

# UV Curing of Pigmented High-Build Wood Coatings Based on Non-Air-Inhibited Unsaturated Polyesters

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# UV Curing of Pigmented High-Build Wood Coatings Based on Non-Air-Inhibited Unsaturated Polyesters

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## Introduction

Pigmented coatings based on non-air-inhibited, unsaturated polyesters (NAI/UPEs) are usually applied (by direct/indirect roll or curtain coater) to medium-density fiberboard using UV flat-line curing equipment and conventional photoinitiators. Until now, such coatings could not be completely cured at thicknesses beyond 4 mils because the titanium dioxide (TiO<sub>2</sub>) pigment kept the UV light from penetrating deeply enough. One attempt to solve this problem—dual-curing—allowed thicker films to be cured but required managing two separate curing steps.

This paper shows that the proper choice of resins, the UV equipment, and photoinitiator allows acceptable cure of wood coatings as thick as 11.8 mils and with pigment-to-binder ratio of up to 0.3.

## Discussion

This section details the choices of NAI/UPE, UV-cure equipment, and UV photoinitiator that led to improvements in through-cure.

### TRADITIONAL UNSATURATED POLYESTERS

Traditional air drying unsaturated polyesters are polycondensation products based on saturated and unsaturated dicarboxylic acids, such as maleic or fumaric acids, and primary bivalent alcohols. Typically, these systems are dissolved in styrene, which reacts with and crosslinks the unsaturated resin when a dryer system, i.e., a cobalt salt and an organic peroxide, is used. The cobalt salt decomposes the peroxide to form free radicals, R<sup>•</sup>, which initiate the crosslinking of the system.<sup>2</sup> This reaction mechanism is described in Figure 1.

These types of systems are two-component coatings with the cobalt in the formu-

lated product and the peroxide added just prior to use. They have a short pot life which is typically about 5-10 min. They also have a problem with surface drying; the coatings' surface does not cure and will be sticky because the oxygen in the air inhibits the free radical mechanism. A mechanism for oxygen termination is given in Figure 2.

To overcome this effect, a paraffin wax is usually added to the formulation. While the system is curing, the paraffin wax migrates to the surface. Oxygen from the atmosphere is excluded; thus, chain termination is prevented. This technique works but requires removal of the wax since the wax leaves a low gloss appearance. The surface must then be sanded and polished to get a high-gloss appearance. This additional sanding and polishing is very labor intensive.

Work in the mid 1950s<sup>2</sup> saw the development of NAI/UPEs that cured without the aid of waxes. These unsaturated polyesters would have the same hardness and chemical resistance of traditional unsaturated polyesters and would give a high gloss without sanding and polishing. The oxygen inhibition could be prevented through the introduction of allyl ether groups to the modified fumarates. Figure 3 shows a reaction mechanism on the surface.

The radical R<sup>•</sup> attacks the allyl ether forming the allyl ether radical (Step A). This allyl ether radical can then react with a hydrogen atom (Step B), and in conjunction with another allyl ether radical and oxygen, form hydroperoxides which will aid in the further development of new radicals in the presence of a cobalt drier (Step C).

A reaction path within the film is shown in Figure 4. The radical R<sup>•</sup> attacks the allyl ether forming the allyl ether radical (Step A). This radical then attacks the double bond of a fumaric acid group (Step B) forming a radical that can in time form the three-dimensional network of the polymer.<sup>3</sup>

How these two separate reactions may take place within the coating is described in Figure 5. On the surface, the oxygen actually aids in the cure due to the allyl

