INVESTIGATION INTO THE REDUCTION OF FOXING STAINS IN PAPER

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Advisors: Richard Wolbers and Joan Irving

Winterthur/University of Delaware Program in Art Conservation

ANAGPIC 2018, Queen's University

THE OBJECTS

BT Recto, normal illumination

Description

- *Le Ballon* (left) and *Le Pigeon* (right)
- Chine collé lithographs on wove paper
- 23.5 x 16.3 inches

Provenance

- 1870 - 1871
- Lithographs by Émile Vernier
- After paintings by Pierre Puvis de Chavannes
- Published by Lemercier & Cie, Paris

S.O.S.!

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- Pervasive foxing
- Risk of delamination

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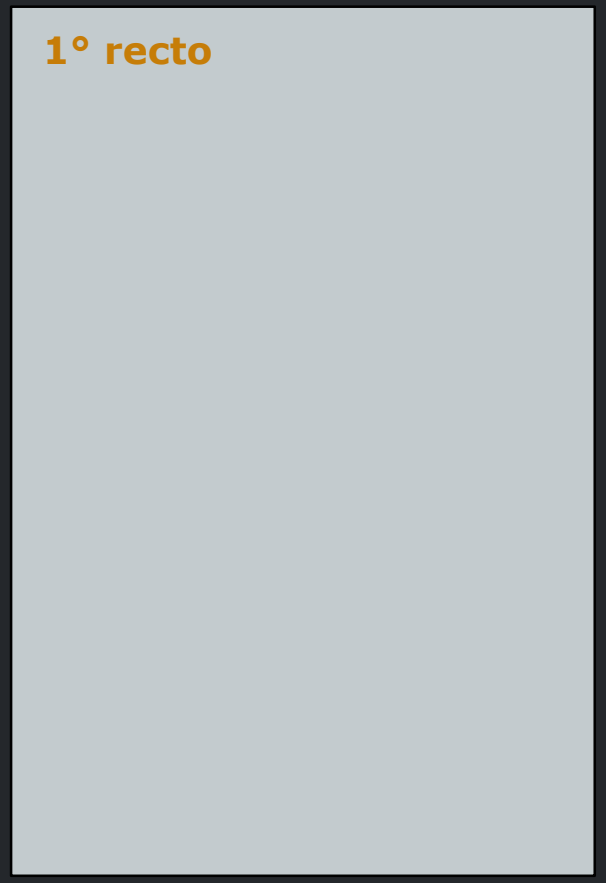
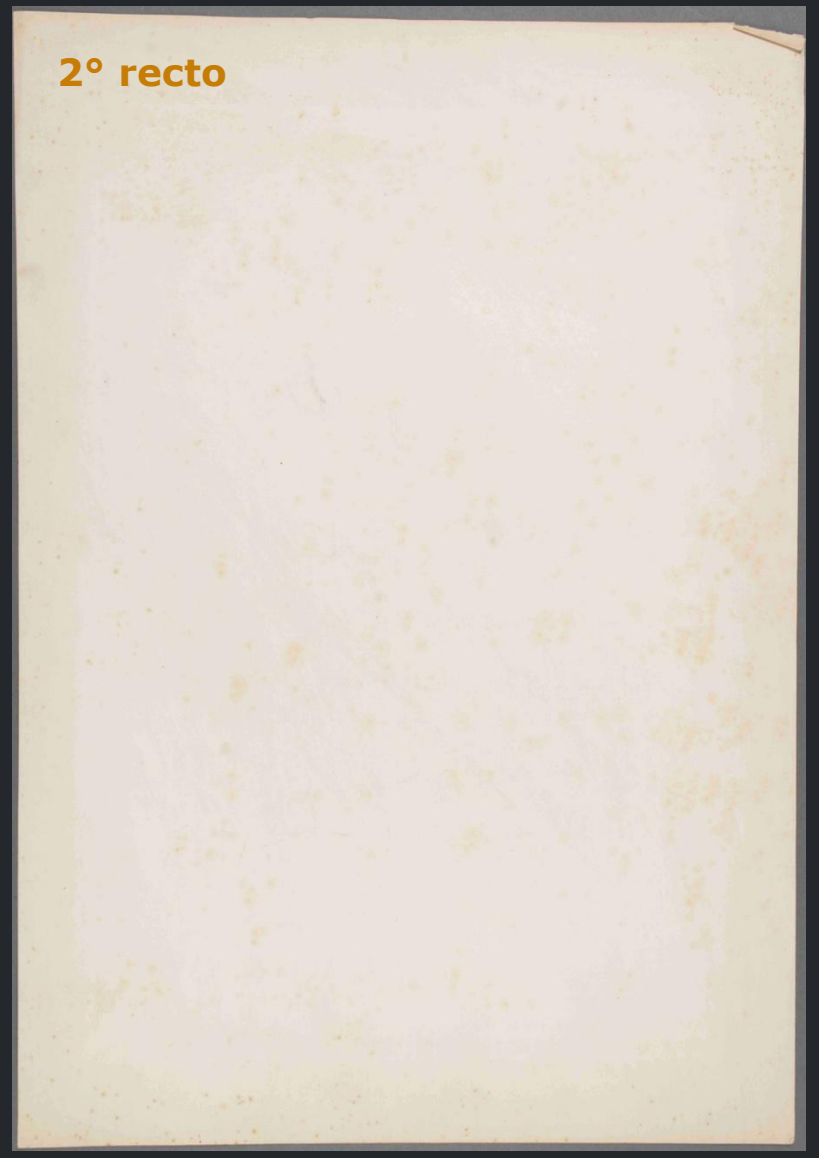
CHINE COLLÉ

Technique:

- Damp 2° support

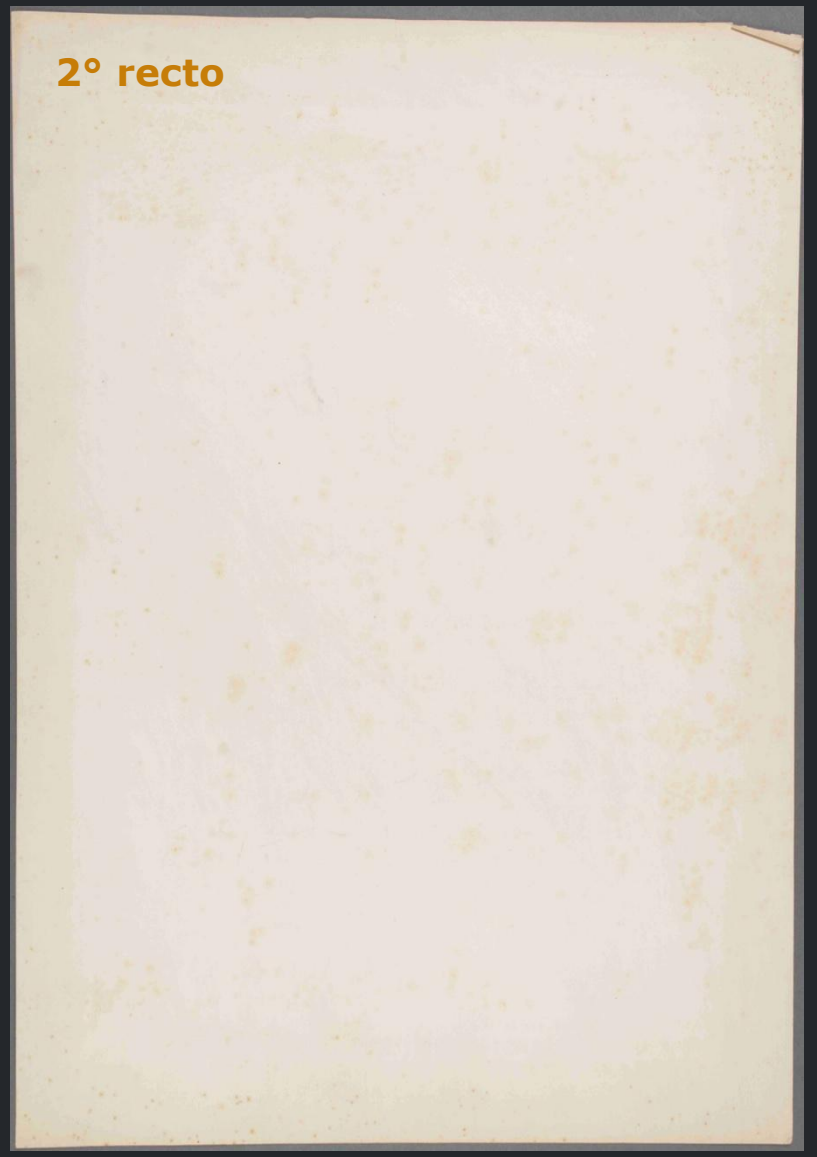




CHINE COLLÉ

Technique:

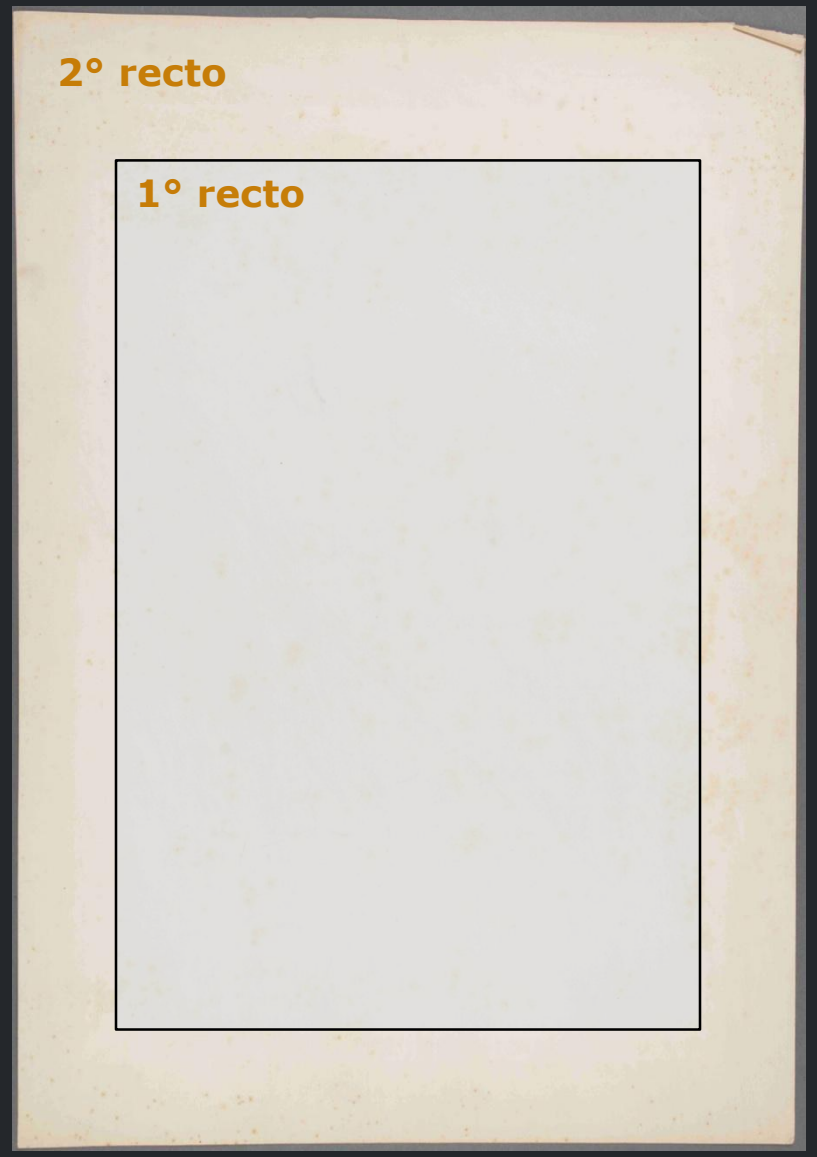
- Damp 2° support
- Pasted verso of 1° support



CHINE COLLÉ

Technique:

- Damp 2° support
- Pasted verso of 1° support
- 1° support placed on 2°



CHINE COLLÉ

Technique:

- Damp 2° support
- Pasted verso of 1° support
- 1° support placed on 2°
- Plate printed on 1° as objects are pressed together

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Risk of delamination in aqueous treatment due to water-soluble adhesive

THE ARTISTS

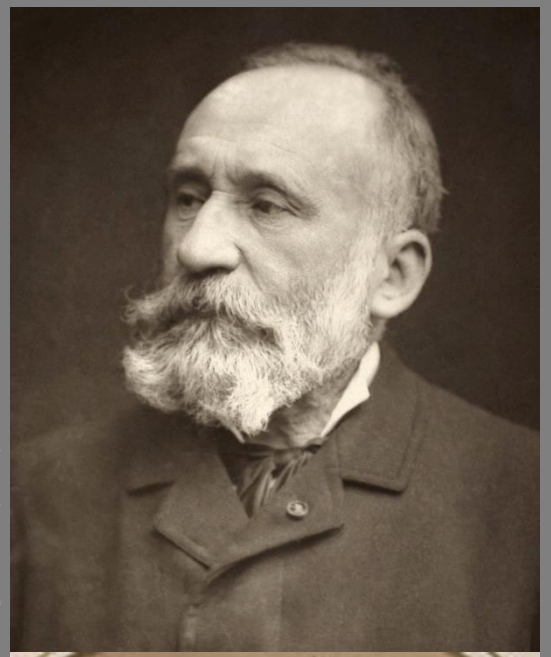
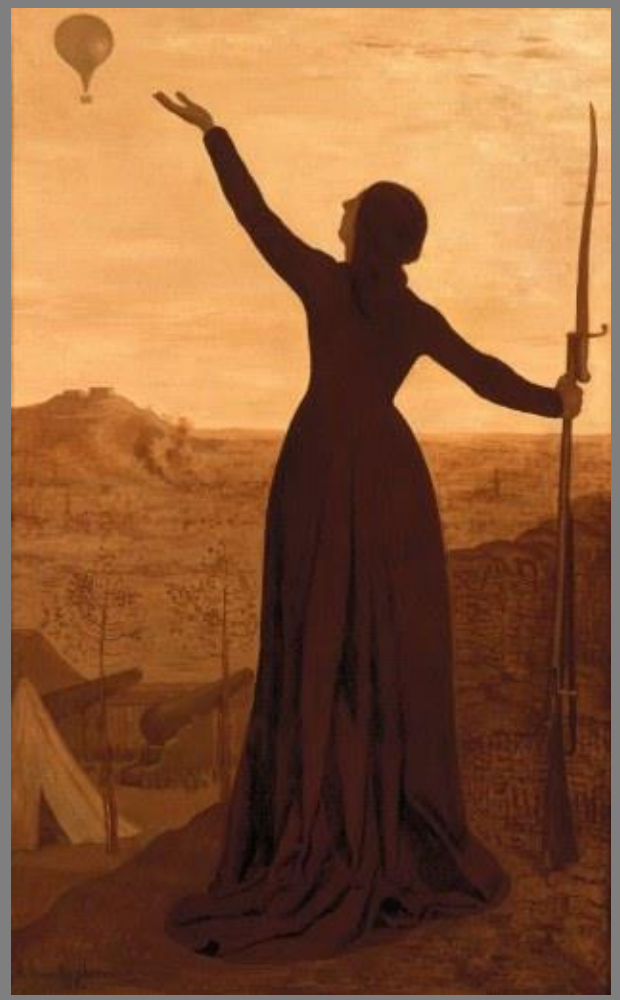


Image courtesy Wikipediaa

Pierre Puvis de Chavannes
1824 - 1898

http://www.peintres-ecouen.com/emile-louis-vernier-e/a

Émile Vernier
1829 - 1887

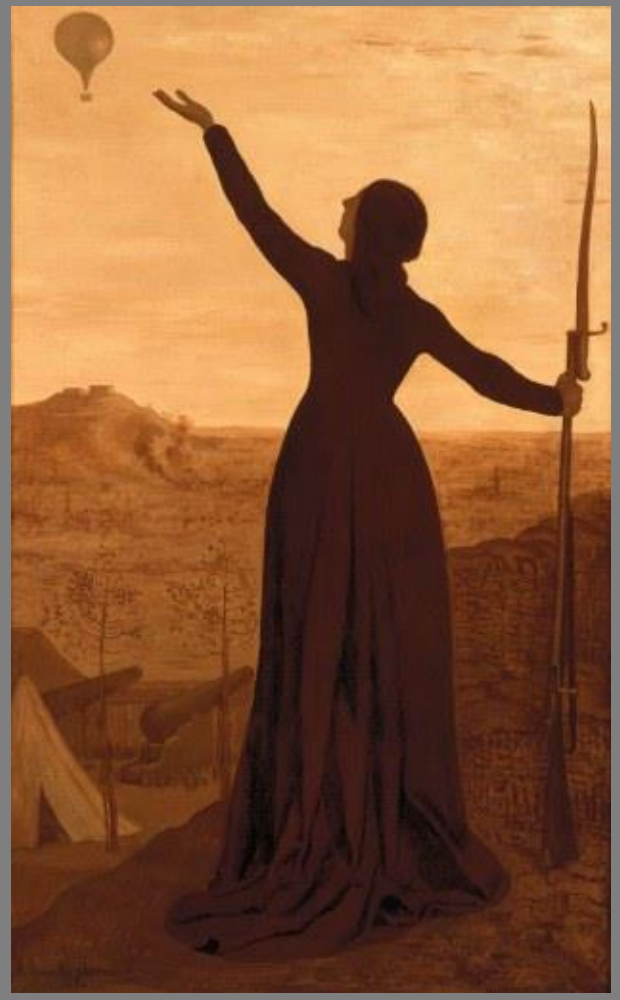


Images courtesy L'Histoire Pa L'Image

THE SETTING

Franco-Prussian War

- 19 July 1870 – 10 May 1871
- Paris under siege
- Messages carried by balloons and pigeons
- Images to uplift Parisian people
- Immediately reproduced for distribution

