Physicochemical investigation of chemical paint removers II: Role and mechanism of phenol in the removal of polyurethane coatings

Christopher N. Young*, Clive R. Clayton

Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794

James H. Wynne, James P. Yesinowski, Grant C. Daniels

Chemistry Division, U.S. Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375

Purpose: Commercial military paint stripper is effective because it contains phenol; in order to replace it, one must first understand the mechanism of action/interaction with the coating.

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*Christopher N. Young may be reached at: Christopher.young@alumni.stonybrook.edu

Abstract

Thermal and spectroscopic techniques have been used to study the interactions of phenol with model polyurethane coatings. Previous work has pointed to phenol as the principal source of polymer degradation in methylene chloride / phenol paint stripping mixtures. Thermal analysis demonstrates that the addition of phenol leads to severe depression in T_g and outright coating failure. Exposure appears to cause chain scission, leading to significant weight loss during thermal analysis. XPS confirms the deposition of methylcellulose stabilizer at the surface, but also indicates breaches in the conformal coating which we attribute to polyurethane degradation. Raman and ATR-FTIR spectroscopy confirm chemical modification of the polyurethane by phenol, leading to the proposed model of degradation by nucleophilic attack.

1. Introduction

The current formulation of chemical paint removers based on methylene chloride and phenol has proven extremely effective in the removal of polymeric coatings. These solvents also present significant challenges in modern use due to their adverse impacts on health and the environment. Recent regulations have elevated the urgency for less-hazardous paint removal techniques. While media blasting and laser ablation accomplish this objective, these methods are

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4 slow and require significant (expensive) retooling of current operations. Solvent-based methods
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6 currently rely on reformulation to replace methylene chloride and phenol with benzyl alcohol
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8 and anisole [1]. This mixture requires an order of magnitude more time to perform adequate
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10 paint removal (several hours vs. minutes). In order to determine optimal replacement solvents,
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12 one must first understand the mechanism of the target compound.
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17 These authors have previously discussed the changes caused by the presence of
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19 methylene chloride (MC) in model military top-coatings [2]. In short, it was found that
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21 methylene chloride appears to swell the polyurethane polymer, evidently by solvating the
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23 carbonyl groups responsible for cross-linkage. This solvation effect is demonstrated through
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25 observation of Raman broadening of the carbonyl stretching peak, through the reduced rotational
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27 mobility of methylene chloride within the swollen polymer by both ^1H and ^2H NMR (of the
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29 deuterated methylene chloride molecule), and by increased polymer segmental motion by ^1H
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31 NMR. However, while methylene chloride can be observed to swell the coating during
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33 exposure, there is only a minimal subsequent change in T_g after drying; drying and swelling
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35 relaxation appear to occur within minutes of the cessation of solvent exposure. When one
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37 considers the nature of the effects of methylene chloride in combination with ethanol and water,
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39 along with the previous assessment of the active ingredients of these paint removers (see
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41 Introduction section of [2]), it is logical to hypothesize that the addition of phenol is primarily
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43 responsible for significant irreversible degradation in the polymeric coating.
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52 Phenol is a relatively small alcohol that has demonstrated a strong ability to penetrate
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54 organic coatings and materials [3]. In addition to its penetrative characteristics, phenol offers
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56 numerous other advantages as a component of paint strippers. It is soluble in water, ethanol, and
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58 methylene chloride, and is capable of forming hydrogen bonds due to electron delocalization
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4 from the phenyl ring onto the oxygen atom. This delocalization also makes phenol a weak
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6 organic acid, which facilitates possible nucleophilic attack. Despite this acidity, no corrosive
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8 effects have been observed due to phenol, which leads to its suitability in aerospace applications.
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10 It has been speculated that phenol serves as a co-solvent to enhance the functionality of the
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12 primary solvent (here, methylene chloride) [4].
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17 Recent work by Croll has presented solvent-based paint removal from a mechanical
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19 disbondment perspective, with the Flory-Rehner equation and Griffith fracture criteria used to
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21 interpret removal from the perspective of the cohesive and adhesive properties of the polymer
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23 [5]. Others have described the role of substrate receptor group density on adhesion [6-8],
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25 lending a chemical underpinning to disbondment. While these findings offer an explanation for
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27 removal, they do not address the chemical processes which may occur within the coating during
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29 solvent exposure, thereby leading to apparent chemical degradation. Extensive studies have been
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31 undertaken concerning the degradation of military coatings by water [9], accelerated weathering
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33 [10-15], and physical aging [16]. While polyurethanes are commonly considered susceptible to
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35 phenol exposure, the specific mechanism of attack has not been elucidated.
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42 In this study, we discuss the effects of phenol in combination with other model
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44 formulation components on model military coatings, in order to elucidate the mechanism that
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46 allows phenol to cause irreversible damage to the coating. Model paint-removing systems, based
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48 upon those currently in service, have been constructed to permit analysis of solvent-polymer
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50 interactions with a minimum of interference. Differential Scanning Calorimetry (DSC) and
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52 Thermogravimetric Analysis (TGA) were used to monitor the change in polymer thermal
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54 properties. Vibrational spectroscopy techniques (specifically FTIR and Raman) were used to
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56 interrogate the chemical changes in the coating following solvent exposure.
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2. Materials and Methods

