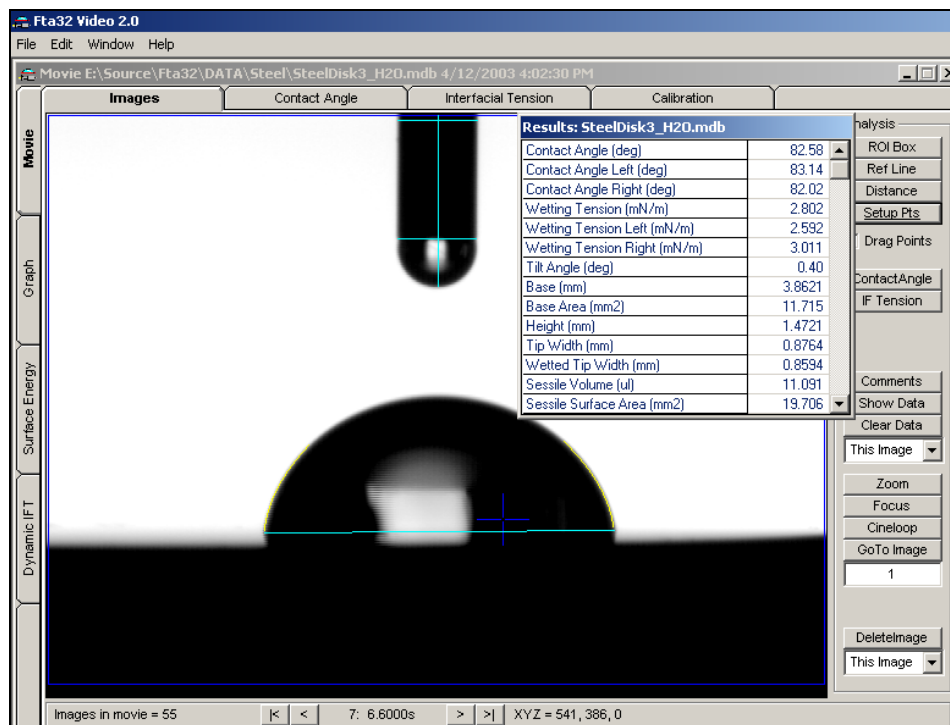


Contact Angle and Surface Energy Measurements on Steel

July 19, 2003

Four precision steel coupons were tested on an FTA200 for contact angle and surface energy. The samples were ground smooth and appeared clean, which is what makes the following results interesting.

The following image shows a typical sessile drop on the sample. The test liquid was water.

