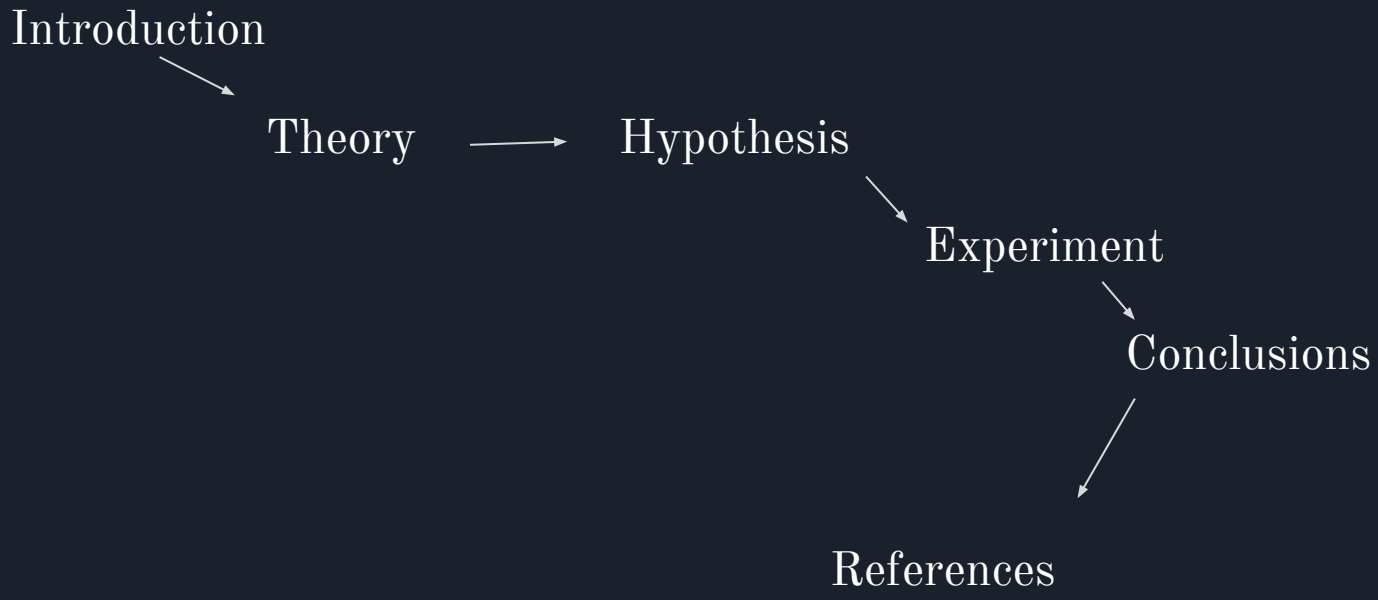
3. Photography with iron salts
Report Greece - Menelaos Raptis

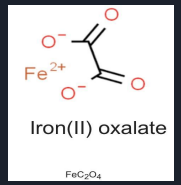
Hellenic Physical Society
I.Y.N.T. 2020

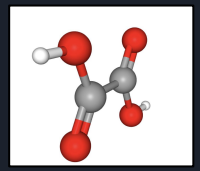
1953
ΕΚΠΑΙΔΕΥΤΗΡΙΑ
ΦΡΥΓΑΝΙΩΤΗ

Contents

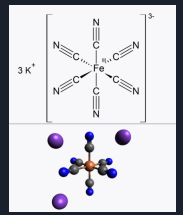

Introduction
Theory
Hypothesis
Experiment
Conclusions
References

Problem to be investigated



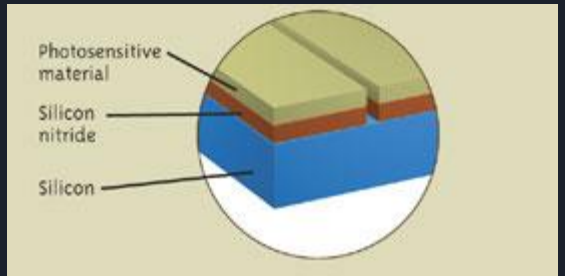


Mix 10 parts of ferrous oxalate (25% aqueous solution), 7 parts of concentrated ammonia solution, and 20 parts of saturated solution of oxalic acid to produce a photosensitive iron complex. Prepare separately a 25% solution of potassium ferricyanide. A sheet of paper saturated with a mix of these two solutions can be exposed to light and produce an image.