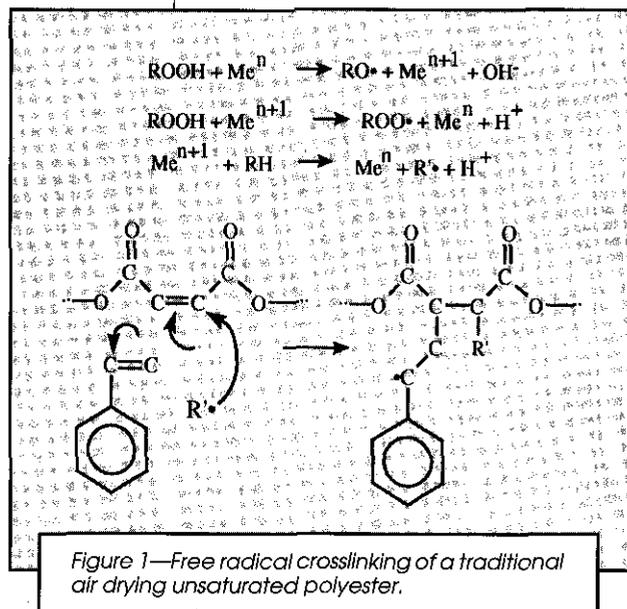


Figure 1—Free radical crosslinking of a traditional air drying unsaturated polyester.

ether groups. Below this surface, the copolymerization of styrene and fumaric acid groups occurs without being inhibited.<sup>4</sup>

### UV-CURING OF NAI/UPEs

**UV-Curing Mechanism:** The most significant method of cure for these NAI/UPEs is through the use of UV light and photoinitiators. This free radical-cure mechanism allows for instantaneous cure of the NAI/

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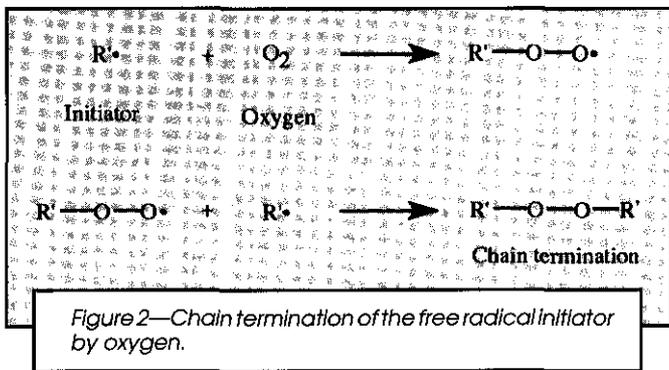


Figure 2—Chain termination of the free radical initiator by oxygen.

UPEs. It eliminates any difficulties due to ingredients in certain woods that can inhibit the peroxide/cobalt cure mechanism. It also has the added advantage of working as a one-component system and not requiring inert gas to prevent oxygen from inhibiting surface cure. Typical photoinitiators for a NAI/UPE are those based on hydroxy propiophenones.

The cleavage reaction of 2-hydroxy-2-methyl-1-phenyl-propan-1-one when it is photolyzed is given in Figure 6.

This cleavage goes through a very short triplet state and then decomposes by  $\alpha$ -splitting to give a benzoyl radical and a 2-hydroxy-2-propyl radical.<sup>5</sup>

### UV-CURE EQUIPMENT

The improvement reported here—the ability to cure thick films at high pigment loadings—was largely a result of changing from standard UV arc-lamp ovens to UV ovens that have long- and short-wave electrodeless bulbs—bulbs with energy outputs of up to 600 watts per inch.

In standard arc lamp ovens, the UV light is blocked by the TiO<sub>2</sub> (rutile) pigment in the coating and cannot penetrate much beyond approximately 4 mils (Figure 7).<sup>6</sup>

Some improvement came with gallium-doped, low-wattage, long-wave fluorescent

lines—thicker pigmented films still did not develop full hardness.

The electrodeless bulbs described here, however, develop full hardness at up to 11.8 mils and at pigment-to-binder ratios of 0.3.

### UV PHOTOINITIATORS

A second improvement can be made in choosing the proper UV photoinitiator.

European researchers found that the photoinitiators used in unpigmented wood coatings (see Table 1, photoinitiators A, B, and C) cannot initiate cure of pigmented coatings because they activate in the same UV range that is blocked by the TiO<sub>2</sub> (rutile) pigment.

