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Physicochemical investigation of chemical paint removers: Interactions of methylene chloride with polyurethane coatings

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ABSTRACT

A variety of thermal and spectroscopic techniques have been used to investigate interactions of the widely-used paint-stripping solvent methylene chloride upon model polyurethane coatings. Thermal analysis reveals that methylene chloride penetrates and swells the polymer film and leads to a slight depression in the glass transition temperature (T_g) after drying. The ^{1}H NMR spectra and T_1 and $T_{1\rho}$ relaxation times show that methylene chloride is responsible for increased polymer segmental motion in the polymer due to swelling, and indicate intimate contact between the methylene chloride molecules and the polymer, with no liquid-like pools of the solvent observed. The quadrupolar-echo ^{2}H NMR spectra of CD_2Cl_2 in the polyurethane over a temperature range of 24 °C to −27 °C reveal a lengthening of the rotational correlation times of the methylene chloride by over four orders of magnitude compared to the neat liquid, indicating restricted mobility due to an interaction with the polymer. Although this interaction is likely due to the electric dipoles in the solvent and the polymer backbone, the absence of significant residual nuclear quadrupole couplings due to a high degree of ordering or solvent immobilization shows that the interaction strength is weak compared to thermal energy (kT). Raman spectroscopy indicates that methylene chloride causes swelling by interacting with the carbonyl group responsible for inter-chain bonding, thus permitting dilation. FTIR and Raman spectroscopy demonstrated that methylene chloride leads to no irreversible chemical changes in the coating. A common cellulosic chemical stabilizer used in commercial paint removers has been found by XPS to deposit as a thin conformal but heterogeneous coating on the surface of the polymer, suggesting a possible important function to retard evaporation while allowing some permeation.

Purpose: Commercial military paint stripper is effective because it contains methylene chloride; in order to replace it, understanding its mechanism of action/interaction with the coating is crucial.

1. Introduction

Chemical paint strippers based on methylene chloride and phenol are widely used to remove polymeric coatings. These strippers are highly effective, inexpensive and have minimal impact on the substrate. However, environmental and health concerns have dictated a need to find suitable replacements. This is a significant issue in the restoration of historic artwork and furniture, where careful design of solvent systems through the use of Hansen solubility parameters is employed in removing coatings while protecting the delicate substrate [1]. Unfortunately, efforts to replace solvent based paint removers in military applications have only produced less effective alternatives [2]. Methods such as solid particle blasting and laser ablation [3] 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. Efforts to replace methylene chloride and phenol by other components in solvent-based paint strippers have been largely unsuccessful. The subsequent solvent systems are often less effective, as is seen with alkali or acid based mixtures [4].

There are few published studies in the scientific literature on the mechanism or mechanisms by which methylene chloride and other components of paint strippers work to remove polymeric coatings. The conclusion has been that solvent-based paint removing formulations wet the paint surface and then penetrate the layers to the underlying substrate by diffusion through the coating [5,6]. Small

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molar volume solvents, e.g. water and methylene chloride, are presumed to penetrate the coating by more easily fitting into spaces between the polymer chains and diffusing through these spaces and channels. A recent paper by Croll [7] discusses the current state of knowledge and considers the effect that swelling by solvents has on "the cohesive and adhesive properties of a crosslinked polymer network." In this work, the Flory–Rehner and the Griffith equations are used to estimate the reduction in strength and resistance to fracture caused by swelling. The swelling effects of vapor-phase methylene chloride in polyurethanes was noted by Volkov et al. [8] using FTIR, where an increase in the amount of free (relative to hydrogen-bonded) carbonyl groups was observed, suggesting that this swelling can occur by interfering with inter-chain hydrogen bonding.