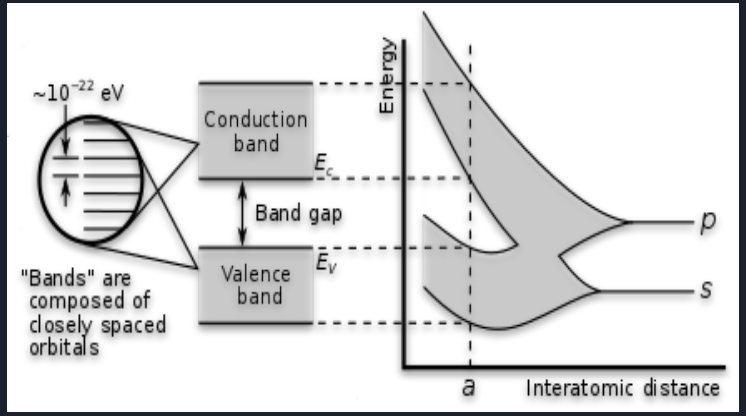


When do we call a material “photosensitive”

Photosensitive materials attain properties that are distinctively different from those of non-excited materials. By absorbing energy from light, these materials temporarily change their solid-state, molecular and/or interfacial properties. If the interface is sufficiently photoactive, these materials may also react with their molecular environments and generate chemical energy in the form of energy-rich compounds.



The discovery of photosensitivity in 1978 by K.O Hill triggered the development of new optical elements, mainly in fibers and waveguides. The principle of photosensitivity relies on the exposure of a material with energy larger than its bandgap. The linear (or nonlinear) interaction generates a change of the material structure that induces a local refractive index change.



What is generally Cyanotype ?

And why referring to this procedure ?

Cyanotype is a photographic printing process that produces a cyan-blue print.

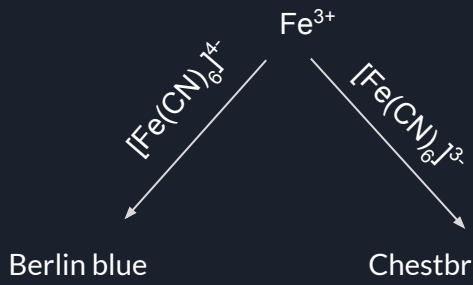
Engineers used the process well into the 20th century as a simple and low-cost process to produce copies of drawings, referred to as blueprints. The process used two chemicals : ferric ammonium citrate and potassium ferricyanide.

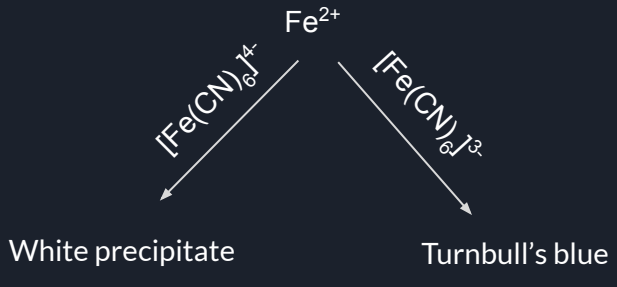
In the experiment given we use ferrous ammonium oxalate and potassium ferricyanide.

The combination of UV light and the citrate reduces the iron(III) to iron(II). This is followed by a complex reaction of the iron(II) complex with ferricyanide. The result is an insoluble, blue dye known as Prussian Blue. **Color change**

In the experiment

Interesting...Combinations





In our experiments we have both Berlin blue (=Prussian Blue) and Turnbull's Blue and their color difference is negligible. There is also a chemical balance between them :

$$Fe_3[Fe(CN)_6]_3 \leftrightharpoons Fe_4[Fe(CN)_6]_3$$

(Turnbull) (Prussian)

