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Some Reflections on the Use of Organic Solvents in Conservation

By Alan Phenix

As I sat and pondered how to tackle this article, it occurred to me that it was almost exactly 27 years ago when I first used organic solvents in the conservation treatment of a work of art. That was in London in 1982, and I was a first-year graduate student of paintings conservation doing my first cleaning of a painting, gently rolling a solvent-laden swab over the surface of the picture to remove discoloured varnish. A few weeks later, I would be varnishing the picture using solvent-borne resin varnishes and retouching (inpainting) with solvent-soluble resin paint media. Although I had frequently used organic solvents previously as an undergraduate student of chemistry, these were my first experiences of using this class of chemicals for the purposes of conservation-restoration. Much has changed in the field of solvents since 1982, and the following is an attempt to pick out a few of the more significant developments that have occurred since then.

In those first practical conservation treatments using solvents, I would have chosen from a fairly limited range of substances: white (mineral) spirits, toluene, xylene, propan-2-ol, ethanol (or a commercially-available grade of it), acetone, and perhaps the occasional 'exotic' such as diacetone alcohol (4-hydroxy-4-methylpentan-2-one), cellosolve (2-ethoxyethanol, ethylene glycol monethyl ether), or cellosolve acetate (2-ethoxyethylethanoate). I think I tested dichloromethane (methylene chloride) for overpaint removal, but did not actually use it in a treatment. If I were to do the same treatments now, quite a few of the solvents listed above would not be among my selection. Cellosolve, cellosolve acetate, and toluene, in particular, would be gone: all are known reproductive hazards, and there exist similar solvents to each which have near-identical solvency properties, but which are intrinsically less hazardous. The safer, logical substitute for cellosolve and its acetate are 1-methoxypropan-2-ol (also known as propylene glycol monomethyl ether, Methyl Proxitol™ [Shell], Arcosolv™ PM [Lyondell], Dowanol™ PM [Dow]) and its corresponding acetate. Xylene (dimethylbenzene, mixed isomers), superficially, is the obvious substitute for toluene.

Xylene

As the article on p. 12 describes, xylene is not, at present, classed as a known human carcinogen, nor as a reproductive hazard. North American long-term (8 hour TWA) occupational exposure limits (ACGIH TLV, OSHA PEL,

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NIOSH REL) for xylene isomers are set at 100ppm, (435 mg/m^3), which is indicative of solvent generally in the category of intermediate health hazard [1]. To my mind, however, xylene is one of the more difficult solvents to evaluate with regard to health risk. A complicating factor is that many commercial grades contain substantial proportions (up to 30%) of ethylbenzene, which is a suspect carcinogen [2]. If, for peace of mind, one wants to avoid, or at least limit, problems deriving from ethylbenzene in products of mixed isomers xylene, with a bit of searching it is possible to find xylene products from laboratory chemical suppliers that are reportedly low in ethylbenzene. A quick search of MSDS sheets for general laboratory grade xylene products in the ranges offered by big U.S. lab suppliers identified, for example, a Fisher Scientific product with just 4% ethylbenzene. Other low ethylbenzene products could, no doubt, be found with a little more probing.

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
TLV	Threshold Limit Value
OSHA	Occupational Safety and Health Administration (U.S.)
PEL	Permissible Exposure Limit
NIOSH	National Institute for Occupational Safety and Health (U.S.)
REL	Recommended Exposure Limit
ppm	Parts per million
mg/m^3	milligrams per cubic meter of air
IARC	International Agency for Research on Cancer
MSDS	Material Safety Data Sheet
TWA	Time Weighted Average (typically 8-hour)
WEL	Workplace Exposure Limit (U.K.)
MEL	Maximum Exposure Limit (U.K.)
EU	European Union
EEC	European Economic Commission

Aromatic Hydrocarbons: Other Problems of Minor Constituents

Many conservators are familiar with aromatic naphthas: proprietary aromatic hydrocarbon solvent products, such as Shellsol™ A100, Shellsol™ A150, ExxonMobil's Aromatic (in Europe Solvesso™) 100, 150, 200, etc [3]. These solvents, which are higher boiling point analogues of toluene and xylene composed mostly of mixtures of aromatic hydrocarbons (aromatic 100 grades mostly C9-10 aromatic hydrocarbons; aromatic 150 grades mostly C10-11 aromatic hydrocarbons; and aromatic 200 grades mostly C10-14 aromatics), have similar solvency properties to the pure compounds and can be very useful in situations where lower volatility and slower evaporation are desirable. These are good solvents for acrylic resins, such as Paraloid™ B72, and most waxes. But most regular grades of the higher boiling point aromatic naphthas (150 and 200 grades) contain moderate amounts, usually 8 - 12%, of naphthalene.

