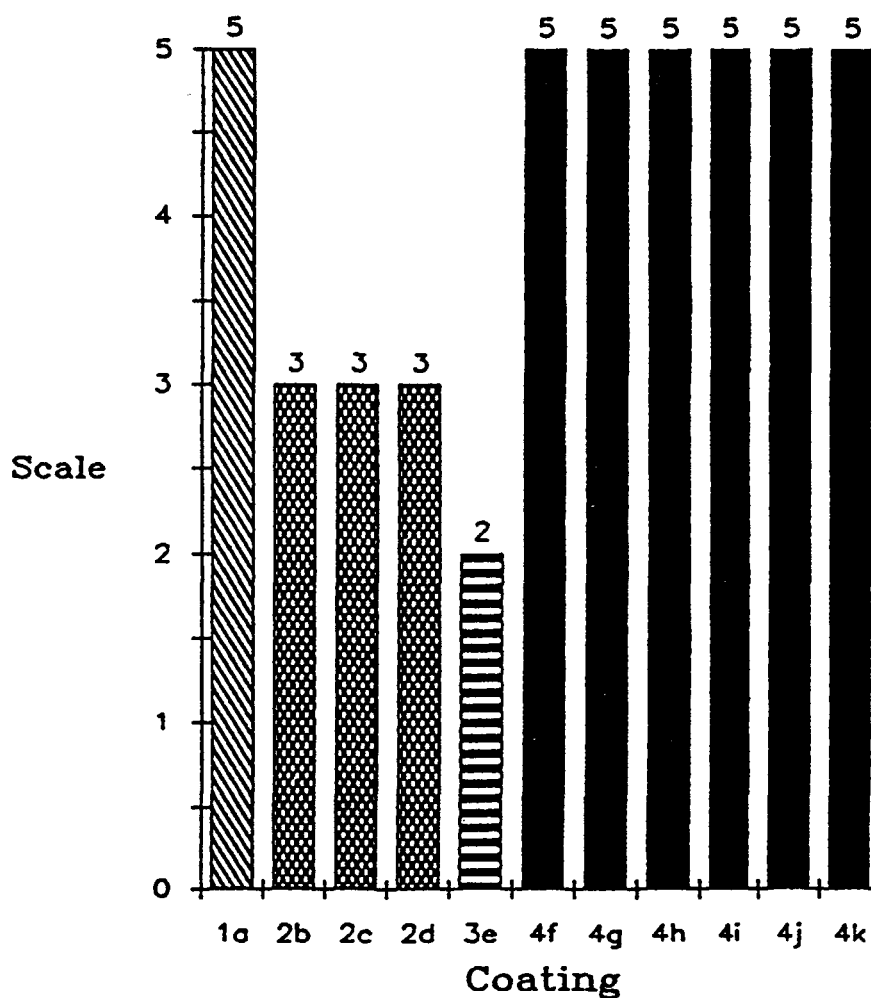
**Figure 8** Conical flexibility (elongation; ASTM D 522) data of various high solids, melamine-based coating systems (1a-4k).

conformationally adjust its rigid structure, is unable to offset the stress applied to the coating system during this ASTM test. Consequently, when 11 perpendicular crosscuts were made through the coating,

down into the metal substrate, as required by the crosshatch adhesion tape test of ASTM D 2794, the force applied to the coating system was greater than were the adhesive forces bonding the coating to the

Coating Component Weight Percentages											
System:	1a	2b	2c	2d	3a	4f	4g	4h	4i	4j	4k
PE(OH) <sub>2</sub>	70	0	0	0	0	65	60	55	50	45	40
NI(Pc)(ROH) <sub>4</sub>	0	70	50	30	0	5	10	15	20	25	30
H <sub>2</sub> O	30	30	50	70	100	30	30	30	30	30	30

### Crosshatch Adhesion



**Figure 9** Crosshatch adhesion data (ASTM D 3359) of various high-solids, melamine-based coating systems (1a-4k).

metal substrate. As a result, the pressure-sensitive tape easily removed the nonadhered coating sections.

All three brittle, melamine-cured, hydroxylated phthalocyanine coatings (2b-2d) were observed to flake-off the surface of the steel substrate at around

15% (3 rating), while the highly cross-linked, self-condensed, melamine-control coating (**3e**) was observed to display the highest degree of adhesion loss, 35% (ASTM rating of 2), which is presented graphically in Figure 9.

Likewise, it is not surprising that these same trends are repeated in coating impact resistance values shown in Figure 10. Upon dropping a 4 lb steel cylinder, vertically through a height-calibrated guide shaft, onto the backside of a coated panel (ASTM D 2794), films **2b–3e** readily cracked at 40 in.-lb or less. These values, in general, are considered to be well below the minimal acceptance value for a protective coating.<sup>32</sup> Only the traditional, high-solids, melamine-cured, polyester coating (**1a**) and its hydroxylated phthalocyanine blends (**4f–4k**), with polyester concentrations ranging from 65 to 40% solids, were observed to withstand the maximum applied impact force of 160 in.-lb without failure.

Thus far, no discernible difference between the industrially used, high-solids, control system (**1a**) and the newly formulated, melamine-cured, phthalocyanine/polyester coatings (**4f–4k**) has been observed. In fact, the only difference between these two types of systems appears to be with respect to their color. Whereas the traditional coating (**1a**) is observed to be translucent and water-clear, the hydroxylated phthalocyanine coatings (**4f–4k**) are noted to be opaque and dark bluish-green in color. Figure 11, however, displays an additional important difference between the two hydroxylated systems. The recorded Tukon hardness values of these two systems (**1a** and **4f–4k**) are observed to be dramatically influenced by the concentration level of the hydroxylated phthalocyanine within the melamine-based coating system. As shown in Figure 11, the traditional, high-solids, polyester coating (**1a**) is observed to display the lowest level of hardness of all the coating systems evaluated, with the exception of **4f**, which also displays a Knoop Hardness Number (K.H.N.) of 3. These hardness values were determined by mechanically lowering a diamond-shaped scribe onto the coated panel for a set period of time and measuring the resulting length of the indentation with a filar micrometer endpiece. The filar units were then converted to a corresponding K.H.N., as described in ASTM method D 1474. Figure 11 also shows that all of the nonpolyester-containing resins (**2b–3e**) display hardness values greater than or equal to 25 K.H.N. Although this may appear to be a desirable property for a protective coating system, these coatings have previously been shown to fail with respect to virtually every other

coating performance evaluation. Consequently, further investigations of these systems were not warranted. However, in the case of the melamine-cured, hydroxylated phthalocyanine/polyester coating (**4f–4k**) values, the exponential increase in recorded Tukon hardness values suggests some potential applications for these systems.

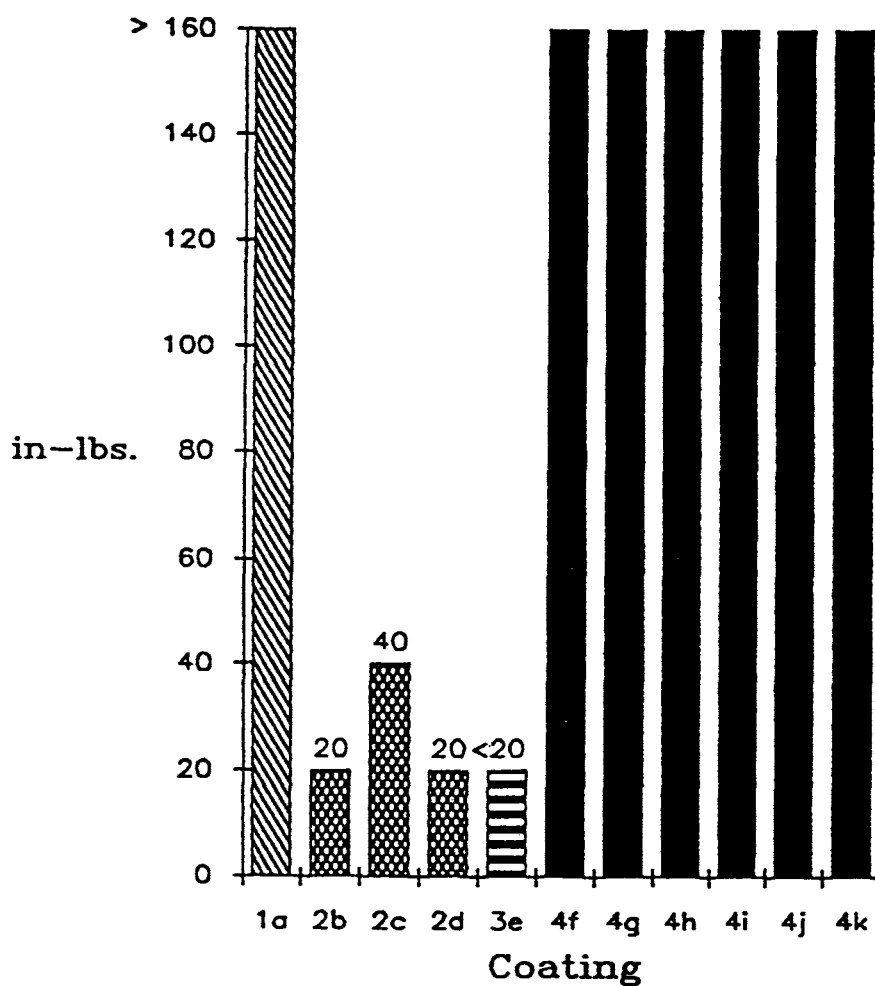
According to previous liquid crystalline, melamine-cured, polyester-coating studies,<sup>35</sup> which also have the capacity to simultaneously display high-impact resistance and Tukon hardness values, a relationship between this behavior and a coating's chip resistance is suggested. This is important, since many melamine-based systems are currently being reduced in the automotive coatings market due to their low hardness values ( $\leq 3$  K.H.N.) and failing chip-resistant character.<sup>36</sup> Use of a new, high-solids, melamine-cured, hydroxylated phthalocyanine/polyester protective undercoat, however, could potentially enhance the overall chip-resistant character of the melamine-based automotive systems. In general, coatings with K.H.N.s of 12 or greater and impact resistance values in excess of 80 in.-lb have been targeted as systems that have the potential ability to serve the automotive market.<sup>37</sup> Based upon this guideline, three hydroxylated phthalocyanine coating systems, **4i–4k**, appear to be optimum candidates for further chip-resistance studies that require use of a standardized gravel projecting machine (ASTM D 3170).

A literature review of mechanical stress analysis methods<sup>38</sup> and experimentally obtained dynamic mechanical thermal analysis (DMTA) data suggest that these new phthalocyanine cross-linked coatings may also have potential applications at elevated temperatures. A typical DMTA thermogram is obtained by applying an oscillatory strain ( $\epsilon$ ) at a set frequency to a free film and measuring the resulting stress ( $\sigma$ ) and phase difference or lag ( $\delta$ ) between the applied strain. The dampening behavior of the coatings was monitored by an interfaced computer and the mechanical loss spectrum ( $\tan \delta$ ) was obtained by increasing the temperature at a constant rate, while measuring the response of the coating to a sinusoidal tensile force. As the temperature increased, both of the cross-linked samples were observed to undergo a transition from a glassy to a rubbery state, which are indicated by  $\tan \delta$  maximums. In general, the resulting peak maximum of a mechanical loss spectrum is assigned to the glass transition temperature ( $T_g$ ) of the polymeric sample, which, in turn, Hill<sup>39</sup> directly correlated with increases in coating impact resistance values.

Apparently, incorporation of a tetrahydroxylated

Coating Component Weight Percentages											
System:	1a	2b	2c	2d	3e	4f	4g	4h	4i	4j	4k
PE(OH) <sub>2</sub>	70	0	0	0	0	65	60	55	50	45	40
Ni(Pc)(ROH) <sub>4</sub>	0	70	50	30	0	5	10	15	20	25	30
MDMI	30	30	50	70	100	30	30	30	30	30	30

*Reverse Impact Resistance*



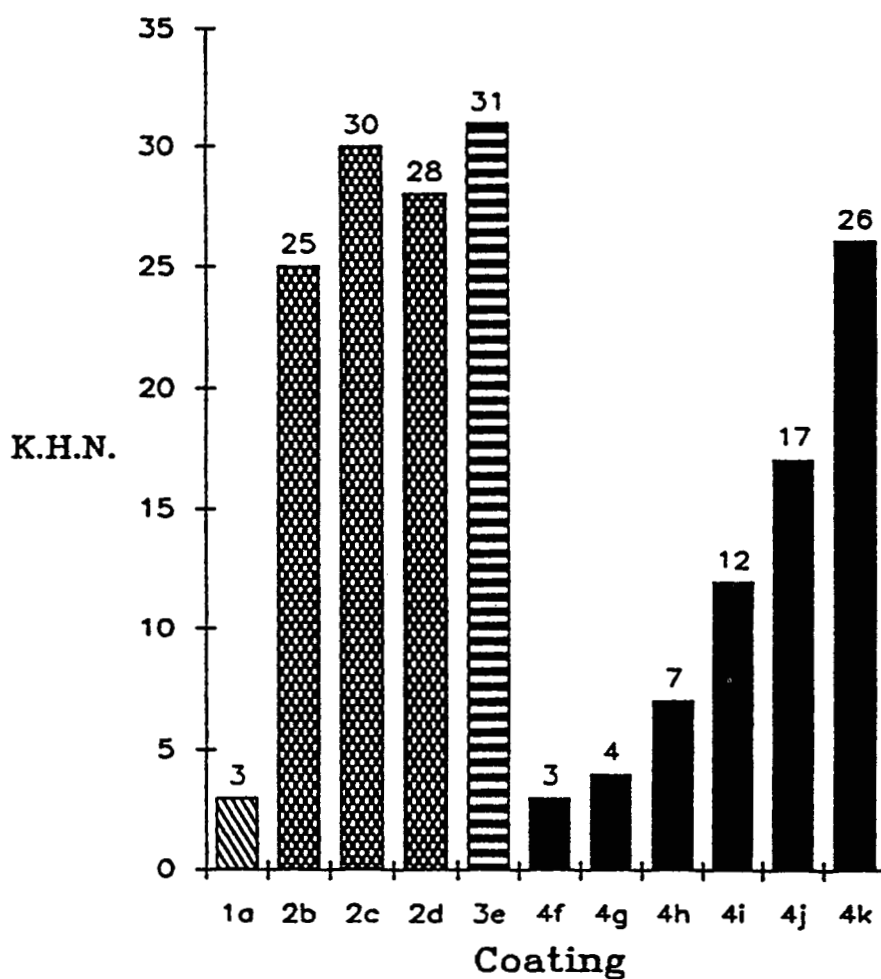
**Figure 10** Reverse impact resistance data (ASTM D 2794) of various high-solids, melamine-based coating systems (1a-4k).

phthalocyanine into a high-solids, melamine-based, polyester system leads to a broadening of the coating's tan  $\delta$  curve. This is shown in Figure 12, traces

a and b, for coating systems 1a and 4k, respectively. The physical interpretation of this phenomenon is attributed to the fact that the cross-linked phthal-

Coating Component Weight Percentages											
System:	1a	2b	2c	2d	3e	4f	4g	4h	4i	4j	4k
PE(OH) <sub>2</sub>	70	0	0	0	0	65	60	55	50	45	40
Ni(Fe)(ROH) <sub>2</sub>	0	70	50	30	0	5	10	15	20	25	30
EPDM	30	30	50	70	100	30	30	30	30	30	30

### *Tukon Hardness*



**Figure 11** Tukon hardness data (ASTM D 1474) of various high-solids, melamine-based coating systems (1a-4k).

ocyanine coating (4k) can more readily convert absorbed mechanical energy into heat, not only under ambient temperature conditions, but also at elevated

temperatures well beyond 150°C. This mechanical loss behavior suggests that a hydroxylated phthalocyanine coating system, such as 4k, may have the

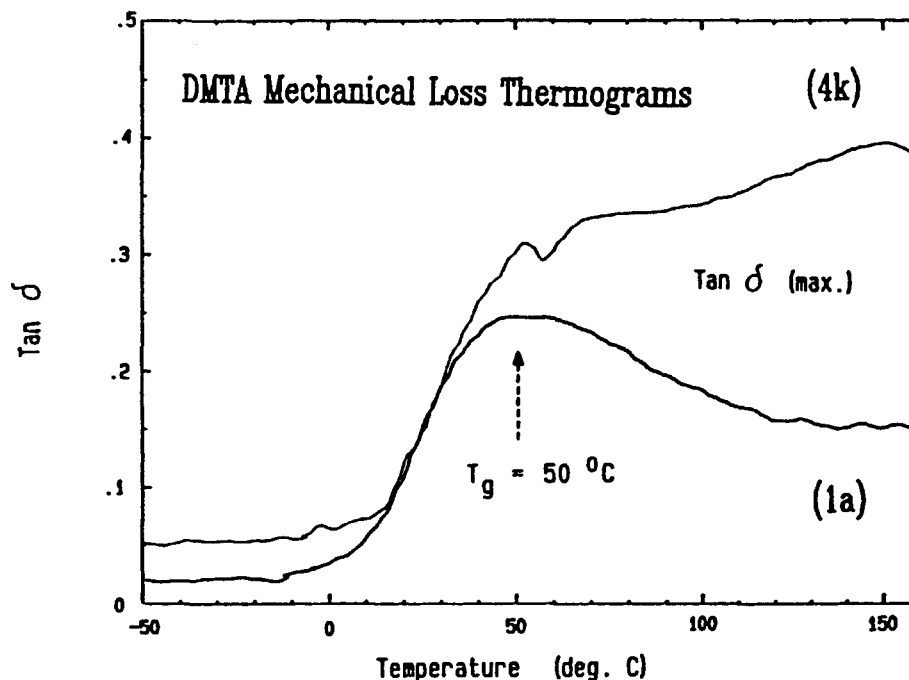


Figure 12 Experimentally determined DMTA thermogram  $\tan \delta$  curves of coating systems 1a and 4k.

additional capacity to serve in end-use applications where opaque coatings with the ability to dissipate sudden mechanical deformation at high temperatures are required.

## CONCLUSIONS

A convenient procedure for the synthesis of a tetrahydroxylated nickel phthalocyanine was reported. A tetracarboxylated nickel phthalocyanine was first prepared by a polycyclotetramerization reaction of trimellitic anhydride with nickel sulfate. Hydroxylation was achieved by reacting the carboxylic acid end groups of the carboxylated phthalocyanine,  $\text{Ni}(\text{Pc})(\text{COOH})_4$ , with a commercially available monofunctional epoxide, Glydex N-10. PA FTIR spectroscopy and elemental analysis were used to verify the resulting tetrahydroxylated phthalocyanine's structure and chemical content.

Once hydroxylated, the phthalocyanine moiety was solvated with methyl isobutyl ketone and formulated into several high-solids, melamine-based coating systems (Table II, systems 2b-2d). A low molecular weight polyester diol was also incorporated into a series of high-solids, melamine-based, hydroxylated phthalocyanine coating systems at various concentration levels, e.g., 40-65 wt % solids (systems 4f-4k), in an attempt to influence certain

coating performance properties. The optimized molecular weight polyester resin was also formulated with HMMM in the absence of hydroxylated phthalocyanine (system 1a), in an effort to represent a high-solids coating formulation that is currently used by the coatings industry today. Lastly, a self-condensed melamine coating system (3e) was prepared to serve as a nonhydroxylated, high-solids, control coating. All the resulting coating formulations were observed to display adequate application-viscosity (at  $10,000 \text{ s}^{-1}$ ) levels at/or below 0.1 Pas and nonvolatile organic content levels near 70 wt % total solids. Hence, they can be classified as high-solids coating systems that comply with governmental restriction on pollution emission levels.

Upon curing at  $150^\circ\text{C}$  for 30 min, all the curing systems were observed to undergo extensive cross-link formation, which was monitored on a molecular level by PA FTIR spectroscopy and on a macroscopic level by solvent resistance studies. Additional test results, which were performed in accordance to standardized ASTM procedures, indicated that the melamine-cured, hydroxylated phthalocyanine/polyester coatings (4f-4k) performed just as well in their elongating, adhesive, and impact-resistant behavior as did a traditional, high-solids, melamine-cured, polyester control coating (1a). The hydroxylated phthalocyanine system (4g-4k), however, differed from this control by displaying superior in-



dentation hardness values and a broader glass transition thermogram. The extent of this behavior appeared to be proportional to the phthalocyanine concentration level,  $[\text{Ni}(\text{Pc})(\text{ROH})_4]$ , within the coating system. Consequently, incorporation of a hydroxylated phthalocyanine reactant into a high-solids coating cannot only serve as an effective means of pigmenting the film, but it can also serve as an effective means of controlling the overall performance of the conventional, melamine-based system.

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