The solvent penetration into cross-linked polymeric networks that is a key aspect of the paint-stripping process is related to an area that has received some attention, the permeation of small molecules, usually gaseous, through polymer membranes. In particular, the ability of a small molecule to enter a polymer matrix presupposes the existence of some "unoccupied volume" (the term "free volume" is also used, although its definition may vary), i.e. cavities consisting of open space outside the van der Waals radii of the atoms of the polymer [9–12]. Theoretical simulations of polymer chains having a given packing density have yielded histograms of the percentage of free volume vs. the volume of the maximum-size sphere fitting in the cavity. As an example of such results, for polypropylene 20° below its T_g of $-20\,^{\circ}$C the largest cavity volume thus calculated is ca. 27 Å^3 (corresponding to a diameter of 3.7 Å), although a more representative volume of 9 Å^3 (corresponding diameter 2.6 Å) represents the approximate median point in terms of free volume fraction available [12]. These dimensions can be compared to those of the methylene chloride molecule, which closely approximates a prolate ellipsoid in shape [13]. The effective radius along the Cl–Cl vector direction is 3.3 Å, and thus two axes in the molecule present a long dimension of twice this radius, or 6.6 Å. A comparison of this dimension with those calculated from the free volumes [12,14] demonstrates that even though methylene chloride may be a "small" molecule, it is too large to fit into the existing free volume cavities (of this polymer at least), and thus must exert its effect by a dynamic process of swelling the polymer to create more space for solvent molecules. However, the connectedness of such cavities through "throats" or "necks" to form a percolation pathway is also crucially important, and it is likely that polymer dynamics also plays a role by modulating the size of such openings to transiently allow a small molecule to penetrate. Once this process has begun, at least in the case of liquid solvents, one expects a continuing expansion of the polymer by the swelling that facilitates further penetration by the solvent molecules. The ability of molecules to penetrate into a polymer can be predicted by comparing their Hansen solubility parameters, where solvents and polymers with similar values are more likely to be compatible. Given the relatively complex interactions that may occur between the polar methylene chloride molecule and polyurethane, these Hansen values must be used over the simpler Hildebrand solubility parameters [15]. As one might expect given its effectiveness, the Hansen solubility parameters of methylene chloride (δ_d: 18.2 MPa$^{0.5}$, δ_p: 6.3 MPa$^{0.5}$, δ_h: 6.1 MPa$^{0.5}$) [16] are very similar to those of polyurethane (δ_d: 18.0 MPa$^{0.5}$, δ_p: 6.3 MPa$^{0.5}$, δ_h: 6.3 MPa$^{0.5}$) [17].

This paper begins to fill the knowledge gap regarding the molecular-level interactions important to the action of paint strippers by using a combination of techniques to characterize the interaction of methylene chloride with model polyurethane topcoats. Model paint-removing systems, based upon those formulations currently in use, are constructed to permit analysis of solvent–polymer interactions with a minimum of interference. One of the crucial changes taking place during this solvent-induced swelling process is the transition from a glassy polymer (i.e. one below its glass transition temperature T_g) to an elastomer (or rubbery state) above T_g, with small irreversible changes to T_g occurring. Differential Scanning Calorimetry (DSC) was used to monitor this change, and solid-state proton (^{1}H) Nuclear Magnetic Resonance (NMR) spectroscopy to follow the increase in the polymer segmental dynamics associated with the transition to an elastomeric state. Vibrational spectroscopy (specifically FTIR and Raman) was used to survey for chemical changes in the polymer resulting from the solvent swelling. Solid-state deuterium (^{2}H) NMR of isotopically-labeled methylene chloride (CD_2Cl_2) was used to specifically observe this component and to obtain information about its physical state in the topcoat polymer network. Finally, XPS identified heterogeneous coating characteristics of a commonly-used cellulosic stabilizer that may serve an important function.

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 to 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) and MIL-PRF-85285 (coating PU-2). The coatings were unsupported free films, with a final thickness of approximately 127 μm (5 mils) (see Table 2). 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 application 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 102 μm (4 mils) thickness in one application trapped too many bubbles in the coating as it cured. All formulas were ultimately sprayed in multiple layers on release paper allowing 16–24 h cure time between each layer and a final seven day cure time. This minimized bubble formation and created coatings of the desired thickness. The clear coatings were prepared on release paper and subsequently removed for evaluation.

2.2. Solvent exposure of coatings for thermal and spectroscopic analysis

Approximately two centimeter squares of each coating were cut and placed into individual scintillation vials. To each vial the respective solvent or solvent mixture was added until the coating was completely covered (~10 mL). After exposure, the liquid was decanted, the surface of the coating rinsed with 5 mL EtOH to remove any impurities that may have been extracted and remained on the surface, and the coating allowed to air dry in the vial for >2 weeks. Samples were visually observed to be dry prior to analysis. Non-NMR experiments were performed on samples exposed for 2 h, with an additional set of samples exposed for 2 days analyzed by DSC. For the vibrational spectroscopic study of swollen coatings, square samples were exposed to solution for several hours to ensure maximum solvent ingress, then removed and analyzed immediately without drying.