

Prediction of Adhesion and Wetting from Lewis Acid Base Measurements

(As Presented at TPOs in Automotive 2000)

by Roger P. Woodward, Ph.D.

First Ten Ångstroms, Inc., 465 Dinwiddie Street, Portsmouth, VA 23704. Tel: 1.757.393.1584

www.firsttenangstroms.com

Introduction

The Lewis acid/base theory is the best available model to predict adhesion and wetting from laboratory data. Our goal is to relate the engineering variables of adhesion and wetting to the chemistry variables of surface tension and surface energy. We will carefully enumerate the forces involved, how they are categorized by the acid base theory, and then briefly explore the nature of the underlying relationships to engineering variables, how to make the measurements, and the successes and failures of the theory.

Review of Adhesion

The term *adhesion* refers to the attraction the molecules of one material feel to the molecules of a different material. The attraction molecules of one material feel toward other molecules of the same material is *cohesion*. The surface tension of a liquid is a measure of its cohesion. The analogous term for a solid is surface energy, although some use surface tension irrespective of the liquid or solid state.

We would like to know two things industrially:

- if we have two pure and clean materials, what is the adhesion between them? This may be re-phrased: what is the best we can do between them?
- what external influences (such as contaminants or oxidation) reduce adhesion and by how much?

The ideal situation is to have a theory to predict adhesion from independently measured characteristics of the materials involved at the interface, say, paint and a polymer. By independently, we mean we would like to characterize the paint *without reference to the polymer* and we like to characterize the polymer

without reference to the paint, then compute the adhesion between them. The current theory can provide guidelines and explanations, but not always a complete explanation. The Lewis acid/base theory is the current state of the art in understanding.

Atoms are held in larger structures called molecules by two types of bonds: ionic and covalent. Similarly molecules are held in larger structures (liquids and solids) by cohesive and adhesive forces which are termed *intermolecular forces*. Something like 20 such forces have been identified, but only a few are significant and we ignore the others. The dominant forces are primarily electrostatic in origin, so loosely speaking, everything is held together by static electricity.

Forces of Adhesion

- atoms are held in molecules by covalent and ionic bonds
- intermolecular forces hold molecules together in condensed matter
- intermolecular forces are primarily Coulomb (electrostatic) in nature
- most covalent bonds have a residual charge, or ionic character: electronegativity
- the many intermolecular forces are grouped into the LW (Lifshitz-van der Waals) and AB (acid/base) force collections

The theory divides intermolecular forces into two principal groups. The various names have fine shades of meaning, but are normally used interchangeably:

- LW = Lifshitz-van der Waals \approx London \approx non-polar \approx dispersive forces
- AB = (Lewis) acid/base \approx polar forces

Dispersion Forces

- Lifshitz-van der Waals Forces
- act on all atoms and molecules, including totally neutral ones
- can act over long distances (to 100Å) and can orient molecules
- can be repulsive in addition to attractive
- include dispersion, retardation, orientation, and induction energies

Acid/Base Forces

- Lewis acid/base bonds (also described as electron donor-acceptor bonds)
- a Lewis acid accepts a pair of electrons to form a covalent bond
- $A + B \rightleftharpoons A:B$ (reversible)
- act over short range ($<3\text{Å}$)
- force is strong function of distance
- hydrogen bonding is common example, but not only type possible

The most important thing to know is that dispersion forces are always present, but that acid/base forces, which may or may not be present, contribute most of industrial adhesion. PTFE (“Teflon”) is wholly dispersive and is difficult to glue. A metal or a plasma treated polymer will have significant polar components and will offer good adhesion. Water is highly polar and many oils are wholly dispersive.

