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# New polyester polyols for two component coatings for high performance protective and industrial OEM coatings.

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## ABSTRACT/INTRODUCTION

In the past, polyester polyols were limited in use for protective and industrial OEM topcoats due to performance limitations. Generally, weathering, chemical resistance, and hydrolysis resistance were problems that limited adoption for high-performance coating systems. Eastman Tetrashield$^{TM}$ resins demonstrate superior performance to both conventional polyester and high performance acrylic resins. Tetrashield resins, based on a novel monomer, deliver extended corrosion, weathering, and chemical resistance in environmentally-compliant formulations.

This paper will review how a unique monomer composition delivers improved properties for high performance topcoats. The work presented will detail:

- How resin properties increase performance for two component high performance coatings used in general industrial and protective coating applications
- How monomer selection impacts acid/base hydrolysis resistance and chemical resistance
- How monomer composition affects weathering and photo degradation

Keywords: Corrosion, Weathering, Protective, Tetrashield

## EXPERIMENTAL PROCEDURE

The resins developed for use in protective and general industrial coatings use a unique monomer, TMCD (2, 2, 4, 4 tetramethyl cyclobutane diol). This monomer delivers improved weathering, hardness, cure response, and chemical resistance. The structure of the TMCD monomer is shown below:

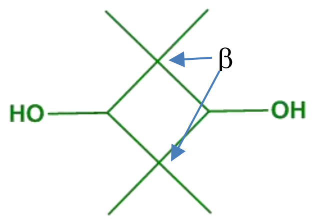


Figure 1 TMCD molecule

### Chemical resistance

The incorporation of TMCD into the copolyester provides resins with distinctive hydrolysis resistance. The tetramethyl structure, when reacted into a polyester, is very sterically shielded resulting in excellent chemical and hydrolysis resistance. Model polyesters made from TMCD and other common diols were tested to verify hydrolysis resistance.

A series of homopolymers were made from the following glycols commonly used in coatings:

Table 1 Homopolymers made for hydrolysis testing

| ID. | Glycol | Diacid/methyl ester | Mn |
|---|---|---|---|
| EG – TPA | Ethylene glycol | Dimethyl terephthalate | 38981 |
| BD – TPA | 1, 4 butane diol | Dimethyl terephthalate | 40388 |
| NPG – TPA | Neopentyl Glycol | Dimethyl terephthalate | 53218 |
| TMCD – TPA | 2, 2, 4, 4 tetramethyl 1, 3 cyclobutane diol | Dimethyl terephthalate | 23988 |

Terephthalic acid (TPA) was used because it provides a convenient marker for UV detection in LC-MS. All samples were crystalline except for the TMCD polymer which was mostly amorphous. The polymers were ground to an average particle size of 1.2-2.8 mm. To test hydrolysis resistance, 0.5 g of each polymer was placed in 1 mL of 0.03M NaOH (aq.) for 24 hours at 95 °C. Details of the analysis are shown in Appendix 1.

After 24 hours, the water solution was analyzed by liquid chromatography mass spectroscopy for TPA content. As shown in Figure 2, “Base hydrolysis LC-MS”, the homopolymer containing TMCD glycol shows significantly less hydrolysis (less TPA in solution) than the polymers containing the other glycols, demonstrating very good hydrolysis resistance to a strong base.

