An Aromatics-Free Hydrocarbon Solvent / Diluent for Laropal® A 81 and Gamblin Conservation Colors

by Alan Phenix and Agata Graczyk

The commercially available, low molecular weight (LMW), urea-aldehyde resin Laropal® A81, made by BASF, has become an established material for conservation-restoration treatment of painted works of art. Evaluated first as binder for retouching (inpainting) paints (de la Rie et al 2000; de la Rie 2002) and eventually commercialized in the range of Gamblin Conservation Colors,[1] Laropal® A81 is increasingly finding use too as a picture varnish, perhaps partly because of the lack of availability of another LMW resin intended for that purpose.

Whether used as retouching medium or varnish, Laropal® A 81 needs a solvent for application; according to the manufacturer's datasheet[2] it is soluble in "alcohols, esters, ketones, and aromatic hydrocarbons; aliphatic hydrocarbons – solutions tend to separate at temperatures below 15°C, adding 2-5% of an aromatic solvent produces stable solutions."

Conservators know from experience, however, that a pure aliphatic hydrocarbon solvent has insufficient solvent power/polarity, under normal studio conditions, to dissolve Laropal® A 81 properly, and they almost always need to choose another solvent altogether, blend with one or more polar oxygenated solvents, or increase the proportion of aromatics appreciably above the 2-5% level suggested by BASF.[3]

As has been ably demonstrated, with the assistance of the Teas chart, by Greg Smith and Ronald Johnson in a previous WAAC Newsletter (Smith & Johnson 2008), for Laropal® A81 to dissolve in a mineral spirits-type solvent there generally needs to be ca. 30% aromatic hydrocarbons present.[4] Since most aliphatic mineral spirits products nowadays have low proportions of aromatics, topping up the aromatics by adding xylenes to ca. 30% is the simple, usual solution.

Boosting polarity/solvent power by using oxygenated solvents such as alcohols as diluents for Laropal® A 81 is not generally a problem in terms of risk to the underlying strata when the application is retouching/inpainting, but for varnishing, especially by brush, there are definite benefits to using a solvent/diluent that is as inactive on the sub-strata as possible, and 100% aliphatic hydrocarbons have a distinct advantage in this respect because of their low solvent power and swelling effect (Phenix 2002; Phenix 2013).

It would be advantageous too, from the point of view of human health and olfactory comfort, to have the option of a 100% aliphatic hydrocarbon solvent for Laropal® A81 and Gamblin Conservation Colors. We think we may have a solution to the problem of dissolving Laropal® A81 in 100% aliphatic hydrocarbons.

In the PSG session at AIC Miami in May this year we presented a paper that reported on work we have been doing towards a new solubility descriptor system which retains some of the graphic accessibility of the Teas fractional solubility parameter system with its familiar ternary diagram, while hopefully improving on the discrimination of solvency effects.

The essence of the approach is to take as the main descriptors of the solubility behavior of organic liquids two properties that can be quite easily measured using not-too-elaborate instrumentation: refractive index (*n*) and the normalized Reichardt solvatochromic solvent polarity parameter, E_T^N (Reichardt 2011).[5]

When presented graphically in a simple *x*-*y* diagram, the combination of these two measurable properties seems to separate organic liquids remarkably well in terms of their solubility character.[6] The graphic visualization can be applied also to mixtures of solvents, though one of the main outcomes of our study is that the representation of mixtures is far from linear and ideal.

Even before combining it with Reichardt polarity parameter E_T^N into the new, composite scheme, we were aware that refractive index (*n*) alone was quite a sensitive discriminator of solvent power for the general class of hydrocarbon liquids. Refractive index is connected with, and an indicator of, the *polarizability* of organic substances;[7] that is, the disposition for the electron cloud of the molecules to be distorted from normal shape by an external electric field. With regard to

1. http://www.conservationcolors.com/

2. http://worldaccount.basf.com/wa/NAFTA/Catalog/FunctionalPolymers/doc4/BASF/PRD/30041405/.pdf?title=Laropal_A_81_Dec_2010&asset_type=ti/pdf&language=EN&urn=urn:documentum:eCommerce_sol_EU:09007bb28008474f.pdf

3. Typical solvents/diluents suggested for Gamblin Conservation Colors® include: ethanol, iso-propanol (propan-2-ol), methoxypropanol (PGME; Dowanol PM), methoxypropyl acetate, (PGMEA; Dowanol PMA), ethyl lactate, diacetone alcohol, and mineral spirits of 30-40% aromatics.

4. Smith & Johnson 2008 present a full Teas fractional solubility diagram for Laropal® A81 as their Appendix 1, plus a detail of the non-polar region as their Figure 2.

