Advice & Counsel

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Methods of Measuring Surface Tension

Dear Advice and Counsel:
What techniques are available for measuring surface tension in chromium plating solutions for monitoring compliance with chromium MACT standards?
Signed, Tense Plater

Dear Tense:

The surface tension requirement was written into the U.S. Environmental Protection Agency's (EPA) Chromium MACT, because in the process of chromium plating, gas bubbles generated rise to the surface of the tank solution and burst. Upon bursting, tiny droplets of chromic acid are emitted. The greater the surface tension of the solution, the larger these droplets will be. Consequently, more chromic acid vapor is emitted. Surfactants (wetting agents) are surface active agents that reduce the surface tension of a liquid and diminish the formation of these droplets. Most fume suppressants contain a surfactant.

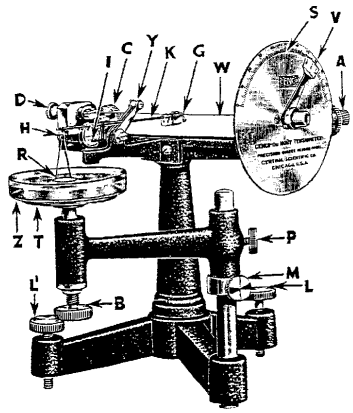
The chromium MACT for decorative chrome platers has provided an option of consistently meeting 45 dynes/cm for compliance. The surface tension of water is approximately 73 dynes/cm. The surface tension of a 33 oz/gal chromium plating solution, containing no fume suppressant, has a surface tension of about 70 dynes/cm.

Frequent surface tension measurements of the plating bath are required initially, up to one time every four hr for the first 40 hr of operation. If, at any time, one measurement is higher than 45 dynes/cm, the frequency of measurements must resume to once every four hr.

Techniques of Measurement

There are dynamic and static ways of measuring surface tension. Dynamic techniques measure the way the surface tension of a fluid changes in relation to the surface tension of a different fluid, such as measurement taken with a stalagmometer. Static techniques examine surface tension in equilibrium, such as those measurements taken with a tensiometer. Method 306B of the regulations allow surface tension to be measured by a tensiometer, a stalagmometer, or "any other device suitable for measuring surface tension." Note that the regulation requires the instruction from the manufacture of the device be kept with the log book. If a precision ring tensiometer is used, a copy of ASTM Method D 1331-89, "Standard Methods for Surface Tension of Solutions of Surface Active Agents," must be kept with the log book.

Tensiometer



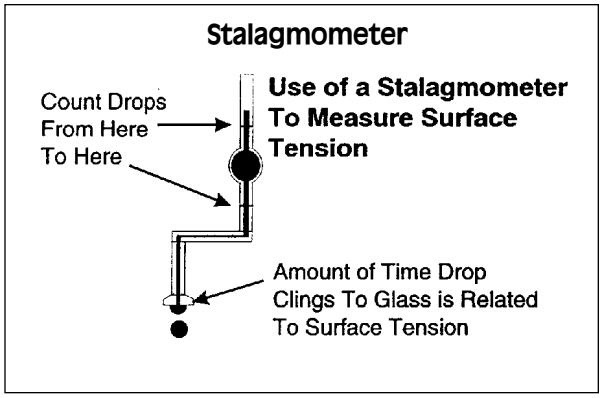
A—Torsion Screw
B—Sample Table Screw
C—Torsion Wire Adjust
D—Tension Screw
G—Torsion Arm Balancing Nut
H—Torsion Arm Ring Hook
K—Torsion Arm
I—Torsion Level Indicator
R—Platinum Ring
S—Graduated Dial
T—Sample Table
V—Vernier Index
W—Torsion Wire
Y—Upper Torsion Arm Stop
Z—Sample Vessel

Tensiometers

The oldest and most familiar way of measuring surface tension is with the du Nouy precision tensiometer, also known as the "ring method." This type of tensiometer is named after the French physicist who designed the original tensiometer in the 1800s. Tensiometers are essentially torsion balances that apply a slowly increasing force to a very accurately constructed platinum-iridium ring in contact with the surface of 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 is proportional to surface tension. The amount of the force is indicated upon a graduated scale that, when calibrated, gives readings in dynes of force per cm. If a facility uses a tensiometer, Method 306B in EPA's chromium MACT requires following ASTM D1331-56, the standard test method procedure for surface tension measurement.

