ANAYTICAL EVALUATION AND MECHANISTIC ELUCIDATION FOR SOLVENT DEGRADATION OF POLYMERIC MATERIALS

by

Grant C. Daniels A Thesis Submitted to the Graduate Faculty of George Mason University in Partial Fulfillment of The Requirements for the Degree of Master of Science Chemistry

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Analytical Evaluation and Mechanistic Elucidation for Solvent Degradation of Polymeric Materials

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at George Mason University

By

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DEDICATION

This is dedicated to my wonderful fiancé, Lindsay, for her never-ending love and support.

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I would like to thank all the people that made this possible including my fiancé Lindsay, my parents for their support, and Dr. James Wynne for the opportunity to do this work and all his invaluable help. I'd like to thank Dr. Gerald Weatherspoon for his insights and attention to detail, Dr. Robert Cozzens for his acumen and many suggestions and Dr. Robert Honeychuck for all the helpful feedback and the Strategic Environmental Research and Development Program for its finical support.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	vii
LIST OF TABLES	viii
LIST OF ABBREVIATIONS	ix
ABSTRACT	
1 Deckemburg	1
1. Background	1
1.1 Polymeric Coatings	1
1.2 Solvent Removal of Polymeric Coatings	2
1.3 Polyurethanes	4
2. Thesis	6
2.1 Thesis Statement	6
3. Methods	7
3.1 Polymeric Coatings	7
3.2 Solvent Selection	12
3.3 Sample Exposure	14
3.4 Thermal Analysis	16
Differential Scanning Calorimetry (DSC)	16
Thermogravimetric Analysis (TGA)	16
3.5 Spectroscopy	16
Fourier Transformed Infrared Spectroscopy-Attenuated Total Reflectance (FI	TR-
ATR)	16
Raman Spectroscopy	17
Solid-State Nuclear Magnetic Resonance (NMR)	17
Near Edge X-ray Absorption Fine Structure (NEXAFS)	/ I
S.0 Microscopy	10 18
Confocal Laser Microscopy (SEM)	10
3 7 Goniometry	10
Contact Angle	
4. Results and Discussion	20
4.1 Control Coatings Analysis	20
4.2 MC Exposure	
4.3 MC and Ethanol Exposure	

4.4 MC and Phenol Exposure	
4.5 MC, Ethanol and Phenol Exposure	
4.6 MC, Ethanol and Water Exposure	
4.7 MC, Ethanol, Phenol and Methocel Exposure	47
4.8 MC, Ethanol, Phenol, Water and Methocel Exposure	55
5. Conclusion	61
References	63

LIST OF FIGURES

Figure Pag	ge
Figure 1: Polyurethane reaction example.	. 4
Figure 2: Confocal images of unexposed MIL-PRF-53039 and MIL-PRF-85285 2	20
Figure 3: NEXAFS C K-edge spectrum of unexposed, fully-formulated MIL-PRF-85285	5.
	21
Figure 4: SEM images of unexposed control and MC exposed MIL-530392	24
Figure 5: Raman comparison of control clear and MC exposed clear MIL-PRF-852852	26
Figure 6: Proton NMR T1 vs. temperature for MIL-PRF-53039 before and after 5-minute	e
exposure to MC2	27
Figure 7: NEXAFS C K-edge spectrum of MC-exposed, fully-formulated MIL-PRF-	
85285, around the outer perimeter of the methylene chloride droplet	29
Figure 8: NEXAFS C K-edge spectrum of MC-exposed, fully-formulated MIL-PRF-	
85285, within the area of the methylene chloride droplet	30
Figure 9: TGA curves of MIL PRF-85285 exposed to MC/Ethanol and MC.	34
Figure 10: Confocal laser image of partial formulation of MIL-PRF-85285 unexposed,	
left, and partial formulation of MIL-PRF-85285 exposed to MC/Phenol,	
right3	35
Figure 11: FTIR-ATR of clear MIL-PRF-53039 exposed to MC and phenol 3	37
Figure 12: Theoretical coating degradation pathway from nucleophilic attack by phenol3	38
Figure 13: NEXAFS C K-edge spectrum of methylene chloride/ethanol/phenol-exposed	,
fully-formulated MIL-PRF-85285	39
Figure 14: SEM images of MIL-PRF-53039 exposed to MC/Ethanol/Water/Methocel	
solution	43
Figure 15: Water contact angle and surface free energy of exposed MIL-PRF-852854	45
Figure 16: TGA curves of MIL-PRF-85285 exposed to MC, MC/EtOH and	
MC/EtOH/H ₂ O	46
Figure 17: Confocal laser image of partial formulation of MIL-PRF-53039, left, and full	Ĺ
formulation of MIL-PRF-85285 exposed to MC, ethanol, phenol and	
methocel, right	48
Figure 18: TGA curves of MIL-PRF-53039 exposed to MC, MC/Ethanol/Phenol, and	
MC/Ethanol/ Phenol/Methocel.	50
Figure 19: TGA curves of MIL-PRF-85285 exposed to MC, MC/Ethanol/Phenol and	
MC/Ethanol/Phenol/Methocel	51
Figure 20: SEM images of MIL-PRF-53039 exposed to MC, ethanol, water, phenol and	
methocel solution5	56
Figure 21: TGA curves of MIL-PRF-85285 exposed to solvent solutions5	58
Figure 22: TGA curves of MIL-PRF-53039 exposed to solvent solutions5	59

LIST OF TABLES

Table Page
Table 1: MIL-PRF-53039 Full Formulation: Single Component Aliphatic Polyurethane
CARC
Table 2: MIL-PRF-85285 Full Formulation: High Solids Polyurethane Topcoat9
Table 3: MIL-PRF-53039 Clear Formulation: Single Component Aliphatic Polyurethane
CARC
Table 4: MIL-PRF-85285 Clear Formulation: High Solids Polyurethane Topcoat 12
Table 5: Composition of Solvent Solutions
Table 6: NEXAFS C K-edge peak assignments
Table 7: DR ratio of unexposed and MC exposed MIL-PRF-85285
Table 8: Tg (°C) of Coatings Exposed to MC and MC/Phenol
Table 9: Tg (°C) of Coatings Exposed to MC/Phenol and MC/Ethanol/Phenol 40
Table 10: Roughness of Full Formulation Coatings Exposed to Solution of
MC/Ethanol/Phenol
Table 11: Tg (°C) of MC/Ethanol/Phenol and MC/Ethanol/Phenol/Methocel exposures. 49
Table 12: Contact angle and wetting of MC, ethanol and phenol droplet on unexposed
coatings
Table 13: Contact angle and wetting of MC, ethanol and phenol droplet on coatings
exposed to MC, ethanol, water, phenol and methocel
Table 14: Tg (°C) of Coatings Exposed to MC/Ethanol/Phenol, MC/Ethanol/Phenol and
MC/Ethanol/Phenol/Methocel

LIST OF ABBREVIATIONS

ATR
a.u.
CARC
DR
DSC
FTIR
LARIAT
MC
MIL-PRF
NEXAFS
NMR
SEM
Tg
TGA
UV
wt%

ABSTRACT

ANAYTICAL EVALUATION AND MECHANISTIC ELUCIDATION FOR SOLVENT DEGRADATION OF POLYMERIC MATERIALS

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George Mason University 2014

Thesis Director: Dr. Gerald Weatherspoon

Polymeric coating materials have been used for decades to protect various substrates from degradation, such as corrosion, which can cause failure of important aspects in vehicles and buildings. The proper removal of polymeric coating materials is as important as their protection of underlying substrates since improper removal will damage the substrate. Methylene chloride and phenol based removers have been utilized for this purpose for over 50 years. During which time little understanding of the mechanism for the degradation of polymeric materials from these solvents has been developed. This work employed two military polyurethane coatings in three different formulations: full, partial and clear. Simplified formulations and control mixtures of solvents commonly used in methylene chloride and phenol removers were developed in order to deconvolute analysis of the complex polymeric material and the solvent systems. The polymeric coatings were exposed to the different solvents and solvent solutions. Analyses were conducted utilizing multiple techniques to determine the mechanism for the degradation of polymeric coatings.

These analyses revealed that methylene chloride solvated and swelled the coating while phenol degraded the polymer by nucleophilic attack. It was also determined that the addition of water to the solution significantly increased degradation. The enhanced degradation arose from the water molecule abstracting the proton from phenol, which increased its nucleophilicity.

