A Novel Approach to Cleaning II: Extending the Modular Cleaning Program to Solvent Gels and Free Solvents, Part 1

by Chris Stavroudis and Tiarna Doherty

This article has been divided into two parts. This first section deals with principles of solubility and presents the interactive graphical display created to illustrate solubility parameters. The second will discuss the formulation of Carbopal gels and use of the Modular Cleaning Program.

Abstract

The Modular Cleaning Program (MCP) was originally conceived to assist the conservator in the formulation and selection of aqueous cleaning systems. Upon using the system, it became apparent that many of the advantages of the approach could also be applied to both solvent gels and free solvents.

The two overarching principles of the MCP are the use of small amounts of stock solutions that can be mixed to make a large number of test cleaning solutions and the use of physical constants as a basis for all calculations. The conservator decides on a cleaning strategy and uses the program to work though variables to determine the optimal cleaning system. The computer takes care of the bookkeeping issues associated with formulating complex mixtures. The software provides a context showing which parameters may be changed in a cleaning, and the conservator chooses the direction of the testing.

Using small volumes of test solutions offers advantages in cost, ecological impact, and heath and safety by minimizing exposure and waste. The speed and ease with which test solutions can be formulated allows many more cleaning options to be tested and evaluated than was previously practical when each test solution had to be made from scratch.

This paper will focus on the design of the solvent and solvent gel capabilities of the program, which will enable a conservator to approach a cleaning using a mixture of free solvents or a set of stock solvent gels that can be mixed together.

The MCP incorporates a new theory for formulating solvent gels. The theory, based on empirical observation, postulates physical-chemical structures for Carbopol-based gels. These structures have been used to calculate the gel formulations. A group of solvent gels has been integrated into the new graphical display of solvent parameters, allowing the conservator to navigate visually through the selection of gel combinations. These features are not fully integrated into the current version of the MCP, but are included in the next version which is being debugged as you read this.

The clearance of Carbopol-based gels will also be addressed within the database. Recommendations for clearance mixtures will be based on the solubility range of the Carbopol/amine present in the gel or gel mixtures and are calculated in Hansen Solubility Space. As yet, this feature is not incorporated into the database, but research is ongoing.

Introduction

The Modular Cleaning Program evolved as an extension of the Gels Research Project at the Getty Conservation Institute. Valerie Dorge, Dusan Stulik, and Richard Wolbers wished to codify, in the form of a "logic tree," the thought process that a conservator would follow to arrive at a successful gel cleaning (Dorge 2004).

Using the logic tree concept as a basis, Chris Stavroudis developed the first version of the MCP, which dealt with aqueous cleaning. It incorporated the use of concentrated stock solutions in set amounts (the "modules") that could be mixed into a wide range of test solutions. The modular system reduced the time necessary to test variables and, more significantly, enabled the conservator to fine tune a cleaning system. After demonstrating the prototype MCP at the Getty Museum, Tiarna Doherty and Stavroudis discussed adapting the methodology to cleaning with solvent gels. The concept was discussed extensively with Richard Wolbers, who also thought there was considerable potential in the idea.

A number of methods were tested for quickly preparing a solvent gel of any polarity from pre-mixed components (Appendix B). It was determined that the most workable approach was to use pre-mixed gelled solvents that could be combined with each other. As with the aqueous system, the conservator would use the stock solvent gels to mix a small amount of almost any solvent gel necessary for testing in a matter of minutes.

In an analogy with inpainting, the set of stock gels can be thought of as the palette, and the individual gels are the different paints. By mixing differing amounts of the paints together, the conservator can match any color within the gamut of the inpainting palette. Similarly, by mixing different amounts of solvent gels in the solvent gel set together, a test gel of any intermediate solvent strength can be formulated. The gel palette differs from paints in one significant way, however. While any paint in the same medium can be mixed with any other, regardless of where they fall on the spectrum, gels need to have compatible polarities. Accommodating this requirement meant widening the solubility range of each stock gel.

The ability to create a gel for a solvent blend depends on the amine used to neutralize the Carbopol and the polarity of the solvent mixture. Typically, Ethomeen C/25 (polyethoxylated cocoamine), Ethomeen C/12 (di ethanol cocoamine), or Armeen 2C (dicocoamine) are the bases used to react with the polyacrylic acid groups that constitute the Carbopol polymer. The amines are also surfactants and the differences in the hydrophilic and hydrophobic character of each determines the polarity of the Carbopol/amine combination. If the polarity of the Carbopol/amine combination is compatible with that of the solvent mixture, the Carbopol polymer, along with its neutralizing amines, can unfurl and impart a three-dimensional framework to hold the solvents in a gel. However if the polarities are incompatible, the gel collapses into a mixture of sticky goo floating in solvent.