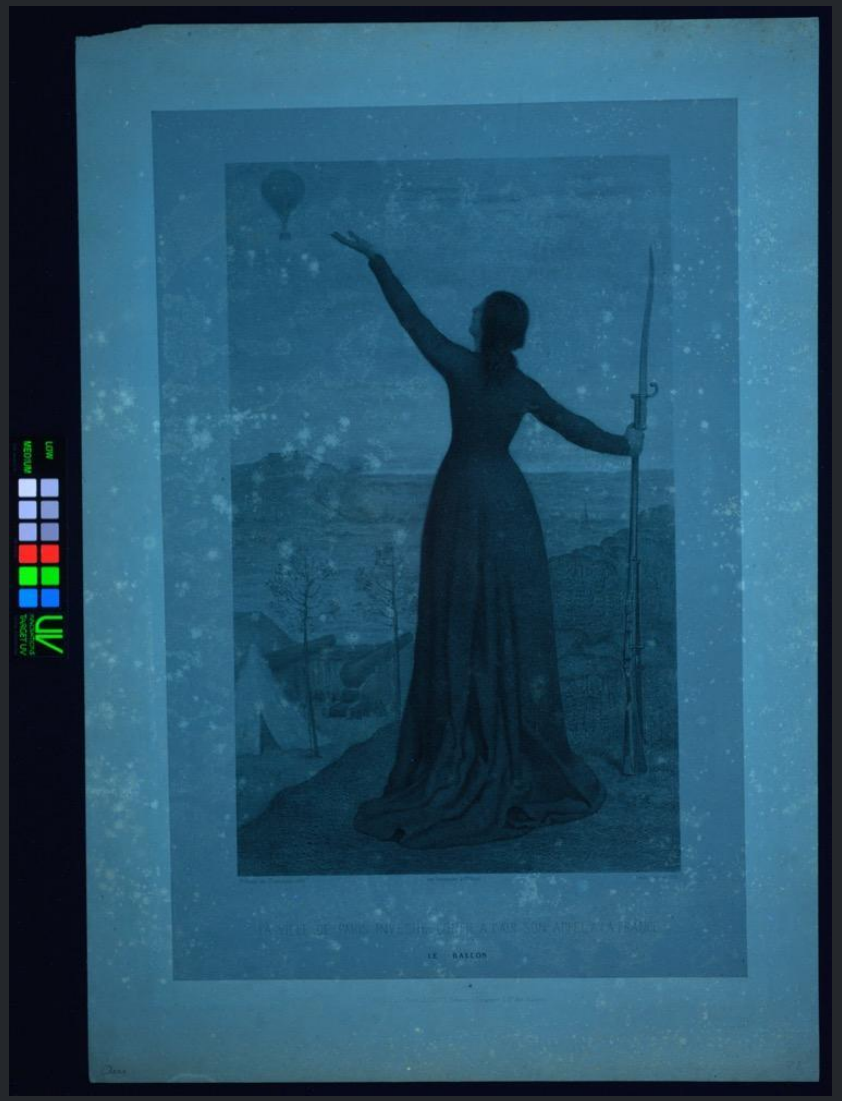


Images courtesy L'Histoire Pa L'Image

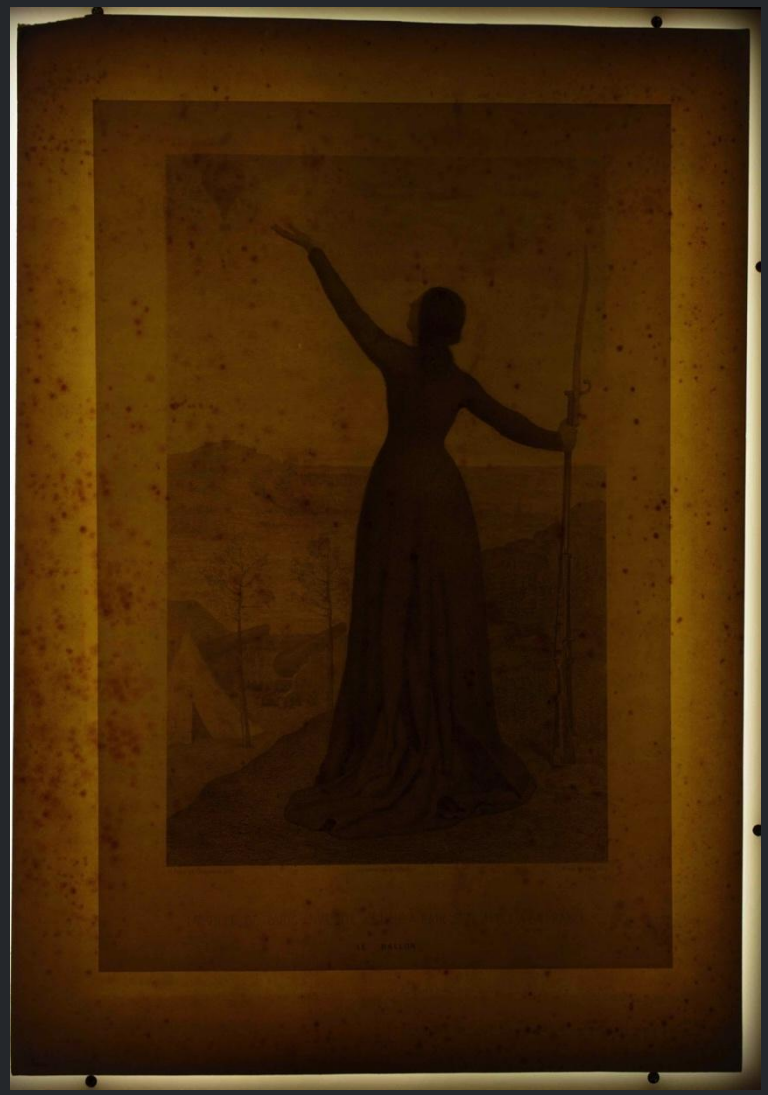
LE BALLON

BT Recto, normal illumination

BT Recto, UV illumination



BT Recto, transmitted illumination



LE PIGEON

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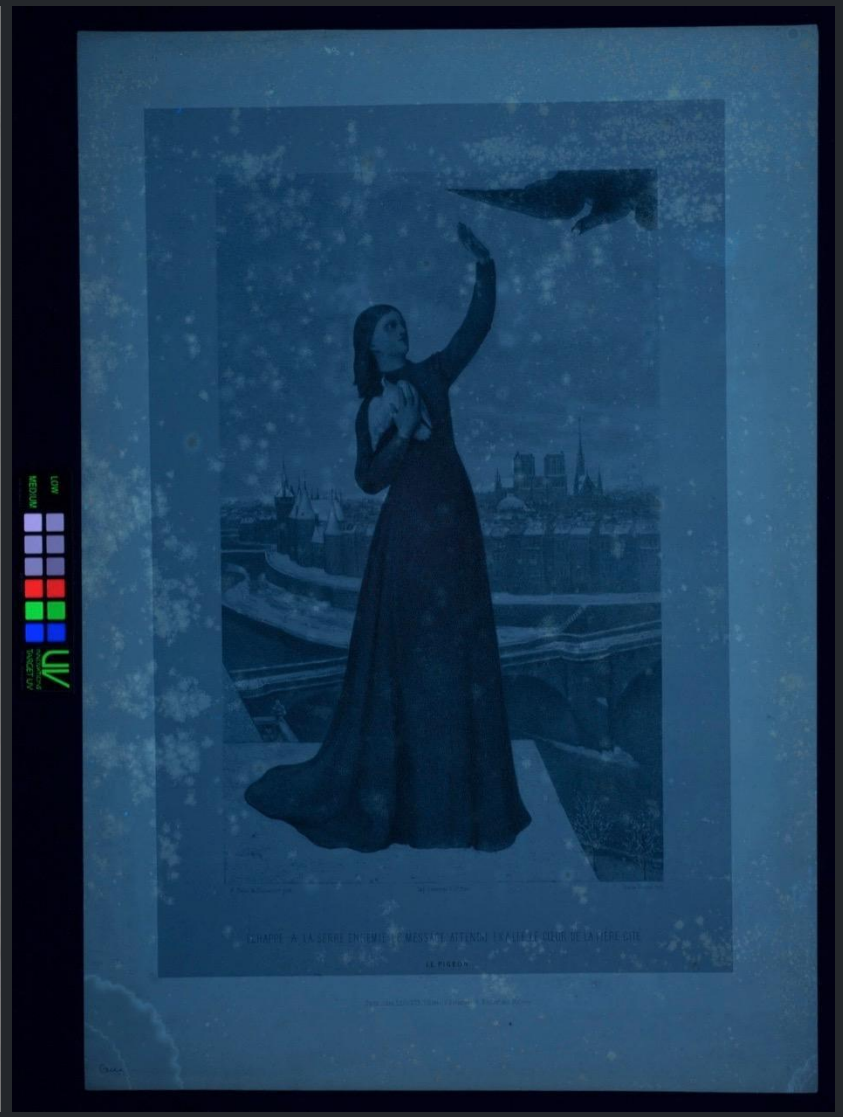

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WHAT IS FOXING?

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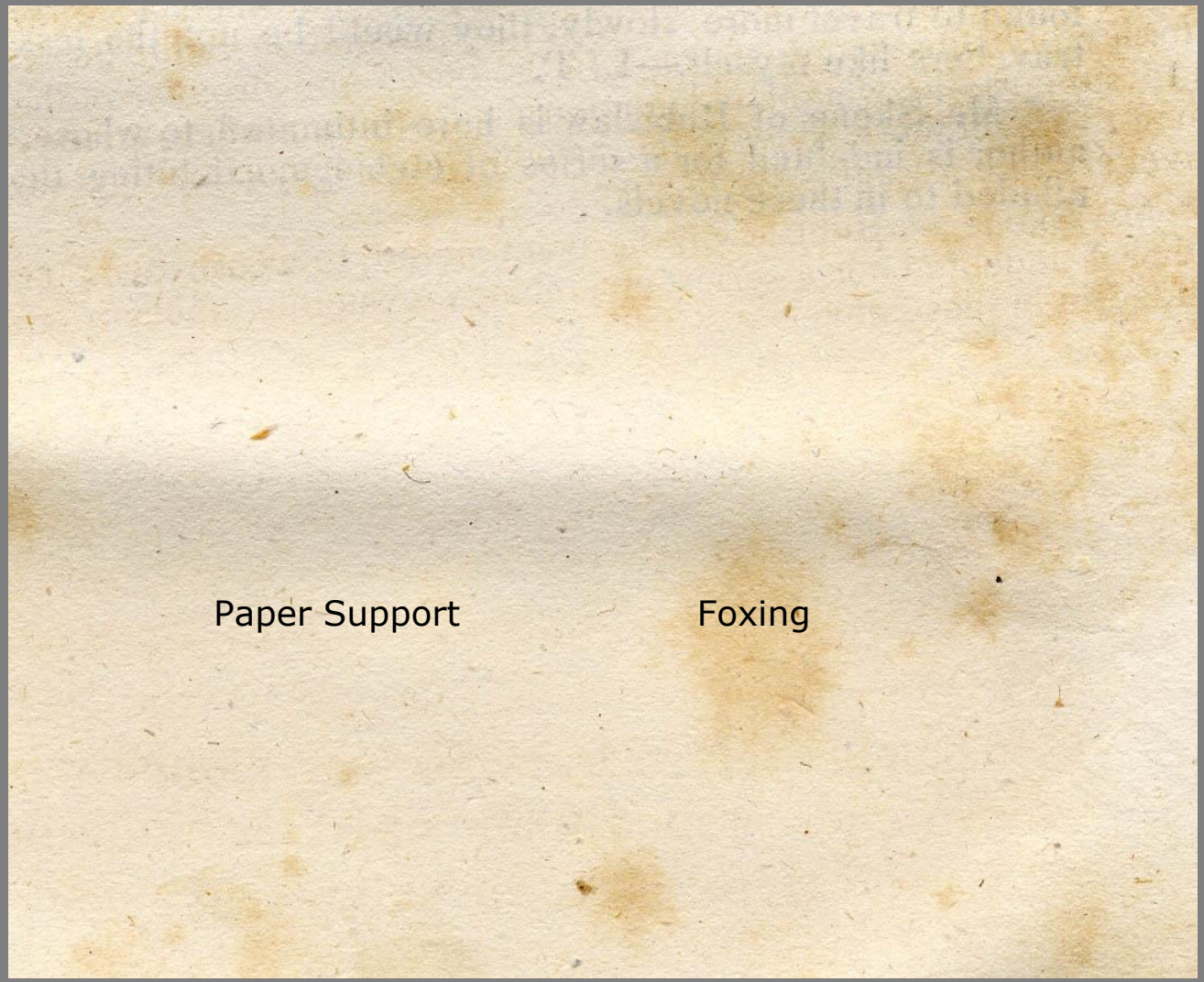


Image courtesy of Joan Irving

Detail: Foxing, normal illumination

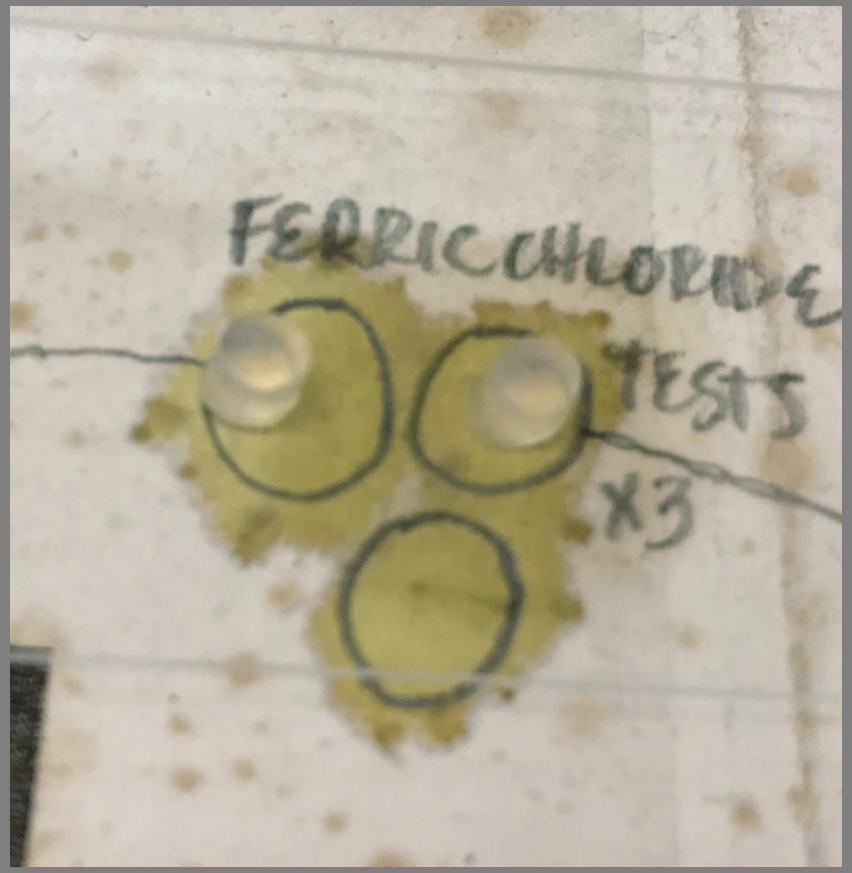
Detail: Foxing, long-wave UV illumination

ART + SCIENCE

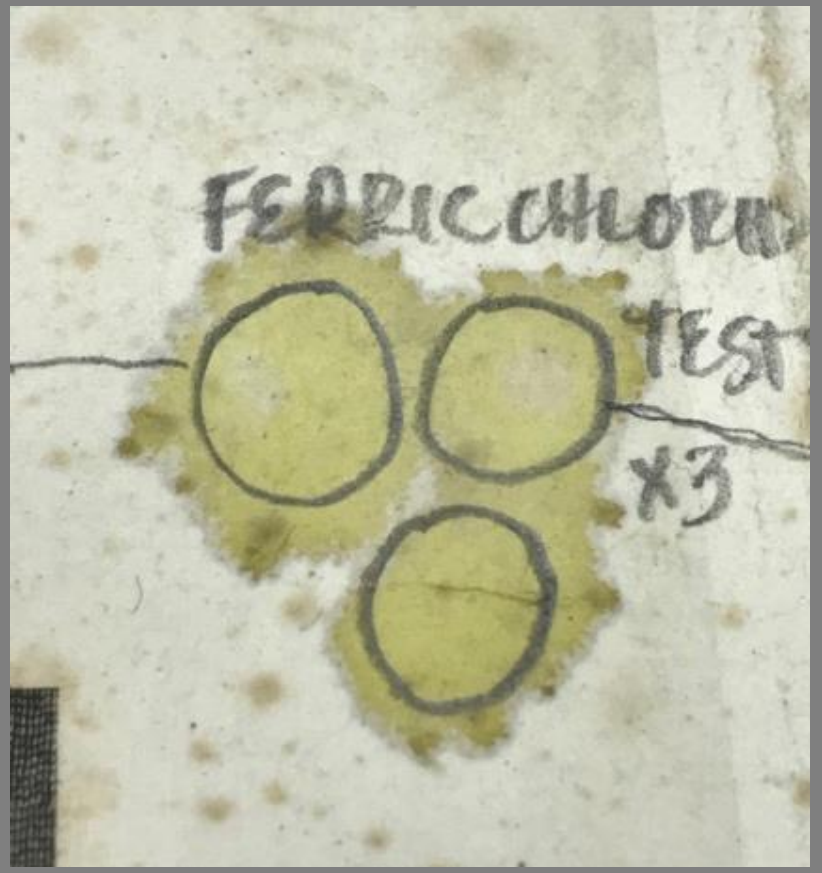
Treatments for 2nd year Paper Conservation

