AN INVESTIGATION INTO THE USE OF IONIC LIQUIDS FOR THE REMOVAL OF SURFACE COATINGS:

Improving the Cleaning Efficacy of Low-toxicity Molecular Solvents with 1-Ethyl-3-methylimidazolium Ethyl Sulfate.

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Queen's University

MOTIVATION : REDUCING TOXICITY OF SOLVENTS FOR COATING REMOVAL

- Organic/Molecular Solvents
- Inhalation, Skin Absorption
- DMF, MEK
    - Irritants and Nerve Toxins
- How can we find less harmful alternatives for strong solvents?

PA 449

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MOTIVATION : REDUCING TOXICITY OF SOLVENTS FOR COATING REMOVAL

- Organic solvents are ubiquitous to the practice of paintings conservation.
- The volatility of organic solvents, and their ability to permeate skin and other membranes of the body create several possible exposure routes for these chemicals.
- These solvents are often irritants (skin, eyes, membranes, airways, etc.), nerve toxins, and carcinogens. Additionally, they are often eco-toxic and carry significant flammability risks.
- Especially strong solvents like methylene chloride, dimethyl formamide, and methyl ethyl ketone are particularly harmful to our health and the environment, so how can we strive to remove them from our work practice?

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- **Reduce Exposure by Method**
  - Respirators + Ventilation
  - Gels
  - Compresses
- **Substitution: Other active agents**
  - Resin Soaps
  - Enzymes
- **Substitution: Organic for Less Hazardous Organic**
  - Ex. Xylene, Acetone, and MEK
  - Vs. Toluene, Cellosolve, and Methylene Chloride

REDUCING SOLVENT EXPOSURE

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REDUCING SOLVENT EXPOSURE

- **Reduce Exposure by Method**
  - We can over come the mobility of the solvent (and thus mitigate exposure routes) using:
    - barriers against absorption into the body (respirators and gloves)
    - ventilation to draw away volatized solvent
    - or prevent evaporation by keeping the solvent in a physical matrix (gels and compresses)
- **Substitution: use alternative, water-borne, active agents that are innocuous to the practitioner**
  - For example, resin soaps and enzymes are non-volatile, and typically much less hazardous to work with than organic solvents
- **Substitution: less harmful organic solvents**
  - For example, in place of aromatics like toluene, use xylenes. For polar organics like Cellosolve and/or Methylene Chloride use acetone and/or MEK.

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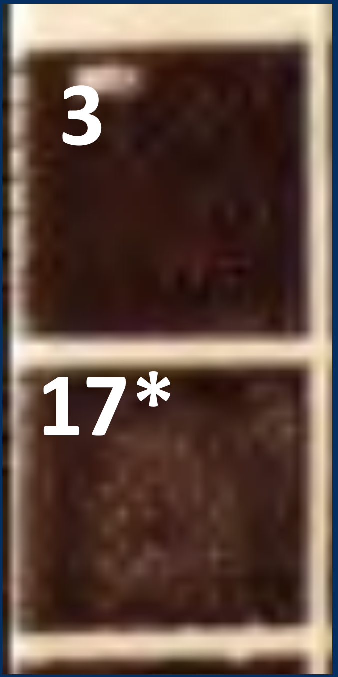
Varnish Sample Boards



Successful Removal Of natural resin varnishes – but upwards of 15 min+ dropwise cleaning

Historical Painting

Table 1 Results of varnish removal with several ILs[a]

Ionic liquids	Dammar	Retouching varnish	PVAc varnish
[bmim][DCA]	+	+	+
[bmim][BF_4]	−	−	+
[bmim][TfO]	−	−	±
[bmim][TFA]	±	−	±
[omim][Cl]	+	+	−
[Aliquat][DCA]	±	±	−
[Aliquat][Cl]	±	±	−

← $87.6/g

vs. Gold $42/g

← Inexpensive but toxic and corrosive

VARNISH REMOVAL FROM PAINTINGS USING IONIC LIQUIDS

PACHECO, PEREIRA, BRANCO AND PAROLA, 2013.

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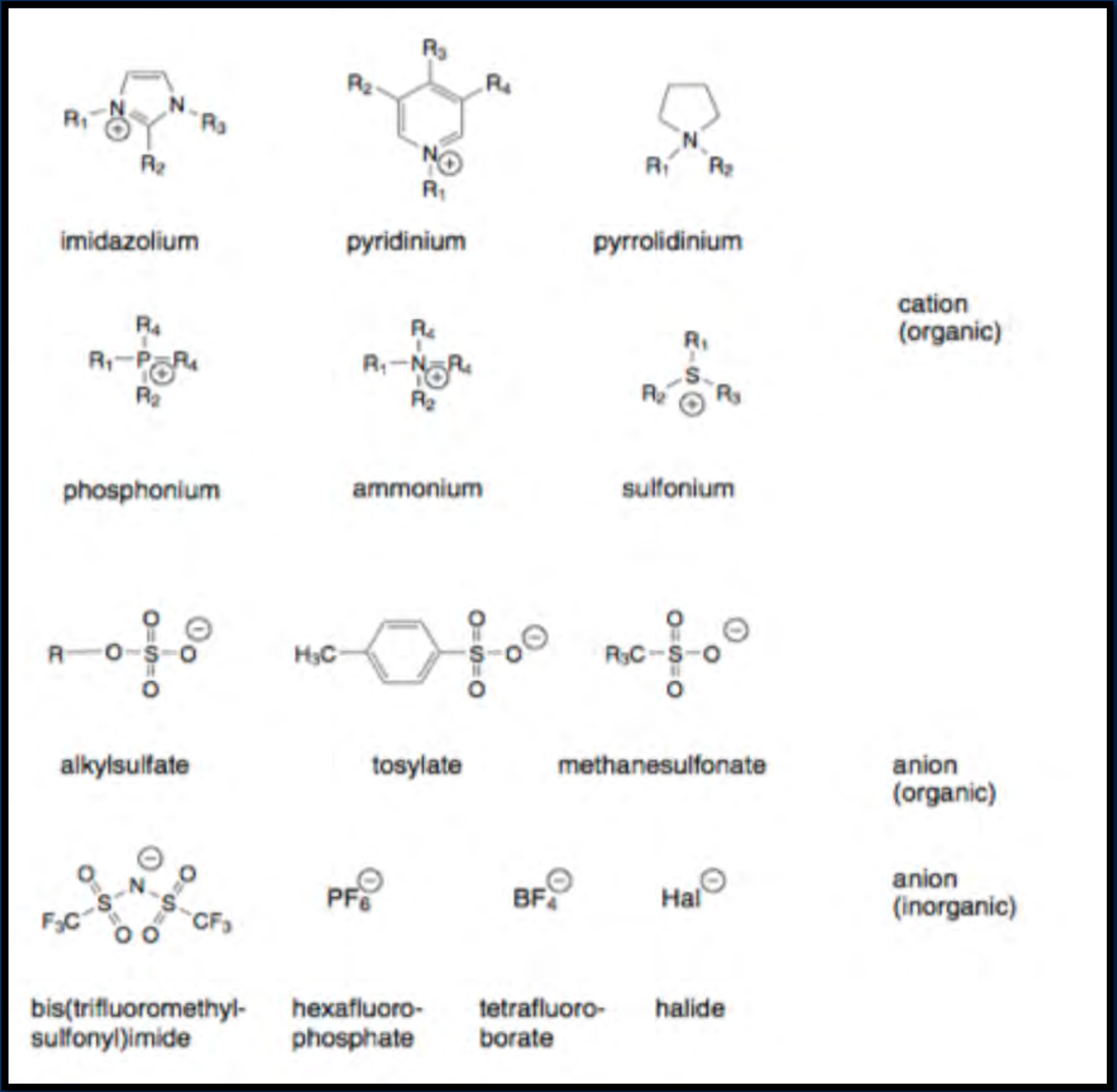
VARNISH REMOVAL FROM PAINTINGS USING IONIC LIQUIDS

- Seminal research by Pacheco, Pereira, Branco and Parola (2013) introduced a novel class of fluids called ionic liquids to the conservation field.
- These fluids were able to remove natural resin varnishes from painted surfaces (both historical paintings, and constructed test surfaces).
- Marked drawbacks to the materials and cleaning methodology were noted.
  - Cleaning was undertaken dropwise, and could take upwards of 15 minutes, with several reapplications necessary to clean a very small area.
  - Successful fluids were often incredibly costly, not readily available, and/or corrosive and toxic.
- What made these novel chemicals of interest to paintings conservation?



"Enabling Technologies: Ionic Liquids," 2002.

Working Advantages:

- Non-volatile
- Non-flammable
- Some are non-toxic
- Noted solvents of organic and polymeric materials

Disadvantages:

- Cost
- Can be eco-toxic, non-biodegradable

INTRODUCTION TO IONIC LIQUIDS

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INTRODUCTION TO IONIC LIQUIDS

Pacheco et. al. (2013) had employed ionic liquids following several academic and industrial STEM fields that had pioneered its research and use as an alternative to organic solvents. When compared to traditional organic solvents, ionic liquids held several advantages for the practitioner. Ionic liquids are:

- Non-volatile (exposure is limited to just physical contact)
- Non-flammable

And can be selected for further desirable properties:

- Non-toxic, and even non-irritating
- Noted solvents of organic and polymeric materials

Disadvantages are currently cost, due to the complicated synthesis of these entirely man made compounds. They may also be eco-toxic, and non-biodegradable, with limited study of their afterlife. Additionally, their intensive synthesis generates significant waste products that likely make these chemicals currently less ‘green’ and ‘eco-friendly’ than consciously selected traditional organic solvents.

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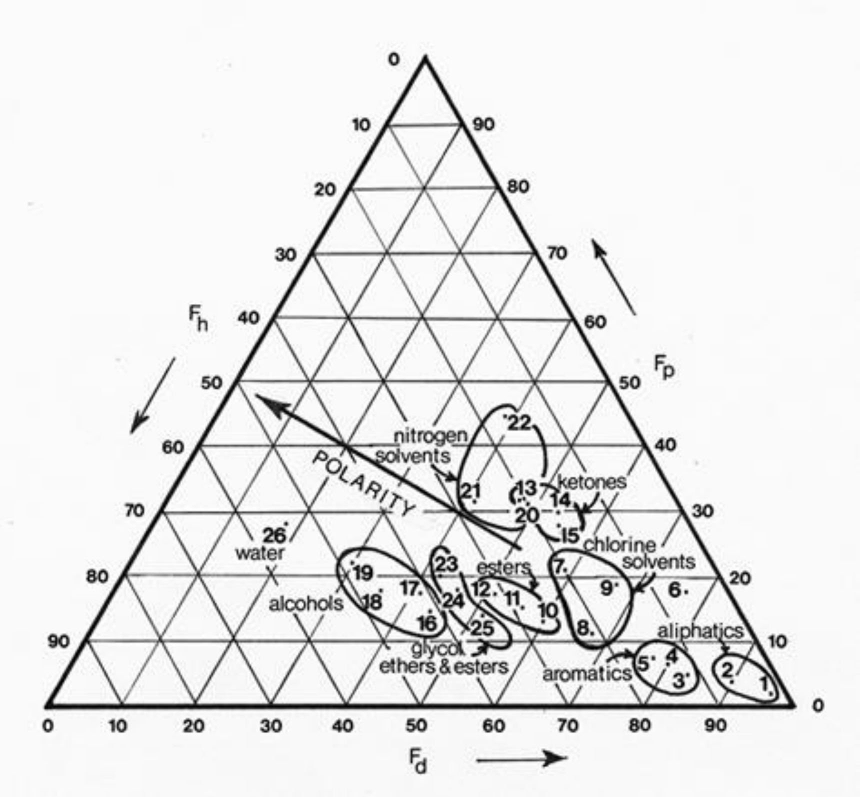
- In order to improve our use of ionic liquids we have to understand **why they work or don't work**
- **Solubility is an incredibly complicated phenomena**
  - Electrostatic forces: dispersion, polarity, hydrogen bonding
  - Structural similarity
  - Penetration rate
  - Acidity and basicity: chemical reactivity
  - Etc.
- What we can do is **quantify the solvent's qualities**

IONIC LIQUIDS: WHY DO THEY WORK?

