

International Baccalaureate

Extended Essay - Chemistry

How does the anodising time affect the thickness of the oxide layer and therefore the amount of dye absorbed when (Type II) dye anodising aluminium?

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Abstract:

This investigation attempts to answer the question "How does the anodising time affect the thickness of the anodic oxide layer and therefore the amount of dye absorbed when Type II anodising aluminium?". By measuring the change in concentration of a dye solution when the aluminium is dyed using colourimetry, the anodic oxide layer thickness can be estimated.

Pieces of aluminium sheeting were anodised at 16 Volts and 3 Amps for lengths of time between 20 and 40 minutes. The anodised sheets were then left in dilute dye solutions for 24 hours and the change in concentration of the dye solutions was indirectly measured using a colourimeter to measure change in transmittance. These change in transmittance values were then converted to change in absorbance values and plotted against the anodising time in order to determine the experimental relationship between the two variables. The values of change in absorbance were interpreted as being directly proportional to the oxide layer thicknesses on the anodised piece.

This investigation concludes that for between 20 and 40 minutes of anodising time, the experimental relationship is quadratic, and that 40 minutes will develop the thickest oxide layer out of the times tested. Unfortunately, the investigation was limited because of the small range of times tested, and that there was no deviation from the relationship seen at longer or shorter times.

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1 - Outline of the Investigation:

1.1 Aim:

To compare the thickness of the anodic oxide layer when changing the anodising time under controlled conditions, in order to determine the experimental relationship between the anodising time and anodic oxide layer thickness to determine the optimum anodising time for type II anodising with a current density of $1.5\text{A}/\text{dm}^2$ and a cell voltage of 16.

1.2 Research question:

How does the anodising time affect the thickness of the anodic oxide layer and therefore the amount of dye absorbed when Type II anodising aluminium?

2.1 - Introduction:

Anodising is becoming an increasingly popular finish for aluminium. It is a cheap and durable finish that is relatively easy to apply. As demand for aluminium surges, anodising has become increasingly cheap and simple to do with little experience in the industry.

Anodised surfaces are used commonly in the aeronautical industry to provide a strong, corrosive resistant surface, and in diving and sea equipment for its resistance against corrosion by salt water. Nowadays, people all over the world are anodising at home in their garages using simple equipment that can be bought from a hardware store.

I chose this topic because of my interest in materials science. A book that led to the development of my passion for chemistry was a book by materials scientist Mark Miodownik about the materials that shape our world today. When reading about metals and alloys, I was intrigued by the how something that seemed so simple could in fact be quite complicated. I never could have imagined that alloys could harden over time, as in precipitation hardening alloys. Ever since I have been interested in materials and when brainstorming possible EE topics, I immediately thought of materials science. I chose anodising for this EE as it is a very common aluminium finish and is used to treat a huge range of aluminium products, but does not have a large amount of published research on the topic, making it hard for individuals without experience to anodise.

2.2 Background research

2.21 Types of anodising:

There are 3 different types of aluminium anodising; Type I, II and III. Type I is chromic acid anodising, which gives a thin oxide layer (approximately 2 microns) and is very resistant to corrosion. Because of the thin oxide layer type 1 anodising creates, it is unsuitable for dyeing and is mostly used in the aerospace industry (*Introduction*). This type of anodising is mainly done on an industrial scale with the appropriate safety measures, as chromic acid is carcinogenic, mutagenic and incredibly toxic (*MSDS Chromic*).

Type II anodising is done at 20°C in a bath of concentrated sulphuric acid. Type II anodising creates a thicker oxide layer of approximately 20 microns (*Higgins, Raymond*) that is more suitable for dyeing.

Type III anodising, often called hard coat anodising is similar to type II anodising, but the sulphuric acid anodising bath is cooled to 0°C. This reduces the activity of the sulphuric acid bath, allowing the oxide layer to grow thicker than in type II anodising. This type of anodising has many different applications but is not often dyed as the colour produced is uneven and unattractive (*Introduction*).

For this EE, I will be using type II anodising to anodise 10x10cm aluminium sheets.

2.22 Colourimetry:

I decided to use colourimetry to determine the oxide layer thickness because it was the simplest and easiest way to measure it. The oxide layer itself is so thin that it can't be measured conventionally with a micrometre or any form of readily available measuring device. A property of the anodised surface is that it readily accepts dyes onto the surface because of its porous nature. This way, the oxide layer thickness can be easily measured by the amount of dye the aluminium absorbs into the surface by measuring how much dye is taken out of a dye solution by a piece of anodised aluminium.

Colourimetry is the determination of the concentration of a solution based on its colour and wavelengths of light that the solution absorbs. A ray of monochromatic light is shone through a sample of the solution and a value for absorbance or transmittance is calculated from how much of the original light makes it through to the detector (*Arnold, Ben*). Transmittance is calculated from the formula $T = \frac{I}{I_0}$, where T is the transmittance, I is the intensity of light received at the detector and I_0 is the intensity of light emitted. While the transmittance represents the amount of light that makes it through the solution, the absorbance is the amount of light that is absorbed by the sample, and can also be used to find the exact concentration of a solution using the Beer-Lambert law:

$$A = \epsilon l c$$

Where A is absorbance, ϵ is the molar absorption constant, l is the path length and c is concentration. Transmittance is similar to Absorbance, and it can be derived from absorbance using the following formula:

$$A = -\log_{10}T \qquad T = 10^{-A}$$

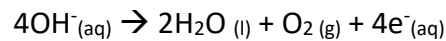
(Absorption spectra)

In my experiment, ϵ and l are constants as I always use the same sized cuvettes and I keep the type of dye constant throughout. Because of this, it can be said that A is proportional to c . I can therefore use the change in Absorbance as the change in concentration of the solution. The values will not be true values of change in concentration but the graphical relationship will be the same.

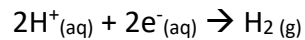
A dark green dye was used because of its strong colour which allowed me to easily see if the anodising has been successful, even when the piece has not been anodised for a long time. The colourimeter was therefore set to 635nm (red), a wavelength that will be absorbed by the dye. I chose the red wavelength over a blue wavelength as the green dye could possibly be a mix of some green and blue pigments.