In order to extend the solubility range, the idea was developed of using two bases to neutralize the Carbopol in a gel. This is the rationale and genesis of the so-called "dual neutralization gel" which we will discuss later. An additional benefit from widening the solubility range of each gel is that a wider range of solvent mixtures could be used to clear the gel.

To formulate a gel-based test cleaning system it was necessary that solubility theory be incorporated into the MCP. Providing this information would allow the MCP to be used for solvent-based cleaning as well as serve as a framework for discussing the clearance of solvent gels. For the MCP to support solubility theory, physical constants from various sources had to be added to the database. As will be discussed shortly, these physical constants are used to calculate solubility parameters and predict solvent behavior.

Solubility

Solubility theory can best be considered an extension of the fundamental concept: "like dissolves like." The more a solvent and solute are chemically similar at the molecular level, the better the solvent will dissolve the solute. Of course, solubility is much more complicated than that, which can be seen in the complexity of the numerous solubility theories offered in the literature and the several systems developed to describe the behavior, i.e. solubility parameters, of a solvent. (Feller, Stolow, & Jones 1959; Torraca 1978; Hedley 1980; Burke 1984; Blank & Stavroudis 1989; Phenix 1998). Here, only solubility theory as it relates to the MCP will be discussed.

The single Hildebrand solubility parameter, ∂, is an aggregate measure of all intermolecular forces attracting one molecule to another. It is worth mentioning that Hildebrand and Scott proposed an equation (see Appendix A) that gives an estimate of ∂ based on the boiling point of a solvent. This serves to further emphasize the relationship between the process of evaporation and solubility. It also means that with minimal information, simply knowing a solvent's boiling point, molecular weight and density, we can estimate its solubility parameter.

However, the Hildebrand system has limitations, as can be seen when considering two very different solvents like n-propanol and dimethylformamide, which have nearly identical Hildebrand solubility parameters and yet have very different characteristics in cleaning works of art. Intermolecular forces arise from more than one sort of attraction and each form of attraction contributes to the total intermolecular force.

Charles Hansen took Hildebrand's solubility parameter and resolved it into three component parameters, proposing that the total energy holding molecules together was the sum of the energy arising from three component forces: dispersion forces, dipolar forces, and hydrogen bonding forces. Hansen's three parameters are related to the total (Hildebrand) solubility parameter by the equation:

$$\partial^2 = \partial d^2 + \partial p^2 + \partial h^2$$

The MCP uses Hansen's solubility theory as the basis for calculations involving solvents and solvent gels. Because the MCP enables the conservator to manipulate solvent mixtures and gels using solubility theory, it is worthwhile to review the component forces in Hansen, Teas, and other similar theories.

Dispersion forces (∂d) are the intermolecular forces that attract all molecules to one another. They are comparatively weak and are responsible for hydrocarbons like heptane being liquid and larger molecules, like waxes, being solids. Also called London or van der Waals forces, they are explained by quantum mechanics. When molecules are in close proximity, the electron cloud of one molecule induces a distortion in the adjacent molecule's electron cloud. The distortion causes a net attractive force despite the fact that the electron clouds should really repel one another. Van der Waals forces are related to the surface area of a molecule and function only at close distances. So greater structural similarity between solvent and solute allows molecules to pack closer together and have more area in common, thereby increasing the van der Waals attractive force.

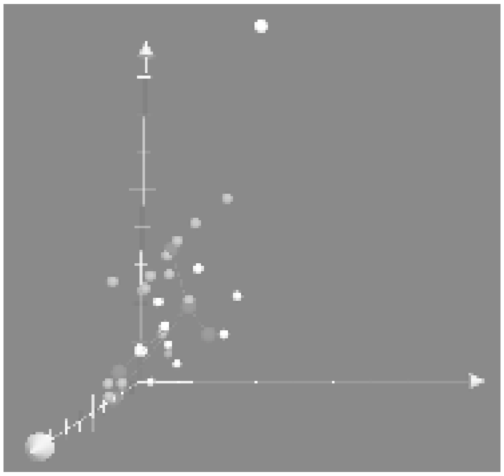
Dipolar forces (∂p) are often, and incorrectly, referred to as polar forces, as the actual phenomenon of polarity results from a combination of forces. Adding to the confusion, because the subscript 'd' is already taken for dispersion forces, they are noted by the subscript 'p'. Dipolar forces arise from electrostatic attractions between molecules. They arise from permanent dipoles created by the molecular structure, where partial positive charge is separated in space from partial negative charge in the same molecule. Partial positive charges on one molecule are attracted to the partial negative charges on an adjacent molecule. Dipoles can also be induced into molecules that don't normally possess a permanent dipole resulting in a net attractive force between the molecules. Dipolar forces are the predominant intermolecular force in ketones.

