Advice & Counsel

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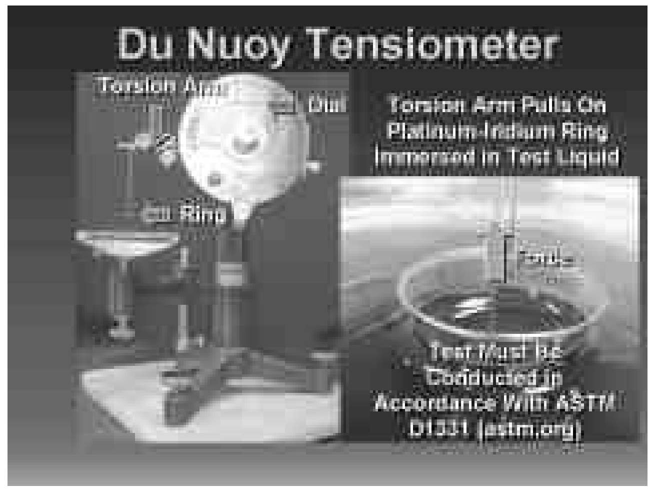
Surface Tension & The Chromium MACT



Dear Advice & Counsel,
At a recent AESF branch meeting, a speaker mentioned that EPA has reduced the surface tension requirement for decorative chromium platers to 35 dynes/cm from the existing 45 dynes/cm. I have three questions:

1. Was this speaker correct?
2. If my ring tensiometer readings have been between 35 and 45 dynes/cm in the past, will I be considered out of compliance?
3. What is surface tension anyway?

Signed,
Columbo Trainee

Dear Trainee,
The answer to the first question is "NO." That's the good news. The bad news is that EPA is *considering* lowering the surface tension requirement to 35 dynes/cm, *IF* you use a ring tensiometer instead of a stalagmometer to monitor your hexavalent chromium plating solution. The source of this change is believed to be a paper titled, "Report on Observed Differences in Dynes/Centimeter Readings of Various Chromium MACT Method 306B Surface Tension Measuring Devices," by James E. Hensley, Industrial Technology Institute, and David York, Diamond Chrome Plating. The paper was presented at AESF Week 2001.

These researchers found that a ring tensiometer provides consistently lower surface tension readings when compared to a stalagmometer. Because the EPA used stalagmometer readings to come up with the 45 dynes/cm minimum, it is now considering the change.

The answer to your second question is "NO," as far as I know.

Your third question requires a longer answer. Let's begin by defining surface tension. A beaker of water contains billions of water molecules. Those molecules that are within the water are surrounded by other molecules, while the water molecules at the surface are only joined by water molecules below and by the air above. This creates an imbalance of forces. The molecules at the surface respond to this imbalance by exerting a strong attractive force on other molecules around them.

A fluid will therefore behave as if it were covered by a thin membrane when it is exposed to the air. This is what causes water to form a round (as opposed to a cube) droplet, if we pour a small amount into the air. A sphere minimizes the surface area exposed to the air for a given volume of water. The higher the surface tension, the larger the water droplet; the lower the surface tension, the smaller the droplet. This translates well to your chromium process, in that by lowering the surface tension of the plating solution, the gas bubbles are made very small. When tiny bubbles burst at the top of the plating solution, there is little energy available for producing mist.

The force that is produced by the attractive forces of surface fluid molecules is called *surface tension*. Surface tension is this force measured along a perpendicular path along a line of unit length. The units are typically dynes-per-centimeter (***not*** dynes-per-square-centimeter, as some inaccurately say it). The surface tension of liquids varies with temperature. It is therefore necessary to report the temperature of the liquids upon which the measurement was made, along with the dynes/cm.

There are numerous methods of measuring surface tension, and EPA allows any method that is equivalent to a stalagmometer (equivalency might need to be proven). The first method we will describe is your ring tensiometer.

The ring tensiometer is more formally known as the Du Nuoy ring tensiometer, named after the French physicist who designed the original instrument in the 1800s. All tensiometers are essentially torsion balances that apply a slowly increasing force to a very accurately constructed platinum-iridium ring, which is in contact with the liquid under measurement.

The tensiometer pulls on the ring on the surface of the solution and measures the force it takes to break it from the surface. This force (subject to a correction we will discuss later) is proportional to surface tension. The amount of the force is indicated upon a graduated scale, which, when calibrated, provides direct readings in dynes of force per centimeter.

If your facility has opted to use a tensiometer, EPA requires that it be operated in accordance with ASTM D1331. A copy is available for purchase at www.astm.org.

