# Polyester Weatherability: Coupling Frontier Molecular Orbital Calculations of Oxidative Stability with Accelerated Testing

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## INTRODUCTION

A variety of accelerated weathering techniques have been developed and utilized over the last 40 years of coatings research in an effort to predict "real" weatherability of all coating systems in a short period of time.[1-4] Accurate predictive capabilities have obvious practical benefits because coating warranties are based upon real performance. New resins and new coating systems must go through long-term testing prior to market introduction unless accelerated performance data can be used reliably as a predictor of long-term durability.

Just as conventional accelerated test methodologies help guide developmental coatings projects, accepted theoretical polymer degradation mechanisms[5,6] provide the conceptual foundation which also guides research efforts. In our recent work with polyesters based upon 2-methyl-1,3-propanediol (MPD) we observed some unusual exceptions to well founded concepts. Specifically, well cited Norrish Type II degradation mechanisms imply that polyesters containing diols with beta-hydrogens will degrade rapidly under UV radiation;[7,8] however, our testing of polyesters based upon MPD, which contains a beta-hydrogen, contradicts this theory.

$$\underset{\text{(MPD)}}{HO-CH_2-\underset{\overset{|}{CH_3}}{CH}-CH_2-OH}$$
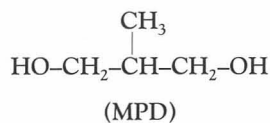
In addition, for polyesters with different levels of isophthalic acid in the polyester backbone, we have seen contradicting test results from different test procedures.

In order to address the contradictions in test results and the contradictions with accepted theory, we focused our attention on developing accelerated weathering data on several coating systems by several different techniques. Florida exposures were also initiated. In addition, we addressed the many mechanisms of polymer degradation and, ultimately, we utilized frontier molecular orbital calculation (FMOC) methods to identify the oxidative weak links.

In utilizing FMOC, we obtained relative values of oxidative stability for the different bonds in the polyester. Some of these values were highly unexpected, but the values fit very

A series of polyesters were formulated into melamine baking enamels and evaluated by QUV-B, QUV-A, Xenon arc, Emmaqua® NTW, and Florida exposures in order to determine the effect of polyester composition on outdoor durability. Specifically, 2-methyl-1,3-propanediol was compared to propylene glycol and neopentyl glycol in several compositions that utilized adipic acid, isophthalic acid, and phthalic anhydride as the diacid constituents. Unexpected positive results for polyesters based upon 2-methyl-1,3-propanediol led to a detailed analysis of polyester decomposition mechanisms and raised questions concerning the true significance of beta-hydrogen degradation pathways. Semiempirical frontier molecular orbital calculations demonstrated that the beta-hydrogen of diols and diol esters are less susceptible to oxidative attack than the alpha hydrogens. The molecular orbital calculations fit well with experimental evidence and provided a deeper understanding of the effect that the components of polyesters have upon the exterior durability of the coating.

well with the experimental evidence. This coupling of the molecular orbital calculations with the test results enabled a better understanding of the impact that different components of the polyester have upon the polyester weatherability and provided added insight into the relative importance of differ-

**Table 1—Polyester Compositions for Coil Coatings**

| Components | PE-100 | PE-200 | PE-500 | PE-2186 |
|---|---|---|---|---|
| **Weight Ratios** | | | | |
| Neopentyl glycol | 411.4 | — | — | — |
| 2-Methyl-1,3-propanediol | — | 376.8 | — | 366.7 |
| Propylene glycol | — | — | 349.9 | — |
| Isophthalic acid | 308.3 | 325.9 | 340.5 | 554.2 |
| Phthalic anhydride | 126.6 | 133.8 | 139.8 | — |
| Adipic acid | 153.7 | 162.5 | 169.8 | 79.1 |
| | | | | |
| **Properties** | | | | |
| Acid no. (mg KOH/g) | 6.7 | 6.8 | 5. | 6.5 |
| Hydroxyl no. (mg KOH/g) | 26 | 28 | 40 | 23 |
| Mol. wt. (no. avg.) | 2200 | 2300 | 1370 | 3200 |
| % Solids[a] | 65 | 65 | 65 | 62 |
| Viscosity (Gardner/Holdt) | Z | Y/Z | V/W | Z4 |
| Glass transition temp. (°C) | 7 | -5 | 5 | 13 |
| | | | | |
| **Enamel Constants** | | | | |
| Pigment/binder[b] | 1.0/1.0 | 1.0/1.0 | 1.0/1. | 1.0/1.0 |
| Polyester/melamine[c] | 9/1 | 9/1 | 9/1 | 9/1 |
| Catalyst/binder | 0.5% | 0.5% | 0.5% | 0.5% |
| Wt. % solids (det.) | 67 | 68 | 65 | 62 |
| Viscosity, Zahn #4 (sec) | 22 | 21 | 9 | 44 |

(a) 3/1 Aromatic 150, propylene glycol monomethyl ether acetate.
(b) Kronos® 2090 Titanium Dioxide (Kronos, Inc.).
(c) Cymel® 303 hexamethoxymethylol melamine (American Cyanamid).

ent degradation pathways. This added insight builds upon a rich conceptual framework of polymer degradation theories and introduces the possibility of utilizing molecular orbital calculations as a new tool to guide future research and product development efforts. Details of this analysis are reported here.

## EXPERIMENTAL

All polyesters were synthesized at 210°C in a two-liter round bottom flask equipped with stirrer, sampling port, thermocouple, nitrogen purge, and a packed, partial condenser. Propylene glycol (PG) and MPD were obtained from ARCO Chemical Co. Other raw materials for the polyesters were obtained from Aldrich Chemical Co. Hydrated monobutyl tin oxide was obtained from Elf Atochem. Kronos® 2090 (registered tradename of Kronos, Inc.) grade of titanium dioxide was used for pigmented coatings.

Compositions and properties of the resins for coil coatings and the coil coating enamel constants are provided in *Table* 1. The coil enamels were cured at 245°C for 75 sec. *Table* 2 lists compositions and properties for the polyesters intended for high-solids[10] and the respective high-solids baking enamel constants. The high-solids coatings were cured at 149°C for 30 min. Chromate treated aluminum test panels were used for accelerated

weathering analysis and humidity testing. Iron phosphated steel test panels were used for the salt spray corrosion testing.

Accelerated weathering testing with UV-B313 and UV-A340 bulbs were performed in a QUV chamber under cycling conditions of eight hours UV radiation at 60°C followed by four hours of humidity at 50°C. Xenon arc accelerated weathering was conducted in an Atlas weatherometer with borosilicate inner and outer filters. Xenon conditions were 102 min of light followed by 18 min of light and water spray with 0.35W/m² radiation, 50% relative humidity, and 63°C black panel temperature. Emmaqua®NTW (registered tradename of Heraeus DSET Laboratories) was run in accordance with ASTM D 4141-82, Procedure C by Heraeus DSET Laboratories, Inc. Florida exposures were also conducted by Heraeus DSET Laboratories in accordance with ASTM G7-89 with a 26° exposure angle.