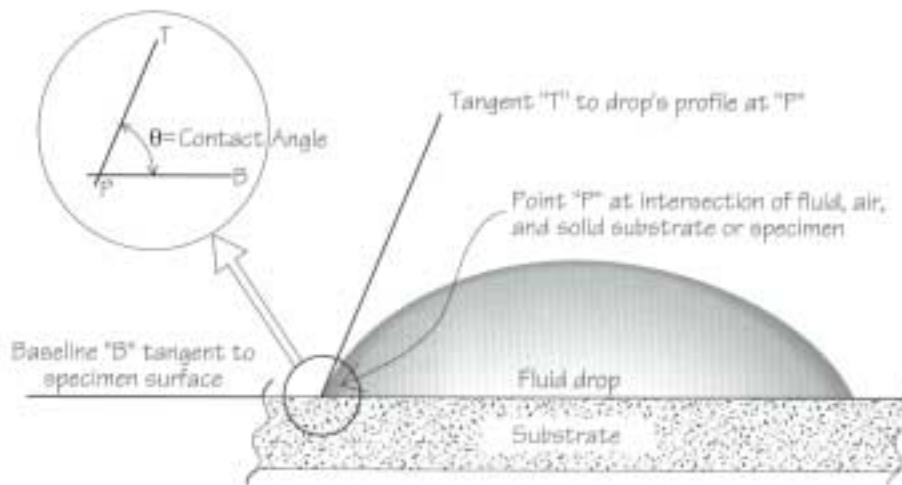
We will use the theory to compute adhesion from surface tensions and surface energies.

Surface Tension and Surface Energy Measurements

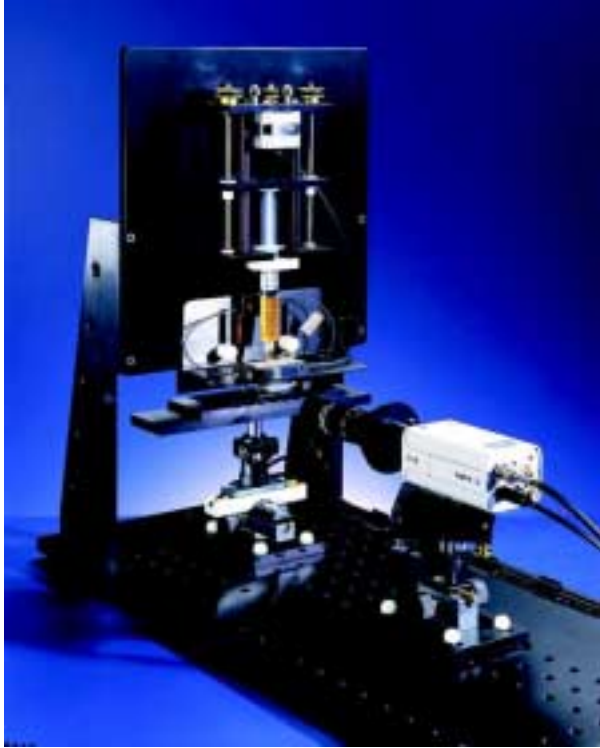
Surface tensions of liquids can be measured by the shape of a small drop of the liquid or by the force imparted on a platinum plate dipped in the liquid. The first method is called drop shape, or Bashforth-Adams after the people who first solved the equations. It typically uses a video system to capture an image and software to precisely measure the shape. The second method is called the force balance or Du Nouy ring or Wilhelmy plate, again after the individuals who first perfected the techniques. There are other variations on these approaches involving pressures and the weight of drops falling off small tips. Surface tensions of liquids can be obtained exactly because the only forces acting on the drop are gravity and surface tension, and the drop will assume a shape that balances the two.

Contact angles describe the shape of a small drop of liquid in contact with a solid. The drop will spread out until the liquid’s cohesion is balanced by its adhesion to the solid. Contact angles are the most practical way to characterize surface energies of solids. As before, drop shape or force on a plate can be used. Unfortunately, surface energy can not be obtained directly from contact angle data alone because the solid will not deform under the stress of surface tension. Nevertheless, there is a way to an approximate answer.

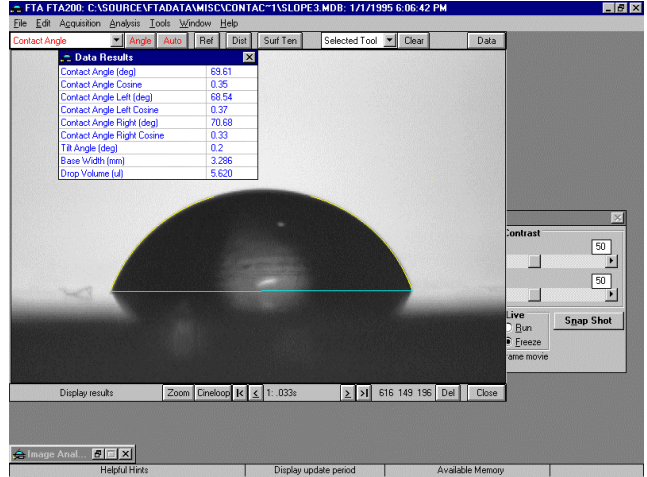
Drop shape is a convenient method to measure contact angles on industrial samples. The illustrations on the next page show two arrangements and example images on flat and sloped specimens. Software can automatically compensate for sloping surfaces, so the drop shape method is convenient for complex parts.