Old Methods:

- **Hansen Solubility Parameter(s)**
  - Dispersion Forces (d), Dipolar Intermolecular Forces (p), Hydrogen Bonds (h)
- **Hildebrand Solubility Parameter**
  - Quantifies van der Waals forces
  - Similar values indicate solubility between solute and solvent

From *COOL Conservation*



Teas Chart of Solvents
(Based on Hansen Parameters)

Solvent	δ (SI)
n-Hexane	14.9
White spirit	16.1
Turpentine	16.6
Xylene	18.2
Toluene	18.3
Methyl ethyl ketone	19.3
Acetone	19.7
Methylene chloride	20.2
Pyridine	21.7
Cellosolve®	21.9
Dimethylformamide	24.7
Methyl alcohol	29.7
Water	48.0

Hildebrand Values

HOW DO WE COMPARE SOLVENTS?

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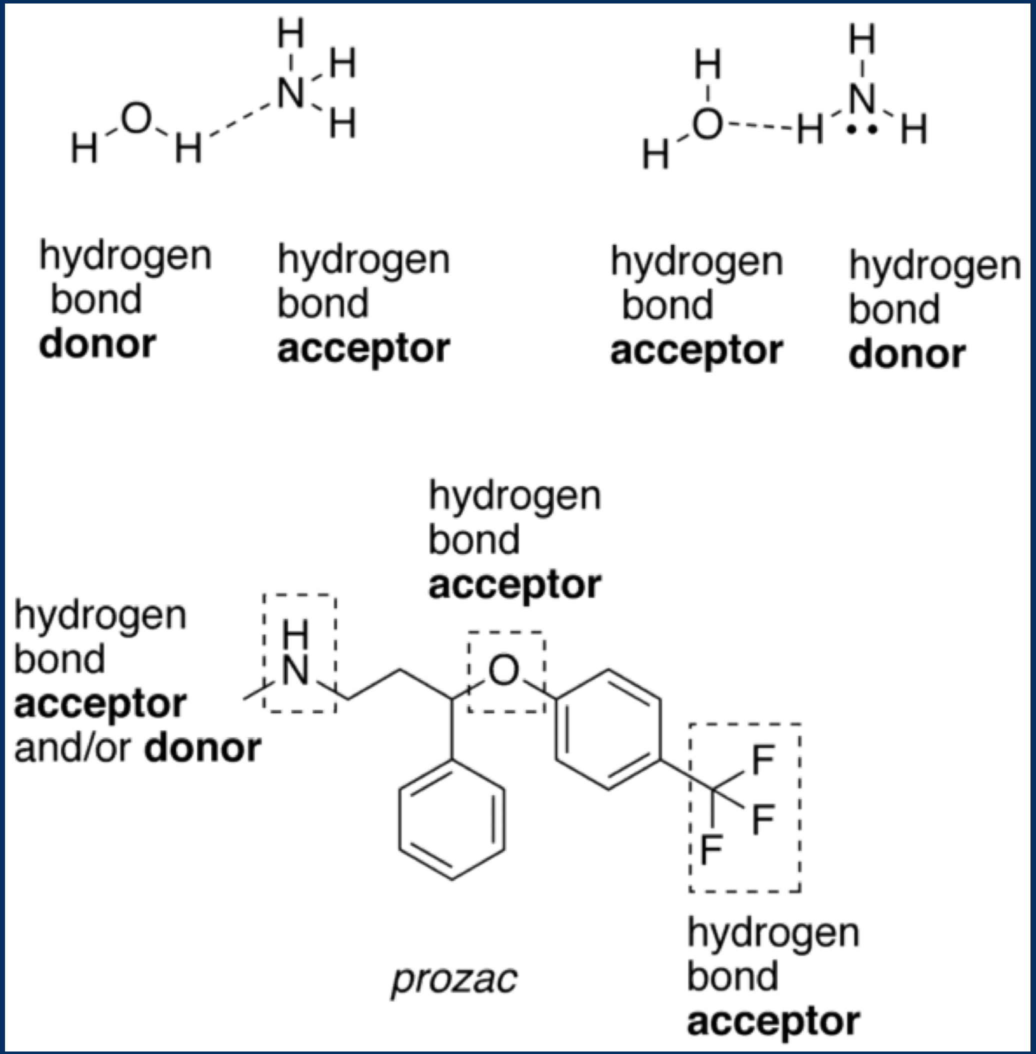
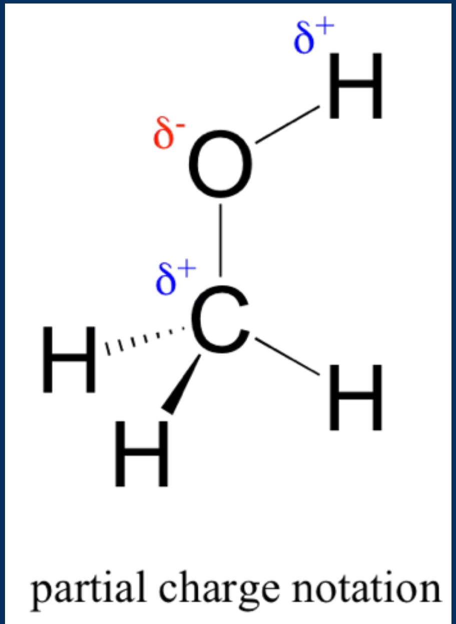


https://commons.wikimedia.org/wiki/File:WikipediaHDonorAcceptor.png

Three Parameters

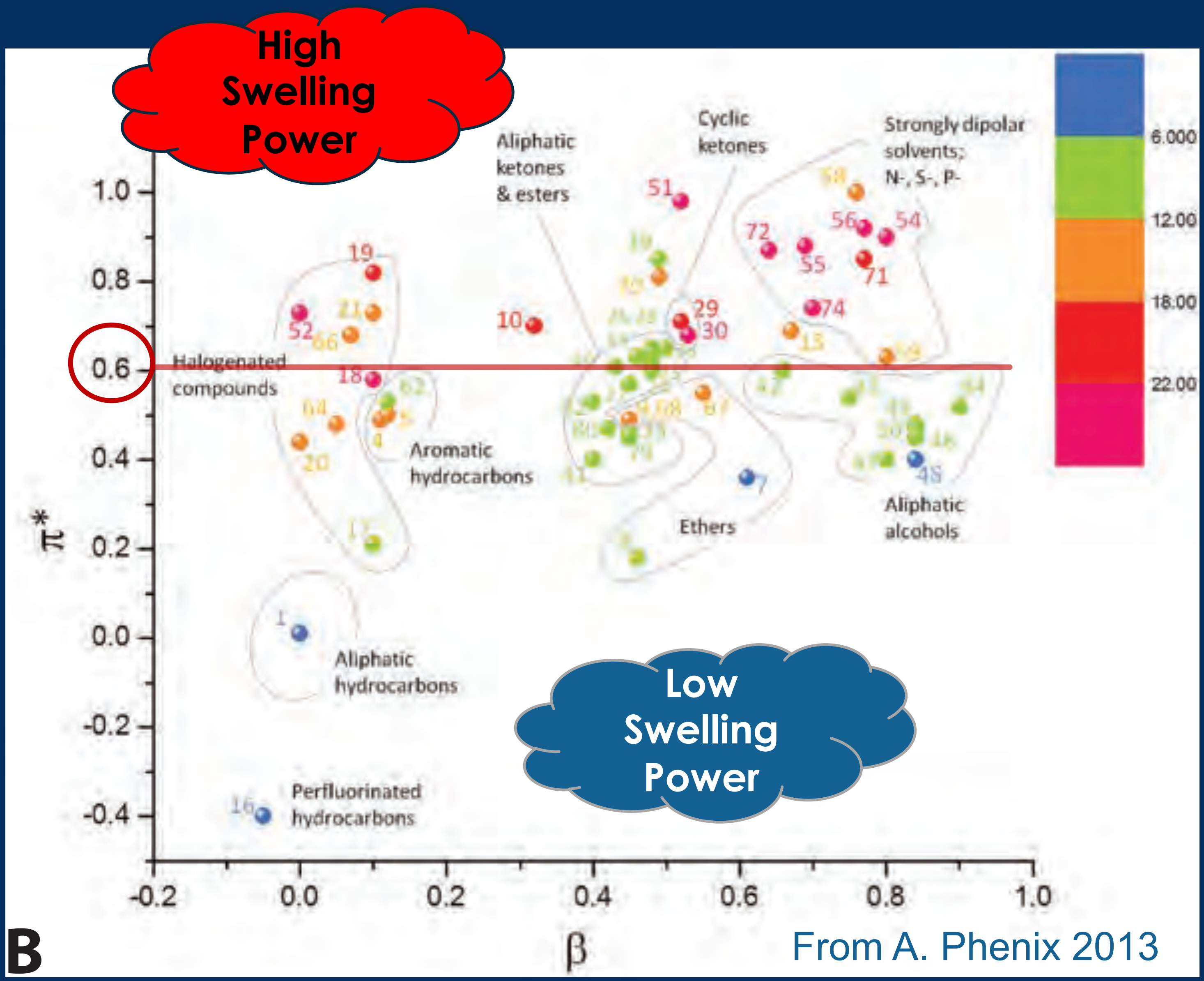
- **Alpha**
  - Hydrogen Bond Donating Ability
- **Beta**
  - Hydrogen Bond Accepting Ability
- **Pi***
  - Polarity
  - (And Polarizability)

KAT is now considered to be the most comprehensive means of quantifying solvent properties



http://chemwiki.ucdavis.edu/

NEW: KAMLET-TAFT SOLVENT PARAMETERS



Strong Solvents According to Paint Swelling Ability (Phenix 2013)

- Alpha - lacks any correlation to solvent families and swelling ability
- Beta – groups solvents by chemical families, but doesn't directly influence swelling power
- **Pi* > 0.6 = 'Strong solvents'**
  - **Indicates swelling power**

KAMLET-TAFT SOLVENT PARAMETERS

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SOLVENT PARAMETERS: KAMLET-TAFT

KAT parameters are now considered to be the most comprehensive means of quantifying solvent properties. Conservators have more typically employed, and continue to use, Hildebrand and Hansen systems that form the basis of the Teas chart.

Allen Phenix introduced KAT parameters to conservators, publishing his extensive studies on the correlation of paint swelling and KAT values.