Naphthalene is classified by the IARC (International Agency for Research on Cancer) as a category 2B carcinogen (possibly carcinogenic to humans) and, in the U.S., products containing greater than 0.1 weight percent naphthalene are required to reflect this classification on the Material Safety Data Sheet (MSDS). As well as being a category 2B carcinogen, naphthalene is a compound that is quite smelly; and being a planar aromatic molecule it adsorbs strongly onto surfaces, including hair and clothing. This problem can be reduced by using special grades of the high flash aromatic naphthas which have lower naphthalene contents. ExxonMobil, for example, manufactures ND (naphthalene depleted) grades of Aromatic 150 and 200 which have naphthalene contents of less than 1% w/w. ExxonMobil has at times also produced ULN (ultra-low naphthalene) grades containing less than 0.1%, about which I have heard positive comments from conservators. Although not presently reported in the range of products offered in North America on the ExxonMobil products website, I understand that some specialist industrial chemicals distributors can still obtain supplies of ULN Aromatic 150 and 200 on request [4].

Naphthenic Hydrocarbon Solvents

Finding safer, effective alternatives to aromatic hydrocarbon solvents remains a challenge, both for conservators as users and for the solvent manufacturers. By virtue of their chemistry, aromatic hydrocarbons have particularly good solvency properties in relation to their polarity; from the technical point of view, they are often hard to replace with alternatives that match in performance. A common approach to substitution of aromatics is to combine a non-aromatic (i.e. aliphatic) hydrocarbon solvent with, usually, minor amounts of a more polar solvent, typically from the group of alcohols, ketones, esters, or other oxygenated solvents. In this situation, there is an advantage to using an aliphatic hydrocarbon solvent with the strongest solvency properties. That position is held by saturated, cyclic hydrocarbon compounds: cyclohexane and its higher homologues, decalin, and related compounds, which are known in industry as cycloparaffinic or naphthenic hydrocarbons. Several specialty naphthenic solvent products are - or at least have been - available in the U.S. Some conservators may be familiar with two Shell products from this class that were near 100% cycloparaffins, Cypar™ 7 and Cypar™ 9, but unfortunately these solvents are now obsolete and have not been replaced with alternative grades [5]. Indeed, considering the good solvency and low health hazards of naphthenic solvents, it is interesting - though frustrating - that the major U.S.

hydrocarbon solvents manufacturers (Shell, ExxonMobil) currently do not offer many products of this type. ExxonMobil offers a naphthenic solvent with interesting and useful properties, Nappar™ 10 (bp. 155-190°C) in Europe and the Asia/Pacific region, but no similar product appears in the ExxonMobil range for North America. However, some naphthenic hydrocarbon solvents are available here in the U.S. in the form of products specifically formulated as replacements for xylene. One such product is Formula 83™ (boiling range: 119-145˚C / 246-293˚F) which is marketed as a substitute for xylene as a clearing solvent in histology [6].

Solvent Mixtures: Azeotropes

There are two main technical challenges to creating safer substitutes for aromatics by blending other solvents. One is to reproduce the same level of solvent power. The other is to control evaporation of the various individual components, which may have different boiling points or boiling ranges and rates of evaporation. The latter issue is especially important for solvent-based coatings (paints, varnishes, consolidants) where dry film properties may be strongly affected by any differential solvent evaporation. One solution to the problem of ensuring uniform evaporation of multi-component combinations is to use an azeotropic solvent mixture. A useful characteristic of an azeotrope is that the components evaporate at the same rate and the composition is maintained during the course of evaporation. In the past few years there has been a definite increase in applications of azeotropes within conservation, and this area of solvent technology offers still more potential for practical conservation operations, especially application of solvent-borne resin coatings, such as varnishes and retouching/inpainting media [7]. For paintings conservation practice, a reproducible azeotropic mixture of an aliphatic hydrocarbon solvent and a polar, oxygenated solvent which had a boiling point of about 150˚C and a polarity/solvent power similar to xylene would be really useful as a diluent, for example, for the Gamblin Conservation Colors. I'm sure one must exist.