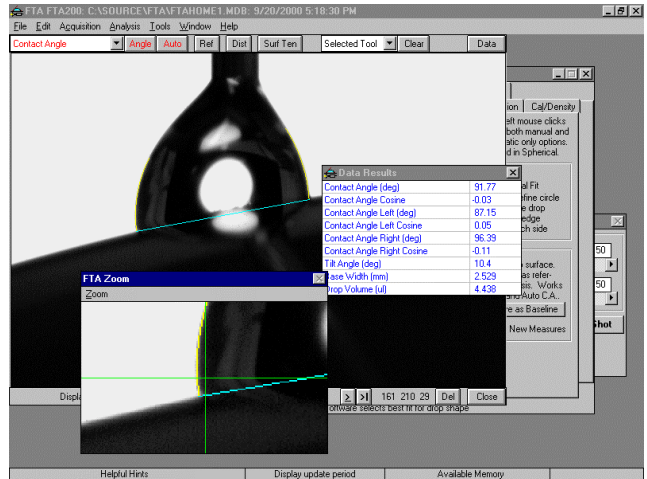
Contact Angle Measurement



Video System with Horizontal Camera



Example Contact Angle Image



Contact Angle Measurement on Slope



Video System with Vertical Camera

Young's equation describes the balance of forces at the liquid-vapor-solid three-phase line (the "edge"):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

We see that we can measure θ , and we can look up or measure γ_{LV} , so we can compute *one* unknown (one equation, one unknown). This means we can compute the difference

$$\gamma_{SV} - \gamma_{SL}$$

but not the individual values γ_{SV} and γ_{SL} . Since, in general, we need to know the individual values, we need *another* equation. This other equation is supplied by a surface energy theory. There are several available theories, of which the Lewis acid/base is the most sophisticated and the one which takes the most effort to apply.

All of the theories start with the Young-Dupre equation relating contact angle to work of adhesion. This is also the way we tie contact angles back into adhesion values.

Young-Dupre Equation for Adhesion

$$W_a = \gamma_{LV} (1 + \cos\theta)$$

- between liquid and solid
- W_a = work to separate surfaces

To provide the "missing equation," combining rules are hypothesized to describe how the forces interact. The details are outlined in Table 1, but the important points are 1) assumptions are made and 2) two separate relationships are used: the geometric mean and the harmonic mean, to combine forces. You will see these used to describe theories, such as the *Owens-Wendt geometric mean*.

Combining Rules

- how to compute forces between substances, knowing individual energies
- for LW systems, Fowkes showed the work of adhesion to be *exactly* $W_A^{LW} = (\gamma_1^{LW} \times \gamma_2^{LW})^{1/2}$
- first assumption: total work of adhesion is *sum* of LW and AB terms $W_A = W_A^{LW} + W_A^{AB}$
- second assumption: AB forces combine geometrically like LW forces do:
 $W_A^{AB} = (\gamma_1^A \times \gamma_2^B)^{1/2} + (\gamma_1^B \times \gamma_2^A)^{1/2}$
 A = acid = electron acceptor = proton
- "the acidity of a solid's surface... is the ability to convert an adsorbed base into its conjugate acid" (Voytec Gutowski)

The theories differ in how many liquids are used and how many components are computed. The simpler theories do not compute all possible components—they lump some of them together into larger groups, a convenience but also an inaccuracy. The analysis method is to:

1. make contact angle measurements with one or more liquids
2. choose a theory and let software solve equations

Table 1. Competing Theories

Theory	Liquids	Rule	γ	γ^{LW}	γ^{AB}	γ^A	γ^B
Girifalco, et.al.	1	Geometric	•				
Wu	2	Harmonic	•	•	•		
Owens-Wendt	2	Geometric	•	•	•		
Lewis AB	3	Geometric	•	•		•	•

Obtaining Surface Energies from Contact Angles

- contact angles are but one way of obtaining energies, but often easiest
- because of "missing equation" in Young's force balance, must use theories
- these theories relate contact angles to energies by same arguments as W_A
- exception: Wu's harmonic theory uses $(\gamma_1^A \times \gamma_2^B) / (\gamma_1^A + \gamma_2^B)$ rather than square root of product
- also, different theories compute different numbers of energy components

Practical Considerations

Only a few test liquids are used because only they have sufficiently high surface tension to not wet out entirely (have zero contact angle), have high boiling points, and are reasonably safe.

