CALCIUM - PHYTATE TREATMENT AGENT

General Phytic acid, or *myo*-inositol hexakisphosphate (IP6) is a strong chelator (complexing agent) of important minerals such as calcium, magnesium, iron and zinc. In nature, it functions as storage for phosphorus in plants, especially in the hulls of nuts and seeds. Phytic acid can exchange its 12 protons against metal ions. Phytic acid is a strong acid and therefore should not be used for treating ink corroded artefacts as such. Consequently it is first transferred into calcium phytate, a salt of phytic acid. The calcium phytate prepared in this recipe, contains on average 2.5 calcium ions and 7 protons per phytate structure. During application of the aqueous calcium phytate solution to ink corroded artefacts, the calcium ions are exchanged for "free", harmful iron(II) and iron(III) ions. The reaction products are iron-phytate complexes. They are special, since they do not catalyse the oxidative degradation of cellulose. During this process, the iron-gall ink complex is not destroyed.

Reaction with other transition metals Calcium phytate also can exchange calcium ions against other transition metals, e.g. copper. Copper phytates however do not block the catalytic activity and therefore remain to be harmful. As copper phytates are soluble, an aqueous treatment will remove them.

Phytic acid concentration When purchasing phytic acid, the concentration of the solution should be known (usually either 40 or 50 w.%). If the concentration is unknown, please note the charge number of the product and contact the supplier before ordering. Usually, the supplier will be able to tell the concentration of the phytic acid solution (w.%). The amount of phytic acid that is required to produce calcium phytate is depending on the concentration of phytic acid (see table 1). The final concentration is 1.75 mmol/l calcium phytate, equivalent to 0.116% phytic acid.

Concentration of phytic acid solution	Phytic acid solution	CaCO3	Demin. water
20 %	5,76 g	0.44 g	c. 1 l
30 %	3,84 g	0.44 g	c. 1 l
40 %	2.88 g	0.44 g	c. 1 l
45 %	2,56 g	0.44 g	c. 1 l
50 %	2.30 g	0.44 g	c. 1 l

Table 1: Necessary quantity of phytic acid, calcium carbonate and demineralised water to produce 1 Liter of calcium phytate.

Adjusting the pH of calcium phytate A calcium phytate solution prepared according to this recipe is too acid to be applied to artefacts. Consequently, the solution needs to be neutralized. Neutralization with calcium carbonate and calcium hydroxide would cause the precipitation of tri- and tetra calcium phytate, leaving insufficient phytate in solution to complex iron(II) and iron(III) ions. Therefore, the solution needs to be neutralized with ammonia, until a pH between pH 5.0 and pH 5.8 is reached.

Addition of ethanol or iso-propanol Strong ink corrosion reduces the wettability of the paper. To improve the penetration of the calcium phytate solution, ethanol or iso-propanol can be added. Ethanol can be mixed with the phytate solution up to a volume ratio of 1:1.

Combination with deacidification Treatment with calcium phytate does not stop the acid-catalysed hydrolysis of cellulose, the other process responsible for ink corrosion. Therefore, the treatment with aqueous calcium phytate always has to be followed by a subsequent deacidification. As iron-gall ink seems to be unstable above pH = 9, we can not recommend aqueous magnesium-bicarbonate solutions for deacidification. They render too alkaline values to the ink and paper. An aqueous calcium-bicarbonate solution, saturated with carbon dioxide is preferred. When treating with this solution, ink and paper never reach values above pH = 8.5. Unfortunately, a combination of complexation and deacidification into one step is not possible.

Shelf life

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Phytic acid solution: A concentrated phytic acid solution (40-50 w.%) has a brown colour which gradually darkens upon storage over years. To prevent this, it is advised either to dilute this solution with distilled water to a (known) concentration under 20 w.%, or to store the concentrated solution in a refrigerator at a temperature below 10ºC.
Calcium phytate solution: Acid to neutral pH-levels might stimulate the growth of micro organisms in calcium phytate solutions. According to our experiences, some solutions developed mold already after a few days, some remained stable for months, depending on the sterility of the container used for storage. We suggest to always apply fresh solutions. The addition of ethanol to the solution prevents mold formation.