## ACCELERATED WEATHERING TEST RESULTS

### Coil Coating Resins

The initial accelerated weathering tests for the neopentyl glycol (NG), the MPD, and the PG resin systems designed for coil coating applications were reported in 1990.[9] The preliminary results fit well with established theories of Norrish Type II degradation. MPD and PG resins, with the beta-hydrogen in the diol link of the polyester, degraded faster than the NG based polyester resin. However, in a repeat experiment, the performance of the resins reversed themselves and the MPD resins maintained their gloss for a longer duration than the NG and PG resins (*Figure* 1.)

**Table 2—Polyester Compositions and High-Solids Coatings**

| Components | C-NG | C-2050 | C-2075 | C-2088 | C-2100 |
|---|---|---|---|---|---|
| **Molar Ratios** | | | | | |
| Neopentyl glycol | 6.12 | — | — | — | — |
| 2-Methyl-1,3-propanediol | — | 6.12 | 6.12 | 6.12 | 6.12 |
| Isophthalic acid | 2.19 | 2.19 | 3.28 | 3.85 | 4.38 |
| Adipic acid | 2.19 | 2.19 | 1.10 | 0.53 | — |
| Trimethylol propane | 0.587 | 0.587 | 0.587 | 0.587 | 0.587 |
| | | | | | |
| **Properties** | | | | | |
| Acid no. (mg KOH/g) | 3.3 | 5.2 | 1.1 | 2.2 | 1.1 |
| Hydroxyl no. (mg KOH/g) | 246 | 260 | 247 | 248 | 240 |
| Mol. wt. (no. avg.) | 833 | 730 | 792 | 759 | 792 |
| % Solids (xylene) | 79.2 | 79.5 | 80.1 | 80.4 | 81.1 |
| Viscosity (Gardner/Holdt) | Y/Z | V/W | Z1 | Z4 | Z6/Z7 |
| | | | | | |
| **Enamel Constants** | | | | | |
| Pigment/binder | 0.7/1.0 | 0.7/1.0 | 0.7/1.0 | 0.7/1.0 | 0.7/1.0 |
| Polyester/melamine | 65/35 | 65/35 | 65/35 | 65/35 | 65/35 |
| Catalyst/binder | 0.37% | 0.37% | 0.37% | 0.37% | 0.37% |
| Wt. % solids (det.) | 78.2 | 78.2 | 78.7 | 79.0 | 79.3 |
| Density (lbs/gal) | 11.6 | 11.8 | 11.9 | 11.9 | 11.4 |
| VOC (lbs/gal) | 2.53 | 2.57 | 2.53 | 2.50 | 2.46 |
| Viscosity, Zahn #4 (sec) | 15 | 16 | 9 | 27 | 37 |
| Shelf stability, 6 months | Hazy | Clear | Clear | Clear | Clear |
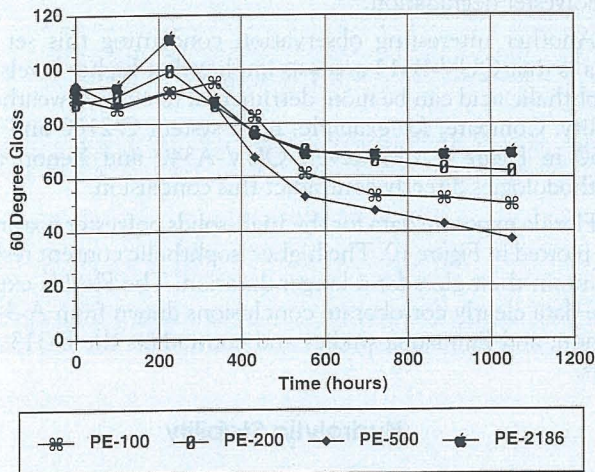
Figure 1—QUV-B313 test results for coil coatings.



Figure 3—Xenon arc test results for coil coatings.

Because of these anomalies, we expanded the scope of our analyses to include other accelerated weathering techniques. The QUV-A340, Xenon arc, and Emmaqua NTW analyses of the four test coil resins are provided in *Figures* 2, 3, and 4, respectively. By QUV-A340, both MPD resins outperform the NG and PG resins. Xenon arc analysis also shows the PG resin to be the weakest, and the MPD resins roughly comparable to the NG in performance for the first 2400 hr. The Emmaqua NTW analysis indicates that the PG resin has the best weatherability and the high isophthalic content MPD resin, PE-2186, is superior to the NG resin.

These four accelerated test procedures yield contradicting conclusions on the weatherability of these four resin systems. Florida exposure data for two of these resins is provided in *Figure* 5. Clearly, the MPD based polyester is maintaining gloss as well as the neopentyl glycol based polyester. In reality, what we may be looking at are very minor differences in performance among four different polyesters of compa-

rable molecular weight. In real terms, we may be simply splitting hairs in trying to define which of these four resins is the "best."

Most importantly, based upon these results, we see no clear evidence that supports the theory that the Norrish Type II degradation pathway is a dominating factor in polyester environmental degradation.

## High-Solids Resins

The accelerated weathering data for the five high-solids polyesters are provided in *Figures* 6-9. QUV-B313 technology indicates that the NG system is superior to the MPD resins and, thus, substantiates the Norrish Type II degradation theory. However, the results of the QUV-A340, Xenon arc, and Emmaqua NTW studies clearly and strongly contradict the QUV-B313 test results. As with the coil resin systems, these three test procedures raise strong reservations concerning the
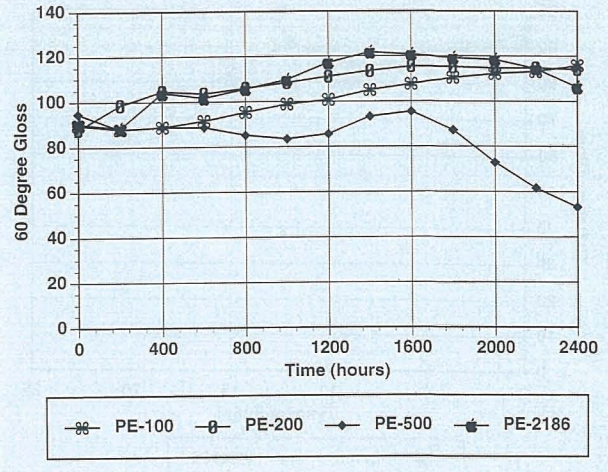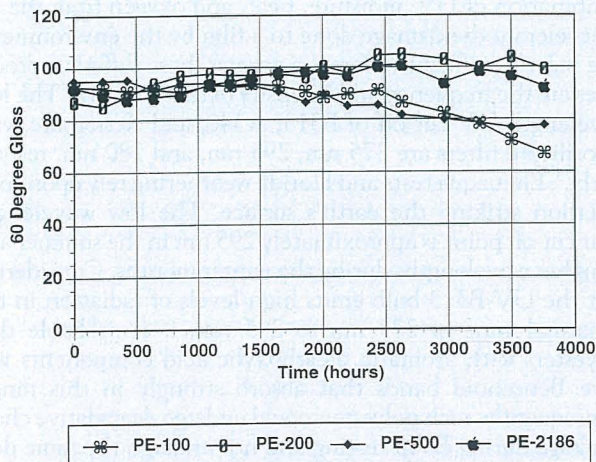


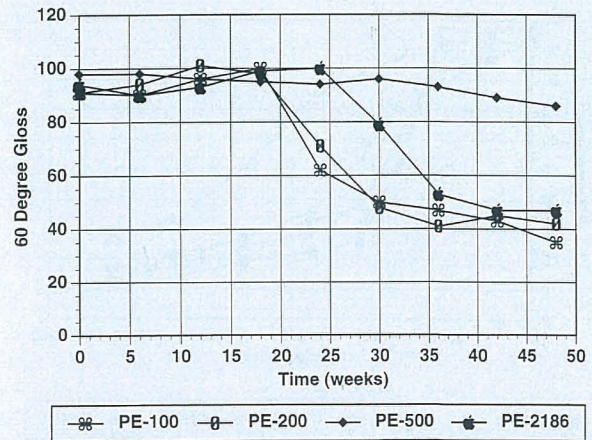Figure 2—QUV-A340 test results for coil coatings.