In the experiment

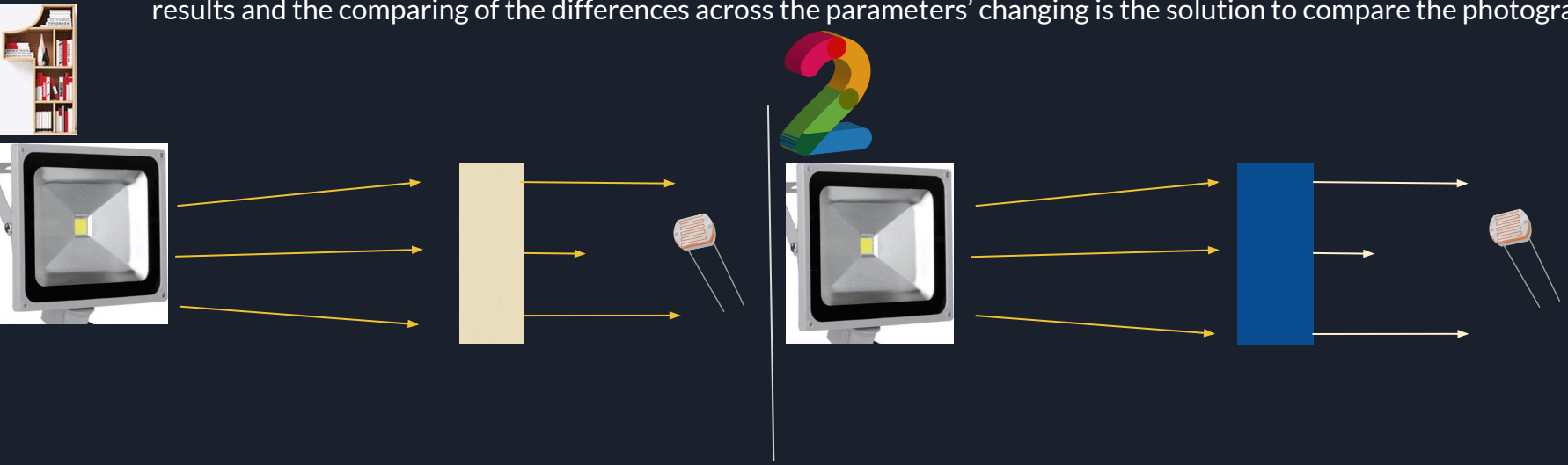
Hypothesis

- We wait to observe a higher shade number with higher concentration of the solutions
- We wait to observe better results referring to the contrast control by using papers with more absorbent surface
- Higher temperature ⟶ more electronic traps ⟶ higher photosensitivity
- We will not observe change in the color if we'll let the paper under a led light bulb
- With a higher speed of the air current we wait a bigger amount of water to be evaporated
- Higher speed of evaporation of the liquid ⟶ lower optical density
- The lower the pH the more intense the final result

Experimental Procedure
Compering Results

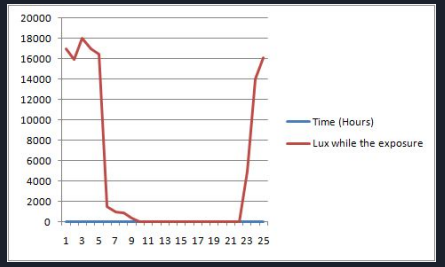
It would be very subjective to compare the results with a naked eye and in this contest we are all looking for something really valid and scientific.

I put a projector in a dark room and in a distance of 10 meters of the paper in question. Behind the paper exists an arduino photoresistor. Firstly, I measured the resistance written from the sensor with the paper which has the solution of the problem statement. Then, I did the same after the formation of the photograph. The difference between the two results and the comparing of the differences across the parameters' changing is the solution to compare the photographs.



Experimental Procedure

1st experiment - Original experiment



Ingredients

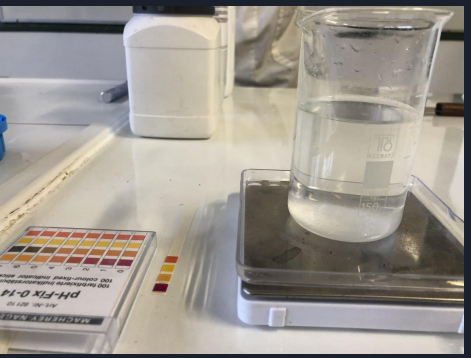
1) Ferrous Oxalate 12,5gr/50ml (10 parts)
2) Concentrated Ammonia Solution (7 parts)
3) Saturated solution of oxalic acid (20 parts)

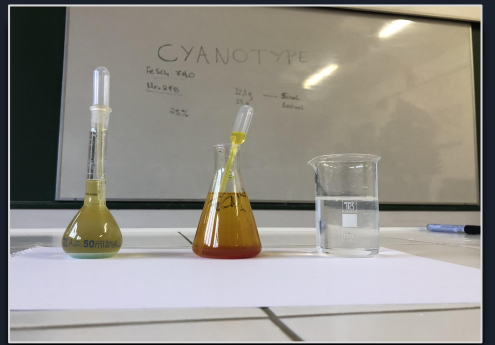
A

4) Potassium Ferricyanide (25% solution)