Safety precautions The general safety precautions for the storage and handling of acids and bases are valid for the concentrated phytic acid solution, resp. concentrated ammonium hydroxide solution.

Suppliers

Reagent	Firm	Address
Phytic acid, 40 wt% aq. solution	Sigma-Aldrich Cy, Ltd	See: www.sigma-aldrich.com
Calcium carbonate, 99+%, A.C.S. Reagent	Sigma-Aldrich Cy, Ltd	See: www.sigma-aldrich.com
Ammonium hydroxide solution, A.C.S. reagent, 28-30% NH_3	Sigma-Aldrich Cy, Ltd	See: www.sigma-aldrich.com
Ethanol 96%, A.C.S. reagent	Sigma-Aldrich Cy, Ltd	See: www.sigma-aldrich.com

Further reading

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Ink Corrosion: Comparison of Currently Used Aqueous Treatments for Paper Objects, In: Preprints der IADA, 9th IADA Congress, Copenhagen, August 16-21, 1999, Internationale Arbeitsgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren, Copenhagen (1999): 121-129.

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PREPARATION OF 5 LITRES OF A CALCIUM - PHYTATE TREATMENT AGENT

Chemicals

- Phytic Acid solution, 40 *or* 50%
- Calcium Carbonate powder ($CaCO_3$)
- Demineralised or distilled water (will be referred to as demineralised water in the text)
- Aqueous solution of Ammonia (Ammonium Hydroxide NH_4OH)
- pH-test strips (pH 0-6)

Materials and equipment

- laboratory balance (readability at least 0.1 g)
- glass pipette
- 1 L glass beaker
- 250 ml glass beaker
- 50 ml glass beaker
- 2 x 25 ml glass beakers
- metal spatula or spoon
- glass rod
- 5 L storage container for the Calcium Phytate solution
- a tray for immersion treatment that can contain 5L
- label

Procedure

- **Weighing of 14.4 g of Phytic acid solution when using the 40% solution *or* 11.6 g when using the 50% solution**

- Pour some of the Phytic acid (ca. 15 ml) from the original container into a 25 ml glass beaker
- Take a 250 ml glass beaker as weighing vessel
- Check if the balance pan is clean and dry
- Place the 250 ml glass beaker on the laboratory balance
- Tare the balance
- Transfer the phytic acid from the 25 ml glass beaker into the 250 ml glass beaker, using a glass pipette, until the required amount is reached
- Dispose of excess phytic acid from the 25 ml beaker into a special waste container for acids

- **Weighing of 2.2 g of Calcium Carbonate powder**

- Take a 25 ml glass beaker as weighing vessel
- Check if the balance pan is clean and dry
- Place the 25 ml beaker on the laboratory balance
- Tare the balance
- Add Calcium Carbonate powder into the 25 ml glass beaker using a spatula until 2.2 g are reached

- **Measuring the aqueous solution of Ammonia (without balance)**

- Take a 50 ml glass beaker
- Pour ca. 40 ml of Ammonium Hydroxide (1.25%) into the glass beaker
- NB: When higher concentrations of Ammonium Hydroxide are used, less solution will be required

- **Dissolving of Calcium Carbonate powder in Phytic Acid**

- Take small amounts of Calcium Carbonate powder with a spatula
- Add it to the Phytic Acid in the 250 ml glass beaker
- Stir with a glass rod, so that the two components mix, foam develops due to formation of CO_2
- Continue stirring while adding small amounts of Calcium Carbonate powder, each time add only a little amount to prevent formation of lumps
- Stir until all of the Calcium Carbonate is dissolved. The resulting Calcium Phytate is highly concentrated and is pinkish-brown coloured with a foamy consistency