2.23 The science of anodising:

When anodising in sulphuric acid, oxygen gas is formed on the surface of the aluminium anode:

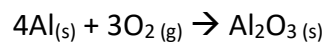


Hydrogen gas is formed at the cathode.

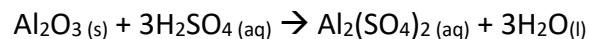


For type II aluminium anodising, lead is the suggested cathode material because it does not react with sulphuric acid, and can be reused extensively.

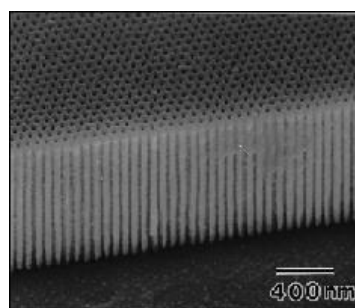
The oxygen that forms on the surface of the aluminium anode reacts with the aluminium to form a layer of aluminium oxide.



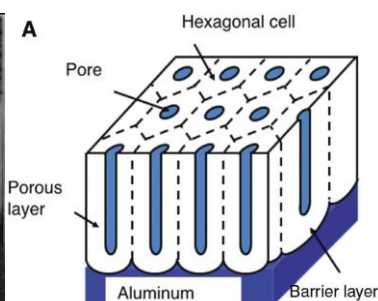
At the same time, the sulphuric acid in the anodising bath is breaking down the aluminium oxide into soluble aluminium sulphate.



This dual action forms an anodic aluminium oxide layer that has a hexagonal pore structure. This porous structure allows dyes to be integrated and absorbed onto the surface of the aluminium, and therefore allows the anodised aluminium to be dyed.



(Type 2 Anodising)



(Role of Anodic Oxide)

After anodising, these pores are left open and dipping into dye will result in the dye being integrated into the surface of the aluminium.



A piece of anodised aluminium that has been dyed blue

(Anodised Coloured Blue)

Once the dye has 'soaked in', the piece can be sealed so the dye doesn't leach by boiling the piece in water or a professional sealing solution for 20 minutes to an hour, which closes the pores and traps dye inside (*Anodizing World*). In the sealing process, aluminium oxide from the porous anodised oxide layer reacts to form aluminium hydroxide, a less dense compound which 'swells' and seals the pores, trapping dyes inside.

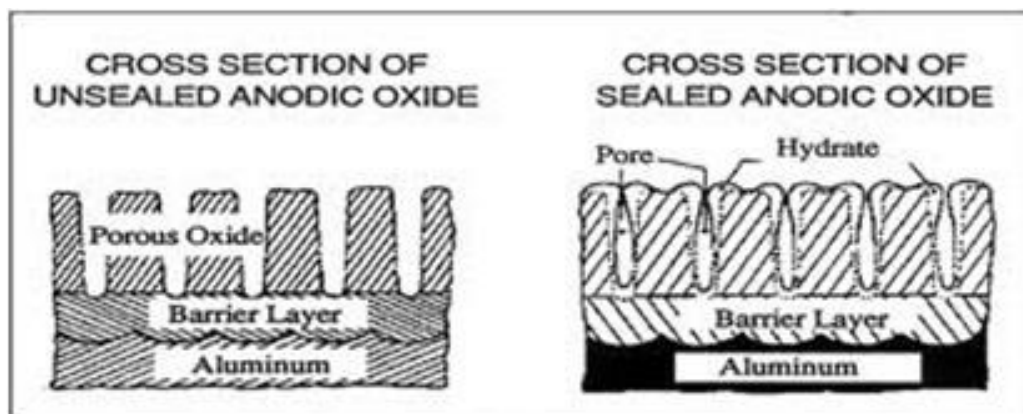
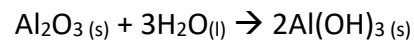


Diagram showing the effects of sealing on the anodic oxide layer of type II anodized aluminium (*Anodizing Sealant*)

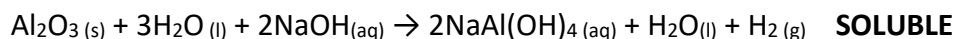
3 - Preliminary testing:

During the preliminary testing, I ran into many problems. Anodising is very sensitive, meaning that if certain steps of the method are skipped, the anodising will fail. Originally, I had not considered the degreasing step to remove surface grease, and my anodising continuously failed until I incorporated that step into my method (Check appendix section 8.4 for photos of improper degreasing). Besides that, a lot of minor 'calibrating' was also needed in order for it to work properly. Taking an extra minute off my etching time (I originally etched for 7 minutes) resulted in an inconsistent anodised finish. The end anodised piece relies on many different factors that I had not previously considered. A lot of these errors were caused by a lack of readily available research and information on the topic. It therefore took many hours of lab work and research, trying various different methods, to develop a working method. My original method was using incorrect voltages, currents and electrolytes. Only after extensive research at a public library and accessing several books on anodising, did I manage to gain information on the vital steps I was missing and perfected my method.

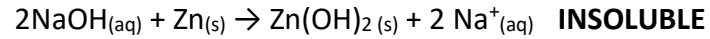
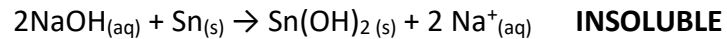
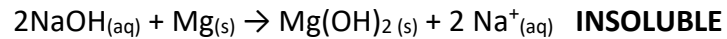
3.1 Justification of methodology designed from preliminary trials:

Before anodising, there are a number of vital steps that need to occur in order to prepare the aluminium surface properly. The existing aluminium oxide layer needs to be removed to make way for the one that will be built up by anodising in an acid etch. Before the aluminium is etched however, the surface must be cleaned with a degreaser such as detergent to remove any oils from the surface, as the etching solution cannot break them down. Surface grease will prevent the surface from etching evenly. Commercial degreasing solutions usually contain non-etch alkalis that remove the surface dirt and grease but do not affect the aluminium (*Peterson, David S.*). I decided however that using detergent would be just as effective, would reduce cost and save time as commercial degreasing solutions are a niche product and are hard to find.