B

Ph. r. - B. & A.	Photoresistance
Before	853
After	850
Difference	negligible

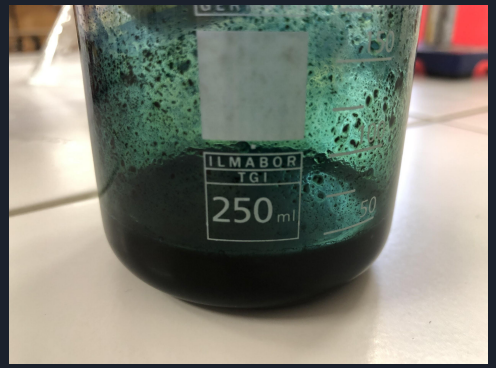


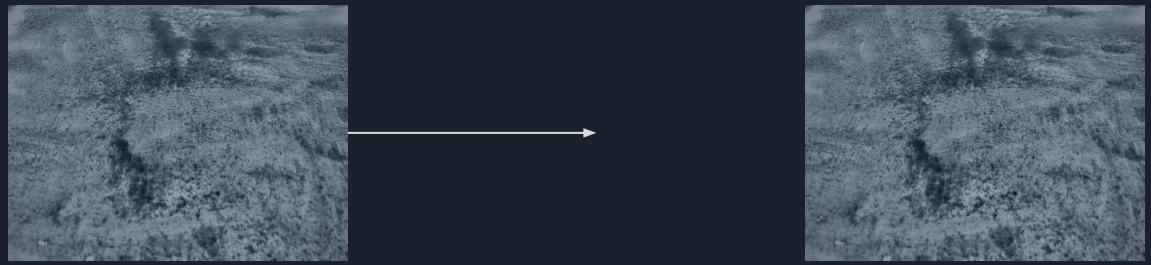


Experimental Procedure

1st experiment - Original experiment

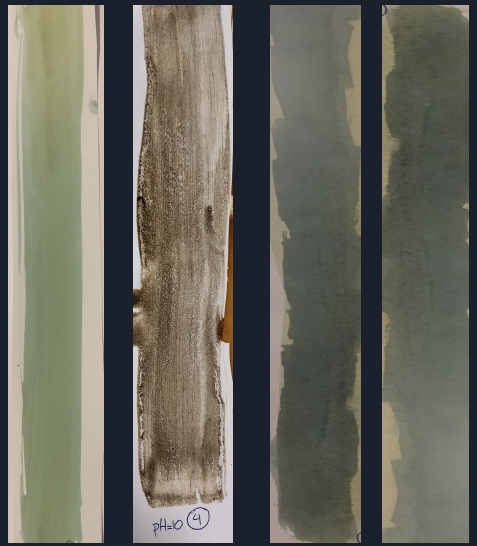
The problem uses Iron(II) with Potassium Ferricyanide. That means we will observe from the start the Turnbull's blue (which is the same in color with Prussian blue). That is what we hypothetically wait to see after the exposure of the paper in the UV. In my experiment that didn't work.