5. The E_T^N parameter is an empirical scale of solvent polarity parameter obtained from UV/Vis spectroscopic measurements of a solvatochromic pyridinium-N-phenolate betaine dye (Reichardt's dye) in solution. Normalized polarity values (E_T^N), which cover a scale from 0.0 to 1.00, are derived by calculation from the position of the longest-wavelength intramolecular charge transfer absorption band of the dyestuff dissolved in the test solvent.

6. The Reichardt E_T polarity parameters are understood to be independent of polarizability (Laurence et al 1994: 5815; Machado, Stock, & Reichardt 2014: 10441); thus E_T^N and *n* are complementary descriptors of solvent character.

7. Polarizability and refractive index are related according to the Lorenz-Lorentz equation (Reichardt, 2011: 14).

solubility, *polarizability* reflects the tendency of the solvent molecules to acquire induced polarity in proximity to a dipole; solvents with relatively high refractive index and high polarizability, such as aromatic hydrocarbons, are capable of strong dispersion force interactions.

Within the family of linear aliphatic hydrocarbon liquids, refractive index increases progressively from 1.3723 for *n*-hexane up to 1.4195 and above for *n*-dodecane and higher homologues. Cycloparaffinic (alicyclic; naphthenic) hydrocarbons are always higher refractive index than their linear counterparts. The greater solvent power of aromatic hydrocarbons is reflected by the magnitude of their refractive indices: for example, the value for toluene is 1.491; xylene 1.4933-1.5030 depending on the isomer (Table 1). Linear aliphatic hydrocarbons, including *n*-hexane,

Table 1. Refractive indices of hydrocarbon solvents: pure substances, proprietary products, and blends.

	Refractive index at 25°C	Solvent for Laropal® A81?
Pure Hydrocarbons		
n-hexane	1.3723	×
n-heptane	1.3851	×
iso-octane	1.3890	×
n-octane	1.3951	×
n-decane	1.4097	×
n-dodecane	1.4195	×
cyclohexane	1.4235	✓
methylcyclohexane	1.423	✓
toluene	1.4941	✓
xylene (isomers)	1.4933 - 1.5030	✓
Commercial products		
Benzine (petroleum naphtha)	1.4063	×
CBG Formula 83 ™	1.4142	×
Shellsol D38	1.4180	×
Shellsol D40	1.4200	×
Mixtures		
Shellsol D38 : xylene 80 : 20	1.4310	×
Shellsol D38 : xylene 70 : 30	1.4379	✓
Shellsol D38 : xylene 60 : 40	1.4450	✓

n-heptane, *n*-decane, *n*-dodecane, and aliphatic mineral spirits products composed of them, such as VM&P naphtha (refractive index = 1.407), petroleum benzine (refractive index = 1.406),[8] and Shellsol D38 (refractive index = 1.4180), are not in themselves capable of dissolving Laropal® A81. As we have seen, it takes an addition of ca. 30% aromatics to Shellsol D38 to increase solvent power sufficiently to dissolve the resin: a 70:30 v/v mixture of Shellsol D38 and xylene has a refractive index of 1.4380.[9]

However, cyclohexane (refractive index = 1.4235) and its relative methylcyclohexane (refractive index = 1.423) can fully dissolve Laropal® A81. These cycloparaffinic solvents seemingly represent the limit of solubility of the resin on the non-polar side. With boiling points respectively of 80.7 °C (177.3 °F) and 101 °C (214 °F), cyclohexane and methylcyclohexane are rather too volatile, though, for most practical applications; something slower evaporating would be more useful.

Proprietary hydrocarbon solvents that were aromatics-free and composed substantially of cycloparaffins – such things as Shell's Cypar 9 and ExxonMobil's European product Nappar 10 – used to be available until quite recently, but these are discontinued and there seem now to be no products of this type on the market. Even products marketed as substitutes for aromatics, like CBG Formula 83™ (refractive index = 1.4142)[10] lack the solvent power to dissolve Laropal® A81. We have, therefore, been looking at other options within the cycloparaffinic hydrocarbons range, using refractive index as a guide to determine the necessary solvent power.

On the basis that the cycloparaffins have the highest refractive indices and greatest solvent power in the class of aliphatic hydrocarbons, we looked to see if any homologues larger than cyclohexane were commercially available.