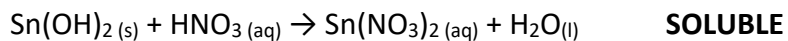
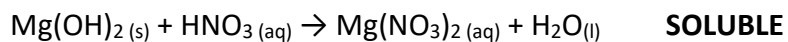
The surface must then be etched for 8-10 minutes in concentrated sodium hydroxide (*Chesterfield, "Alkaline"*) to remove the pre-existing oxide layer and any surface impurities in the aluminium (*Brown, Colin D.*), most commonly Magnesium, Silicon, Zinc, Tin and Manganese.



Although the reaction between sodium hydroxide and aluminium produces highly soluble sodium aluminate $[\text{NaAl}(\text{OH})_4]$, many metal hydroxides that are produced when the alloying elements in the aluminium sheet react with sodium hydroxide [mainly $\text{Mg}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ and $\text{Sn}(\text{OH})_2$] are highly insoluble and form a film over the aluminium piece called 'smut'.



If this layer of smut remains on the surface of the aluminium, the aluminium will fail to anodise properly. The surface 'smut' must be removed by dipping the piece briefly in a desmutting solution, which is usually nitric acid (*Chesterfield, "Smut"*).



Once the aluminium has been prepared according to the steps above, it is ready to be anodised.

Several sources suggest a sulphuric acid electrolyte with a concentration ranging from 10-20% by weight (w/w), with several suggesting 15% (*Polmear I.J ; Higgins, Raymond*). The anodising failed when trialled with 10% concentration so a 15% concentration was chosen. These metallurgy books also suggested a current density ranging between 1-2 A/dm² and a cell voltage ranging between 12 and 24 Volts. I chose a current density of 1.5 A/dm², as this value is in the centre of the suggested range, and are therefore likely a common choice in industry. I chose a cell voltage of 16 Volts because it was near the centre of the recommended range, but was also the upper limit of what was deemed safe to use in a school laboratory.

After anodising, the piece needs to be neutralised to remove any surface acid. I followed a popular online anodising forum's advice and neutralised by dipping the piece into a solution of sodium bicarbonate (*Introduction*).

The piece was then dyed in a dye solution. During pre-trials, I tested out various dye solution concentrations and soon realised that to see any considerable change in concentration, the solution would have to be much more dilute than any solutions used in industry and therefore would need to be dyed for a much longer period of time because of the low concentration. Even relatively low concentrations relative to concentrations used in industry that I tried had such a low transmittance that the colourimeter couldn't measure it. After testing out several different dye concentrations, I settled on 2 cm³ in 900cm³ (2.2M), which gave me the best results as it was reasonably concentrated, but the colourimeter could easily measure the transmittance accurately.

3.2 Experimental variables

Table 1 - Experimental Variables

Type of variable	Variable	Method of controlling
Independent	Anodising time	Time was measured using an accurate stopwatch
Dependant	Change in %Transmittance of dye solution	Aluminium dyeing time and dye solution were kept constant.
Controlled	Current	A variable resistor and an ammeter were added in series to the circuit, allowing me to keep the current to 3A.
	Voltage	The power pack used had variable voltage of 0-25 volts, allowing me to keep the voltage at 16V. A voltmeter was also connected in the circuit to confirm the voltage.
	Concentration of anodising solution	The same acid concentration (15%) was used for all anodisings.
	Temperature	The same lab was used to collect all results ($\approx 25^\circ$)

3.21 Justification of experimental variables:

I chose to change the anodising time for this EE because of its simplicity. Originally, I wanted to change the anodising voltage, but as the voltage range suggested by many sources is so large, and because it isn't considered in any anodising calculations, I decided against it. I believe it would have been more relevant because of the limited amount of published research into the area, but in order to measure any noticeable difference, I would need a large range of voltages, and high voltages would be dangerous without proper equipment.

In order to collect precise and accurate results, several variables were controlled. The current and voltage were kept constant throughout all trials in order to make sure that it does not affect the oxide layer thickness so that we can say any difference in oxide layer thicknesses is due only to the change in time period. This was controlled by using a variable voltage power pack and adding a variable resistor to the circuit, allowing me to control both the voltage and the current independently.

In addition to controlling the power input, the concentration of the sulphuric acid solution was kept constant, as the concentration of sulphuric acid has a large effect on the oxide layer thickness.

4 Methodology:

4.1 Apparatus:

5cm ³ syringe (± 0.05 cm ³)	1dm ³ beaker
Dropper pipettes	30dm ³ container (anodising bath)
Colourimeter ($\pm 0.01\%$ T)	Wires and crocodile clips
Plastic cuvettes (width 1 cm)	Ammeter (± 0.001 A)
Variable voltage (1-25V) 8.5A max power supply	Voltmeter (± 0.001 V)
3 plastic trays (20x30cm)	Electronic Balance (± 0.001 g)
1L Volumetric flask (± 0.8 cm ³)	25 cm ³ measuring cylinder (± 0.1 cm ³)

4.2 Chemicals:

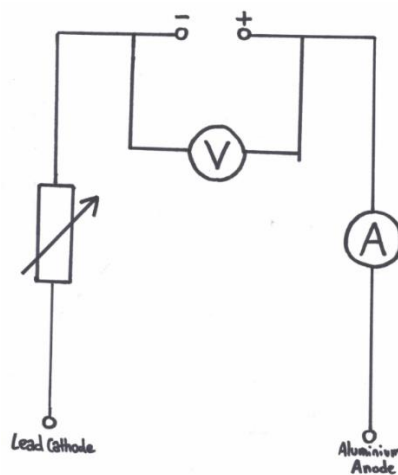
Per anodising:

Note: Acid and lead are reused for multiple experiments.