Hydrogen bonding interactions (∂h) are the strongest of the intermolecular forces. Hydrogen bonds are temporary bonds that form between hydrogen atoms attached to a strongly electronegative atom (O, N, F) in one molecule and another strongly electronegative atom in an adjacent molecule (or, in larger molecules, in the same molecule). This temporary bond forms because the first strongly electronegative atom pulls the electron cloud from around the hydrogen molecule, leaving a somewhat exposed proton nucleus. If a strongly electronegative atom in an adjacent molecule likewise has pulled the electron clouds from atoms within its molecule, it will have acquired a partial negative charge, and will be attracted to the partial positive charge of the hydrogen proton. Hydrogen bonding is predominant in alcohols.

Unfortunately, hydrogen bonds behave more like an acid-base reaction than a simple attractive force, and this is a weakness of the Hansen solubility theory. However, in most cases, the Hansen partial solubility parameters work fairly well, and they are used in the solubility calculations in the MCP.

J.P. Teas took Hansen's three partial solubility parameters, normalized them, and then plotted them on a triangular graph. The Teas diagram offers a graphical view of solvent strength that is well known to conservators. There are many excellent references in the conservation literature that discuss the use of the Teas diagram (Burke 1984; Torraca 1978; Hedley 1980), four computer programs that make calculations based on the Teas parameters (Henry 1989; Bertolli and Cremonesi; Ormsby; GELOdata) as well as treatments of solubility theory much more comprehensive than that presented here (Phenix 1998; Phenix and Sutherland 2001; Phenix 2002). Unfortunately, the Teas chart has other problems (Phenix 1998; Blank and Stavroudis 1989) which compound the limitations of Hansen partial solubility parameters, hence the use of the Hansen parameters for calculations in the MCP.

There are buttons in the MCP to display the solvent positions in Hansen 3 dimensional space or on a 2 dimensional Teas diagram. (As of this writing the 2 dimensional plotting does not yet work.) The feature only works on the Macintosh platform and uses the program "Grapher.app" which is included with current Mac operating system software. The process is a bit cumbersome, but allows visualization of Hansen space and the solvent mixture being considered (figure 1).



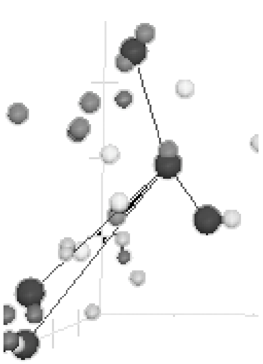


Figure 1
A view of Hansen space as visualized by Grapher.app.

The enlarged detail, with the background converted to white, shows the lines connecting the four component solvents to the mixture of the four in the center.

Various tabulated Hildebrand and Hansen solubility parameters have been entered into the MCP. Where sufficient raw data is available, the MCP also calculates the Hildebrand and Hansen solubility parameters via a number of calculations as explained in Appendix 1. The MCP preferentially uses the published, tabulated values from: "Hansen and Beerbower's 1971 Parameters for Liquids at 25°C" as published in Barton, Table 11 (1991).

There is one more complication to mention: the formation of azeotropes. An azeotrope is a particular mixture of solvents that has a boiling point minimum (or maximum) lower (or greater) than the starting components. As conservators, we are only interested in azeotropes that show a minimum boiling point. Hildebrand solubility parameter can be calculated from a solvent's boiling point. The boiling point of an azeotrope is lower than either of the component solvents. This means that an azeotropic mixture of solvents will have an anomalous solubility parameter. This anomaly is not calculated for in the MCP. However, the MCP does alert the conservator of any binary or ternary azeotropes that might exist for the mixture under consideration.

