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CONDUCTING SURFACE TENSION MEASUREMENTS FOR COMPLIANCE WITH CHROMIUM MACT

ABSTRACT:
Conducting surface tension measurements to consistently meet 45 dynes/centimeter is a compliance option for decorative chromium plating facilities under the USEPA's National Emission Standards for Chromium Emissions (MACT Standard). It is important to understand the various techniques and procedures for measuring surface tension in order to find a suitable method for your shop.

LIST OF SLIDES

01 . AESF Slide
02. Title Slide
03. Definition of Surface Tension
04. Diagram of Chrome Emissions
05. USEPA's Method 306B
06. Schematic of Frequency of Measurements
07. Techniques of Measurement
08. Du Nouy Ring Tensiometer, diagram
09. Du Nouy Ring Tensiometer, photo
10. Equipment List
11. Cleaning Ring Tensiometer
12. Calibrating Ring Tensiometer
13. Calibrating Ring Tensiometer (cont.)
14. Advantages/Disadvantages of Tensiometers
15. Other Types of "Tensiometers"
16. Stalagmometer, photo
17. List of Equipment for Stalagmometer
18. List of Equipment for Stalagmometer
19. Cleaning Stalagmometer
20. Procedure Using Stalagmometer
21. Calculation of Surface Tension w/Stalagmometer
22 Advantages/Disadvantages of Stalagmometer
23. Capillary Tube Apparatus, photo
24. Equipment List
25. Cleaning Capillary Tube
26. Procedure Using Capillary Tube Apparatus
27. Calculation of Surface Tension w/Capillary Tube
28. Advantages/Disadvantages of Tensiometers
29. Summary

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Slide 1

Conducting Surface Tension Measurements for Compliance with Chromium MACT

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Slide 2

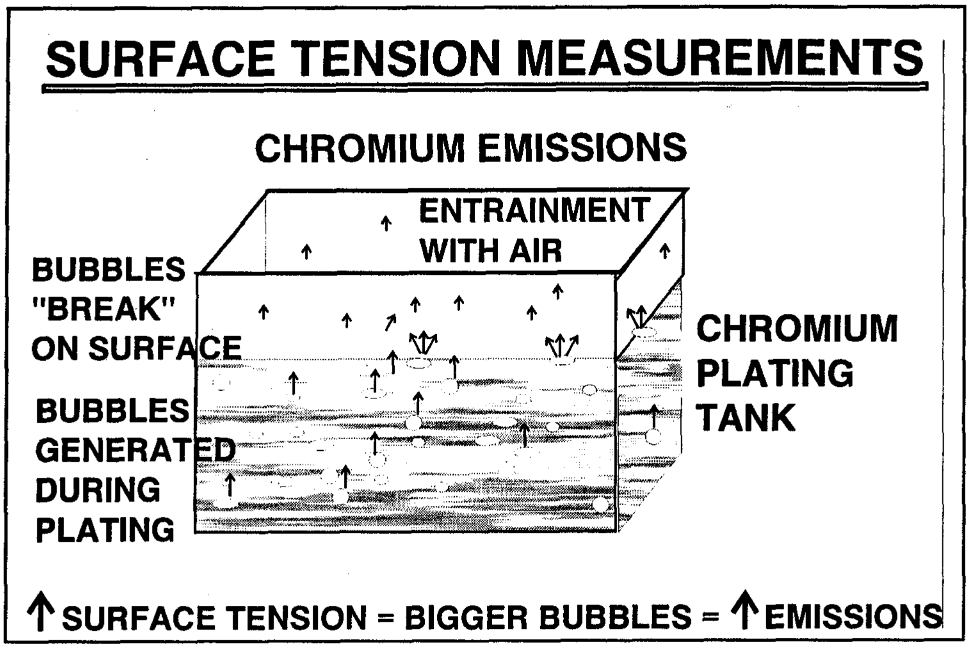
WHAT IS SURFACE TENSION?

- Makes surface of fluid behave as if its covered by a thin membrane
- Result of surface molecules contracting
- Force forms droplets, bubbles
- Usually measured in dynes/cm

Slide 3

WHAT IS SURFACE TENSION?

Surface tension is the property of a liquid in contact with air or vapor that makes it behave as if it were covered with a thin membrane under tension. For example, if you were to fill a glass of water, and carefully place a thin razor blade onto the top of the water, it would float for a short time due to this pseudo-membrane that supports it. This "tension" at the surface results from intermolecular forces within the solution that cause the exposed surface to contract to the smallest possible area. This is because a molecule in the interior of a solution interacts with other molecules equally, from all sides, whereas a molecule at the surface of liquid is only affected by the molecules below it. The property of surface tension is responsible for the formation of liquid droplets, soap bubbles, and menisci (the curved upward or downward appearance of a column of liquid). Surface tension is defined as the force acting over the surface of the solution per unit length of the surface perpendicular to the force. It is usually measured in dynes per centimeter.



Slide 4

The surface tension requirement was written into the USEPA Chromium MACT because during chromium plating, gas bubbles generated during the process rise to the surface of the tank solution and burst. Upon bursting, tiny droplets of chromic acid become entrained in the air and are emitted. The greater the surface tension of a solution, the larger these droplets will be. Consequently, more chromic acid vapor is emitted. Surfactants (aka "wetting agents") are surface active agents that reduce the surface tension of a liquid and diminishes the formation of these droplets. Most fume suppressants contain a surfactant. The use of these products is discussed at length later.