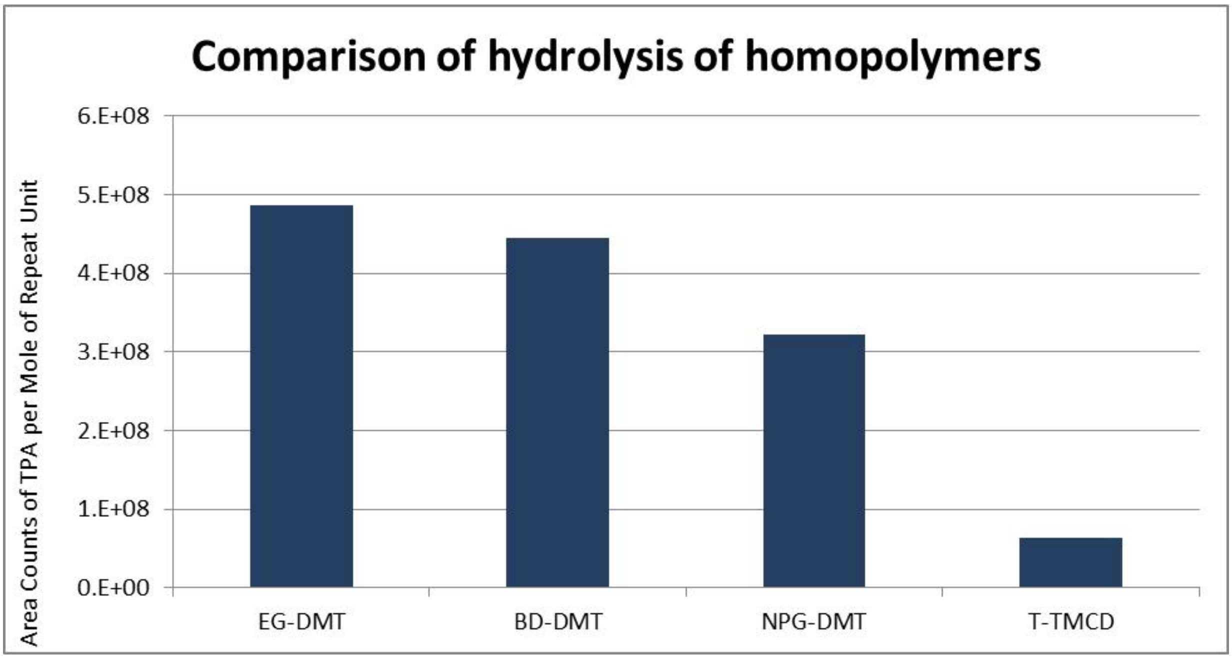


Figure 2 Base hydrolysis LC-MS

In order to demonstrate the resistance of TMCD-based resins to hydrolysis, polyesters with varying levels of TMCD were formulated into white monocoats and exposed to concentrated sulfuric acid (watch glass). Figure 3 shows that by incorporating TMCD into polyester polyols, one can improve acid resistance of the final coating. This proof point, when combined with the base hydrolysis study above, demonstrates excellent hydrolytic stability.


Figure 3 36 Day 50% $H_2SO_4$ exposure, Left, PE coating no TMCD, middle the same resin with partial replacement of the glycol by TMCD, right, 100% of the glycol replaced by TMCD

## Chemical resistance:

For topcoats used in harsh or extreme environments, chemical and fluid resistance is critical to ensure long term performance and protection. For benchmark testing, TMCD-based resins were compared to commercial acrylic and polyester resins crosslinked with hexamethylene diisocyanate trimer (HDI, Desmodur 3390TM, Covestro). The paints were coated on phosphated steel panels at 75 micron dry film and allowed to cure at 70F 40% humidity for 7 days. Chemical insults were applied to the paints and covered with a 25 MM watch glass. After 7 days, the paints were visually rated for damage after scraping with a wooden tongue depressor. Ratings are 10 – no visible mark, 7 - obvious visible damage and softening of the film, 5 - obvious visible damage, paint can be easily scraped by tongue depressor, 3 - paint can be scraped down to metal, 1 - coating destroyed.

Each coating was tested with 1N NaOH and 1N Sulfuric acid and all performed well after seven days under a watch glass at 72F, 40% relative humidity.

However, when tested with General Motors (GM) brake fluid and Skydrol™ aviation hydraulic fluid, the chemical resistance of the TMCD-based polyol showed significantly better performance (Figure 4). This is consistent with the expected chemical/hydrolysis resistance imparted by use of TMCD in the copolyester.