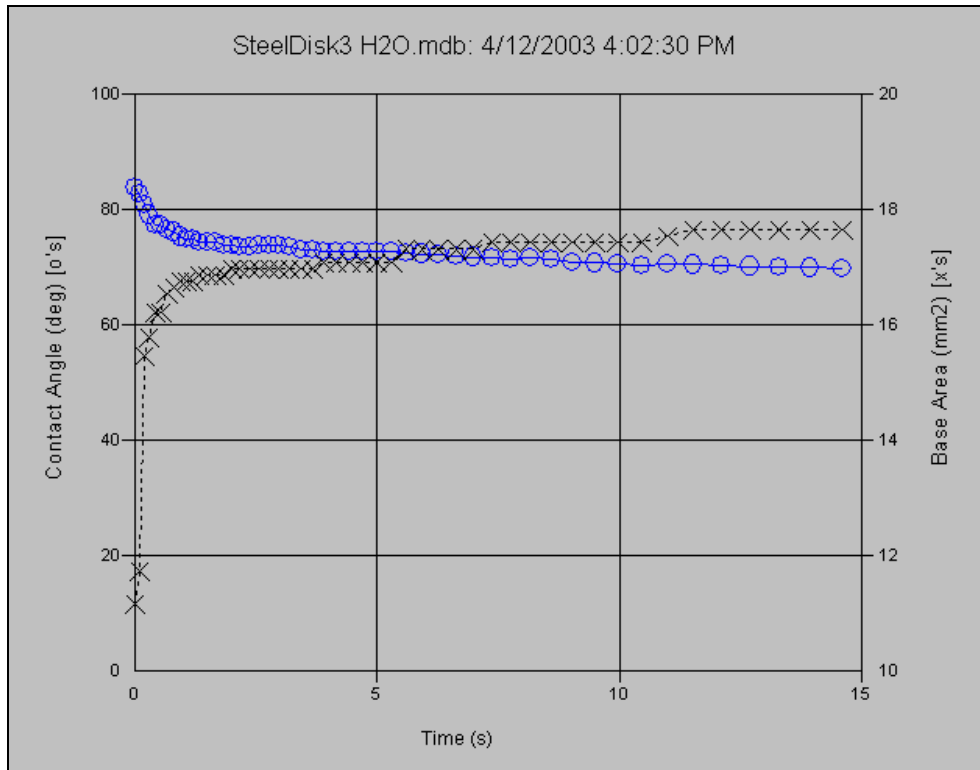


Contact angle of water on steel sample

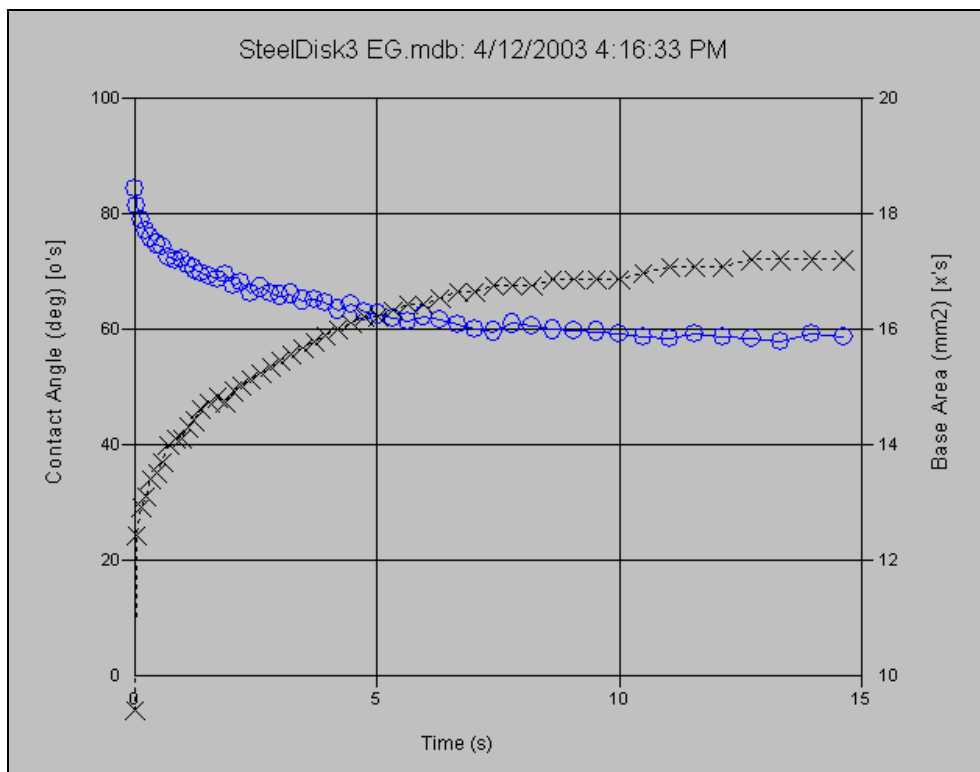
The samples were tested with water, ethylene glycol and formamide. In all cases the test liquids spread after being deposited on the surface. This typically indicates one of three conditions:

- penetration into the surface
- adsorption of test liquid vapor onto surface, or
- the test liquid is dissolving the surface or reacting chemically with it