MEASURING SURFACE TENSION

USEPA'S METHOD 306B

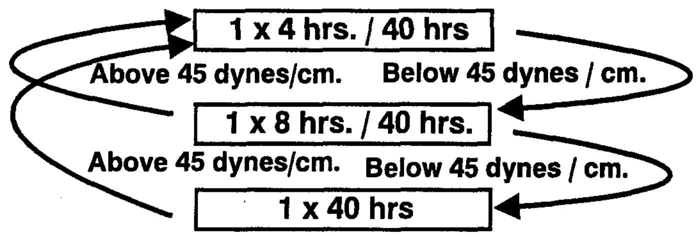
- 45 DYNES/CM LIMIT
- PROGRESSIVE FREQUENCY OF MEASUREMENTS
- LOG BOOK CONTAINING:
    - S.T. MEASUREMENTS
    - FUME SUPPRESSANT ADDS
    - MFG. INSTRUCTIONS
    - COPY OF ASTM D1331-89

Slide 5

The Chromium MACT for decorative chrome platers has provided an option of consistently meeting 45 dynes/centimeter 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 around 70 dynes/cm.

SURFACE TENSION MEASUREMENTS

FREQUENCY OF MEASUREMENTS



- **Any measurement over 45 dynes / cm., must return to 4 hour frequency for 40 hours of compliance**
- **Longest interval - One measurement in 40 hrs.**

Slide 6

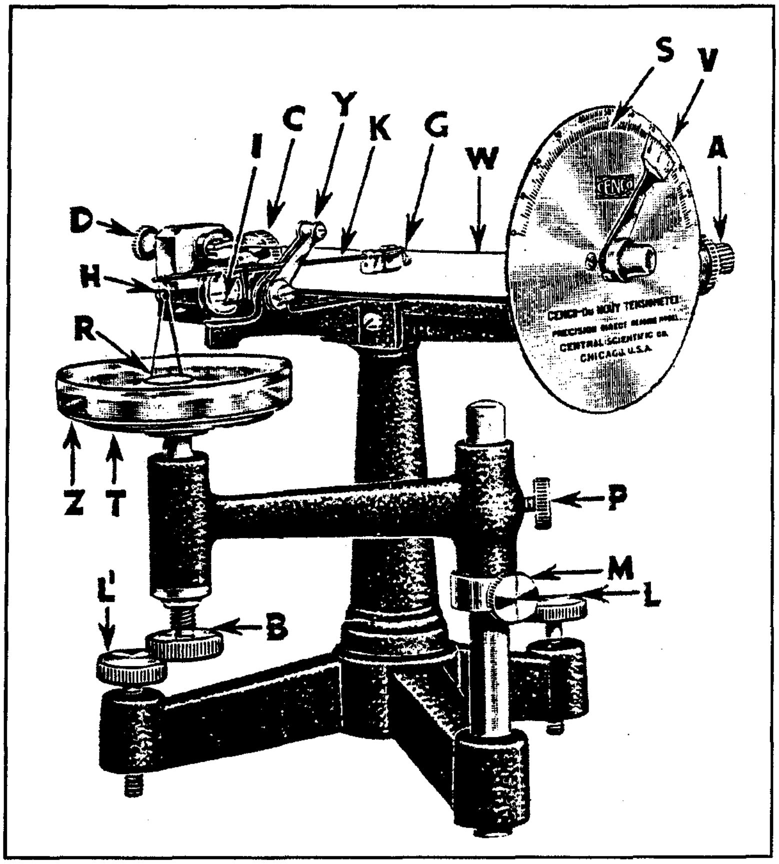
Frequent surface tension measurements of the plating bath are required initially, up to one time every four hours for the first forty hours of operation. The frequency of measurements decreases as compliance is maintained. If, at any time, one measurement is higher than 45 dynes/centimeter, the frequency of measurements must resume to once every four hours.

TECHNIQUES OF MEASUREMENT
• du Nouy "Ring" Tensiometer
• Stalagmometer
• Capillary Tube
• Any other "suitable" device

Slide 7

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 measurements taken with a stalagmometer. Static techniques of measurement 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 using a tensiometer, a stalagmometer, or "any other device suitable for measuring surface tension". Please note that the regulation requires that the instruction from the manufacture of the device must be kept with the log book. If you are using a precision ring tensiometer, a copy of ASTM Method D 1331-89, Standard Methods for Surface Tension of Solutions of Surface Active Agents (see Appendix A) must be kept with the log book.



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

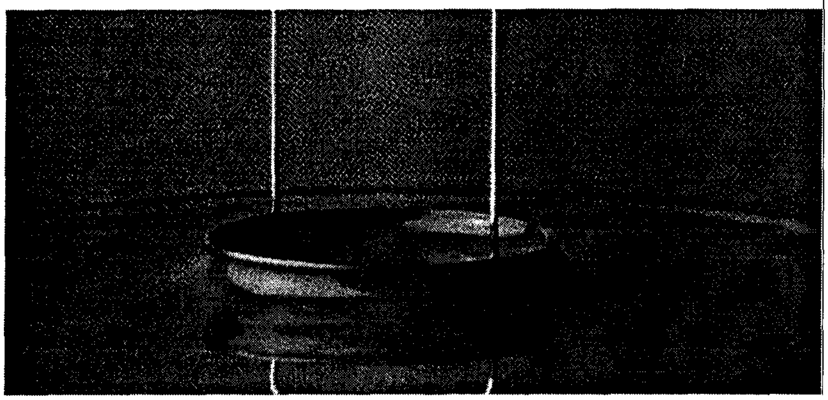
Y- Upper Torsion Arm Stop

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 1800's. 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 which, when calibrated, gives readings in dynes of force per centimeter. If your facility has opted to use a tensiometer, Method 306B in USEPA's Chromium MACT requires that you follow ASTM D1331-56, the standard test method procedure for surface tension measurement. Copies of this method are attached in Appendix A.