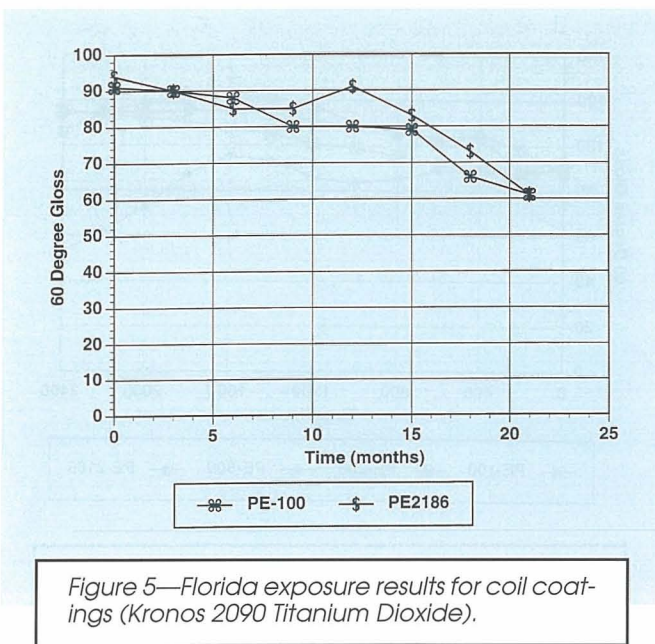Figure 4—Emmaqua® NTW test results for coil coatings.

Figure 5—Florida exposure results for coil coatings (Kronos 2090 Titanium Dioxide).

**Table 3—Cleveland Humidity and Salt Spray Corrosion for High-Solids Coatings**

| | | Salt Spray Corrosion[a] | |
|---|---|---|---|
| Resin Code | Humidity Results[b] Δ60° Gloss | Rust Creepage | Blistering (Size/Frequency) |
| C-NG | +1.5% | 1/16 in. | Large/Moderate |
| C-2050 | +1.0% | 3/16 in. | Large/Moderate |
| C-2075 | +1.0% | 1/8 in. | Large/Few |
| C-2088 | +2.6% | 1/8 in. | Medium/Few |
| C-2100 | −3.0% | 1/8 in. | Small/Few |

(a) 800 hr total time, 5% NaCl; cycles of 1 h rmist, 1 hr drying; 50°C.
(b) 5000 hr total time in Cleveland humidity chamber; cycles of 8 hr humidity, 4 hr drying, 50°C.



Figure 6—QUV-B test results for high-solids coatings.

significance of the Norrish Type II chain scission mechanism in polyester degradation.

Another interesting observation concerning this set of data is that QUV-B313 analysis implies that higher levels of isophthalic acid can be more detrimental to coating weatherability. Compare, for example, resin system C-2100 and C-2050 in *Figure 6*. However, QUV-A340 and Xenon arc methodologies directly contradict this conclusion.

Florida exposure data for the high-solids polyester coatings are plotted in *Figure 10*. The higher isophthalic content resins maintain their gloss for a longer duration. The Florida exposure data clearly corroborate conclusions drawn from A-340, Xenon, and Emmaqua studies and contradicts the B-313 results.

## Hydrolytic Stability

Turpin[11] reported that steric hindrance is a major controlling factor in the rate hydrolysis of polyester binders. However, his study was limited to polyesters that were fully compatibilized in an aqueous medium to ensure high concentrations of water. In reality, the hydrolysis of polyester binders in coatings applications will be dependent upon the inherent rate of hydrolysis *and* the equilibrium water concentration within the coating. This equilibrium water concentration will be low and inversely proportional to hydrophobicity of the resin. Also, harder coatings based upon high glass transition temperature resins will have less internal free volume at the molecular level for water absorption.[12] Higher isophthalic content in the polyester should lead to a more hydrophobic character and a higher glass transition temperature; therefore, higher isophthalic content polyesters should have better hydrolytic resistance.

*Table 3* reports the salt spray corrosion testing and Cleveland humidity testing of these same test resins. Humidity alone does not seem to harm the polyester. Salt spray corrosion data show some differences which support our premise that higher isophthalic content polyesters are inherently more hydrolytically stable.