20 dm ³ 15% w/w Sulphuric Acid	2cm ³ Rit brand dark green dye
500cm ³ 2M Sodium Hydroxide	Deionised water
500cm ³ 1M Nitric Acid	
10x10cm sheets of aluminium	
3x7cm Lead sheet/cathode	
10g solid Sodium bicarbonate	

4.3 Method:

1. Clean the piece of aluminium with hot water and detergent and dry thoroughly with paper towel.
2. Transfer the aluminium into a plastic tray containing 500cm³ 2M NaOH and etch for 8 - 10 minutes.
3. Transfer the aluminium into a plastic tray containing 500cm³ 1M HNO₃ and leave/Desmut the aluminium of for 1-2 minutes.
4. Set up the anodising power supply circuit according to the circuit diagram below:



5. Put the aluminium into an anodising bath (30dm³) containing 20dm³ of 15% w/w sulphuric acid. Connect the aluminium to the positive electrode and a piece of lead sheet (1:3 Cathode: Anode surface area ratio) to the negative (*Anodizing Anode*). Ensure that the crocodile clip connection to the anode is not in the acid bath.
6. Anodise for 20 minutes on 3A 16V, continuously maintaining current and voltage.
7. Measure out 1000cm³ of deionised water in a volumetric flask. Remove 100 cm³ using a measuring cylinder and transfer the remaining 900 cm³ into a 1dm³ beaker.
8. Measure out 2cm³ of Rit dye using a syringe and add to the 1dm³ beaker. Stir the solution, and fill a cuvette with the solution using a dropper pipette.

9. After the anodising has finished, transfer the aluminium from the anodising bath into a plastic tray containing 500cm³ dilute sodium bicarbonate solution and neutralise for 1 minute.
10. Transfer the aluminium into the 1dm³ beaker with the dye solution. Let it dye for 24 hours.
11. After 24 hours, stir the solution and remove aluminium. Fill a plastic cuvette with the dye solution and measure %Transmittance value using the colourimeter.
12. Use the colourimeter to measure the %Transmittance of the sample taken in step 8.
13. Repeat for 20, 25, 30, 35 and 40 minutes and repeat 3 times for each length of time.

Notes: Carry out all steps in a fume cupboard. Colourimeter has been set to 635nm in all steps. Rinse aluminium in 'fresh' deionised water after each step for 1-2 minutes.

4.4 Safety

2M Sodium Hydroxide, 15% w/w sulphuric acid and 1M Nitric acid: (*Nitric ; Sodium Hydroxide ; Safety*)

- Corrosive and irritant and can cause severe skin burns and eye damage.
 - If skin comes into contact with these solutions, rinse thoroughly in cold water.
 - Lab coat must be worn at all times to reduce chance of contact with skin.
 - If eyes come into contact with any of these solutions, rinse eyes for several minutes and call a doctor.
 - Eye protection must be worn at all times.
- Dispose of into a chemical waste bin. Do not mix acids and bases together, and keep away from metals.
- If a spillage occurs, immediately make sure it is neutralised and cleaned up.

Hydrogen (evolved from etching and anodising) (*Material*)

- Highly explosive and flammable
 - Carry out all anodising and etching steps in a fume cupboard.

Solid sodium bicarbonate

- None

Lead (*Material Safety Data Sheet Lead*)

- Slightly hazardous if comes into contact with skin
 - If skin comes into contact with lead, wash with water
 - Always handle lead cathode with tongs.

Aluminium

- Take care for sharp edges and corners that could cut.

5 Data:**5.1 Raw Data:**

Note: anomalous results have been struck out below and are not used in any calculations.

Table 2 – Raw data

Anodising Time (min) ± 0.2	%Transmittance before ± 0.01	%Transmittance after ± 0.01	%Transmittance change ± 0.02	Average change in %Transmittance ± 0.02
20.0	4.08	7.4	3.32	3.18
	4.08	7.00	2.92	
	4.02	7.32	3.30	
25.0	3.99	7.18	3.19	3.38
	4.04	9.71	5.67	
	4.01	7.53	3.52	
	3.99	7.43	3.44	
30.0	3.98	5.38	1.4	3.63
	4.05	7.61	3.56	
	4.02	4.31	0.29	
	4.01	9.45	5.44	
	4.07	7.59	3.52	
	3.92	7.74	3.82	
35.0	3.95	9.13	5.18	5.23
	4.03	9.41	5.38	
	4.15	9.29	5.14	
40.0	3.86	9.01	5.15	6.25
	4.01	10.48	6.47	
	4.16	10.4	6.24	
	4.01	7.51	3.5	
	4.04	10.07	6.03	

5.2 Processed Data:

To determine the relationship between anodising time and oxide layer thickness, values that are proportional to the amount of dye absorbed or the change in the concentration of the solution when dyeing should be used. The raw values that were measured in the experiment were %Transmittance values. These %Transmittance values are not directly proportional to the concentration of the solution (as discussed in section 2.2). These %Transmittance values were therefore converted to Absorbance values before being plotted on a graph against anodising time.

%Transmittance values were converted to Absorbance values using the following formula:

$$A = 2 - \log_{10} \%T$$

E.g. Using 20 minute trial 1 - %T before:

$$2 - \log_{10} 4.08 = 1.39$$

These values were then used to calculate a change in absorbance value for each experiment, which was then averaged and plotted against anodising time in Graph 1

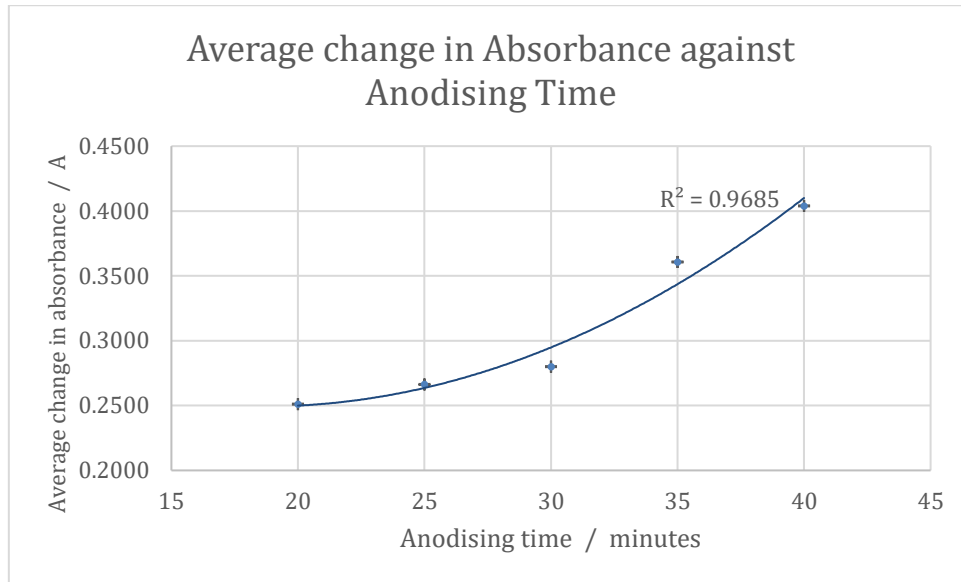
$$\textit{Change in Absorbance} = \textit{Final Absorbance} - \textit{Initial Absorbance}$$