SURFACE TENSION MEASUREMENTS



Slide 9

The pull on the tensiometer ring is obtained by applying a torque to a fine wire, fixed at one end and attached at the other end to the movable index, which is driven by a small gear. This type of drive permits precise adjustment of the twisting action needed for measurement. An arm of steel tubing clamped to the center of the torsion wire applies the force to the ring suspended from its outer end. The theory of the ring method of surface tension measurement depends upon the ring being wet by the liquid it is immersed into.

EQUIPMENT

In order to prepare for a surface tension measurement with a tensiometer, you will need the following items:

LIST OF EQUIPMENT:
1- Tensiometer w/ undamaged platinum ring
1- Clean sampling vessel
1- Bunsen burner
1- Forceps
1- Calculator
1- Calibrating weight (see below)
1- Thermometer
50 mL plating solution
50 mL methyl alcohol

Slide 10

NOTE: Safety warning! Methyl alcohol is flammable. Please keep alcohol away from the bunsen burner, and make sure that the ring is triple rinsed with water prior to flaming.

CLEANING TENSIOMETER

- CLEAN RING & VESSEL CRITICAL
- INSPECT RING FOR BENDS, CRACKS
- RINSE RING AND VESSEL W/ METHYL ALCOHOL
- TRIPLE RINSE WITH DI WATER
- FLAME RING OVER BUNSEN BURNER

Slide 11

CLEANING

The most critical part of obtaining an accurate measurement of the tensiometer is making sure the platinum ring is free of dirt, and bends. The platinum ring is the most critical component of the tensiometer, and should be handled with care. The ring should always be handled with forceps or tweezers. Prior to beginning the test, rinse the ring with methyl alcohol, then rinse three times with deionized water, and place over the flame of a bunsen burner (or similar source of heat) for a short time. Allow the ring to cool prior to beginning the test.

CALIBRATING TENSIOMETER
• MAKE SURE TENSIOMETER IS LEVEL • ADJUST DIAL TO ZERO • PLACE WEIGHT ACROSS RING • ADJUST TORSION ARM UNTIL INDEX LEVEL IS OPPOSITE REF. LINE • RECORD READING • CALCULATE

Slide 12

CALIBRATION OF TENSIOMETER

To calibrate the tensiometer you may first need to adjust the length of the torsion arm so that the dial scale will read directly in dynes per centimeter. You will then need to ensure that the tensiometer is level, either by bolting it to a flat platform, or tightening it with clamps around the benchtop being used. Slowly pull the wire tight with the tension knob, and adjust the reading and the vernier to zero. Insert the platinum metal ring in the holder, and carefully place an accurately measured weight (no less than 500 mg and no greater than 800 mg) across the ring. If you do not have a weight, you can crumple a small piece of aluminum, weigh it on a digital balance, and if it is between 500 and 800 mg, use that in place of a weight. Carefully place the weight on the ring, and turn the rear adjusting screw until the index level of the arm is opposite of reference line of the mirror. Record this dial reading.

CALIBRATING TENSIOMETER (CONT.)

$$y = (M \times g)/2L$$

where:

- y = surface tension in dynes per centimeter
- M = weight placed on ring, in grams
- g = gravity constant (980.3 in Chicago)
- L = mean circumference of the ring (check w/mfg. usually 4 cm)

Slide 13

The above equation is used for calibrating your tensiometer. If the previously recorded reading (taken w/weight) is greater than the calculated value, then the tensiometer needs to be adjusted by shortening the torsion arm. If the recorded reading is less than the calculated value, the arm needs to be lengthened. Once the arm is adjusted, re-calibrate the tensiometer using the same procedure as before, until the recorded value matches the calculated value.

PROCEDURE USING TENSIOMETER

Prior to beginning your test, you should note the concentration of your chromium plating solution, and the quantity of surfactant used. Care should also be taken that the plating solution is physically homogeneous, particularly with solutions containing surface-active material in order to avoid unrepresentative measurement. Record the temperature of the liquid, and the date that the bath was last made-up. The surface tension of chromium plating solutions and other liquids increases with a decrease in temperature and vice-versa. It is necessary to report the temperature of the liquids upon which the temperature of the liquid.

After you have cleaned and calibrated the tensiometer, you are ready to begin the test on your chromium plating solution. Verify that the tensiometer is level, and insert the clean platinum ring that is to be used in the measurement. Place solution to be tested to clean sample vessel, and place vessel onto sample platform. Raise the platform with the adjusting screw until the ring is submerged. Once the ring is submerged, lower the platform slowly, while simultaneously applying torsion to the wire with the dial adjusting knob. These simultaneous adjustments must be carefully proportioned so that the ring system remains constantly in its zero position. As the "breaking point" between the solution and the ring approaches slower, smaller, and more careful adjustments must be made to the tensiometer. When the solution "breaks" (when it detaches from the ring), stop making adjustments, and record the dial reading. ASTM 1331 requires you to make at least two measurements, and more measurements may be necessary if the variation between readings is large.

CALCULATION OF SURFACE TENSION WITH TENSIOMETER

The dial reading obtained is actually an uncorrected or "apparent" surface tension reading. The reading must be corrected for the resistance at the contours of the liquid surface in the area of the ring at the instant of breakaway. This resistance causes a slightly higher surface tension reading. This correcting factor, F, is usually too small to vary the whole number measured directly from the tensiometer. However, the correction factor has been provided in Appendix A, if needed.