Experimental Procedure

2nd experiment - Ferrous with Ferrocyanide, pH



5

Before	780
After	520
Difference	33,33%

4

Before	656
After	602
Difference	negligible

2

Before	902
After	544
Difference	37,6%

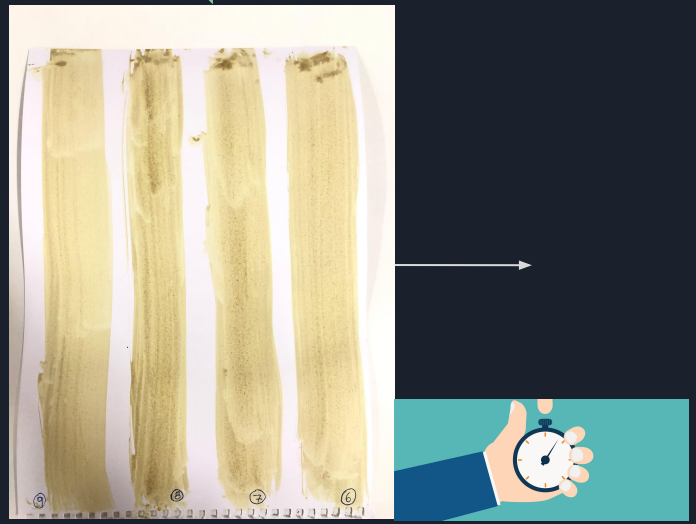
3

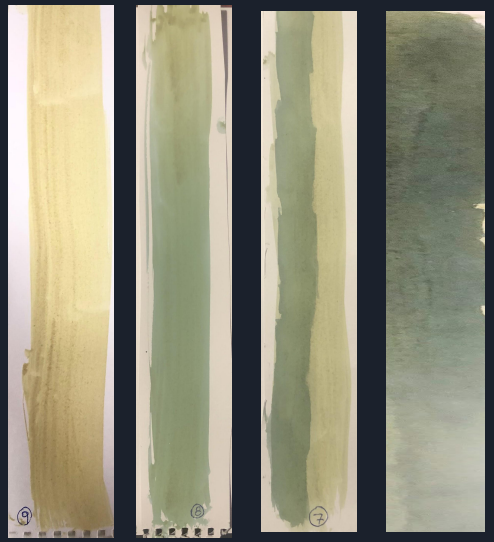
Before	871
After	563
Difference	35,3%

2 : pH = 0, **3** : pH = 1, **4** : pH = 10, **5** : pH=9 & it was 1 week-made so that also test if it works with a relevantly old solution

Experimental Procedure

3rd experiment - Ferrous with Ferrocyanide, radiation





6: exposed for 6h, **7** :exposed for 12h with two sides (a: was exposed to intense sunlight, b: to weak sunlight), **8**: Exposed to a UV lamp for 24 hours, **9**: to a led bulb for 24 hours

9

Before	856
After	855
Difference	negligible

8

Before	850
After	788
Difference	10,1%

6

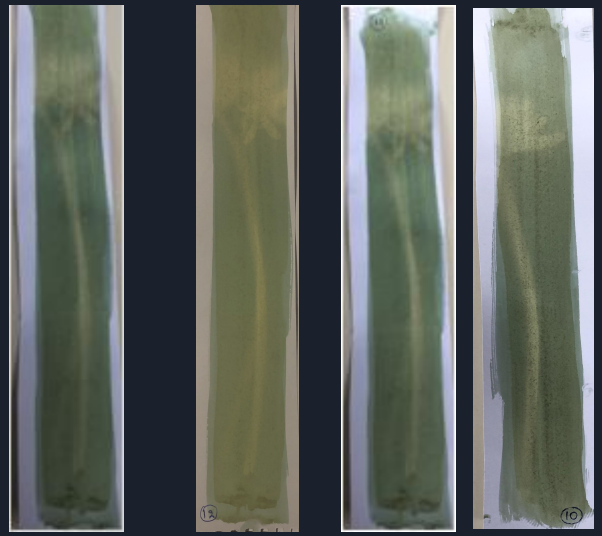
Before	831
After	621
Difference	25,2%

7

Before	825(a) / 825(b)
After	509 / 581
Difference	38,2% / 29,5%

Experimental Procedure

4th experiment - Ferrous with Ferrocyanide, dry



10 : was dried by the air of the room,
11: was dried with a radiator with its surface up (room light), **12:** in a radiator with its surface down, **13:** in a radiator with its surface up (light of sun)

temp :25 ℃

10

Before	868
After	543
Difference	37,4%

13

Before	866
After	529
Difference	38,8%

12

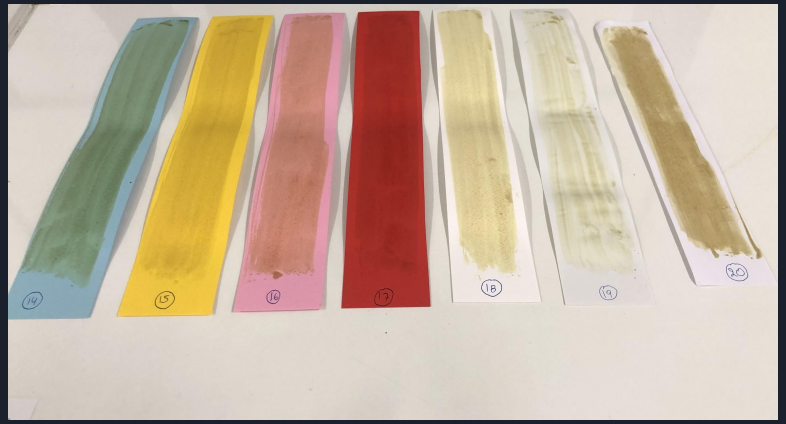
Before	868
After	540
Difference	37,7%

11

Before	865
After	540
Difference	37,5%

Experimental Procedure

5th experiment - Ferrous with Ferrocyanide, types of paper



14: blue hot pressed paper, 15: yellow[...], 16: pink[...], **17**: red [...], 18: white [...] , **19**: Glazed paper, **20**: Bond paper