Advantages & Disadvantages Of Tensiometers

The du Nouy tensiometer is the easiest and most accurate (+/- .05 dynes/cm) method of measuring surface tension. It only requires a small amount of solution for the measurement. Purchasing a tensiometer, however, can be cost prohibitive. Most basic models are $2,000–$3,000, but can be as much as $12,000 for more sophisticated pieces of equipment (*e.g.*, digital readouts). Extreme care must also be taken to avoid any damage to the platinum ring. Even a slight bend in the ring can be costly. It's usually about $300 to replace the ring alone. One facility has had difficulty conducting the surface tension measurements because machining vibrations from the shop were causing their solutions to



"break" sooner, thus yielding erroneous tensiometer readings.

There are other types of tensiometers on the market. They are, however, typically more expensive than a manual du Nouy tensiometer. The Wilhelmy Plate method uses a vertical plate of known perimeter that is attached to a balance, and the force due to wetting is measured. The Bubble Pressure method measures the maximum pressure of a bubble produced in the fluid and relates this pressure to surface tension. The Pendant Drop method is similar to the stalagmometer, but analyzes the geometry of each drop optically and relates this to surface tension.

Stalagmometer

A stalagmometer is a piece of equipment that uses a "dripping" technique for measuring surface tension. This method is also known as the "drop weight" method of measuring surface tension, because drops of solution drip from the tip of the stalagmometer and are counted to measure the surface tension of the solution. A stalagmometer is basically a pipette with a wide, flat tip that allows large droplets of reproducible size to form slowly, and finally drop. The weight of each drop is calculable from the total volume of the pipette, from the number of drops that fall, and from the density of the sample. For practical purposes, however, it is easier to count the number of drops that fall, the density of the sample, and the surface tension of water, which is used as a reference liquid for factory standardization of the stalagmometer.

Advantages and Disadvantages Of Stalagmometers

Stalagmometers are inexpensive, easy to use and to replace. Unfortunately, the process may take up to an hour to complete, after cleaning the apparatus and calculating the surface tension. For those facilities that will be monitoring every four hr, the time factor for conducting the test may not be cost effective in the long run.

Capillary Tube

A capillary tube is a tube with a very small bore (about 0.5 mm) in which liquid will rise because of the surface tension of that particular liquid. A capillary tube designed for surface tension measurements usually consists of a 250 mm glass capillary tube, graduated from 0–10 cm in 1 mm increments. The glass capillary tube is held inside a larger outer tube with a small cork. The outer tube is open at one end with a glass side-arm opening at the top to hold the rubber tubing. The principle of this technique is that, if a liquid wets a solid material, it will rise along the vertical surface of that material in contact with the liquid. This phenomenon is called "capillarity" and can be related to surface tension.

Advantages and Disadvantages Of Capillary Tubes

This apparatus is an economical and convenient system for measuring the surface tension of chromium plating solutions. The apparatus is extremely easy to break, and there are many opportunities during set-up, cleaning and conducting the test to do so. It has been our experience with one manufacturer that the tubing, rubber stopper, and rubber valve are not provided with the glassware. Set-up can be very time consuming if these items are not readily available.

Choose Carefully

The three techniques listed here are the easiest and most economical techniques for metal finishers. Remember, if you use any technique other that the ring precision tensiometer, you must keep the manufacturer's information with the equipment. Maintain all data in a single log book for good organization, and don't forget that one non-compliant reading will result in increasing the required measurement frequency to once every four hr for 40 hr of operation.

All three techniques are described in detail in *Chromium Emission Regulations and Compliance Information for Decorative Chromium Platers*, a manual published for the 1995 AESF Chromium Summit. The manual is $75 for AESF members and $100 for non-members. Order number is 20-305. To order by credit card, call AESF Publications Sales at 1-800/334-2052.

Author's note: There is some confusion about the chromium MACT standards, because EPA has proposed to defer for five years the date that chromium platers will be required to obtain a Title 5 permit. The proposed change only applies to the Title 5 permit. All other regulations and deadlines are still in effect and must be complied with by decorative and hard chromium platers. ***P&SF***

Acknowledgment:

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Chromium Colloquium & Course in Chromium Plating For Industrial Applications

Sheraton Cleveland City Centre
777 St. Clair Ave.
Cleveland, OH 44114
Ph: 217/771-7600

Course—March 25–26, 1996
Registration: $480 for AESF members; $580 for non-members.

Colloquium—March 27–28, 1996
Registration: $350 for AESF members; $450 for non-members.

$100 tabletops (in session room; requires registration of booth personnel).

For information: AESF Educational Services (Phone: 407/281-6441).

Capillary Tube

Suface Tension Apparatus

Includes 250mm borosilicate glass capillary tube (graduated from 0 to 10 cm in 1mm div.) and outer tube. Graduations are engraved. Capillary tube is held inside outer tube by means of a cork. Outer tube accomodates rubber tubing. Determine surface tension from height of liquid in capillary tube.