ADVANTAGES OF RING METHOD:

- ACCURATE
- RAPID MEASUREMENT
- EASY TO USE

DISADVANTAGES OF RING METHOD:

- EXPENSIVE
- SENSITIVE TO INDUSTRIAL ENVIRONMENT
- FRAGILE RING

Slide 14

ADVANTAGES/DISADVANTAGES

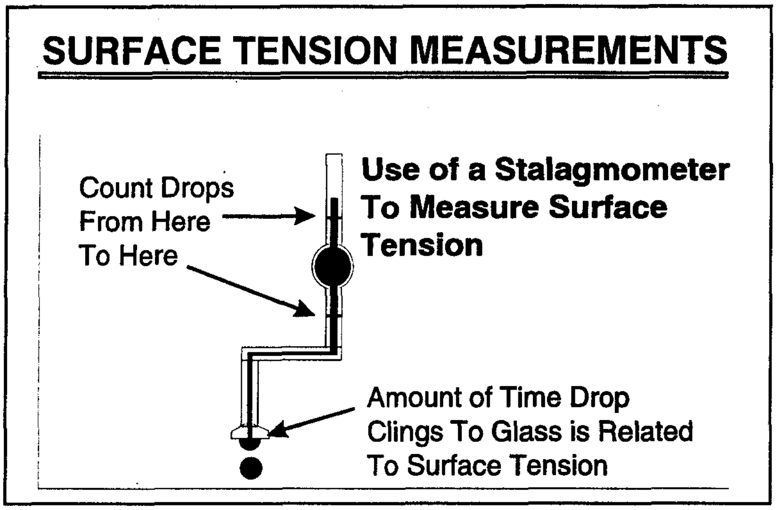
The du Nouy tensiometer is the easiest and most accurate (+/- .05 dynes/ centimeter) method of measuring surface tension. It only requires a small amount of solution for the measurement. Purchasing a tensiometer, however, can be cost prohibitive. Most basic models are $2000 - $3000, but can be as much as $12,000 for more sophisticated pieces of equipment (i.e. digital readouts). Also, extreme care must 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 difficultly conducting the surface tension measurements because machining vibrations from the shop was causing their solutions to "break" sooner, thus yielding erroneous tensiometer readings.

OTHER TYPES OF TENSIOMETERS:

- Wilhelmy Plate Method
- Bubble Pressure Method
- Pendant Drop Method

Slide 15

There are other types of tensiometers on the market, however, they are typically significantly more expensive than a manual duNouy 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.



Slide 16

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 drops which 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.

EQUIPMENT

You should plan on the surface tension reading with the stalagmometer to take approximately a half hour, including cleaning of the equipment. Cleaning of the stalagmometer is crucial to getting an accurate reading (and saving time!). In order to get set up for this test you will need the following equipment:

EQUIPMENT LIST:

1- Stalagmometer
1- Ring Stand
1- Rubber Bulb w/three-way valve
1- Thermometer Clamp
1- Base Stand
1- Hydrometer for Chromium
6- 150 mL beakers
7- Gloves, Personal Protective Equipment
8- Device for counting droplets (optional)

Slide 17

Most suppliers of stalagmometers will be able to provide you with a "package" for a little bit more money that will include the base stand, the ring stand, the thermometer clamp, rubber bulb, and any other equipment in addition to the stalagmometer that you may need to conduct the test.

You will need the following solutions:

EQUIPMENT LIST (cont.)

150 mL	Chromium Plating Solution, taken directly from bath
150 mL	Concentrated Nitric Acid
150 mL	Methyl Alcohol
150 mL	Deionized Water

Slide 18

NOTE: **Safety warning!** Because of the use of concentrated nitric acid and other dangerous chemicals, when conducting this test, you should wear the appropriate personal protective equipment (i.e. gloves, safety glasses, lab coat). Also, the nitric acid can emit noxious fumes, so conduct this test underneath a ventilated hood.

CLEANING OF STALAGMOMETER

- SET UP ON STAND W/BULB
- UNDER HOOD, DRAW HNO_3 INTO STALAGMOMETER PAST TOP ETCHED LINE
- DRAIN AFTER 5 MIN.
- TRIPLE RINSE W/ DI WATER
- RINSE W/ METHYL ALCOHOL
- ALLOW TO DRY FOR 10 MIN.

Slide 19

CLEANING OF STALAGMOMETER

Cleaning the stalagmometer is crucial to a successful surface tension reading. The manufacturer of your stalagmometer should supply you with directions on the best way to clean the stalagmometer. In order to clean the stalagmometer, place it into the stand. Under a ventilated fume hood, place 150 mL of concentrated nitric acid into the beaker. Immerse lower end of the stalagmometer deep into beaker of nitric acid (if it is not deep enough, you may suck air into the stalagmometer and have to start over). Squeeze the rubber bulb and when collapsed, place bulb on the top end of the stalagmometer. Carefully release the bulb, and slowly draw in the nitric acid past the top etched line on the stalagmometer. Allow the nitric acid to remain in the stalagmometer for 5 minutes. After 5 minutes, raise the stalagmometer in the stand so that the lower tip is out of the nitric acid solution. Remove the bulb and drain solution back into the beaker. For faster draining you may turn the stalagmometer upside-down, but be extremely carefully not to spill any solution. After nitric acid is drained, using the same procedure above, rinse stalagmometer 3-4 times with deionized water until you notice that inside of the stalagmometer is "water break" free. Using the same procedure, rinse stalagmometer with methyl alcohol and allow to dry completely (about five minutes).

PROCEDURE USING STALAGMOMETER:

- Measure S.G. w/ Hydrometer
- Draw solution into stalag. past top etched line
- Drain to top etched line
- Drain from top etched line to bottom etched line, counting # of drops that fall in between
- Calculate surface tension

Slide 20

TEST PROCEDURE

Fill 150 mL beaker with solution taken directly from chromium plating tank. Using a hydrometer, measure the specific gravity of the chromium plating solution. This measurement will need to be used in your calculation, so you should write it down. Using the same procedure for cleaning the stalagmometer, immerse the lower tip of the stalagmometer deep into the chromium solution. Wipe the tip of the stalagmometer by touching it against the side of a beaker. Release finger tip to allow solution to drain, counting the number of drops of solution that fall in the beaker. Do this until the solution in the stalagmometer reaches the bottom etched line. Write the number of drops down onto a piece of paper.

CALCULATING SURFACE TENSION WITH STALAGMOMETER

After conducting the test, you should have the written down the number of drops of sample counted, the water drop number, engraved on the stalagmometer, the density of sample, measured with hydrometer, the density of water at 25° C, and the surface tension of water at 25° C.

Surface tension measured with stalagmometer can be calculated with the following equation:

CALCULATION OF SURFACE TENSION WITH STALAGMOMETER:

$$S = \frac{(Sw)\ (Nw)\ (D)}{(N)}$$

where:

S	=	S.T. of sample, dynes/cm
Sw	=	S.T. of water (73)
N	=	#of drops of sample counted
Nw	=	Water drop number, engraved on the stalagmometer
D	=	Density of sample, g/mL

Slide 21

Surface tension measured with stalagmometer can be calculated by plugging our information into our equation written above. The number you will calculate from this equation will give you the surface tension of your solution (S) in dynes per centimeter.

ADVANTAGES OF STALAGMOMETER:

- INEXPENSIVE
- EASY TO USE

DISADVANTAGES:

- TIME CONSUMING
- EASY TO BREAK
- NOT AS ACCURATE AS TENSIOMETER

Slide 22

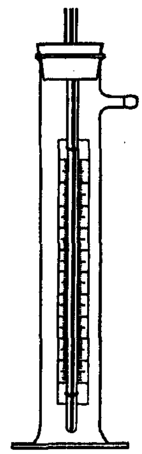
ADVANTAGES/DISADVANTAGES OF STALAGMOMETERS

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

SURFACE TENSION MEASUREMENTS

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.



Slide 23

CAPILLARY TUBE

A capillary tube is a tube with a very small bore (about 0.5 mm) in which a liquid will rise due to the surface tension 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 phenomena is called capillarity and can be related to surface tension.

EQUIPMENT

To prepare for the surface tension measurement with the capillary tube, you will need the following equipment:

EQUIPMENT LIST:

1 - Capillary Tube
1 - Outer Tube w/fretted nozzle
1 - Rubber hose
1 - Rubber Bulb w/3-way valve
1 - Rubber Stopper
1 - Magnifying Glass
1 - Calculator

Slide 24

NOTE: Safety warning! Use only a rubber bulb with a three-way valve to perform this test. Do NOT use your mouth to move to blow or suck on the tubing of this device, despite manufacturer's instructions. Using your mouth could result in ingesting some solution which would cause severe internal damage. Also, this process involves moving the solution up and down the open-ended capillary tube. If the solution is moved too high in the capillary, it could spill out the top, potentially exposing your skin to acid. Take precaution when conducting this test by using the appropriate personal protective equipment.

CLEANING CAPILLARY TUBE:

- CLEAN USING NITRIC ACID
- TRIPLE RINSE WITH DI WATER
- RINSE WITH METHYL ALCOHOL
- DRY FOR 5 MIN.

Slide 25

CLEANING

As with the other equipment, the capillary tube must be thoroughly cleaned prior to beginning the test. Fill the outer tube with nitric acid. Attach rubber bulb to rubber tubing and slowly squeeze bulb to "push" the acid through the capillary. Release bulb, and let acid drain into outer tube. Drain acid from outer tube and rinse with DI water. Using the same procedure for the nitric acid, rinse the capillary and outer tube with DI water three times. Finally, rinse methanol and let dry for 5 minutes.

PROCEDURE USING CAPILLARY TUBE:

- RINSE W/SAMPLE
- SUBMERGE CAPILLARY
- BLOW INTO TUBING AND ALLOW CAPILLARY MENISCUS TO COME TO EQUILIBRIUM
- MEASURE HEIGHT DIFFERENCE (IN CM) BETWEEN LOWER MENISCUS IN OUTER TUBE AND HIGHER MENISCUS IN CAPILLARY (NEED MAGNIFYING GLASS)
- REPEAT

Slide 26

PROCEDURE

Place approximately 100 mL of plating solution sample into the outer tube. Insert the capillary tube (with the cork) into the outer tube so that the lower end of the capillary tube is submerged. Affix the rubber tubing with rubber bulb to the sidearm, and carefully squeeze bulb so that the sample moves completely up and down the capillary tube. This ensures that the capillary tube is thoroughly wetted. Blow into the tubing again and allow the curved upward surface inside the capillary to come to equilibrium. Using reading glass, measure the distance (graduated on the tube in centimeters) between the lower meniscus in the outer tube and the upper meniscus in the capillary. Repeat this procedure. Next, detached the bulb, collapse it, and reattach onto the tubing. Release the valve on the bulb to allow the solution to be pulled down in the capillary. Allow the meniscus to come to equilibrium. Once again using the reading glass, measure the distance between the lower meniscus in the outer tube, and the upper meniscus in the capillary. Repeat this procedure. This procedure results in four measurements. Average the four measurements to determine the average height difference between menisci.

CALCULATION

Surface tension can be calculated from the rise in the capillary tube with the following equation:

CALCULATION WITH CAPILLARY TUBE:

$$y = 1/2\ (h)(r)(d)(g)$$

<u>where:</u>

y = surface tension (dynes per centimeter)

h = height difference between menisci, as measured (cm)

r = radius of capillary (given by manufacturer)

d = density of sample (g/cm^3)

g = acceleration of gravity (980.3 cm/sec^2 in Chicago)

Slide 27

CAPILLARY TUBE:

ADVANTAGES

- INEXPENSIVE

DISADVANTAGES:

- NOT VERY ACCURATE
- BREAKS EASY

Slide 28

ADVANTAGES/DISADVANTAGES OF CAPILLARY TUBES

This apparatus is can very economical and convenient system for measuring the surface tension of your chromium plating bath. 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. This can make for a time consuming set-up if you do not have these items readily available.

SUMMARY:

- FIND METHOD BEST FOR YOU
- ACCURATE LOG BOOK
- MONITOR SURFACTANT ADDITIONS
- ONE NON-COMPLIANCE READING = READING EVERY 4 HRS FOR 40 HRS.

Slide 29

The three techniques described in this lecture comprise the easiest and most economical techniques for metal finishers. Remember that if you use any technique other than the ring precision tensiometer, you must keep the manufacturer's information with the equipment. Maintain all of your data in a single log book for good organization. Also, don't forget that one non-compliant reading will result in the increasing the measurement frequency to once every 4 hours for forty hours of operation.

APPENDIX A

Designation: D 1331 – 56 (Reapproved 1980)

Standard Test Methods for
SURFACE AND INTERFACIAL TENSION OF SOLUTIONS OF SURFACE-ACTIVE AGENTS[1]

This standard is issued under the fixed designation D 1331; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These methods cover the determination of surface tension and interfacial tension of solutions of surface-active agents, as defined in ASTM Definitions D 459, Terms Relating to Soaps and Other Detergents.[2] Two methods are covered as follows:

Method A. Surface Tension.

Method B. Interfacial Tension.

1.2 Method A is written primarily to cover aqueous solutions of surface-active agents, but is also applicable to nonaqueous solutions and mixed solvent solutions. Method B is applicable to two-phase solutions. More than one solute component may be present, including solute components that are not in themselves surface-active.

2. Apparatus

2.1 *Tensiometer*—Either the du Nouy precision tensiometer or the du Nouy interfacial tensiometer, equipped with either the 4 or the 6-cm circumference platinum ring, as furnished by the manufacturer, may be used. The tensiometer shall be placed on a sturdy support that is free from vibrations and other disturbances such as wind, sunlight, and heat. The wire of the ring shall be in one plane, free of bends or irregularities, and circular. When set in the instrument, the plane of the ring shall be horizontal, that is, parallel to the surface plane of the liquid being tested.

2.2 *Sample Container*—The vessel for holding the liquid shall be not less than 6 cm in diameter, and sufficiently large to ensure that the contact angle between the ring and the interface is zero.

3. Preparation of Apparatus

3.1 Clean all glassware thoroughly. The use of fresh chromic-sulfuric acid cleaning mixture, followed by a thorough rinsing in distilled water, is recommended.

3.2 Clean the platinum ring by rinsing thoroughly in a suitable solvent and in distilled water, before taking a set of measurements. Allow the ring to dry, and then heat to white heat in the oxidizing portion of a gas flame.

4. Calibration of Apparatus

4.1 The tensiometer is, in fact, a torsion balance, and the absolute accuracy depends on the length of the torsion arm, which is adjustable. Torsion may be applied to the wire by means of either the dial-adjusting screw (which controls the dial reading) or a rear adjusting screw. Calibration consists essentially in adjusting the length of the torsion arm so that the dial scale will read directly in dynes per centimeter. The precision tensiometer shall be calibrated in accordance with the following: 4.1.1 to 4.1.3; the interfacial tensiometer shall be calibrated in accordance with 4.1.1 to 4.1.4.

4.1.1 Level the tensiometer. A liquid level of the type employed on analytical balances may be used. Place the level on the table that holds the sample for testing, and adjust the leg

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[1] These methods are under the jurisdiction of ASTM Committee D-12 on Soaps and Other Detergents.

Current edition effective Sept. 10, 1956. Originally issued 1954. Replaces D 1331 - 54 T.

[2] *1983 Annual Book of ASTM Standards*, Vol 15.04.

screws of the tensiometer until the table is horizontal. Pull the torsion wire taut by means of the tension screw, and adjust the dial reading and the vernier to zero. Insert the platinum ring in the holder, and place a small piece of paper across the ring. This will serve as a platform to hold the calibrating weight. Turn the rear adjusting screw of the torsion wire until the index level of the arm is opposite the reference line of the mirror; this automatically compensates for the weight of the paper platform. Next, place an accurately standardized weight of between 500 and 800 mg on the paper platform and turn the dial-adjusting screw until the index level of the arm is opposite the reference line of the mirror. Record the dial reading to 0.10 division. Call this "gamma-c."

4.1.2 Calculate what the reading "gamma-c" obtained in 4.1.1 *should be* when the tensiometer is properly adjusted, as follows (Note 1):

$$\gamma_c = (M \times g)/2L$$

where:

M = weight placed on the paper platform, in grams,

g = gravity constant (Note 2), in cgs units, and

L = mean circumference of the ring (furnished by the manufacturer with each ring).

If the recorded dial reading "gamma-c" is greater than the calculated value, the torsion arm should be shortened. If "gamma-c" is less than the calculated value, the torsion arm should be lengthened. Repeat the calibration procedure, readjusting the zero position after each change in the length of the torsion arm, until the dial reading agrees with the calculated value. Each unit of the scale now represents a pull on the ring of 1 dyne/cm. Note that a conversion factor, F (see 4.1.3), must be multiplied by the scale reading to give corrected surface tension in dynes per centimeter.

NOTE 1 *Example*—If M is exactly 0.600 g and L is 4.00 cm:

$$\gamma_c = (0.600 \times 980.3)/(2 \times 4.00) = 73.52 \text{ dynes/cm}$$

NOTE 2—The gravity constant is 980.3 at Chicago; in other localities it will differ very slightly from this value.

4.1.3 After the tensiometer has been calibrated, it is convenient to calculate the number of grams total pull on the ring that is represented by each scale division. This is done simply by dividing the scale reading into the weight used for calibration (Note 3). This value is used in the calculation of the conversion factor, F, mentioned in 4.1.2.

NOTE 3—In the example given in Note 1, each scale unit after calibration represents:

$$0.600/73.52 = 0.008161 \text{ g}$$

4.1.4 *Interfacial Tensiometer*—With the interfacial tensiometer, the same principle of calibrating by adjusting the length of the torsion arm also applies. This instrument has, however, in addition to the torsion arm, a torsion-arm counterbalance. Adjust the length of this counterbalance to coincide with that of the torsion arm itself, in order that the vertical members of the assembly may remain in line.

METHOD A. SURFACE TENSION

5. Procedure

5.1 After the tensiometer has been calibrated, check the level and insert the cleaned platinum ring (Note 4) that will be used in the measurement. Check the plane of the ring, and set the dial and vernier at zero. Adjust the rear adjusting screw so that the index level of the arm is opposite the reference mark on the mirror, that is, the ring system is at the zero position.

NOTE 4—Extreme care must be taken to have the sample vessel and platinum ring clean. Contamination of the liquid surface by dust or other atmospheric impurities during measurement should be avoided.

5.2 Place the solution to be tested (Note 5), contained in the thoroughly cleaned vessel (Note 4), on the sample platform. Raise the sample platform by means of its adjusting screw until the ring is just submerged.

NOTE 5—Since the surface tension of a solution is a function of the concentration, care must be taken that the concentration is adjusted and recorded within known limits. The presence of solutes other than the surface-active agent should be ascertained and reported qualitatively and quantitatively, insofar as possible. This includes hardness components in the water. Care should be taken that the solution is physically homogeneous. Measurements made near or above the cloud point or other critical solubility points can be in serious error. This is ticularly true when the solute is a surface-active material.

5.3 Lower the platform slowly, at the same time applying torsion to the wire by means of the dial-adjusting screw. These simultaneous adjustments must be carefully proportioned so that the ring system remains constantly in its zero position. As the breaking point is approached, the adjustments must be made more carefully and more slowly. Record the dial reading when the ring detaches from the surface.

5.4 Make at least two measurements. Additional measurements shall be made if indicated by the over-all variation obtained, the total number of readings to be determined by the magnitude of that variation.

5.5 Record the temperature of the solution and the age of the surface at the time of testing. Since the submerging of the ring (5.2) may constitute a significant disturbance of the surface, take the age as the elapsed time between submersion and breakaway of the ring. The accuracy of this time observation may be indicated in the usual manner. In most cases an accuracy of ±5 s is reasonable, and sufficient for this method.

6. Calculation and Report

6.1 The dial reading, obtained from a measurement carried out in the foregoing manner with a calibrated instrument, is actually the pull per linear centimeter on the ring (both inner and outer circumference being considered) at the break-point, expressed in dynes. This value, called the uncorrected surface tension, must be multiplied by a correcting factor, F, to give the corrected surface tension. F is a function of the contours of the liquid surface in the neighborhood of the ring at the instant of breakaway. It can be numerically specified in terms of R, the mean radius, in centimeters, of the ring; r, the radius, in centimeters, of the wire from which the ring is made; and V, the maximum volume of liquid elevated above the free surface of the liquid. For liquids of low surface tension, such as surface-active agents, F is, in general, appreciably less than unity. It must, therefore, be ascertained and applied. Values of F in terms of two compounded parameters, R^3/V and R/r have been compiled and tabulated by Harkins and Jordan.[3] In order to look up F in the tables, the values of these two parameters must be calculated. Values for R and r are furnished by the manufacturer with each ring. The value of V is calculated from the following equation:

$$V = M/(D - d)$$

where:

M = weight of liquid raised above free surface of the liquid,
D = density of liquid, and
d = density of air saturated with vapor of the liquid.

To calculate M, multiply the tensiometer dial reading by the factor which converts this reading into grams pull on the ring, as calculated in 4.1.3. The factor D can be measured by the usual procedures, and the value d can be obtained from published data. The corrected surface tension in dynes per centimeter is obtained by multiplying the uncorrected surface tension value by F.

6.2 Unless specified, the surface tension values reported shall be corrected values. Report also the temperature at which the measurement was made. If it is desired to report the surface tension value of an aqueous solution at some standard temperature, for example, 25 C, and the measurement was actually made at a temperature within about 3 C of this value (that is, 22 to 28 C), a correction factor of 0.14 dynes/cm · deg C may be used. Subtract this correction factor from the surface tension when the temperature of the test is lower than the reported temperature, and add it to the surface tension when the temperature of the test is higher than the reported temperature. This value for the correction factor is not valid for nonaqueous liquids, and should be used only where the solvent is preponderantly water.

Method B. Interfacial Tension

7. Procedure

7.1 Determine interfacial tension as described in Section 5 for surface tension, with the following modifications:

7.1.1 Always move the ring from the aqueous side of the interface through to the nonaqueous side. With liquids lighter than water, it is accordingly possible to use the precision tensiometer as well as the interfacial tensiometer. With liquids heavier than water, where the ring must be pushed downward, the interfacial tensiometer should be used.

7.1.2 Use fresh solutions and a freshly cleaned ring for each determination.

7.1.3 When operating with a liquid heavier than the aqueous solution, place the two-layer system in the sample vessel and place the ring in the upper (aqueous) layer. Make the measurement by turning the torsion wire counter-clockwise and simultaneously keeping the ring system in the zero position, as in the measurement of surface tension, until the ring breaks through the interface.

7.1.4 When operating with a liquid (oil) lighter than the aqueous solution, first place the aqueous solution in the sample vessel and immerse the ring therein. Carefully pour the oil on top of the aqueous solution to form the two-layer system. Contact between the oil and the ring should be avoided during this operation. After allowing sufficient time for the interfacial tension to come to its equilibrium value (Note 6), make the measurement in the same manner as that used for measuring surface tension.

Note 6—Since the interfacial energy of a newly formed liquid-liquid interface generally requires some time to reach its equilibrium value, it is advisable to wait at least 5 min after the interface is formed before taking a measurement.

8. Calculation and Report

8.1 As in the case of surface tension, a correction factor, F, must be multiplied by the dial reading (pull on the ring in dynes) in order to obtain the corrected value for interfacial tension. Values for F have been published by Zuidema and Waters.[4] The factor F is, in this case, a function of the densities of the two liquids as well as of R and r, the radius of the ring and that of the wire, respectively.

8.2 Unless specified, interfacial tension values reported shall be corrected values. Report and adequately specify the nature of the nonaqueous liquid (oil) used in the determination. Also report the temperature at which the determination was made. In contrast to surface tension values, interfacial tension values cannot adequately be corrected for small temperature deviations by means of a simple formula.

[3] Harkins, W. D., and Jordan, H. F., "A Method for Determination of Surface and Interfacial Tension from the Maximum Pull on a Ring," *Journal Am. Chemical Soc.*, Vol 52, 1930, p. 1751. These tables are also published in *Physical Methods of Organic Chemistry*, Interscience Publishers, Inc., New York, N. Y., Vol 1, 1945, pp. 182-184.

[4] Zuidema, H. H., and Waters, G. W., "A Ring Method for Determination of Interfacial Tension," *Industrial and Engineering Chemistry*, Analytical Edition, Vol 13, 1941, p. 312.

CORRECTION FACTOR FOR TENSIOMETER

The reading given by the ring tensiometer dial is apparent surface tension. Actual surface tension is found by applying a correction factor. The tensiometer measures the amount of force required to pull the ring through a liquid surface. Resistance, by the nature of the ring, and from sample density, produces a slightly higher surface tension reading.

The correction factor offsets properties of both ring and sample at the point of detachment.

The difference between actual and apparent readings is typically less than six percent. Some readings, however, may differ from the true value by as much as 30 percent.

$$A = P * F$$

Where:

- A = Actual Surface Tension
- P = Apparent Surface Tension (dial reading)
- F = Correction Factor

Determine the correction factor with the following formula:

$$F = 0.7250 + \frac{0.0145(P)}{C^2 (D-d)} + 0.04534 - \frac{1.67(r)}{R}$$

Where:

- F = Correction Factor
- P = Apparent Surface Tension (dial reading)
- C = Ring Circumference (usually 4 cm)
- D = Density of Lower Phase (Sample)
- d = Density of Upper Phase (Air)
- R = Radius of Ring
- r = Radius of Ring Wire

You will most likely need to verify the R and r values with the manufacturer.

METHOD 306-B
SURFACE TENSION MEASUREMENT AND RECORD~EEPING FOR CHROMIUM PLATING TANRS USED AT ELECTROPLATING AND ANODIZING FACILITIES

1. Applicability and Principle

1.1 Applicability. This method is applicable to all decorative plating and anodizing operations where a wetting agent is used in the tank as the primary mechanism for reducing emissions from the surface of the solution.

1.2 Principle. During an electroplating or anodizing operation, gas bubbles generated during the process rise to the surface of the tank liquid and burst. Upon bursting, tiny droplets of chromic acid become entrained in ambient air. The addition of a wetting agent to the tank bath reduces the surface tension of the liquid and diminishes the formation of these droplets.

2. Apparatus

2.1 Stalagmometer. Any commercially available stalagmometer or equivalent surface tension measuring device may be used to measure the surface tension of the plating or anodizing tank liquid.

2.2 Preciser tensiometer. A Preciser tensiometer may be used to measure the surface tension of the tank liquid provided the procedures specified in ASTM D 1331-89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents (incorporated by reference--see 63.14) are followed.

3. Procedure

3.1 The surface tension of the tank bath may be measured by using a Preciser tensiometer, a stalagmometer or any other device suitable for measuring surface tension in dynes per centimeter. If the Preciser tensiometer is used, the instructions given in ASTM D 1331-89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents (incorporated by reference--see 63.14) must be followed. If a stalagmometer or other device is used to measure surface tension, the instructions that came with the measuring device must be followed.

3.2 (a) Measurements of the bath surface tension are done using a progressive system which minimizes the number of surface tension measurements required when the proper surface tension is maintained. Initially, measurements must be made every 4 hours of tank operation for the first 40 hours of tank operation after the compliance date. Once there are no exceedances during 40 hours of tank operation, measurements may be conducted once every 8 hours of tank operation. Once there are no exceedances during 40 hours of tank operation, measurements may be conducted once every 40 hours of tank operation on an on-going basis, until an exceedance occurs. The maximum time interval for measurements is once every 40 hours of tank operation.

(b) If a measurement of the surface tension of the solution is above the 40 dynes per centimeter limit, the time interval reverts back to the original monitoring schedule of once every 4 hours. A subsequent decrease in frequency would then be allowed according to the previous paragraph.

4. Recordkeeping

4.1 Log book of surface tension measurements and fume suppressant additions. The surface tension of the plating or anodizing tank bath must be measured as specified in section 3.2. The measurements must be recorded in the log book. In addition to the record of surface tension measurements, the frequency of fume suppressant maintenance additions and the amount of fume suppressant added during each maintenance addition will be recorded in the log book. The log book will be readily available for inspection by regulatory personnel.

4.2 Instructions for apparatus used in measuring surface tension. Also included with the log book must be a copy of the instructions for the apparatus used for measuring the surface tension of the plating or anodizing bath. If a Preciser tensiometer is used, a copy of ASTM D 1331-89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents (incorporated by reference--see 63.14) must be included with the log book. If a stalagmometer or other surface tension measuring device is used, the instructions that came with the apparatus must be included with the log book.