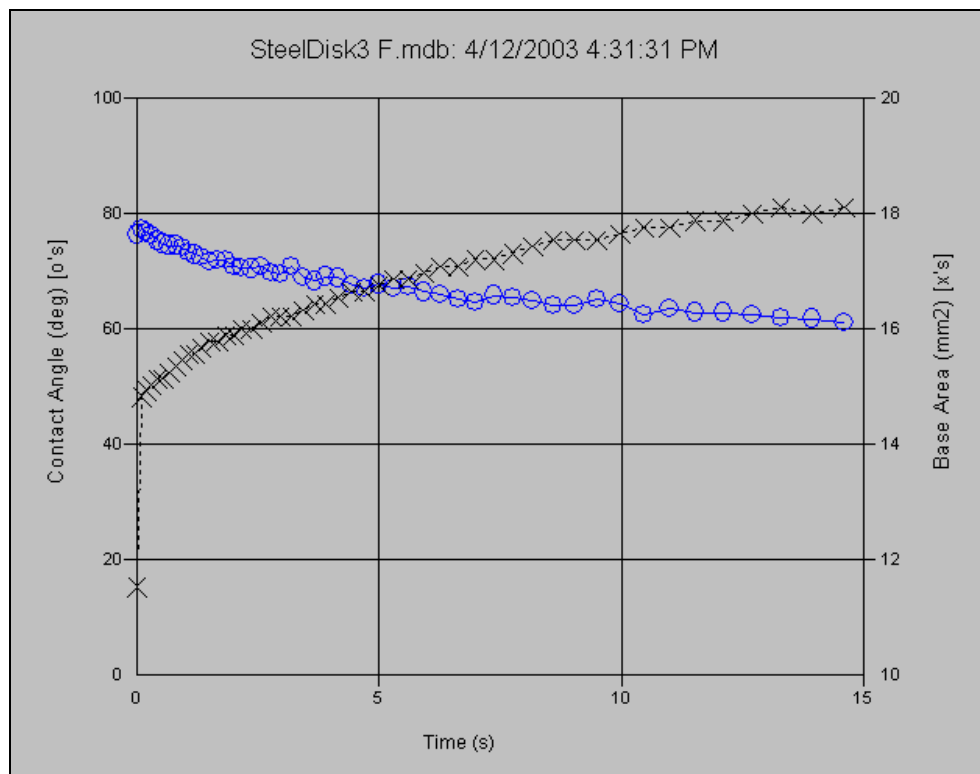
The following graphs show the contact angles of the three test liquids on one of the samples.



Contact angle ('o' symbols) and sessile drop base area ('x' symbols) for water



Contact angle and base area for ethylene glycol



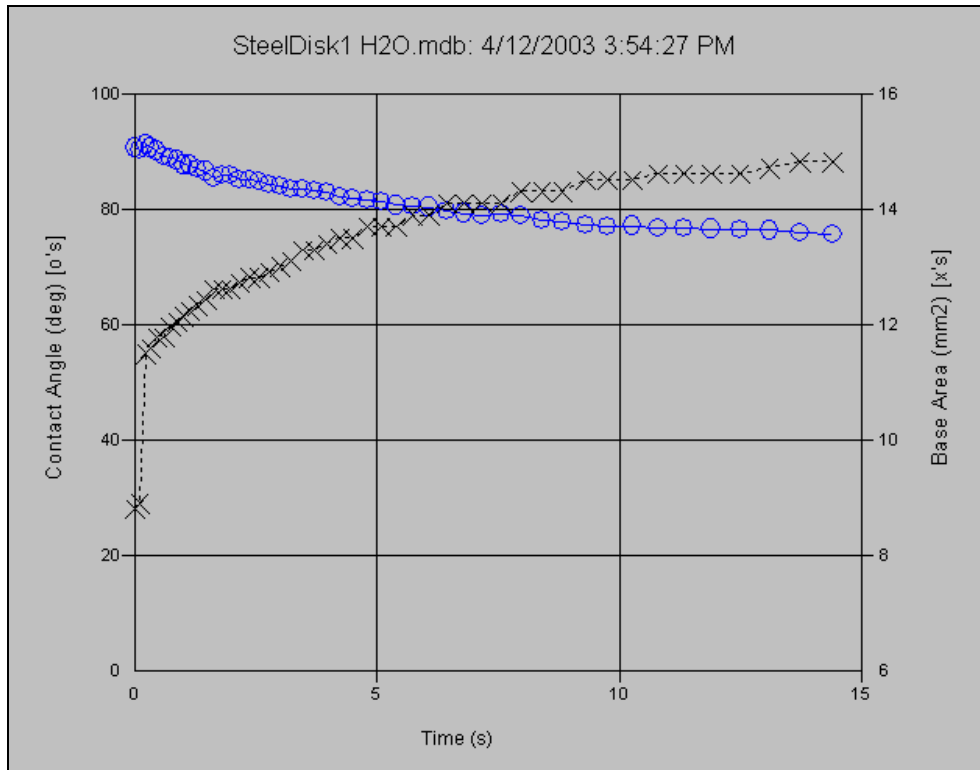
Contact angle and base area for formamide

All four samples behaved in a similar way. Notice that all three test liquids spread. And, finally, let us repeat the samples appeared clean.