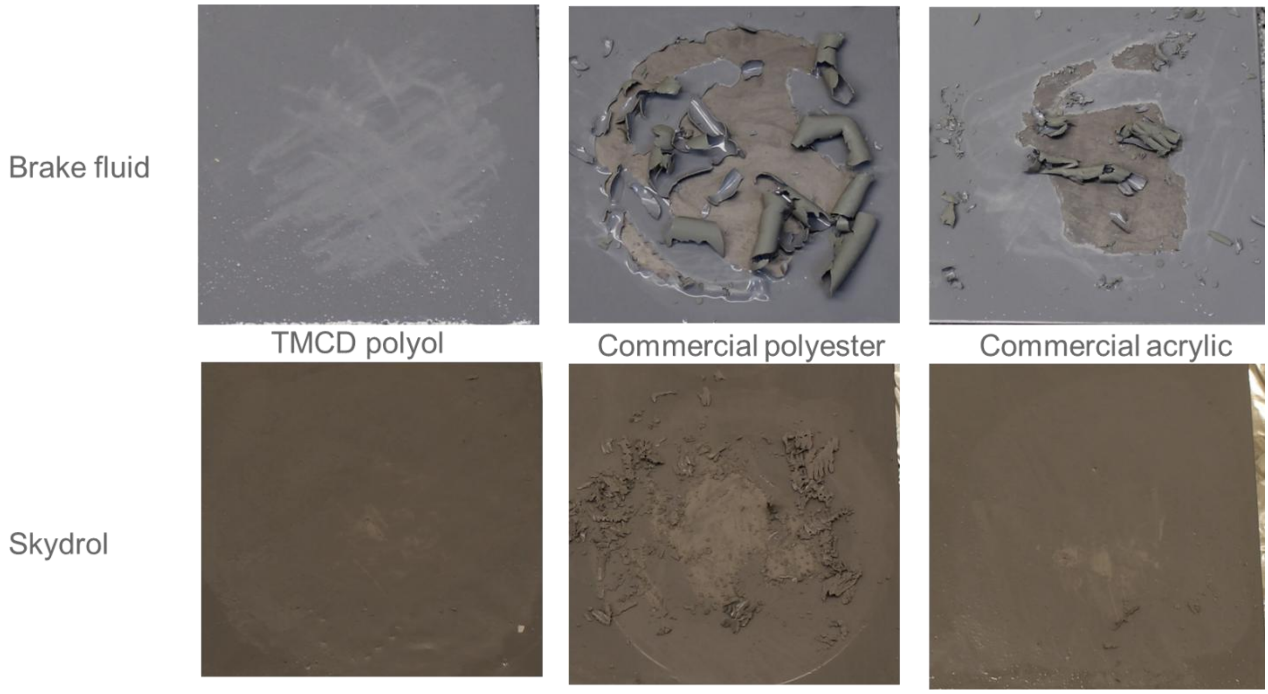


Figure 4 Chemical resistance after 7 days under a watch glass, then scraped

## Improved moisture diffusion:

Exterior two-component (2K) topcoats face a difficult challenge, as they are often expected to perform for ten or even twenty years. Improved moisture barrier properties are necessary to improve performance, because high-moisture diffusion reduces weathering, adhesion and corrosion resistance of the film. The TMCD-based polyol was benchmarked against a commercial acrylic resin in a clear HDI cross-linked film. The water vapor transmission rate was determined via ASTM E-96. As shown in Figure 5, the water vapor transmission rate of the TMCD-based resin is half that of the commercial acrylic resin.