Aging and Solubility

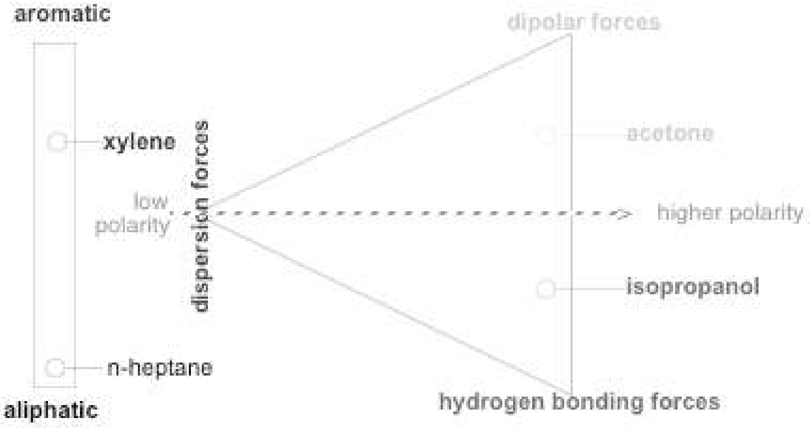
So, after all of the theoretical discussion, one is back to "like dissolves like," with the proviso that "like" be evaluated on a decidedly chemical basis. Of the many "cleaning" scenarios in conservation, probably the most common is dissolving one material from another where the second material was deposited in a "mild" solvent but the coating, adhesive, or paint has changed with time and no longer dissolves in the solvent in which it was deposited. The change in solubility of the second material upon ageing is typically caused by any of four possible chemical changes. An organic material can oxidize, form double, often conjugated double, bonds (i.e., yellow), increase in molecular weight by cross-linking, or reduce its molecular weight by chain scission. (Only the first two are of significant interest in this discussion.)

In a very simplistic way, oxidation of paint or varnish can be considered as the addition of alcohol or ketone groups (or both when forming a carboxylic acid) to the material. To re-dissolve oxidized material, the polarity of the solvent has to increase by moving towards either higher dipolar strength solvents or higher hydrogen bonding solvents (or both). Ultimately, oxidation can require such high polarity solvents that an aqueous cleaning system may be considered.

Similarly, yellowing can be thought of as the addition of unsaturation (double bonds) to the structure. It might be too broad a generalization of "like dissolves like," but it is a convenient oversimplification to try to re-dissolve yellowed material by increasing the proportions of double bonds by increasing the aromatic character of the solvent.

Applying Solubility Theory

It was necessary to make some adaptations to the original MCP so that it would work with solvents, both free solvents



To use the diagram – which, please remember, is designed to be a tool and not a new theory – one selects a solvent to represent each solvent class: aromatic, aliphatic, dipolar, and hydrogen bonding. Then by changing the proportions of these solvents the database can calculate the polarity and aromaticity of the solvent mixture. In the MCP, the polarity triangle and A/A bar are interactive. As the composition of the test solvent is changed, the position of the dots (one in the polarity triangle and one in the A/A bar) move, providing a visual reference for the conservator.

Figure 2. The graphical display which illustrates solubility space in the MCP. There are two separate but related elements in the diagram: the polarity triangle and the aromatic/aliphatic (A/A) bar.

and gels. Adding data on solvents to the MCP was easy, although tracking down many of the physical constants required referring to a number of different reference sources (Lide 2002; Weast 1972; Budavari 1989; Gmehling et al. 2004). Adding the algorithms for working with mixtures of solvents in Hansen space, calculating Teas values and NFPA hazard ratings was more of a challenge. The most difficult task was to come up with an interface that made sense of the numbers generated by the computer and an intuitive means for the conservator to interact with the model.

As always when three variables are interacting, the best way to illustrate it is in three dimensions. Unfortunately, practically speaking this is awkward to display and interpret.

Hence, the most significant change in the MCP is an interactive, graphical display of solvent parameters (figure 2) for working with both solvent mixtures and solvent gels. This display is based on Hansen solubility parameters and a new parameter, which we have called the aromatic/aliphatic index. This diagram does not represent a new solubility theory but is a visualization tool for the conservator. You will notice that a few familiar solvents have been indicated on the diagram.

Examining the polarity triangle one sees that the three apexes are labeled dispersion forces, dipolar forces, and hydrogen bonding forces. While this may superficially resemble the Teas Diagram, it is not the same at all. The horizontal line from the left apex represents increasing polarity (in the broader sense of the term) and is the source of the triangle's name. The increased polarity results from increasing hydrogen bonding forces, dipolar forces, or both. This trend can be thought of corresponding to oxidation in our simple model of the aging of organic materials.