2.1. Chemicals and Coatings

All chemicals were reagent grade and used without further purification. Mixtures were prepared by weight percent according with Table 1.

Solution	Compound	Methylene Chloride	Ethanol	Water	Phenol	Methocel
	Commercial paint stripper ^a	60.6	5.8	7.8	15.8	1.2
D	MC, EtOH, H ₂ O, PhOH	67	6	9	18	1.2
E	EtOH, PhOH	0	27	0	73	0
F	MC, PhOH	79	0	0	21	0

Table 1: List of control formulations by weight percent.

^a Contains also, Toluene (1.3%), sodium petroleum sulfonate (5.5%) and paraffin wax (1.9%). Methocel is used to enhance solvent phase miscibility and to increase viscosity.

Current military coatings were selected for study, in the form of two polyurethane topcoats, based upon military specifications MIL-DTL-53039 (coating PU-1, an aliphatic isocyanate-based polyurethane with polyester extenders) and MIL-PRF-85285 (PU-2, a polyisocyanate-based polyurethane with polyether extenders); these coatings are designed to meet the referenced specifications, so their exact formulation may not be described in further detail. The coatings were unsupported free films, with a final thickness of approximately 5 mils (see Table 2). The simplification of the otherwise complex coating system was prepared to allow for ease of analysis. Coatings used in this study were clear films, without pigments, fillers and pigment related dispersion and wetting agents. Antifoaming agents were retained to facilitate sample preparation. Current formulations were used based on the same raw materials and binder ratios used in the commercial product. However, the solvent ratios were altered to compensate for the change in surface tension, viscosity and other properties resulting from the removal of the pigments and other components. Initial attempts at applications without this alteration of solvent

ratios using conventional spray equipment and settings failed due to the high viscosity of the formulations. A drawdown mechanism for creating coatings also failed as creating films of the approximate 4 mil thickness in one application trapped too many curing-generated gas bubbles in the coating. All formulas were ultimately sprayed in multiple layers on release paper allowing 16-24 hour cure time between each layer and a final seven day cure time. This minimized the presence of bubbles and created coatings of the desired thickness. The clear coatings were prepared on release paper and subsequently removed for evaluation.

Coating	Coating Type	Military Specification	Final thickness (mm)	Specific coating description
PU-1	Polyurethane	MIL-DTL-53039	0.13	single component aliphatic polyurethane CARC topcoat
PU-2	Polyurethane	MIL-PRF-85285	0.13	two component high solids polyurethane topcoat

Table 2: List and description of prepared coatings.