Aqueous Cleaning Methods Seminar with Richard Wolbers

AQUEOUS CLEANING SEMINAR – PRELIMINARY TESTING



With agarose plugs



After

First experiment on expendable foxed print:

- Drops of ferric chloride (iron (III) form) were applied to sample
- Agarose gel plugs containing ascorbic acid and EDTA were placed on the ferric chloride spots
- The gel was effective: proves iron (III) can be reduced and chelated

PRELIMINARY TESTING

Other expendable examples of foxed prints were treated using various reducing agents, chelators, and enzymes

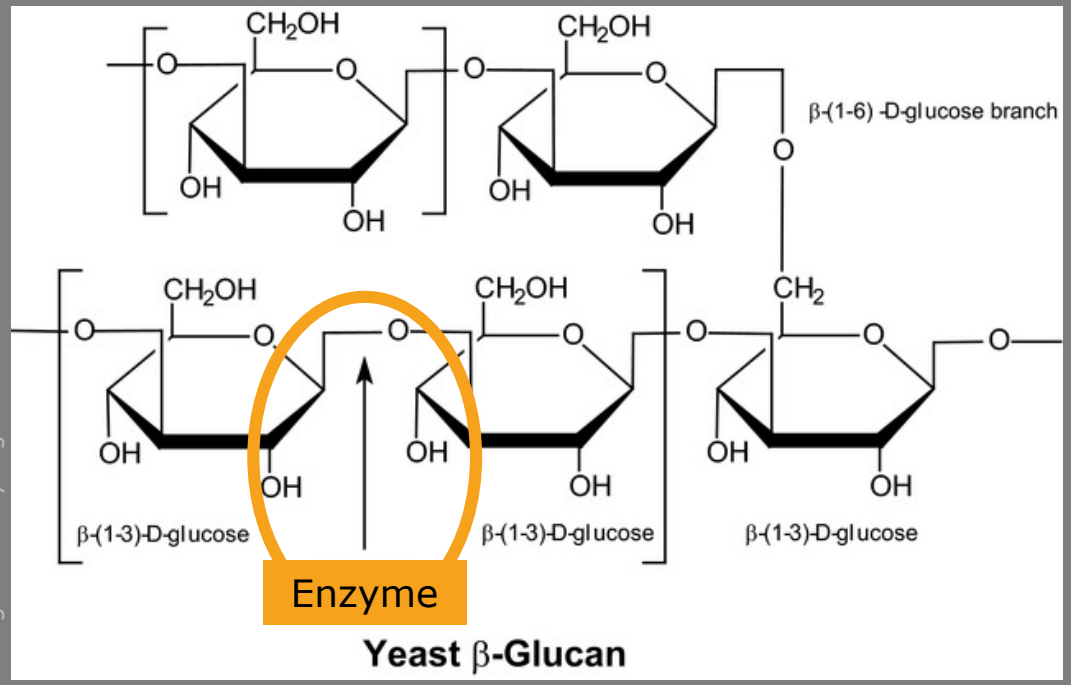


Image courtesy Sigma Aldrich

Enzyme specificity

- Enzyme hydrolyzes poly-β(1→3)-glucose
- Lysing enzyme blend contains β-glucanase, cellulase, protease, and chitinase activities; industrial quality
- Lyticase is more targeted; premium quality

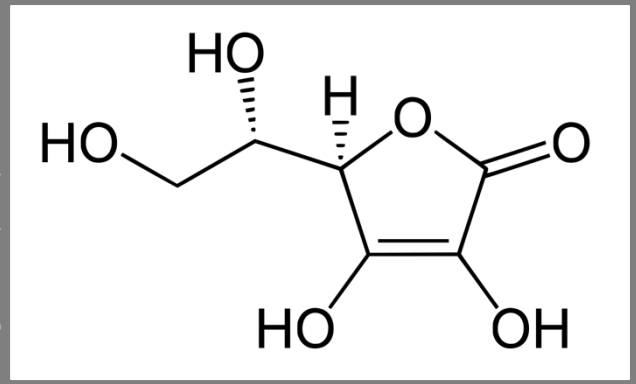


Image courtesy Wikipedia

Ascorbic acid

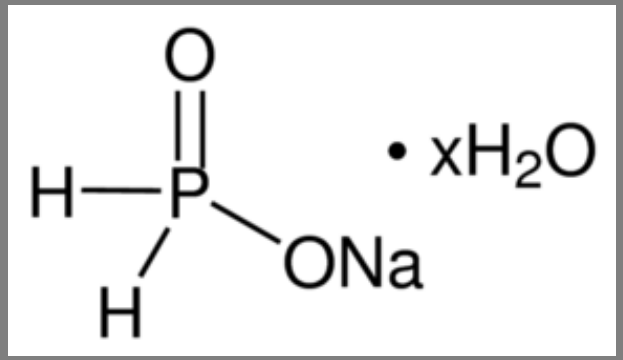


Image courtesy Sigma Aldrich

Sodium hypophosphite

PRELIMINARY TESTING

Other expendable examples of foxed prints were treated using various reducing agents, chelators, and enzymes

Richard Wolbers and Madison Brockman pour in the enzyme solution

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The expendable examples are:

1. placed into a DI bath containing the reducing agent and chelator,

Richard Wolbers and Madison Brockman pour in the enzyme solution

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1. placed into a DI bath containing the reducing agent and chelator,
2. rinsed in DI water,

Richard Wolbers and Madison Brockman pour in the enzyme solution

PRELIMINARY TESTING

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The expendable examples are:

1. placed into a DI bath containing the reducing agent and chelator,
2. rinsed in DI water,
3. then placed in a DI bath containing the enzyme.

Richard Wolbers and Madison Brockman pour in the enzyme solution

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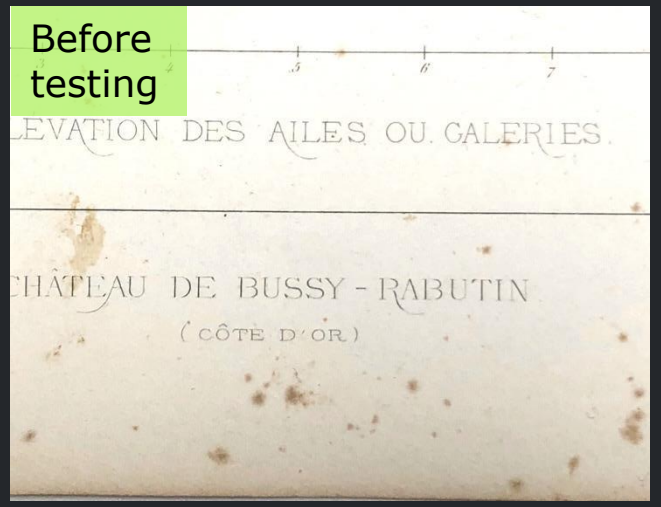

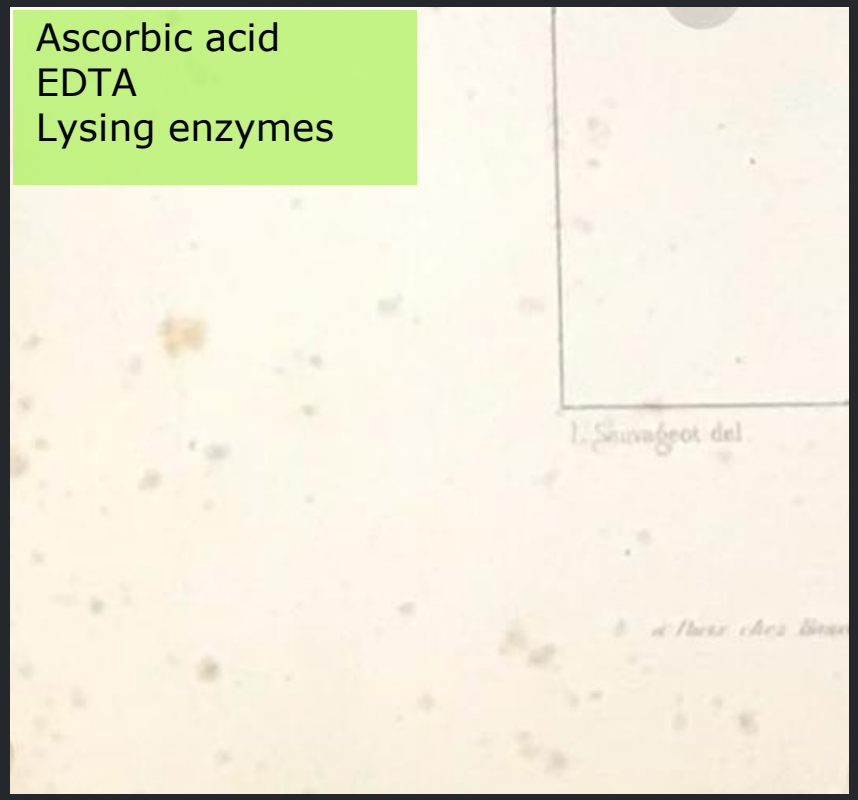

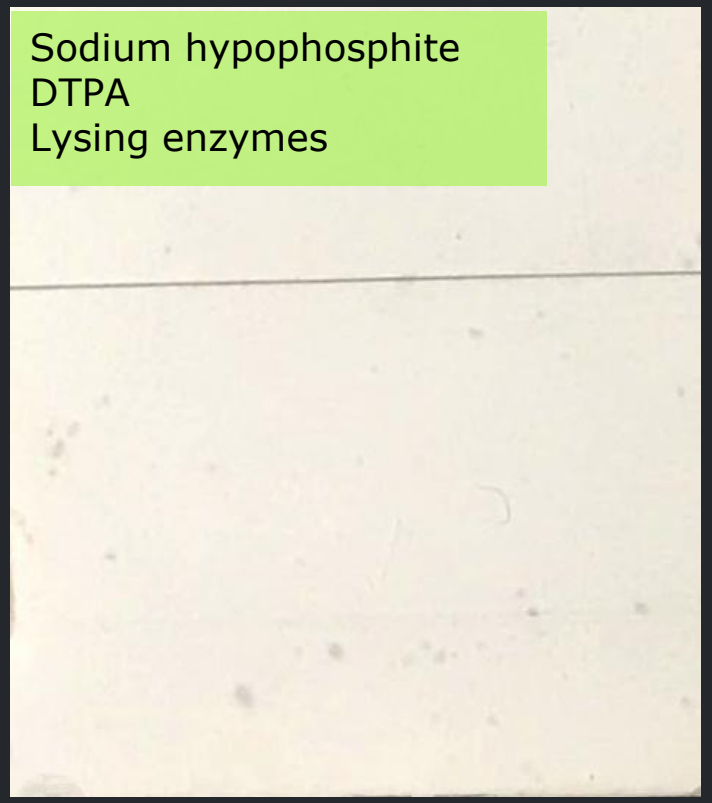

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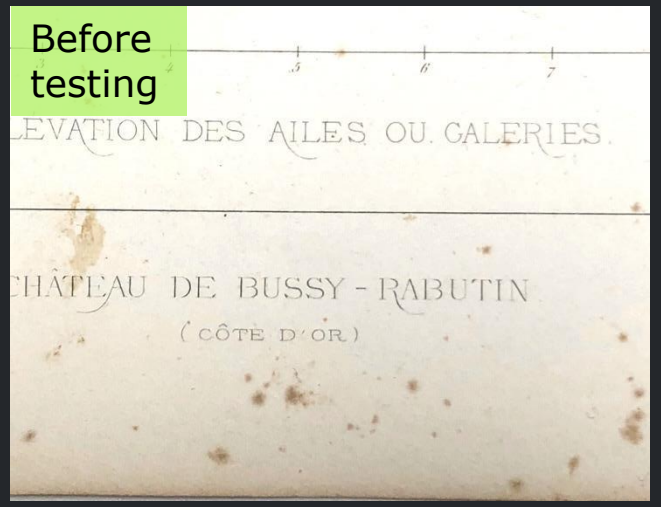