- PI*, quantifies the polar and dipolar nature of the molecule
- Beta, quantifies the hydrogen bond accepting ability of the molecule
- Alpha, quantifies the hydrogen bond donating ability of the molecule

As with the Teas chart, polarity is the key factor in correlating KAT values with paint swelling. Solvents with a Pi* value (polarity) greater than 0.6 are considered to have a strong swelling power.

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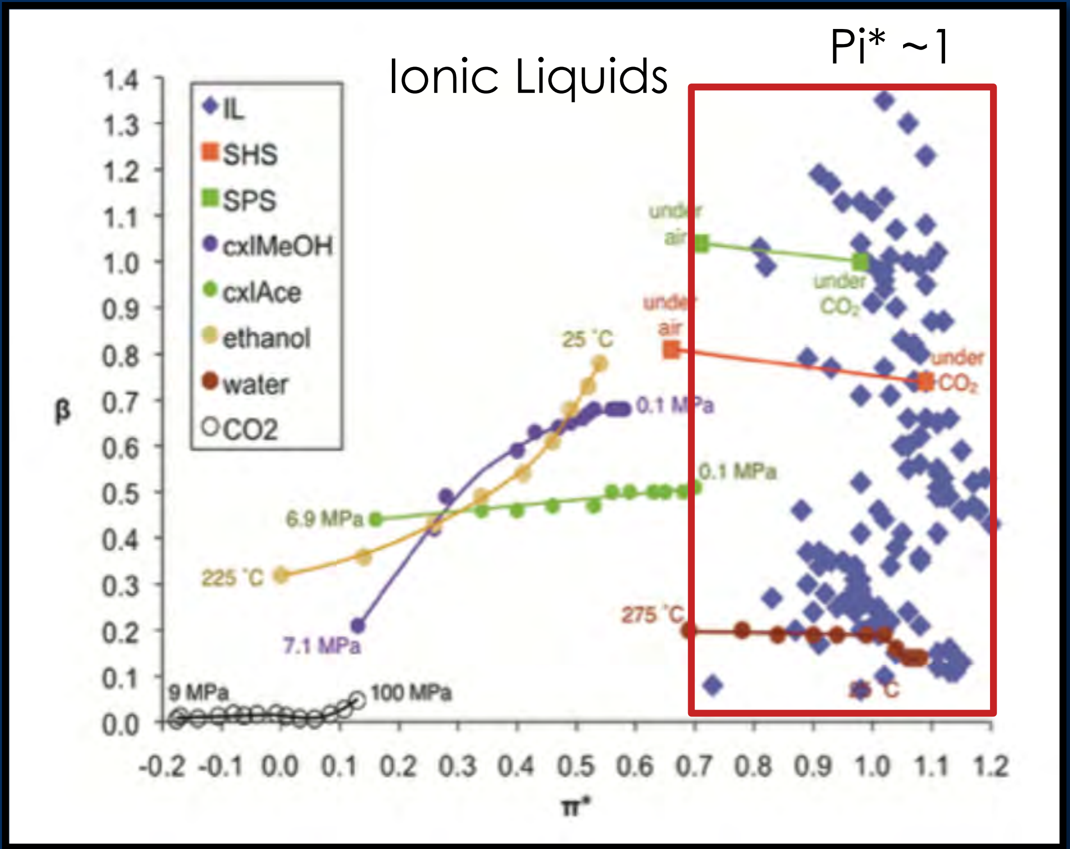
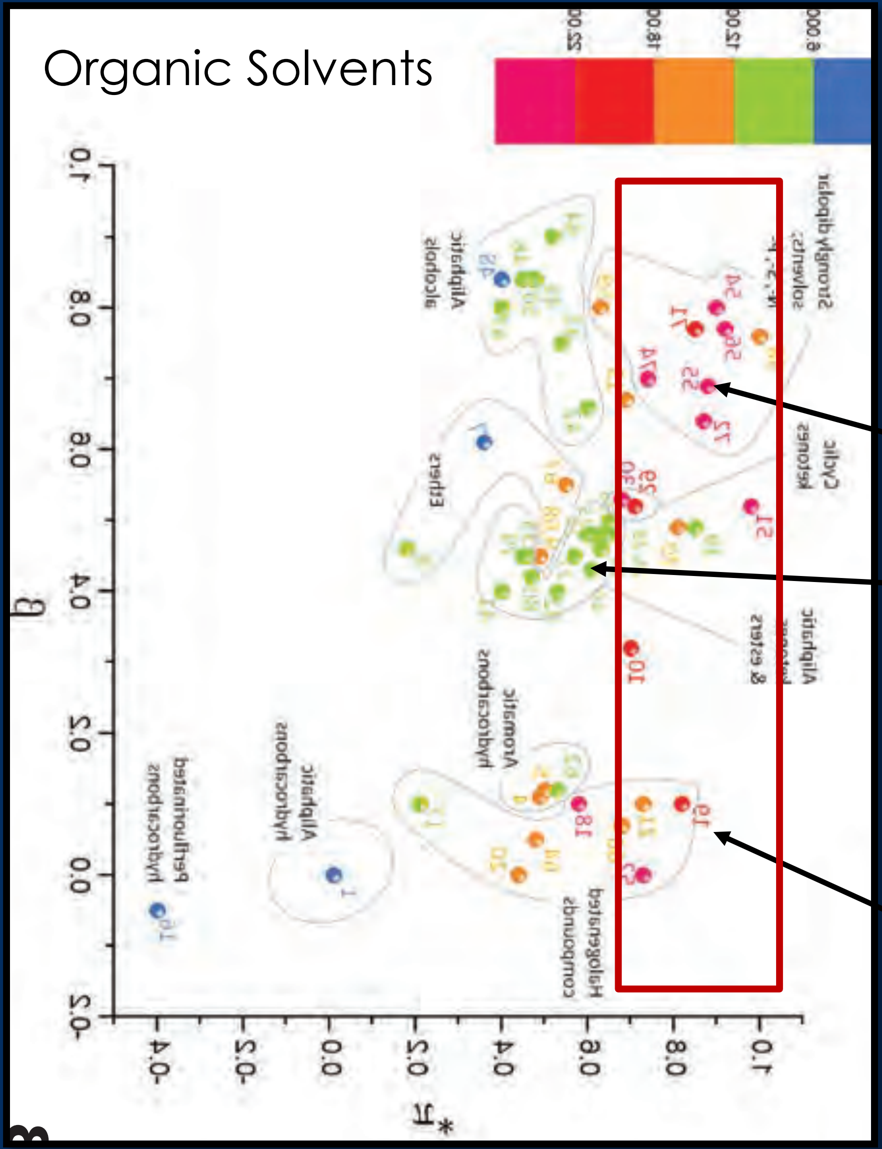
Jessop et. al. 2012; Phenix 2013





For Organic Solvents
>0.6 = strong

DMF (~0.9)

MEK (~0.6)

Dichloromethane
~0.8

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Any ionic liquid should do - select for a non-toxic, affordable option

SUBSTITUTION STRATEGY?

SUBSTITUTION STRATEGY?

Ionic liquids occupy a distinct region of solvent values: 0.81 ≥ Pi* ≥ 1.20, with a wide range of Beta values.

In theory, any ionic liquid should therefore have a strong swelling and solvency action on paint films and other coatings. If an ionic liquid is selected to be accessible, affordable, and non-toxic, we will have found a viable, safer option for the cleaning of painted surfaces.

Pacheco et al. 2013 pioneered the use of such ionic liquids, providing seminal research to build upon. How could this research be furthered for the benefit of conservators?

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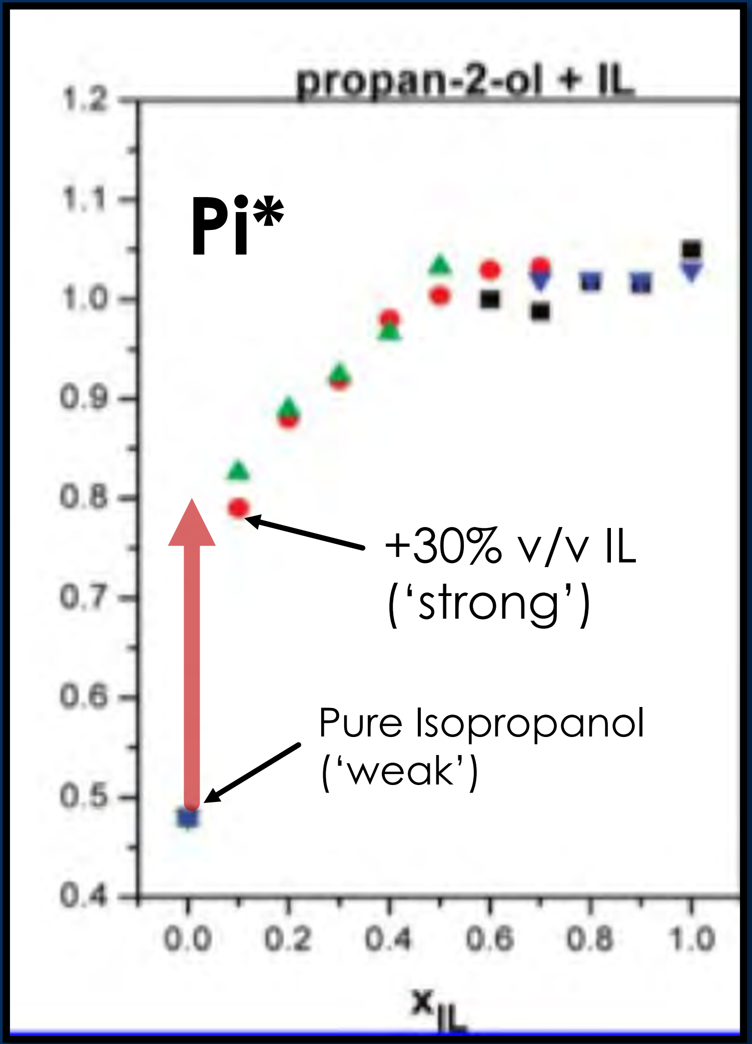
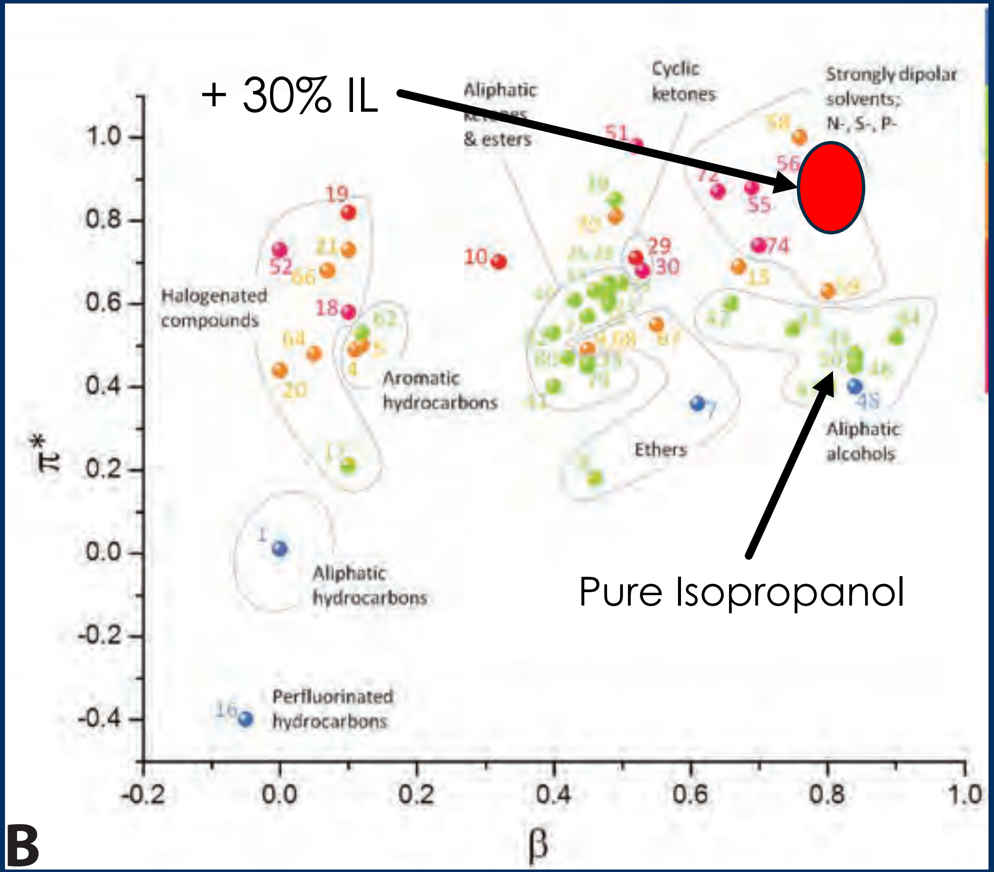


Forunato et. al. 2010.