2.2. Sample Exposure

Approximately two centimeter squares of each free coating film were cut and placed into individual scintillation vials. To each vial the respective solvent or solvent mixture was added until the film was completely covered (~10 mL). After exposure, the liquid was decanted, the surface of the film rinsed with 5 mL EtOH to remove any impurities that may have been extracted and remained on the surface, and the film allowed to air dry in the open vial for >2weeks. Samples were visually observed to be dry prior to analysis. DSC, TGA, Raman, FTIR, and XPS experiments were performed on samples exposed for 2 h, with an additional set of samples exposed for 2 days analyzed by DSC.

2.3. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (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 Instruments Tzero aluminum pans, with an empty aluminum pan used as reference. Samples were analyzed twice from -90 °C to 150 °C at a heating rate of 20 °C/min. All data reported were taken from the second scan in order to minimize the effect of shape memory. Glass transition temperatures were determined using TA Universal Analysis program.

2.4. Thermogravimetric Analysis (TGA)

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

2.5. FTIR-ATR

FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a Smart Performer ATR attachment using a germanium crystal and constant pressure tower, and also with a Smart iTR attachment using a zinc selenide crystal and constant pressure tower. A DTGS detector collected 64 scans of the sample. Data acquisition and analysis was performed using the Thermo Scientific OMNIC software suite.

2.6. Raman

Raman analysis was carried out using a Nicolet Almega dispersive spectrometer coupled to an Olympus microscope with 10x and 100x objective lenses, and also using a WiTec α -500 confocal Raman microspectrometer with 20x and 100x objective lenses. The sample was scanned 128 times using a 1s collection time, with the spectra analyzed using the Thermo Scientific OMNIC software suite. Samples were placed on quartz slides to reduce background interference. In the case of the solvated coatings, samples were placed on a quartz slide with additional solvent, then covered with a second quartz slide to maintain sample geometry and diffuse solvent evaporation away from the objective. Additional solvated samples were analyzed by adhering the sample to the inner face of a quartz cuvette, which was then capped and placed horizontally for analysis. Efforts were made to minimize sample heating while performing analysis.

2.7. Entrapped Vapor and Supernatant GC-MS

Vapor above a free coating film (headspace) in an air tight vial was injected into the GCMS after the vial had been heated at approximately 80 °C for 30 minutes. The GCMS system was an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass selective detector operating in electron ionization mode and an Agilent 7693A autoinjector. The column utilized was an Agilent HP-5MS (5% phenyl) methylpolysiloxane film. The carrier gas was helium with a flow rate of 1 mL·min⁻¹. The injection volume was 10 μ L with a split injection ratio of 50:1. The temperature program has an initial temperature of 35 °C for one minute, then 10 °C per minute ramp to 90 °C with a three minute post run hold at 250 °C. The injection port temperature, MS quad temperature, and source temperature were 220 °C, 150 °C and 230 °C, respectively. The detector was set to scan a mass range from 20 to 500 m/z . For analysis of the

supernatant liquid after exposure of a free coating film, the initial oven temperature was 50 °C held for one minute, then ramped up to 300 °C at 15 °C per minute.

2.8. XPS

X-ray photoelectron spectra were obtained using a VG ESCA-3 Mk. II system under ultra-high vacuum (10^{-9} Torr $\equiv 10^{-7}$ Pa). X-rays were generated from a magnesium anode at 6 kV with a filament current of 20 mA. A pass energy of 20 eV was applied to emitted photoelectrons for analysis. Scans for each region were executed with a spacing of 0.1 eV and a 100ms dwell time; each scan was repeated 50 times and co-added, using the VGX900i control program. Spectra were calibrated using the adventitious carbon peak at 284.5 eV. Analysis was performed using the CasaXPS software package.

2.9 Microscopy

Optical micrographs were obtained using an Olympus OLS4000 3D Measuring Laser Confocal Microscope. Scanning electron micrographs were obtained using an FEI LEO SEM with backscatter detector.