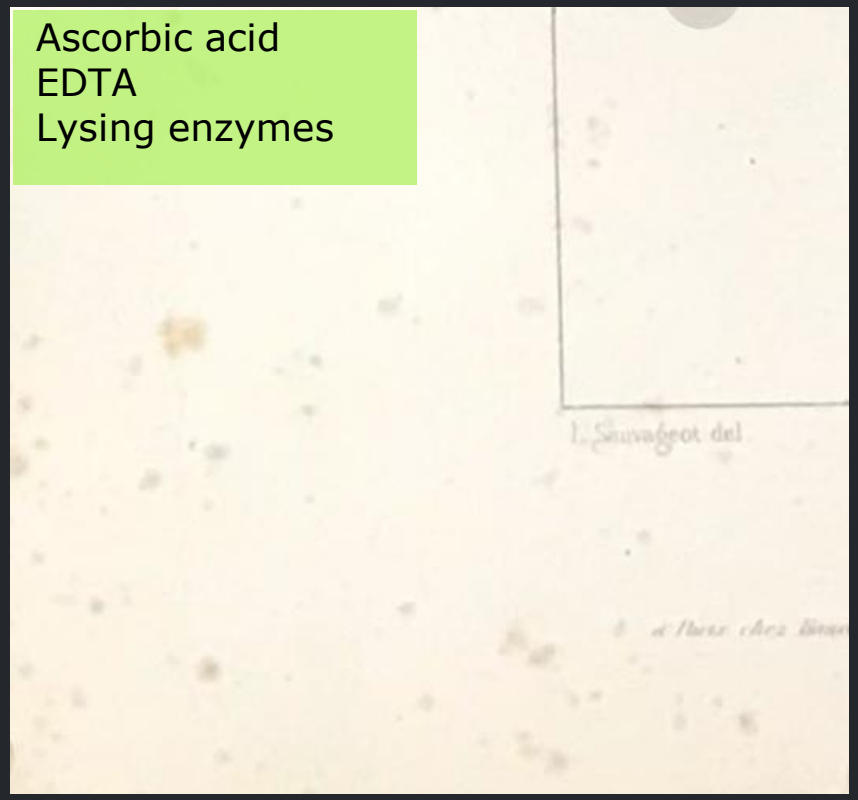

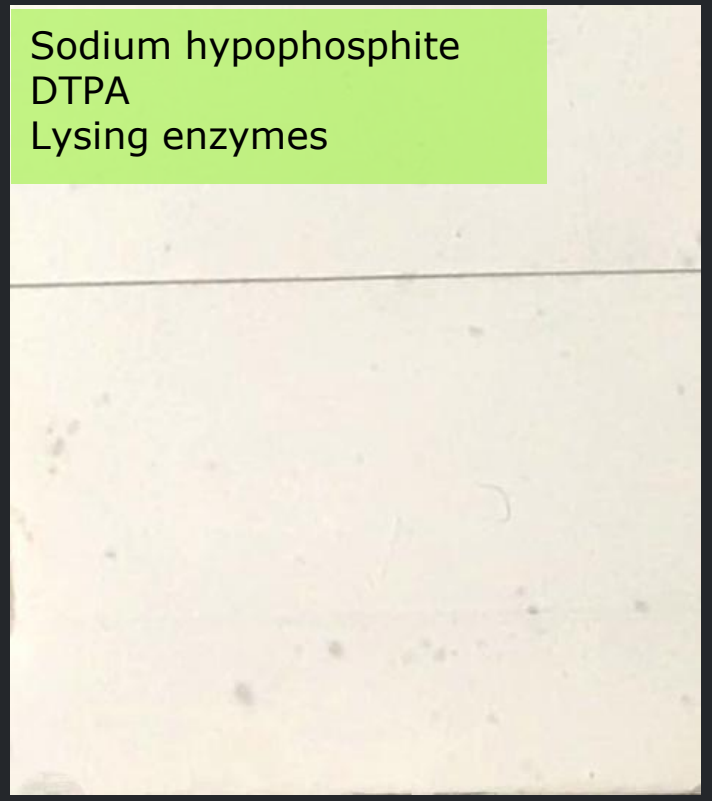

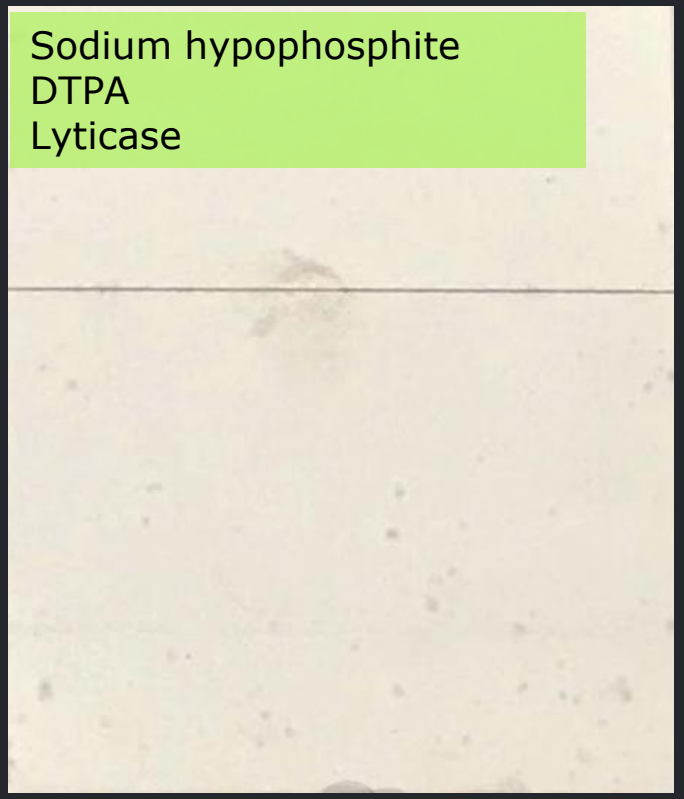

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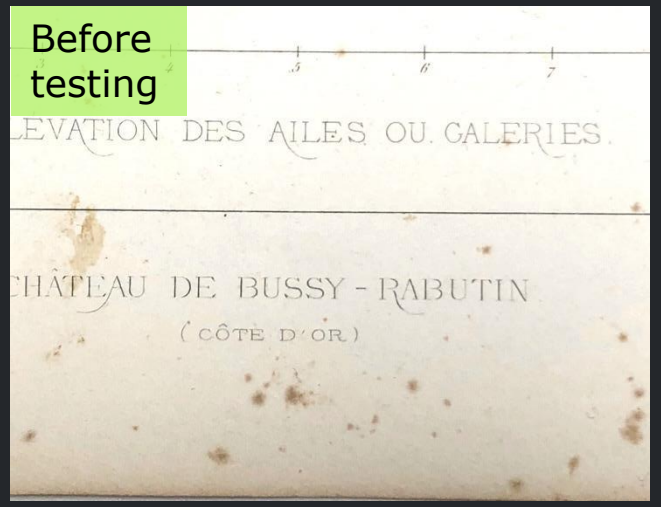
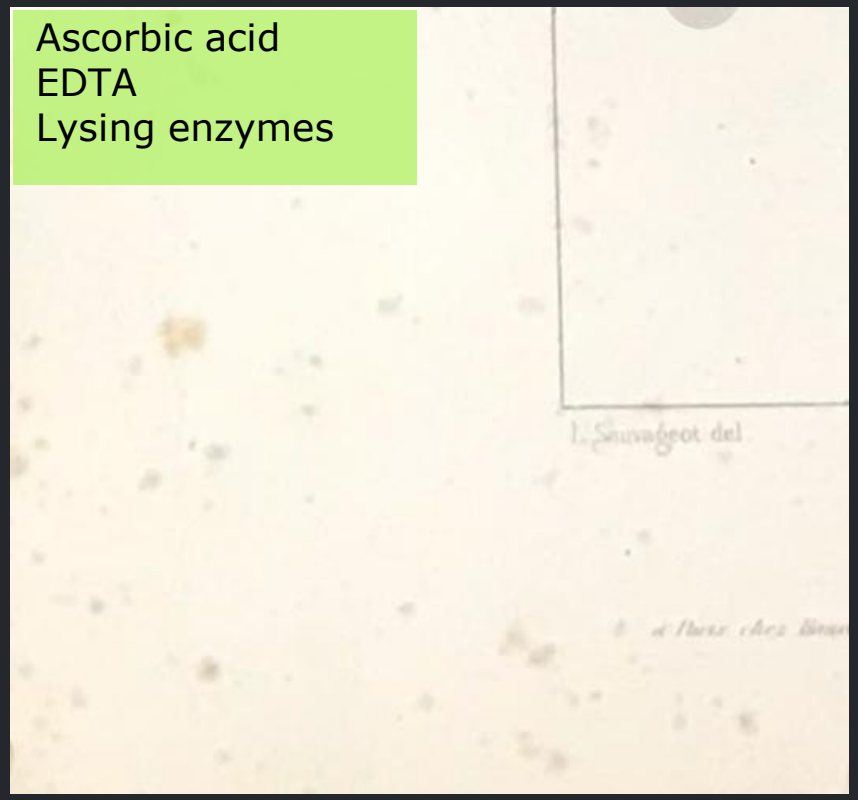
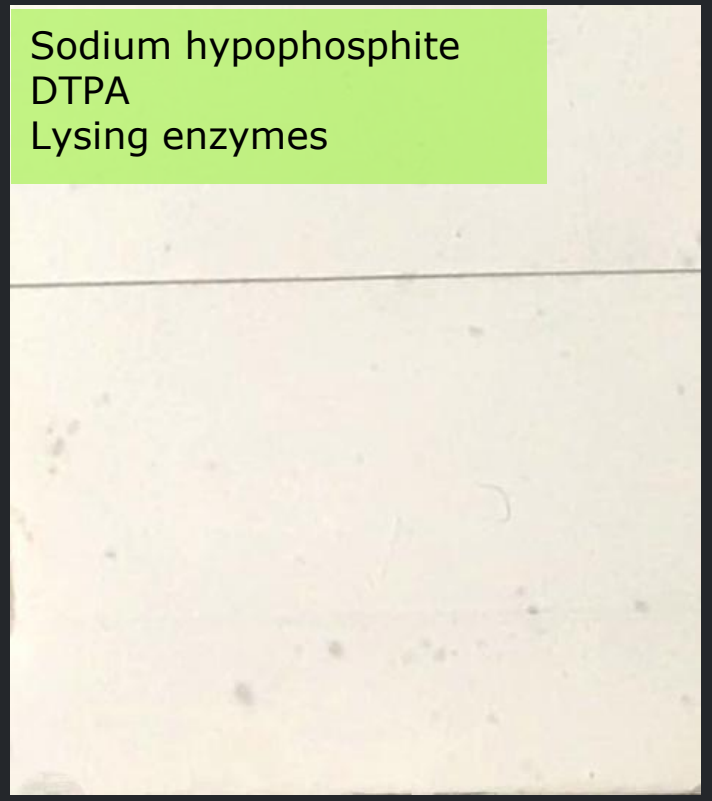
Before testing



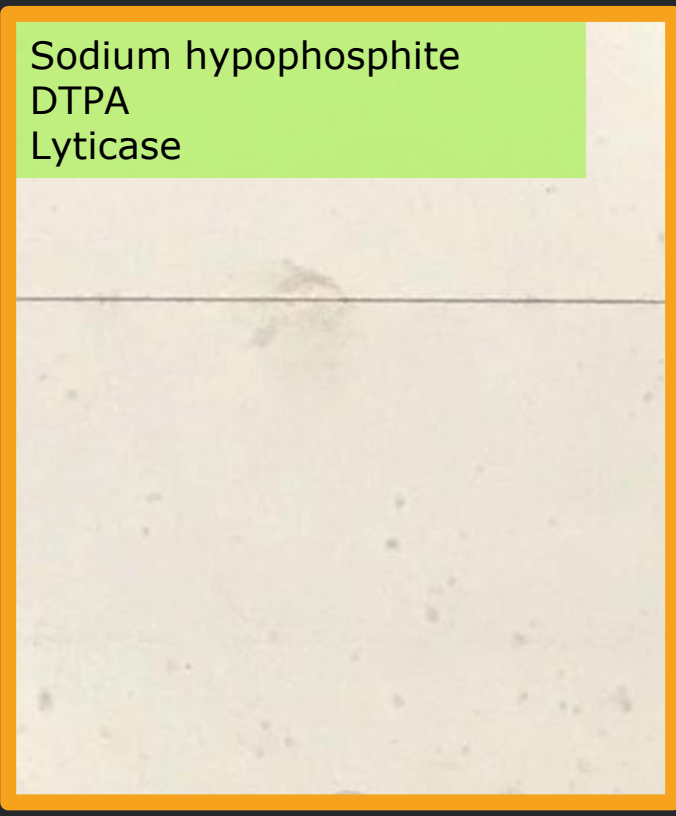
Ascorbic acid
EDTA
Lysing enzymes



Sodium hypophosphite
DTPA
Lysing enzymes



Sodium hypophosphite
DTPA
Lyticase



TREATMENT PROTOCOL

- Step 1: Pre-rinse
- Step 2: Reducing agent and chelator solution
- Step 3: Rinse
- Step 4: Enzyme solution
- Step 5: Final rinse

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GELS CONFERENCE

International conference in conservation science

- Held in London, UK
- 24 countries represented
- 42 papers presented:
  - paper
  - paintings
  - objects
  - textiles
  - new research
- Numerous other posters presented
- Polysaccharide, polyacrylic, and novel gel systems

GELS CONFERENCE

Agar Street!

International conference in conservation science held in London, UK

WHY GEL?

WHY GEL?

Three common polysaccharide gels

Contact angle tests on different papers

Images courtesy Michelle Sullivan

Moisture Control

- Can act as a reservoir for solutions
- Can act as a poultice for degradation products

WHY GEL?

Image courtesy of Joan Irving

Moisture Control

- Can act as a reservoir for solutions
- Can act as a poultice for degradation products

Physical Restriction

- Can be cast in large sheets
- Gel sheet can cover entire object
- Weight may prevent layer separation

WHY AGAROSE?

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Chemical structure of agarose

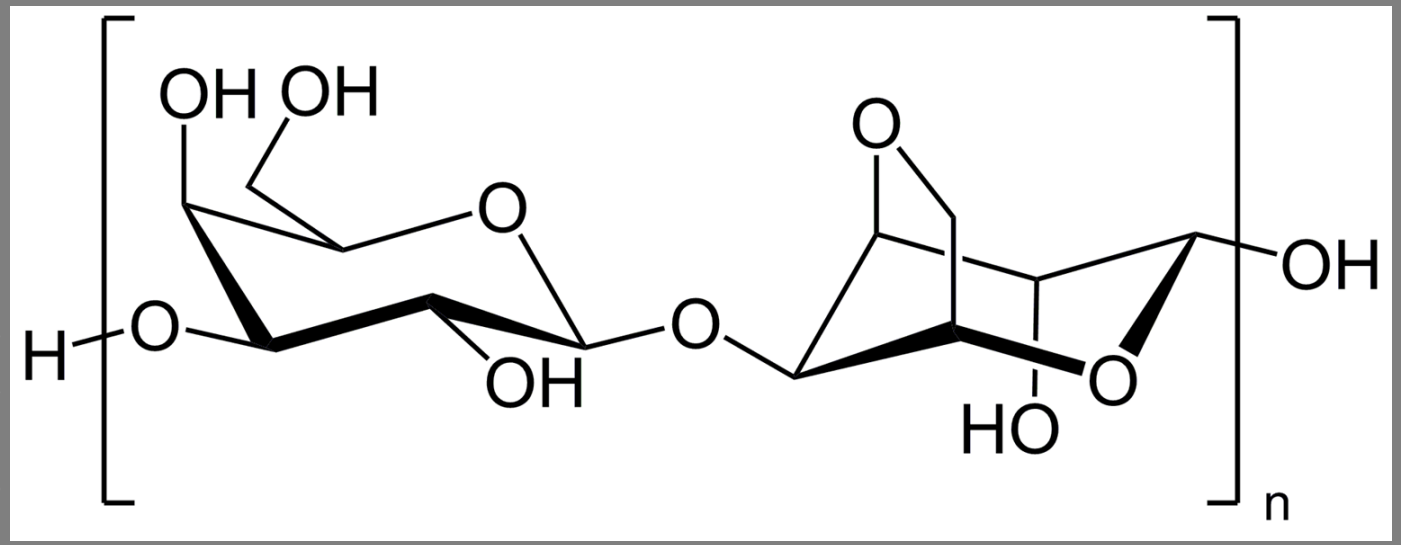

Image courtesy Wikipedia

Solution Compatibility

- Agarose is a neutral gel
- Can carry ionic and enzymatic solutions

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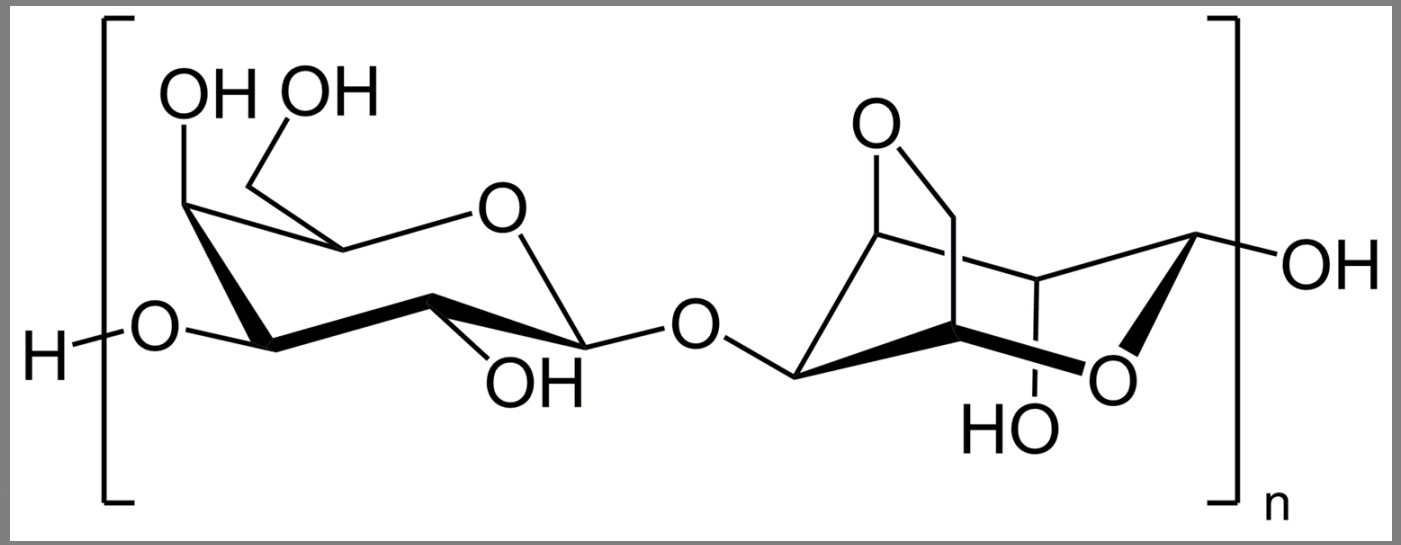

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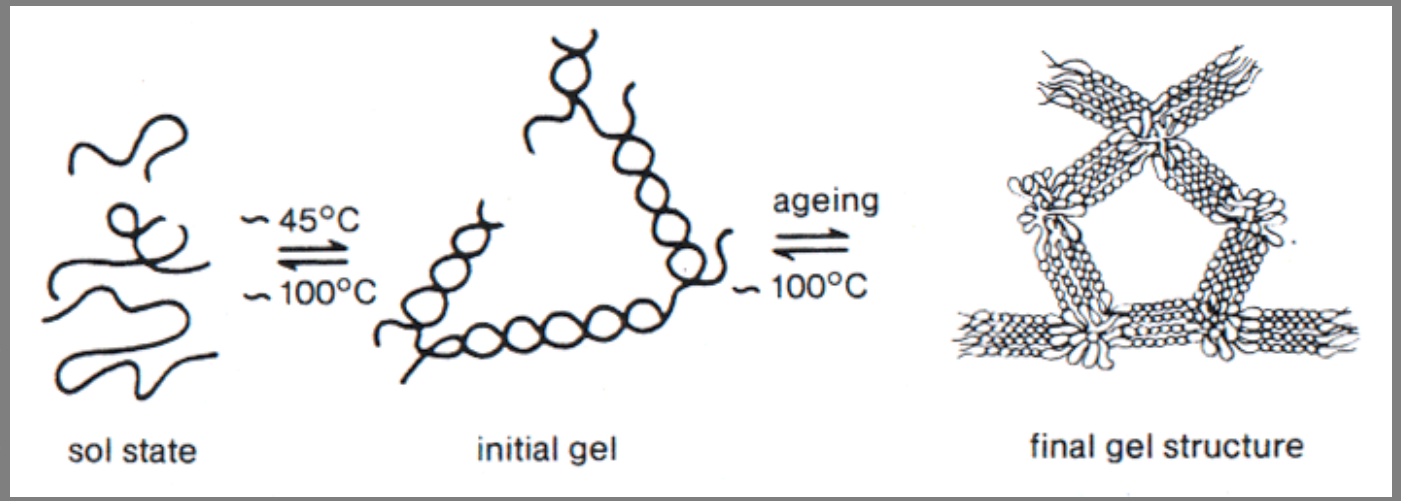

Image courtesy www.siumed.edu

Solution Compatibility

- Agarose is a neutral gel
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Capillarity

- Pore size can be decreased with increasing concentration
- Pore size determines capillary force
- Ex: 5% w/v gel releases moisture slower than 1% w/v gel

TWINS…

BT Recto,
normal illumination

“SEPARATED AT BATH”

SUCTION TABLE

TEK-WIPE

“SEPARATED AT BATH”

COMPARISON

- Photodocumentation
- Surface cleaning
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

SUCTION TABLE

- All rinse solutions sprayed on object under suction
- Gels applied to object for 20 minutes:
  - Under suction for 5 minutes
  - No suction for 10 minutes
  - Under suction for 5 minutes

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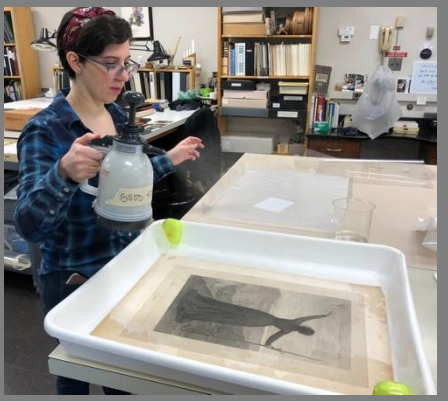

TEK-WIPE

- TEK-Wipe kept damp with rinse solutions
- Gels applied to object:
  - 30 minutes of contact time
  - No Mylar or other covering material