Properties of Binary Mixtures: Ionic Liquids + Low Toxicity Organic Solvents

- Example: Isopropanol + IL
  - = 'Stronger' Solvent
  - Increase Pi* value of Isopropanol
  - Retain Beta value
  - Unique action of both solvents
  - Decrease viscosity of IL
  - Increase penetrating power of IL
  - Less IL = less cost



Hypothesis: Binary mixtures of IL in isopropanol will solvate fresh and/or aged coatings of paint, varnish, and/or adhesives more effectively than isopropanol alone.

NEW FRONTIERS: BINARY MIXTURES?

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NEW FRONTIERS: BINARY MIXTURES?

Based on more recent literature, binary mixtures of low-toxicity organic solvents and ionic liquids were proposed as novel cleaning agents.

- The small addition of strongly polar ionic liquid (30 % v/v) to isopropanol has been shown to result in a solvent mixture with a similarly high Pi* value as the ionic liquid alone. It was hoped that these strongly polar mixtures, with intermediate physical properties, could better be exploited for the cleaning of painted surfaces than either alone.
- The lowered viscosity of the mixture (vs. viscous pure ionic liquids) should encourage faster diffusion/penetration which has been identified as a key factor in swelling paint films.
- Additionally, the proposed mixtures may prove effective for dissolving aged overpaint due to their ionic character. As paint films age, they become increasing ionic and polar. Disruption of cohesion may be more important than solvation. The proposed mixture may be able to simultaneously swell and disrupt the cohesion of an aged paint film, solvating it for easy removal.
- By using significantly less ionic liquid, the mixtures would be less costly than pure ionic liquids.

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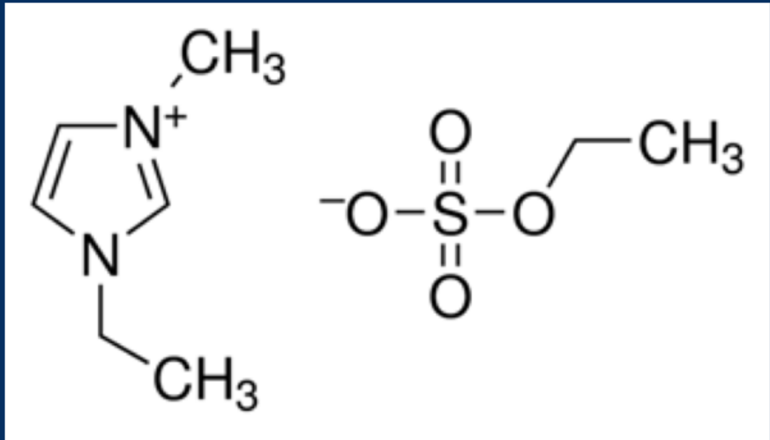

www.sigmaaldrich.com/

IONIC LIQUID SELECTION:

1-ETHYL-3-METHYL-IMIDAZOLIUM ETHYL SULFATE (EMIN ES)

- Always liquid at room temperature (will not freeze)
- Completely non-toxic and non-volatile
- Relatively affordable
- Readily miscible with water, isopropanol and acetone
- Has a high Pi* and Beta value
- Has a polar head and non-polar alkyl chains
    - Allows for the solvation of a wide range polar and non-polar, organic and inorganic, and organometallic solutes

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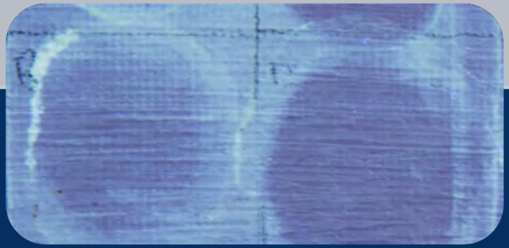
EXPERIMENTAL DESIGN

1) Measure Kamlet-Taft parameters

- solvation probe dyes and spectrophotometer
- Determine if ‘stronger’ solvent is being formed
- Determine optimal proportions

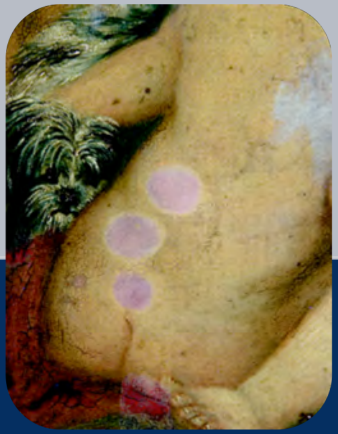
2) Test efficacy of 30% EMIN ES vs. pure isopropanol on naturally aged varnish samples

- Swab tests
- Macro and micro photographs – UV and normal
- Color and gloss measurements
- Range of varnishes – mostly natural



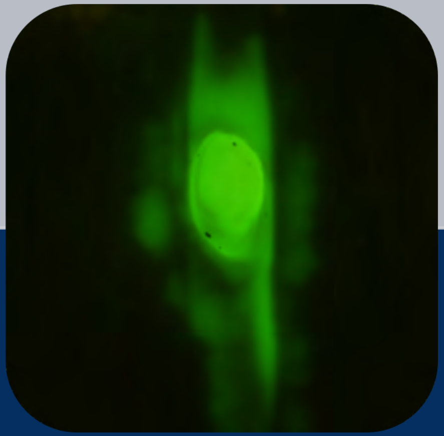
3) Test cases: test paintings available at Queen’s MAC

- 30% EMIN ES vs. isopropanol
- Natural resin varnish coatings
- Overpaint
- Grimy soiling



4) Residue Testing

- Rhodamine 123 Fluorescent Dye
- Surface and cross-sectional analysis



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EXPERIMENTAL DESIGN

1) Measure Kamlet-Taft Paramters

- Determine if the predicated behavior of EMIN ES in isopropanol holds true in practice. Is the addition of EMIN ES to isopropanol creating a strongly polar mixture?
- Determine the best ratio to use in subsequent testing.

2) Test the efficacy of the resulting mixture on naturally aged varnish samples

- Determine the effects of the mixture on a wide range naturally aged varnish samples, and on constructed paint surfaces.
- Compare with the efficacy of pure isopropanol

3) Determine the efficacy of the mixture on authentic paintings

- Determine the effects of the mixture on a range of naturally aged coatings and paintings that reflect typical surfaces encountered in paintings conservation.

4) Residue testing

- Due to the non-volatile nature of the ionic liquid, clearance may present a major issue with the use of these cleaning alternatives.

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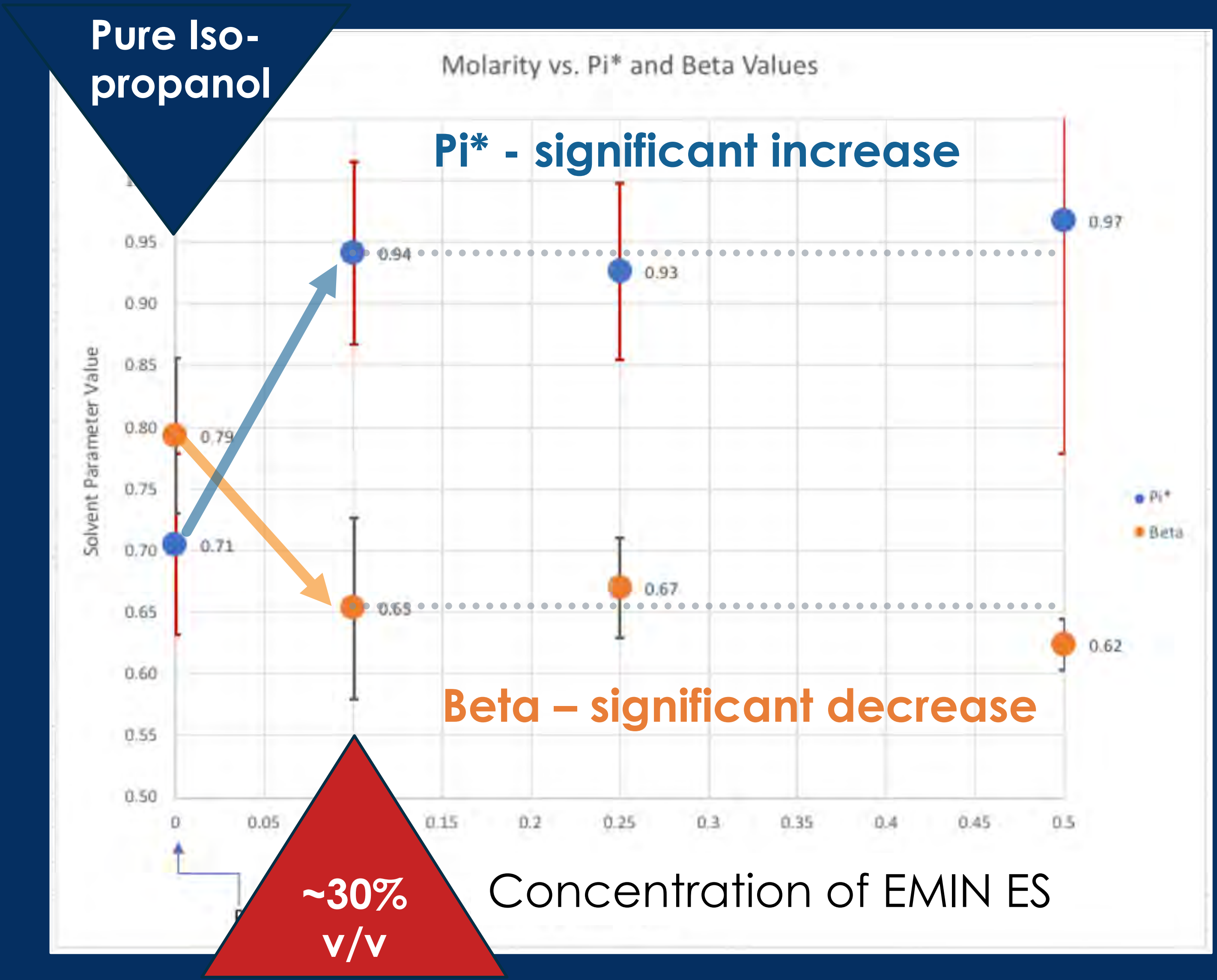