3. Results and Discussion

3.1 Thermal properties

In Table 3, the changes in T_g due to exposure to the prepared phenol solvent mixtures are shown. Phenol produces significant, irreversible deterioration of the coating observed through multiple technique including SEM and confocal microscopy, as highlighted in Figure 1. Its addition leads to T_g depressions of well over 50 °C, which results in a soft, easily-torn film at room temperature. In the case of coating PU-2, the clear film became so swollen and soft that

removal of the film from solution was impossible. One would expect that solvent system D would lead to decomposition in the fully-formulated coating as well, or at least lead to the greatest T_g depression. We explain this based on the nature of the coating: fully-formulated PU-2 has a glass transition temperature of 0 °C, indicating that it is highly flexible in the presence of various standard fillers and pigments used in the coating system, such as celite and titanium dioxide. We speculate that the encapsulation of these fillers within the polyurethane matrix serves to provide some minimal flexible cohesion which is unaffected by phenol; further research into the critical concentration of fillers is required. The application of solvent system F to free-standing films of fully-formulated PU-1 leads to significant degradation and apparent failure by shear force. While plasticization is occurring due to the presence of phenol, these effects are too significant to be accounted for solely by this mechanism; a later section will discuss the spectroscopic evidence for polymer degradation.

Figure 1 - SEM (left) and optical (right) micrographs of clear PU-1 exposed to solvent system D, highlighting the significant apparent damage to the coating.

Solvent Exposure	PU-1 Polyurethane Topcoat		PU-2 Polyurethane Topcoat	
	Clear coating	Fully formulated coating	Clear coating	Fully formulated coating
Control	87	60	51	0
MC/EtOH/Water/PhOH* (D)	-11	-8	DECOMP	-38
EtOH/PhOH (E)	-9	-13	-25	-45
MC/PhOH (F)	-4	-2	-30	-54

Table 3 – T_g values in degrees Celsius for clear and fully-formulated polyurethane coatings exposed to phenol-containing solutions.

* - Solvent mixture stabilized with Methocel

3.2 Solvent persistence

The exposed coatings acquire a light purple tint (shown in Figure 2) as a result of exposure, indicative of the presence of impure solid phenol within the polymer matrix. Coatings also produce a strong odor of phenol after several months of drying, indicating solvent retention. Small samples of exposed films were heated in sealed vials, and the subsequent headspace gas was analyzed using GC-MS, where the presence of phenol was confirmed.

Figure 2 – Clear coating PU-1 (MIL-53039) after exposure to solvent system D for 2 h with subsequent drying, showing a purple tint indicative of impure solid phenol.

Thermogravimetric analysis (TGA) was performed on all exposed coatings, with an unexposed coating serving as control. Curves are presented in Figure 2, with phenol-containing solvent results overlaid against those from solvent blends without phenol. Following exposure to solvent mixtures containing phenol, each coating shows a significant loss of weight before

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4 reaching 125 °C. The boiling point of phenol is well above this point (181 °C), which suggests
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6 that phenol is causing significant chain scission within the sample, with subsequent outgassing of
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8 low-molecular weight degradation products. The mass loss at ~125 °C is believed to be
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10 ultimately caused by chain scission and not entrapped water/solvent. Sublimation of phenol may
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12 be affecting the TGA curves of the sample; however, the intercalation and incorporation of the
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14 phenol would lead to much slower rate of sublimation due to hindered migration through the
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16 polymer matrix as compared to that of pure solid phenol. A mass loss of 50-60% from the
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18 sample by 125 °C indicates, along with other data provided, that degradation of the free film has
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20 occurred. This was concluded after head space analysis yielded no signs of organic solvent, yet
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22 the limits of detection of GPC were not sufficient to detect substantial molecular weight extracts
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24 or oligomers believed to be evolving from the thermal process. The smaller mass loss at ~125
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26 °C for samples not exposed to phenol might be accounted for by migration of unreacted products
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28 or short-chain segments not cross-linked during curing.
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Figure 3 – TGA curves of coatings PU-1 (top) and PU-2 (bottom) exposed to solvent systems D, E, and F; as well as systems A, B, and C (100% MC, 91% MC / 9% EtOH, and 82% MC / 8% EtOH / 10% H₂O, respectively) from past work [2].