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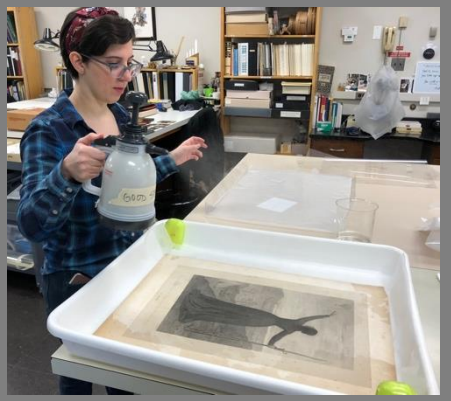

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Surface cleaning with cosmetic sponges and white vinyl eraser crumbs

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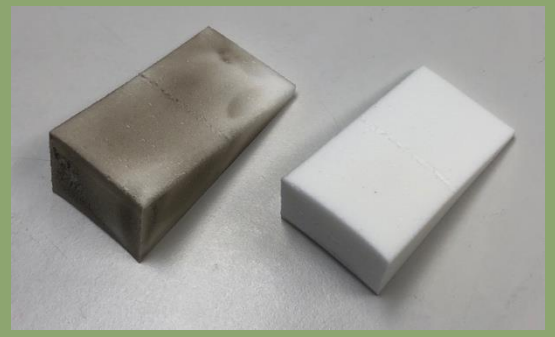

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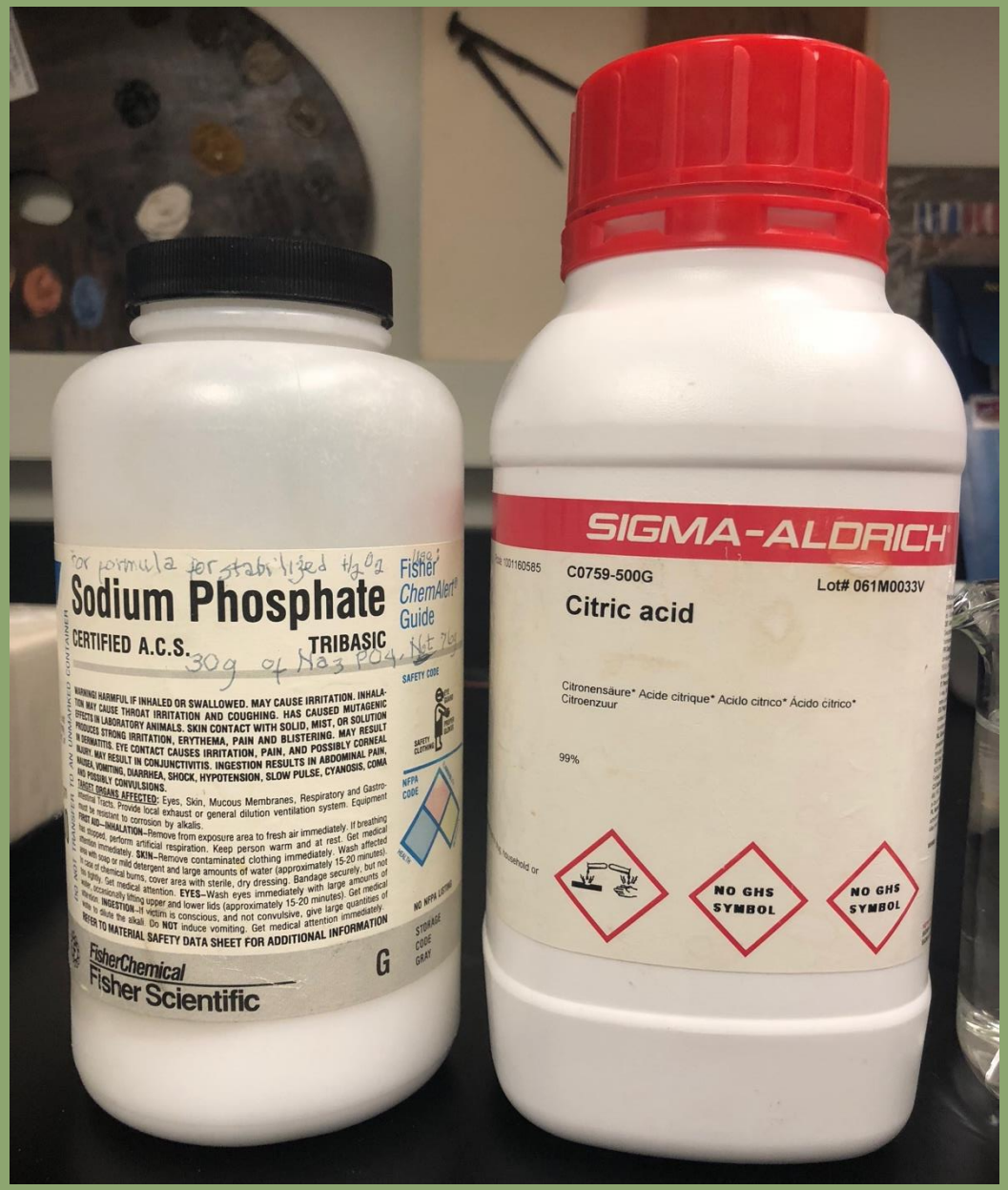
Created buffered solution as base for gel solutions using sodium phosphate and citric acid



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Added DTPA and $NaPO_2H_2 \cdot H_2O$ to half of the buffered solution for the reducing/chelating gel

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- Mend tears
- Humidification/flattening as necessary

Pouring hot agarose gel into Mylar trays

SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- **Materials preparation**
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Using a squeegee to ensure an even thickness of the agarose gel

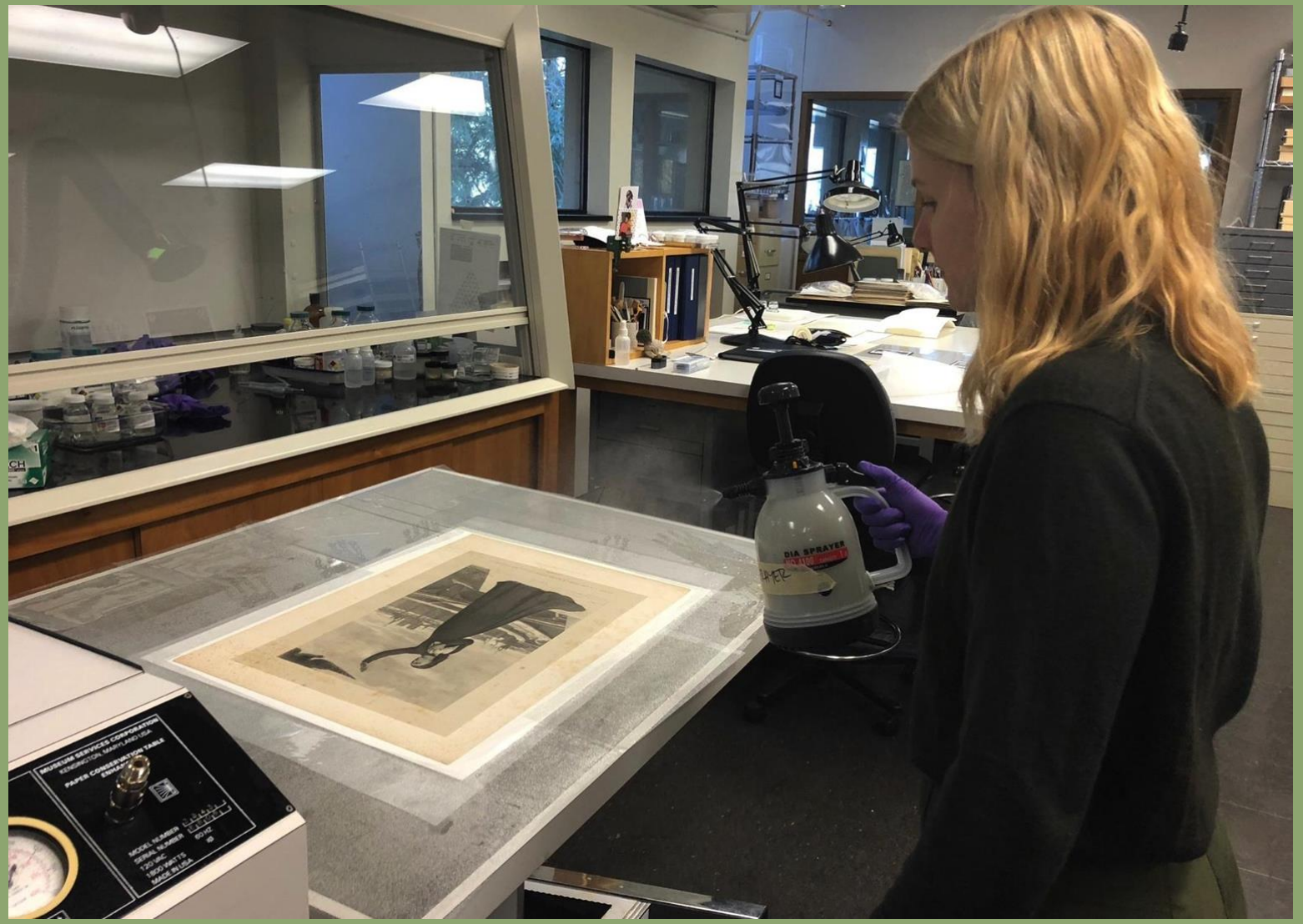
SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- **Pre-rinse with buffered solution, pH 6**
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Pre-rinsing using Dia sprayer

Solution: DI water with sodium citrate and citric acid, buffered to pH 6 and conductivity isotonic to print



SUCTION TABLE

OVERALL STEPS

- Photodocumentation
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- Overall humidification
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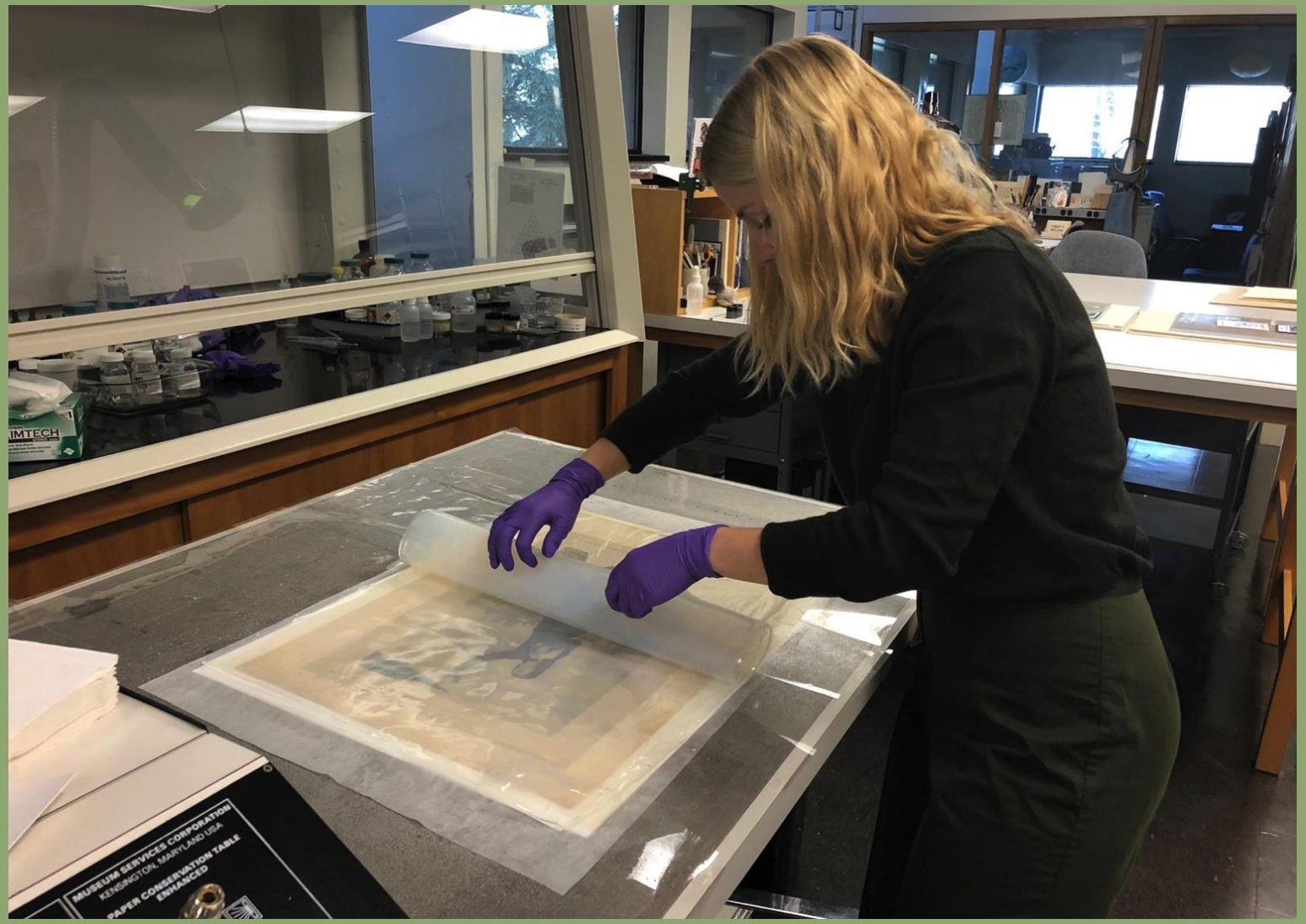
- **Reducing/chelating gel, pH 7.5**
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Applying first agarose sheet atop *gampi* barrier layer

Solution: Buffered solution, DTPA, and $NaPO_2H_2 \cdot H_2O$ adjusted to pH 7.5 with NaOH



SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
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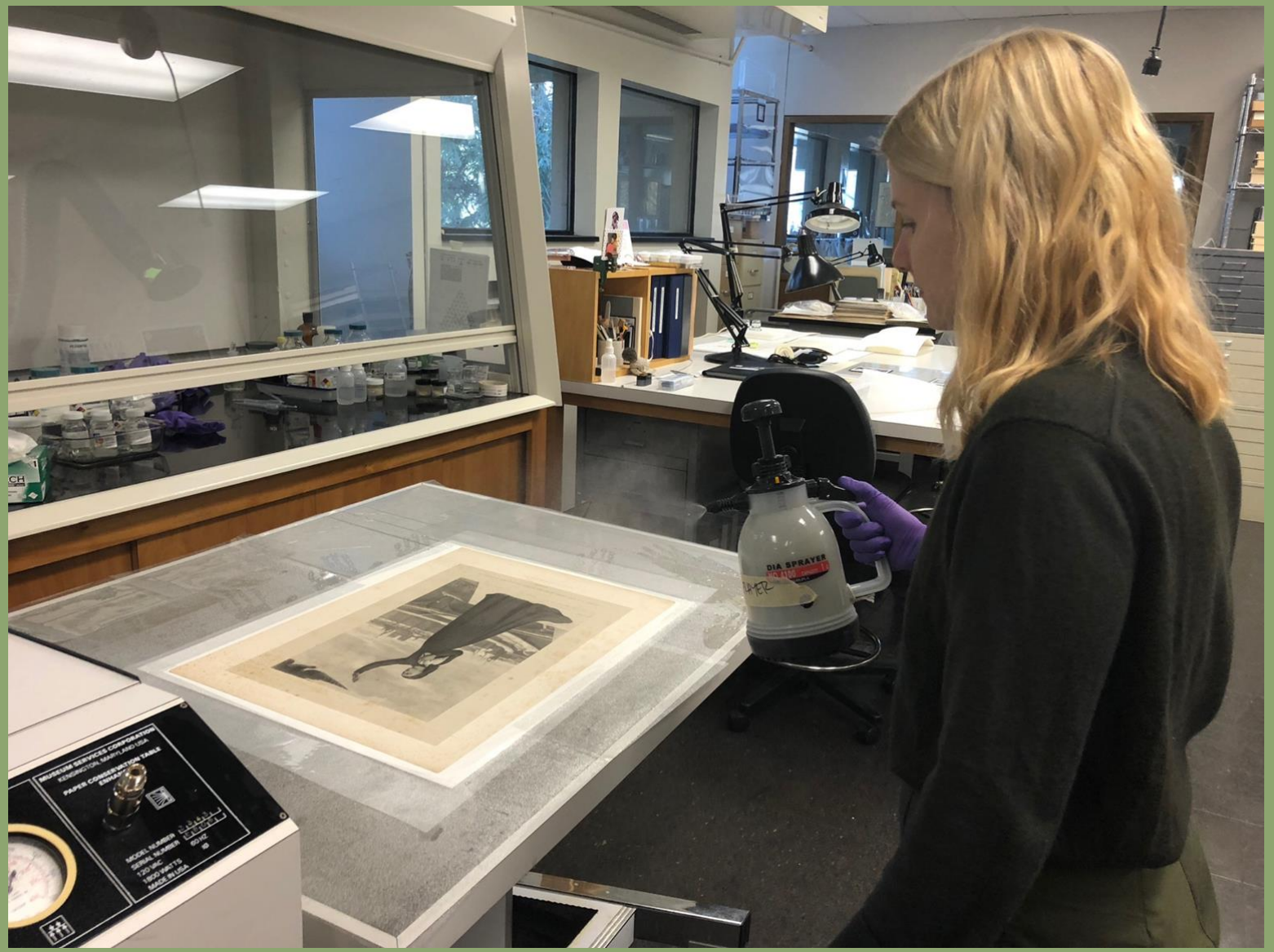
- **Rinse with buffered solution, pH 6**
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Rinsing with Dia sprayer

Solution: DI water with sodium citrate and citric acid, buffered to pH 6



SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- **Enzyme gel, pH 7.5**
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Applying second agarose sheet atop *gampi* barrier layer