## Comparison of Test Methodologies

Each of the accelerated test methodologies utilizes the combination of UV, moisture, heat, and oxygen from the air to accelerate the damage done to a film by the environment. The most significant difference among these different procedures are the frequency and intensity of the UV light. The low wavelength UV cut off of B313, A340, and Xenon arc with borosilicate filters are 275 nm, 295 nm, and 280 nm, respectively.[3] Emmaqua tests and Florida weathering rely upon solar radiation striking the earth's surface. The low wavelength solar cut off point is approximately 295 nm in the summer and at higher wavelengths during the winter months. Considering that the UV-B313 bulb emits high levels of radiation in the unnatural zone of 275 nm to 295 nm, it is probable that polyesters with aromatic dicarboxylic acid components will have Benzenoid bands that absorb strongly in this range. Consequently, such polyesters could undergo degradative chain breakage during B313 testing and not undergo the same degradation during external usage. Therefore, we specifically consider B313 accelerated weathering to be wholly inappropriate for isophthalate based polyesters and we place more trust in the QUV-A340 and Emmaqua NTW techniques.
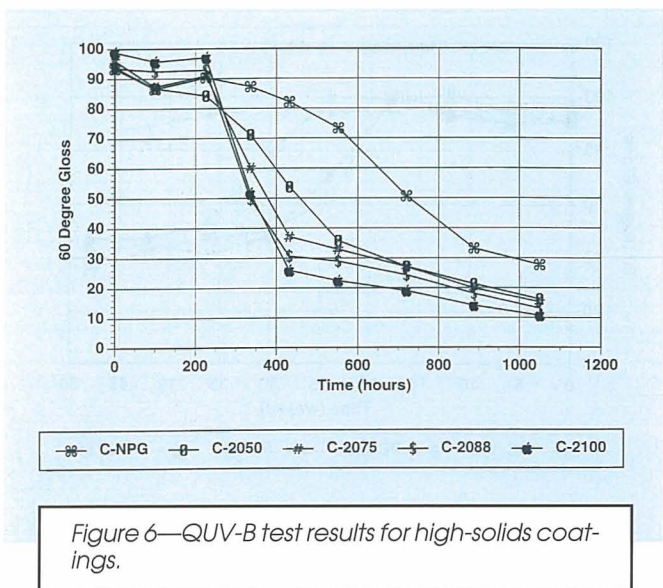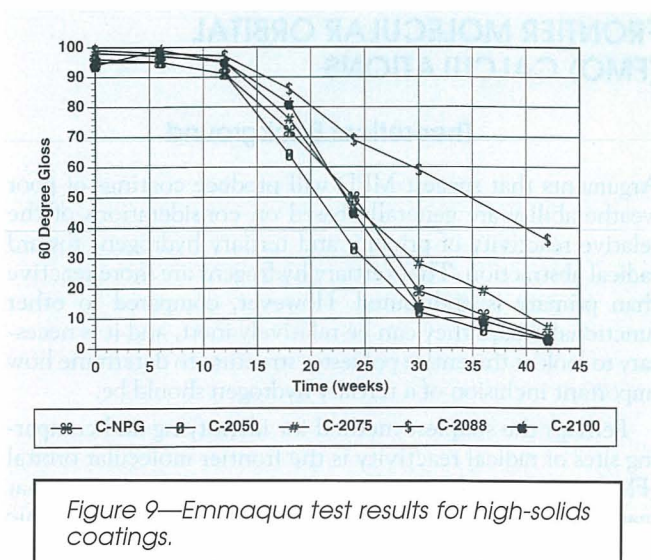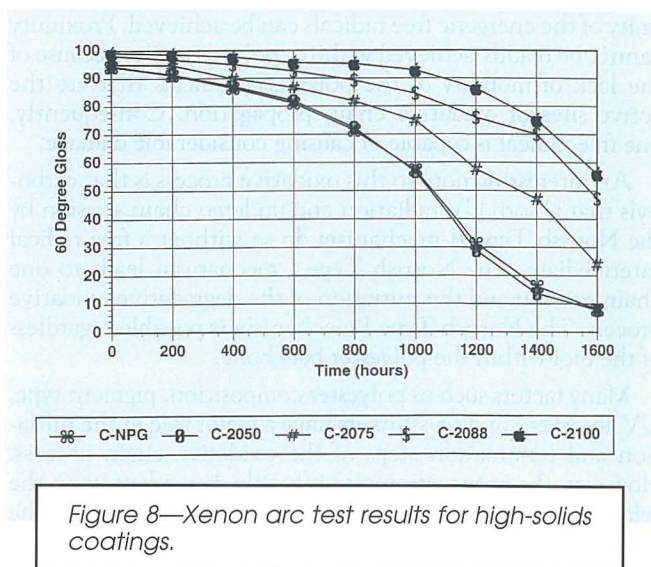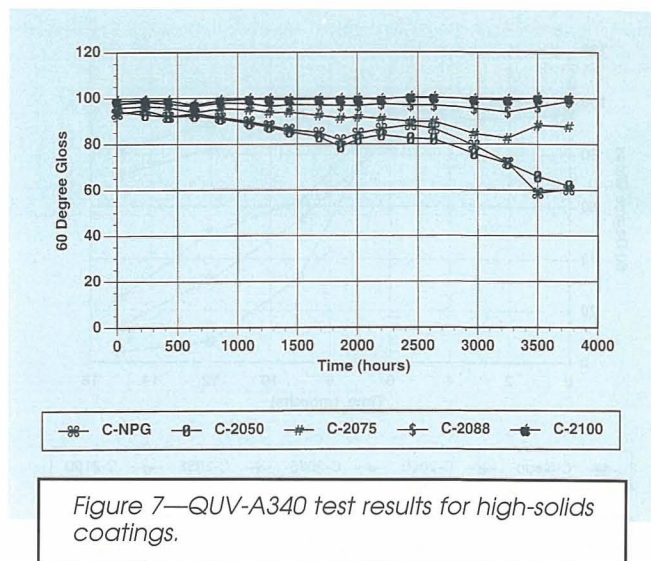
## POLYESTER DEGRADATION MECHANISMS

Oxidative free radical reactions are a dominating factor in the polymer chain cleavage which leads to the loss of physical properties and erosion of organic coatings. We have used frontier molecular orbital computations (FMOC) in order to identify sites in the polyester backbone that are most vulnerable to oxidative attack. However, the significance of FMOC to this work and perhaps future studies gains perspective by first reviewing the commonly accepted polymer degradation pathways.

Common degradation pathways of polymeric materials include radiolysis, photolysis, hydrolysis, and thermal or mechanical cleavage of polymer chains. For the purpose of evaluating coatings, radiolysis can be largely ignored because shortwave UV, X-ray, and electron radiation are not prevalent at the earth's surface and are not expected to be realistic contributors to degradation of a coating. Thermal degradation is generally irrelevant because most coatings see very mild temperatures—particularly compared to the elevated temperatures of polyester resin manufacturing processes. Mechanical degradation due to shearing forces also has no relevancy to coatings.

Hydrolysis, as we mentioned previously, is an important issue for polyester coatings; however, the humidity testing alone shows no great differences regarding the choice of diol in the polyester backbone. Increasing the isophthalic content in the polyester seems to improve the coating's resistance to salt fog but we suspect that this effect is due to an increase in glass transition temperature and hydrophobicity of the resin. Nonetheless, this effect of higher isophthalic content on salt fog resistance is small and the net effect of changing from NG to MPD is very minor.

Photolysis is the absorption of UV radiation with subsequent bond cleavage; however, UV absorption is typically low without absorbing chromophores. For polyesters, the carbonyl site can act as a very weakly absorbing chromophore. Absorption can lead to Norrish Type II chain scission depicted in *Figure* 11 or the energy absorbed could decay through nondegradative energy transfers. If the quantum yield for the Norrish Type II mechanism is high, then PG and MPD based polyesters would fare much worse than an NG based polyester. The accelerated weathering tests and the Florida exposures strongly contradict this premise. Although the Norrish Type II degradation pathway is possible, we are left to believe that other pathways to degradation are contributing to a much greater extent.

Oxidation is the remaining significant pathway to degradation. Oxidative chain reactions have three separate stages: initiation, propagation, and termination.[14] Although not well understood, initiation is believed to occur by the addition of oxygen to an existing free radical. Free radicals are generated by photolysis such as by the Norrish Type I mechanism depicted in *Figure* 11. Once formed, the free radical will add oxygen to form a peroxy radical which can abstract a hydrogen from a carbon-hydrogen bond and generate a new free radical. This is the propagation stage of the free radical chain reaction. In addition, the peroxide that is formed is readily cleaved by UV radiation of approximately 350 nm wavelength to yield two new alkoxy radicals which in turn can abstract hydrogens and create new radicals that will add oxygen. Coupling or disproportionation of the peroxy compounds



Figure 7—QUV-A340 test results for high-solids coatings.



Figure 8—Xenon arc test results for high-solids coatings.



