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

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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 slow and require significant (expensive) retooling of current operations. Solvent-based methods currently rely on reformulation to replace methylene chloride and phenol with benzyl alcohol and anisole [1]. This mixture requires an order of magnitude more time to perform adequate paint removal (several hours vs. minutes). In order to determine optimal replacement solvents, one must first understand the mechanism of the target compound.

These authors have previously discussed the changes caused by the presence of methylene chloride (MC) in model military top-coatings [2]. In short, it was found that methylene chloride appears to swell the polyurethane polymer, evidently by solvating the carbonyl groups responsible for cross-linkage. This solvation effect is demonstrated through observation of Raman broadening of the carbonyl stretching peak, through the reduced rotational mobility of methylene chloride within the swollen polymer by both ^{1}H and ^{2}H NMR (of the deuterated methylene chloride molecule), and by increased polymer segmental motion by ^{1}H NMR. However, while methylene chloride can be observed to swell the coating during exposure, there is only a minimal subsequent change in T_g after drying; drying and swelling relaxation appear to occur within minutes of the cessation of solvent exposure. When one considers the nature of the effects of methylene chloride in combination with ethanol and water, along with the previous assessment of the active ingredients of these paint removers (see Introduction section of [2]), it is logical to hypothesize that the addition of phenol is primarily responsible for significant irreversible degradation in the polymeric coating.

Phenol is a relatively small alcohol that has demonstrated a strong ability to penetrate organic coatings and materials [3]. In addition to its penetrative characteristics, phenol offers numerous other advantages as a component of paint strippers. It is soluble in water, ethanol, and methylene chloride, and is capable of forming hydrogen bonds due to electron delocalization from the phenyl ring onto the oxygen atom. This delocalization also makes phenol a weak organic acid, which facilitates possible nucleophilic attack. Despite this acidity, no corrosive effects have been observed due to phenol, which leads to its suitability in aerospace applications. It has been speculated that phenol serves as a co-solvent to enhance

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the functionality of the primary solvent (here, methylene chloride) [4].

Recent work by Croll has presented solvent-based paint removal from a mechanical disbondment perspective, with the Flory–Rehner equation and Griffith fracture criteria used to interpret removal from the perspective of the cohesive and adhesive properties of the polymer [5]. Others have described the role of substrate receptor group density on adhesion [6–8], lending a chemical underpinning to disbondment. While these findings offer an explanation for removal, they do not address the chemical processes which may occur within the coating during solvent exposure, thereby leading to apparent chemical degradation. Extensive studies have been undertaken concerning the degradation of military coatings by water [9], accelerated weathering [10–15], and physical aging [16]. While polyurethanes are commonly considered susceptible to phenol exposure, the specific mechanism of attack has not been elucidated.

In this study, we discuss the effects of phenol in combination with other model formulation components on model military coatings, in order to elucidate the mechanism that allows phenol to cause irreversible damage to the coating. Model paint-removing systems, based upon those currently in service, have been constructed to permit analysis of solvent–polymer interactions with a minimum of interference. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to monitor the change in polymer thermal properties. Vibrational spectroscopy techniques (specifically FTIR and Raman) were used to interrogate the chemical changes in the coating following solvent exposure.

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.

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 h cure time between each layer and a final 7-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.

2.2. Sample exposure

Approximately 2 cm^2 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^{-1}. 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^{-1}. 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^{-1}. 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 were performed using the Thermo Scientific OMNIC software suite.

Table 1
List of control formulations by weight percent.

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_2O, PhOH	67	6	9	18	1.2
E	EtOH, PhOH	0	27	0	73	0
F	MC, PhOH	79	0	0	21	0

[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.