Solution: Buffered solution at pH 7.5 with lyticase enymes

SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- **Final calcinated rinse, pH 8**
- Mend tears
- Humidification/flattening as necessary

Rinsing with Dia sprayer

Solution: Calcinated filtered tap water, adjusted to pH 8 with $Ca(OH)_2$

SUCTION TABLE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

After final rinse, print was placed into a drying stack

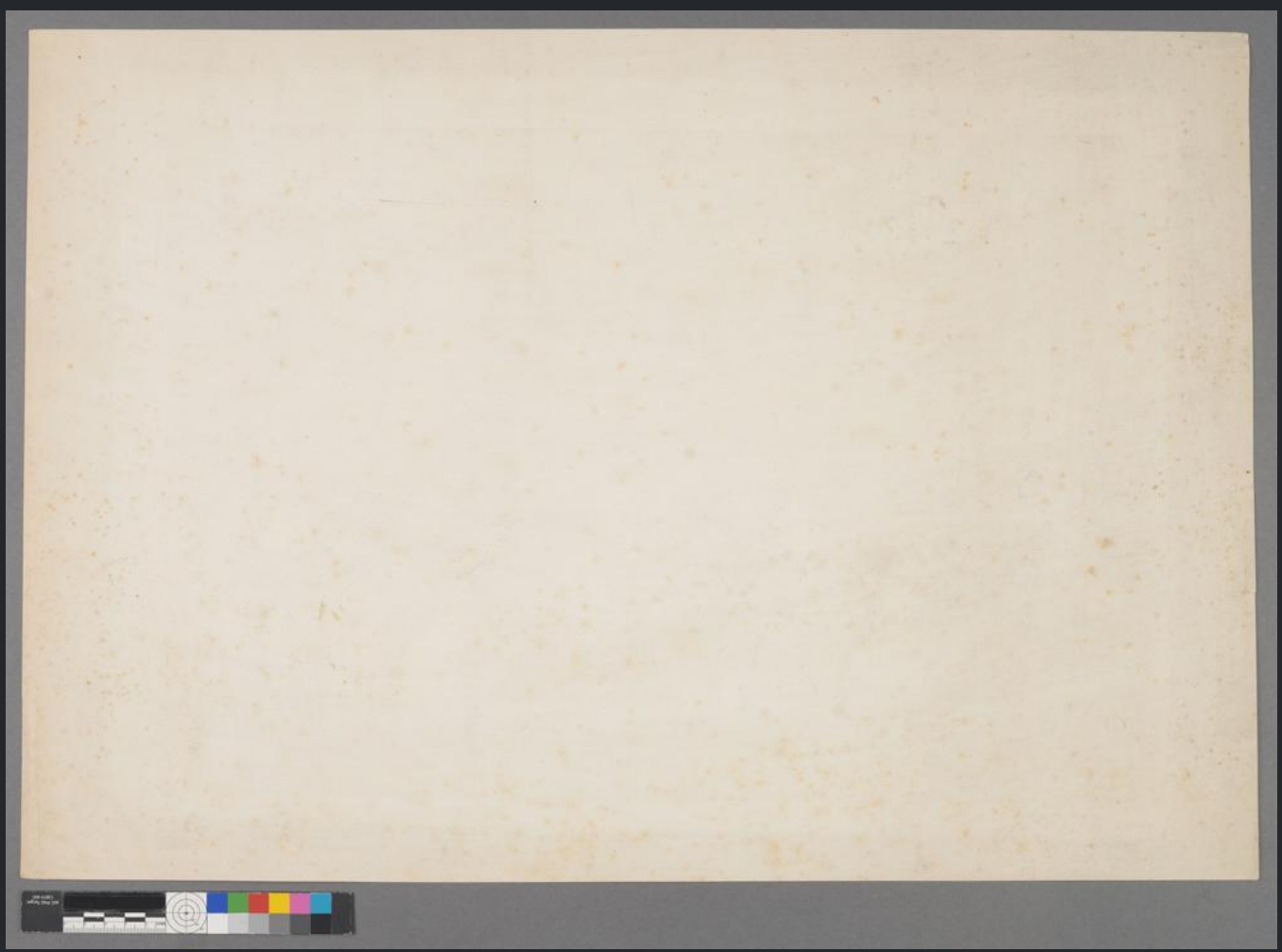
RESULTS

"Le Pigeon," BT

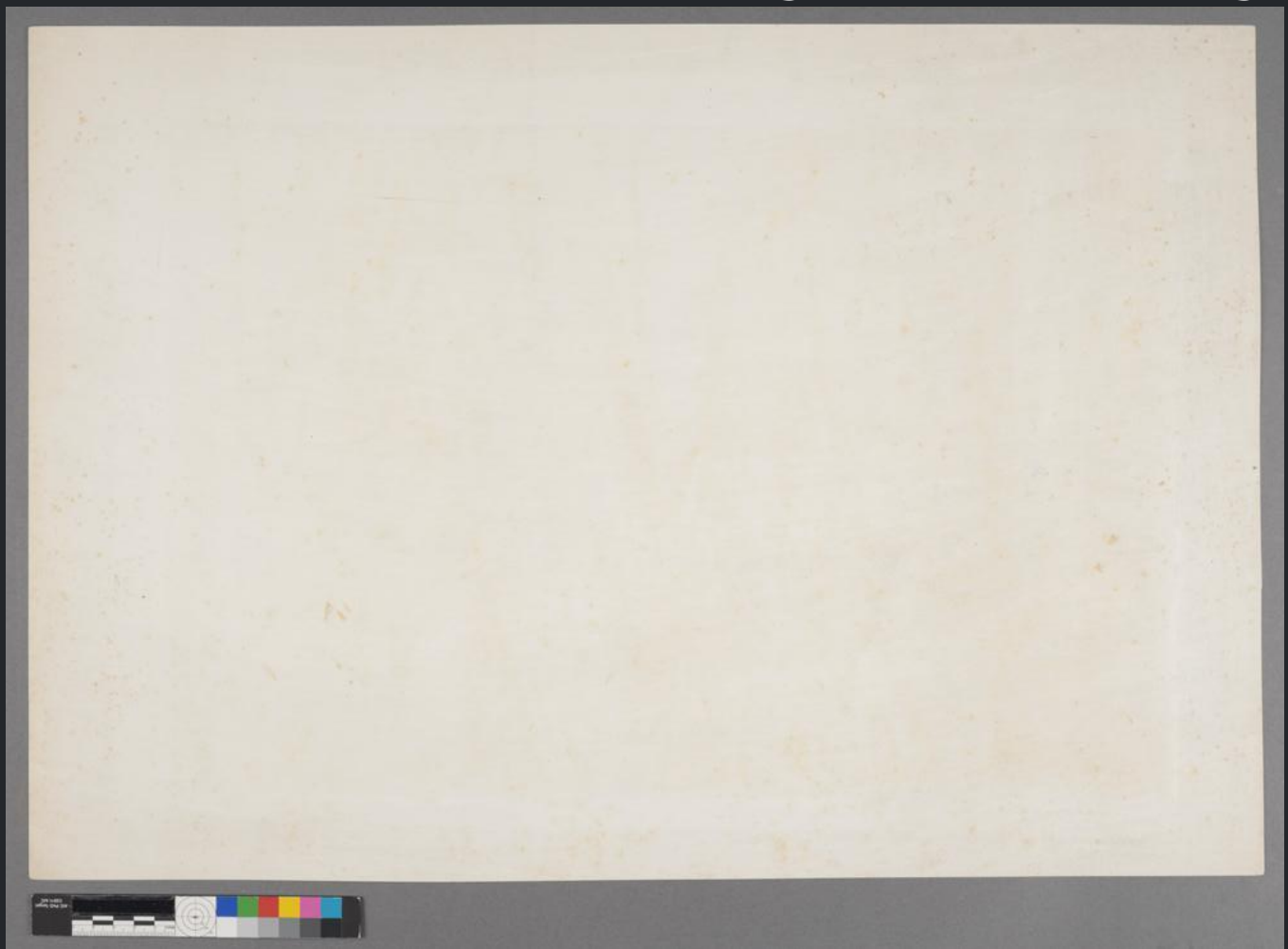
"Le Pigeon," DT after bathing

RESULTS

“Le Pigeon,” BT

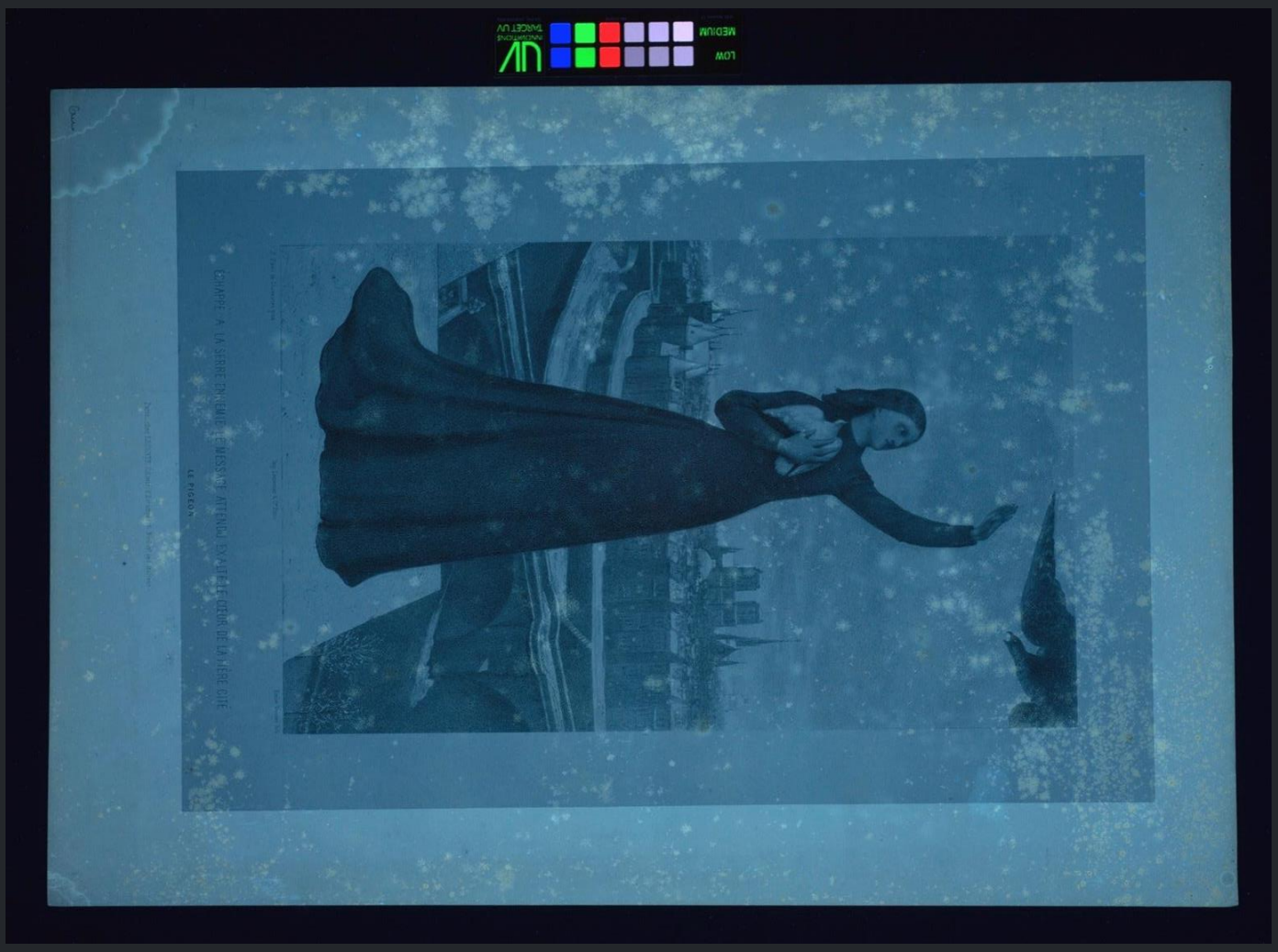


“Le Pigeon,” DT after bathing

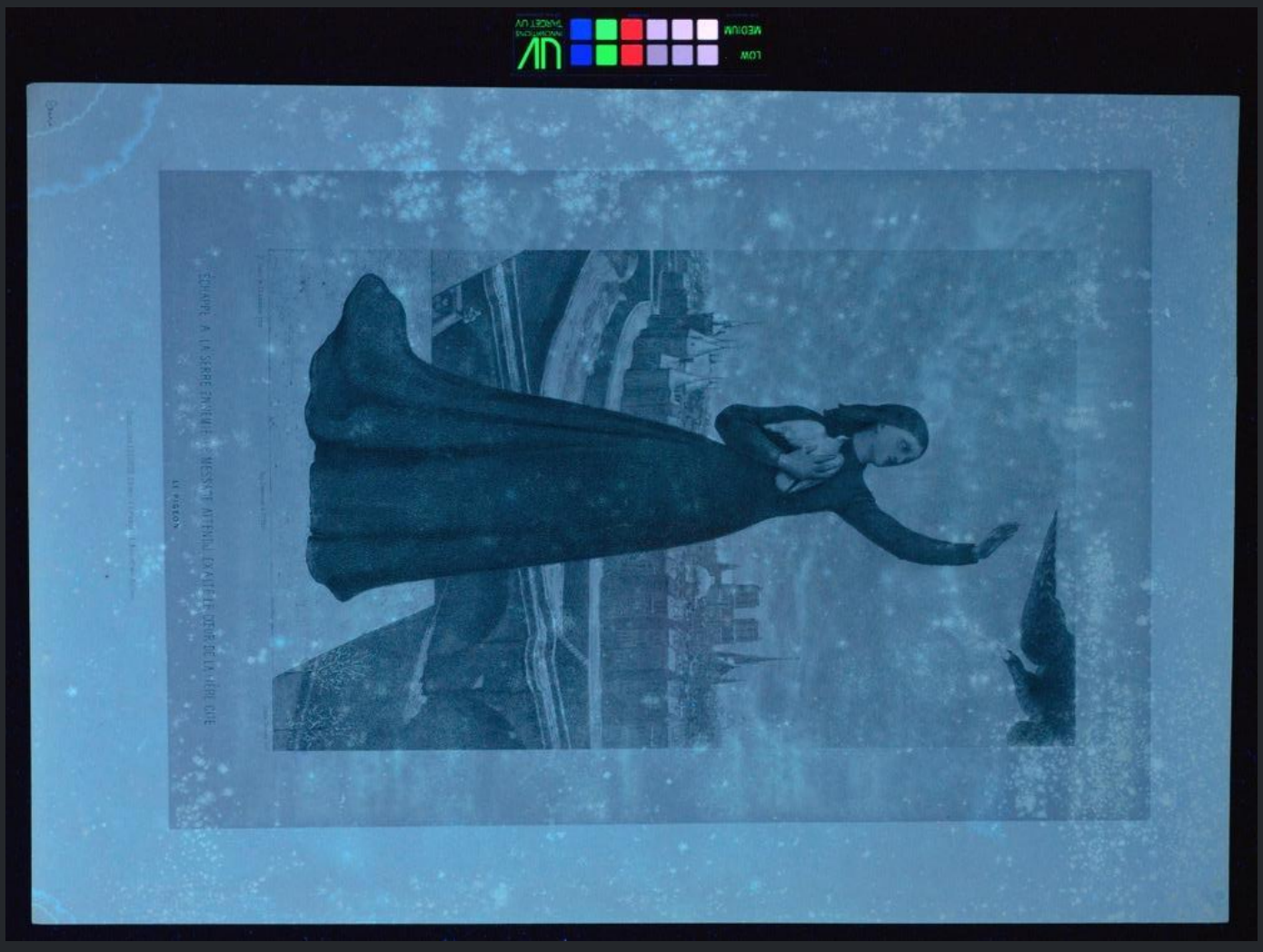


UV

"Le Pigeon," BT



"Le Pigeon," DT after bathing



UV

“Le Pigeon,” BT

“Le Pigeon,” DT after bathing

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- **Surface cleaning**
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Surface cleaning with cosmetic sponges and white vinyl eraser crumbs

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- **Materials preparation**
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
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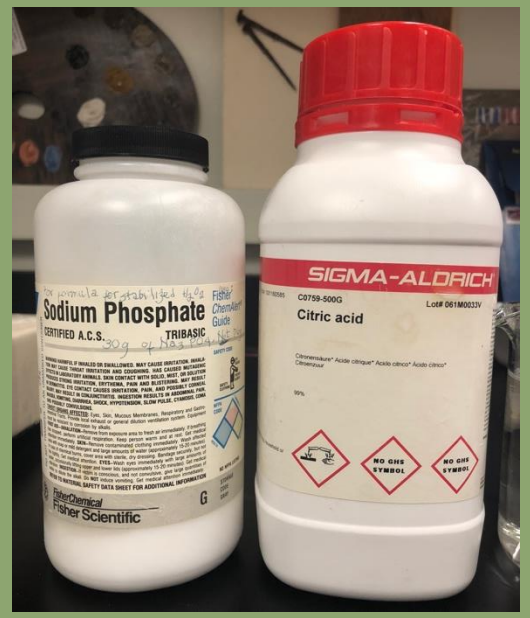
- Humidification/flattening as necessary



TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- **Pre-rinse with buffered solution, pH 6**
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Preparing the bathing chamber by saturating the TEK-Wipe in the pre-rinse solution

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- **Pre-rinse with buffered solution, pH 6**
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Using a squeegee to ensure even saturation and planarity of the TEK-Wipe

