Extended Abstract—The Use of Ionic Liquids for Varnish Removal: Effectiveness and Risk Evaluation

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INTRODUCTION

The development of less harmful cleaning methods, both for health and the environment, is one of the major concerns for conservators and restorers (McCann, 1992). Therefore, the possibility of replacing volatile and toxic organic solvents by ionic liquids (ILs) could contribute to safer procedures. Ionic liquids can be defined as organic salts with melting points below 100°C, constituted by an organic cation and an inorganic or organic anion. Some of the properties of ILs (Branco et al., 2002; Rogers and Seddon, 2002; Wilkes, 2002; Poole, 2004; Dupont, 2005) can be useful for the conservation of paintings. For example, their low volatility reduces the risks to health and the environment, their high viscosity may inhibit the penetration into the pictorial layers, and their adjustable miscibility with water or less toxic solvents (e.g., alcohols) allows their removal with safer solvents. This study evaluated the effects and consequences of possible cleaning operations with ILs. The effectiveness and risk evaluation was carried out through the application of different types of ILs in mock-ups prepared with various painting materials and varnishes.

MATERIALS AND METHODS

The samples aimed to mimic real cases in oil paintings. To assess the role of the colorants, the colors used in the test systems were selected on the basis of the predicted pigment effect on oil drying and aging. For example, lead white acts as a drier and promotes the reticulation of the polymer, which makes the paint less vulnerable to solvents, whereas red lake and Vandyke brown are slower driers (Carlyle, 2001) that inhibit drying of the oil and make the paint layer more sensitive to the effect of the cleaning products. Three different varnishes were applied over three sections of a 17-year-old oil paint sample, half with lead white and half with Vandyke brown. The three varnishes were a natural resin (dammar) and two synthetic varnishes, polyvinyl acetate (PVAc) and cyclohexanone resin (Retouching Varnish, Talens).

To reproduce the materials and techniques found in modern and contemporary art, a painting mock-up was prepared with an acrylic medium, poly(*n*-butyl acrylate-methyl

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methacrylate) (Rembrandt Acrylic Colours, Talens), and coated with an acrylic varnish, poly(isobutyl methacrylate) (Acrylic Varnish Matt, Talens). The varnish was applied 1 month after the application of the acrylic paint and left to dry for approximately 1 month before cleaning tests were carried out.

The ILs were chosen according to the polarity of the liquid itself and the nature of the paint layers and varnishes to be removed. A total of 13 commercial ILs were tested (Aldrich, Solchemar). The cleaning tests were performed under a stereomicroscope (Olympus SZx12) in three steps: (1) application of the IL to the surface, (2) after 10 minutes, removal with a dry swab, and (3) rinsing with a water-wetted swab.

Images of the surface were obtained with an optical microscope (Axioplan 2) that provides information about varnish removal effectiveness. This method was also used to examine paint cross sections. The results were assessed by Fourier transform infrared microspectroscopy (FTIR; Nexus and Continuum-Nicolet) in the transmitted and attenuated total reflection (ATR) modes. These analytical methods allowed verification of complete varnish removal and detection of eventual IL residues left on the surface.

RESULTS AND CONCLUSIONS

The following ILs did not prove to be effective: [C_2OHmim][BF_4], [C_5O_2mim][Cl], [emim][$EtSO_4$], [emim][$MOEOEtSO_4$], [$P_{6,6,6,14}$][Cl], and [choline][Ac]. None of these ionic liquids were efficient in the removal of the Acrylic Varnish Matt, and therefore, the mimicked modern paints were not examined further in this study. The ILs that proved to be effective in the cleaning tests are listed in Table 1, where the results obtained are also summarized.

In Figure 1 the removal of PVAc varnish with [bmim][BF_4] as characterized by optical microscopy and FTIR-ATR is shown. In this particular case, the IL was removed with a swab embedded in water, but in the cases of the Aliquat ILs, water and

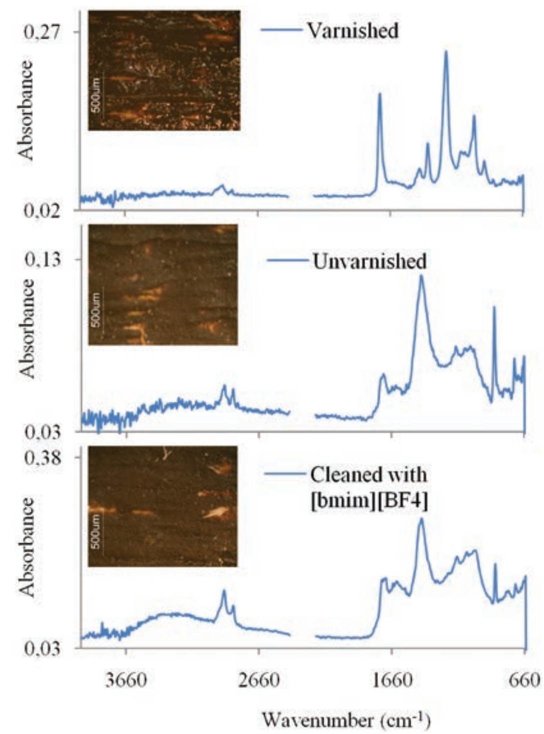
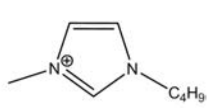
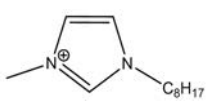
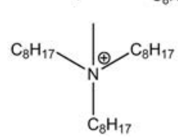


FIGURE 1. Optical microscope images and FTIR-ATR spectra during the removal of the PVAc varnish from oil paint with [bmim][BF_4].

TABLE 1. Results of effective varnish removal from over oil paint with several ionic liquids. M = more effective removal; L = less effective removal.

Ionic liquids	Cation	Anion	Dammar	Retouching varnish	PVAc Varnish
[bmim][DCA]		NC—N$^{\ominus}$—CN	M	M	M
[bmim][BF_4]		$BF_4^{\ominus}$			M
[bmim][TfO]		$CF_3SO_3^{\ominus}$			L
[bmim][TFA]		$CF_3COO^{\ominus}$			L
[omim][Cl]		$Cl^{\ominus}$	M	M	
[Aliquat®][DCA]		NC—N$^{\ominus}$—CN	L	M	
[Aliquat®][Cl]		$Cl^{\ominus}$		M	

ethanol mixtures were required because of the low solubility of these ILs in water.

One important issue to consider is the presence of IL residues left by the cleaning procedure. The FTIR-ATR was useful for detecting ILs with specific signals, such as those containing dicyanamide (DCA) (CN stretching at 2160 cm^{-1}; Hummel, 2002). For example, when cleaning the dammar varnish with [bmim][DCA], IR signals of DCA could be detected in some points. Other techniques such as spectrofluorimetry are being exploited to further reveal the presence of residues.

The results presented suggest the potential of ILs as cleaning agents for varnish removal in paintings. For each varnish it was possible to identify at least one IL that efficiently removed it.

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