E.g. Using 20 minute trial 1 – Absorbance before and after:

$$1.39 - 1.13 = -0.24$$

Graph 1 - Graph showing change in absorbance against anodising time with a linear line of best fit:

Note: The values have been plotted as positive values to improve the clarity of the graph:



The full table of values plotted on this graph can be found in Appendix section 9.2 (pg32)

These change in absorbance values could be converted into concentrations using the beer-lambert law, but these values however are not useful in determining the relationship between anodic oxide layer thickness and anodising time due to the large uncertainty in the values, with the largest uncertainty being 30% [Appendix section 9.3 or pg 39]. Because Absorbance is directly proportional to concentration, the relationship of each (respectively) with anodising time will be the same.

$$A = \epsilon lc$$

$$c = \frac{A}{\epsilon l}$$

If change in absorbance values and therefore change in concentration values are considered a direct measure of or as directly proportional to the anodic oxide thickness, we can take the relationship between change in absorbance and anodising time as the

relationship between anodising time and oxide layer thickness. Graph 1 shows that the relationship between anodising time and oxide layer thickness is not linear, but quadratic.

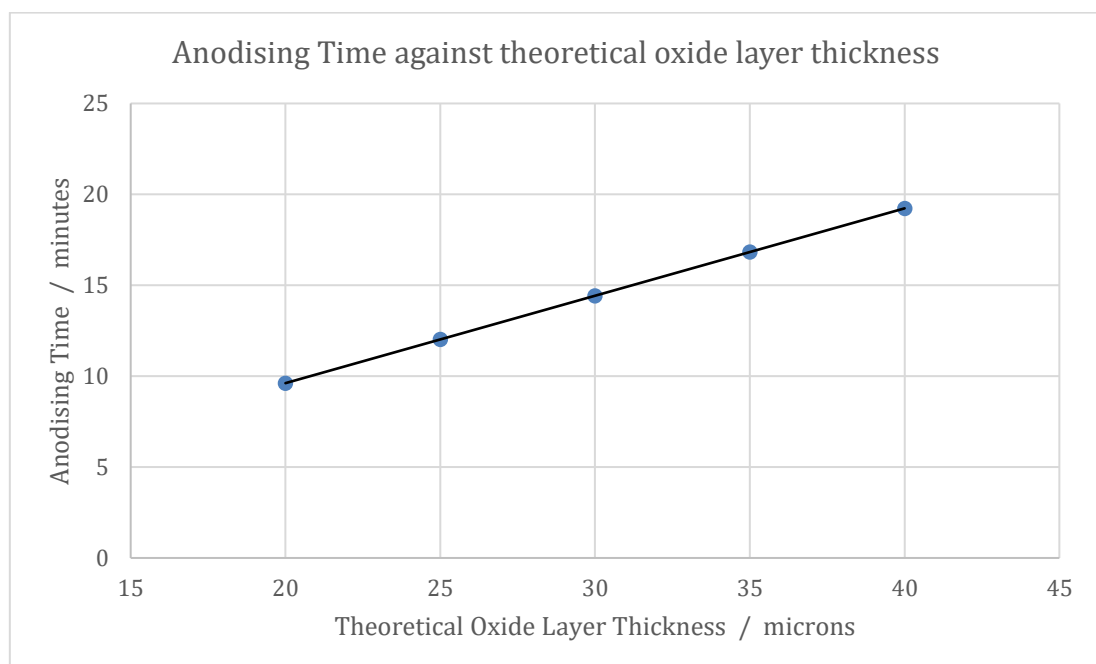
5.3 Theoretical oxide layer thickness

A common equation used in industry to calculate the thickness of an anodic oxide layer when type II anodising is the '312 rule' (Chesterfield, "Calculating"). It is used to calculate specific anodising times for certain thicknesses of oxide layers required for different anodised products:

$$\text{anodising time} = \frac{\text{microns} \times 3.12}{\text{current density}}$$

This formula relates the oxide layer thickness to the anodising time and the current density. This formula suggests a linear relationship between the anodising time and the oxide layer thickness:

Graph 2 – Graph showing theoretical oxide layer thickness (312 rule) against anodising time:



Values used in this graph can be found in Appendix section 9.3, pg 41.

My experimental data suggests that this is not an accurate model, and that Anodising time is proportional to the oxide layer thickness squared.

6 Conclusions and discussions:

Research Question: How does the anodising time affect the thickness of the anodic oxide layer and therefore the amount of dye absorbed when Type II anodising aluminium?

The experimental data taken during the experiment concludes that there is a quadratic relationship between anodising time and the thickness of the oxide layer between 20 and 40 minutes of anodising time. This suggests that as the time increases, the rate at which the oxide layer forms accelerates.

This quadratic relationship could however be because the sulphuric acid bath was not renewed after every anodising, decreasing the concentration of the acid which therefore increased the oxide layer thickness independently of the time. My assumption was that the anodising would have a negligible effect on the concentration of the anodising solution. If I was to replace the electrolyte every time I anodised, I would have to use over 300 litres of sulphuric acid to complete my results, which is impractical and dangerous to handle.

If my experimental data is correct, the experimental relationship has been seen to differ from pre-existing theory, possibly offering a new insight into the workings of anodising.

7 Evaluation

7.1 Strengths and Limitations

This experimental data is strong because of the low uncertainty in change in absorbance values. The range of change in %Transmittance values for each anodising was also small, suggesting that random errors in the experiment were minimal. Another strength of this investigation was the quality of the secondary sources used. Many of them are referred to often in industry, and are therefore accurate and precise. There was also a good range of sources from different mediums such as forums, websites and books.

A significant issue with the experiment however, was that the same sulphuric acid was used for a large number of anodisings. It is likely that the decrease in concentration of the sulphuric acid had a significant effect on the thickness of the oxide layer, and could account for the quadratic relationship seen, as the experiments with lower anodising time were done first.