But two new photoinitiators, photoinitiators D and E, activate above the 380 nm cutoff of TiO<sub>2</sub> and therefore can activate cure of thick, heavily pigmented coatings (Figure 9). These photoinitiators with NAI/UPEs have been used commercially in Italy for the last five years<sup>7-9</sup> (Figure 10).

This study used photoinitiator D, which is a solid and dissolves in the resin systems free monomer, in the following systems: UV topcoat, UV sealer, air dry topcoat, and solvent-borne resin. Photoinitiator E, which is

a liquid version of photoinitiator D, was used for the water reducible and 100% solids UV topcoat.

UV-curable NAI/UPEs are available in three forms: those that contain styrene, those that are reduced in solvent and do not contain styrene, and those that are water-reducible but contain no styrene or solvent (VOC about 0.2 lbs/gal). The latest development of NAI/UPEs is a low-viscosity product containing no styrene, solvent, or water—only resin and UV photoinitiator. Many NAI/UPEs produce fully cured, high-build coatings (up to about 11.2 mils WFT) in systems with pigment-to-binder ratios of up to 0.3.

## Experimental

### SAMPLE AND FILM PREPARATION

Samples were prepared by grinding rutile TiO<sub>2</sub> into the resin solution, then drawing them down on glass and UV curing them. The degree of cure was measured by the Koenig pendulum hardness instrument. In addition, hardness was measured four days later to see if there had been any post cure.

### TEST PROTOCOL, UV-CURING DEVICES

Films were cured using three different types of UV exposures: a UV-arc lamp oven (Figure 11) for its spectral curve; TLO3 bulbs (Figure 8) followed by a UV-arc lamp oven; and an electrodeless oven using a gallium-doped V bulb (Figure 12) followed by a D bulb (Figure 13). In addition, each UV-curing device was evaluated at two different UV energy dosages.

Table 2 gives the energy dosage that each film received during the curing process.

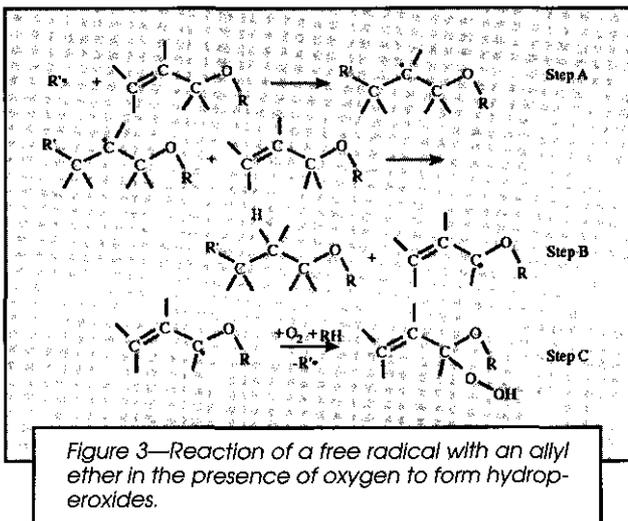


Figure 3—Reaction of a free radical with an allyl ether in the presence of oxygen to form hydroperoxides.