Table 2. Typical Test Liquids

Liquid	γ	γ^{LW}	γ^{AB}	γ^A	γ^B
Water	72.8	21.8	51	25.5	25.5
Glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
Methylene Iodide	50.8	50.8	0	0	0
Ethylene Glycol	48	29	19	1.92	47

Contact angle measurements can be carried out to an accuracy of about one degree. Most surfaces have natural variations of several degrees, so measurement accuracy is not normally the limiting factor. Table 3 shows highest accuracy is required for angles near 90°.

Most workers average over 5 to 10 measurements; that is, they place drops on 5 to 10 separate locations (not 5 to 10 drops on the same location!). Sometimes negative energies are reported by the surface energy equations. This is not necessarily incorrect, but the possibility of inaccurate angle data should be checked.

Angle	Degrees for Error in Cosine of Angle =			
	0.01 0.5%	0.02 1%	0.05 2.5%	0.10 5%
$\theta=90^\circ$ $ \cos\theta =0$	0.58	1.15	2.86	5.73
$\theta=75^\circ$ or 105° $ \cos\theta =0.26$	0.59	1.18	2.94	5.59
$\theta=60^\circ$ or 120° $ \cos\theta =0.50$	0.65	1.31	3.25	6.42
$\theta=30^\circ$ or 150° $ \cos\theta =0.86$	1.12	2.21	5.31	10.0
$\theta=0^\circ$ or 180° $ \cos\theta =1.0$	8.10	11.47	18.2	25.8

Obtaining Robust Contact Angle Data

- do not distort drop in placing it on surface
- have drop be large and in focus
- orient camera to obtain clear baseline image
- average over several positions on surface
- inspect time behavior of drop for hydration or reaction or reaction or solution

Negative Energies

- known to exist from AFM measurements
- theoretical basis in energy vs distance curves
- can also arise from “noise” in contact angle data, because of geometric rule
- can also arise from imperfect knowledge of AB components (e.g., water)
- not of consequence when relative values considered

Two examples will follow. The first will use the Lewis acid/base theory and the second will use the Owens-Wendt geometric mean.

Automotive Paint Example

This example compares one-package acrylic and two-package urethane paints cured at one location by directly heated gas ovens and at another location by indirectly heated electric ovens. Contact Angles were measured with video drop shape instrument. The average contact angle of 12 locations was reported for each sample.

Automotive Paint Example

- two tone parts, where second color painted over first on portion of part
- two different basecoat types (1K and 2K) and 2K urethane clearcoat
- two different plants with different ovens: direct gas and indirect electric
- plant using gas ovens has line stoppages up to four hours
- plant using gas ovens had occasional recoatability problems
- surface energy measurements used to quantify surfaces

Table 4. Contact Angle Data

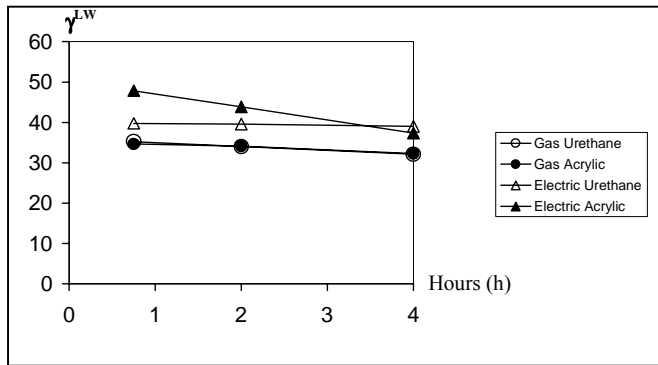
Ovens	Basecoat	Bake Time (hours)	Contact Angle		
			CH ₂ I ₂ (°)	H ₂ O (°)	C ₂ H ₆ O ₂ (°)
Gas	Urethane	0.75	48.3	88.1	74.2
Gas	Urethane	2	50.5	97.4	75.5
Gas	Urethane	4	53.8	98.1	78.6
Gas	Acrylic	0.75	49.3	92.7	73.6
Gas	Acrylic	2	50.3	94.5	75.9
Gas	Acrylic	4	53.5	96.9	78.9
Electric	Urethane	0.75	39.7	81.6	69.2
Electric	Urethane	2	40.1	83.5	70.5
Electric	Urethane	4	41.1	90.3	72.6
Electric	Acrylic	0.75	19.7	82.0	69.9
Electric	Acrylic	2	30.8	84.1	70.5
Electric	Acrylic	4	44.3	87.0	71.4