7.2 Error Analysis

Table 3 – Table showing experimental errors, their significance and possible solutions

Source of Error	Type	Direction (effect on values)	Significance	Possible solutions
Concentration of sulphuric acid anodising bath.	Systematic	Increase	Significant	Replace the anodising solution after 10 uses
Fluctuating current and voltage	Random	None	Medium	Use a constant current source and/or a constant voltage source, that provides a constant current/voltage no matter the resistance
Time measurement (anodising, etching, dyeing)	Random	None	Minor	None
Sunlight (dye solution was kept in an area where sunlight could reach and interact with the solution)	Systematic	Decrease	Minor	Keep the dye solution in a dark area while the aluminium is dyeing in order to prevent possible sunlight interaction with the dye.

Word Count: 105

7.3 Further exploration

One pertinent issue with the experimental data collected was that it doesn't predict the optimum anodising time because the range of times is simply too small, and there is no seen deviation from the relationship in any way. In order to predict the optimum anodising time, the anodising needs to be tested for longer times, at which, the oxide layer cannot grow any thicker because of high resistance in the aluminium due to the thickness of the oxide layer.

Therefore, if I was to repeat or extend this project, I would enlarge the range of anodising times to 'extremes' in order to find the optimum anodising time and optimum oxide layer thickness. Because of time constraints due to the issues during pre-trials, I was not able to take any more than 5 data points for my experimental data, and didn't pick a wide enough range of times. This limits the experiment, as the data gives no suggestion of an optimum value as the curve cannot be extrapolated to find a maximum/optimum time value.

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9 Appendix:

9.1 Raw Data:

Final data including anomalies (average values calculated while excluding the anomalies):

Table 4 – Anodising time against %Transmittance values

Anodising Time (min) ± 0.2	%Transmittance before ± 0.01	%Transmittance after ± 0.01	%Transmittance change ± 0.02	Average change in %Transmittance ± 0.02
20.0	4.08	7.4	3.32	3.18
	4.08	7.00	2.92	
	4.02	7.32	3.30	
25.0	3.99	7.18	3.19	3.38
	4.04	9.71	5.67	
	4.01	7.53	3.52	
	3.99	7.43	3.44	
30.0	3.98	5.38	1.4	3.63
	4.05	7.61	3.56	
	4.02	4.31	0.29	
	4.01	9.45	5.44	
	4.07	7.59	3.52	
	3.92	7.74	3.82	
35.0	3.95	9.13	5.18	5.23
	4.03	9.41	5.38	
	4.15	9.29	5.14	
40.0	3.86	9.01	5.15	6.25
	4.01	10.48	6.47	
	4.16	10.4	6.24	
	4.01	7.51	3.5	
	4.04	10.07	6.03	

9.2 Processed Data:

In order to calculate the change in concentration of the dye solution, we need to convert all the %Transmittance values measured into Absorbance values, as according to the Beer Lambert law (and as explained on page 7), Absorbance is directly proportional to the concentration of the solution.

$$A = -\log_{10}T$$

This equation as rearranged to calculate A from %T:

$$A = 2 - \log_{10}\%T$$

For example (using 20 min trial 1 - T before)

$$\begin{aligned} A &= 2 - \log_{10}4.08 \\ &= 1.35 \end{aligned}$$

Then, from the 3 non-anomalous repeats for each anodising time, a change in Absorbance value was calculated by subtracting the Absorbance of the dye solution before the aluminium was dyed from the Absorbance of the dye solution after the aluminium was dyed:

Table 5 - Table showing %Transmittance and Absorbance values

Anodising time (m) ± 0.166	%Transmittance before ± 0.01	Absorbance before ± 0.004	%Transmittance after ± 0.01	Absorbance after ± 0.004	Change in Absorbance ± 0.007
20	4.08	1.389	7.40	1.131	-0.259
	4.08	1.389	7.00	1.155	-0.234
	4.02	1.396	7.32	1.136	-0.260
25	3.99	1.399	7.18	1.144	-0.255
	4.01	1.397	7.53	1.123	-0.273
	3.99	1.399	7.43	1.129	-0.270
30	4.05	1.393	7.61	1.119	-0.274
	4.07	1.390	7.59	1.120	-0.271
	3.92	1.407	7.74	1.111	-0.300
35	3.95	1.403	9.13	1.040	-0.364
	4.03	1.395	9.41	1.026	-0.368
	4.15	1.382	9.29	1.032	-0.350
40	4.01	1.397	10.48	0.980	-0.417
	4.16	1.381	10.40	0.983	-0.398
	4.04	1.394	10.07	0.997	-0.397

For each time period, an average change in absorbance was calculated from the 3 repeats of each time:

Table 6 - Table showing average absorbance values calculated from 3 repeats for each time:

Anodising time (m) ± 0.2	Change in Absorbance ± 0.007	Average change in Absorbance ± 0.007
20.0	-0.259	-0.251
	-0.234	
	-0.260	
25.0	-0.255	-0.266
	-0.273	
	-0.270	
30.0	-0.274	-0.280
	-0.271	
	-0.300	
35.0	-0.364	-0.361
	-0.368	
	-0.350	
40.0	-0.417	-0.404
	-0.398	
	-0.397	

Using the Beer-Lambert Law, the exact concentrations can be calculated from the absorbance values by dividing the absorbance by the path length multiplied by the Molar Absorptivity constant.

The molar absorptivity constant was then found by measuring the absorbance of a solution of known concentration and dividing it by the path length and the concentration of the solution.

$$A = \epsilon l c$$

$$\epsilon = \frac{A}{l c}$$

All dye solutions made were made by adding 2mL of dye to 900cm³ of deionised water. From an average value for the %Transmittance of the beginning solutions that were made, a value for ϵ can be calculated. The concentration of the solution however cannot be measured in mol/dm³ as the dye is not a pure substance with a calculable molar mass. Therefore, the concentration has been calculated as mL/dm³.