1. BACKGROUND

1.1 Polymeric Coatings

The explosion in the variety of polymers in the last 100 years has led to a huge diversity of polymeric materials and their applications.¹ One of the main uses for polymeric materials through much of human history has been as coatings.² Polymeric coatings are thin layers of macromolecular material adsorbed onto a substrate that have been utilized for decorative, functional and protective purposes.³ Originally, these polymeric coatings were made from natural resins and unsaturated oils, but by the 1930s synthetic polymeric materials were produced.⁴ Inclusion of additives and the development of different polymers have led to a large increase in polymeric materials used for coating applications.^{5,6} Most of the coating applications center on protecting or enhancing a substrate, thereby resulting in better performance.^{3,7} However, polymer coatings lose their functionality over time and eventually require replacement.⁸ While many different substrates exist, a main form of substrate degradation against which polymeric coatings must protect is metal corrosion.³ due to the use of many different metals as building materials in industry and for vehicles. A prime example of substrate degradation are vehicles exposed to harsh environments. In order to prevent the degradation of the metal, a polymeric coating is applied to the vehicle. The polymeric coating provides the protection needed to safeguard against weathering, thereby allowing the vehicle to maintain its needed properties. The Navy, which uses protective polymeric coatings in harsh maritime environments, estimates that degradation of vehicles cost several billion dollars per year.⁹ This is but one example of the many ways that polymeric coatings protect substrates. To ensure adequate substrate protection, the polymeric coating needs to be removed periodically and replaced.⁷ It is imperative that removal of the coating does not damage the underlying substrate. Multiple methods exist to remove polymeric coatings that can be grouped into two broad categories: physical and chemical. Physical methods include sand blasting and other physical removal, while chemical methods involve solvent degradation of the coating and subsequent adhesive loss of the polymeric coating.

1.2 Solvent Removal of Polymeric Coatings

The main chemical coating removers for the last 50 years have contained methylene chloride (MC) and phenol as the primary constituents.¹⁰ Methylene chloride, which is a suspected carcinogen, breaks down into toxic carbon monoxide in the body and can cause neurological damage with high exposure.¹¹ Even though MC has been shown to be toxic to fish and other marine life, it was found not to bioaccumulate in the environment.¹² Phenol has been shown to reduce red blood cell count and affects the kidneys, liver, immune and nervous systems.¹³ Studies have shown that phenol exposure causes adverse effects on embryonic development, which is another major health concern of phenol exposure.^{14,15} Phenol is acutely toxic to many different aquatic organisms and can reside in waterways for hundreds of days.^{16,17} The environmental and health concerns of MC and phenol have prompted the need for suitable replacements. Unfortunately, efforts to replace the solvents in many applications have only produced less effective alternatives.¹⁸ Many of these alternatives are physical methods that create their own hazards: particle blasting

produces toxic dust, laser ablation requires protection from the laser, and both are more cumbersome and expensive than solvent-based removal.¹⁹ Attempts utilizing chemicals to replace MC and phenol have led to more environmentally friendly alternatives at the sacrifice of performance, price, and substrate damage.¹⁸ The most effective replacements utilize acidic or basic chemicals to enhance the degradation of the coating. However, the non-neutral pH of these systems increase the degradation of the substrate, resulting in increased damage and subsequent higher overall costs.²⁰

Despite the history of use for MC and phenol, the mechanism of polymeric coatings removal has not been fully characterized.²¹ One major area of investigation has been to analyze physical changes in regard to adhesion loss. Some research has shown that solventbased solutions wet the polymeric coating surface and then penetrate the layers of the polymeric coating down to the substrate through diffusion.^{22,23} It is thought that the small molar volume solvents, *i.e.* water and MC, are able to penetrate the coating by more easily "fitting" into spaces between the polymer molecules and diffusing through these spaces and channels.²⁴ As the solvent penetrates the coating it causes swelling. The swelling induces adhesion loss through expansion of the polymer network, leading to the reduction of intermolecular forces including hydrogen bonds and dispersion forces present in the polymeric coating.²⁵ Generally, swelling reduces the amount of additional stress necessary to fracture the coating by increasing the strain on the polymer network. Experimentally, this is observed by the ease of scraping off a solvated coating versus a dry coating from a substrate. Volkov, V. and coworkers have investigated the chemical interactions between solvents and coatings, including evidence of the influence solvents have on the polymer

structure.²⁶ These studies have primarily concentrated on the solubility of polymeric coatings in various solvents and solvent solutions; little work has looked at polymeric coating degradation.²⁷

1.3 Polyurethanes

Many different types of polymeric coatings are used commercially. One of the most employed protective polymeric coatings are polyurethanes.²⁸ Polyurethanes are usually made by reacting isocyanates and polyols as seen in Figure 1. Polyols are molecules that contain multiple free -OH groups. Polyols can be monomeric molecules or polymers of a wide range of molecular weights.^{2,4}



Figure 1: Polyurethane reaction example.

Polyurethanes are highly customizable to many applications through alteration of the chain length and branching of monomers, as well as through the addition of different chain extenders to the monomers. The customization of polyurethanes allows for the development of protecting coatings for many different substrates and diverse environments.²⁹ The military utilizes this customization to make engineered polyurethanes

for protection of aircraft and vehicles. Two polyurethane coatings of interest are Air Force top coat (MIL-PRF-85285) and Chemical Agent Resistant Coating (CARC or MIL-PRF-53039). Both of these coatings are durable and used in harsh environments. MIL-PRF-85285 is resistant to heat, solvent, jet fuel and hydraulic fluid, humidity up to 49 °C and possesses de-icing properties.³⁰ MIL-PRF-53039 is resistant to water, acid, bleach and hydrocarbon fluid.³¹ The durable nature of these coatings has made them even more difficult to remove when using alternatives to MC and phenol. The broad use and diverse properties of these polyurethanes make them ideal for degradation analysis. Thus, the knowledge of the mechanism for degradation of these types of coating will assist in the development and application of alternative polymeric coating removers.

2. THESIS

2.1 Thesis Statement

The ability to remove and replace polymeric coatings with minimal substrate damage is essential for continued substrate protection, especially on metal substrates. Methylene chloride and phenol based paint removal mixtures have shown a great ability to remove durable, complex and resilient coatings with minimal substrate damage. Yet, the mechanism of how MC and phenol based mixtures remove polymeric coatings has never been fully understood. The two polyurethane coatings that where evaluated are Air Force top coat (MIL-PRF-85285) and CARC (MIL-PRF-53039). These polyurethane coatings are engineered to endure extreme conditions and thus still require the use of MC and phenol for their removal. Knowledge of the fundamental mechanism for MC and phenol mixtures degradation of polymeric coatings will provide significant insight into the development of more environmentally friendly alternatives.

The evaluation of MC and phenol paint remover required a multifaceted approach. The two aforementioned polyurethane coatings are complex systems that contain fillers, pigments and flattening agents added to the polymer. In order to help with the analysis of the polymer degradation, clear coatings with no fillers, pigments, or flattening agents were made for each polyurethane. Partially formulated coatings that contained only the polymer and pigments were also made to help understand the mechanism. A systematic stepwise approach allowed for identification of the effect of each component on the coating systems, which then permitted analysis of the complex solutions.

3. METHODS

3.1 Polymeric Coatings

Currently employed military coatings were selected for this study. Two military polyurethane coatings (MIL-SPEC: 53039 and 85285) were analyzed since they represent functional polymeric coatings and have known specifications. These polymeric coatings are engineered to handle extreme temperature changes, chemical conditions and weathering. MIL-SPEC 53039 is a single component polyurethane system and the MIL-SPEC 85285 is a two component system with a polyester extender reacted with a premade polyurethane. Commercial polymeric coatings like these polyurethanes contain not only the polymer, but also various pigments, fillers, flattening compounds and wetting agents to ensure compatibility of the coating. To reduce complications, some of this work employed control coatings made without any extra components. Films of fully formulated MIL-SPEC coatings were also studied. The two polyurethane topcoats were utilized as unsupported coatings (free films), with a film thickness of approximately five mils. Full formulation of the coatings can be found in Tables 1-2.

Raw Material	wt%	Raw Material	wt%
Polyurethane	31	Cobalt titanate spinel	0.4
Dispersant	1	Methyl isoamyl ketone	23.5
Rheology modifier	0.1	VM&P naphtha	3.2
Flow modifier	<0.1	Xylene	1.4
Surfactant	0.1	<i>n</i> -Butyl acetate	1.3
Dibutyl tin dilaurate	0.5	Aromatic 100	1.3
Celite	18.5	Mineral spirits	1.2
Imsil	3.6	Propylene glycol	0.1
TiO ₂	9.5	Isobutyl ketone	0.1
Iron oxide hydrate	2.5	<i>n</i> -Butyl acid phosphate	0.1
Carbazole dioxazine violet	<0.1	Bentone	0.5

 Table 1: MIL-PRF-53039 Full Formulation: Single Component Aliphatic Polyurethane

 CARC.

Part A Raw Material	wt%	Part B Raw Material	wt%
Methyl <i>n</i> -propyl ketone	1	Polyurethane resin	43
Methyl <i>n</i> -amyl ketone	7	<i>n</i> -Butyl acetate	1.6
Antioxidant	0.3		
UV absorber	0.5		
UV stabilizer	1		
Polyester solution #1	19.3		
Cellosolve acetyl butyrate	0.6		
Surfactant	0.1		
1% Thickener in xylene	0.2		
Thixotropic agent	0.2		
Dispersing agent	0.3		
TiO ₂	20.5		
Polyester solution #2	4.4		

Table 2: MIL-PRF-85285 Full Formulation: High Solids Polyurethane Topcoat.