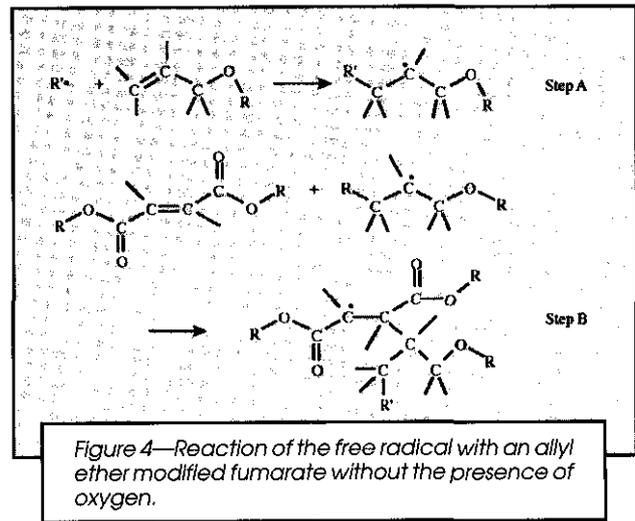
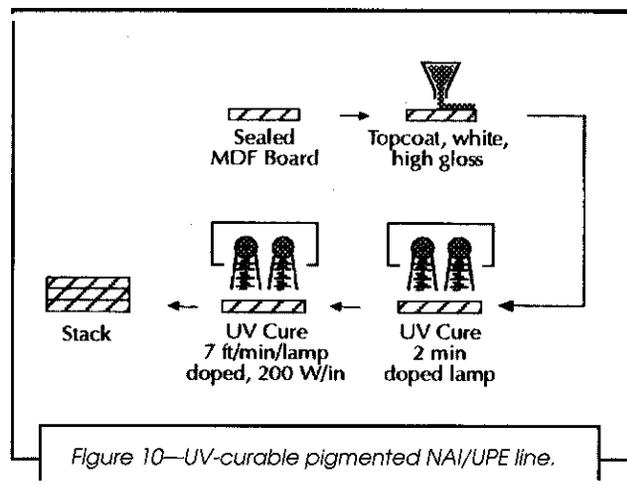
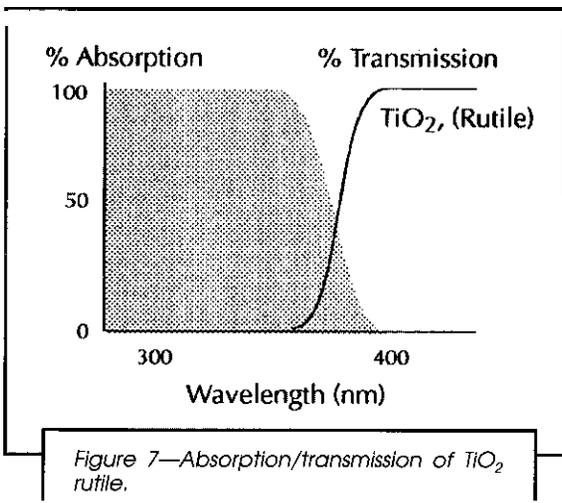
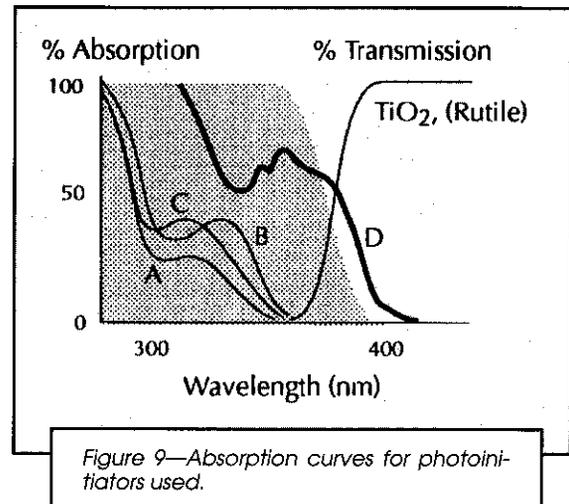
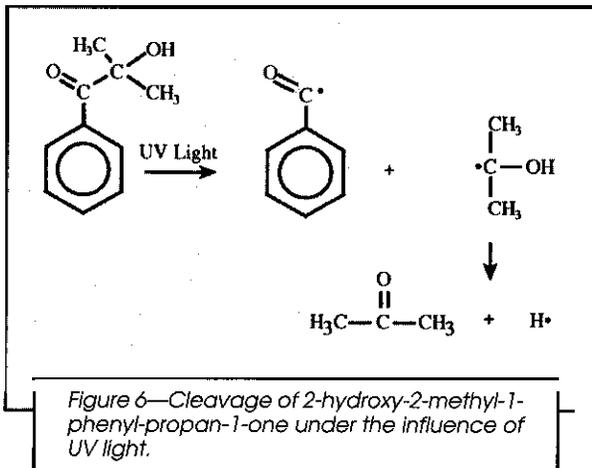