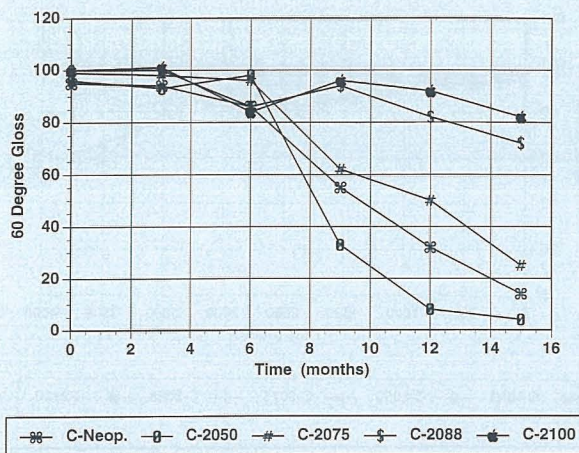Figure 9—Emmaqua test results for high-solids coatings.

Figure 10—Florida exposure results for high-solids coatings.

terminates the chain reaction process, but only if close proximity of the energetic free radicals can be achieved. Proximity cannot be readily achieved within a polymeric film because of the lack of mobility of the polymeric radicals that are the active sites of oxidative chain propagation. Consequently, one free radical is capable of causing considerable damage.

An interesting note to this oxidative process is that carbonyls that absorb UV radiation and undergo chain scission by the Norrish Type II mechanism do so without a free radical intermediate. The Norrish Type I mechanism leads to one chain scission and the initiation of the degradative oxidative process. The Norrish Type I mechanism is possible regardless of the diol within the polyester backbone.

Many factors such as polyester composition, pigment type, UV absorbers, and crosslinkers have a major role in the initiation and termination steps of the oxidative chain process. However, the propagation rate is highly dependent upon the relative lability of individual carbon-hydrogen bonds in the polyester backbone. This relative lability is consequently a vital link to the relative weatherability of different coatings. FMOC can predict this relative lability.

## FRONTIER MOLECULAR ORBITAL (FMO) CALCULATIONS

### Theoretical Background

Arguments that suggest MPD will produce coatings of poor weatherability are generally based on considerations of the relative reactivity of primary and tertiary hydrogens toward radical abstraction. That tertiary hydrogens are more reactive than primary is undisputed. However, compared to other functional groups they can be relatively inert, and it is necessary to look at the entire polyester structure to determine how important inclusion of a tertiary hydrogen should be.

Perhaps the simplest method for identifying and comparing sites of radical reactivity is the frontier molecular orbital (FMO) method of Fukui.[15] Its fundamental premise is that reactivity is determined by a special function of the electronic density at a particular atom. Mechanistic details need not be

known, only the general expression for the molecular orbitals. Furthermore, much of the reactivity is determined by only two orbitals: the highest occupied and lowest unoccupied molecular orbitals.

For a full understanding of what is essentially a simple concept, a brief review of molecular orbital theory is in order. Most modern quantum calculations treat the electrons as if they were delocalized throughout the molecule. The actual probability that an electron will occupy a particular point in space is then determined by a set of "molecular" orbitals constructed by taking linear combinations of atomic orbitals (LCAO) from the original atoms.

$$\Psi_x = \Sigma\, c_i \phi_i \tag{1}$$

Here, $\Psi_x$ represents a given molecular orbital, and $\phi_i$ is an atomic orbital on a particular atom. Given the level of rigor, all or only selected atomic orbitals can be used. Each resulting molecular orbital has a discrete energy value, and the coefficients, $c_i$, are determined as to minimize the total energy. The coefficients can be positive, negative, or zero, and among other things, are related to the electronic density at a given atomic site.

A consequence of the mathematical treatment of the LCAO method, details of which can be found in virtually any book on molecular orbital theory,[16] is that the final number of molecular orbitals is equal to the original number of atomic orbitals. In keeping with the Pauli exclusion principle, no more than two electrons can occupy a given orbital, and in a ground state molecule, the lowest energy molecular orbitals are filled first.

A simple example of a molecular orbital calculation is shown in *Figure 12*. Four separate hydrogen atoms, each with a single s orbital, and two carbon atoms with a valence orbital configuration of $sp_x p_y p_z$ are combined to form the ethylene molecule. In this representation only valence orbitals and electrons are used. The highest occupied molecular orbital (HOMO) has the formula $0.7p_z + 0.7p_z$, where $p_z$ represents the mathematical expression for the carbon $2p_z$ orbital. In terms familiar to organic chemists, this orbital holds the molecule's $\pi$-electrons which are responsible for the characteristic reactivity of ethylene. The orbital of next highest energy (the lowest unoccupied molecular orbital or LUMO) has the formula $0.7p_z - 0.7p_z$ and can accept the electrons from an attacking nucleophile or radical.

The fundamental postulate of the frontier orbital method is that molecular reactivity is largely, but not necessarily exclusively, determined by the geometry, or more strictly, by the coefficients, of the HOMO and the LUMO. Why the
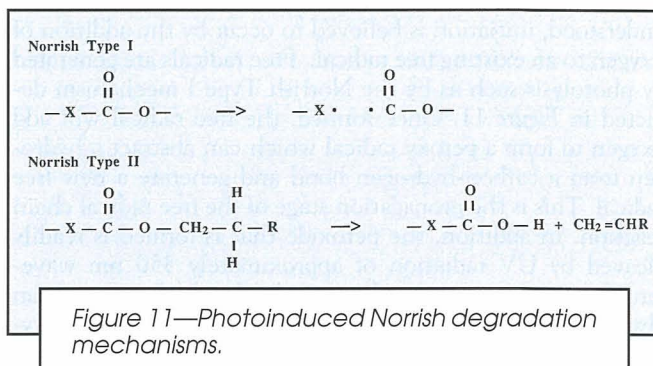


Figure 11—Photoinduced Norrish degradation mechanisms.

**Table 4—Frontier Densities of MPD and NG Diacetates**

| Atom | Group | Frontier Density (Electron/Site) | |
| --- | --- | --- | --- |
| | | NG | MPD |
| H | $\underline{C}H_3$ (diol) | 0.004 | 0.005 |
| H(beta) | C$\underline{H}$ | — | 0.017 |
| H(alpha) | C$\underline{H}_2$ | 0.051 | 0.050 |
| C | $\underline{C}H_3$ (diol) | 0.020 | 0.024 |
| C | $\underline{C}$-C$_4$ | 0.039 | — |
| C | $\underline{C}$-C$_3$H | — | 0.042 |
| C | $\underline{C}H_2$-O | 0.072 | 0.068 |
| O-sp3 | Ester | 0.271 | 0.261 |
| C | Carbonyl | 0.010 | 0.010 |
| O-sp2 | Carbonyl | 0.441 | 0.454 |
| C | Acetate | 0.047 | 0.048 |
| H | Acetate | 0.002 | 0.003 |

reactivity is largely restricted to these orbitals is fairly easy to rationalize. Removing an electron from an orbital below the HOMO would simply require additional energy, as would introducing an electron into an unoccupied orbital above the LUMO. Therefore, sites of reactivity, whether nucleophilic, electrophilic, or radical, can be determined to a large extent by simply examining the HOMO and LUMO.