The contact angles of Table 4 were then converted into Lewis acid/base data by the software and are shown in Table 5. Notice three fluids were used: methylene iodide, water, and formamide.

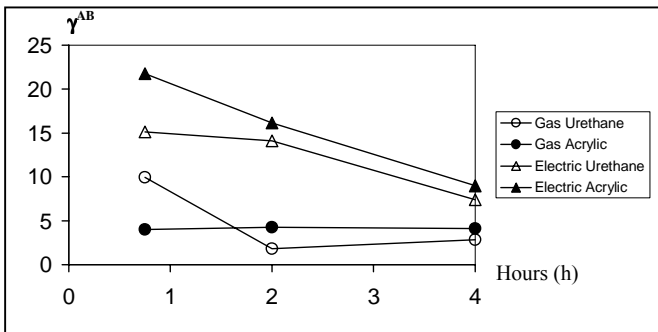
The gas ovens lowered the surface energies and this resulted in occasional over coating problems. As a function of bake time, the dispersive (LW) and acid/base (AB) surface energies for the samples are plotted in graphs on the next page. The dispersive energies are not affected by bake time the way AB polar energies are. Since adhesion is dependent on polar (acid/base) bonding to a large degree, this is an important result.

Table 5. Surface Energy Data

	Oven	Basecoat	Bake Time (hrs)	γ_s^{LW} mN/m	γ_s^+ mN/m	γ_s^- mN/m	γ_s^{AB} mN/m	γ_s mN/m
○	Gas	Urethane	0.75	35.22	1.24	20.04	9.96	45.18
	Gas	Urethane	2	33.99	0.3	2.86	1.84	35.83
	Gas	Urethane	4	32.13	0.47	4.40	2.87	35.00
●	Gas	Acrylic	0.75	34.66	0.05	8.03	4.02	38.68
	Gas	Acrylic	4	32.3	0.65	6.53	4.12	36.42
△	Electric	Urethane	0.75	39.76	1.81	31.63	15.14	54.90
	Electric	Urethane	2	39.56	1.79	27.78	14.09	53.65
	Electric	Urethane	4	39.05	1.13	12.08	7.39	46.44
▲	Electric	Acrylic	0.75	47.87	3.58	33.03	21.76	69.63
	Electric	Acrylic	2	43.89	2.47	26.37	16.15	60.04
	Electric	Acrylic	4	37.38	1.10	18.34	9.00	46.38



Dispersive Energies with Bake Time



Polar Energies with Bake Time

Aircraft Paint Example

This problem was a little different from the previous one. Injection molded components experienced adhesion problems sometimes. This was traced to silicone mold release remaining on the part's surface. The customer desired a simple means of screening incoming parts for silicone contamination.

Aircraft Paint Example

- injection molded part
- residual silicone mold release agent caused subsequent coating adhesion problems
- these adhesion problems only appeared later as field failures
- silicone could be identified by XPS
- customer wanted lower cost screening test
- surface energy measurements used to quantify surface

Table 6. Contact Angle and Surface Energy Data

Angles (°) and Tensions/Energies (mN/m)	Sample #1	Sample #2
Water contact angle	89.8	91.2
Methylene iodide contact angle	32.5	43.8
Water wetting tension	0.25	-1.52
Methylene iodide wetting tension	42.8	36.7
Total surface energy (Owens-Wendt)	43.8	38.6
Dispersive surface energy	43.2	37.6
Polar surface energy	0.6	1.0

Sample #2 was contaminated by the silicone. It has a distinctly higher contact angle for methylene iodide (43° versus 32.5°). Since methylene iodide has no polar component, the dispersive silicone offers much less adhesion than the underlying surface.

Reference

For a complete discussion of adhesion theory, see L.H. Lee, "Fundamentals of Adhesion", ISBN 0-306-43470-9.