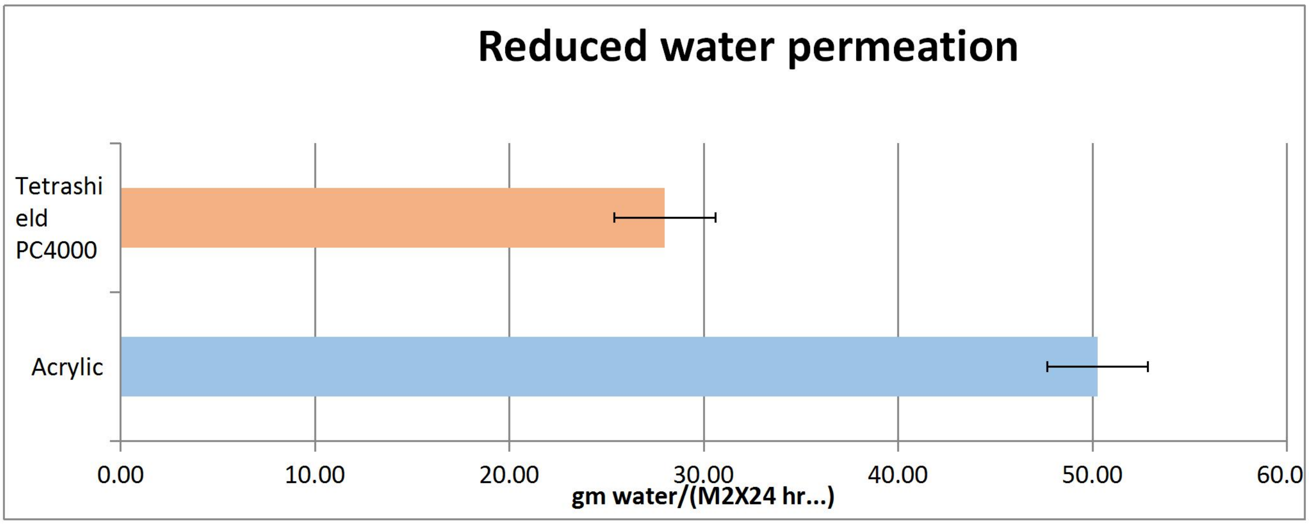


Figure 5 Water vapor transmission rates (ASTM E-96) comparing a coating prepared using Tetrashield PC4000 to a standard protective coating acrylic polyol cross-linked with Desmodur 3390 (Covestro).

## Demonstrated weathering characteristics

In weathering of aliphatic polyesters, β hydrogens on carbons two bonds away from the ether group of an ester, are susceptible to photo oxidation (see Figure 1). Because of TMCD's unique tetramethyl structure, the absence of β hydrogens significantly reduces photo degradation of resins that incorporate TMCD. Additionally, the improved moisture barrier and hydrolysis resistance combine to enable very good weathering performance compared to commercial automotive and industrial acrylics as shown below in automotive clearcoat formulations.

