UV-Sensitive Paper

Blueprint for Chemical Change

Introduction

Make your own ultraviolet-sensitive paper and develop images of any object you want! Reproduce the ultraviolet light–activated redox reaction used in traditional blueprinting. Images appear in just minutes and are permanent.

Concepts

- Oxidation-reduction
- Photochemistry

Materials

Iron(III) nitrate solution, $Fe(NO_3)_3$, 0.10 M, 10 mL Oxalic acid solution, $H_2C_2O_4$, 0.15 M, 10 mL Potassium ferricyanide solution, $K_3Fe(CN)_6$, 0.10 M, 10 mL Corrugated cardboard, at least 8-cm square, 2 pieces Filter paper, 7-cm diameter Graduated cylinders, 10-mL, 2 Non-metallic, opaque objects Paper towels Stirring rod Tongs or forceps Weighing dishes, 39" × 39", plastic, 2

Safety Precautions

Potassium ferricyanide solution causes mild skin and eye irritation. Iron(III) nitrate solution causes skin and serious eye irritation. Oxalic acid is harmful if swallowed and causes severe skin burns and eye damage. Do not breathe dust or fumes. Combining Solutions 1 and 2 will dye the skin a dark blue. The product, Prussian blue, is nontoxic and the color will fade with time. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Please review current Safety Data Sheets for additional safety, handling, and disposal information.

Procedure

Part A. Preparing UV-Sensitive Paper

Collect various non-metallic objects to place on the paper. Opaque objects work best.

- 1. Measure 10 mL of 0.10 M iron(III) nitrate solution and pour it into a large weighing dish.
- 2. Measure 10 mL of 0.15 M oxalic acid solution. Combine it with the iron(III) nitrate in the weighing dish and mix well with a stirring rod. This solution, which is now iron(III) oxalate, will be Solution 1. Set the dish aside for use in step 4.
- 3. Measure 10 mL of 0.10 M potassium ferricyanide solution and pour it into a separate weighing dish. This will be Solution 2.
- 4. Use a pair of tongs or forceps to soak a piece of filter paper in Solution 1. As soon as the paper is saturated, remove the filter paper and blot it on a paper towel.
- 5. Take the same piece of filter paper and dip it in Solution 2, turning it over to wet both sides. Remove it and blot it on a paper towel.
- 6. Place the treated filter paper on a piece of cardboard. Cover it with a second piece of cardboard.

Part B. Developing Images on the Treated Paper

- 7. Locate both a sunny area and a cloudy or shaded area outside.
- 8. Bring a non-metallic object and the treated filter paper into the shaded area. Remove the top piece of cardboard and quickly place the object on the treated paper. *Note:* Doing this in the shade will block the paper from direct sunlight and give crisper images.

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- 9. With the object sitting on the treated paper on the cardboard, move to a sunny area. Set the paper in the sunlight, exposing it to bright, direct sunlight until the paper turns a dark blue color. This step will take about five minutes, depending on the amount of sunshine.
- 10. After the paper is developed, remove the object and cover the paper with the top cardboard piece.
- 11. Bring the "blueprint" paper indoors (out of the sunlight). Holding the paper with tongs, gently rinse it with very cold water for a few minutes to remove excess iron(III) ions. Rinse until the solution turns clear and the blueprint paper turns a lighter shade of blue.
- 12. Repeat steps 4–11, trying a variety of different objects.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. Iron(III) oxalate may be rinsed down the drain with excess water according to Flinn Suggested Disposal Method #26b. Provide a disposal container for leftover Solution 2. Potassium ferricyanide solution may be oxidized according to Flinn Suggested Disposal Method #14.

NGSS Alignment

This laboratory activity relates to the following Next Generation Science Standards (2013):

Disciplinary Core Ideas: High School HS-PS1 Matter and Its Interactions PS1.A: Structure and Properties of Matter PS1.B: Chemical Reactions HS-PS3 Energy PS3.A: Definitions of Energy PS3.B: Conservation of Energy and Energy Transfer HS-PS4 Waves and Their Applications in Technologies for Information Transfer PS4.B: Electromagnetic Radiation

Science and Engineering Practices

Developing and using models Planning and carrying out investigations Constructing explanations and designing solutions

Crosscutting Concepts

Cause and effect Energy and matter Stability and change

Tips

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- Carefully read the chemical labels before preparing the solutions for this lab. Iron(III) nitrate is also called ferric nitrate, and potassium ferricyanide is also call potassium hexacyanoferrate(III). Note also that potassium ferricyanide is different than potassium ferrocyanide.
- Perform this demonstration on a sunny day so the students will be able to develop their images outside. A sunny day will provide for the fastest developing of the images; however, an overcast day will set the stage for additional discussion of ultraviolet radiation.
- If your situation prohibits students from going outside, try developing the paper using an artificial ultraviolet "black" light.
- Blueprinting is the standard method used to copy pre-construction drawings. The older method of blueprinting, which is illustrated in this activity, produces white lines against a blue background. The drawing to be copied is drawn on a special transparent paper or plastic. This drawing is then placed on top of the chemically treated "blueprint" paper and exposed to strong light. The areas of the blueprint paper that are protected by the lines on the drawing are not exposed to light and remain white, while the rest of the paper turns blue. A newer method of blueprinting, which utilizes diazonium salt chemistry, produces blue lines against a white background.