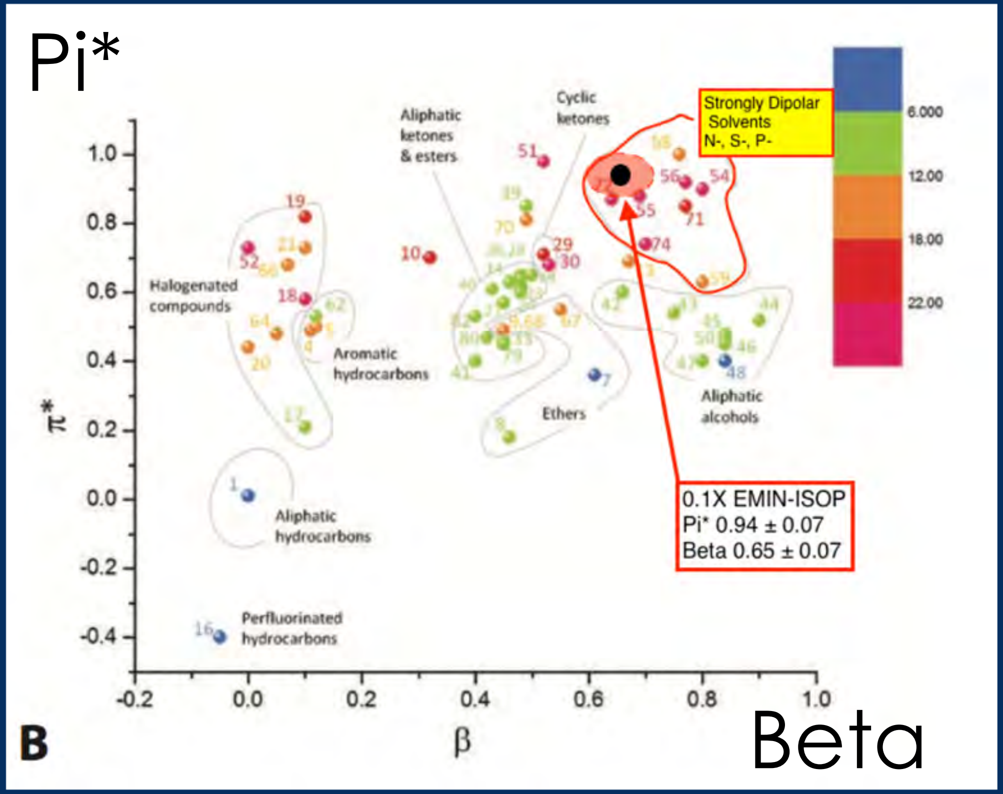

Modified from Phenix (2013). Pg. 75.

RESULTS 1: **SOLVENT PARAMETERS**

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RESULTS 1: SOLVENT PARAMETERS

- Solvent probe dyes (4-Nitroanisole and 4-Nitroaniline) are employed to determine the PI* and Beta values of EMIN ES and isopropanol mixtures across a range of concentrations. The dye's solvation/interaction with the solvents produces shifts in the absorbance spectrum that can be quantified and correlated to its polarity (Pi*) and hydrogen bond accepting ability (Beta).
- Even a small fraction of EMIN ES added to isopropanol (0.1 parts by molar fraction) produced a strong boost in the Pi* value, measured at 0.94 ± 0.07 (vs. pure isopropanol 0.71 ± 0.07). Greater mole fractions produce no significant increase in Pi*.
- While the Pi* value increases significantly at 0.1X, the Beta value significantly decreases, measured at 0.65 ± 0.07 (vs. pure isopropanol 0.79 ± 0.06).
- Considering Phenix's correlation of swelling power to Pi* and Beta values, the measured values of 0.94 Pi* and 0.65 Beta would put the mixture in the same region as strongly dipolar organic solvents, comparable to 'super solvents' like pyridine.
- A mixture of approximately 30% EMIN ES in isopropanol (v/v) was selected as the strongest possible binary mixture to continue testing with (~0.1 parts by molar fraction).

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RESULTS 2: CCI WORKSHOP VARNISH SAMPLES

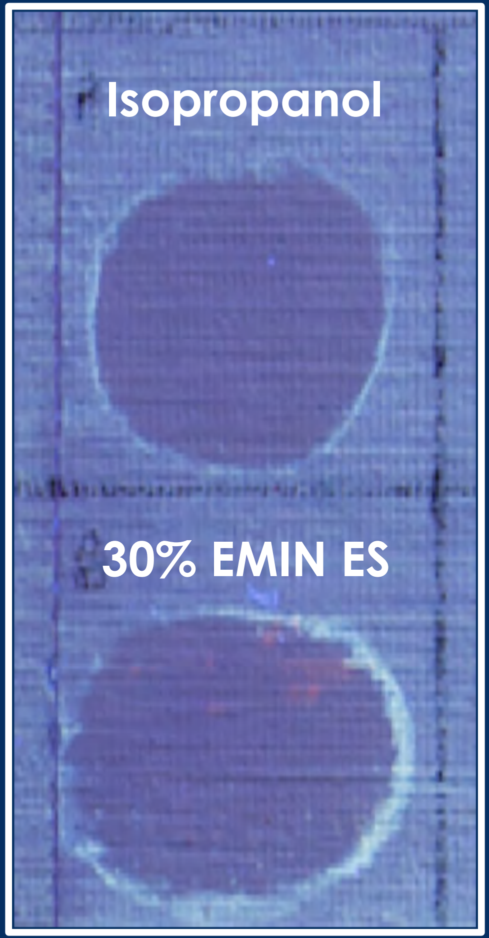
Experimental:

- Naturally aged 24 years
- Flake White and Van Dyke Brown Brown in Oil (Winton)
- Natural and Synthetic Varnishes

Results:

- Dyke Brown samples –too sensitive to solvents - not suitable for solvent cleaning
- Most natural resins that were soluble in 30% EMIN ES were also soluble in pure isopropanol – Mastic, Dammar, etc.
- **30% EMIN ES was slightly more effective at solvating copal varnishes, and markedly less effective at solvating Paraloid B-72**

Dammar Varnish



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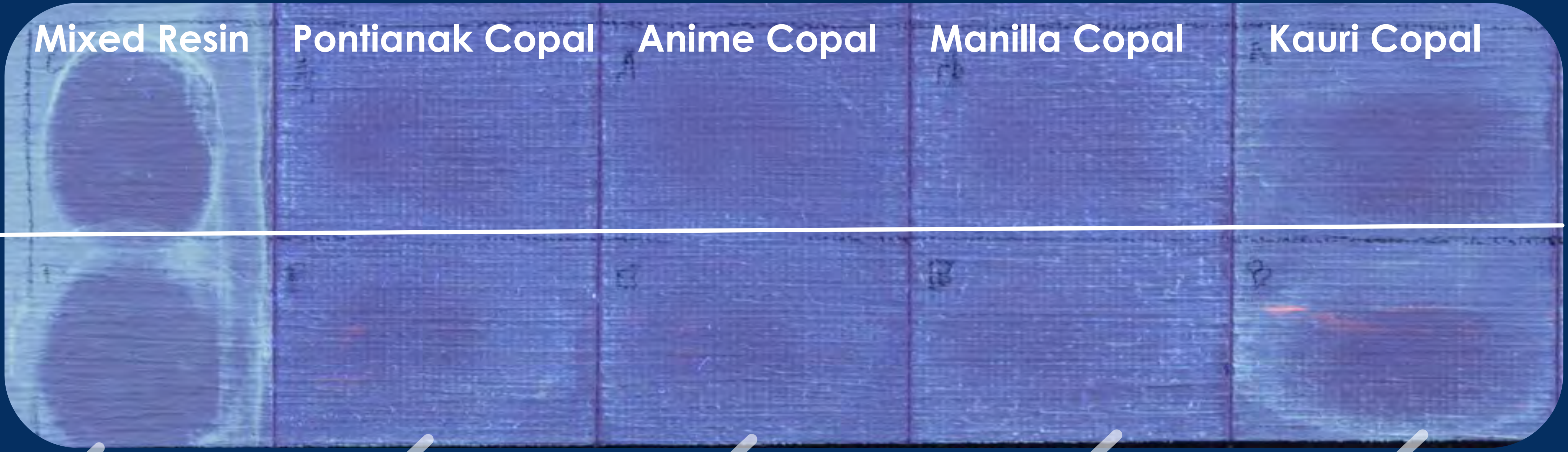
- UV illumination

Isopropanol

30% EMIN ES



RESULTS: VARNISH SAMPLES – FLAKE WHITE

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SWAB TEST WITH ACETONE – COPAL VARNISHES

- Performs better than 30% EMIN ES, with significantly less swabbing time and mechanical action

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RESULTS 2: VARNISH SAMPLES

- A wide range of naturally aged varnishes were tested upon to compare the action of pure isopropanol vs. the 30% (v/v) EMIN ES.
- All natural resin varnishes were soluble in both pure isopropanol and 30% EMIN ES, expect for copal varnishes.
- UV florescence of copal varnishes shows that most of these varnishes were merely being disturbed by the solvents tested. This is evidenced by a lack of fluorescing material being transferred on to the cleaning swabs.
- Kauri copal however, shows a notable difference. The EMIN ES test site was cleaner, with more varnish deposited on the swab and the edges of the test site. This suggests the EMIN ES mixture was solvating the varnish more effectively than isopropanol alone.
- Acetone more readily and effectively solvated the copal varnishes, with much less mechanical swabbing action than either isopropanol or the 30% EMIN ES.

