C 141 (Expt. No. 10)

NAME : _____ **BATCH :** _____
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Cyanotype Blue Printing

AIM

To study the photochemical reduction of ferric oxalate in cyanotype blue printing.

THEORY

The **cyanotype** or **"blueprint" photographic process** is one of several alternative photographic methods, which **relies on the photoreduction of ferric ions.** Cyanotypes are quite long-lasting and are normally blue.

Cyanotype chemistry relies on 2 distinct reactions :

(a) ferric ions present in organic-iron complexes are reduced by light (for example, ammonium ferric citrate and ammonium ferric oxalate) ;

(b) the ferrous ions formed are allowed to react with potassium ferricyanide to form an insoluble blue compound called Prussian blue, $Fe_4[Fe(CN)_6]_3 . 15 H_2O$.

The structure of **Prussian blue** has **hexacoordinate Fe (II)** *bound through the carbon atoms*, and **hexacoordinate Fe (III)** *bound through the nitrogen atoms*, forming an **extended cubic framework**.

To achieve stoichiometry, one - fourth of the Fe (II) sites are occupied by water molecules. This reduces the number of bridging cyanide groups, and water molecules occupy the otherwise empty ligand positions thus created. There are also water molecules in some cubic sites in the crystal lattice.

The chemical equations for the reactions involved in blueprinting with ferric oxalate are as follows :

(a) Under UV – light, **ferric oxalate** (or its ammonium salt) gets ***reduced*** to **ferrous oxalate**, with the release of CO_2 ,

$$\mathbf{2\,(NH_4)_3\,Fe\,(C_2O_4)_3 \longrightarrow 2\,CO_2 + 2\,Fe\,(C_2O_4) + 3\,(NH_4)_2\,(C_2O_4)}$$

(ferric) (ferrous)

(b) The **ferrous iron** reacts with **potassium ferricyanide** to form **ferroferricyanide (Prussian blue),**

$$Fe(C_2O_4) + K_3Fe(CN)_6 \longrightarrow K\,Fe\,[Fe(CN)_6] + K_2(C_2O_4)$$

$$8\,K\,Fe\,[Fe(CN)_6] \leftrightarrow 2\,Fe_4\,[Fe(CN)_6]_3 + 2\,K_4\,Fe(CN)_6$$

MATERIALS REQUIRED

Oxalic acid, diammonium hydrogen phosphate, ferric chloride, potassium ferricyanide, potassium dichromate, HCl solution

PROCEDURE

1. Pour **50 ml** of **0.5 M oxalic acid** into a 250 ml beaker.
   Add **10 ml** of **3.5 M diammonium hydrogen phosphate** solution,
   and **mix well**.**Keep the beaker in subdued light.**
2. Add **50 ml** of **ferric chloride** while stirring.
   If a precipitate is formed, further stirring should dissolve it.
   Keep this **solution inside the cupboard**, since the **ferric oxalate is sensitive to light.**
3. Immerse **4** pieces of bond paper **(4" x 2.5")** in the freshly prepared sensitizing solution (**ammonium iron oxalate** solution).
   Rotate the beaker and make sure that the paper is thoroughly wet.
4. **Remove the wet pieces of paper**, and place them **between sheets of filter paper.** **<u>This should be done as quickly as possible</u>.**
5. After the paper has dried, remove it from the filter paper sheets.
6. **Place the opaque object on the top of the sensitized paper, and compress it between sheets of glass.**
   Expose to sunlight.
   The **time required for exposure** of a normal **print in bright sunlight** is about **4 – 5 minutes**.
   During printing, do not hold the glass plates, but lay them on the desk, windowsill, or any flat surface.
7. **After the exposure**, **smoothly dip the paper** into **50 ml** of **0.1 M potassium ferricyanide solution**, kept in a wide-mouthed dish.

8. Remove the paper and **dip it** in **50 ml** of **0.03 M potassium dichromate solution for 1 minute.**
9. **Wash the paper first in 0.1 M HCl, and then in tap water.**

Make a series of 2 – 3 exposures, varying the time of exposure to optimize the best conditions.

Use these conditions to obtain the most satisfactory pictures.

Record the Time of Exposure for each picture.