The value for the frontier density at a particular atom is shown in equation (2). The expression shown is somewhat more general than the original derivation which was developed for $\pi$-electron systems.[15b]

$$F = \frac{(2-n_r) \sum\limits_{i=1}^{N} n_i c_i^2 e^{-\alpha(e_H-e_i)}}{2 \sum\limits_{i=1}^{N} c_i^2 e^{-\alpha(e_H-e_i)}} + \frac{n_r \sum\limits_{i=1}^{N} (2-n_r) n_i c_i^2 e^{-\alpha(e_L-e_i)}}{2 \sum\limits_{i=1}^{N} (2-n_r) c_i^2 e^{-\alpha(e_H-e_i)}} \quad (2)$$

F is the frontier density at a particular atom, and the $c_i$ values are the coefficients from each molecular orbital at that atom. $e_H$, $e_L$, and $e_i$ refer respectively to the energies of the HOMO, LUMO, and the remaining occupied orbitals. $\alpha$ is a somewhat arbitrary scaling factor which was set by Fukui at 3.0 and is normally kept at that value. N is the total number of occupied orbitals in the molecule, and $n_r$ is the number of electrons contributed from the attacking molecule. For radicals, $n_r$ is 1.

The exponential terms assure that the greatest contribution to the frontier density will be from the HOMO and LUMOs, but they also allow for other orbitals to have an influence. The closer in energy the orbital is to the HOMO or LUMO, the more of an effect it will have. Therefore, although examination of the HOMO and LUMO is useful for locating centers of reactivity, other orbitals may make significant contributions. It should also be recognized that the second term, which deals with the contribution from the LUMO, vanishes when dealing with an electrophilic reagent ($n_r$ = 2), as does the term for the HOMO when the reaction involves a nucleophile ($n_r$ = 0). For radical reactions ($n_r$ = 1) both terms involving the HOMO and LUMO are retained.

Simply put, the FMO method predicts reactions are most likely to occur at sites where the coefficients of the HOMO and LUMO are largest. Nucleophiles donate electrons to the LUMO, electrophiles accept electrons from the HOMO, and radicals are treated as reacting readily at both. Other orbitals contribute to reactivity depending on how close their energy is to the HOMO or LUMO.

## The MNDO-PM3 Method

Strictly speaking, any molecular orbital method, regardless of how approximate, can be used to calculate a frontier density. However, the PM3 molecular orbital method of Stewart,[17] based on the earlier MNDO method of Dewar and Thiel[18] was used. As with all semiempirical methods, the quantum mechanical integrals are not calculated explicitly, but are either ignored or treated as parameters. Since the main emphasis of the MNDO method is for calculating ground state energies, the parameterization is based on experimental heats of formation. Stewart's modification has reduced the root mean error of the heats of formation of organic compounds to 7-8 kcal/mole, which is a considerable improvement over the previous AM1 reparameterization.[19] Although the latter calculations are perhaps still more widely used, the PM3 method is rapidly becoming prominent.

Without doubt, the MNDO method and its later developments are the most useful semiempirical methods for calculating ground state properties of organic molecules. It has been applied to literally thousands of applications involving neutral molecules, radicals, and ions.[20] Its primary appeal is that it is available in one form or another at minimal cost, it is rapid, available on an increasing number of platforms, and can be used by the nonspecialist with relative ease.

## FMO Calculations—Computational Procedures

All PM3 calculations were carried out on the ground state with total geometry optimization. They were run using the MOPAC version implemented on the Tektronix CAChe Worksystem™ loaded onto a Macintosh Quadra 950 enhanced with RP88 coprocessors. Although some algorithmic
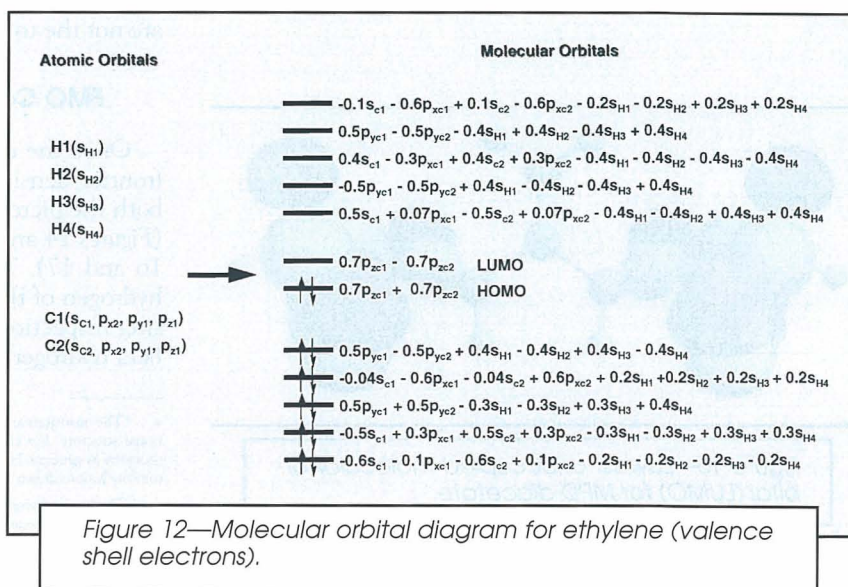
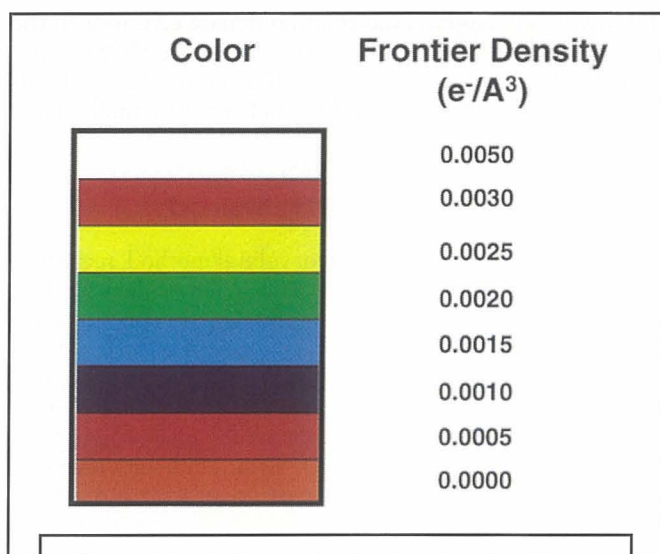Figure 12—Molecular orbital diagram for ethylene (valence shell electrons).

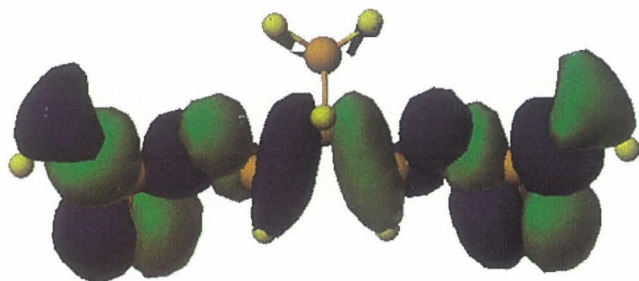Figure 13—Color codes for frontier density.