Cyclooctane, in particular, has some useful properties: refractive index 1.4557; boiling point 149°C (300°F).[11] When tested, cyclooctane was found to comfortably dissolve Laropal® A81, as might have been predicted from its refractive index value. Usefully, cyclooctane presents no special health risks: according to the new Globally Harmonized System (GHS) for classification and labelling of hazardous substances, it carries just the 'Warning' signal word, and the hazard statement '*H226 Flammable liquid and vapour.*'

We think this combination of properties makes cyclooctane a good choice as solvent/diluent for Laropal® A81; likewise for products made from that resin, specifically the Gamblin Conservation Colors. Admittedly, cyclooctane is not especially cheap at about $50 for 100 ml or $125 for 500ml, but there are some adaptations that can be done for economization.

With a refractive index for cyclooctane of 1.4557, there is quite a bit of latitude in terms of the non-polar solubility limit of Laropal® A81 (demanding a r.i. of around 1.430) to 'dilute' it by blending with a hydrocarbon solvent having lower r.i./solvent power.

8. Products called Petroleum benzine, like that offered by Fisher Chemical, seem to correspond to ASTM Standard D3735 specification for VM&P Naphtha HT.

9. An 80:20 v/v mixture of Shellsol D38 and xylene (r.i. 1.4310) was not capable of dissolving Laropal® A81under normal lab conditions.

10. http://www.cbgtechnologies.com/clearing-solvent.aspx

11. Cyclooctane is available in the US from Sigma-Aldrich: catalog number C109401.

Petroleum benzine (= VM&P naphtha) is an obvious choice as the co-solvent on grounds of having a boiling range (119-140°C; 246-284°F) a little below that of cyclooctane, and relatively good solvent power because of >50% cycloparaffins already in the product. A 50:50 v/v mixture, for example, of cyclooctane and petroleum benzine, with a measured refractive index of 1.4322, was found still to dissolve Laropal® A81 effectively and to produce a coherent dry film of resin on evaporation.

By contrast, a 40:60 v/v mixture of cyclooctane and petroleum benzine, with a refractive index of 1.4276, just lacks the solvent power necessary to dissolve the resin. So, with Fisher Chemical 'benzine' (Cat. No. 264-20) selling for just $12 per 500ml, the possibility of 50:50 blending of benzine with cyclooctane offers quite a saving on cost for preparing a functional, aromatics-free hydrocarbon solvent/diluent for Laropal® A81 and the Gamblin Conservation Colors.

Finally, since conservators are familiar with the representation of resin solubility in the form of regions within the ternary Teas fractional solubility parameter diagram (see Smith & Johnson, 2008: 14, 17; Horie 2010: 402), we thought it useful to compare the Teas chart rendering of Laropal® A81 solubility with that of our new *x-y* graphic presentation of normalized Reichardt solvatochromic polarity parameter, E_T^N, plotted against refractive index (*n*).

Using the solubility data reported by Smith & Johnson 2008, and E_T^N and refractive index data obtained from Marcus 1998 and other sources, our graphic rendering of the solubility of Laropal® A81 in pure solvents is given in Figure 1. We should note, though, that the solubility of the resin in binary solvent mixtures would almost certainly not plot coherently with this plot of solubility in pure solvents.