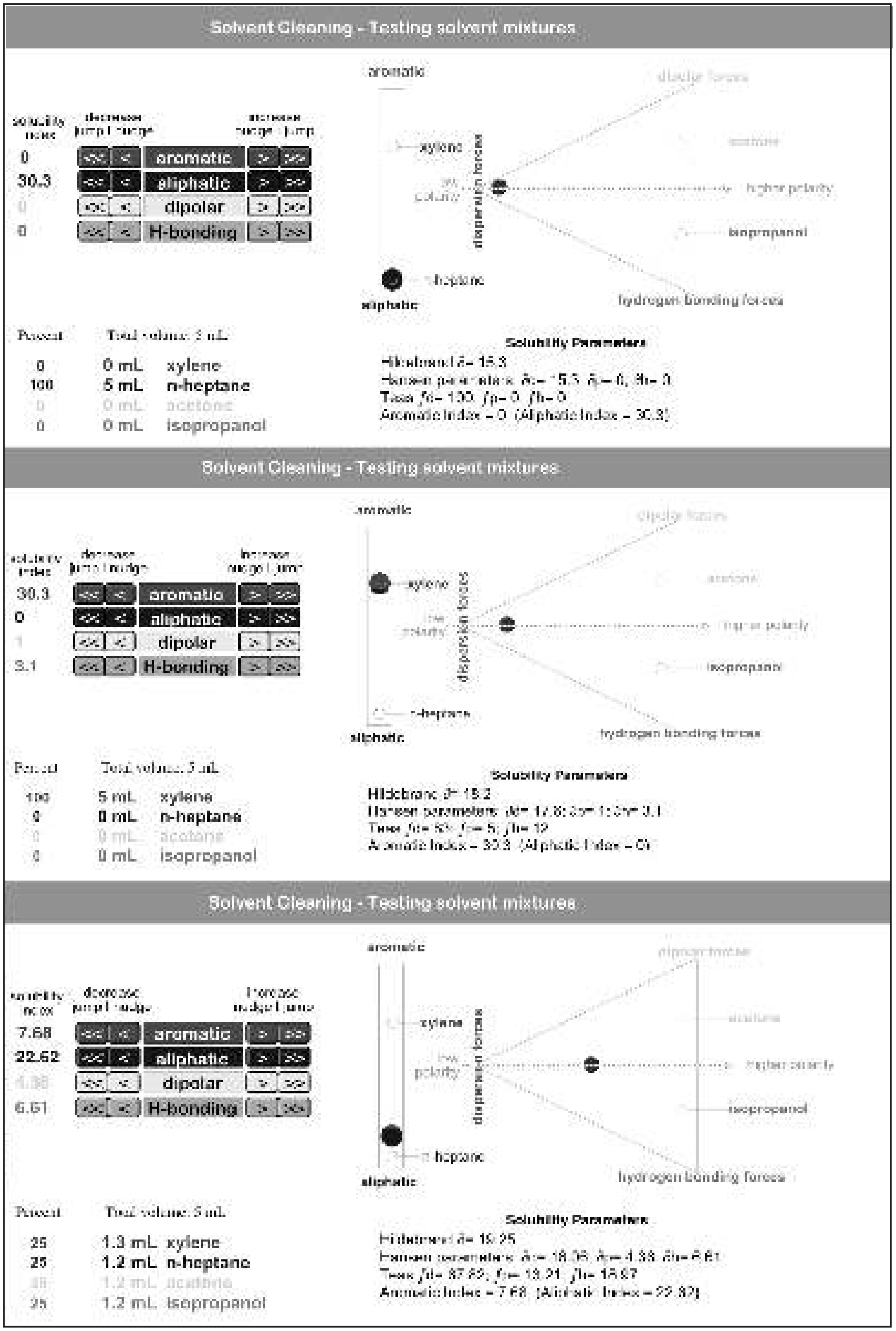
The previous discussion of aging posits that yellowing is attributable to the formation of double bond and that double bonds require aromatic content to solubilize them. From the perspective of the conservator, solubility theory is not entirely satisfying in reflecting the subtlety of differences between aromatic and aliphatic solvents. To demonstrate the influence of the y axis dispersion forces, the vertical axis of the diagram has been detached, as it were, and laid flat.