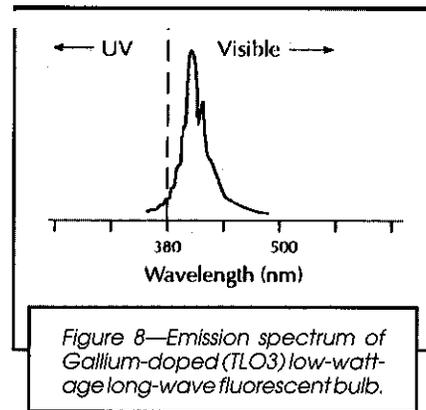
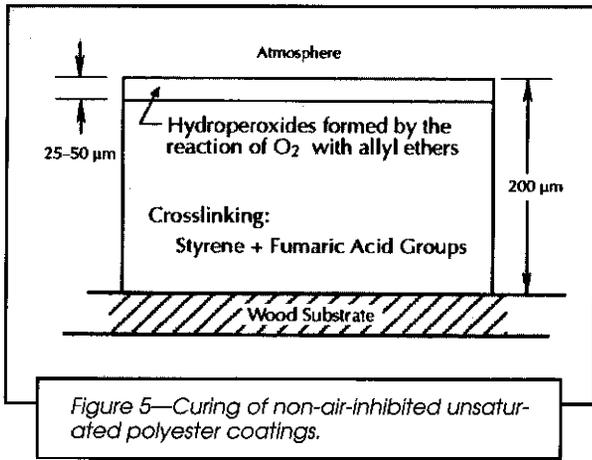
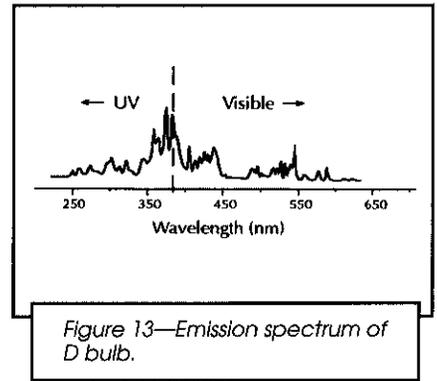
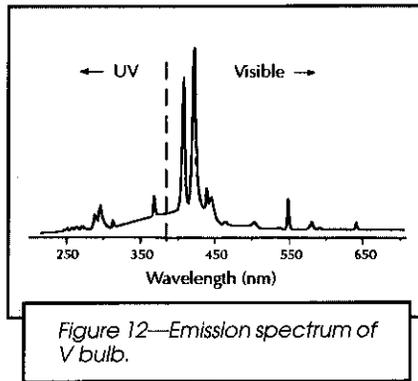
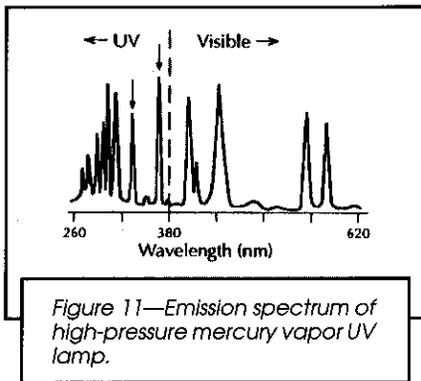