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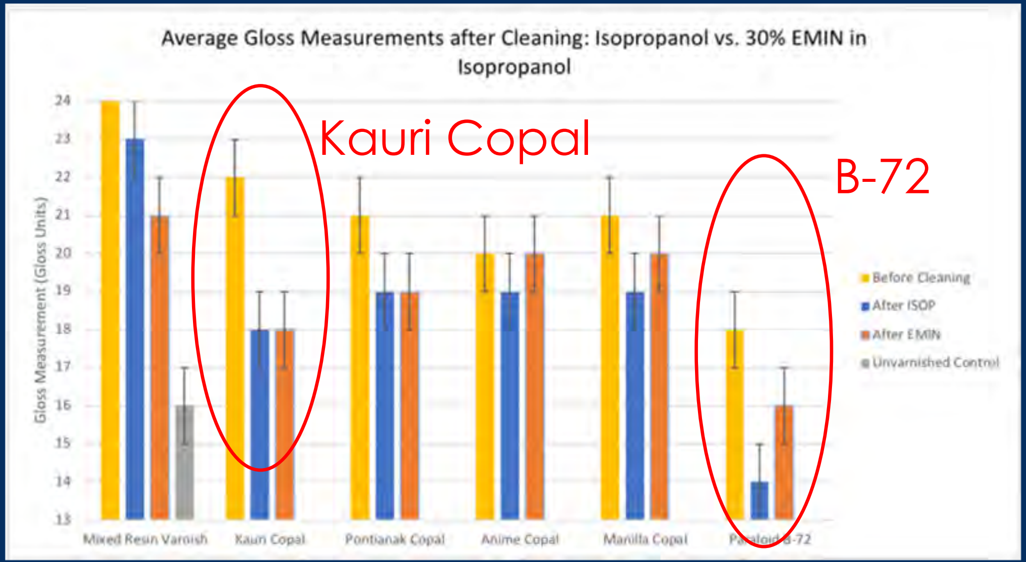
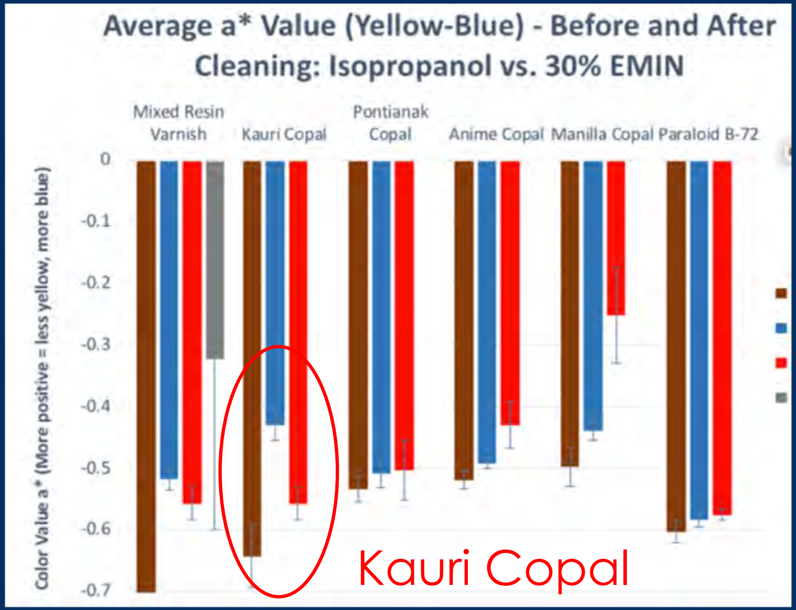
Gloss

- Before Cleaning
- After ISOP
- After EMIN
- Unvarnished Control



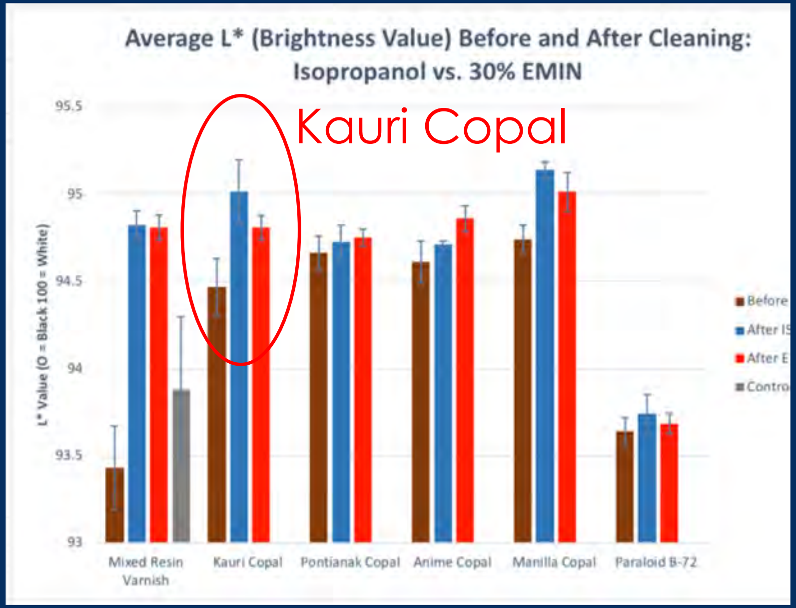
a*



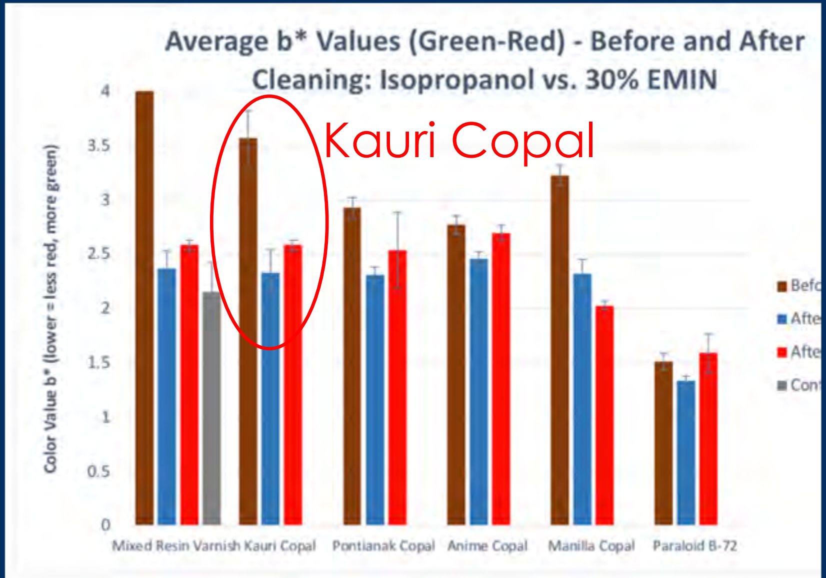
Color

L*

- Before Cleaning
- After ISOP
- After EMIN
- Control



b*



RESULTS 2: VARNISH SAMPLES – FLAKE WHITE

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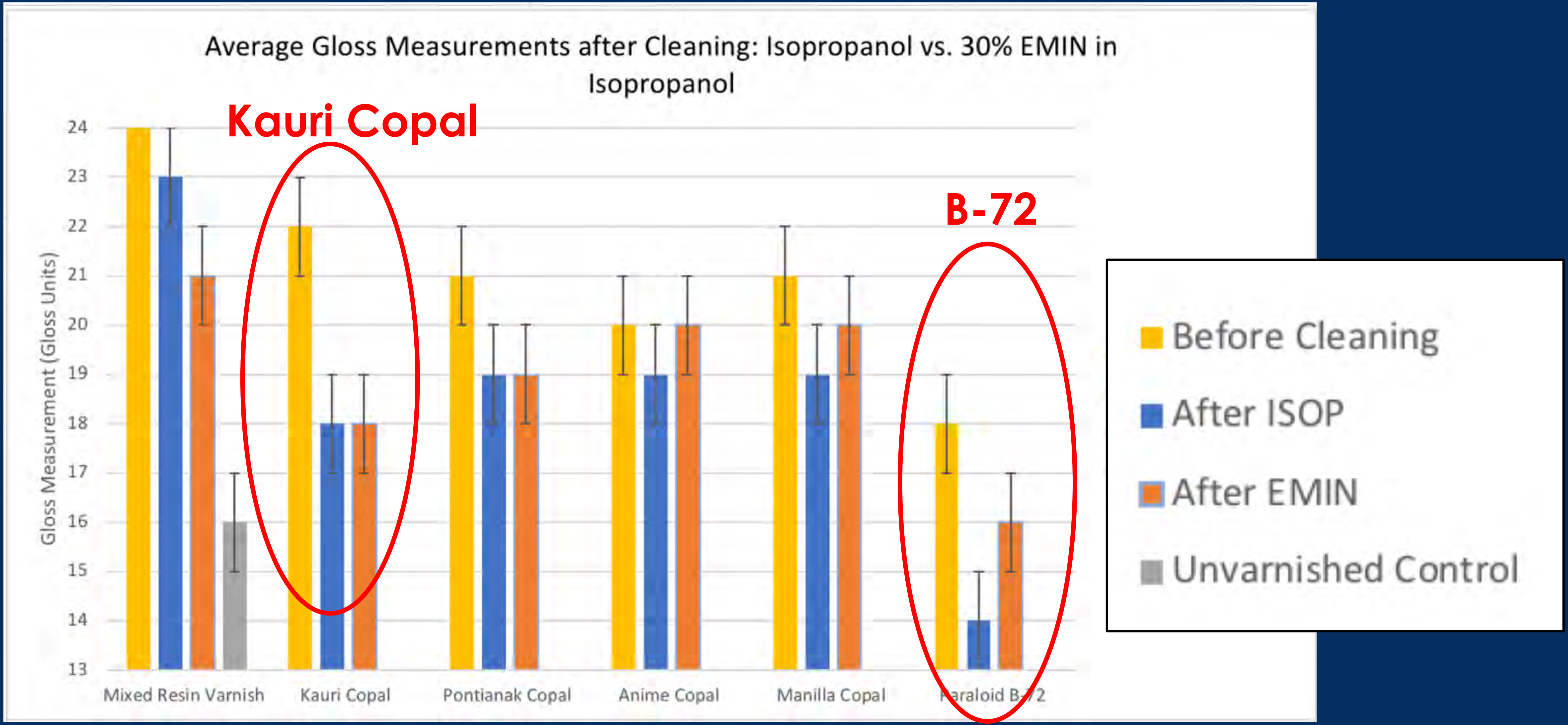

GLOSS VALUES: KAURI COPAL AND B-72

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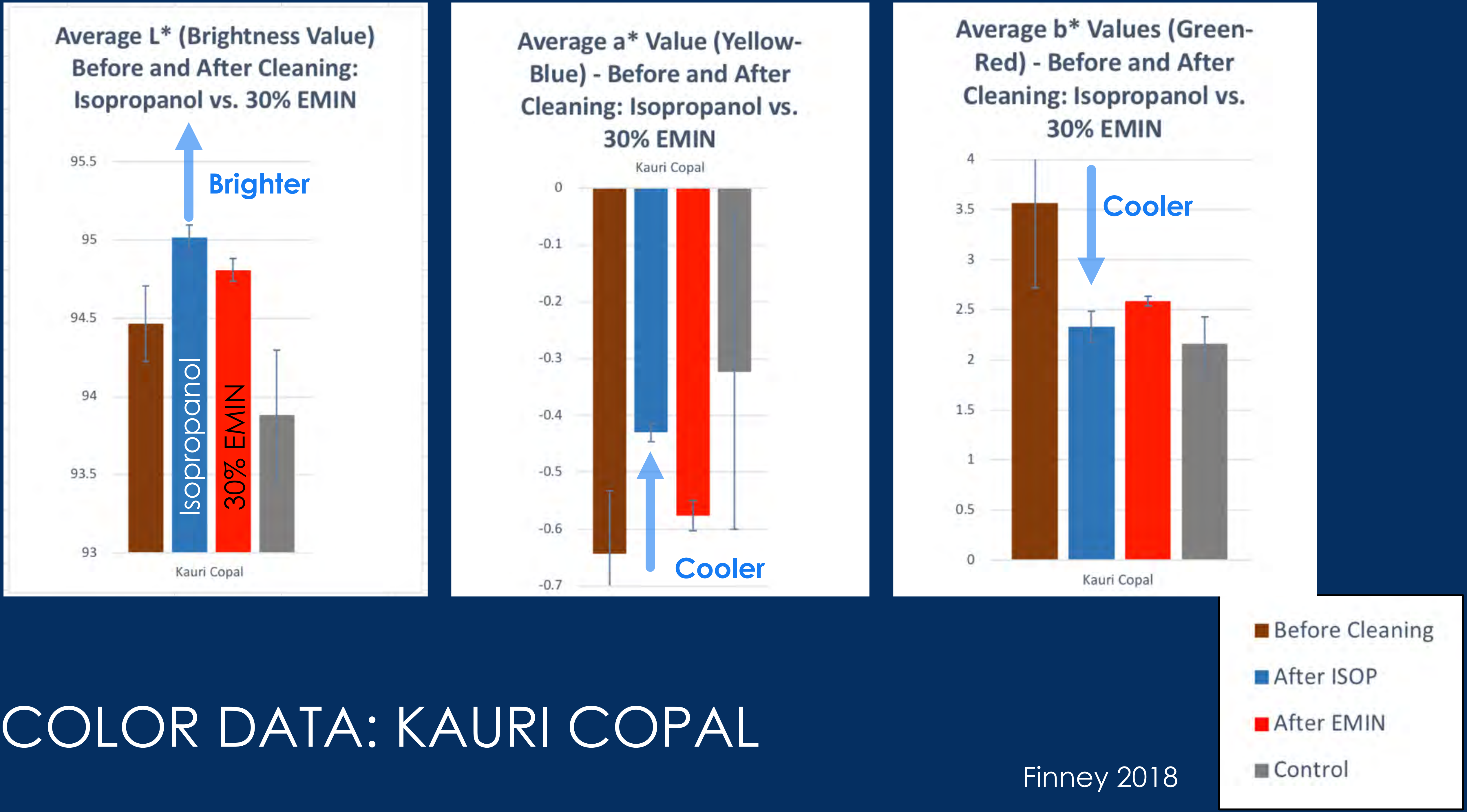