- **Dissolving Calcium Phytate with water**

- Pour a small quantity of demineralised water into the 250 ml glass beaker with the Calcium Phytate
- Stir with the glass rod
- Add more water and stir
- Pour this solution into a 1L glass beaker
- Clean the 250 ml glass beaker by adding water and pouring the resulting solution into the 1L glass beaker until no residues are left, to ensure that all of the Calcium Phytate solution is transferred
- Fill the glass beaker up to 1 L with demineralised or distilled water

- **Preparing the immersion tray with the Calcium Phytate solution**

- Pour the content of the 1L beaker into the tray that will be used for the immersion treatment
- Add another 3.5 L of demineralised water to the tray
- Slowly add some of the Ammonia solution with a glass pipette, remember that not all of the Ammonia needs to be used ! Be aware that once too much Ammonia has been added the Calcium Phytate solution can not be used anymore
- Stir the solution within the tray with a glass rod
- Check the pH-value of the solution using pH-indicator strips
- Add Ammonia until the pH reached a value of ca. 5.5. The liquid will become slightly milky, indicating that the a suspension has formed due to the precipitation of some Calcium Phytate
- Add the remaining demineralised water (should be less than 0.5 L)
- Label the tray

When the solution is not to be used on the same day, transfer the solution to a container for storage.

- **Transfer solution to a storage bottle**

- Pour the solution through a funnel into the storage bottle
- Label the storage bottle (Calcium Phytate solution + date)

- **Clean all equipment**

- Clean up the balance and the area around the balance
- Pour the leftover of the Ammonia into the sink
- Rinse the beakers, glass rod, funnel, pipette and spoon or spatula in demineralised water and let them dry

PREPARATION OF 5 LITRES OF A CALCIUM - PHYTATE TREATMENT AGENT

Weigh, into a 250 ml glass beaker, the necessary amount of Phytic Acid using a glass pipette

Weigh the necessary amount of Calcium Carbonate into a 25 ml glass beaker

Add a small amount of the Calcium Carbonate to the Phytic Acid

Stir with a glass rod. Foam develops due to the formation of CO_2.

Continue to add small amounts of Calcium Carbonate.

While stirring, Calcium Carbonate dissolves in the Phytic Acid.

After adding half of the required amount of Calcium Carbonate.

Add more Calcium Carbonate, stir, add more Calcium Carbonate, stir, …

… until all Ca-Carbonate is added.

Stir, until all Calcium Carbonate is dissolved in the Phytic Acid.

Slowly add some demineralised water to the Calcium Phytate “foam”, stir.

Continue to dilute the Calcium Phytate with water.

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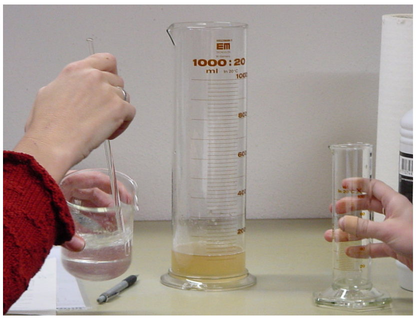
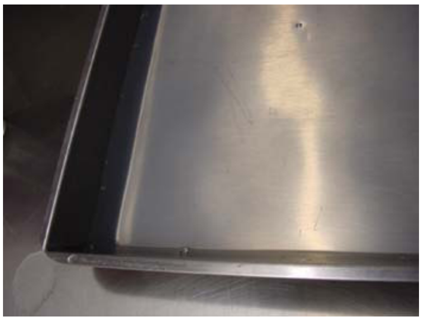
Pour the solution into a 1L beaker


Clean the 250 ml beaker with demineralised water and add this to the 1L beaker. Add water until the 1 L mark is reached


Add the prepared 1 L of calcium phytate solution to the tray


Add 3.5 L of demineralised water


The solution is clear and colourless


Add some Ammonium Hydroxide using a glass pipette, stir


Measure the pH-value using indicator strips


Add more Ammonium Hydroxide and check the pH


The final pH-value should be 5.5-5.8


Add remaining water


Calcium phytate is ready

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