When the proportions of a solution change, and its inter- and intra-molecular forces change, two dots appear on the new version of the diagram. One, on the triangle, demonstrates its character relative to dipole forces and hydrogen bonding (solution polarity), while dispersion forces are demonstrated on the aromatic/aliphatic bar. (The A/A bar is not an actual measure of the dispersion forces, but reflects the ratio of aromatic to aliphatic in the solution. See Appendix B for a discussion of how the aromatic/aliphatic index is determined.) When the proportions change again, these move simultaneously to show the new set of behavior characteristics. (figure 3)

The next installment of this article will present our ad-hoc theory of Cabopol based solvent gel formation and will discuss how this empirically derived model is used in the MCP to assist with solvent gel formulation. We will then discuss in further detail how an understanding of solubility theory can suggest approaches to cleaning with solvents and solvent gels and how the MCP can assist with formulating cleaning systems. We will also consider how future research will allow us to determine the solvent mixtures that will most effectively clear a specific solvent gel formulation by using Hansen solubility space calculations to determine how "good" a solvent or solvent mixture will be at keeping a given gel in a happy place, from a solubility perspective.

The MCP is available as freeware. Conservators must register before the software will work in an effort to keep non-professionals from thinking that a computer program can substitute for a professional conservator.

x



solubility index	
0	aromatic
30.3	aliphatic
0	dipolar
0	H-bonding

Percent	Total volume: 5 mL	
0	0 mL	xylene
100	5 mL	n-heptane
0	0 mL	acetone
0	0 mL	isopropanol

Solubility Parameters

Hildebrand δ= 15.3
Hansen parameters: δd= 15.3, δp= 0, δh= 0
Teas fd= 100, fp= 0, fh= 0
Aromatic Index = 0 (Aliphatic Index = 30.3)

solubility index	
30.3	aromatic
0	aliphatic
1	dipolar
3.1	H-bonding

Percent	Total volume: 5 mL	
100	5 mL	xylene
0	0 mL	n-heptane
0	0 mL	acetone
0	0 mL	isopropanol

Solubility Parameters

Hildebrand δ= 18.2
Hansen parameters: δd= 17.8; δp= 1; δh= 3.1
Teas fd= 83; fp= 5; fh= 12
Aromatic Index = 30.3 (Aliphatic Index = 0)

solubility index	
7.68	aromatic
22.62	aliphatic
4.38	dipolar
6.61	H-bonding

Percent	Total volume: 5 mL	
25	1.3 mL	xylene
25	1.2 mL	n-heptane
25	1.2 mL	acetone
25	1.2 mL	isopropanol

Solubility Parameters

Hildebrand δ= 19.25
Hansen parameters: δd= 18.06, δp= 4.38, δh= 6.61
Teas fd= 67.62; fp= 13.21, fh= 18.67
Aromatic Index = 7.68 (Aliphatic Index = 22.62)

Figure 3. Three views of the solvent cleaning screen in the MCP, showing n-heptane alone, xylene alone, and a 1:1:1:1 mixture of n-heptane : xylene : isopropanol : acetone

Slightly Technical Appendices:

Appendix A – Solubility Parameter Calculations

To calculate the Hildebrand solubility parameter of a solvent, one looks up values for the enthalpy of vaporization, its molecular weight and density. The MCP calculates the Hildebrand solubility parameter from the following equation:

$$\partial = [(\Delta H - RT)/V_m]^{1/2}$$

V_m, the molar volume, is simply the molecular weight of the solvent divided by its density, R is the gas constant, and T is the temperature in degrees Kelvin. However, ΔH, the enthalpy of vaporization is a complicated quantity to measure experimentally. Hildebrand and Scott proposed an empirical equation that relates the enthalpy of evaporation to the boiling point of the solvent:

$$\Delta H \approx -12340 + 99.2(T_b) + 0.084(T_b)^2$$

where T_b is the boiling point of the solvent in degrees Kelvin.

In earlier versions of Hansen's work, he proposed equations to determine the dipolar and hydrogen bonding parameters based on measurable constants. Hansen used the Böttcher equation to generate estimates for the dipolar solubility parameter via:

$$\partial_p = 2.0455 * [(12108 / V_m^2) * (\varepsilon - 1) /(2\varepsilon + n_D^2) * (n_D^2 + 2) * \mu 2]^{1/2}$$

where ε is the dielectric constant, n_D is the index of refraction, and μ is the dipole moment of the solvent (Hansen 1967, p. 25).

Likewise, Hansen proposed that the hydrogen bonding partial solubility parameter could be calculated for alcohols by dividing the energy of a hydrogen bond (5000 cal., determined from the IR spectra for a typical H---OH hydrogen bond) by the molar volume:

$$\partial_h = 2.0455 * [5000 * A/V_m]^{1/2}$$

where A is the total number of alcohol groups in the molecule (Hansen 1967, p. 24). In both equations, the factor 2.0455 converts from older cgs units of $[\mathrm{cal/cm^3}]^{1/2}$ to the S.I. units of $[\mathrm{MPa}]^{1/2}$ where MPa are megaPascals.

The MCP calculates the Hildebrand solubility parameter from both measured ΔH values and the boiling points of the solvents if there are sufficient physical constants in the database. If additional constants are available, it will also calculate the dipolar and hydrogen bond Hansen parameters from the above equations and calculate the dispersion parameter by difference. Many of the constants have been located in reference sources, but not all information is available for all solvents. Mixed solvents, such as mineral spirits, etc., of course don't possess these values as we are not privy to the chemical composition of these solvent mixtures but the manufacturer often provides the Hildebrand solubility parameter.

Appendix B – The Aromatic/Aliphatic Index

One way to estimate the difference in energy between aromatic and aliphatic compounds is to compare benzene and cyclohexane. Examining the pattern of the heat of hydrogenation between cyclohexane, cylohexene, and cyclohexadiene and extrapolating that pattern to a non-existent, non-aromatic, cyclohexatriene, and then comparing that value to benzene, one finds a resonance energy of 36 kcal from the formation of an aromatic ring. This value is also consistent with the heat of combustion (Morrison and Boyd 1973, p. 323).

Paralleling the way Hansen originally defined the hydrogen bonding partial solubility parameter (above), we have proposed an aromatic/aliphatic index as the resonance energy of an aromatic ring divided by 6 (for the six carbons in both molecules) times the number of aromatic atoms (#A) in the molecule and then multiplied by the number of aromatic atoms divided by the total number of carbons (#C).

$$\text{Aromatic index} = 2.0455 * [36{,}000 * (\#A/6) * (\#A/\#C) / V_m]^{1/2}$$

While this definition is arbitrary, a list of aromatic solvents and their aromatic/aliphatic indices feels right in terms of practical solvent power. Table 1 shows the aromatic/aliphatic index for a number of familiar solvents along with their aniline point, kauri-butanol number, Reichardt's E_T^N values, and Freed's Spectral Polarity Index, P_s.

There are certainly other ways of formulating a ranking of aromatic strength, and from the perspective of the MCP, any could be used. (And if a more sensible schema is proposed, it could be incorporated into the MCP.) Unfortunately, the Percent Aromatic value that is often found in solvent specifications is quite misleading. ASTM defines the value of percent aromatic as the volume percent of a constituent component that contains an aromatic structure. So, by that definition, xylene, toluene, and benzene are all 100% aromatic.

Table 1 The Aromatic/aliphatic index compared with other polarity measurements.

Solvent	Aromatic/ aliphatic index	% of benzene	Aniline point	% of heptane	Kauri butanol #	% of benzene	E_T^N	% of benzene	P_s	% of benzene
Benzene	41.1	100%	22°F	14%	112	100%	0.111	100%	6.95	100%
Toluene	34.9	85%	47°F	30%	105	94%	0.099	89%	6.58	95%
Xylene	30.3	74%	48°F	31%	98	88%	0.074	67%	6.27	90%
Diethyl benzene	24.1	59%								
heptane	0	0%	154°F	100%	30	27%	0.012	11%	2.77	40%

Acknowledgements

The authors would like to thank Alan Phenix for his discerning comments and suggestions and Carolyn Tallent for an extraordinary amount of editorial collaboration.

References

Barton, A.F.M. 1983. *CRC Handbook of Solubility Parameters and other Cohesion Parameters*. Boca Raton: CRC Press, LLC.

Barton, A.F.M. 1991. *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, 2nd Edition. Boca Raton: CRC Press, LLC.

Bertolli, I. and Cremonesi, P. 1999. Un approccio più scientifico alla pulitura dei dipinti. Triansol ®: il Triangolo delle solubilità, un software per il restauro. *Progetto Restauro,* 10: 42–45.

Blank, S. and Stavroudis, C. 1989. Solvents and Sensibility, Parts 1-3. *WAAC Newsletter,* 11(2): 2-10.