3.3 Spectroscopy of exposed polyurethanes – solvent system D

Polyurethane is observed to degrade significantly after exposure to phenol-containing solvent mixtures. In Figure 3, we present ATR-FTIR spectra of coating PU-1 exposed to mixture D, which causes the greatest T_g depression in this system. There is spectral evidence of a significant residue of hydroxypropyl methylcellulose on the surface of the material; as mentioned in the previous paper, this masks many changes which occur in the coating. The spectrum demonstrates significant attenuation of the signal (or peak, or absorption) from the

polyurethane binder, with the primary signatures coming from methylcellulose and phenol (most notably observed by the presence of C-O and C-O-C peaks between 1000 and 1250 cm^{-1} , and C=C at 1596 cm^{-1}). It is difficult to evaluate chemical changes in these samples with such a shallow depth of analysis.

Also in Figure 3, the complementary spectrum from Raman analysis is presented. Herein, we see the similar evolution of C-O-C due to methylcellulose, in addition to the numerous persistent peaks due to phenol (such as those at 1595 and 1000 cm^{-1} , indicating C=C aromatic and aromatic ring breathing, respectively). The peak at 1000 cm^{-1} is caused by aromatic ring breathing, and its growth is attributable to the presence of phenol. The overall difficulty in this analysis arises because the most likely chemical changes in the coating are generally masked by similar bonds in methylcellulose and phenol – these common peaks are indicated in the FTIR spectrum.

Figure 4 - (left) ATR-FTIR and (right) Raman spectra of clear coating PU-1 before and after exposure to solvent system D. In the FTIR spectrum, peaks which occur from phenol are labeled with **P**, and peaks which occur from methylcellulose are labeled with **M**.

XPS spectra of coatings exposed to solvent system D are dominated by the presence of methylcellulose at the surface, rendering a more detailed chemical investigation difficult. In Figure 5, we present a comparison of the XPS C1s spectrum between the neat coating, the coating after exposure to solvent system C (consisting of methylene chloride, ethanol, water, and methylcellulose, studied in our previous work [2]), and the coating after exposure to solvent system D. The spectral features after each exposure are quite similar, although the peak indicating C=O is slightly stronger after exposure in system D, possibly a result of degradation of the coating leading to breaches in the conformal film of methylcellulose.

Figure 5 – XPS C1s spectra of fully-formulated PU-1 unexposed (top left), exposed to solvent system C (top right), and exposed to solvent system D (below left).

3.4 Spectroscopy of exposed polyurethanes – solvent system F

In order to isolate the effects of phenol, coatings were exposed to a solvent system without methylcellulose; while this system is marginally less effective than solvent system D, the interactions of phenol are likely to be similar in nature. The ATR-FTIR spectra of system PU-2 before and after exposure to solvent system F are shown in Figure 5; the preponderance of phenol in the sample does skew the peak intensities of the polymer, rendering quantitative analysis difficult. Several changes in the spectrum are immediately obvious. Prior to exposure, the larger peak at 1684 cm^{-1} is attributed to hydrogen-bonded urethane carbonyl [17], and the shoulder at 1728 cm^{-1} indicates ester carbonyl from the polyester-polyol extender [14]. The peak at 1645 cm^{-1} indicates hydrogen-bonded urea [18] (resulting from the polyisocyanate form of the precursor, hexamethylene diisocyanate, which is in the form of a biuret (i.e. $-(\text{HN-CO-})_2\text{N-}$) for this application, and from the inevitable formation of urea as a result of isocyanate-water reactions) [19].

After exposure, the hydrogen-bonded urethane peak splits into two peaks at 1670 and 1687 cm^{-1} . Based on the splitting pattern, we propose that the peak at 1687 cm^{-1} corresponds to hydrogen-bonded urethane carbonyl as before (and thus shifted to a small degree due to steric effects of the presence of phenol), and that the peak at 1670 cm^{-1} corresponds to a urethane carbonyl vibration near a chain end, of the form $\text{NR}_2\text{-CO-O-Ar}$ (resembling phenyl carbamate). The carbonyl position for phenyl carbamate occurs slightly above 1700 cm^{-1} ; given the usual pattern of roughly $20\text{-}25\text{ cm}^{-1}$ shift depending on the degree of hydrogen bonding [20], it is reasonable to suggest this position as a possible location.