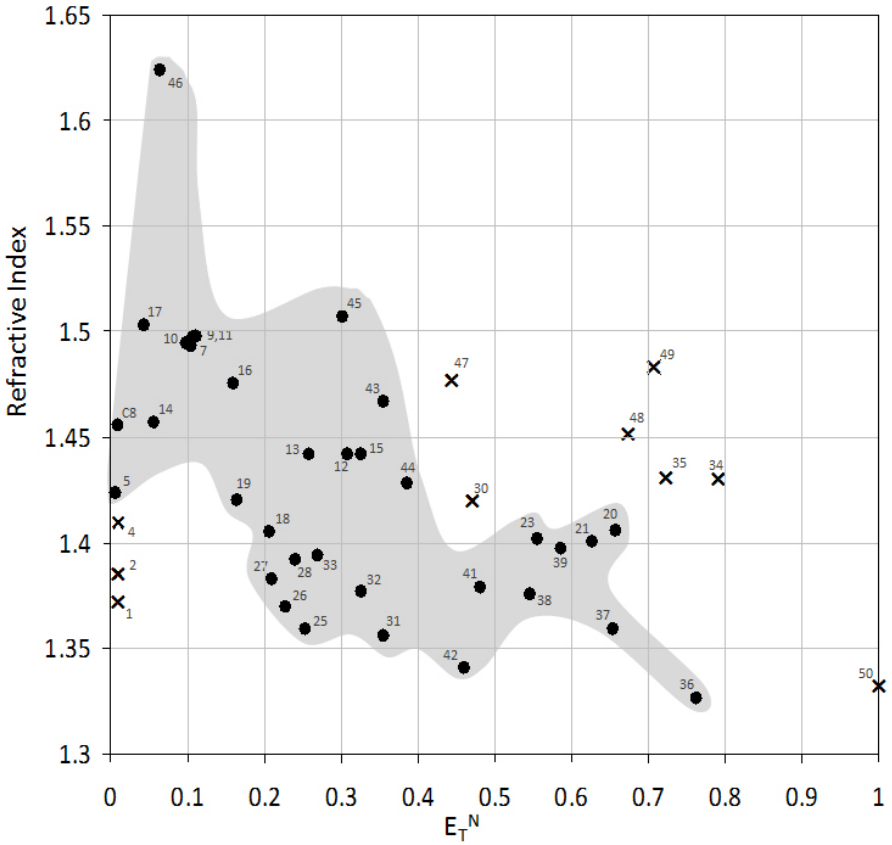

Figure 1. Solubility region of Laropal® A81 expressed in terms of refractive index and normalized Reichardt solvatochromic solvent polarity parameter, E_T^N. Data on refractive index and E_T^N mostly from Marcus 1998. For key to solvents, see table below. Individual solvents numbered same as in Smith & Johnson 2008; cyclooctane included here as solvent C8.

#	Solvent	E_T^N	n
1	n-hexane	0.009	1.3723
2	n-heptane	0.012	1.3851
4	Aliphatic mineral spirits (Shellsol D38)	0.009[w]	1.4180*
5	cyclohexane	0.006	1.4235
7	ethylbenzene	0.105	1.4932
C8	cyclooctane	0.006^	1.4557*
9	benzene	0.111	1.4979
10	toluene	0.099	1.4941
11	xylenes (mixed isomers)	0.106	1.4970*
12	dichloromethane`	0.309	1.442
13	chloroform	0.259	1.442
14	tetrachloromethane	0.057	1.457
15	1,2-dichloroethane	0.327	1.457
16	trichloroethylene	0.16	1.475
17	tetrachloroethylene	0.043	1.503
18	tetrahydrofuran	0.207	0.207
19	1,4-dioxane	0.164	1.4203
20	2-ethoxyethanol (cellosolve)	0.657	1.4057
21	2-methoxyethanol (methyl cellosolve)	0.627	1.4002
23	1-methoxypropan-2-ol	0.556*	1.402*
25	methyl acetate	0.253	1.3589
26	ethyl acetate	0.228	1.3698
27	*iso*-propyl acetate	0.21	1.3828
28	*n*-butyl acetate	0.241	1.3918
30	propylene carbonate	0.472	1.419
31	acetone	0.355	1.356
32	butanone (MEK)	0.327	1.3769
33	methyl iso-butyl ketone (MIK)	0.269	1.3936
34	ethylene glycol	0.79	1.4306
35	propylene glycol	0.722	1.4314
36	methanol	0.762	1.3265
37	ethanol	0.654	1.3594
38	*iso*-propanol	0.546	1.3752
39	*n*-butanol	0.586	1.3974
41	nitromethane	0.481	1.379
42	acetonitrile	0.46	1.341
43	N-methyl-2-pyrrolidone	0.355	1.467
44	N,N-dimethylformamide	0.386	1.428
45	pyridine	0.302	1.507
46	carbon disulfide	0.065	1.624
47	dimethyl sulfoxide	0.444	1.477
48	ethanolamine	0.673	1.452
49	triethanolamine	0.707	1.483
50	water	1.0	1.3325

^ Estimated by comparison with cyclohexane

[w] Estimated by comparison with n-decane

* Our measured values

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In mathematics you don't understand things,
you just get used to them.

Johann von Neumann

A New Conservation Tool

The conservators at Birmingham Museums Trust have been using thorns to clean decorative metalwork, such as vesta cases, coins, buttons, and in particular the Staffordshire Hoard, for the past few years.

Why thorns?

The idea of using thorns for the Staffordshire Hoard objects was first considered as gramophone records were historically played with thorns, suggesting that it may be a suitable material to trial.

Steel implements such as scalpels, picks, and pins are commonly seen in a conservator's toolkit, but these tools are much harder than the hoard gold and silver alloy objects and are therefore not suitable due to the risk of scratching and possible marking the gold.

Many hoard objects already have a number of surface scratches, but the majority of these are the result of manufacture construction marks or from the subsequent removal of their component parts from the original objects in the 7th century. Thorns have become the perfect solution for the conservation of the 4000 fragments and objects that make up the Staffordshire Hoard.

The benefit of thorns

Thorns have the advantage of having very fine, naturally sharp but flexible points that can get into very small areas. Many hoard objects have very fine cloisonné or filigree decoration, and a tiny implement is required to remove soil around these decorative features.

A selection of different thorns ready for action