17

Before	341
After	215
Difference	37,1%

16

Before	358
After	240
Difference	33%

14

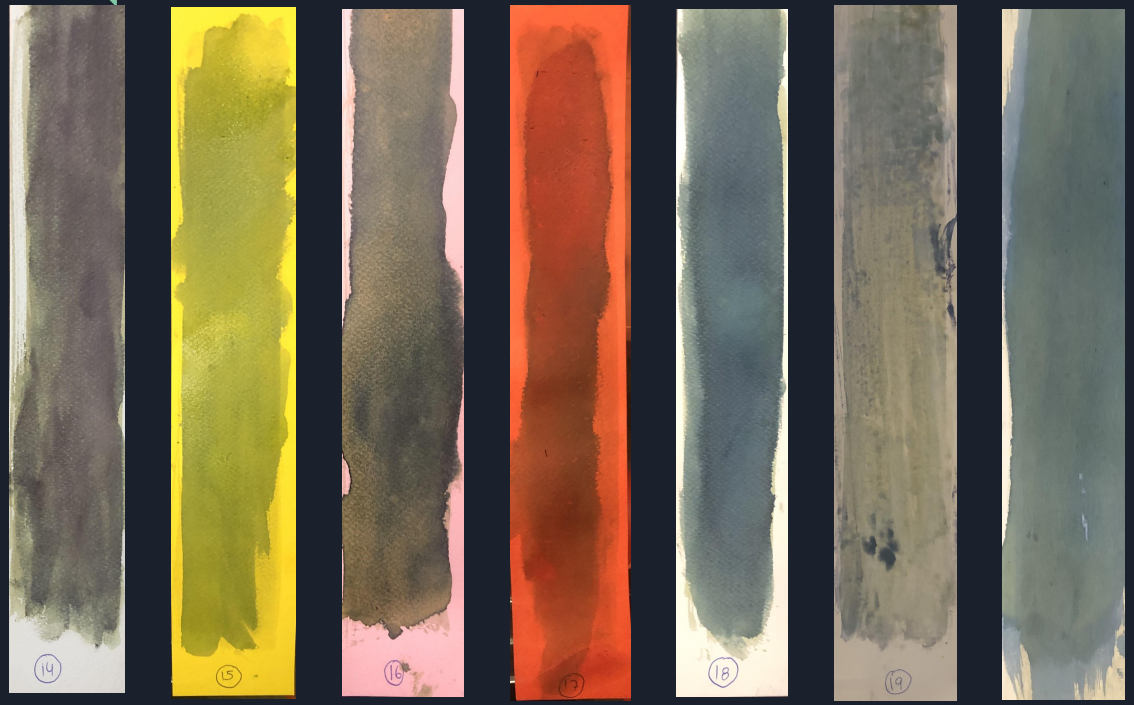
Before	383
After	249
Difference	35%

15

Before	394
After	268
Difference	32,2%

Experimental Procedure

5th experiment



20

Before	955
After	593
Difference	36,2%

19

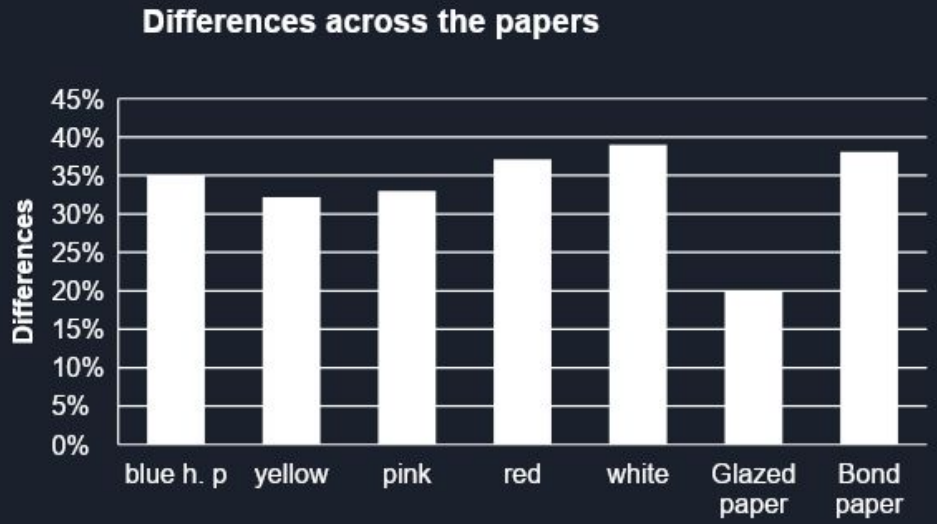
Before	881
After	705
Difference	20%

18

Before	543
After	332
Difference	39%

Experimental Procedure

5th experiment - Ferrous with Ferrocyanide, types of paper



Experimental Procedure

6th experiment - Traditional way, Ferric Ammonium Citrate & P. Ferricyanide

Recipe #1

This is the original created by John Herschel in 1842 :

Solution A :

- Ferric Ammonium Citrate 200 gm
- Distilled Water to make 1000 ml

Solution B :

- Potassium Ferricyanide 160 gm
- Distilled Water to make 1000ml

Recipe #2

Variation using more concentrated solutions :

Solution A :

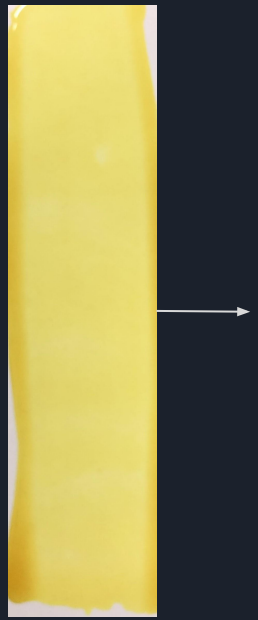
- Ferric Ammonium Citrate 360 gm
- Distilled Water to make 1000 ml

Solution B :

- Potassium Ferricyanide 200 gm
- Distilled Water to make 1000ml

Experimental Procedure

7th experiment - Traditional way & UV



Flowers to spot the difference

Flowers to spot the difference

Before	877
After	614
Difference	30,2%

It was exposed to UV for 8 minutes

Conclusions

- Iron(II) combined with Ferricyanide gives Turnbull’s blue from the beginning