A new shoulder is formed at 1265 cm^{-1} ; it is recognized that aryl monosubstitution increases the wavenumber in asymmetric C-O-C stretching vibrations [21], thus further

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4 supporting the phenyl carbamate model. The amide II peak centered at 1540 cm^{-1} is significantly
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6 decreased, and reduces into two peaks at 1530 and 1555 cm^{-1} , which might plausibly be
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8 attributed to the hydrogen bonding in dilute solution [21]. The DSC data presented above
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10 supports this notion, as the strongly depressed T_g value indicated in Table 3 suggests some
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12 measure of polymer chain cleavage to so severely impact the material. GC-MS of the
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14 supernatant for films exposed to solvent system F revealed a shoulder peak on phenol indicative
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16 of carbamic acid, methyl-, phenyl ester. While small, the peak for carbamic acid supports the
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18 notion that this change occurs as a result of nucleophilic attack, as explained schematically in
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20 Figure 7, due to the weak acidity of the phenol molecule. The peaks which correspond to O-H
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22 stretching around $3370 - 3500\text{ cm}^{-1}$ do increase in intensity, but this increase is also influenced
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24 by the presence of unbound phenol, as noted through GC/MS headspace analysis discussed
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26 earlier. Generally, the presence of both residual phenol and existing esters masks many changes
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28 we would otherwise hope to detect in the coating, but the observation of urethane carbonyl peak
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30 splitting and the development of a new C-O-C shoulder both support this reaction mechanism.
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32 By eliminating the presence of methylcellulose, we confirm that these observed changes are
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34 caused by a chemical reaction, rather than cellulosic deposition at the surface as seen with
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36 stabilized solvent blends.
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Figure 6 - (left) ATR-FTIR spectra of PU-2 before and after exposure to solvent system F; (right) a magnified view of the fingerprint region of these spectra.

Figure 7 – Proposed nucleophilic attack of phenol on polyurethane.

A comparable effect is observable in coating PU-1, presented in Figure 7. The carbonyl peak at 1683 cm^{-1} is split into two peaks at 1687 and 1670 cm^{-1} , suggesting the same mechanism seen in PU-2. It is more straightforward to resolve the shoulder at 1265 cm^{-1} in this sample, as it is not crowded by the presence of other C-O-C polyester peaks due to the extender polymer chosen (here, usually polyethylene or a derivative), although the presence of phenol does still generate several peaks nearby. From the thermal data, we know that the degradative performance of phenol is enhanced by the addition of a small amount of water. This seems likely to be due to the enhanced acidity of phenol in the presence of water. The Raman spectrum

of this exposure (Figure 8) is dominated by the presence of phenol, and since it is not as sensitive as FTIR to the changes observed in this degradation, it does not shed any additional light on the situation.

Figure 8 - (left) ATR-FTIR spectra of PU-1 before and after exposure to solvent system F for 2h; (right) a magnified view of the fingerprint region of these spectra

Figure 9 – Raman spectra of clear PU-1 before and after exposure to solvent system F.

4. Conclusions

The addition of phenol to a model paint stripping solution results in significant, irreversible depression of T_g in exposed military coating systems. Phenol is retained in the sample for months after exposure, and can be detected by GC-MS analysis and a simple odor test. There is significant mass loss from the exposed coating at a much lower elevated temperature than can simply be accounted for by phenol evacuation, suggesting that a chemical reaction by phenol is resulting in chain scission and subsequent removal of the shortened chains. ATR-FTIR spectroscopy highlights a change in the degree and type of carbonyl/amine hydrogen bonding of the coating, as well as the development of a new aromatic ether peak, which allows

us to suggest a model for degradation based on nucleophilic attack of the urethane linkage by the weakly-acidic phenol molecule.

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