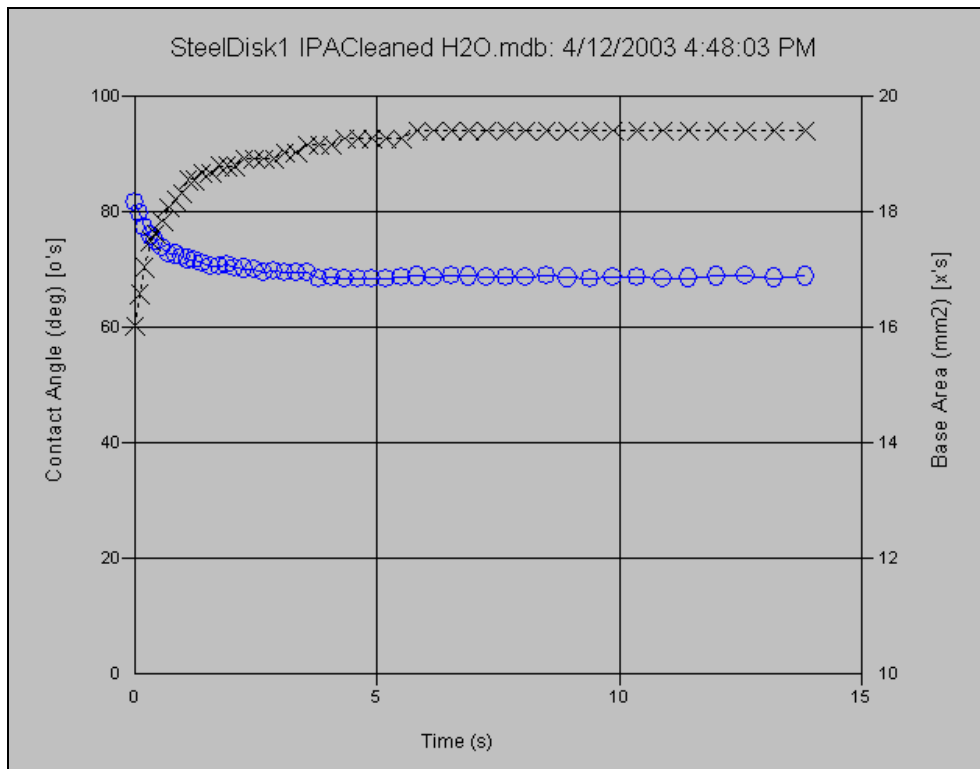
The samples were then cleaned in a 99% isopropyl alcohol (IPA) bath, dried, and then tested with water again. The following two graphs show the water contact angle data on sample #1, as received, and after the IPA wash. While the response is different, it still shows spreading over time. The other samples behaved similarly. From this we conclude the IPA wash affected the surface but did not clean it thoroughly.

The samples were next cleaned with a methyl ethyl ketone (MEK) wash. This was more successful. The third graph in the series shows the water contact angle data after the MEK wash. The flatness of the graphs are remarkable: there is no spreading of the solvent on the sample after deposition. The contact angle is also lower, indicating a higher surface energy. We would normally expect organic contamination to have a lower surface energy and therefore a higher contact angle, but this is a rule-of-thumb and not as convincing as the change in the shape of the time curves.

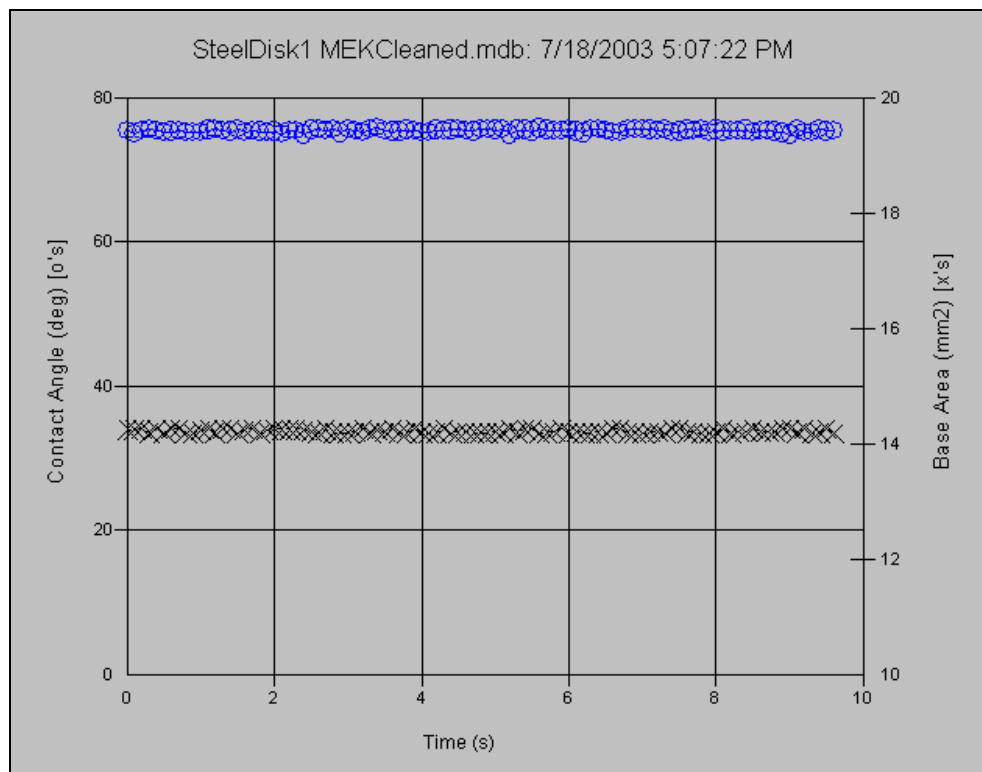
This set of data is an excellent example of contact angle data revealing contamination on precision parts that otherwise appear clean.