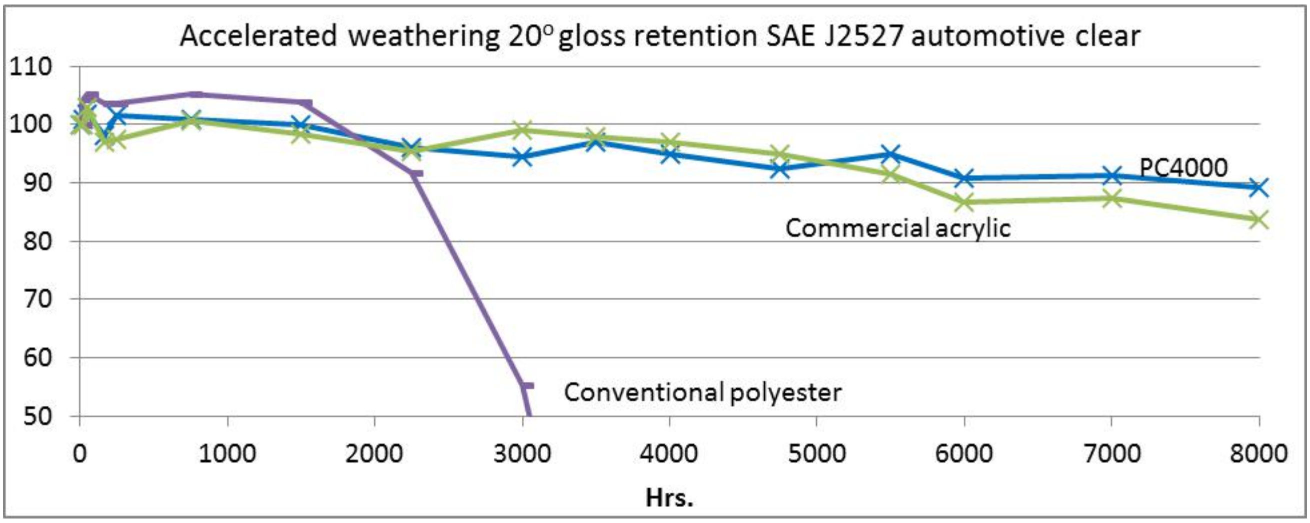


Figure 6 Xenon SAE 2527 weathering

To further understand the weathering capability of copolyesters that contain TMCD, a test method developed by Ford motor company called “Photo oxidation Testing” (POV) was used (1) (2). This technique uses photoacoustic infrared spectroscopy to monitor the increase in photo oxidation products on the surface of coatings, specifically it monitors the increase in the R-OH and R-NH stretch regions with reference to internal C-H stretch. For more information, please see the papers referenced below (1, 2).

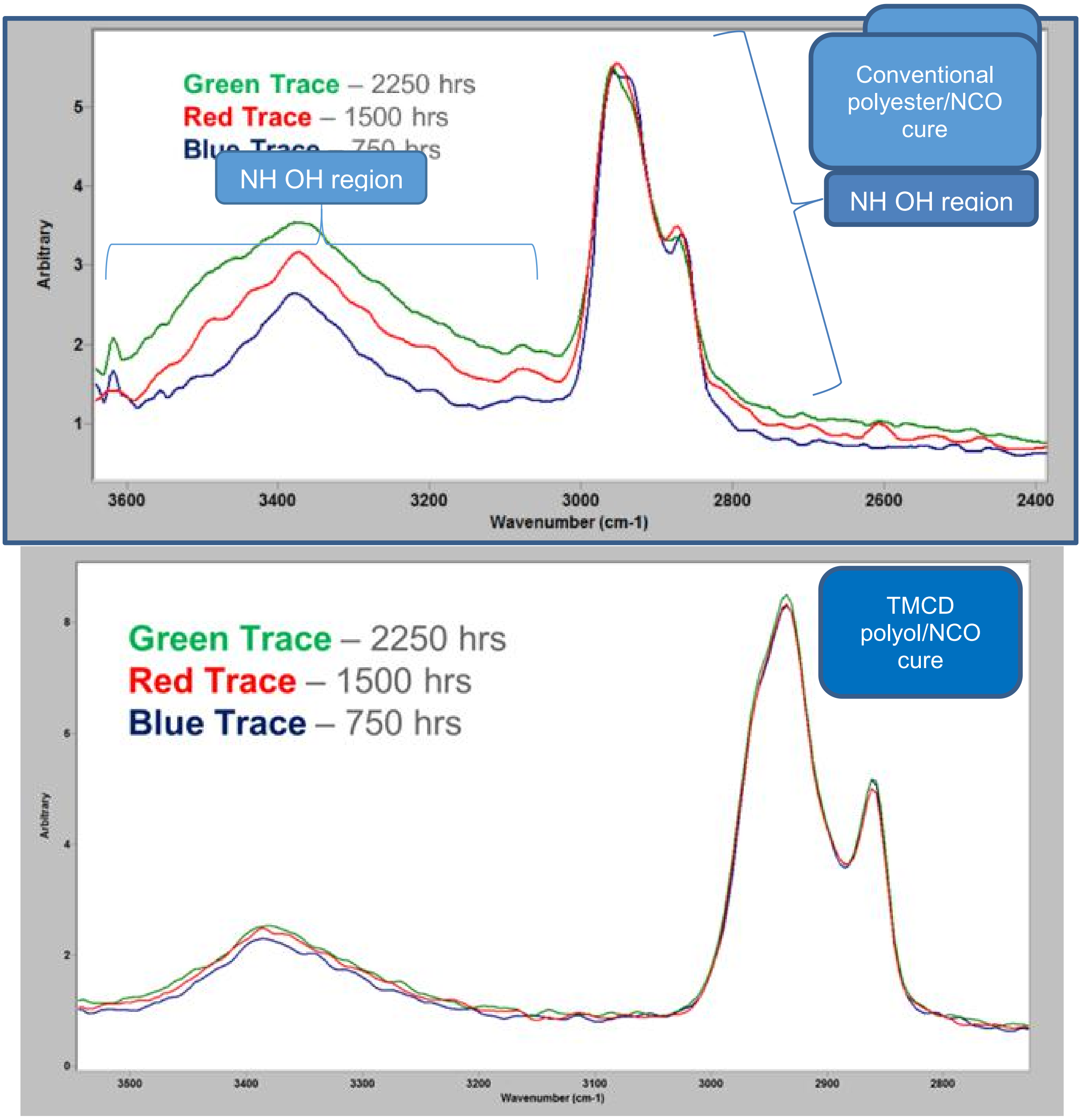


**Figure 7 – Photoacoustic IR of weathered clearcoats comparing acrylics and conventional polyesters to TMCD polyols**

Ford found that the increase in the area under the NH/OH region is linear with time and can be used to determine which coatings are photo oxidizing faster. This test protocol was used to develop a new automotive Xenon test cycle, ASTM D7869. This is shown above by the changes in the NH/OH regions in the spectra over time. Here the TMCD polyol shows the least amount of change.

Figure 8 is the photo oxidation over time for a conventional polyester polyol, a conventional acrylic polyol, and a TMCD-based resin. This clearly shows that the TMCD-based resin is photo oxidizing at a rate lower than the conventional acrylic and significantly lower than commercial weatherable polyesters.

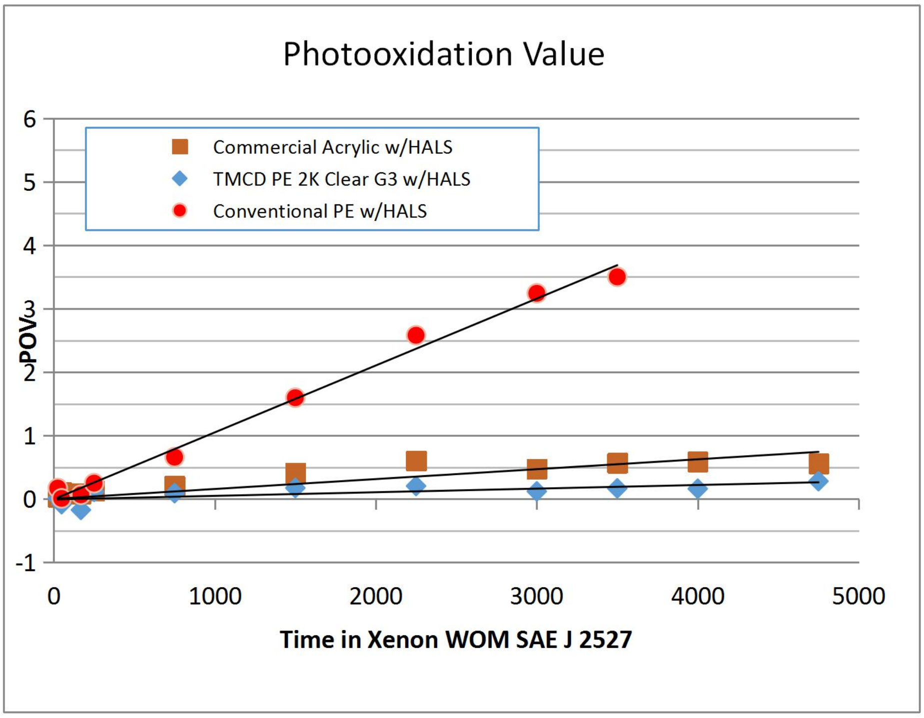


**Figure 8 Photo oxidation of clearcoats over time**

## Corrosion

TMCD-based coating over SP10 shot blasted steel shows very good direct-to-metal corrosion. At 1000 hrs. of salt spray corrosion (ASTM B117), the TMCD-based coating exhibits about 1/3 the scribe undercut corrosion as the acrylic control (Figure 9).

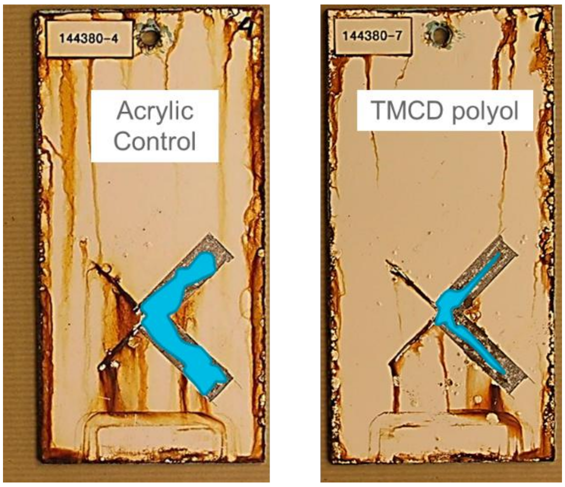


Figure 9 1000 hrs. ASTM B117 Salt spray. Paint stripped to highlight scribe undercut (blue)

## Commercial Resins and Prototype Formula

Eastman has successfully launched Tetrashield™ resins for protective and general industrial coatings. Additionally, starting point formulations are available and can be optimized for specific performance and application properties.

### CONCLUSIONS

Eastman has developed a unique resin platform that provides balanced performance characteristics when formulated into two-component, isocyanate cure, general industrial and protective coatings. These resins demonstrate:

- Very good weathering
- Formulation latitude for cure and pot life
- Exceptional chemical resistance
- Improved moisture barrier properties
- Good corrosion resistance
- High-solids formulation capabilities for VOC compliance

This technology is available under the Eastman Tetrashield$^{TM}$ brand.

## Appendix 1 - LC MS analysis

The hydrolysis experiments were performed with NaOH in water (0.03 M). Synthesized homopolymers were exposed to alkaline solutions for 24 hours at 95 °C in an oven. Once removed from the oven, the water solution and oligomers were fully dissolved in DMSO so that both the hydrolysate (disodium terephalate) and oligomers could be observed in the same chromatogram. This solution was then neutralized with an equivalent amount of phosphoric acid to quench the reaction. These samples were injected directly into the liquid chromatography-mass spectrometer (LC-MS). The acidic mobile phase rapidly converted the disodium terephalate into terephthalic acid.

The samples were analyzed using LC-MS. The chromatographic separation was achieved using a HP Series 1100 liquid chromatograph (LC), which was fitted with a Zorbax XDB-C18 (4.6x50 mm, 1.8u) column. A post-column diode array detector was used to detect the analytes. The initial conditions of the mobile phase were 97% water (with 0.1% formic acid) and 3% acetonitrile (with 0.1% formic acid). Mass spectra were acquired with a Micromass LCT mass spectrometer, which was coupled to the LC.

1. An improved accelerated weathering protocol to anticipate Florida exposure behavior of coatings. **M. Nichols et al. Ford Motor Company.** 2013, Journal of Coatings Technology Research, pp. 10(2) 153-173.

2. On the use of Fourier transform infrared spectroscopy and ultravilot spectroscopy to assess the weathering performance of isolated clearcoats from different chemical families. **J. Gerlock et al.** Polymer Degradation and Stability, 1998, Vols. (62) 225-234.