Polarity Indicators

The polarity of an organic solvent cannot be measured absolutely, but to some degree it can be deduced from other measurable physical properties, such as the dipole moment (μ; unit = Debye, D) or the dielectric constant (ε, also called *relative permittivity*; dimensionless). Dipole moments of solvents fall within the approximate range 0 – 5 D. The dielectric constant ranges from about 2 for solvents with low polarity such as tetrachloromethane, up to 80 for water.

A number of solvent polarity scales rely on the property of *solvatochromism*, a term which is used to describe a pronounced shift in an absorption band in the uv/visible spectrum of a compound as a consequence of a change in the polarity of the medium. Reichardt proposed a scale of solvent polarity, E_T, based on colour changes caused in a pyridinium-N-phenoxide betaine dyestuff in solution. The Reichardt E_T scale has the dimension of kcal/mol and ranges from about 30 for non-polar solvents, such as paraffins, to 63 for water. More recently, Reichardt's normalised polarity values, E_T^N, have been recommended. E_T^N values range from zero for very non-polar liquids, such as tetramethylsilane, up to 1.00 for water.

Solvatochromatographic parameters (π^*, α, β) of Kamlet, Abboud, Taft and co-workers

Kamlet, Abboud & Taft created a solubility parameter equation - a linear solvation energy relationship (LSER) - that was intended to be able to predict every kind of interaction between solvents and solutes. The solvatochromatographic comparison method, as it was called, was claimed as a means to "unravel, quantify, correlate, and rationalize multiple interacting solvent effects on many types of physicochemical properties and reactivity parameters." The Kamlet, Abboud & Taft system is essentially a three-parameter system that focuses on the strong, polar intermolecular interactions:

- π^* is an index of solvent polarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect;
- α is a scale of hydrogen-bonding donor acidity, which is the ability of the solvent to donate a proton in a solvent-solute hydrogen bond; and
- β is a scale of hydrogen-bonding acceptor basicity, which is the ability of the solvent to accept a proton (or donate an electron pair) in a solvent-solute hydrogen bond.

A fourth, polarizability correction factor, δ, is included for some solvents (e.g. aromatics and polyhalogenated solvents) to correct for differences in the polarizability contribution to π^*.

Halogenated Solvents

Of all the main chemical types of solvents, perhaps the greatest changes in regulation of use have occurred with the halogenated solvents, because of hazards to human health and to the environment. The latter concern derives from the adverse effects of this type of compound on atmospheric ozone and on aquatic organisms. The health hazards associated with the fully halogenated compound tetrachloromethane (carbon tetrachloride) were well known even when I was a conservation student in 1982, and this substance rightly was effectively obsolete by then. However, its sister compound dichloromethane (methylene chloride) has remained an important solvent, primarily as the principal ingredient in many commercial paint and varnish strippers. In most parts of the world, use of dichloromethane is now highly restricted, primarily by very low permissible occupational exposure limits: OSHA PEL values are long-term 25ppm (87 mg/m^3), short-term 125ppm (435 mg/m^3); in the U.S. it is classed as a category 3A carcinogen.

In Europe, at least at the time of writing, use of dichloromethane is less tightly controlled by occupational exposure limits (UK WEL/MEL 8hr TWA long-term 100ppm (350 mg/m^3), short-term 300ppm (1060 mg/m^3), and its classification as a carcinogen is less firmly imposed: dichloromethane is a Category 3 carcinogen in the EU where it is assigned the risk phase R40 'Limited evidence of carcinogenic effect'. However, this situation is changing rapidly, and it is probable that by June 2009 legislation will be in place within the EU that prohibits the supply of dichloromethane-based paint strippers to the general public and to professional users [8].