Budavari, S. ed. 1989. *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 12th Edition. Whitehouse Station: Merck & Co.

Burke, J. 1984. Solubility Parameters: Theory and Application. *The Book and Paper Group Annual,* 3: 13-58.

Dorge, V. ed. 2004. *Solvent Gels for the Cleaning of Works of Art*. Los Angeles: Getty Publications.

Feller, R., Stolow, N., and Jones, E. 1959. *On Picture Varnishes and Their Solvents*. Washington: National Gallery of Art.

Freed, B.K., Biesecker, J., and Middleton, W.J. Spectral Polarity Index: A New Method for Determining the Relative Polarity of Solvents. *Journal of Fluorine Chemistry*, 48: 63-75.

GELOdata website. SOLVATOR© software. URL: www.gelodata.de.

Gmehling, J, Menke, J., Krafczyk, J., and Fischer, K. 2004. *Azeotropic Data, Parts 1-3,* 2nd Edition. Weinheim: Wiley-VCH Verlag GmbH.

Hansen, Charles M. 1967. *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient: Their Importance in Surface Coating Formulation*. Copenhagen: Danish Technical Press.

Hansen, Charles M. 2000. *Hansen Solubility Parameters. A User's Handbook*. Boca Raton: CRC Press, LLC.

Hedley, G. 1980. Solubility Parameters and Varnish Removal: A Survey. *The Conservator,* 4:12-18.

Henry, W. 1995. Application Development for the Conservation Laboratory. In: *Advances in Preservation and Access, Vol. II,* ed. B. Buckner Higginbotham, Medford, Learned Information, Inc.: 156–179.

Henry, W. 1989. TeasTime. (Computer software, obsolete but available from http://palimpsest.stanford.edu/packages/).

Lide, D. R., ed. 2002. *CRC Handbook of Chemistry and Physics,* 83rd Edition Boca Raton. CRC Press, LLC.

McGlinchy, C. 2002. Boundaries of the Teas Solubility Concept. *WAAC Newsletter,* 24(2): 17-19.

Morrison, R.T. and Boyd, R.N. 1973. *Organic Chemistry, 3rd Edition*. Boston: Allyn and Bacon, Inc.

Nelson, R.C., Hemwall, R.W., and Edwards, G.D. 1970. Treatment of Hydrogen Bonding in Predicting Miscibility. *Journal of Paint Technology,* 42(550):636-643.

Ormsby, M. 2001. Solvent Solver Program. *AIC News* 26(5):6.

Ormsby, M. 2004. Solvent Solver: A Calculator for Working with Teas Fractional Solubility Parameters. http://palimpsest.stanford.edu/packages/solvent_solver.html.

Phenix, A. 1998. Solubility Parameters and the Cleaning of Paintings: an Update and Review. *Zeitschrift für Kunsttechnologie und Konservierung,* 12(2):387-408.

Phenix, A. and Sutherland, K. 2001. The Cleaning of Paintings: Effects of Organic Solvents on Oil Paint Films. *Reviews in Conservation,* 2:47-60.

Phenix, A. 2002. The Swelling of Artists' Paints by Organic Solvents and the Cleaning of Paintings: Recent Perspectives, Future Directions. *2002 AIC Paintings Specialty Group Postprints,* Miami FL June 6-11: 71-86.

Phenix, A. 2002. The Swelling of Artists' Paints in Organic Solvents. Part 1: A Simple Method for Measuring the Inplane Swelling of Unsupported Paint Films. *Journal of the American Institute for Conservation,* 41:43-60.

Phenix, A. 2002. The Swelling of Artists' Paints in Organic Solvents. Part 2: Comparative Swelling Powers of Selected Organic Solvents and Solvent Mixtures. *Journal of the American Institute for Conservation,* 41:61-90.

Teas, J.P. 1968. Graphic Analysis of Resin Solubilities. *Journal of Paint Technology,* 40(516):19-25.

Torraca, G. 1978. *Solubility and Solvents for Conservation Problems*. Rome: ICCROM.

Weast, R.C., ed. 1972. CRC *Handbook of Chemistry and Physics, 53rd Edition*. Cleveland: The Chemical Rubber Co.

Wolbers, R. 1988. *Notes for Workshop on New Methods in the Cleaning of Paintings*. Unpublished manuscript. The Getty Conservation Institute, Los Angeles.

Wolbers, R. 2002. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.