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- **Pre-rinse with buffered solution, pH 6**
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
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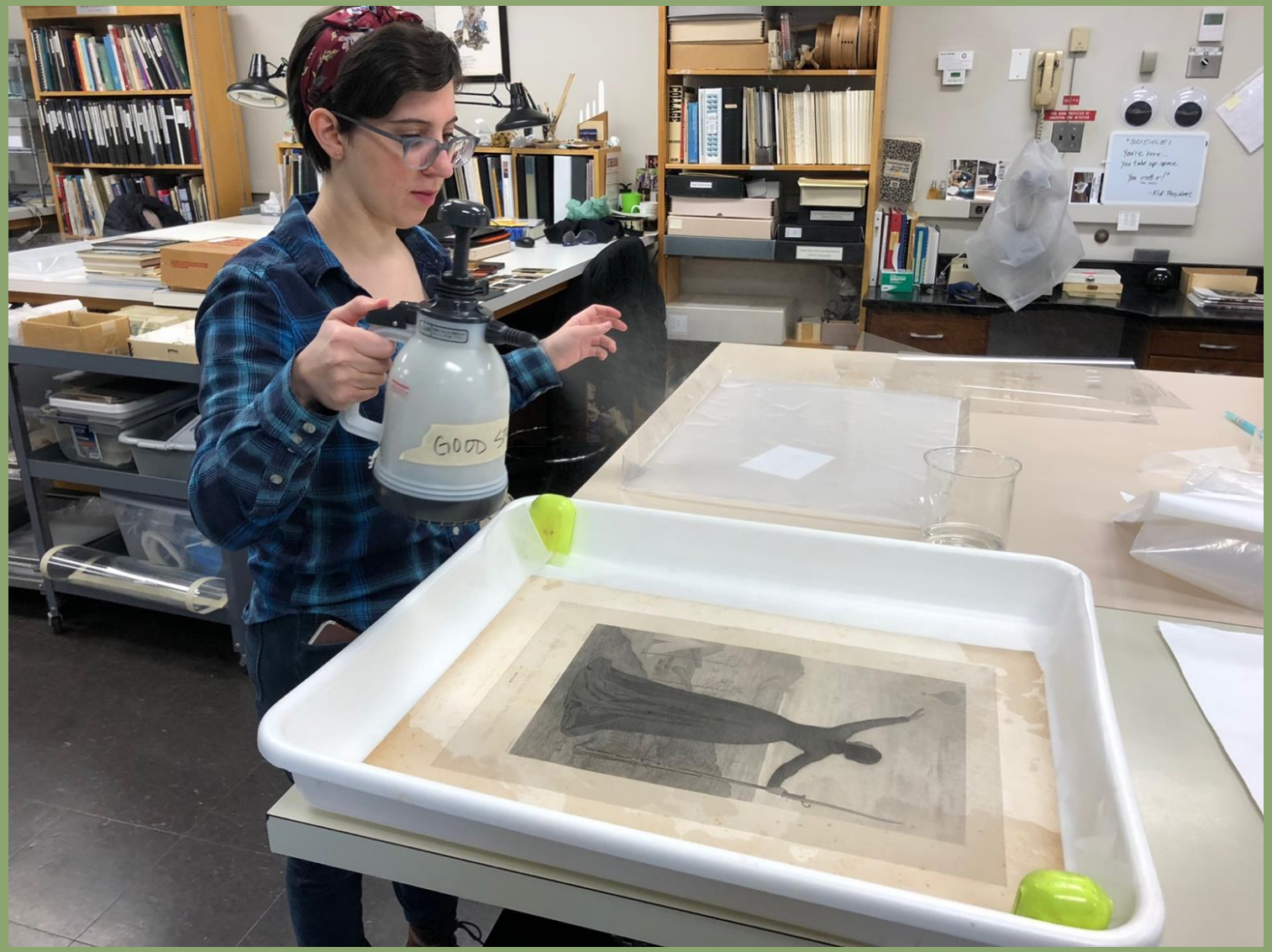

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- **Reducing/chelating gel, pH 7.5**
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- Mend tears
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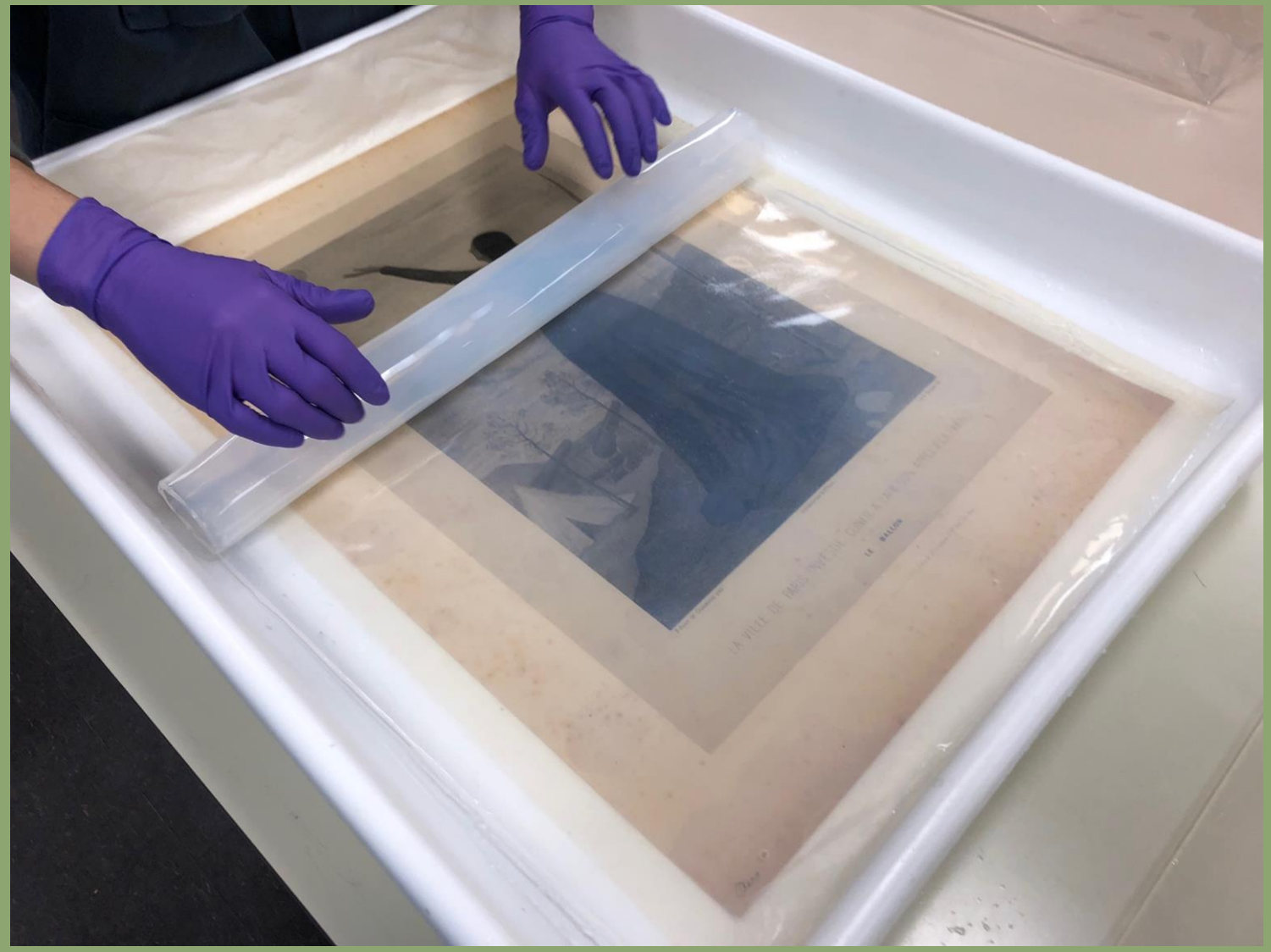
Applying first agarose sheet atop *gampi* barrier layer

Solution: Buffered solution, DTPA, and $NaPO_2H_2 \cdot H_2O$ adjusted to pH 7.5 with NaOH



TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
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- **Rinse with buffered solution, pH 6**
- Enzyme gel, pH 7.5
- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

Changing TEK-Wipe, saturated with rinse solution

(And having fun!)

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
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Applying second agarose sheet atop *gampi* barrier layer

Solution: Buffered solution at pH 7.5 with lyticase enzymes

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
- Enzyme gel, pH 7.5
- **Final calcinated rinse, pH 8**
- Mend tears
- Humidification/flattening as necessary

Changing TEK-Wipe, saturated with final rinse solution

Solution: Calcinated filtered tap water, adjusted to pH 8 with $Ca(OH)_2$

TEK-WIPE

OVERALL STEPS

- Photodocumentation
- Surface cleaning
- Materials preparation
- Overall humidification
- Pre-rinse with buffered solution, pH 6
- Reducing/chelating gel, pH 7.5
- Rinse with buffered solution, pH 6
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- Final calcinated rinse, pH 8
- Mend tears
- Humidification/flattening as necessary