Figure 4—Reaction of the free radical with an allyl ether modified fumarate without the presence of oxygen.





## Data Analysis

### UV TOPCOAT BASED ON NAI/UPE RESINS

Appendix 1, Figures A-F show that hardness development generally decreases with increasing film thickness and pigment-to-binder ratio. This trend is especially evident in the UV-arc lamp series (Appendix 1, Figures A & B), where no cure was measured above 8 mils WFT with 0.3 pigment-to-binder ratio.

Post cure occurred in most cases. This post curing can actually be a benefit with the NAI/UPE: the initial lower hardness will make it easier to sand and polish the coating if that becomes necessary, as is the case when the coating is applied in a dusty environment.

### UV SEALER BASED ON NAI/UPE RESINS

The UV sealer based on NAI/UPE gave the best hardness development of all the pigmented NAI/UPEs tested. Appendix 2, Figures A-F show the development of hardness achieved with arc lamp, TLO3/arc-lamp and electrodeless V and D bulbs.

The UV sealer NAI/UPE also showed the greatest amount of post cure of all the systems tested, and developed the highest hardness (165 sec initial to 180 sec after four days) at the most critical point of the testing matrix (about 11.8 mils at a pigment-to-binder ratio of 0.3). Cure criteria were easily met when the coating was subjected to the electrodeless V and D bulbs at 600 W. This resin system is especially designed for UV cure.

### UV CURE OF AIR-DRY/ NAI/UPE TOPCOAT

For various processing reasons, furniture manufacturers choose to UV-cure pigmented coatings that are not specifically designed for UV cure.

Some will dual-cure these systems both by air drying with cobalt salt and perox-

ide and by UV curing. We found that coatings cured in this way do not harden fast enough (see Appendix 3, Figures A-E) for four of the six techniques for unpigmented systems listed in Table 2. However, the coatings cured with the TLO3 and arc lamp at 300 W developed hardness better (Appendix 3, Figure D) than the coatings cured with electrodeless V and D bulbs at 300 W (Appendix 3, Figure E). Interestingly, at 600 W, the air dry NAI/UPE produced the best hardness under the electrodeless V and D bulbs at 600 W (Appendix 3, Figure F).

### SOLVENT-BORNE NAI/UPE RESINS

We tested solvent-containing NAI/UPE resins as alternatives to reactive monomer-based resins. These NAI/UPE products can be cured either by cobalt salt and peroxide or by UV. Curing by UV, however, requires a flash off time to remove solvents before the cure (Appendix 4, Figures A-F). P/B values of "0.0" for the electrodeless V and D oven were not tested (Appendix 4, Figures E & F).

### WATER-REDUCIBLE NAI/UPE RESINS

Water-reducible NAI/UPEs, which contain no styrene or solvent, have the same properties as products that contain these diluents. A 3-mil coating based on such products requires a five-minute flash off at 150°F to remove the water before UV cure,<sup>10</sup> and this flash-off time increases as the film becomes thicker. Formulations for this product have VOCs as low as 0.2 lbs/gal (Appendix 5, Figures A-F).

### HIGHLY PIGMENTED, 100% SOLIDS UV-TOPCOAT BASED ON NAI/UPE RESINS

A new product that avoids solvent, water, or styrene is the 100%-solids NAI/UPE. Coatings based on this recently developed product can be UV cured as well as air cured.

This NAI/UPE can tolerate only a liquid photoinitiator because it has no styrene or solvent to dissolve a solid photoinitiator. The formulations tested contained the liquid photoinitiator E instead of the solid

Table 1—Key to Photoinitiators

Code	Photoinitiators
A	1-Hydroxycyclohexyl phenyl ketone
B	2,2-Dimethoxy-2-phenyl acetophenone
C	Benzoin isopropyl ether
D	2,4,6-Trimethylbenzoyldiphenoyl-phosphine oxide (solid)
E	Proprietary blend of aromatic ketone (liquid)