Water contact angle on sample as received, before any wash



Water contact angle on sample after IPA wash



Water contact angle on sample after MEK wash

The initial, before cleaning, and final, after cleaning, contact angles for the four samples are listed in the table.

| Sample number | Initial CA (°) | Final CA (°) |
|---------------|----------------|--------------|
| 1 | 90.8 | 75.4 |
| 2 | 85.6 | 77.7 |
| 3 | 83.7 | 75.8 |
| 4 | 93.7 | 73.7 |

The mean of the final contact angles is 75.7, the standard deviation 1.6, and the coefficient of variance is 2.1%.

An attempt was made to characterize the initial (uncleaned) surfaces using Lewis acid/base analysis and Owens-Wendt analysis. We know that these analyses require thermal equilibrium and that we do not have equilibrium when the drops continue to spread. Nevertheless, may people try to apply these equations in circumstances where the underlying assumptions are not met.

Sometimes workers feel that if they use either the initial contact angle (before the liquid spreads) or the final value after spreading, then the results will be better. The following table shows the acid/base and dispersive/polar components for each of the samples, using both the initial and final time values, all before any cleaning was performed. The energies computed using the final values for the contact angles (i.e., after spreading) are naturally different but not necessarily

more reliable. For Lewis acid/base analysis, negative values are obtained for the acid components when using the initial contact angles. These negative values are not seen when using the contact angles after spreading. Negative values would indicate repulsion and are considered suspect by many. A final point of contention is that the acid/base non-polar (i.e., dispersive) components should be similar to those for Owens-Wendt analysis. The Owens-Wendt analysis was performed using the water and ethylene glycol contact angle data.

| Sample | Lewis A/B NonPolar (mN/m) | Lewis A/B Acid (mN/m) | Lewis A/B Base (mN/m) | Owens-Wendt NonPolar (mN/m) | Owens-Wendt Polar (mN/m) |
|-----------|---------------------------|-----------------------|-----------------------|-----------------------------|--------------------------|
| 1 initial | 52.43 | -4.359 | 6.392 | 5.963 | 11.90 |
| 1 final | 37.18 | 0 | 13.55 | 4.497 | 25.47 |
| 2 initial | 62.59 | -8.281 | 11.06 | 1.968 | 20.90 |
| 2 final | 36.58 | 0 | 20.10 | 6.308 | 30.28 |
| 3 initial | 68.24 | -11.52 | 14.06 | 0.4906 | 26.99 |
| 3 final | 33.63 | 0 | 17.43 | 7.567 | 24.40 |
| 4 initial | 64.18 | -6.644 | 3.681 | 8.356 | 8.305 |
| 4 final | 43.67 | 1.257E-2 | 4.812 | 18.36 | 10.32 |

What should one make of this kind of situation? Understand that the surface energy equations are based on important thermal equilibrium assumptions and they should not be used when the contact angle time graphs are varying as they are with these (uncleaned) samples.

However... the contact angle data itself is valid and is very revealing. We learn from the spreading that there is some coating on the surface interacting with the test liquids. This is important information in itself. Secondly, after successfully cleaning the samples, we see that there is a correlation between contact angle and cleanliness. This is something that has been found to be true on many surfaces, although the exact details must be established by empirical means.