Discussion

The preparation of UV-sensitive paper in this activity involves the combination of two iron salts—iron(III) oxalate, $Fe_2(C_2O_4)_3$, and potassium ferricyanide, $K_3Fe(CN)_6$. Iron(III) oxalate is prepared by combining iron(III) nitrate and oxalic acid, as shown in Equation 1.

$$2Fe(NO_3)_3(aq) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 6HNO_3(aq) \qquad Equation 1$$

Exposing porous paper saturated with iron(III) oxalate and potassium ferricyanide solutions to UV light results in a breakdown of the iron(III) oxalate to produce iron(II) ions (Equations 2a and 2b). Iron(II) ions combine with $Fe(CN)_6^{3-}$ ions from potassium ferricyanide, resulting in the characteristic dark blue color of the exposed part of the paper. The dark blue color is due to a mixed iron(II)–iron(III) compound (see Equation 3). In the areas where the paper is covered by an opaque object (and protected from UV light), this reaction does not occur and the paper retains its original color.

Solutions of iron(III) oxalate, $Fe_2(C_2O_4)_3$, contain several complex ions of Fe^{3+} . One of these ions is $[Fe(C_2O_4)(H_2O)_4]^+$, which can be simplified as $Fe(C_2O_4)^+$. When irradiated with UV light, this ion undergoes an internal electron transfer from the oxalate ligand $(C_2O_4^{2-})$ to iron(III), resulting in an iron(II) ion and an oxalate radical anion (Equation 2a):

The $(C_2O_4)^{--}$ radical anion is very unstable and decomposes into CO_2 and the CO_2^{--} radical anion, which dimerizes to regenerate $(C_2O_4)^{2--}$, the oxalate anion (Equation 2b). The oxalate anion is stable.

$$2\operatorname{Fe}(\operatorname{C}_{2}\operatorname{O}_{4})^{+}(\operatorname{aq}) \xrightarrow{\operatorname{UV}} 2\operatorname{Fe}^{2+}(\operatorname{aq}) + 2\operatorname{CO}_{2}(\operatorname{g}) + \operatorname{C}_{2}\operatorname{O}_{4}^{2-}(\operatorname{aq}) \qquad \qquad Equation \ 2b$$

The resulting Fe²⁺ ions react with hexacyanoferrate(III) ions to produce Turnbull's blue, also known as Prussian blue.

$$Fe^{2+}(aq) + Fe(CN)_6^{3-}(aq) \rightarrow Prussian blue$$
 Equation 3

Prussian blue and Turnbull's blue have been shown by X-ray crystallography to be the same compound. It is a mixed iron(II)– iron(III) compound that is best described as "ferric ferrocyanide," with the formula $Fe_4[Fe(CN)_6]_3$. The structure consists of a cubic array of iron ions with cyanide ions along the cube edges and water molecules in the cubes.

The general principle involved in making UV-sensitive paper is similar to that used in the photographic process. Instead of iron salts, black and white photography uses silver salts coated on cellulose acetate paper. Silver is easily and quickly reduced from Ag⁺ to Ag(s) when exposed to light. When film is exposed to light, the areas exposed to the most light form the most silver atoms and thus appear black on the negative. Areas that have not been exposed to light appear white on the negative because no silver ions have been reduced. The fixing and washing processes remove the excess reactants, preventing further darkening of the negative. Producing a black and white photograph from the negative involves shining light through the negative onto a fresh sheet of photosensitive paper.

Questions for Class Discussion

- 1. Why is it best to store iron(III) oxalate and other photographic chemicals in brown or dark-colored bottles? (*The brown bottles help filter out UV light, extending the life of the chemical.*)
- 2. Why does the lab work on overcast days as well as on clear days? (Ultraviolet radiation can and does penetrate the clouds.)
- 3. Explain why slow deterioration of poorly rinsed blueprints or photographs may result. (Unreacted chemicals left on the paper will react with the light, ruining the image on the print.)
- 4. Where is the best place for storing photographs? What would you predict sunlight would do to photographs? Why? (Photographs are best stored in a dark area out of the sunlight. Sunlight would gradually lighten the image causing it to fade.)
- 5. Why doesn't typical classroom lighting develop the prints? (Higher energy ultraviolet rays, which are not present in fluorescent or incandescent light, are needed to develop the print.)

Materials for UV-Sensitive Paper are available from Flinn Scientific, Inc.

Catalog No.	Description
AP6155	Making UV—Sensitive Paper Student Laboratory Kit
F0047	Iron (III) Nitrate Solution, 0.1 M, 500 mL
Q0005	Oxalic Acid, 100 g
P0165	Potassium Ferricyanide Solution, 0.1 M, 500 mL

Consult your Flinn Scientific Catalog/Reference Manual for current prices.

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