$$A = 2 - \log_{10} \%T = 2 - \log_{10} 4.04 = 1.39$$

$$conc. = \frac{mL}{dm^3} = \frac{2}{0.9} = 2.22$$

$$\epsilon = \frac{A}{l c} = \frac{1.39}{1 \times 2.22}$$

$$\epsilon = 0.626$$

From this ϵ value, a real concentration value in mL/dm³ for the dye solutions after the aluminium has been dyed can be calculated its absorbance and the value of ϵ calculated, for example:

$$A = \epsilon l c$$

$$c = \frac{A}{\epsilon l}$$

Using the example of 20-minute anodising time trial 1:

$$\frac{1.1308}{0.626 \times 1} = 1.8060 \text{ mL/dm}^3$$

Table 7 - table showing initial and final absorbance, initial and final concentration, change in concentration and an average change in concentration:

Anodising Time ± 0.166	Initial absorbance ± 0.004	Concentration before ± 0.06	Final absorbance ± 0.004	Concentration after $\pm 3\%$	Change in concentration ± 0.1	Average change in concentration ± 0.1
20.0	1.39	2.22	1.131	1.81	-0.4	-0.4
	1.39	2.22	1.155	1.84	-0.4	
	1.40	2.22	1.136	1.81	-0.4	
25.0	1.40	2.22	1.144	1.83	-0.4	-0.4
	1.40	2.22	1.123	1.79	-0.4	
	1.40	2.22	1.129	1.80	-0.4	
30.0	1.39	2.22	1.119	1.79	-0.4	-0.4
	1.39	2.22	1.120	1.79	-0.4	
	1.41	2.22	1.111	1.77	-0.4	
35.0	1.40	2.22	1.040	1.66	-0.6	-0.6
	1.39	2.22	1.026	1.64	-0.6	
	1.38	2.22	1.032	1.65	-0.6	
40.0	1.40	2.22	0.980	1.56	-0.7	-0.6
	1.38	2.22	0.983	1.57	-0.7	
	1.39	2.22	0.997	1.59	-0.6	

9.3 Uncertainties:

Anodising time was measured using a digital stopwatch with an uncertainty of ± 0.01 seconds, however the human error increases this value to ± 0.5 s.

The uncertainty of the syringe used to measure the 2mL of dye had an uncertainty of ± 0.05 mL, or $\pm 2.5\%$. The uncertainty of the 25cm³ measuring cylinder is ± 0.01 cm³, but when measuring 100cm³, the raw uncertainty becomes ± 0.4 cm³. The raw uncertainty of the 1L volumetric flask is ± 0.8 cm³. Therefore, when measuring 900mL using the two pieces of equipment, the uncertainty is ± 1.2 cm³.

$$1000 \pm 0.8 - 25 \pm 0.1 - 25 \pm 0.1 - 25 \pm 0.1 - 25 \pm 0.1 = 900 \pm 1.2 \text{ cm}^3$$

This value is then divided by the mL of dye to find the concentration in mL/dm³. The raw uncertainties are converted to percentage uncertainties and added.

$$\text{conc.} = \frac{\text{mL}}{\text{dm}^3} = \frac{2 \pm 2.5\%}{0.9 \pm 0.133\%} = 2.22 \pm 2.63\%$$

The colourimeter used has an uncertainty of ± 0.01 %Transmittance. These %Transmittance values were then used to calculate absorbance values for the dye solutions:

$$A = 2 - \log_{10} \%T$$

In this case, the percentage uncertainty of the %T value is the same as the same as the percentage uncertainty of the absorbance value.

$$\text{E.g. } A = 2 - \log_{10} 4.01 \pm 0.25\% = 1.40 \pm 0.25\%$$

Table 8 - Table showing raw and percentage uncertainties for %T values and A values for the initial solution:

Anodising Time	%Transmittance	Raw uncertainty	% uncertainty	Absorbance	Raw uncertainty	% uncertainty
20.0	4.08	0.01	0.2	0.6107	0.0001	0.01
	4.08	0.01	0.2	0.6107	0.0001	0.01
	4.02	0.01	0.2	0.6042	0.0001	0.01
25.0	3.99	0.01	0.3	0.6010	0.0001	0.01
	4.01	0.01	0.2	0.6031	0.0001	0.01
	3.99	0.01	0.3	0.6010	0.0001	0.01
30.0	4.05	0.01	0.2	0.6075	0.0001	0.01
	4.07	0.01	0.2	0.6096	0.0001	0.01
	3.92	0.01	0.3	0.5933	0.0001	0.01
35.0	3.95	0.01	0.3	0.5966	0.0001	0.01
	4.03	0.01	0.2	0.6053	0.0001	0.01
	4.15	0.01	0.2	0.6180	0.0001	0.01
40.0	4.01	0.01	0.2	0.6031	0.0001	0.01
	4.16	0.01	0.2	0.6191	0.0001	0.01
	4.04	0.01	0.2	0.6064	0.0001	0.01

Table 9 - Table showing raw and percentage uncertainties for %T values and A values for the final solution:

Anodising Time	%Transmittance	Raw uncertainty	% uncertainty	Absorbance	Raw uncertainty	% uncertainty
20.0	7.40	0.01	0.1	1.1308	0.002	0.1
	7.00	0.01	0.1	1.1549	0.002	0.1
	7.32	0.01	0.1	1.1355	0.002	0.1
25.0	7.18	0.01	0.1	1.1439	0.002	0.1
	7.53	0.01	0.1	1.1232	0.002	0.1
	7.43	0.01	0.1	1.1290	0.002	0.1
30.0	7.61	0.01	0.1	1.1186	0.002	0.1
	7.59	0.01	0.1	1.1198	0.002	0.1
	7.74	0.01	0.1	1.1113	0.001	0.1
35.0	9.13	0.01	0.1	1.0395	0.001	0.1

	9.41	0.01	0.1	1.0264	0.001	0.1
	9.29	0.01	0.1	1.0320	0.001	0.1
40.0	10.48	0.01	0.1	0.9796	0.001	0.1
	10.40	0.01	0.1	0.9830	0.001	0.1
	10.07	0.01	0.1	0.9970	0.001	0.1

The absorbance values for the initial and final solutions are then subtracted from each other to get the change in absorbance.