The move away from dichloromethane as the basis of paint strippers has been underway for some time [9] and it seems likely that commercial developments will continue apace in light of the probable changes in European regulations. For many years, conservators have explored alternatives to dichloromethane for use in paint removal. One group of solvents which seems promising is that of dibasic esters (DBEs), which includes such compounds as dimethyl adipate, dimethyl succinate and dimethyl glutarate [10]. Although they have rather high boiling points and probably don't quite match the solvency/swelling power of dichloromethane, it is likely that these environmentally-friendly, water-miscible solvents will become increasingly familiar in years to come. DBEs are now seemingly used in quite a number of commercial paint stripper products, usually in combination with other solvents, often strongly dipolar, highly active substances, such as N-methyl-2-pyrrolidone (NMP), dimethylsulphoxide (DMSO), propylene carbonate and the like [11].

Green Solvents

The dibasic esters mentioned above are sometimes referred to as 'green' solvents or biosolvents, since they are mostly manufactured from biological, usually plant, sources. Another increasingly popular green solvent is ethyl lactate (ethyl 2-hydroxypropanoate), which finds use in products such as degreasers, paint strippers, and graffiti removers. Current interest in green solvents (and in 'green chemistry', generally) among both chemists and within the industry is escalating to the point where whole journals, books, and conferences are devoted to these subjects [12].

Although some principal areas of green solvent chemistry research, such as ionic liquids, will be of marginal relevance to conservation, the emergence of new, environment-friendly organic solvents is worth keeping an eye on. For example, it was interesting to discover that Sigma-Aldrich is now marketing two products, 2-methyltetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME), specifically as 'green' alternatives. Additionally, supercritical carbon dioxide is now finally being used in conservation, mostly for cleaning purposes, after delays in acceptance that perhaps can be attributed to cost and accessibility of the necessary equipment [13]. Liquid carbon dioxide is just one of several approaches that have been adopted as a substitute for the once ubiquitous dry cleaning solvent perchloroethylene (1,1,2,2-tetrachloroethene), now also a suspect carcinogen, for which a variety of other solvents have also been proposed: hydrocarbons, *n*-propyl bromide, siloxane (silicone) fluids, and others.

The Teas Fractional Solubility Parameter Diagram

Back in 1982, the primary vehicle for explaining solvent behaviour from the theoretical point of view was the fractional solubility parameter system of J-P Teas and his now familiar triangular solubility diagram, which was first published in 1967. It is interesting that the Teas fractional solubility parameter system remains still the principal system used in conservation for describing solvent power and selectivity, even though its shortcomings are now well established [14]. Currently, the Teas chart is rarely used in fields of science/technology outside of conservation; other solvent descriptor systems are preferred. Nowadays, the focus is on *polarity* and indicators of this chemical characteristic, such as the Reichardt, solvent polarity scales, E_T and E_T^N, and on solvatochromatographic solubility descriptor approaches which, again, focus on various types of polar intermolecular interaction. Of the latter, the π^* (solvent polarity/polarizability), α (hydrogen-bonding donor acidity), β (hydrogen-bonding acceptor basicity) parameters of Kamlet, Abboud, Taft and co-workers are perhaps the most widely recognized.

Alongside other, more scientifically rigorous, solubility parameter systems, there remains a use for the Teas chart within conservation, which is after all a visual discipline. Its primary virtue is that it allows easy graphic representation of solvent characteristics; it's a kind of map - albeit an imperfect one - to safer solubility. The important thing, perhaps, is to understand its theoretical shortcomings insofar as these influence how one uses the map to navigate the murky waters of solubility.

Conclusion

Reflecting on these developments in solvent technology over the past quarter of a century or so, it is evident that conservators now have a much broader range of options open to them when it comes to selecting organic solvents for treatment operations. At one level, better understanding of the shortcomings of some of the customary solvents has been complemented by increased awareness of effective, safer, less-polluting alternatives. But I have become aware, too, that some misconceptions about solvents pervade the discipline of conservation. The notion that "all organic solvents are toxic," which one encounters occasionally in our field, is one such example which does not hold up under close analysis.

It might be observed also that, as a field, we are still perhaps a little too attached to a rather outdated theoretical framework (i.e. the Teas chart) for understanding the properties and activity of organic liquids as solvents, and we have some collective catching up to do in order to properly integrate current perspectives on solvency science into conservation theory and practice.