Simplified formulations of the corresponding complex coating systems were prepared in order to isolate specific variables and identified their effects. Resin binders and curing agents were combined as specified in Tables 3 and 4 to produce clear coat films of the selected military coatings. Each clear coat formulation was produced without pigments, additives, and fillers. In order to cast clear formulations to the required film thickness for analysis, it was necessary to combine solvent components of MIL-SPEC 53039 and MIL-SPEC 85285 in order to achieve a workable spray application viscosity. Elimination of entrapped air or solvents required either the addition of an antifoam agent or the readjustment of the amount of antifoam agent, or both. Antifoam agents were from each formula and added in the proportions specified in Tables 3 and 4.

Raw Material	wt%
Polyurethane	47.4
Dibutyl tin laurate	0.7
Dispersant	0.1
<i>n</i> -Butyl acetate	2
Methyl isoamyl ketone	38.2
Surfactant	0.2
Flow modifier	0.1
Rheology modifier	<0.1
VM&P naphtha	4.8
Xylene	2.1
Aromatic 100	2
Mineral spirits	2
Propylene glycol	0.0
Isobutyl ketone	0.2
<i>n</i> -Butyl acid phosphate	0.2

 Table 3: MIL-PRF-53039 Clear Formulation: Single Component Aliphatic Polyurethane

 CARC.

			1
Part A Raw Material	wt%	Part B Raw Material	wt%
Polyester solution #1	24.4	Polyurethane resin	54.4
Polyester solution #2	5.5	<i>n</i> -Butyl acetate	2
Methyl <i>n</i> -amyl ketone	8.9		
Methyl <i>n</i> -propyl ketone	1.3		
Antioxidant	0.4		
UV absorber	0.6		
UV stabilizer	1.3		
Cellosolve acetyl butyrate	0.8		
Surfactant	0.2		
1% Thickener in xylene	0.2		

Table 4: MIL-PRF-85285 Clear Formulation: High Solids Polyurethane Topcoat.

The formulas were compounded to achieve continuous, anomaly-free films of the desired thickness by utilizing the identical rheology and flow modifiers specified in each formula. In order to determine the possible effects of the fillers and flattening agents, preliminary studies were performed on partial formulations that consisted of the clear formulations specified coatings with pigments added. All coatings were prepared on release paper for facile removal and evaluation of free films.

3.2 Solvent Selection

MC and phenol based paint removers contain many supplementary components in addition to the primary solvents. To aide analysis, control solutions with a range of increasing complexities were prepared to mimic the real paint remover formulation. Components of the commercially available remover and the different formulations that were prepared are listed in Table 5. Spectroscopic analysis of the coatings was performed using attenuated total reflectance-Fourier transform infrared (ATR-FTIR), nuclear magnetic resonance (NMR), Raman and near edge X-ray adsorption fine structure (NEXAFS) spectroscopies. These techniques identified chemical changes to the coating upon exposure to solvents, especially to the polymer backbone. Confocal microscopy, SEM and contact angle allow for surface analysis of the coatings. Surface analysis permits chemical and physical evidence of degradation of the coatings to be found and interpreted. Bulk characterization of the coatings utilized differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) afforded the determination of the extent of degradation throughout the entire polymeric coating. These multiple techniques helped to elucidate the mechanism of solvent facilitated degradation and removal of polymeric materials for MC and phenol based paint removers.

	Weight Percent				
Solvent Formula	methylene chloride	ethanol	water	phenol	methocel ^b
Commercial Coating Remover ^a	60.6	5.8	7.8	15.8	1.2
Methylene Chloride	100				
Methylene Chloride and Phenol	79			21	
Methylene Chloride and Ethanol	91	9			
Methylene Chloride, Ethanol and Phenol	74	7		19	
Methylene Chloride, Ethanol, Water and Methocel	80	8	10		2
Methylene Chloride, Ethanol, Water, Phenol and Methocel	67	6	9	17	1
Methylene Chloride, Ethanol, Phenol and Methocel	73	7		19	1

Table 5: Composition of Solvent Solutions.

^{*a*}Also contains toluene (1.3%), sodium petroleum sulfonate (5.5%) and paraffin wax (1.9%).

^bMethocel added to emulsify into a single phase, with exception of methylene chloride, ethanol, and phenol solution.

The variety of chemicals present in the paint remover further adds to the complexity of the analysis. Different mixture formulations allowed for a systematic approach to identify the effects that various chemicals may have on the degradation process. Similar to characterization of the coatings, multiple analytical techniques were used to help confirm and understand any findings.

3.3 Sample Exposure

Samples for thermal analysis were exposed using the following method. Coupons of approximately 2 cm^2 of each free coating were cut and placed into individual scintillation vials. To each vial was added the respective solvent or solvent mixture (see

Table 1) until the coating was completely covered (~10 mL). After exposure periods of two hours the liquid was decanted, rinsed with absolute ethanol and the coating allowed to air dry in the vial. A rinse with ethanol ensured that no remaining paint removal chemicals were adhered to the surface of the coating prior to analysis. Caution was taken to ensure the coating was completely dry before evaluation.

Vibrational spectroscopy samples were exposed to individual solvents or solvent mixtures for times ranging from 15 minutes to 2 hours. The samples were then air dried thoroughly, for times ranging from 2 hours to 2 weeks, to reduce spectral contamination from residual solvent. Limited samples were taken of saturated coatings using Raman Spectroscopy. NEXAFS samples were prepared by placing a drop of solvent or solvent mixtures on the sample and then dried in the same manner as vibrational spectroscopy samples.

Samples for confocal and contact angle analysis followed the same procedure as the thermal experimental except that they were exposed for 20, 40 and 60 minutes. Samples were rinsed with ethanol and dried for at least a day to ensure complete removal of solvents from the coating. This systematic time trial allowed for a stepwise analysis of the paint remover solutions method of attack on the coating.

¹H solid-state NMR analysis was conducted on polymeric coatings before and after a 5 minute room temperature exposure to MC. Exposures were performed by immersing squares of the cut film in the solvent in a beaker. The film was removed and blotted dry before placing into a 5 mm glass NMR tube, loosely sealed with Teflon tape to minimize evaporation.

3.4 Thermal Analysis Differential Scanning Calorimetry (DSC)

DSC was performed on a TA Instruments Q20 DSC with the DSC Refrigerated Cooling System (RCS) and a purge gas of nitrogen set to 50 mL/min. Samples of approximately 1-2 mg were placed into TA Instrument Tzero Aluminum pans and an empty aluminum pan was used as reference. Samples were run in air from -90 °C to 150 °C at 20 °C/min twice. All data reported were taken from the second cycle in order to erase the thermal memory of the coating. Glass transition temperatures (T_g) were measured using TA Universal Analysis software.

Thermogravimetric Analysis (TGA)

TGA was performed on a TA Instruments Q50 TGA using a platinum sample pan. The analysis was carried out in the presence of oxygen with breathing air used as the sample gas. Nitrogen was used as the purge gas for the balance. Data were recorded from ambient temperature to 700 °C at a 5 °C/min ramp. Plots of percent weight loss versus temperature were constructed to analyze the data.

3.5 Spectroscopy

Fourier Transformed Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR)

FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a Smart Performer ATR attachment with a germanium crystal at 32 scans per spectra. Spectra were recorded from 4000 - 500 cm⁻¹ with a resolution of 2 cm⁻¹, and were analyzed using the Nicolet OMNIC software suite.

Raman Spectroscopy

Samples were analyzed using a Nicolet Almega dispersive Raman spectrometer with 10x objective lens. Either a 785 nm or 532 nm excitation laser was used with the incident laser spot size of less than 3 μ m. The instrument had a range of 100 – 4000 cm⁻¹ Raman shift with a 2 cm⁻¹ resolution.

Solid-State Nuclear Magnetic Resonance (NMR)

Solid state ¹H NMR experiments were carried out on a Bruker Avance DMX-500 NMR spectrometer using a non-spinning high-power ¹H probe with a horizontal 5 mm solenoidal coil containing the glass sample tube. The ¹H NMR spectra and ¹H relaxation times were obtained at 500 MHz (11.7 T field). The ¹H spin-lattice relaxation times (T₁) were measured using a saturation-recovery pulse sequence with typically a dozen different recovery delays, and fitting the recovery curve of the peak intensity using OriginPro 7.0 to a single-exponential recovery curve with time constant T₁. Intensities of static ¹H NMR peaks versus spin-lock times (typically nine values) in a spin-locking pulse sequence were fit using OriginPro 7.0 to a single-exponential decay curve with a decay time constant T₁.

Near Edge X-ray Absorption Fine Structure (NEXAFS)

NEXAFS spectroscopy was performed on Beamline U7A of the National Synchrotron Light Source at Brookhaven National Laboratory to study the carbon K edge of unexposed and exposed coatings. A grid bias voltage of 150 V was used, which provides surface selectivity on the order of several nm, with a spot size of less than 1 mm². Spectra were subsequently pre-/post-edge normalized prior to curve fitting and analysis. Igor Pro software was used to calculate the dichroic ratio of each peak in each sample, utilizing data

collected at 3 angles (20°, 55°, and 90°) relative to the sample. The intensity at 0° was extrapolated from a linear fit of the intensities at the various angles. Hyperspectral acquisition of a large sample area, 12x15 mm², was done on the same Beamline using the Large Area Rapid Imaging Analytical Tool (LARIAT).

3.6 Microscopy

Scanning Electron Microscopy (SEM)

Micrographs were obtained using an FEI Helios Nanolab dual-beam scanning electron microscope with a secondary electron detector. Prior to SEM analysis the surface of samples were coated with a 3 nm layer of gold using a Cressington 108 auto sputter coater equipped with a Cressington MTM20 thickness controller. Accelerating voltage was set between 3 and 5 kV.

Confocal Laser Microscopy

Confocal laser microscopy was performed on an Olympus OLS4000 3D Measuring Laser Microscope with magnification from 108X to 2150X. Images for roughness analysis were taken at 1076X magnification with an area of 715 x 720 μ m² and a height step of 60 nm. Roughness was calculated by the LEXT software using the root mean square deviation from the surface (R_q). The formula for the calculation is shown in equation 1. M is a number of points per profile (scan line), N is the number of profiles and η is the amplitude at point x_i, y_j.

(1)
$$R_{q} = \sqrt{\frac{1}{MN} \sum_{j=1}^{M} \sum_{i=1}^{N} \eta^{2} (x_{i} y_{j})}$$

3.7 Goniometry Contact Angle

Contact angle and surface free energy measurements were obtained on a VCA 2500 using the sessile drop technique, employing liquid drops of 2 μ L. Images of the droplet were taken after 3 seconds and then analyzed using the VCA OptimaXE software. Contact angle was investigated with multiple liquids including triple distilled water, hexadecane and methylene chloride. Surface free energy was determined using the Owens-Wendt theory with water and diiodomethane. Owens-Wendt theory uses two different liquids with known polar and dispersive forces to solve Young's equation determining the surface free energy.³²

4. RESULTS AND DISCUSSION

4.1 Control Coatings Analysis

The different formulations of the coatings MIL-PRF-53039 and MIL-PRF-85285 were analyzed with various techniques, thereby providing a baseline for comparison. The SEM and confocal images (Figure 2) along with the roughness calculations (Equation 1) allowed for analysis of physical changes to the polymer, and pigments and fillers in both the full and partial formulations. FTIR-ATR spectra were obtained for only the clear and partial coating formulations due to spectral interference from the additives in the full formulations. Raman analysis allowed for all coating formulations to be analyzed with minimal spectral interference from the fillers and pigments. Surface energies were calculated from contact angle measurements taken on the unexposed films.



Full Formulation MIL-53039: Roughness 1.86 μmFull Formulation MIL-85285: Roughness 2.11 μmFigure 2: Confocal images of unexposed MIL-PRF-53039 and MIL-PRF-85285.

Due to time restrictions on the synchrotron light source, limited NEXAFS spectra and hyperspectral images of full MIL-PRF-85285 were obtained. Pre- and post-edge correction processes were used on the spectra to allow for comparisons between spectra. The pre-edge was subtracted to remove the overall background, providing the correct intensity of the spectrum. The post-edge correction, which set the long-tail end of the data to an intensity of 1, provided normalization of the data. All spectra analyzed were taken at 55°, which is the "magic angle" to eliminate orientation effects. The spectrum of fully formulated MIL-85285 are presented in Figure 3.



Figure 3: NEXAFS C K-edge spectrum of unexposed, fully-formulated MIL-PRF-85285.

Even though the position and width of peaks were very consistent across samples, a small degree of flexibility in peak fit was allowed to account for the different physicochemical environments in the polymeric coatings. In Figure 3, the C 1s peak observed at 285.4 eV, peak A, correlates to -C=C aromatic π^* , which must be attributed to an additive in the polymer due to MIL-PRF-85825 aliphatic nature.³³ This is due to the presence of UV stabilizing compounds, which consist of conjugated molecules. A single curve fit for this peak was too broad for this technique, with the full width half maximum (FWHM) of 0.8 eV. The fitting two peaks at 285.2 and 285.7 eV, named A1 and A2, respectively, resulted in more reasonable FWHM values of ~0.6 eV for a peaks at such binding energies. Confidence in this assignment was high since the fitted peaks were dissimilar in area, with A1 generally being larger than A2. The small peak at 286.7 eV (B) corroborated the prediction of a molecule resembling benzophenone, a commonly used UV blocker, as it corresponded to the transition seen in a carbonyl which links two aromatic rings.³⁴

	Binding	
	Energy (eV)	Structure
А	285.2, 285.7	C=C aromatic π^*
В	286.8	C=O π^* conjugated systems
С	288	С-Н σ*
D	289.5	С=О π*
Е	290.7	С=О π*, С-N σ*, С=С 2π*
F	293	σ* (C-C)
G	296	σ* (C-C/C-O)
Η	299	σ* (C-C)

Table 6: NEXAFS C K-edge peak assignments.

Peak C, in the carbon K edge spectrum occurred at 288 eV and corresponds to C-H σ^* , which results from absorptions of the long chains of the polyurethanes and polyesters.³⁵ Peak D, at 289.4 eV, was related to C=O π^* absorptions due to the polyurethanes. This peak fit corresponds well for the types of urethane linkages that are often observed as the basis of many structures commonly employed in the formation of polyurethanes from hexamethylene diisocyanate.³⁶ The peak at 290.7 eV, E, appeared to be the aggregate of several peaks: the C=O π^* transition for urethanes, and the C-N σ^* transition. The literature reported that the carbonyl peak should be closer to 290 eV; however, a single peak fit for the addition of the C-N σ^* results in a single peak that is overly broad for this assignment.³⁷ The ionization edge between 290 and 291 eV proved challenging to properly fit, this led to the conclusion to under-fit the curve.³⁸ Additional peaks at ~293, ~296, and ~299 eV (F, G, H) were σ^* transitions which relate to C-C, C-C-/C-O, and C-C, respectively.³⁹ The positions and assignments of these peaks are presented in Table 6. Any changes in these peaks indicates alterations to the polymer coating.

4.2 Methylene Chloride Exposure

MC was selected for initial analysis due to its use as the majority component in the paint removal solutions, despite various other solvents present. The polymeric coatings exposed to MC were thoroughly analyzed to ensure that its method of degradation was understood. Confocal microscopy and SEM images showed no signs of degradation (blisters, cracks, peeling and holes) for the samples exposed to MC when compared to control coatings, as can be seen in Figure 4. In the full coatings some fillers were more

easily observed after exposure to MC, indicating possible solvation of the fillers. The lack of physical signs of deterioration in the images implied that MC did not degrade the coating.



Full Formulation MIL-53039 Control Full Formulation MIL-53039 Exposed to Methylene Chloride Figure 4: SEM images of unexposed control and MC exposed MIL-53039.

Confocal images revealed a sporadic, yet small, increasing trend in surface roughness with respect to exposure time. The surface free energy calculated for the exposed coatings also revealed small sporadic changes with an increasing trend with respect to MC exposure time. Changes in surface roughness of a coating is known to affect surface free energy.⁴⁰ Therefore, it was important to determine whether surface free energy changes were dependent on roughness or surface chemistry. A correlation was observed between roughness and surface free energy, implying that no chemical changes occurred in the coating. FTIR-ATR analysis of coatings exposed to MC was undertaken to ensure
that only the roughness affected surface free energy and not chemical alterations. No peak changes were found on the clear and partial formulations of the coatings. The full formulations were difficult to analyze due to noise from the fillers in the coating. Despite difficulty, surface and near surface analysis showed no chemical or physical degradation.

Bulk coating analysis was performed with DSC and TGA. Glass transitions (T_g) were determined from DSC analysis. Studies have shown that a decreasing T_g indicates polymer degradation.⁴¹ The T_g for the different coating formulations changed slightly, with a range of 0-15 °C, after exposure to MC. In most of the coatings a small increase in the T_g was observed, which was unexpected since decreasing T_g is a sign of polymer degradation. TGA curves of samples exposed to MC exhibited a lower initial degradation point and a small overall increase in the degradation of the polymer throughout the TGA run compared to unexposed samples. Overall, the minor and significant effects detected from the above analyses imply that MC did not cause degradation of the polymer backbone in the coatings. A possible explanation for the observed results could be that the polymer rearranges upon drying. In the full and partial formulations, these results could also arise from the rearrangement of the fillers and pigments in the coating upon solvation from MC.

Confirmation of solvation, rearrangement and further analysis of the role of MC in degradation was undertaken with Raman, solid-state ¹H NMR and NEXAFS. Raman spectra of clear coatings, saturated in MC, were acquired to better understand the effects of MC on the polymer matrix. Spectra of the saturated coatings, shown in Figure 5, exhibit a broadened carbonyl peak at 1758 cm⁻¹.



Figure 5: Raman comparison of control clear (left) and MC exposed clear MIL-PRF-85285 (right).

This peak broadening implies that MC solvated the coating and stretched/swelled (dilated) the carbonyl of the polyurethane. In polyurethanes, the carbonyl hydrogen bonds with hydrogens attached to the nitrogen on adjacent chains. This bonding effect gives polyurethanes many of their properties.⁴ Interaction of MC with the carbonyl weakens these bonds, thereby allowing solvation of the coating. The dilation of the carbonyl could result from the interaction of the MC with the carbonyl through dipole-dipole forces. This caused the polymer chains to move freely and subsequent rearrangement of the polymer network upon drying. The dilation of the carbonyl could also increase the carbonyl's susceptibility to nucleophilic attack.

Solid-state ¹H NMR analysis of MC afforded conformation of Raman results and further analysis of the solvated polymer coatings. Comparing the unexposed clear coating

 T_1 data to the T_1 data of MC exposed clear coating produced several conformations of MC solvation that can be seen in Figure 6.



Figure 6: Proton NMR T_1 vs. temperature for MIL-PRF-53039 before and after 5-minute exposure to MC.

The T_1 of neat methylene chloride was long because it is an isotropic liquid with a short (ns) rotational correlation time, whereas the T_1 of the unexposed polymer film was significantly shorter and typical of non-rigid polymers.⁴² The similarity of the two T_1 values of the coating exposed to MC and the unexposed coating indicated that MC was in intimate atomic-scale contact with the polymer. This intimate contact resulted in the MC having significant proton-proton dipolar coupling to the polymer backbone in the coating, which equalized T_1 values by the process known as spin-diffusion.⁴³ No evidence of free MC in liquid-like pools of any size was found during analysis. The dipolar coupling between the polymer backbone and MC matched the results observed from Raman spectroscopy, in which MC solvated the coating and interacted through dipole forces. The

NMR data provided a strong confirmation that MC only solvated the coating. Further analysis on full formulations was necessary to determine how pigments and fillers effect solvent degradation of polymeric coatings.

NEXAFS spectroscopy of a drop of MC on MIL-PRF-85285 provided further information on the effect of MC on the entire coating. Spectra were taken in three different areas on the coating; inside the MC drop, at the edge of the drop and outside the MC drop. There was no difference between spectra outside the area of the drop and unexposed MIL-PRF-85825 and therefore was used to confirm which areas were influenced by the drop. The spectra of the outer perimeter of the drop, shown in Figure 7, exhibited a significant change.



Figure 7: NEXAFS C K-edge spectrum of MC-exposed, fully-formulated MIL-PRF-85285, around the outer perimeter of the methylene chloride droplet.

While most of the spectrum of the exposed samples was very similar to that of the unexposed sample, a couple of small differences in peak C and peak G were observed, as well as the overall intensity of peak A increased by roughly 50%. MIL-PRF-85285 is an aliphatic polymer, therefore peak A must represent the aromatic fillers that were added to the coating. The significant increase in peak A intensity revealed that not only does MC solvate the polymer but also the additives. This revealed that MC solvated the entire coating, which further indicated that the polymer underwent rearrangement upon drying. The minor variability observed in peak C and peak G were within the experimental error of the instrument and could have resulted from changes in the local environment due to the polymer rearrangement.⁴⁴ The spectrum from inside the droplet area, seen in Figure 8,

revealed a significant decrease in peak A. The depletion of peak A inside the droplet and increase along the edges further highlighted the ability of MC to solvate the entire coating and rearrange the polymer and additives.



Figure 8: NEXAFS C K-edge spectrum of MC-exposed, fully-formulated MIL-PRF-85285, within the area of the methylene chloride droplet.

Peaks C and G had small decreases in intensity similar to the changes on the edge of the droplet. Peak D shifted to a slightly lower binding energy by about 150 meV. Small differences to the peaks could be due the effects on the degree of hydrogen bonding or local steric environment around the carbonyl as a result of polymer swelling and rearrangement. The analysis of the inside and the edge of area exposed to MC strongly suggested that MC solvated the fully formulated coating entirely.

NEXFAS also allowed for the analysis of polymer rearrangement in the coating through evaluation of the dichroic ratio (DR). The DR utilizes the polarized synchrotron radiation of NEXFAS to determine whether the molecular bonds lay parallel or perpendicular to the surface. The perpendicular intensity was determined by recording a spectrum at 90° from the surface. The parallel intensity was calculated using a linear regression from intensities taken at multiple angles.

(2)
$$DR = (I^{\parallel} - I^{\perp})/(I^{\parallel} + I^{\perp})$$

Determination of the DR was done using equation 2, where I^{\parallel} is the intensity of the peak parallel to the surface and I^{\perp} is the intensity of the peak perpendicular to the surface. The DR for surfaces can range from 1, totally parallel, to -1, totally perpendicular.⁴⁵ In polymer systems the DR usually falls between 0 and 0.2.⁴⁶ Changes in the dichroic ratio upon exposure to MC can indicate rearrangement of the polymer chains, as seen in Table 7. The intensities used for the DR were all taken within the MC drop.

MIL-PRF-85285 unexposed								
Peak	A(C=C)	B (C=O)	С (С-Н)	D (C=O)	E (C-O)	F (C-C)	G (C-C)	
R^2	0.9143	0.6505	0.2885	0.3409	0.0469	0.2939	0.2938	
DR	0.0555	-0.2039	0.0037	-0.0027	0.0031	0.0003	-0.0003	
MIL-PRF-85285 MC exposed								
Peak A (C=C) B (C=O) C (C-H) D (C=O) E (C-O) F (C-C) G (C-C)								
R ²	0.9893	0.9615	0.9640	0.8989	0.8306	0.1961	0.1492	
DR	0.2849	-0.1142	0.0489	0.0332	0.4167	0.0123	-0.001	

Table 7: DR ratio of unexposed and MC exposed MIL-PRF-85285.

To ensure accuracy, only the perpendicular linear fits for bonds with a R² higher than 0.85 were considered for analysis. In unexposed MIL-PRF-85285, the C=C bond was the only one with a linear fit that allowed for determination of the bond orientation. The C=C bonds in the coating were associated with the UV stabilizing additives. Orientation of the C=C bonds was slightly toward parallel with the surface. Upon exposure to MC the C=C bonds surface orientation became more parallel. The rearrangement of the additive confirmed that MC solvated both the additives in the coating and the polymer chain. While a direct comparison cannot be made between the remainder of the bonds due to the poor linear fit for the DR, it should be noted that the increase in the R² values of the peaks for the MC exposed coating indicated rearrangement of the coating. The increased R² values highlight that the random orientation of the bonds had rearranged into a more ordered orientation. The DR, along with the NEXAFS analysis, revealed that MC solvated the entire coating and resulted in the rearrangement of the polymeric backbone, fillers and additives in the coatings. Through analysis of Raman Spectroscopy, ¹H-NMR and NEXAFS spectroscopy, MC was shown to not only solvate the polymer but also solvate the fillers and additives in the coating. The solvation led to rearrangement of the coating upon drying.

4.3 MC and Ethanol Exposure

Establishing the role of MC permitted the development and investigation of solutions with additional components. The first solution tested was composed of MC and ethanol, prepared as described in Table 1. The confocal and SEM images for MC and ethanol solution degradation on the different coatings were very similar to the MC exposure. Additionally the minor effects on the T_g and roughness of the MC/ethanol exposed coatings exhibited magnitude and variation similar to the MC exposed samples. Finally, the TGA curve of the MC and ethanol exposure (Figure 9) was almost identical to the MC curve.



Figure 9: TGA curves of MIL PRF-85285 and MIL PRF-53039 exposed to MC (green) and MC/ethanol (blue).

Insignificant differences in the data between the MC exposed coatings and the MC/ethanol exposed coatings were well within experimental error or can be explained by rearrangement of the polymer matrix upon solvation and subsequent drying being a non-ordered/random process. This indicated that ethanol played no active role in degradation of the polymer backbone of the coating and was most likely present in the solution to help with solubility of the various components.

4.4 MC and Phenol Exposure

A solution of MC and phenol was made in order to determine if any degradation was caused by phenol. Exposure of the samples to MC/phenol revealed obvious changes with clear MIL-PRF-53039 as it became very brittle and discolored. Confocal microscopy

of the coatings revealed significant degradation when compared to non-exposed coatings, presented in Figure 10.



Figure 10: Confocal laser image of partial formulation of MIL-PRF-85285 unexposed, left, and partial formulation of MIL-PRF-85285 exposed to MC/Phenol, right.

The drastic transformation in physical appearance of the coating confirmed polymer rearrangement and possible degradation. The development of holes in several locations on the coating indicated that degradation of the polymer backbone had started to occur. Evaluation of the bulk properties of the coatings shows whether these changes only occurred on the surface or if the entire coating had been degraded. The large decrease in T_g values for the coatings exposed to MC/Phenol (Table 8) clearly indicated that the drastic transformation observed on the surfaces of the coatings were also present throughout the entire coating.

	Clear MIL-	Full Formulation	Clear MIL-	Full Formulation
	PRF-53039	MIL-PRF-53039	PRF-85285	MIL-PRF-85285
Control	87	60	51	0
MC	67	76	46	15
MC/Phenol	-4	-2	-25	-53

Table 8: T_g (°C) of coatings exposed to MC and MC/phenol.

The presence of phenol in the mixture led to a large decrease in the T_g that was not observed in MC exposure alone. A sizable decrease was observed in both coatings and all formulations. This large decrease in the T_g showed that the polymer backbone of the coating had been degraded. Phenol is a known nucleophile that can use either the oxygen or the aromatic ring to attack the polymer backbone.⁴⁷ Determination of the chemical changes in the clear and partial formulation coatings was performed through ATR-FTIR analysis. Spectra resulting from exposure to MC and phenol (Figure 11), developed sharp peaks at 1600 cm⁻¹, 1500 cm⁻¹, and a peak at 1225 cm⁻¹.



Figure 11: FTIR-ATR of clear MIL-PRF-53039 exposed to MC and phenol

The peaks at 1600 cm⁻¹ and 1500 cm⁻¹ resulted from carbon-carbon semicircle stretching in the benzene ring of the phenol. The peak at 1225 cm⁻¹ was from the carbon-oxygen-aromatic carbon asymmetric stretching.^{48,49} This peak indicated that the phenol acted as a nucleophile and covalently attached to the polymer backbone of the coating. The peak at 1225 cm⁻¹, while indicating that the phenol was covalently attached to the polymer, did not indicate where phenol attached on the polymer chain. In the MIL-PRF-53039 coating the polyurethane is an aliphatic single component polyurethane. The nucleophilic attack by phenol on this coating would most likely occur with the oxygen on the phenol attacking the carbon of the urethane functional group (Figure 12).



Figure 12: Theoretical coating degradation pathway from nucleophilic attack by phenol

In contrast to MIL-PRF-53039, in the MIL-PRF-85285 coating the polyurethane is bonded to a polyester. In this coating, the phenol could be covalently attached to the carbon of the urethane or the ester. The ester functional group is more vulnerable to nucleophilic attack than a urethane functional group.⁵⁰ This implied that for the MIL-PRF-85285 coating the degradation of the polymer occurred at the polyester. Understanding the primary role that MC and phenol play in the degradation of the polymers provided the necessary information to determine the action that the other solvents undertake in the degradation process.

4.5 MC, Ethanol and Phenol Exposure

Further analysis and observation was required to assist in the formation of conclusions about MC and phenol. Coatings exposed to the solution of MC, ethanol, and phenol demonstrated similar physical degradation in confocal and SEM imaging.

NEXAFS spectroscopy was conducted to determine the possible chemical changes along the surface of the coating. The spectrum obtained for the MC, ethanol and phenol exposure is presented in Figure 13.



Figure 13: NEXAFS C K-edge spectrum of methylene chloride/ethanol/phenol-exposed, fully-formulated MIL-PRF-85285.

The large increase in the ionization edge of the spectrum, from 1.85 a.u. to 2.25 a.u., hindered a direct comparison between the spectrum of MC, ethanol and phenolexposed, fully-formulated MIL-PRF-85285 and the spectra from other exposures. The difficulty arises from the inability to compare peak areas between this spectrum and previous samples because of differences in response factors. Despite this, information was still gained from the NEXAFS analysis. Peak D decreased dramatically in the spectrum to an extent that peak E became the dominant feature surrounding the ionization potential step. The maximum at 290.2 eV of peak D was not observed in previous spectra, while another maximum appeared slightly off center of the peak at 289.4 eV. In contrast, peak D in the unexposed and MC exposed samples exhibited a maximum at 289.5 eV. The shift of the peak maximum to 290.2 eV indicated the formation of a new chemical bond covalently attached to the carbonyl. The aforementioned nucleophilic attack by phenol would result in this shift. The other maximum at 289.4 eV in the spectrum indicated that some unaltered carbonyl was still present in the coating while the majority had been altered and shifted to 290.2 eV. The large decrease in the 289.4 eV peak and the presence of another apparent maximum illustrated that the carbonyl groups in the coating were significantly altered by exposure to MC, ethanol and phenol solution. This confirmed that phenol attacked the polymer backbone of the coating in the full formulation.

Solvent	Clear MIL-	Full Formulation	Clear MIL-	Full Formulation
Exposure	PRF-53039	MIL-PRF-53039	PRF-85285	MIL-PRF-85285
Control	87	60	51	0
MC/Phenol	-4	-2	-25	-53
MC/Ethanol	44	53	16	25
/Phenol				

Table 9: T_g (°C) of coatings exposed to MC/Phenol and MC/Ethanol/Phenol.

Analysis of the bulk properties of the coatings demonstrated that these effects were not observed throughout the bulk of the coating (Table 9). The different effects on T_g from exposure to the MC, ethanol and phenol solution were surprising since the addition of ethanol to the solution appeared to slow down the degradation of the coating. This result was unexpected since the previous investigation of MC and ethanol solution showed that ethanol had no significant effect on the coating. The ethanol in the solution may hydrogen bond with the phenol in the MC, ethanol and phenol solution. The hydrogen bonding would slow the rate of attack of phenol on the coating and may also inhibit the interaction between MC and phenol which subsequently reduces the intercalation of phenol into the coating. Overall, the T_g data revealed that degradation throughout the coating was inhibited in the exposure to the MC, ethanol and phenol solution.

Exposuro Timo	Roughness (µm) of MIL-	Roughness (µm) of MIL-		
Exposure Time	PRF-85285	PRF-53039		
20 min	1.93	2.15		
40 min	1.91	2.01		
60 min	1.55	1.55		

Table 10: Roughness of full formulation coatings exposed to solution of MC/Ethanol/Phenol.

Surface roughness analysis performed on the full formulation coatings, shown in Table 10, indicated that the surface of the coating was affected by the MC, ethanol, and phenol exposure, despite minor alterations of the glass transitions. The roughness of the coating primarily arose from the fillers and inorganic flattening agents, such as TiO₂, present in the coatings. The fillers were suspended in the polymer solution and upon drying, form nano-sized aggregates which the polymer surrounds. This caused the fillers to embed in the polymer and increased the surface roughness.⁵¹ Roughness, R_q, of the partial formulation of MIL-PRF-85285 was 0.07 µm and the roughness of the full

formulation of MIL-PRF-85285 was 2.11 µm. The large increase in roughness observed from the partial formulation to the full formulation of MIL-PRF-85285 demonstrated the drastic effect that the fillers have on the coating. The surface roughness of the coating decreased as it was degraded. The decrease in surface roughness resulted from the formation of pores and cracks, removal of fillers and pigments and the chemical attack on the polymeric backbone of the coating.^{8,52} Degradation of the polymer allowed the fillers to rearrange their orientation or be extracted from the coating by the solvent. Decreased roughness, seen in the full formulation coatings, indicated the polymer backbone was degraded and some fillers may be leaving the coatings. While the T_g data illustrated that the degradation did not occur throughout the bulk coating, the roughness analysis proved that the degradation did occur on the surface of the coating. Reduction in the amount of degradation resulting from exposure to a solution that was composed of more components was unexpected and further confirms that the role of ethanol in the paint remover was to improve solubility of other additives, instead of polymer degradation.

4.6 MC, Ethanol and Water Exposure

A solution of MC, ethanol and water was made to determine if the water in the paint remover also functioned as a nucleophile, similar to phenol. Methocel, which is the trade name for hydroxypropyl methylcellulose, was required to emulsify the MC, ethanol and water solution into a single phase. Methocel is used in commercially available paint removers for this purpose. Confocal and SEM images of all the coatings exposed to the MC, ethanol and water solution revealed irregular dark sections on the coating (Figure 14). Upon further analysis of these regions, it appeared that a film of unknown composition may have been covering the surface of the coating.



Figure 14: SEM images of MIL-PRF-53039 exposed to MC/Ethanol/Water/Methocel solution.