COLOR DATA: KAURI COPAL

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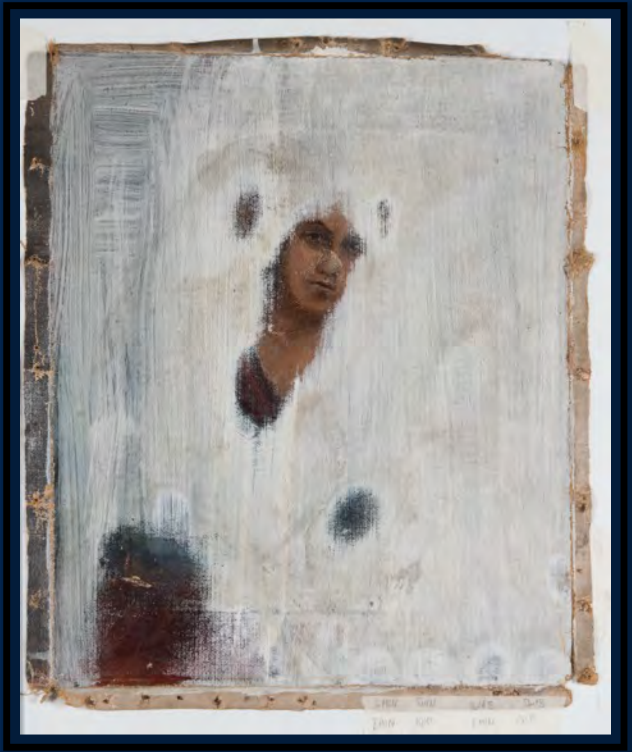
RESULTS 2: VARNISH SAMPLES, COLOR AND GLOSS DATA

- Color and gloss measurements were taken before and after cleaning tests to compare the cleaning efficacy of isopropanol vs. the 30% EMIN ES mixture. A cleaner surface would be matter, with a cooler and brighter color.
- Color and gloss data were largely confusing and contradictory.
- For Kauri copal cleaning tests, the change in gloss is the same for both isopropanol and the 30% EMIN ES solution. Color data suggest that isopropanol was leaving a cooler, brighter, and cleaner surface, despite the observation under UV illumination that EMIN ES was removing more varnish.
- Gloss measurements show the results of testing on Paraloid B-72 better than photos can. Isopropanol completely removed the varnish, while the EMIN ES mixture left a patchy surface, clearly captured in the higher gloss levels measured after cleaning.



RESULTS 3: TEST PAINTINGS

a) Natural Resin Varnishes
b) Grimy Coatings
c) Overpaint and Synthetics (B-72)

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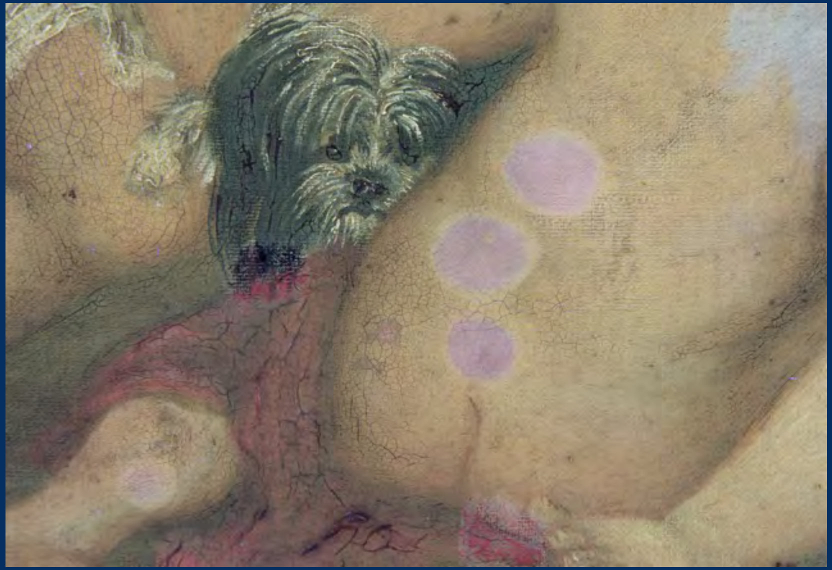
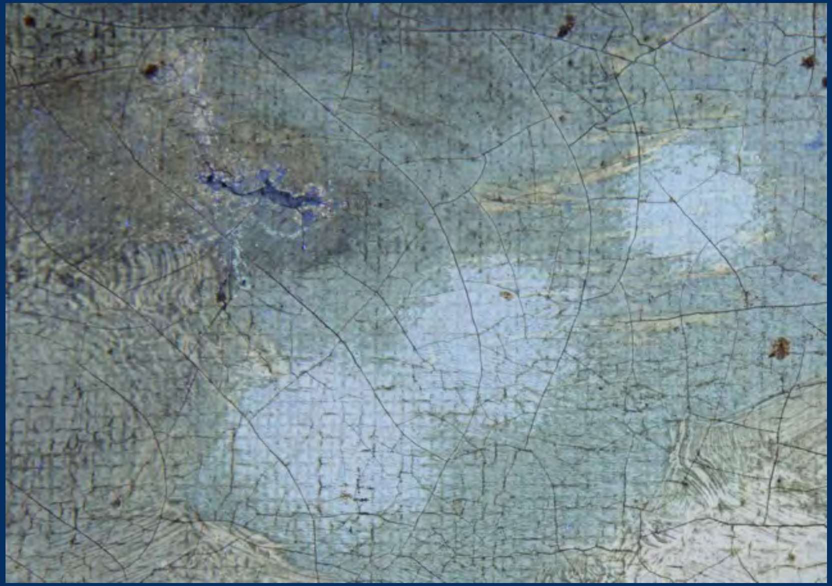
RESULTS 3: TEST PAINTINGS

Four test paintings were selected to encompass a range of coatings. It was hoped that these coatings would represent a range of solubility characteristics. The aim of this phase was to test upon naturally aged, ‘real life’ test cases with varnishes that were very likely applied more than 24 years ago (the age of the CCI varnish board samples). These test cases would allow for a greater understanding of how the experimental EMIN ES mixture interacts with aged coatings and historical paint surfaces.



FT-IR Suggests:

Mastic



Mastic or Dammar

30% EMIN ES vs. Pure Isopropanol:

- Resin is easily soluble in both
- Neither negatively affected the paint layer

A) RESIN VARNISHES

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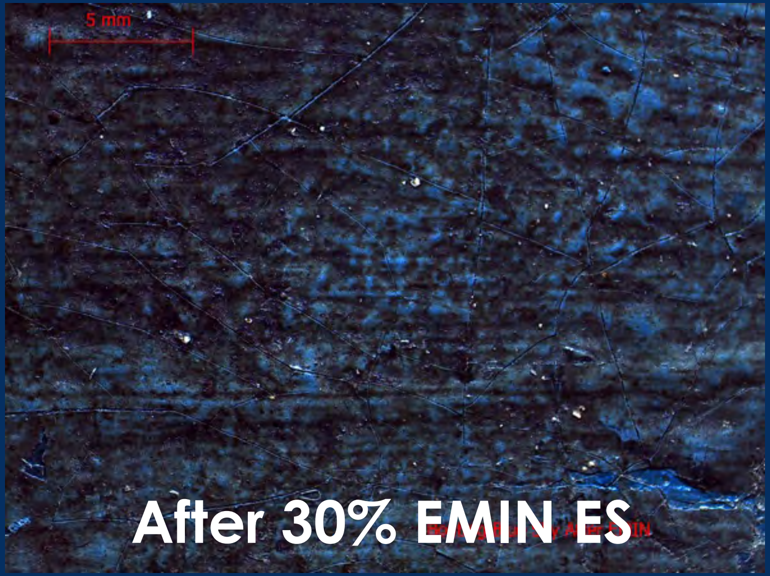
B) GRIMY AND OILY COATINGS

FT-IR Suggests:

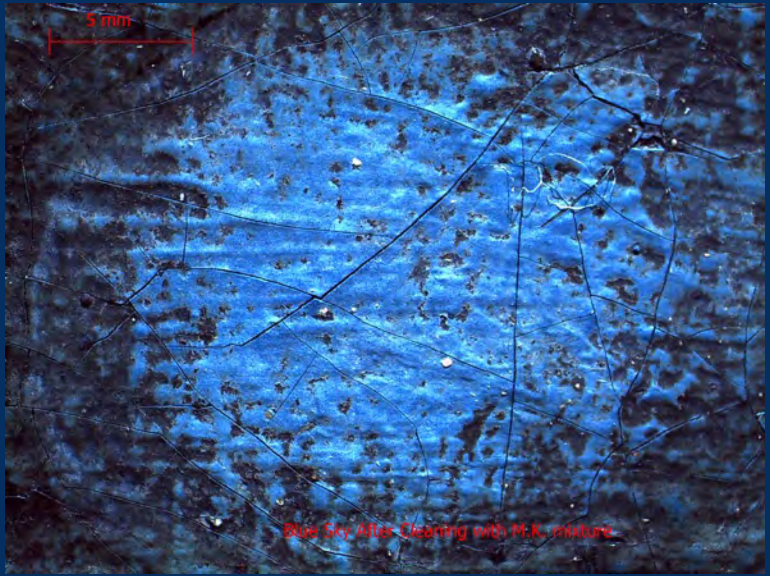
- Dust
- Dirt
- Oily or waxy hydrocarbons

30% EMIN ES vs. Pure Isopropanol:

- Neither are capable of solvating the grimy coating
- Masschelein-Kleiner solution readily solvated (90ml water, 10mL Isopropanol and 3mL 30% NH_4)