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Note: This article follows British style conventions, by author's request.

Notes and References

[1] Permissible levels of xylene in the workplace are more tightly restricted in Europe: for example, the current U.K. long-term (8 hour TWA) Workplace Exposure Limit (WEL) is set at 50ppm (220 mg/m^3).

[2] At the present time (2009), neither toluene nor xylene is available as a specific product in the range of solvents offered in the Americas by Shell Chemicals or by Exxon Mobil. Xylene is manufactured and distributed by Shell in Europe and the Asia/Pacific regions: ethylbenzene content of those products is said to be 10-30%.

[3] These solvents are usually manufactured to be compliant with ASTM D-3734-05 Standard Specification for High-Flash Aromatic naphthas. The suffixes '100' and '150' derive from their approximate flash points in °F.

[4] For example, Univar, Commerce, CA 90040. www.xunivarusa.com

[5] A few current Shell aliphatic hydrocarbon solvents are noted as having high naphthenic content; for example, VM&P Naphtha HT (Americas, 67% cycloparaffins) and Shellsol™ W HT (Americas, 55% cycloparaffins).

[6] CBG Biotech, 2211 Lake Club Drive, Columbus, Ohio 43232. See: http://www.cbgbiotech.com/f83.html

[7] See, for example, Augerson, C. 2000. The use of less toxic solvents in the treatment of a Royal French sleigh, ca. 1720. In *Postprints: AIC Wooden Artifacts Group*, AIC 28th annual meeting, Philadelphia, June 2000. 2-15.

[8] Proposal for a Decision of The European Parliament And Of The Council amending Council Directive 76/769/EEC as regards restrictions on the marketing and use of certain dangerous substances and preparations (Dichloromethane) COM (2008) 80 final; 2008/0033 (COD), Brussels, 14.2.2008.

[9] Wollbrinck, T. 1993. The composition of proprietary paint strippers. *Journal of the American Institute for Conservation* 32 (1): 43-57

[10] Evans, J. 2005. The fine art of stripping: a chemistry problem in conservation. *Chemistry in Australia* (March): 8-11. (http://www.raci.org.au/chemaust/docs/pdf/2005/CiAMarch2005p8.pdf)

[11] See, for example, Invista Dibasic Esters (DBEs) in *Paint Stripping Applications*. http://intermediates.invista.com/doc/files/320/DBE%20for%20Paint%20Stripping%20Applications.pdf

[12] Nelson, W.M. 2003. Green solvents for chemistry: perspectives and practice. Oxford: Oxford University Press.

[13] See, for example, Sousa, M., Melo, M.J., Casimiro, T. and Aguiar-Ricardo, A. 2007. The art of CO_2 for art conservation: a green approach to antique textile cleaning. Green Chem. 9: 943.

[14] Phenix, A. 1998. Solubility parameters and the cleaning of paintings: an update and review. *Zeitschrift für Kunsttechnologie und Konservierung* 12 (2): 387-409

FAIC Samuel H. Kress Foundation Conservation Publication Fellowship

FAIC is pleased to announce that the FAIC Samuel H. Kress Conservation Publication Fellowship Committee has awarded a 2009 fellowship to Mary-Lou E. Florian.

This is the first time that the Fellowship Committee has recommended funding for an author who was previously awarded a Fellowship. Ms. Florian's 1999 Fellowship led to the publication of her widely-used books, "Fungal Facts" and "Protein Facts."

Ms. Florian will be writing on "Cellulosic Facts: Cellulosic Materials in Heritage Objects; Structure, Chemistry, Identification, and Conservation Concerns." The book will be a general reference on the topic, and will cover common cellulosic material used in historic, ethnological, and archaeological textiles, paper, wooden objects, baskets, ropes, etc. The materials' structural morphology, cellular anatomy, and alternation by manufacturing processes, relevant to its physical stability and deterioration, will be presented. The relevant chemistry of cellulose will be discussed in reference to chemical, physical, and biological deterioration. Methods of identification and analysis of deterioration will also be covered.

FAIC anticipates awarding two fellowships in 2010. The application deadline is November 1, 2009. Guidelines and forms can be found on the AIC-FAIC website.