Figure 14—Highest occupied molecular orbital (HOMO) MPD diacetate.
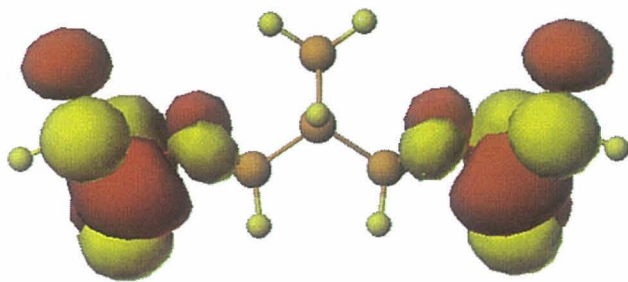


Figure 15—Lowest unoccupied molecular orbital (LUMO) for MPD diacetate.

optimization has been performed by the CAChe scientists and programmers, the parameters are the same as the public domain version. In various tests, we have found no differences in the output.

Details of the operations are available from the software reference manuals, but a general outline will be given here. Atoms for the diacetates of both MPD and NG were selected and connected through the mouse-driven CAChe Editor™ which automatically adjusted the geometries to standard bond lengths and angles. These structures were then used as the input for a single pass molecular mechanics (MM2) sequential search. In this procedure, each bond is rotated through 360° and the minimum energy at each bond is located. Each bond is then set at the value of its minimum, and the search sequence is repeated using full geometry optimization. The conformer with the minimum energy was then used as the input for the molecular orbital calculation.[*]

After the PM3 calculation was completed, the frontier densities were computed using the CAChe Tabulator™ which automatically sums the properly weighted coefficients for each site. It was also used to generate frontier density maps. In forming these surfaces, which are drawn at points of equal total (not frontier) electronic density, the coefficient in Fukui's equation is replaced by the value of the molecular orbital at the particular point in space. In the representation here, the relative density is indicated by the color codes.

The advantage of using the surfaces is that reactive sites are visualized easily. However, it must be kept in mind that they are not the total frontier density as defined by Fukui, and these contours may appear different depending upon which electronic density value is used to define the surface, and small differences in values may not be evident on a map. However, because they show the density at a point in space, narrow regions of reactivity can be identified, even though they may seem somewhat at odds with the total frontier density for the atom.[†] Typically, a number of surfaces are examined to find the one which reveals the greatest contrasts. For the representations shown here, the frontier density was drawn at 0.02 electron/Å[3]. Other electron densities were tested but were found to be less indicative of the site differences. The frontier densities which correspond to the colors on the maps are shown in *Figure* 13. These are for the density at the point on the surface and as discussed in the following are not the total frontier density associated with each atom.

## FMO Calculations—Application to Diol Esters

Once the calculations were completed, the values of the frontier density were tabulated (*Table* 4) and compared to both the pictorial representations of the HOMO and LUMO (*Figures* 14 and 15) and the frontier density surfaces (*Figures* 16 and 17). The immediate conclusions are that the beta hydrogen of the MPD ester is by no means the most reactive site. Inspection of the HOMO and LUMO clearly show the beta hydrogen has a zero coefficient. In the first approxima-

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[*]The quantitative frontier densities reported in *Table* 4 were derived from this minimal conformational structure. For clarity, the qualitative pictorial representations are drawn from the standard geometry as generated by the CAChe Editor. The general appearance of the surfaces and orbitals and the conclusions drawn were not affected.

[†]The largest discrepancy between the map and the tabulated densities are for the carbonyl carbon atoms. However, the area indicating the rapidly changing electron density is restricted to a relatively small area perpendicular to the plane of the carbonyl bond. Therefore the map and the values in *Table* 4 are not contradictory. We wish to thank Dr. Sam Cole of CAChe Scientific for helping us clarify this point.

tion, this indicates that the reaction at that site is expected to be low.

A legitimate question might be raised at this point regarding making comparisons based on the frontier density of different types of atoms. It is certainly possible that the difference in how a radical would interact at atoms as different as oxygen and hydrogen may have an influence on rate. It would be more meaningful to restrict the comparisons to the same type of atoms since they would be more likely to follow similar mechanistic pathways. However, even limiting the comparison to the hydrogen atoms, it is still clear that the beta hydrogen is by no means the one most susceptible to abstraction. The methylene ($CH_2$) hydrogens adjacent to the $sp^3$ oxygen atom, which are common to both MPD and NG esters, have significantly greater frontier density.

Comparing the pictorial representations and the tabulated densities also illustrate the importance of the HOMO and LUMO in the overall frontier density and at the same time show that other orbitals cannot be completely ignored. Even though the HOMO and LUMO coefficients at the beta hydrogen are zero, the overall frontier density indicates the tertiary hydrogen to be more reactive than primary. This difference can be seen to arise from the molecular orbital immediately below the HOMO (HOMO–1, *Figure* 18) where the beta hydrogen has a fairly large nonzero coefficient. However, the HOMO coefficients at the alpha (methylene) hydrogens still have the predominant influence. That reactivity is predicted to occur here preferentially is also shown on the density contour (*Figures* 16 and 17). Therefore, the behavior of polyesters prepared from the two esters should not be expected to be that different.

For a final comparison, we thought it would be interesting to do a similar calculation on an ester of diethylene glycol (DEG), a compound whose coatings are known to weather poorly. Although the hydrophilic nature of the polyol is no doubt a factor in its performance, it will be seen that its oxidative stability is also predicted to be less than MPD or NG.

One difficulty arises here, however. As the number of atoms in a molecule increases, the absolute frontier value at a particular site tends to drop. Therefore, comparing reactivity using frontier densities of two molecules with large size differences is less straightforward. This difficulty can be avoided by selecting a site common to all molecules and scaling all values to the frontier density at that site. As long as nearest and next-nearest neighboring groups are the same, the reactivity of identical groups should be very close. In this way, the frontier densities on different molecules can be compared even if the number of atoms differs considerably.

In the model esters used here, the group common to all is the hydrogen atoms at the acetate group. By averaging and standardizing all values of the acetate hydrogens, and then scaling all values to where the beta hydrogen of MPD is taken to be 1.0, the relative densities of *Table* 5 were derived. Here it clearly shows the ether hydrogens of DEG are significantly more susceptible to radical attack and again, the susceptibility of the beta hydrogen is relatively low.

## FMO Calculations—Conclusions

The conclusion from the frontier analysis is that the beta hydrogen of MPD, although more reactive than a primary
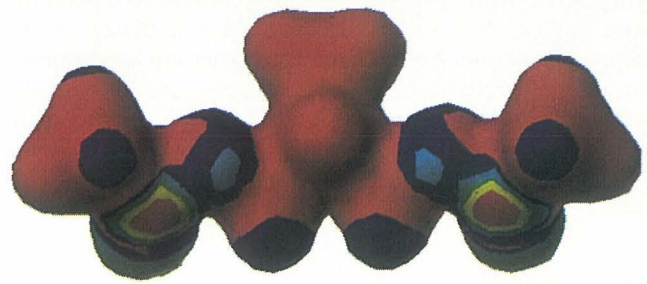
Figure 16—Froniter density contour map of MPD diacetate (isosurface density: $0.02e^-/A^3$).