These dark irregular areas were investigated further using FTIR-ATR. The FTIR-ATR of the exposure of MIL-PRF-53039 coatings to MC, ethanol, water and methocel resulted in reduced peak signals at 1460 cm⁻¹ and 1680 cm⁻¹ and the development of a large peak at 1060 cm⁻¹ when compared to the unexposed control. The reduction of the carbonyl peak, 1680 cm⁻¹, could signify polymer degradation similar to how phenol attacked the polymers. The large peak at 1060 cm⁻¹ is typical of a C-O bond. The presence of the large C-O peak could result from degradation of the polymer or from deposition of a molecule. The reduction on the CH₃ peak (1460 cm⁻¹) would not likely result from degradation since the methyl group is not susceptible to nucleophilic attack. Therefore, it is likely that a film

was deposited onto the coating. Methocel is a cellulose based polymer, which contains multiple C-O bonds and contains no carbonyl functional groups. As such, the FTIR-ATR data implies that methocel could be deposited as a film on the coatings. FTIR-ATR using a germanium crystal only penetrates to a depth of approximately 0.65 μ m.⁵³ The penetration depth highlights that the obtained spectrum could be from both the deposited material and the coating. If methocel had deposited a layer less than 0.65 μ m, this would have resulted in a composite spectrum from the FTIR-ATR. In contrast, NEXAFS spectroscopy has an analytical depth penetration of approximately 10 nm. NEXAFS analysis resulted in a spectrum with no carbonyl, which was consistent with the spectrum of methocel.³⁴ This showed that the methocel deposited on the surface in a layer less than 0.65 μ m in thickness but more than 10 nm. The presence of methocel on the surface limited the utility of both FTIR-ATR and NEXAFS in the evaluation of surface changes.

Contact angle measurements and surface free energy calculations of the exposed coatings revealed any changes to the surface of the coatings due to exposure to the paint remover solutions. Surface free energy calculations indicate the amount of available energy at the surface of the coating. Water contact angle and surface free energy data for the coatings are presented in Figure 15.



Figure 15: Water contact angle (left) and surface free energy (right) of exposed MIL-PRF-85285.

The non-linear behavior of the surface free energy and contact angle data arose from polymer rearrangement upon exposure to remover solvent solutions. The surface free energy and the water contact angles of the coatings exposed to the solution containing methocel deviated significantly from the other solutions. The deviation can be seen in both surface free energy and water contact angle measurements, which highlighted the difference between the MC, ethanol, water and methocel exposure. Despite minor variations, the large differences in values between exposure conditions were consistent over the exposure time. Significant differences in surface energy cannot be attributed to differences in degradation since it was previously shown that the MC, ethanol and phenol solution caused polymer degradation and only a slightly increased the surface free energy. Therefore, it was concluded that methocel deposition was the reason for the large difference in the contact angle and surface free energy observed between the exposure conditions. The surface free energy of methocel is 45 dynes/cm.⁵⁴ This value compared

well to those obtained from coatings exposed to MC, ethanol, water and methocel for 20, 40 and 60 min, 47, 46 and 51 dynes/cm, respectively. The similarity in surface free energy values, C-O peak in FTIR-ATR spectra, and dark regions observed by SEM and confocal images all indicated that methocel was deposited as a thin film on the coatings. The shallow depth of the film reveals that the methocel was present only on the surface and did not penetrate the coating.



Figure 16: TGA curves of MIL-PRF-85285 exposed to MC (green), MC/EtOH (red) and MC/EtOH/H₂O (blue).

The T_g data for the coatings was in 0-26 °C range and the TGA curves (Figure 16) were very similar to those of neat MC and MC/ethanol exposure. This result indicated that exposure did not cause bulk degradation of the coatings and further highlighted the lack of

degradation for the MC, ethanol, water and methocel solution. Even though methocel hindered spectroscopic analysis of degradation, results of the bulk and surface techniques have shown that the water in the solution did not degrade the polymer. The presence of methocel deposition on the coatings was an unexpected result. The film formation on the coatings could have acted as a barrier to solvent evaporation in a way similar to paraffin wax that is normally added to the paint remover, which was omitted to simplify solvent solutions. Thus, further analysis was needed to determine if methocel acted as a barrier for solvent evaporation similar to paraffin wax.

4.7 MC, Ethanol, Phenol and Methocel Exposure

To further determine the role of methocel in the degradation of polymeric coatings, a new solution was prepared that contained MC, ethanol, phenol and methocel. This allowed for a thorough comparison of any effects caused by the presence of methocel. Figure 17 presents confocal images revealed the same dark irregular areas on the surface showing methocel deposition.



Figure 17: Confocal laser image of partial formulation of MIL-PRF-53039, left, and full formulation of MIL-PRF-85285 exposed to MC, ethanol, phenol and methocel, right.

The confirmation of methocel deposition from another solution provided further evidence that methocel always deposits on the surface, regardless of cosolvent composition. The effect of methocel on degradation was determined solely through bulk characterization since the deposited methocel imparted significant spectral interference for spectroscopic analysis. First, the glass transitions for the coatings were determined and are presented in Table 11.

MC/Euranoi/Pitenoi/Intenoi/Intenoie exposures.							
Partial Formulation	MIL-PRF-	Partial Formulation	MIL-PRF-				
MIL-PRF-53039	53039	MIL-PRF-85285	85285				
64	60	65	0				
40	53	31	20				
-10	55	51	2)				
32	36	53	25				
	Partial Formulation MIL-PRF-53039 64 40 32	Partial FormulationMIL-PRF- 53039MIL-PRF-5303953039646040533236	Partial FormulationMIL-PRF-Partial FormulationMIL-PRF-5303953039MIL-PRF-85285646065405331323653				

Table 11: T_g (°C) of coatings subjected to MC/Ethanol/Phenol and MC/Ethanol/Phenol/Methocel exposures.

For both the partial and full formulation of MIL-PRF-53039, exposure to the solution of MC, ethanol, phenol and methocel caused a decrease in the T_g compared to both the MC, ethanol and phenol solution and the unexposed control. The decrease in T_g indicated that a greater amount of degradation had taken place in the coating system. The increased degradation must have been an effect of the methocel since it was the only difference between the two solvent solutions. In contrast to MIL-PRF-53039, both the partial and full formulations of MIL-PRF-85285 exhibited increased T_g when comparing the MC, ethanol, phenol and methocel exposure to the MC, ethanol and phenol exposure. The minor difference in T_g of the full formulation between the two paint remover solutions may have resulted from the methocel affecting polymer rearrangement since changes in T_g for the partial formulation indicated that the methocel had reduced the extent of degradation.



Figure 18: TGA curves of MIL-PRF-53039 exposed to MC (green), MC/Ethanol/Phenol (red), and MC/Ethanol/ Phenol/Methocel (black).

TGA curve analysis was performed in order to deconvolute the differences observed between the exposures of MIL-PRF-53039 and MIL-PRF-85285. In the TGA analysis of MIL-PRF-53039 (Figure 18), results from exposure to MC as well as exposure to MC, ethanol and phenol were compared. The curve of MIL-PRF-53039 exposed to MC, ethanol, phenol and methocel exhibited a higher initial weight loss than from exposure to MC alone and MC, ethanol, and phenol. The higher initial weight loss indicated that the methocel had enhanced the degradation of the coating. The coating that was exposed to MC, ethanol, phenol and methocel exhibited an overall greater weight loss throughout the TGA run compared to those exposed to MC, ethanol and phenol exposure which also indicates increased degradation. Both the higher initial and overall weight loss revealed

that the polymer exposed to MC, ethanol, phenol and methocel was broken down into smaller segments that were more easily liberated from the coating system during heating. The increased degradation from the solution containing methocel indicated that the deposition of methocel along the surface enhanced the degradation of the polymer. TGA measurements performed on MIL-PRF-85285 revealed a different trend, which is presented in Figure 19.



Figure 19: TGA curves of MIL-PRF-85285 exposed to MC (green), MC/Ethanol/Phenol (red) and MC/Ethanol/Phenol/Methocel (black).

The coating that was exposed to MC, ethanol, phenol and methocel exhibited weight loss that began at the same temperature as the exposure without methocel, yet deviated to decreased weight loss at 120 °C. At 330 °C, the sample exposed to MC, ethanol, phenol and methocel began to lose weight more slowly than the sample exposed

to only MC. As such, at 430 °C the sample exposed to MC lost more weight than the sample exposed to MC, ethanol, phenol and methocel. The fact that the MC sample had a greater overall weight loss compared to the MC, ethanol, phenol and methocel sample indicated that methocel was impeding degradation of the coating. MC was shown earlier to not degrade the coating and only cause polymer rearrangement. The fact that the MC exposed sample exhibited a greater total weight loss may have resulted from the deposited methocel impeding the penetration of the solvents into the coating system. The opposite was observed with the MIL-PRF-53039 sample were in methocel may have trapped a significant amount of the solvent solution in the coating network after deposition. A simple experiment was developed to help determine if the solvent solution ingress or egress could be impeded by methocel deposition.

A wetting analysis was performed utilizing contact angle in an effort to find a quantitative or qualitative indication of the effect of methocel on degradation. Samples of both partial and full formulations of MIL-PRF-53093 and MIL-PRF-85285 were exposed to solutions of MC, ethanol and phenol using the contact angle instrument. Drops of the solution were placed on the coating in order to determine the initial contact angle and the total wetting time (Table 12). Complete wetting was defined as the amount of time that passed between placing the drop on the coating until it was no longer visible on the surface.