- Lower pH means a more intense blue
- Usual light bulbs don't affect the color
- Old solutions work too by giving the Prussian blue
- The way of drying of the papers doesn’t affect the experiment significantly
- Higher temperature contributes to raise the photosensitivity
- FAC with P. Ferricyanide works better a lot of times more than the FAO with P. Ferrocyanide
- Higher light intensity & more time of exposure means a more intense result

References

"Exploring Photography – Photographic Processes – Cyanotype". V&A. 2012-11-13. Retrieved 2012-12-22.

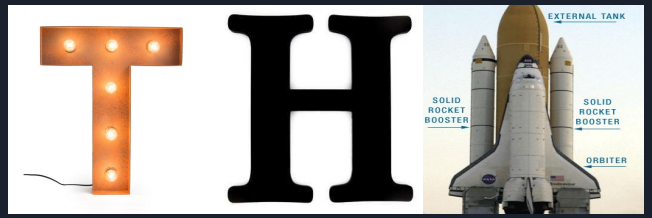
"Victorian Life - 43 Cyanotypes". *Vintage Everyday*. Retrieved 18 August 2019.

"Washington Teasdale". *History of Science Museum, Oxford*. Retrieved 18 August 2019.

Hannavy, John (2013-12-16). *Encyclopedia of Nineteenth-Century Photography*. Routledge. ISBN 9781135873271.

"Exploring Photography – Photographers – Anna Atkins". *V&A*. 2012-11-13. Archived from the original on December 11, 2003. Retrieved 2012-12-22.

"Ge Dunbar, K. R.; Heintz, R. A. (1997). "Chemistry of Transition Metal Cyanide Compounds: Modern Perspectives". *Progress in Inorganic Chemistry*. Progress in Inorganic Chemistry. 45. pp. 283–391. doi:10.1002/9780470166468.ch4. ISBN 9780470166468.neral View of Niagara Falls from Bridge". World Digital Library. Retrieved 11 February 2013.



N

YOU ALL

FOR

YOUR ATTENTION