Table 10 - Table showing raw and percentage uncertainties for initial and final Absorbance values and change in Absorbance values

Anodising Time	Initial Absorbance	Raw uncertainty	Absorbance Final	Raw uncertainty	Change in Absorbance	Raw uncertainty	% uncertainty
20.0	1.389	0.003	1.131	0.002	-0.2586	0.002	0.6
	1.389	0.003	1.155	0.002	-0.2344	0.002	0.7
	1.396	0.004	1.136	0.002	-0.2603	0.002	0.6
25.0	1.399	0.004	1.144	0.002	-0.2552	0.002	0.6
	1.397	0.004	1.123	0.002	-0.2737	0.002	0.6
	1.399	0.004	1.129	0.002	-0.2700	0.002	0.6
30.0	1.393	0.004	1.119	0.002	-0.2739	0.002	0.6
	1.390	0.004	1.120	0.002	-0.2706	0.002	0.6
	1.407	0.004	1.111	0.001	-0.2955	0.002	0.5
35.0	1.403	0.004	1.040	0.001	-0.3639	0.001	0.4
	1.395	0.004	1.026	0.001	-0.3683	0.001	0.4
	1.382	0.003	1.032	0.001	-0.3500	0.001	0.4
40.0	1.397	0.004	0.980	0.001	-0.4172	0.001	0.3
	1.381	0.003	0.983	0.001	-0.3979	0.001	0.3
	1.394	0.003	0.997	0.001	-0.3966	0.001	0.3

The value of ϵ was calculated using the initial concentration (2.22) and an average Absorbance of the initial solutions. The average was calculated by dividing the sum of all the initial absorbances by the number of values (15). This average value had an uncertainty of $\pm 0.255\%$ (the largest % uncertainty of all the absorbance values averaged).

$$A = \epsilon l c$$

$$\epsilon = \frac{A}{l c} = \frac{1.39 \pm 0.255\%}{2.22 \pm 2.63\%} = 0.626 \pm 2.89\%$$

This value was then used to calculate every single final concentration value from its absorbance:

$$\text{E.g. using } c = \frac{A}{\epsilon l} = \frac{1.13 \pm 0.135\%}{0.626 \pm 2.89\%} = 1.81 \pm 3.025\%$$

Table 11 Table showing final concentration values calculated from ϵ value and final absorbance values:

Anodising Time	Final Absorbance	% uncertainty	ϵ value	% Uncertainty	Final concentration	% uncertainty	Raw uncertainty
20.0	1.130	0.1	0.6	3	1.81	3	0.05
	1.155	0.1			1.84	3	0.05
	1.136	0.1			1.81	3	0.05
25.0	1.144	0.1			1.83	3	0.05
	1.123	0.1			1.79	3	0.05
	1.129	0.1			1.80	3	0.05
30.0	1.119	0.1			1.79	3	0.05
	1.120	0.1			1.79	3	0.05
	1.111	0.1			1.77	3	0.05
35.0	1.040	0.1			1.66	3	0.05
	1.026	0.1			1.64	3	0.05
	1.032	0.1			1.65	3	0.05

40.0	0.980	0.1			1.56	3	0.04
	0.983	0.1			1.57	3	0.04
	0.997	0.1			1.59	3	0.05

The initial and final concentrations were then subtracted from each other to find a value for change in concentration:

E.g. for 20-minute trial 1

$$2.22 \pm 0.585 - 1.81 \pm 0.0518 = -0.414 \pm 0.110$$

Table 12 - Table showing raw and percent uncertainties in change in concentration values

Anodising Time	Initial Concentration	raw uncertainty	Final Concentration	Raw Uncertainty	Change in concentration	Raw uncertainty	% uncertainty
20.0	2.22	0.06	1.80	0.05	-0.4	0.1	27
	2.22	0.06	1.84	0.05	-0.45	0.1	30
	2.22	0.06	1.81	0.05	-0.4	0.1	27
25.0	2.22	0.06	1.83	0.05	-0.4	0.1	28
	2.22	0.06	1.79	0.05	-0.4	0.1	26
	2.22	0.06	1.80	0.05	-0.4	0.1	26
30.0	2.22	0.06	1.79	0.05	-0.4	0.1	25
	2.22	0.06	1.79	0.05	-0.4	0.1	25
	2.22	0.06	1.77	0.05	-0.4	0.1	25
35.0	2.22	0.06	1.66	0.05	-0.6	0.1	19
	2.22	0.06	1.64	0.05	-0.6	0.1	18
	2.22	0.06	1.65	0.05	-0.6	0.1	18
40.0	2.22	0.06	1.56	0.04	-0.7	0.1	16
	2.22	0.06	1.57	0.04	-0.7	0.1	16
	2.22	0.06	1.59	0.05	-0.6	0.1	16

Theoretical oxide layer thickness:

We can rearrange the 312-rule formula and use it to find the theoretical oxide layer thicknesses for each anodising time:

$$\text{microns} = \frac{\text{time} \times \text{current density}}{3.12}$$

The current density is calculated by dividing the current (± 0.1) by the surface area in dm^2 . The surface area was measured using a rule ($\pm 0.5\text{mm}$) to measure the length of each side.

$$10 \pm 0.05 \times 10 \pm 0.05 = 100 \pm 0.1\text{cm}^2 = 1 \pm 0.001\text{dm}^2$$

$$1 \pm 0.001 + 1 \pm 0.001 = 2 \pm 0.002 \text{ dm}^2$$

The current was then divided by the surface area to get the current density. Although the ammeter measures to two decimal places, the ammeter fluctuated between currents, so the most accurate it can really be is ± 0.1 .

$$\text{Current density} = \frac{\text{Current}}{\text{Surface Area}} = \frac{3 \pm 3.33\%}{2 \pm 0.1\%} = 1.5 \text{ A/dm}^2 \pm 3.43\%$$

Then the theoretical oxide layer thickness was calculated:

For example, using the 30-minute time trial:

$$\text{microns} = \frac{30 \times 1.5}{3.12}$$

$$= 14.4 \text{ microns}$$

Table 13 - Table showing anodising time against theoretical oxide layer thickness:

Anodising time (min)	Raw Uncertainty	% Uncertainty	Current density (A/dm ²)	% Uncertainty	Oxide layer thickness (μm)	% Uncertainty
20.0	0.2	0.8	1.5	3	9.6	4
25.0	0.2	0.7			12.0	4
30.0	0.2	0.6			14.4	4
35.0	0.2	0.5			16.8	4
40.0	0.2	0.4			19.2	4

9.4 Miscellaneous

Figure 2 – effect of improper degreasing on anodising finish:

