

# CNS Institute for Physics Teachers

<b>Title:</b>	<b>The Clearly Colorful Thin Film Lab (Physics Edition)</b>
<b>Original:</b> <b>Revision:</b>	1 July 2004 24 June 2010
<b>Authors:</b>	Martin Alderman
<b>Appropriate Level:</b>	Regents (enrichment) Honors and AP Physics Science Club
<b>Abstract:</b>	<p>Thin films, like soap bubbles and oil slicks, owe their pretty colors to the process of thin film interference. Anodized Titanium, Scandium, Niobium, and Tantalum also exhibit lovely coloration due to thin film interference associated with the oxide film anodizing creates. These are <i>so</i> lovely, in fact, that they are sometimes used to make jewelry! In this activity, each team of students will observe a sampling of thin films. They will then anodize a small sample of titanium to observe the nature of the electrochemical reaction (anodizing), <math>\text{TiO}_2</math> thin film interference, and the relationship between the thickness of the <math>\text{TiO}_2</math> film formed and the color seen on the metal. Future modules are planned for this experiment, which will add specific quantitative examination of the thin films observed here.</p>
<b>Time Required:</b>	<p>Two 40 minute class periods:</p> <ul style="list-style-type: none"><li>~ 5 minutes: 'engage' the students and introduce the lab</li><li>~ 10 minutes: Soap bubble thin film station</li><li>~ 10 minutes: Nail polish thin film station</li><li>~ 25 minutes: Anodized titanium Thin film station</li><li>~ 25 minutes to explain the basics of thin film interference</li></ul> <p>One 40 minute class period to show a sample thin film interference calculation, and to have students work out another sample with their lab partners.</p>
<b>NY State Standards:</b>	See next page for NY State Standards met and AP Physics content outline items.

## **NY Standards Met:**

This activity on thin film interference addresses the following NYS Standards:

### **STANDARD 1 - Analysis, Inquiry, and Design**

Key Idea 1: The central purpose of scientific inquiry is to develop explanations of natural phenomena in a continuing, creative process.

Key Idea 2: Beyond the use of reasoning and consensus, scientific inquiry involves the testing of proposed explanations involving the use of conventional techniques and procedures and usually requiring considerable ingenuity.

Key Idea 3: The observations made while testing proposed explanations, when analyzed using conventional and invented methods, provide new insights into phenomena.

### **STANDARD 7 - Interdisciplinary Problem Solving CONNECTIONS:**

Key Idea 1: The knowledge and skills of ..., science, and technology are used together to make informed decisions and solve problems, especially those relating to ..., consumer decision making, design, and inquiry into phenomena.

### **STANDARD 4 - Key idea 4.3:**

iii. identify nodes and antinodes in standing waves

vi. predict the superposition of two waves interfering constructively and destructively (indicating nodes, antinodes, and standing waves)

vii. observe, sketch, and interpret the behavior of wave fronts as they reflect, refract, and diffract

viii. draw ray diagrams to represent the reflection and refraction of waves

### **PERFORMANCE INDICATOR 4.3**

4.3c The model of a wave incorporates the characteristics of ..., wavelength,\* ..., and phase.

4.3h When a wave strikes a boundary between two media, reflection\*, transmission, and absorption occur. A transmitted wave may be refracted.

4.3j The absolute index of refraction is inversely proportional to the speed of a wave.\*

4.3m When waves of a similar nature meet, the resulting interference may be explained using the principle of superposition. Standing waves are a special case of interference.

Process Skills: The student will be able to predict the superposition of two waves interfering constructively and destructively (indicating nodes, antinodes, and standing waves) (4.3vi)

Core reference: 4.3c, 4.3f 4.3m

Real-World Application: stereo speakers, surround sound, iridescence (e.g., butterfly wings, soap bubbles)

## **Content Outline for AP Physics B**

IV. Waves and Optics                      A. Wave motion    4. Superposition

### **Course Objectives for AP Physics:**

IV. Waves and Optics                      B. Physical Optics

1. Students should understand the interference and diffraction of waves so they can:

c) Apply the principles of interference to light reflected by thin films to they can:

(1) State under what conditions a phase reversal occurs when light is reflected from the interface between two media of different indices of refraction.

(2) Determine whether rays of monochromatic light reflected from two such interfaces will interfere constructively or destructively, and thereby account for Newton's rings and similar phenomena, and explain how glass may be coated to minimize reflection of visible light.

### **Behavioral Objectives - Physics:**

Upon completion of this lab a student should be able to:

- Identify film thickness, and film substance, as material determinants of the particular colors observed in particular thin films.
- Identify phase shift upon reflection, thickness of film (actual path length), effective thickness of film (actual path length corrected for the influence of refraction), and constructive and destructive interference as the physics factors resulting in colors in thin films.
- Explain the general process whereby thin film interference causes observable colors and patterns of color in soap films, nail polish films, and other thin films using appropriate physics terms and concepts.
- Explain the variation in resistance and current as the Ti anodizing reaction progresses, and the benefit of increasing voltage in stages as in the procedure used.

### **Behavioral Objectives – Chemistry:**

Upon completion of this lab a student should be able to:

- Explain some of the electrochemical process that creates a thin, transparent oxide film on a titanium sample. More details are examined in the chemistry edit of this lab.

### **Teacher Preparation Time Required:**

- 40 minutes (plus time for ordering new material and printing)

### **Class Time Required:**

- 2 class periods
  - ~ 5 minutes: ‘engage’ the students and introduce the lab
  - ~ 10 minutes: Soap bubble thin film station
  - ~ 10 minutes: Nail polish thin film station
  - ~ 25 minutes: Anodized titanium Thin film station
  - ~ 25 minutes to explain the basics of thin film interference.
- 1 class period to show a sample thin film interference calculation, and to have students work out another sample with their lab partners.

### **Materials Needed:**

Soap Film:

- ‘Bubble Stuff’ (commercial ‘bubble stuff’ works well, but it gets better if one mixes equal parts of commercial ‘bubble stuff,’ water, and glycerin)
- ~ 500 ml clear, colorless, smooth, straight-sided bottles (clean, empty, water, soda, milk, or juice bottles with their labels removed)
- Clean plastic drink straws

#### Nail Polish Film:

- Clear nail polish
- A fine tip disposable plastic pipette or eyedropper if the polish does not have a suitable brush
- ¼ sheet (~4 ½" x 6") of black construction paper or black card stock per student (Test the paper for color-fast black tint in advance. A few brands will bleed badly in the water.)
- A cake pan or similar water container (large enough to hold the piece of paper flat in the bottom, black microwaveable plastic trays from frozen food work especially well because of the black background)
- A plastic fork or small spatula to aid in lifting the paper from the water

#### TiO<sub>2</sub> Film:

- A titanium sample (this could be a strip of Ti sheet metal roughly .8-.9 mm thick x .8 cm wide x 8-9 cm long or a Ti wire 2-3mm thick x 8-9 cm long)
- A stainless steel electrode (this could be a strip of SS similar in size to the Ti or it could be a good sized SS bolt or screw ~4-5 cm long.)
- Small strips of 400 grit and finer emery or wet/dry abrasive paper (for cleaning the Ti)
- Isopropyl alcohol (to clean oils, grease, and ink off the Ti)
- One (1) [0.0 – 26.0 V or more] DC Power Supply
- One (1) [0.0 – 26.0 V ± .1 V] Voltmeter w/ leads (one red, one black for simplicity)
- Two (2) ~30 cm Alligator-clip & banana plug leads (one red, one black for simplicity)
- One (1) ~250 ml beaker or plastic cup with enough water to *almost* submerge the Ti
- Water (distilled not required)
- Laundry borax (sodium tetraborate) or washing soda to make the electrolyte. The electrolyte can be made up in advance and re-used many times as it is not depleted when the water is electrolyzed. Dissolve ~1 slightly rounded teaspoon (roughly 7 grams) of sodium tetraborate in 200 ml of water for each student workstation.
- Fine point waterproof marker (Fine point 'Sharpie' markers seem to work best)
- Tape, coffee stirrers, or clothespins (to hold the electrodes in position in the beaker or cup)
- Paper towels to gently dry the Ti after each step

Safety: This is a safe lab to do, but the following is worth being aware of:

- It is *always* good practice to wear safety glasses during labs.
- MSDS – sodium tetraborate: Harmful if swallowed or inhaled. Avoid contact with eyes, skin, and clothing. Avoid breathing dust. Use with adequate ventilation. Wash thoroughly after handling. *The MSDS goes on to say that the risks with this are minor.*
- Electricity: The maximum voltage here is 26 V, and will not push dangerous currents through normal body resistances. 26 V might give a student with wet hands a bit of a start, though, and some care should be used, especially to help students develop good safety habits. Some of the following are more about good habits than safety in this lab.
  - Handle insulated surfaces only, and dry hands are safer hands!
  - Work with one hand at a time in order to avoid becoming part of the circuit.

- If the power supply used in this experiment is capable of higher voltages, extra care must be exercised. *\*Higher voltages will actually yield worse results in this experiment! \**
- Since the connection points for this experiment are un-insulated, be especially careful to avoid short circuits. A short circuit here could make the wires hot enough to cause a burn!
- Spills – Plastic cups are not very stable, so a bit of care is needed here. One can tape the reaction cup to the lab bench, a ring stand, or other support for stability, and encourage students to exercise care not to bump the cups. The laundry borax used in the electrolyte is simple to clean up. It is safe to mop up and can be poured down conventional plumbing.

### **Assumed Prior Knowledge of Students:**

- This is a culminating activity for the unit on waves. Students are assumed to be comfortable with most of the unit on waves, including:
  - basic definitions and conceptual understanding, *excluding thin film* interference.
  - quantitative competence with the law of reflection, Snell's law, and single, double, and multi-slit interference.
- Students are assumed to have studied chemistry at some level, and to be familiar with basic qualitative electrochemistry.
  - (Terms: Redox reaction, electrolyte, electroplate, electrolysis)
  - A chemistry oriented edit of this experiment is available on request.

### **Tips for the Teacher:**

**VERY IMPORTANT:** We have found that students come into this lab with the belief that diffraction and interference *always* occur together. Some seem to think that they are essentially the same thing. This lab is a wonderful example of a case where there is interference, but *diffraction is not involved at all!* Be sure your students understand this important concept: Diffraction and interference are very different physical phenomena!

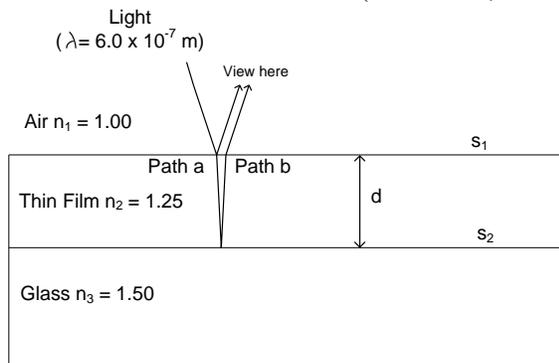
### **[Sample ENGAGE]**

“Check out the beautiful colors in these earrings I just bought for my wife! Aren't they great?! I was wondering how they got such beautiful colors, so I did some snooping. OK, I'm a nerd! Anyway, I found out how they do it! Guess what?! It's Physics!!! It's ALL Physics!!! The color comes from the same phenomenon as the color in soap bubbles and oil films.”

[The even more vivid colors seen in some anodized aluminum are *not* from thin film interference. When aluminum is anodized, the surface of the metal hardens and temporarily becomes quite porous. After being anodized, the aluminum is immediately rinsed and transferred to a dye container where the dye becomes incorporated into the surface of the metal. The coloring is very attractive and quite durable, but again, it is *not* thin film interference.]

**Answers to Questions:** *send request for answers to [cipt\\_contact@cornell.edu](mailto:cipt_contact@cornell.edu)*

AP Physics Exam  
(June 1984, Part II, Number 5 The Solution)



a)  $c = f \lambda$

b) Snell's Law:  $n_1 \lambda_1 = n_2 \lambda_2$

$$f = \frac{c}{\lambda}$$

$$1.00 (6.00 \times 10^{-7} \text{ m}) = 1.25 \lambda_2$$

$$f = \frac{3.0 \times 10^8 \frac{\text{m}}{\text{s}}}{6.0 \times 10^{-7} \text{ m}}$$

$$\lambda_2 = 4.8 \times 10^{-7} \text{ m}$$

$$f = 5.0 \times 10^{14} \text{ Hz}$$

- c<sub>1</sub>) The reflection at  $s_1$  has light hitting a higher index (slower) medium.  
The reflection at  $s_2$  also has light hitting a higher index (slower) medium.

The Phase Shift Rule: When light reflects off a higher index (slower) medium, it experiences a  $180^\circ$  phase shift. This  $180^\circ$  phase shift equals  $\frac{1}{2}$  wavelength of distance. When light reflects off a lower index (faster) medium, *no* phase shift occurs.

Since *both* reflections here have light approaching higher index (slower) media,  $180^\circ$  phase shifts occur during reflection at *both*  $s_1$  and  $s_2$ . Since the light rays start in phase, and both paths experience the same phase shift, *there is no net phase shift here!*

- c<sub>2</sub>) Light goes slower in anything other than a vacuum, causing it to *seem* to travel a longer distance. This is the reason, for instance, that things look larger and closer when viewed underwater.  
Equivalent Optical Path Length =  $nd$ , where  $n$  is the index of refraction, and  $d$  is the distance the light actually travels.

In this problem, path A =  $1.25d$  and path B =  $1.25d$

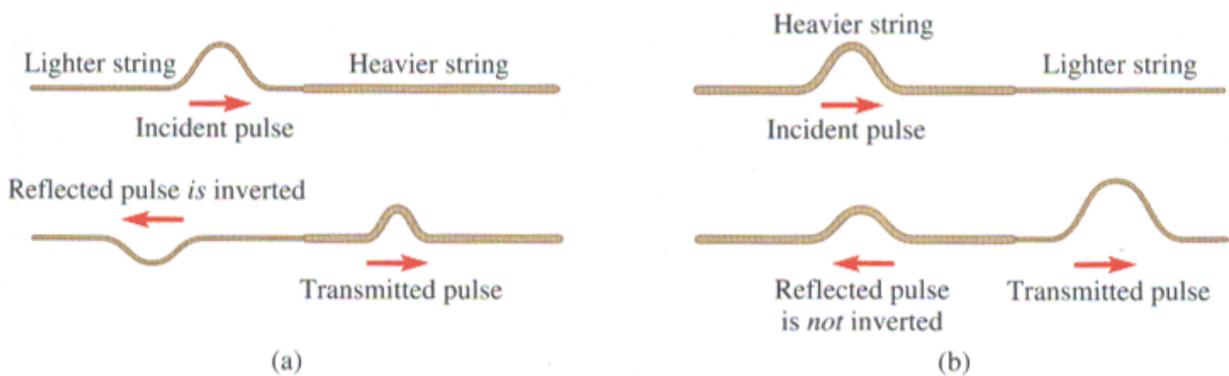
The *total* equivalent optical path length in the thin film of this problem is  $2(1.25d)$  or  $2.50d$

- c<sub>3</sub>) To get a minimum (node), one needs a  $180^\circ$  (or  $\frac{1}{2} \lambda$ ) phase shift. Thus, the path through the thin film must be longer by  $\frac{1}{2} \lambda$ :  $2(1.25d) = (6.0 \times 10^{-7} \text{ m})/2$  yields  $d = 1.2 \times 10^{-7} \text{ m}$
- d) To get a maximum (antinode), one needs a  $360^\circ$  (or  $1 \lambda$ ) phase shift. Thus, the path through the thin film must be longer by  $1 \lambda$ :  $2(1.25d) = (6.0 \times 10^{-7} \text{ m})$  yields  $d = 2.4 \times 10^{-7} \text{ m}$

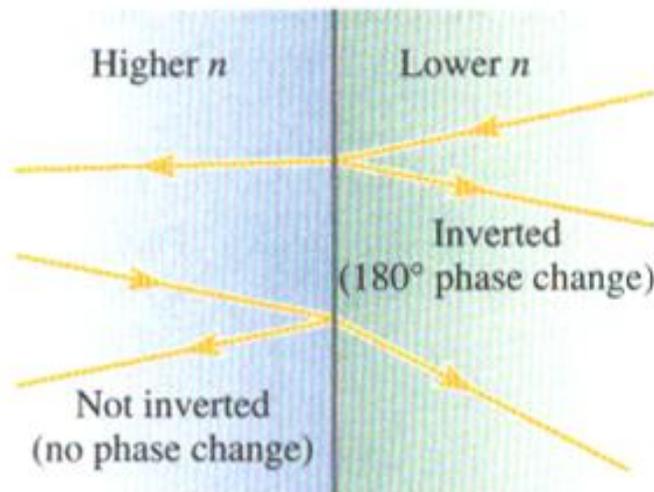


## Interference in Thin Films

Soap Film - This image was taken with a black background and front lighting in order to show only reflected light. Note that the top is a black band. This means that there is destructive interference in that region for all visible wavelengths.

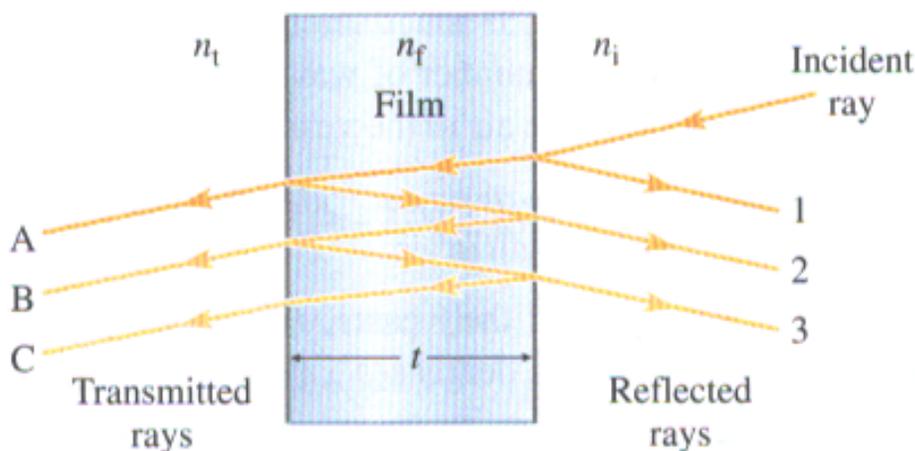


Phase Change Due To Reflection on a string: When a wave pulse on a string reflects off the boundary with a slower medium, one which has more mass per unit length, it is inverted. When a wave pulse goes the other way on a string, and reflects off the boundary with a faster medium, it is *not* inverted.



The same thing happens to EM (electromagnetic) waves: Whenever a wave hits a boundary where the wave speed suddenly changes, reflection occurs. The reflected wave is inverted (phase-shifted  $180^\circ$ ) if it reflects off a slower medium (a medium in which the wave travels more slowly); it is not inverted if it reflects off a faster medium. The transmitted wave is never inverted.

When light reflects from a boundary with a slower medium (higher index of refraction), it is inverted ( $180^\circ$  phase change); when light reflects from a faster medium (lower index of refraction), it is not inverted (no phase change).



One can ignore rays A, B, C, and 3 in this diagram since they do not contain as much light energy as rays 1 & 2.

Do rays 1 & 2 interfere constructively or destructively?

There are two factors to consider:

- a. the relative phase change due to reflection
- b. the extra path length traveled by ray 2 in the film.
  - a. The index of refraction of the film and that of the medium on either side of it determines where phase shifting occurs. It is possible to have a phase shift at the first reflection, at the second reflection, at neither, or at both reflections. If the index of refraction of the film ( $n_f$ ) is between the other two indices ( $n_i$  and  $n_t$ ), there is no relative phase difference due to reflection; either both are inverted or neither is. If the index of the film is the largest or the smallest of the three, then one of the two rays is inverted. In either case there is a relative phase difference of  $180^\circ$ .
  - b. The extra distance traveled by the light going through the film, corrected for the different speed of light in the film, and hence the different wavelength in the film(!), also shifts the phase relationship between the two reflected rays, 1 & 2.

#### Problem-Solving Strategy for Thin Films

- Sketch a ray diagram to show the first two reflected rays. If the problem concerns normal incidence ( $\angle i = 0.0^\circ$ ), draw the incident ray with a small (nonzero) angle of incidence to separate the various rays a bit and allow labeling. Label the indices of refraction.
- Decide whether there is a relative phase difference of  $180^\circ$  between the rays due to reflection.
- If there is no relative phase difference due to reflection, then an extra path length of  $m\lambda$  keeps the two rays in phase, resulting in constructive interference. An extra path length of  $(m + \frac{1}{2})\lambda$  causes destructive interference. Remember that  $\lambda$  is the wavelength *in the film*, since that is the medium in which ray 2 travels the extra distance.
- If there is a  $180^\circ$  relative phase difference due to reflection, then an extra path length of  $m\lambda$  preserves the  $180^\circ$  phase difference and leads to *destructive* interference. An extra path length of  $(m + \frac{1}{2})\lambda$  causes *constructive* interference.
- Remember that ray 2 makes a round-trip in the film. For normal incidence, the extra path length is  $2t$ .

The images and much of the text on these two pages of explanation are from College Physics (Volume II) by Giambattista, Richardson, and Richardson (©2004 McGraw Hill)

Want more on thin films? Try these:

Bubbles:

<http://www.exploratorium.edu/ronh/bubbles/bubbles.html>

[http://www.funsci.com/fun3\\_en/exper2/exper2.htm](http://www.funsci.com/fun3_en/exper2/exper2.htm)

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<http://webexhibits.org/causesofcolor/15.html>

This is an absolutely WONDERFUL website! Great photos and clear explanations of color in butterflies, mother of pearl, peacock feathers, etc.!

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<http://www.opticsexpress.org/ViewMedia.cfm?id=63420&seq=0>.

This is a scientific article that discusses different levels of iridescence in different species of butterfly. Angle of view is an important factor.

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[http://www.hero.ac.uk/uk/research/archives/2005/natural\\_brilliance.cfm](http://www.hero.ac.uk/uk/research/archives/2005/natural_brilliance.cfm)

Interesting analogy of high light emission by butterfly wing to LED emission of light.

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<http://www.wired.com/news/technology/0,68683-0.html>

A news article on use of thin films in making iridescent cosmetics

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[http://www.sciencenews.org/pages/sn\\_arc97/12\\_13\\_97/fob3.htm](http://www.sciencenews.org/pages/sn_arc97/12_13_97/fob3.htm)

Possible use of info from butterfly wing iridescence in mechanical engineering

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Pennisi, E. 1993. Chitin craze. Science News 144(July 31):72.

Peterson, I. 1997. From microdevice to smart dust. Science News 152(July 26):62.

\_\_\_\_\_. 1995. Butterfly blue. Science News 148(Nov. 4):296.

## Equipment List



Item Number	Quantity	Item
1	1	Clear straight-sided bottle
2	1	Bottle of glycerin
3	1	Bottle of bubble solution
4	1	Clean drinking straw
5	1	Black construction paper
6	1	Plastic fork
7	1	Clear nail polish
8	1	Plastic pan
9	1	Small bag of laundry borax
10	2	Coffee stirrers
11	2	Rubber bands
12	1	Fine point Sharpie marker
13	2	Alligator clip to banana plug leads
14	1	Multimeter
15	2	Leads for multimeter
16	1	Plastic cup
17	1	Titanium sample (1/16" diameter rod or 1/40" thick sheet)
18	1	Stainless steel electrode (screw)
19	1	1500-grit abrasive paper
20	1	Variable DC power supply (0 to 25 V or more)
21	1	AC adapter for power supply
22	1	Squeeze bottle for isopropyl alcohol
23	1	Bottle of isopropyl alcohol

# THE CLEARLY COLORFUL THIN FILM LAB

## Soap films

You have blown soap bubbles since you were a little kid, right? Ever watch the eyes of a one to four year-old who is watching the colors swirl in soap bubbles as they float along? They're *almost* magic! In this first section of the lab, your mission is to try to figure out some of 'the rules' for how those pretty colors appear in soap bubbles!

Take a roughly 500 ml clear, colorless, smooth, straight-sided bottle, and gently pour soap & water solution or 'bubble stuff' into the container to a depth of ~2 cm. Be carefully not to shake the bottle; the next step needs a smooth liquid surface to work best!

1. Is the liquid clear and colorless, or is it colored? \_\_\_\_\_

Create a single soap bubble film (a disk across the middle of the bottle) as follows:

- Tilt the bottle and slowly move it around to coat the walls of the bottle with liquid.
  - Dip a beverage straw just into the surface of the liquid in the bottle, tilt the bottle slightly, and blow gently into the straw. After a few tries, it is possible to get a single bubble to grow and form a disk of liquid film spanning the width of the bottle  $\frac{1}{4}$  to  $\frac{1}{2}$  way up. Remove the straw and cap the bottle. Observe the film in a very well illuminated area and fill in the chart below.
  - Place the bottle on a pencil to tilt it a bit off vertical. Wait ~2 minutes.
2. Observe the thin film *carefully* and record colors, patterns, 'dark' areas, etc. in detail.

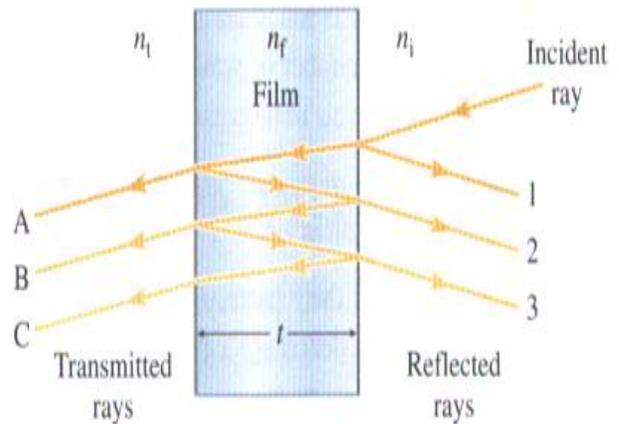
Time	Bottle Position	Observations
Film just created	Vertical viewed from the top of the bubble film	
Film just created	Vertical viewed from bottom of the bubble film	
~2 minutes later	Tilted on a pencil viewed from the top of the bubble film	
~10 minutes later	Tilted on a pencil viewed from the top of the bubble film	

3. The liquid used here is clear and colorless, and yet the film shows beautiful colors *when illuminated with white light!* Considering what white light is, where might the colors be coming from?
4. If the film was illuminated with monochromatic red light instead of white light,
- Formerly red areas would look \_\_\_\_\_
  - Formerly blue areas would look \_\_\_\_\_
5. This film is a liquid, and liquids flow. Use these facts to propose an explanation for the swirling movement of the colors seen in soap bubble films.
6. This film is a liquid, liquid flows, and gravity does effect it. When the bottle is left tilted for a period of time,
- Where does the film become thickest? \_\_\_\_\_
  - Where does the film become thinnest? \_\_\_\_\_
  - If 25 dots could be placed at points that all have the same film thickness, what would their placement look like?  
\_\_\_\_\_  
\_\_\_\_\_
  - What effect does this thickness gradient (transition) appear to have on the color pattern?  
\_\_\_\_\_  
\_\_\_\_\_
  - Describe any complete visible spectrum (ROYGBIV) patterns observed.  
\_\_\_\_\_  
\_\_\_\_\_
7. A clear/colorless or dark/black area will eventually become apparent in the tilted film.
- Roughly when and where in the film does it appear?  
\_\_\_\_\_
  - Does such an area seem to grow larger or shrink with time? \_\_\_\_\_

8. The liquid in the container is clear and colorless, but the thin liquid film is colorful.

a. Write a hypothesis about observed colors, thin films, thickness of films, etc.

A lot goes on here, so read the following carefully! Some of the ambient (surrounding) light approaching the soap film from a particular direction reflects off of the film and some enters the film. Some of the light that enters the film reflects off the back surface of the film and exits, a bit later in time, due to distance traveled, to join the *original* reflected light. The light that goes through the film slows down due to refraction. Finally, the light will also experience a  $180^\circ$  phase shift any time it reflects off a 'slower' medium. All of these factors combine to determine whether the light experiences constructive or destructive interference.



b. Use the reflected ray paths labeled 1 & 2 in the diagram, and knowledge of waves (wavelength, Snell's Law, constructive and destructive interference, etc.) to refine the hypothesis on the last page about **how** the observed colors in thin films occur.

## Nail Polish Films

This section of the lab will create a more permanent thin film and help with development of a hypothesis on colors observed in thin films. Bonus: You get a cool bookmark to take home!

Create a nail polish thin film to observe as follows:

- Fill a shallow, open container to a water depth of 2-3 cm
- Submerge a piece of black paper and hold it submerged with a plastic fork.
- Drop ONE drop of clear nail polish onto the water surface from 5-10 cm up. The nail polish drop should spread out within a couple of seconds, creating an extremely thin film on the surface of the water and revealing a rainbow of colors.
- Carefully and smoothly lift/slide the paper out of the water at an angle, capturing the film on the surface of the paper. Place the paper with your captured nail polish thin film on a paper towel and allow it to dry completely. Be careful, the film is very fragile until it is dry.
- Use the plastic fork to skim out any remaining film and have each lab partner capture a film of his/her own. Try different drop techniques to determine which seems to be best. If a film does not spread out well, simply skim it out and try again.

1. What were the dropping techniques tried, in order from best to worst?

- a. \_\_\_\_\_
- b. \_\_\_\_\_
- c. \_\_\_\_\_
- d. \_\_\_\_\_

2. From the way this film was created, where is it likely to be thickest? \_\_\_\_\_

3. From the way this film was created, where is it likely to be thinnest? \_\_\_\_\_

4. Roughly what shape is the pattern of colors in the nail polish thin films?

\_\_\_\_\_

Observe the nail polish films from various angles to the plane of the paper.

5. What happens to the position where a particular color is seen as the viewing angle changes?

\_\_\_\_\_

6. The path of light into and out of the film is shortest when viewing \_\_\_\_\_

- a. straight towards the paper.
- b. at an angle almost parallel to the paper.

7. How do the observations of nail polish films support the thin film hypothesis developed with soap bubble films? (If the hypothesis is not fully supported, then it must be modified here to explain nail polish films!)

## Titanium Metal with Titanium Dioxide Thin Films

### BACKGROUND

Titanium (Ti) is light in both mass and color. It is a strong, corrosion resistant gray metal. It is so light that it is used in some of the best racing bicycle frames and in jet aircraft! It is also used in everything from surgical implants to jewelry to thin films in nanoscale semiconductor electronic devices and special thin film coatings.

In the nanofabrication of electronic integrated circuits, (computer chips and the like), thin films of material are either deposited on a surface or etched away from a surface, in a very specific pattern. The pattern is obtained by using a mask, a stenciled on pattern which protects the region one wants left unaffected. You will see how a mask is used as part of this lab!

The electrochemical process in this lab, called anodizing, uses a redox reaction to form a thin film of  $\text{TiO}_2$  on a sample of metallic titanium.

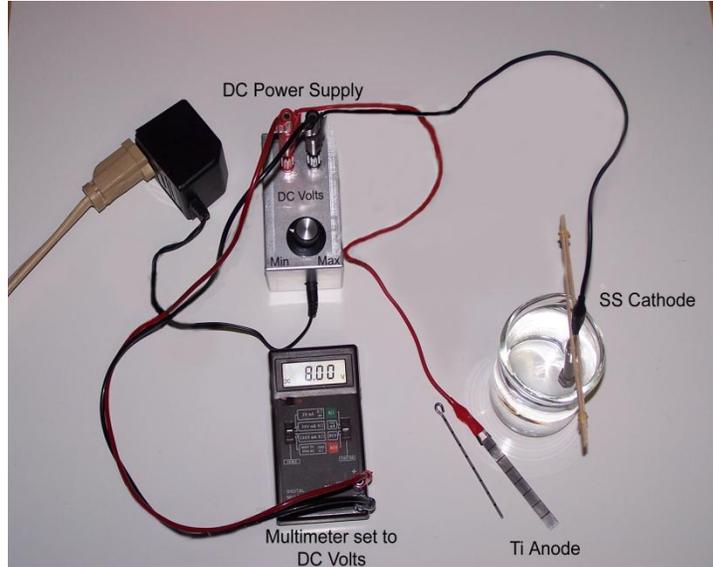
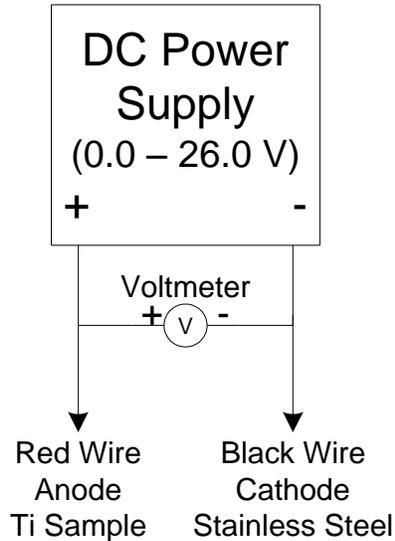
1.  $\text{TiO}_2$  is a clear and colorless material. Predict what will happen when a thin film of  $\text{TiO}_2$  is deposited on Ti metal.
- 
- 

### Creating a $\text{TiO}_2$ thin film on Ti:

#### PREP WORK

- File any sharp edges off the Ti sample. Use fine emery paper or extremely fine wet/dry abrasive paper to polish the Ti as smooth as possible. Start with the smaller number abrasives, and move to the higher numbers. Wetting the abrasive with water that contains a drop of dish soap or a dab of toothpaste can help in the polishing process. The brighter the finish now, the better the results later!
  - Clean oils, grease, and sanding residue from the Ti with a few drops of isopropyl alcohol on a paper towel. After cleaning, handle the Ti by its edges and as little as possible. Fingerprints are oil residues which will get in the way of quality results.
  - Create a mask on the Ti by dabbing waterproof ink fairly thickly onto the metal in the regions to remain Ti grey colored. Fairly thin lines are ok, but must coat the metal well. Draw rings around the Ti wire at 1 cm intervals for reference later in the experiment. If Ti strips are used, draw lines at 1 cm intervals on one side, and whatever pattern you like on the other. Allow time for the ink to dry well!
  - If the teacher has provided a premixed sodium tetraborate electrolyte solution, fill a cup with enough of it to *almost* completely submerge a vertical Ti sample. If you need to mix your own, then dissolve 1 slightly rounded teaspoon of sodium tetraborate in enough water to almost submerge the Ti sample. The exact amounts are *not* critical, and run about 7 grams in about 200 ml of water.
2. As stated, this lab uses an electrochemical reaction. The sodium tetraborate (laundry borax) solution in the *reaction* cup is the electrolyte. The mobile positive and negative ions in the solution make it a good electrical \_\_\_\_\_.

Set up the ‘anodizing system’ as shown in the diagram. Pay careful attention to the colors of the wires used and the following details!



- Once the power supply is turned on, the wires are electrically ‘hot’! The wire ends must not touch each other! Short circuits are a bad thing!
- The Stainless Steel metal strip or bolt (SS) is clamped on the black, negative wire coming from the power supply. It is called the cathode, and is considered ground or zero electrical potential here (0.0 V). There is nothing magic about using the black lead for negative, but everyone does it that way to reduce wiring errors.
- The SS is suspended in the reaction cup solution, the electrolyte, until only the alligator clip and .5 to 1 cm of SS are left un-submerged. Tape or clamp the SS securely in place. Coffee stirrers and rubber bands were used to make the clamp seen in the diagram.
- If an alligator-clip gets wet, rinse it in fresh water, dry it, and continue.
- The Ti metal strip or wire is clamped on the red, positive wire, and is called the anode. Its potential will be set with the power supply control and monitored with the voltmeter. If this is not clear, please ask for clarification!

3. What is a short circuit, and why would it be a bad thing? \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

## ANODIZING

\*\*Be Careful! Do not touch the SS with the Ti!

Keep the alligator clips out of the electrolyte!

The anodizing procedure is repeated using the voltages, and immersion depths in the order listed in the data table. *Study the table, especially the immersion depths*, and proceed as follows:

- Set the power supply to the first voltage specified in the table. The steps **MUST** be done in order!
  - Lower the Ti vertically into the reaction cup to the depth of immersion shown in the table, hold it steady for 30. seconds, and then remove it. Dab the Ti dry above the next immersion line with a paper towel. If you try to dry the whole thing, you will wipe the ink mask off, so don't! Record observations in the chart.
  - Repeat this process, adjusting the voltage to the new value in the table, and *decreasing the amount of Ti immersion by 1.0 cm each time*.
  - Do not touch the metal. The ink mask is not durable! If some of the ink appears to have come off, dry the metal, apply fresh ink, and let it dry before continuing.
  - In the event of problems, sand the Ti clean and start over. The TiO<sub>2</sub> film is very durable, but it will sand off with some effort.
  - Use a few drops of isopropyl alcohol on a scrap of paper towel to clean the ink off the Ti.
4. The ink wipes off the Ti easily, but does the *color* wipe off easily? \_\_\_\_\_
- When done anodizing, pour the sodium tetraborate solution from your reaction cup into the class storage container and clean up your work area.

OPTIONAL READING about the chemistry of the process just completed:

[In chemistry class, you electrolyzed water using two relatively inert electrodes. You observed that hydrogen bubbled off at the negative electrode (the cathode), and oxygen bubbled off at the positive electrode (the anode). The actual chemical reaction was:  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ . If the electrodes are made of reactive materials, they will react! If the anode is made of copper, it will react with the oxygen and make a dark copper oxide film coating the copper. The copper will 'tarnish'. Even though a fairly large number of hydrogen bubbles appeared at the cathode in today's experiment, there were hardly any bubbles of O<sub>2</sub> observed on the Ti anode in this experiment. Where did the oxygen go? In fact, it reacted with the titanium according to the equation:  $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$  (This is actually a redox reaction, which is the combination of the two half-cell reactions:  $\text{Ti} \rightarrow \text{Ti}^{+4} + 4\text{e}^-$  and  $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{-2}$  Note that the charges balance!). Thus, the anodizing process resulted in a thin film of TiO<sub>2</sub> on the surface of the Ti metal.]

No tints or dyes were used here, and yet lovely colors did appear!

5. A copper oxide coating on copper is a dark tarnish. An iron oxide coating on iron is rust, and we *all* know what *that* looks like! A titanium dioxide coating on titanium can't be all the different colors seen on the lab sample. What color is TiO<sub>2</sub>? \_\_\_\_\_

6. While titanium metal conducts electricity very well,  $\text{TiO}_2$  does not! When current flows, the  $\text{TiO}_2$  film grows thicker quite quickly, at first. The thickening film causes the total electrical resistance to (increase, decrease, remain the same), which causes the electrical current to (increase, decrease, remain the same), which causes the chemical reaction rate to (increase, decrease, remain the same). There is almost no current left at the end of each 30. second run. The voltage is increased for each successive process in order to overcome the above changes!
7. Which segment of the titanium sample has the thinnest  $\text{TiO}_2$  film coating? \_\_\_\_\_

8. Increasing thicknesses of  $\text{TiO}_2$  film produced different colors. Explain how this is consistent with the hypothesis developed using soap and nail polish films.

9. Postulate an explanation of how anti-counterfeiting color shifting ink (Observe it from a different angle and it looks like a different color) on modern paper money might work.

10. Postulate an explanation of how the bright iridescent colors seen in butterfly wings might be formed with scales of clear, colorless chitin.

Integrated circuits (ICs) are the small rectangular grey electronic components with many wires seen all over the circuit boards of computers, cell phones, televisions, etc. They contain the equivalent of hundreds, thousands, or even millions of simpler electronic components inside. They are created by layering complex nanoscale patterns of thin films of 'n' (negative) and 'p' (positive) materials on a silicon base. In making the patterns, a mask is lithographically applied to the surface. It is a bit like silk- screen printing on T-shirts reduced to nanoscale. Then

material is either etched away from the areas that are unprotected by the mask or deposited onto the material in those areas. The mask is then removed and the next layer's pattern mask is applied.

11. How is the titanium thin film part of this lab similar to the IC manufacturing process?

12. How is the titanium thin film part of this lab different from the IC manufacturing process?

13. The colors on the titanium in this experiment appeared in a specific order. Jewelry artists working with this medium get the colors they want in the locations they want them. How do they do it, and how might a different order of colors be obtained in this lab experiment?

14. If time and materials permit, try to create a titanium wire with colors in the order:

Blue, gold, purple, gold, blue

15. **VERY IMPORTANT:** List all the cases in this lab experiment where the physics phenomenon of diffraction occurred:

**The Effects of Anodizing Ti for Various Times at Various Potential Differences**

Process Number	Voltage (V)	Time	Amount of Ti submerged	Observations of the anode (Ti)	Observations of the cathode (SS)	Ti color (dry)
1	9	2 mins	All of the sample almost up to the alligator clip			
2a	18	1-2 secs	~ 6 cm			
2b	18	1-2 secs	~5 cm			
2c	18	1-2 secs	~ 4 cm			purple
3	18	2 mins	~ 3 cm			
4	27	2 mins	~ 2 cm			

### The Effects of Anodizing Ti at Various Potential Differences

Time for each process is approximately 30 seconds

Process Number	Voltage (V)	Amount of Ti submerged	Observations of the anode (Ti)	Observations of the cathode (SS)	Ti color (dry)
1	8	All of the sample almost up to the alligator clip			
2	11	~ 6 cm			
3	14	~5 cm			
4	17	~ 4 cm			
5	20	~ 3 cm			
6	23	~ 2 cm			
7	26	~ 1 cm			