The Du Nouy tensiometer is considered the easiest and most accurate method of measuring surface tension. Its accuracy is typically ±.05 dyne/centimeter, and it takes only 1-2 minutes to make a measurement.

This device requires no elaborate cleaning techniques and also requires few, if any, chemicals.

A tensiometer is expensive when compared to other measuring methods. The cost can range from about $3,000 to more than $10,000, depending on features and capabilities. The platinum-iridium ring used by the ring method is $400 and can easily be damaged.

Plant vibrations can produce erroneous results, and industrial environments can easily corrode delicate components.

Calibration

Before using a tensiometer, it must be calibrated. The calibration procedure determines if an adjustment to the torsion arm is required. Calibration is required before using a new instrument, or anytime the instrument has undergone any significant operational change, such as replacement of the torsion wire or replacement of any hardware. It is also a good idea to calibrate the instrument regularly to verify proper operation.

Depending on the level of use, this may be weekly, monthly or annually. Calibrate at least once a year in any case.

Calibration involves placing a known weight on the ring and making a reading. The length of the torsion arm is adjusted until the correct reading is obtained (detailed instructions come with the instrument).

The Ring

The most critical part of the tensiometer is the platinum-iridium ring. Platinum has a contact angle of zero, which ensures repeatable readings, while iridium provides strength to the fragile ring.

The ring must be maintained horizontal to the test fluid, or error is introduced. According to Arthur Adamson in "Physical Chemistry of Surfaces," as little as 2.1-degrees variation can cause a 1.6 percent error.

Damaged or dirty rings will yield inaccurate readings. Because the ring is very expensive to replace, proper care must be emphasized.

The ring can easily be bent during handling, or if it is dropped. For this reason, it should be handled only with locking forceps. The forceps keep the ring clean and reduce the chance of accidental drops.

Always store the ring in its protective wooden case. Open the case carefully to avoid dropping the ring to the floor, which almost always will cause damage (up to $400).

Before making a measurement, the ring should be inspected for the following conditions.

Ring Legs (Stirrups)

Looking at the legs from the side, they should be straight and at a 90-degree angle to the ring itself.

All bottom surfaces of the ring should touch a flat surface when the ring is in a standing position. The ring should be round and free of kinks. Damaged rings should be returned to the manufacturer for repair. For this reason, it is a good idea to always have a spare ring on hand.

The procedure for cleaning the ring can vary to some degree, depending upon the types of liquids that are being evaluated. For chromium, nickel or similar plating solutions, a rinse in deionized water, followed by a rinse in acetone, is a quick cleaning method between samples. The acetone dries the ring in seconds.

For oily liquids, more elaborate cleaning—including a rinse in petroleum naphtha or benzene followed by rinsing in methyl ethyl ketone, followed by heating in a gas burner—is recommended. Flaming the ring in a gas burner assures that all traces of contamination is removed in most cases. This operation can easily damage the ring beyond repair, however. Flame the ring only if you have tested oily liquids or liquids that are difficult to effectively rinse off, or if visible residues are present on the ring after less-rigorous cleaning.

To flame the ring, heat the ring in the oxidizing portion of a gas burner, but only until the ring is dull red, not bright white-hot. This only takes one or two seconds. Excessive heating will warp the ring and possibly cause the ring to detach from the stirrups.

Sample Vessel

The sample vessel can be any one of numerous dishes available from chemical supply houses. Plastic or glass petri dishes, evaporating dishes or watch glasses are most commonly used. The dish should be at least 4.5 cm in diameter. Do not use aluminum pans, because these often are contaminated with a drawing compound that can contaminate the sample and give erroneous readings.

Sample vessels must be clean, or cross-contamination will affect readings. Use a new disposable dish for each sample to avoid cross-contamination. If this cannot readily be done, each used dish requires a through cleaning, followed by a chromic acid soak and rinse prior to re-use.

Correction Factor

The dial reading obtained is actually an uncorrected surface tension reading, but is suitable for most compliance monitoring. The reading can be corrected for the contours of the liquid surface in the area of the ring at the instant of breakaway. The difference between actual and instrument reading is usually less than six percent, but may be as high as 30 percent in rare cases.

For plating solution monitoring, this correcting factor is usually too small to be concerned about, but the equation for calculating it is:

$$F = 0.725\ 0.04534 - \frac{1.69r}{R} + \frac{0.01452P}{C^2\,(D-d)}$$

The values for C, R and r are typically provided by the manufacturer of the ring used in the measurement. D=density of the liquid, d=density of air (normally 0), P= dial reading. ***P&SF***

Note: AESF is producing a CD-based training program on surface tension measurement. It will be available at SUR/FIN® in Chicago.