Unexposed Coatings	Contact Angle (°)	Time for total wetting (s)
MIL-53039	31.9	30
MIL-53039 partial formulation	0.0 ^a	~5
MIL-85285	21.0	18
MIL-85285 partial formulation	16.7	10

Table 12: Contact angle and wetting of MC, ethanol and phenol droplet on unexposed coatings.

a: value not measurable

The unexposed coatings all manifested very short wetting times with the longest, MIL-PRF-53039, being only 30 seconds. The short wetting times were expected since the paint remover was designed to penetrate and degrade the coating. The initial contact angle on MIL-PRF-53039 partial formulation was very low, to such an extent that the droplet spread to wet the surface within the initial measurement time resulting in a contact angle of 0°. The very low contact angles also correlated well with the time frames for complete wetting.

MC/EtOH/H20/PhOH/Methocel Exposed Coatings	Contact Angle (°)	Time for Complete Wetting (s)
MIL-53039	34.1	90
MIL-53039 partial formulation	38.6	125
MIL-85285	41.0	40
MIL-85285 partial formulation	40.7	100

Table 13: Contact angle and wetting of MC, ethanol and phenol droplet on coatings exposed to MC, ethanol, water, phenol and methocel.

In order to analyze the possible effects of methocel deposition, the contact angle and wetting time of coatings exposed to MC, ethanol, water, phenol and methocel were observed (Table 13). The contact angle increased slightly for all the exposed coatings compared to the unexposed coatings. Additionally, all the coatings showed a large increase in the total wetting time, with all times at least doubling. The large increase in wetting time signifies that the MC, ethanol and phenol solution did not penetrate the coatings quickly. The deposition of methocel on the surface of the coatings slowed the ingress of the solvent solution. The effect that causes inhibited ingress can also be viewed to inhibit solvent egress. This means that once the solvent solution is in the coating the deposited methocel film would impede the solutions egress. The ability of methocel to increase the retention of the solvent solution in the coating revealed why the confocal microscope, TGA and T_g data showed that degradation of MIL-PRF-53039 from exposure to MC, ethanol, phenol and methocel solutions degradation observed for MIL-PRF-85285 could have resulted if the methocel deposited faster than the solution penetrated the polymeric coating, thereby slowing degradation. Taking into account the increase in the T_g for the MIL-PRF-85285, which indicated reduced degradation, and the higher initial degradation observed in the TGA suggested that the MC, ethanol, phenol and methocel solution started to degrade the coating, but was then slowed. The role of methocel in solvent ingress/egress was unexpected considering that commercial paint removers contain alternate components like paraffin wax to reduce the solvent egress and methocel is used solely as an emulsifying agent.

4.8 MC, Ethanol, Phenol, Water and Methocel Exposure

A solvent solution containing MC, ethanol, water, phenol and methocel was made to represent the closest formulation to commercial paint remover. Samples exposed to this solution also had methocel deposited on the surface, presented in Figure 20. Clear evidence of degradation was present in the images of the coatings with holes, cracks and blisters along the surface.



Figure 20: SEM images of MIL-PRF-53039 exposed to MC, ethanol, water, phenol and methocel solution.

Upon increasing the magnification, some of the fillers were visible on the surface of the coating indicating that the polymer backbone had degraded significantly. The visible alterations of the coating provided powerful evidence of the solvent solution degrading the coating. The microscopy observations revealed a more sporadic methocel deposition therefore spectroscopic analysis was attempted. FTIR-ATR spectra of exposed samples were very similar to others obtained from exposures with methocel that exhibited a large C-O peak and reduced carbonyl and nitrogen peaks. The deposition of methocel was significant enough to have caused interference in the FTIR-ATR spectra, which required other methods of analysis.

Determination of the T_g for the coatings revealed that the visible alterations observed resulted from degradation. Large changes in the T_g were recorded for all the coatings, presented in Table 14, except clear MIL-PRF-85285, which had decomposed to

the point of no longer remaining as a film. The decomposition of this clear coating provided strong evidence for increased degradation by the MC, ethanol, water, phenol and methocel solvent solution.

Solvent Exposure	MIL-PRF-85285		MIL-PRF-53039			
	Clear	Partial	Full	Clear	Partial	Full
Control	51	65	0	87	64	60
MC/Ethanol /Phenol	22	31	29	44	40	53
MC/Ethanol/ Phenol/Methocel	16	53	25	33	32	36
MC/Ethanol/ Water/Phenol/ Methocel	DECOMP	-19	-38	-11	-25	-8

Table 14: T_g (°C) of Coatings Exposed to MC/Ethanol/Phenol, MC/Ethanol/Phenol and MC/Ethanol/Phenol/Methocel

The large decreases in T_g, the least of which was 38 °C, for exposures to MC, ethanol, water, phenol and methocel convincingly revealed that major degradation of the polymer had occurred. The difference between the glass transitions recorded in the MC, ethanol, water, phenol and methocel exposures and the MC, ethanol, phenol and methocel stemmed from the addition of water. While previous results indicated that water did not

degrade the coating directly, water was the only difference between the two solutions and hence must play an important role in the enhanced degradation observed.

TGA analysis was undertaken to confirm the trends previously observed in the glass transitions. The TGA curves for both MIL-PRF-85285 and MIL-PRF-53039 exposed to MC, ethanol, water, phenol and methocel showed higher overall degradation than other exposures, presented in Figures 21 and 22.



Figure 21: TGA curves of MIL-PRF-85285 exposed to solvent solutions.



Figure 22: TGA curves of MIL-PRF-53039 exposed to solvent solutions.

The large increase in initial degradation of the coatings implied that degradation occurred throughout the entire coating. In MIL-PRF-85285, the TGA curve for MC, ethanol and phenol almost matches the final weight percent of the MC, ethanol, phenol, water and methocel curve. While this indicated that similar degradation had taken place, the higher initial loss and increased loss throughout the TGA curve for MC, ethanol, water, phenol and methocel revealed otherwise. These observations along with the Tg data demonstrated that a greater degree of degradation occurred. In MIL-PRF-53039, the TGA curve for MC, ethanol, water, phenol and methocel solutions. The TGA curves correlated with the observed glass transitions for the solvent solutions. The microscopic physical evidence, decomposition of MIL-PRF-85285 clear coat and thermal analysis all confirm that MC, ethanol, water, phenol and methocel solution caused the most extensive amount of degradation for all

solvent solutions examined. Water was the only addition to solution and appeared to enhance the degradation of the coating, despite MC, ethanol and water samples resulting in no degradation.

Water acting as a base could remove the proton from the phenol. Removal of the proton would make the phenol a stronger nucleophile, thus increasing its ability to attack the polymer backbone of the coating. This would result in an increased degradation of the polymer backbone of the coatings and lead to the increased degradation of the coating. This transformation of the phenol is possible since the pK_a of phenol is 10 and the pK_a of water is 15.7.55 The respective pK_a values indicate that the phenol would lose its hydrogen, acting like a Brønsted acid, and water accept the hydrogen, acting as the Brønsted base. The solvent can play a major role in acid dissociation and the presented pKas are representative for aqueous solutions. MC was the main constituent of the solvent solution causing degradation. The difference in the dipole moment of MC and water affected the pK_a of water and phenol. Elimination of the solvent effect on acid dissociation can be achieved through determination of gas phase acidities. Gas phase acidities represent the amount of energy required to break the hydrogen bond in the molecule creating a proton and molecular ion. Both of these values have already been determined for water (383.74 kcal mol⁻¹) and phenol (340.8 kcal mol⁻¹).⁵⁶ The gas phase acidities of water and phenol revealed that independent of solvent effects phenol was more likely to lose a proton than water. The pK_a and gas phase acidities indicated that phenol likely underwent an acid-base reaction with water and, in the process, created the more nucleophilic phenolate.
5. CONCLUSION

The results and analysis have provided a clear picture of how all the solvents in MC and phenol mixtures caused degradation in polymeric materials. MC penetrated the coating and closely associated/solvated with the polymer backbone. This disrupted the intermolecular bonds in the polymer, thereby increasing the susceptibility of the polymer backbones to nucleophilic attack. NEXAFS showed that MC also solvated the coating additives, further exposing the polymer backbone of the coating to nucleophilic attack. The analysis also demonstrated that phenol was the main active agent of polymer degradation, giving rise to large decreases in the Tg and visible cracks and holes in the polymeric coatings. FTIR-ATR revealed that phenol, acting as a nucleophile, attacked the carbonyl of the polymer, resulting in cleavage of the polymeric backbone. The other components of the MC and phenol based mixture exhibited different effects on the mixture properties and degree of degradation. Analysis of solutions containing ethanol indicated that its role in these solvent solutions was to enhance the solubility of the other constituents. Methocel, added initially to facilitate solubility, was discovered to deposit as a film on the surface of the polymeric coatings. Utilizing contact angle and wetting analysis, it was shown that the methocel could significantly impede solvent escape from the coating. It was also determined that the addition of water to the control solution significantly increased both initial and overall degradation. The enhanced degradation resulted from water facilitated

proton abstraction from phenol, amplifying its nucleophilicity. The systematic analysis of solvent degradation on the polymeric coatings has successfully elucidated the mechanistic role of MC and phenol based mixtures.

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