Table 2—Energy Dosage Received by Coating During Curing

UV Oven Type <sup>a</sup>	Bulb, Watt/in.	UV Energy Dosage, J/cm <sup>2</sup>
UV-arc oven	200	0.352
UV-arc oven	300	0.587
TLO3 UV-arc oven	200	0.352
TLO3 UV-arc oven	300	0.587
Electrodeless V and D	300	V = 0.105 D = 0.287
Electrodeless V and D	600	V = 1.533 D = 3.658

(a) Line speed on all ovens was 6 ft per min.

photoinitiator D, Table 1. The solid photoinitiator D, however, should give the best through-cure if a method can be found to incorporate it into this NAI/UPE. Coatings produced with the liquid photoinitiator at higher film builds and pigment-to-binder ratios developed less than adequate hardness (Appendix 6, Figures A-F). Future work will focus on finding more effective liquid photoinitiators.

**Conclusions**

Pigmented wood coatings based on NAI/UPE can be UV cured: at thicknesses of up to 11.8 mils and at pigment-to-binder ratios of up to 0.3; and in styrene, solvent, or water, or as 100% solids. Pigmented NAI/UPE coatings are best UV cured with electrodeless V and D bulbs and photoinitiator D or E.

We tested high-film builds and pigment-to-binder ratios under lab conditions. We

will conduct plant trials on wooden substrates to verify the lab tests.

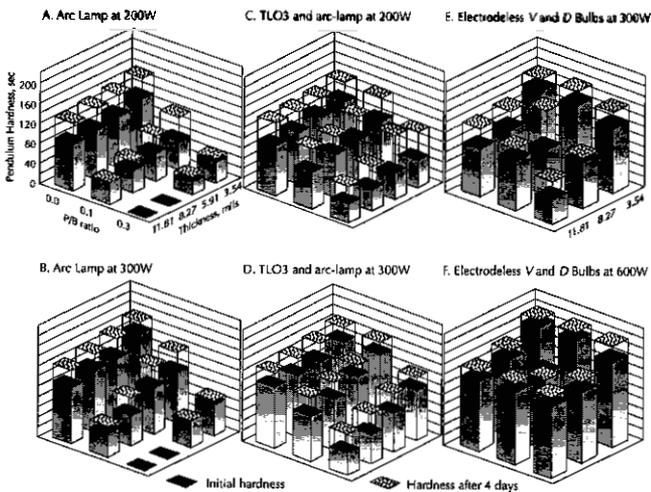
**Acknowledgment**

Special thanks to Patrick J. McFarlane for his dedicated and timely lab work in carrying out the experiments.

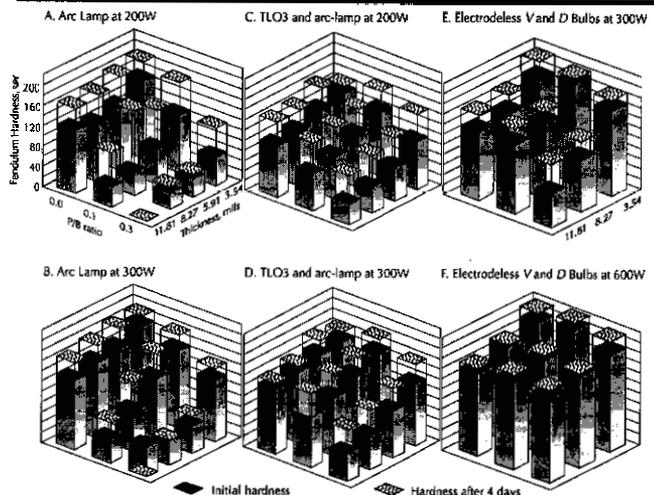
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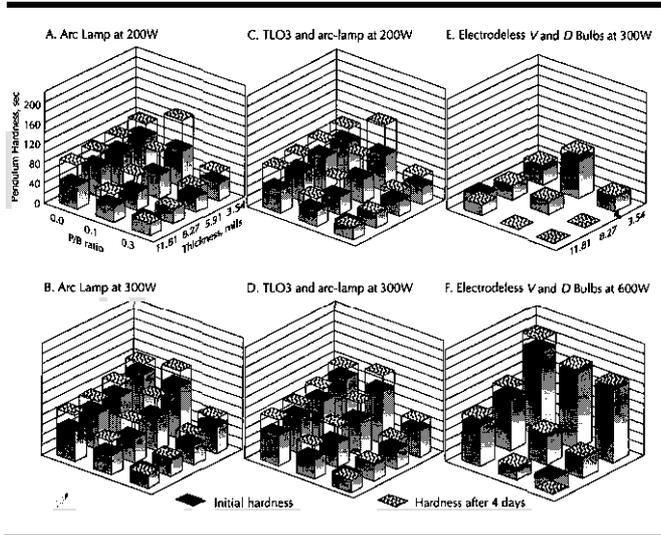
**Appendix 1—UV Curing of Topcoat Based on Non-Air-Inhibited Unsaturated Polyester**



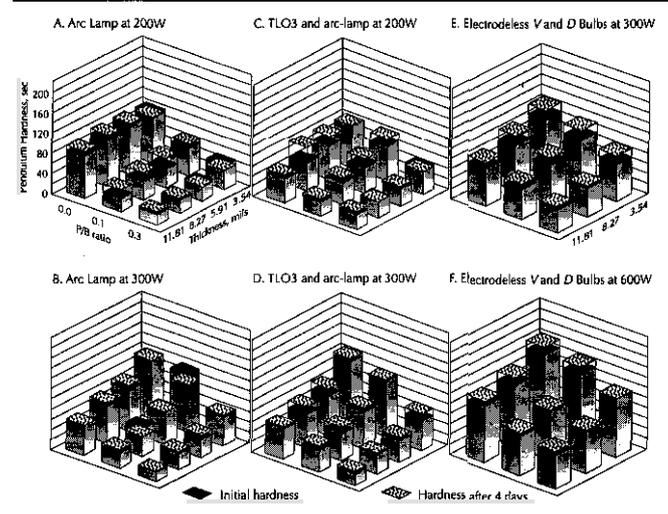
**Appendix 2—UV Curing of Sealer Coating Based on Non-Air-Inhibited Unsaturated Polyester**



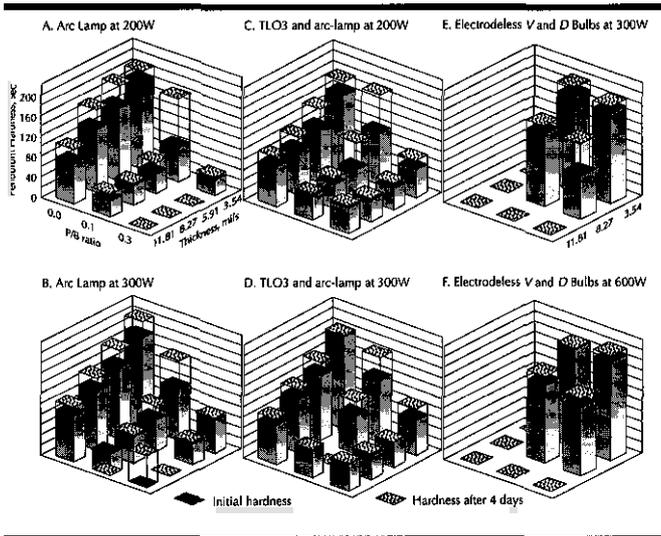
**Appendix 3—UV Curing of Air-Dry Topcoat Based on Non-Air-Inhibited Unsaturated Polyester**



**Appendix 5—UV Curing of Water-Reducible Coating Based on Non-Air-Inhibited Unsaturated Polyester**



**Appendix 4—UV Curing of Solvent-Borne Coating Based on Non-Air-Inhibited Unsaturated Polyester**



**Appendix 6—UV Curing of 100% Solids UV Topcoat Based on Non-Air-Inhibited Unsaturated Polyester**