**Table 5—Comparison of Relative Frontier Densities for Selected Hydrogen Atoms of MPG, NG, and DEG Esters**

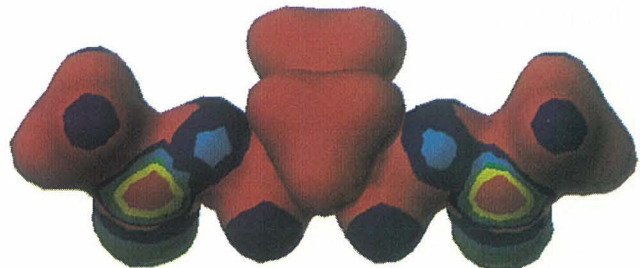| | Frontier Density (Electrons)/Hydrogen | | |
|---|---|---|---|
| Diol | $CH_2$ Ether | $CH_2$ Ester | $CH_3$ Acetate |
| MPD | — | 2.87 | 0.15 |
| NG | — | 2.34 | 0.14 |
| DEG | 7.84 | 1.81 | 0.14 |
| Beta (MPD) = 1.0 | | | |

Figure 17—Frontier density contour map of NG diacetate (isosurface density: $0.02e^-/A^3$).

Figure 18—HOMO-1 for MPD diacetate.

hydrocarbon hydrogen, should not be considered *a priori* the weak link in an oxidative decomposition pathway for the polyester structure. Sites common to other aliphatic polyesters are predicted to be more susceptible to radical degradation. This is fully consistent with the results of the experimental weathering trials which show that an optimized coating will not be unusually prone to weathering because MPD is substituted for NG.

## SUMMARY

As a result of unexpected accelerated weathering data, we sought to better understand the fundamentals of the degradative processes that impact polyester coatings. We ultimately used FMOC to help in this investigation and, as a result, we developed some fresh insights into the mechanisms of polyester environmental decay.

We believe the predominant degradative process is oxidation by free radical chain propagation mechanisms. UV light can initiate this degradative process by cleaving carbon-carbon bonds or peroxide bonds, but it is the relative lability of different carbon-hydrogen bonds that impacts the propagation rate and ultimate rate of damage to a polyester film. Among polyesters, the FMOC analysis clearly indicates that the carbon-hydrogen bonds adjacent to the ester links are the most vulnerable to oxidate attack. That is, the oxidative weak links are the alpha hydrogens on the diol.

Thus, FMOC would predict that only minor differences in polyester weatherability would be observed if NG was replaced with MPD. Any differences would probably be due to changes in hydrophobicity and glass transition temperature of the final coating. The accelerated testing results correlate well with these predictions.

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*CHARLES F. COOPER is currently Research Advisor for ARCO Chemical Company where he has been employed since 1980. Although his Ph.D. from University of Missouri-Rolla was in traditional experimental organic chemistry, he developed an early interest in using computational methods to assist and interpret his experimental work. After post-doctoral studies with the late Professor Paul Gassman at the University of Minnesota, Dr. Cooper came to ARCO Chemical where he has continued to investigate the usefulness of combining computational methods with practical experimental programs.*

With this good correlation between experimental evidence and theoretical computations, we have a stronger insight into the controlling mechanisms of polyester degradation. We hope that this added insight into degradative processes can be productively applied to other polyester resins, as well as coatings with very different binder systems. FMOC methodology has proven to be a valuable asset in building a stronger conceptual framework of polymer degradation and, as such, can be a valuable tool in future weathering studies.

### References

(1) Schmid, E.V., *Exterior Durability of Organic Coatings*, FMJ International Publication Limited, Surrey, England, 1988.
(2) Brennan, P.J., *J. Vinyl Techn.*, *12*, No. 2, 73 (1990).
(3) Brennan, P. and Fedor, C., "Sunlight, UV and Accelerated Weathering," presented at SPE Automotive RETEC, November 1987.
(4) Grossman, G., "Correlation of Laboratory to Natural Weathering," JOURNAL OF COATINGS TECHNOLOGY, *49*, No. 633, 45 (1977).
(5) Carlsson, D.J. and Wiles, D.M., "Degradation" in *Encyclopedia of Polymer Science and Engineering, Vol. 4*, p. 630, Mark, H. F., Bikales, N. M., Overberger, C.G., and Menges, G. (Eds.), Wiley-Interscience, New York, 1986.
(6) Lenz, R.W., "Degradation of Polymers" in *Organic Chemistry of Synthetic High Polymers*, Wiley-Interscience, New York, 1967.
(7) Ibid., p. 750.
(8) Johnson, L.K. and Sade, W.T., "New Monomers for Polyester Powder Coating Resins," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 826, 19 (1993).
(9) Sullivan, C.J., Dehm, D.C., Reich, E.E., and Dillon, M. E., "Polyester Resins Based upon 2-Methyl-1,2-Propanediol," JOURNAL OF COATINGS TECHNOLOGY, *62*, No. 791, 37 (1990).
(10) Eastman Chemical Co. Publication, *High-Solids, Polyester-Based Melamine Cross-linked Coating*, 1988.
(11) Turpin, E.T., "Hydrolysis of Water Dispersible Resins," JOURNAL OF PAINT TECHNOLOGY, *47*, No. 602, 40 (1975).
(12) Aklonis, J.J., MacKnight, W.J., and Shen, M., *Introduction to Polymer Viscoelasticity*, pp. 60-87, Wiley-Interscience, New York, 1972.
(13) Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, 3rd Edition, pp. 231-236, John Wiley & Sons, Inc., New York, 1974.
(14) Mielewski, D.F., Bauer, D.R., and Gerlock, J.L., *Polymer Preprints, 30*, pp. 144-145, September 1989.
(15) Fukui, K., Yonezawa, T., Nagata, C., and Singu, H., *J. Chem. Phys.*, 11, 1433 (1953).
(16) (a) Stewart, J. J. P., *J. Comput. Chem.*, 10 (2), 209 (1989);
(b) Stewart, J. J. P., *J. Comput. Chem.*, 10 (2), 221 (1989);
(c) Stewart, J. J. P., MOPAC Program Ver. 6.0—Quantum Chemistry Program Exchange, University of Indiana; adapted and modified by CAChe Scientific (Tektronix), Beaverton, OR.
(17) Stewart, J.J.P., "Semiempirical Molecular Orbital Methods," in *Reviews in Computational Chemistry*, Chapter 2, p. 45, Kipkowitz, K. B. and Boyd, D. B. (Eds.), VCH Publishers, Inc., 1990.
(18) Dewar, M.J.S. and Thiel, W., *J. Amer. Chem. Soc.*, 99, 4899 (1977).
(19) Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Amer. Chem. Soc.*, 107, 3902 (1985).
(20) Three recent and interesting applications of the MNDO method (including PM3 calculations) as applied to studies concerning radicals and ions are:
(a) Jonsonn, M., Lind, J., Merenyi, G., and Eriksen, T.E., *J. Chem. Soc., Perkin Trans.*, 2, 1994, p. 2149;
(b) Andreoli, R., Gavioli, G.B., Borsari, M., and Fontanesi, C., *J. Chem. Soc., Faraday Trans.*, 90 (21), 3241-4 (1994);
(c) Bando, P., Martin, N., Segura, J.L., Seoane, C., Orti, E., Viruela, P.M., Viruela, R., Albert, A., and Cano, F.H., *J. Org. Chem.*, 59 (16), p. 4618 (1994).