After 30% EMIN ES



After M.K. Ammoniated Solution

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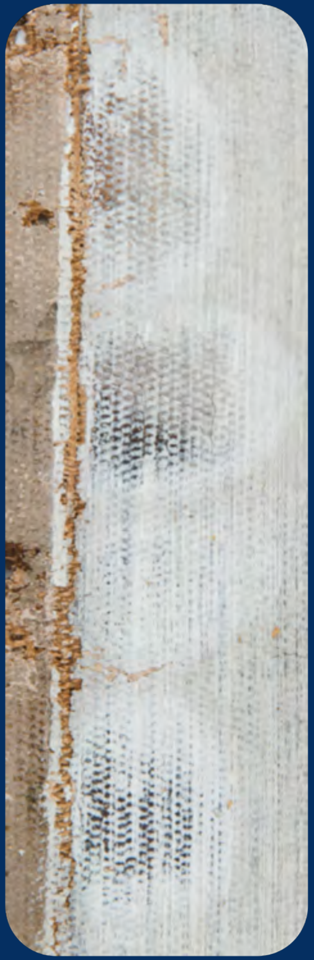
FT-IR Suggests:
- Paraloid B-72
- Lead white carbonate and drying oil

30% EMIN ES vs. Pure Isopropanol:

- Both remove B-72 with aggressive swabbing
- Neither are effective at removing the overpaint
- Gelling does not improve the action
- Acetone, MEK, and M.K. are all more effective



Acetone

Methyl Ethyl Ketone

Toluene

M.K. Solution: Ammonia/Water /Isopropanol

Swabbing with EMIN ES,

Brushing with isopropanol in Velvesil Plus Gel

Brushing with 30% EMIN ES in Velvesil Plus Gel

C) OVERPAINT AND SYNTHETICS

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RESULTS 3: TEST PAINTINGS

- Results mirrored the varnish board testing, EMIN ES could solvate the same natural resin coatings as isopropanol, without causing any noted harm to any paint layers.
- Neither pure isopropanol, nor the 30% EMIN ES mixture were effective at removing grimy soiling with organic components, nor tenacious overpaint.
- It was found that 30% EMIN ES in isopropanol could easily be incorporated in Vevesil Plus to make a stable gel mixture, but this had no increased efficacy on tenacious overpaint.
- When the Kamlet-Taft parameters were quantified in part one, the values suggested a similarity to methyl ethyl ketone, a solvent typically reserved for the removal of overpaints. Results do not support this comparison, as MEK manages to break through the lead white overpaint tested, while EMIN ES cannot without a great deal of physical action.

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Method:

- Tag solvent with Rhodamine 123
- Remove varnish coating from sample board
- Clear with isopropanol x3

Results:

- Trapped in pores
- Infused into varnish at edges of test sites

RESULTS 4) **CLEARANCE TESTING**

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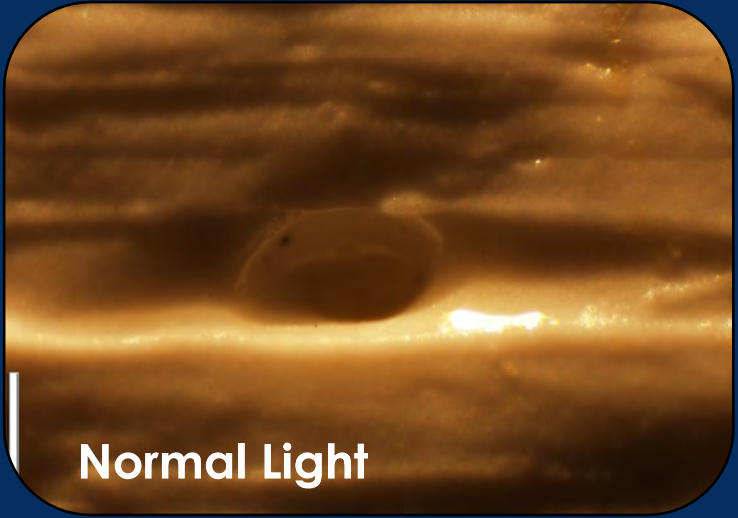
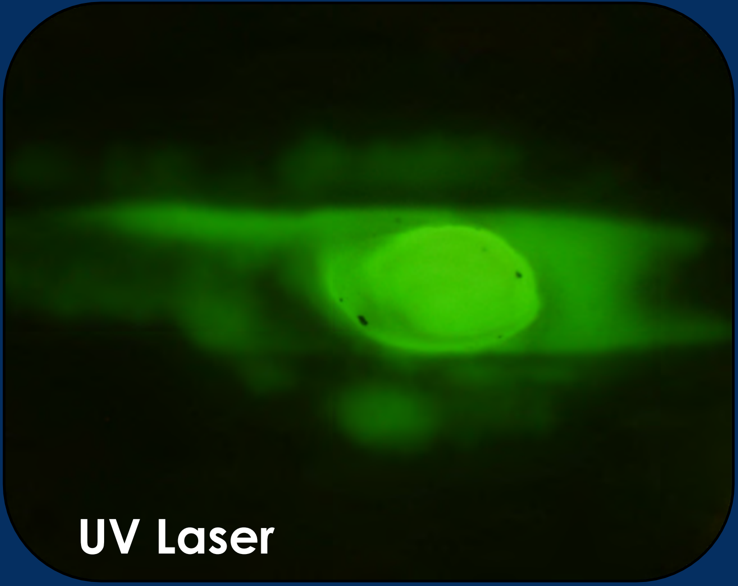
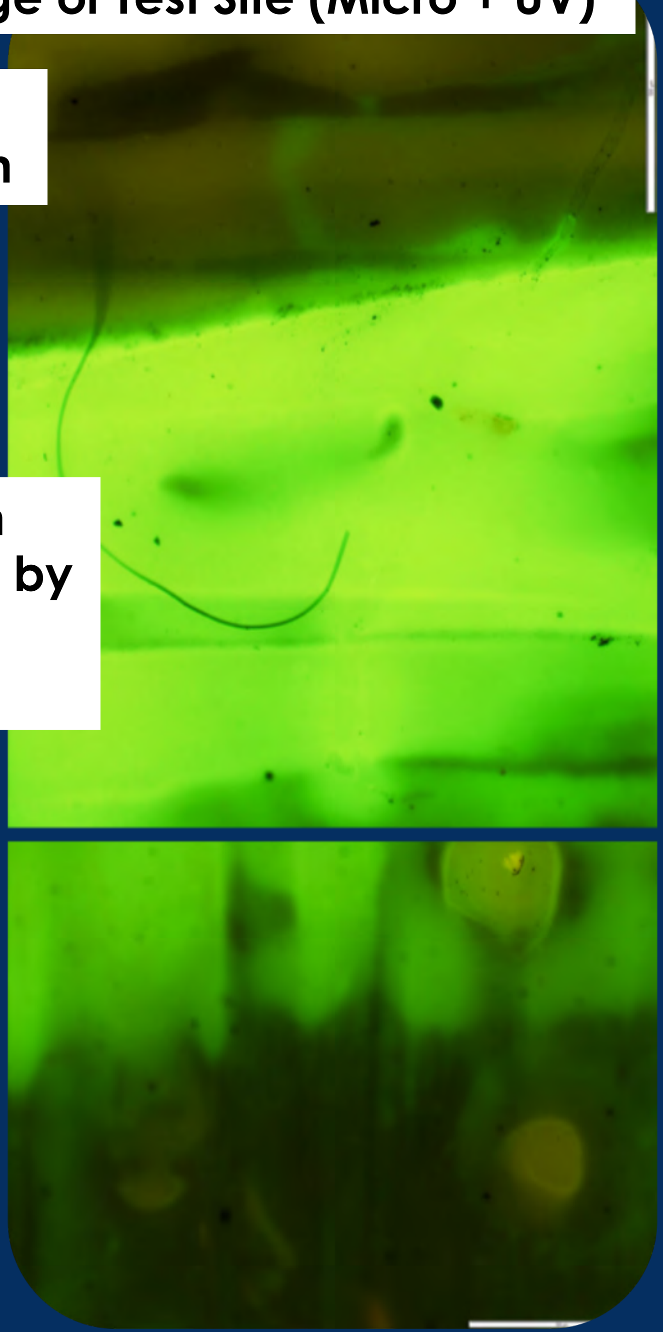
Micro-images: pore in flake white sample - post cleaning with dye tagged solvent





Edge of Test Site (Micro + UV)



RESULTS 4: CLEARANCE TESTING WITH RHODAMINE 123 FLUORESCENT DYE

- In order to assess the clearance of the experimental EMIN ES mixture from the surface of painted works, a fluorescent dye tracer dye may be employed to tag the solvent. Often Rhodamine B is utilized for this purpose. Employing the tagged solvent in a cleaning test allows for the surface to be assessed by florescence microscopy to determine if any non-volatile solvent remains.
- After clearing the surface of the flake white sample with isopropanol, examination with UV illumination showed several pores still contained the tagged solvent mixture. Additionally, the edges of the test sites, where varnish still remained, showed a marked amount of florescence. Here the solvent mixture has incorporated into the edges of the test site, by solvation and reformation, or diffusion of the solvent mixture into the resin.
- The long term effects of lingering EMIN ES in paint and varnish films is unknown, but given its solvent like qualities, it is possible the trapped ionic liquid could cause detrimental, irreversible changes.

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Results:

- Although Kamlet-Taft parameters suggested a 'stronger' solvent – **experimental testing showed a lack of improved efficacy** on coatings
- Non-volatile ionic liquid presented clearance issues

CONCLUSION:

Conclusions:

- **Lack of correlation between Kamlet-Taft parameters and cleaning action** suggests we must be cautious when attempting to quantify the properties of inorganic or other atypical solvents
- **Expense** and lack of efficacy of EMIN ES mixtures suggest an **end to its use in conservation research**
- **Clearance issues casts doubt** not only on the future use of EMIN ES, but **on all non-volatile ionic liquids**

Future of Solvent Research:

- Low toxicity, volatile, organic solvents borrowed from cosmetics industry

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CONCLUSIONS:

- The results of this study have strongly suggested that the addition of EMIN ES is not an effective means of improving the cleaning efficacy of isopropanol. Despite the strong nature of the mixture as predicted by measuring its solvent parameters, practical testing failed to show any significant increase in cleaning efficacy that would merit the use of this ionic liquid. Furthermore, clearance issues suggest this cleaning system is inappropriate for paint surfaces, especially porous ones.
- The lack of correlation between the measured Kamlet-Taft parameters and the action of the experimental mixture is perhaps one of the most interesting aspects of this research. It suggests a complicated relationship between such parameters and solubility. Especially when dealing with non-organics, these measurement systems may not be able to guide conservators in solvent selection.
- Ionic liquids may present exciting new possibilities in several STEM fields, but given the inefficacy of EMIN ES, a rare example of an affordable, non-toxic ionic liquid, these fluids may not be useful in the field of paintings conservation. Judicious use of organic solvents still remains one of the best options for coatings removal. In the near future conservators may be looking increasingly more to alternative solvents borrowed from the cosmetics industry. These solvents tend to be less toxic, more accessible and affordable, as well as biodegradable and not eco-toxic.

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Thank You

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