After final rinse, print was placed into a drying stack

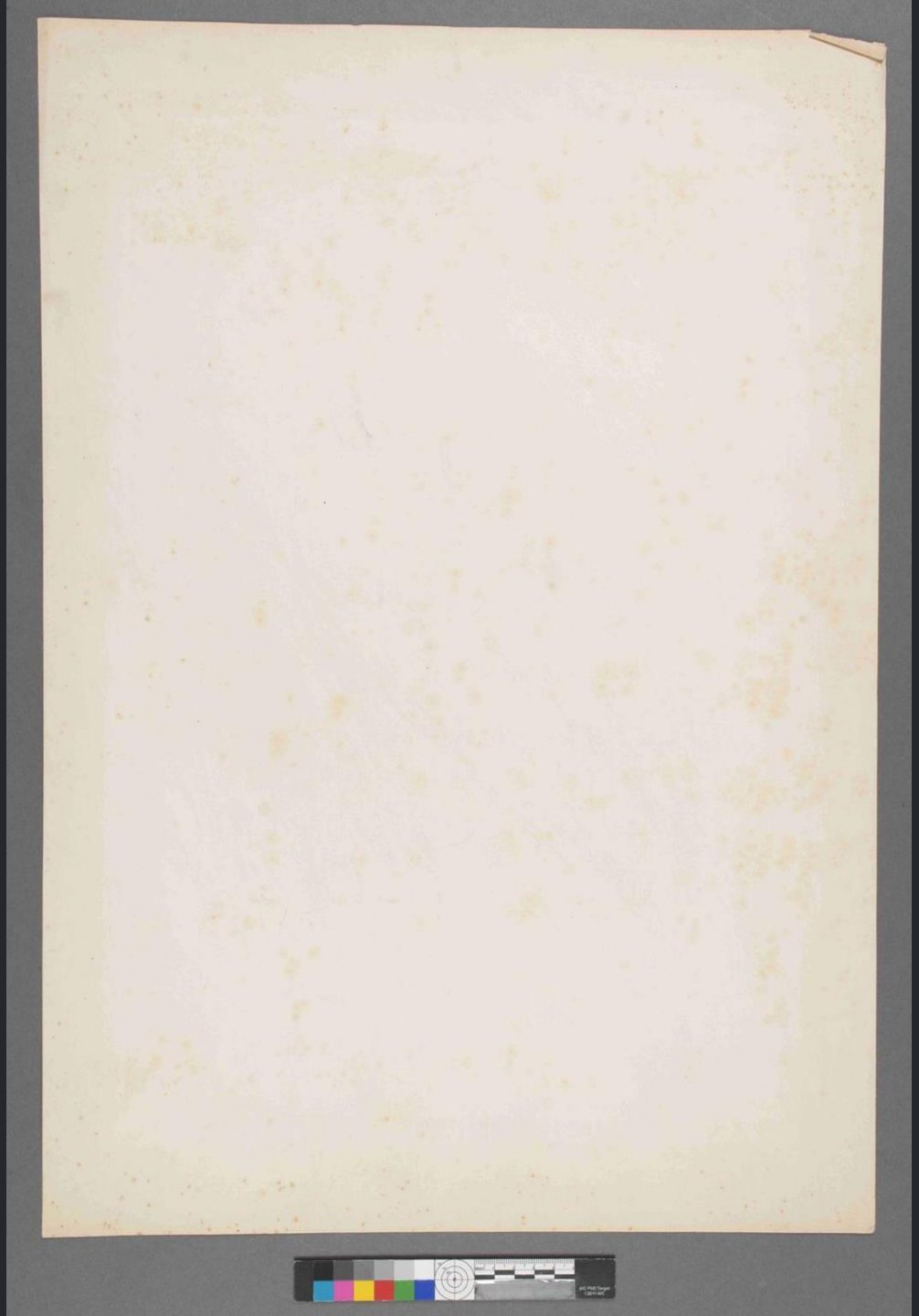
RESULTS

"Le Ballon," BT

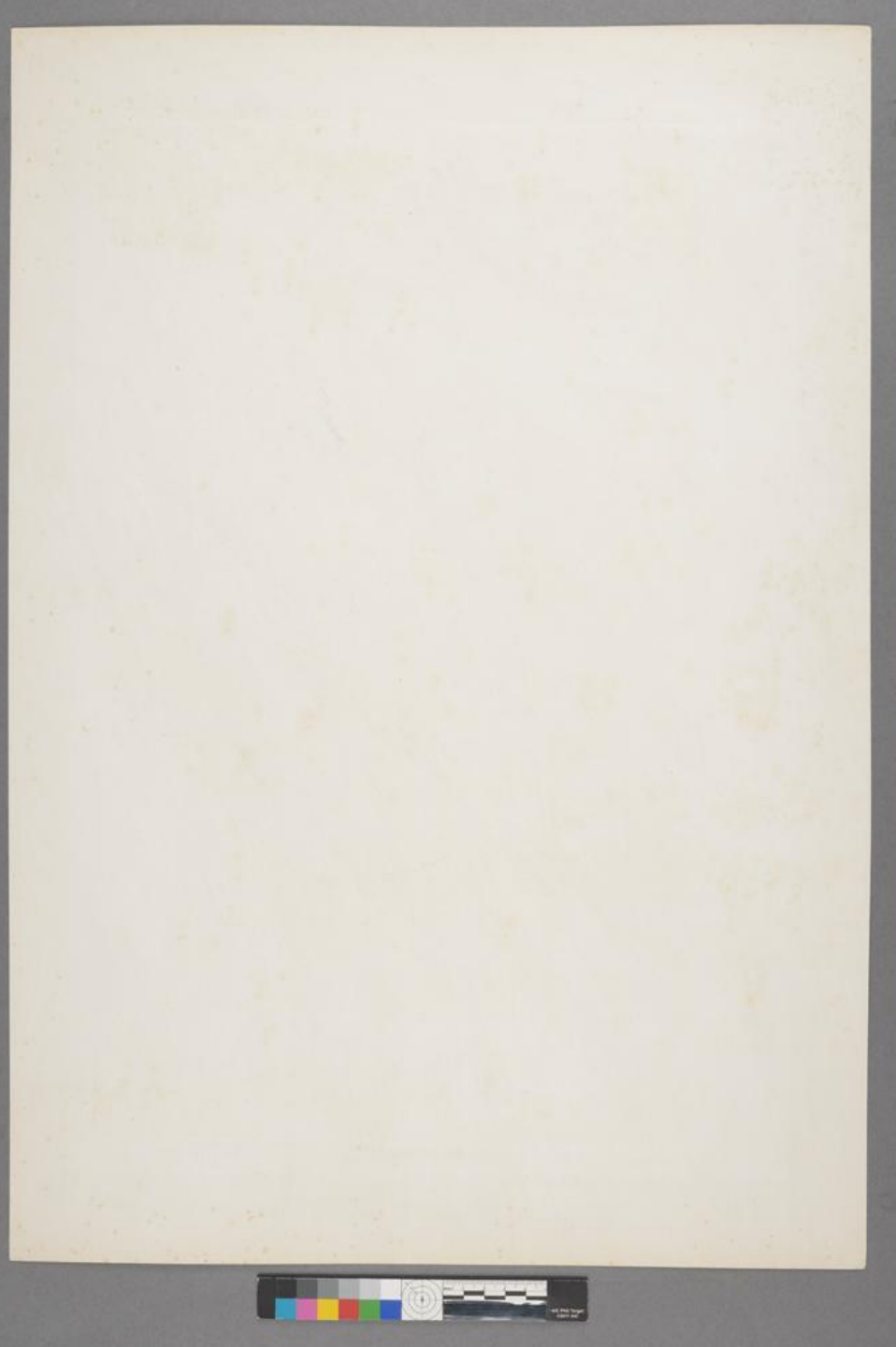
"Le Ballon," DT after bathing

RESULTS

"Le Ballon," BT

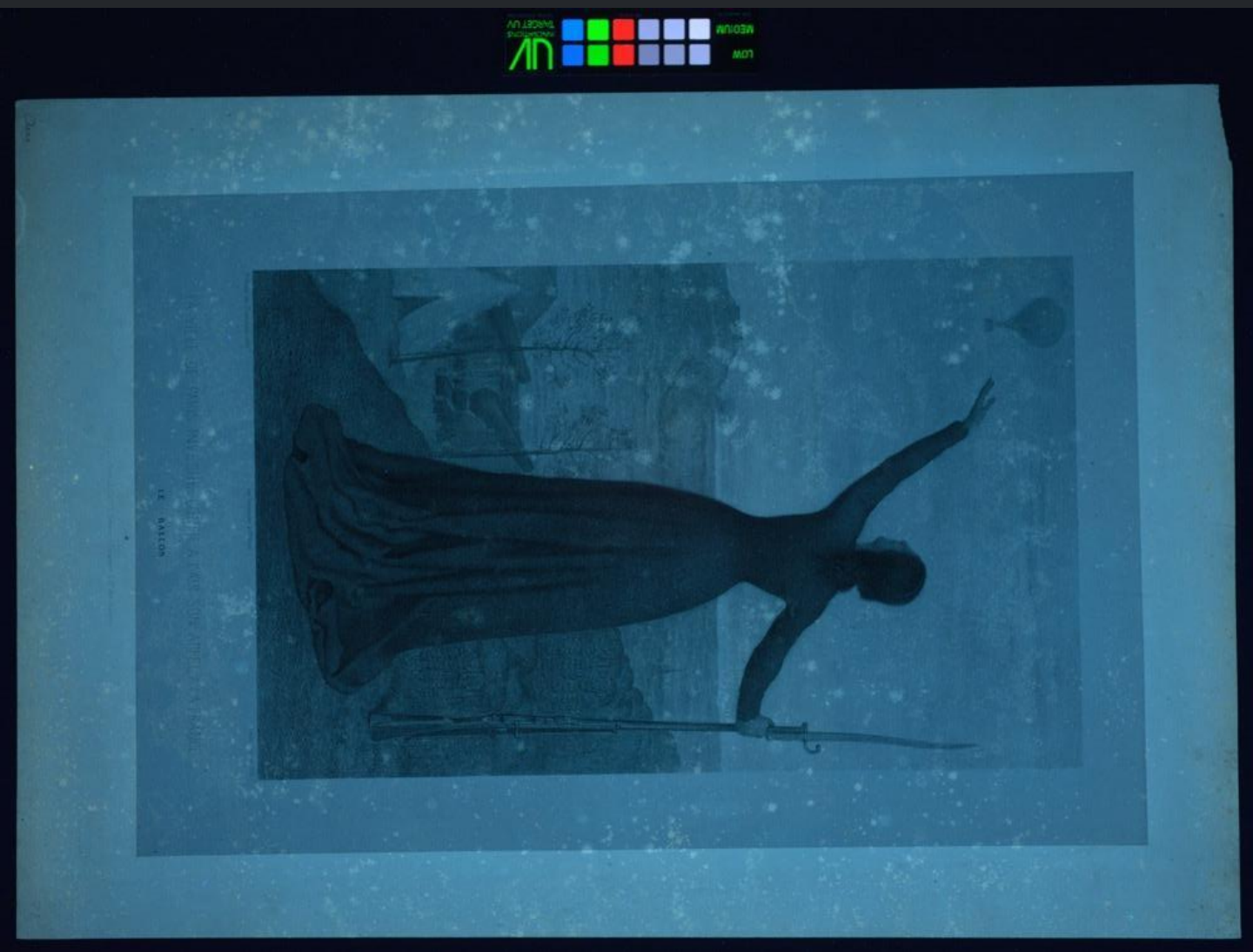


"Le Ballon," DT after bathing

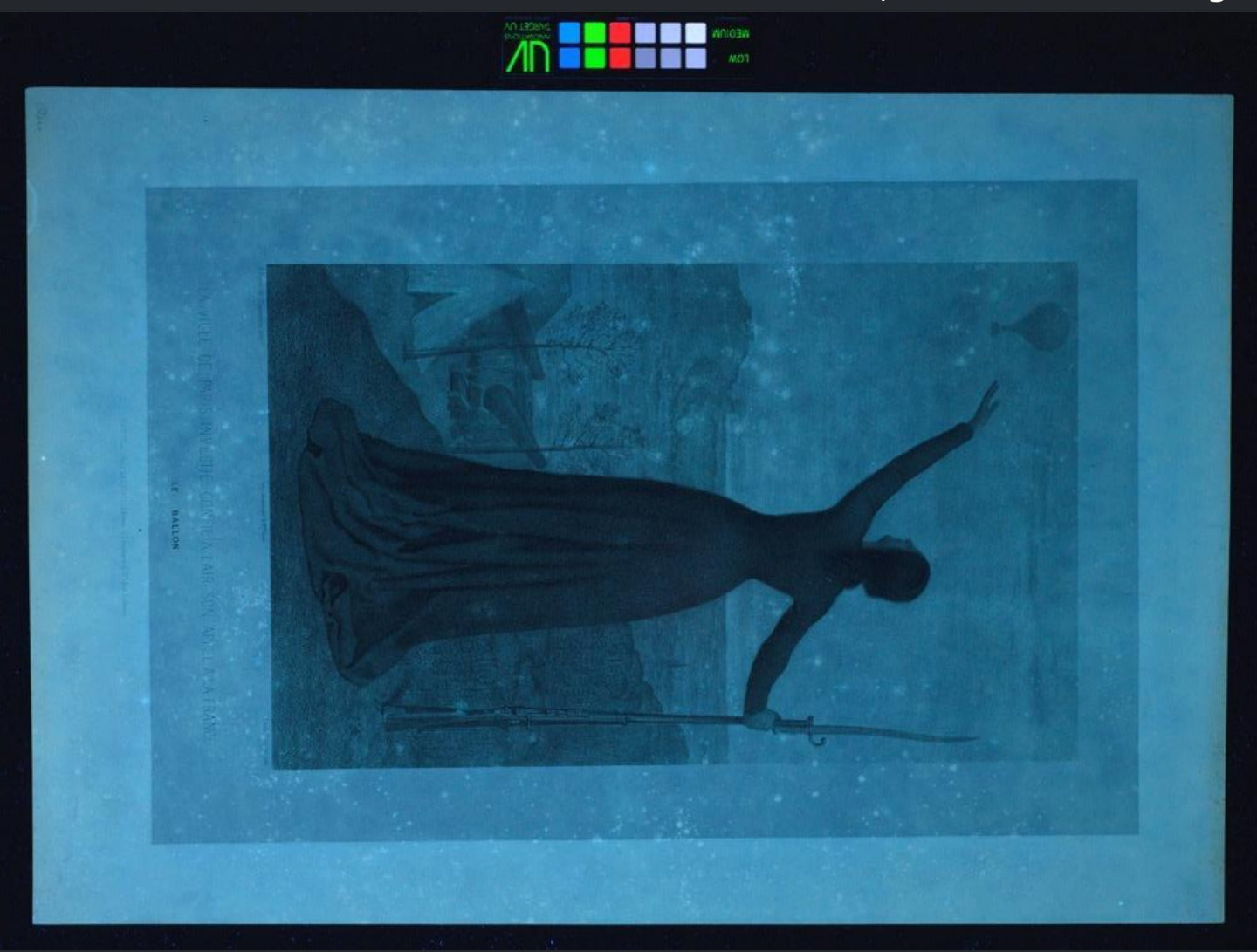


UV

“Le Ballon,” BT



“Le Ballon,” DT after bathing



UV

“Le Ballon,” BT

“Le Ballon,” DT after bathing

RESULTS

RESULTS

Colorimetry

Minolta CR-221

Locations

- 1° support
- 2° support
- 1° support foxing
- 2° support foxing
- D_{max} image
- D_{min} image

RESULTS

Brightening

Secondary support

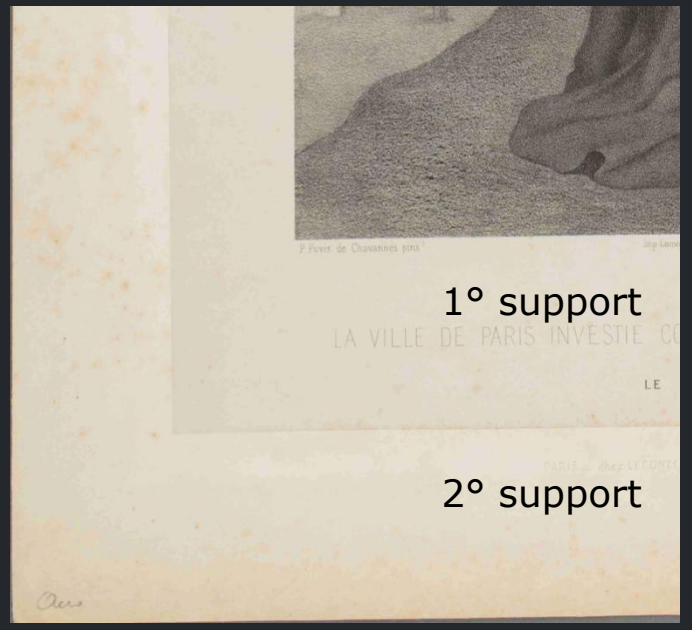
- "Le Ballon" Δ L* = 2.09
- "Le Pigeon" Δ L* = 2.03

- "Le Ballon" Δ b* = -2.10
- "Le Pigeon" Δ b* = -3.23

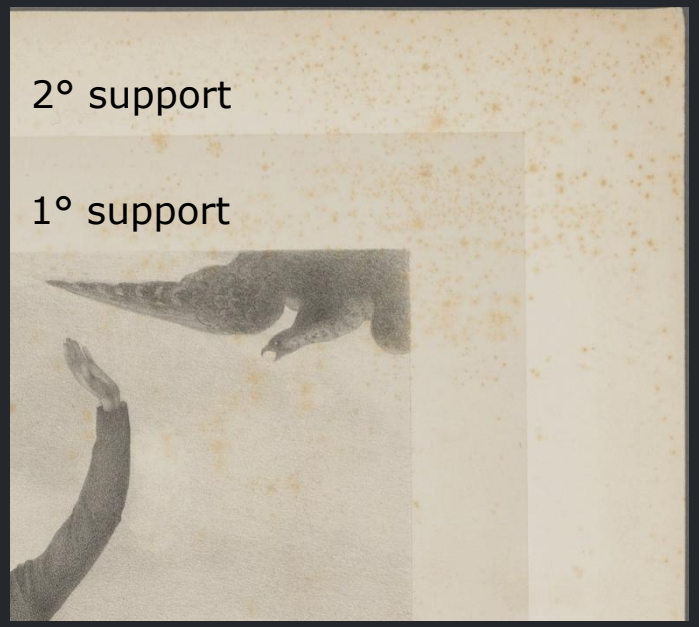
BT

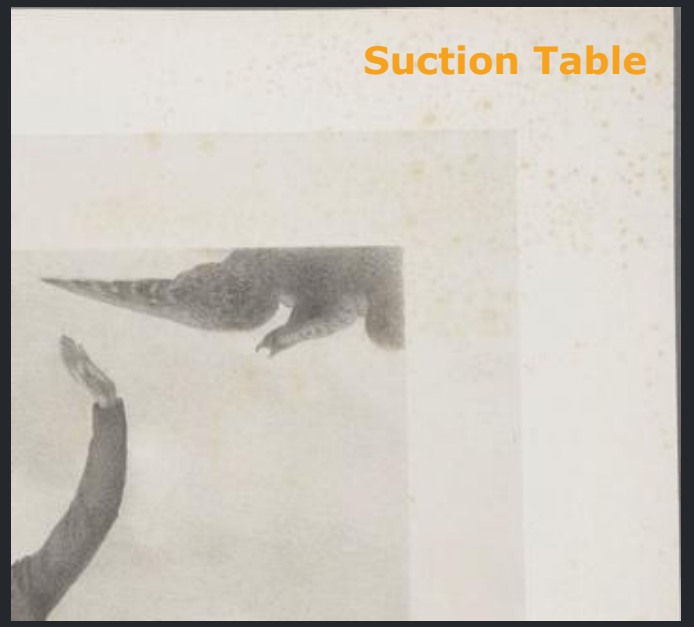
DT

"Le Ballon"



"Le Pigeon"





RESULTS

Brightening

Secondary support

- "Le Ballon" Δ L* = 2.09
- "Le Pigeon" Δ L* = 2.03

- "Le Ballon" Δ b* = -2.10
- "Le Pigeon" Δ b* = -3.23

Foxing Reduction

Secondary support foxing

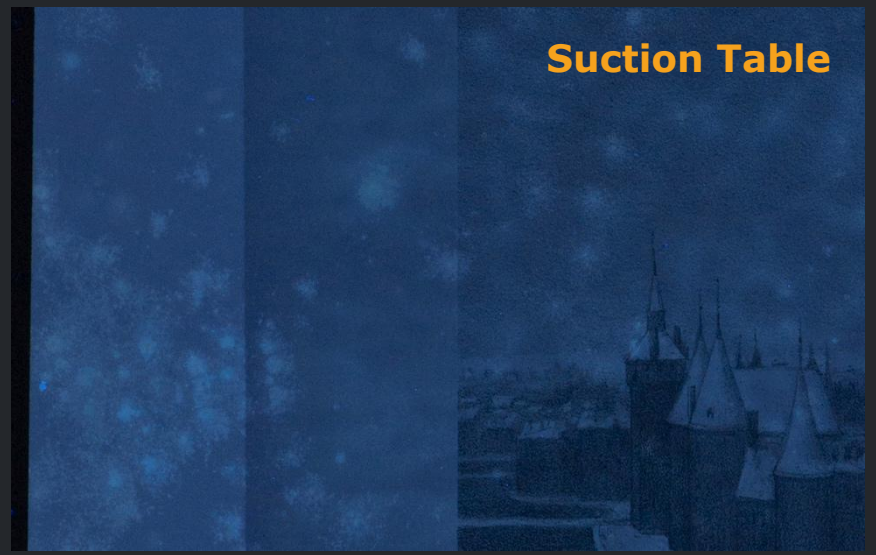
- "Le Ballon" Δ L* = 4.94
- "Le Pigeon" Δ L* = 1.03

- "Le Ballon" Δ b* = -4.63
- "Le Pigeon" Δ b* = -0.91

UV

"Le Ballon"

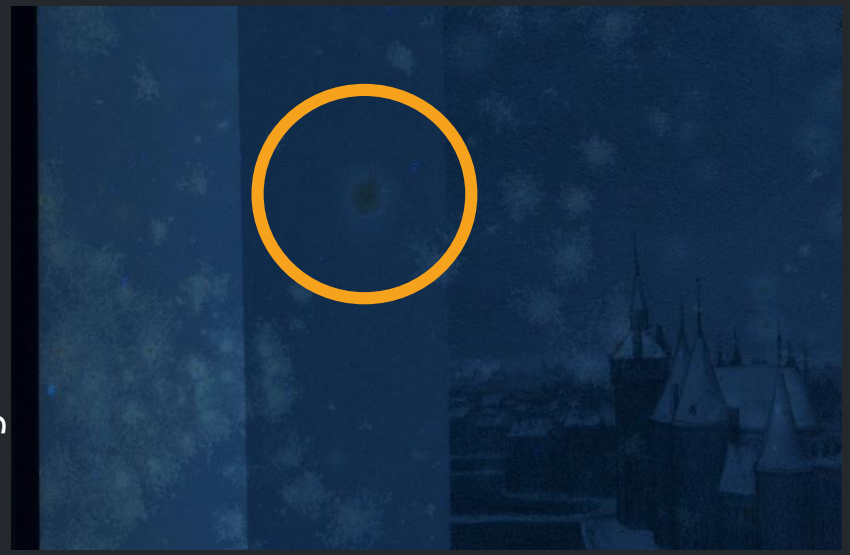
"Le Pigeon"

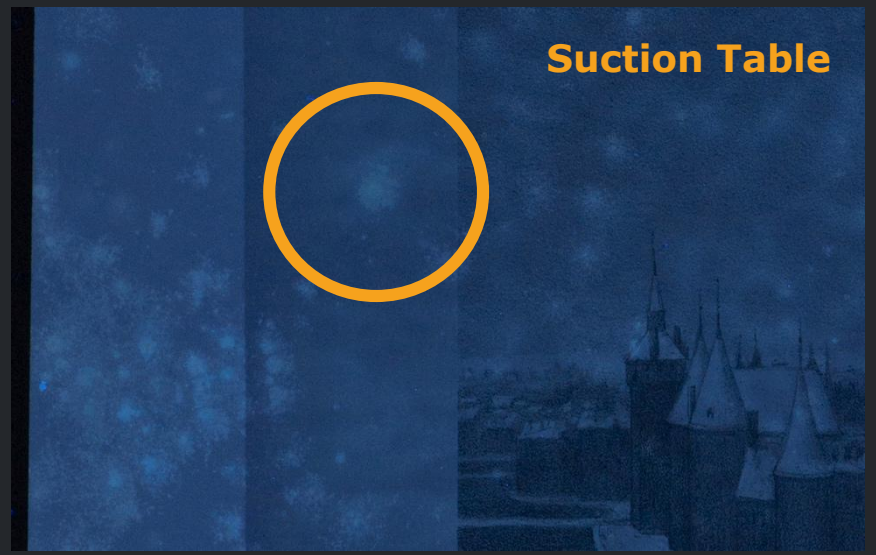


UV

"Le Ballon"

"Le Pigeon"





DISCUSSION

DELIVERY METHOD COMPARISON

SUCTION TABLE

TEK-WIPE

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time

TIME

TEK-WIPE

- Longer total treatment time

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time
- Conservator is active through the entire treatment

TIME

INTENSITY

TEK-WIPE

- Longer total treatment time
- Conservator is active only for bath changes

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time
- Conservator is active through the entire treatment
- Gel functions as a reservoir

TIME

INTENSITY

MOISTURE CONTROL

TEK-WIPE

- Longer total treatment time
- Conservator is active only for bath changes
- Gel functions as a poultice

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time
- Conservator is active through the entire treatment
- Gel functions as a reservoir
- Weight of gel and pull from suction

TIME

INTENSITY

MOISTURE CONTROL

PRESSURE

TEK-WIPE

- Longer total treatment time
- Conservator is active only for bath changes
- Gel functions as a poultice
- Weight of gel alone

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time
- Conservator is active through the entire treatment
- Gel functions as a reservoir
- Weight of gel and pull from suction
- Potential for more rinse solution to be delivered in spray form

TIME

INTENSITY

MOISTURE CONTROL

PRESSURE

DEGREE OF RINSING

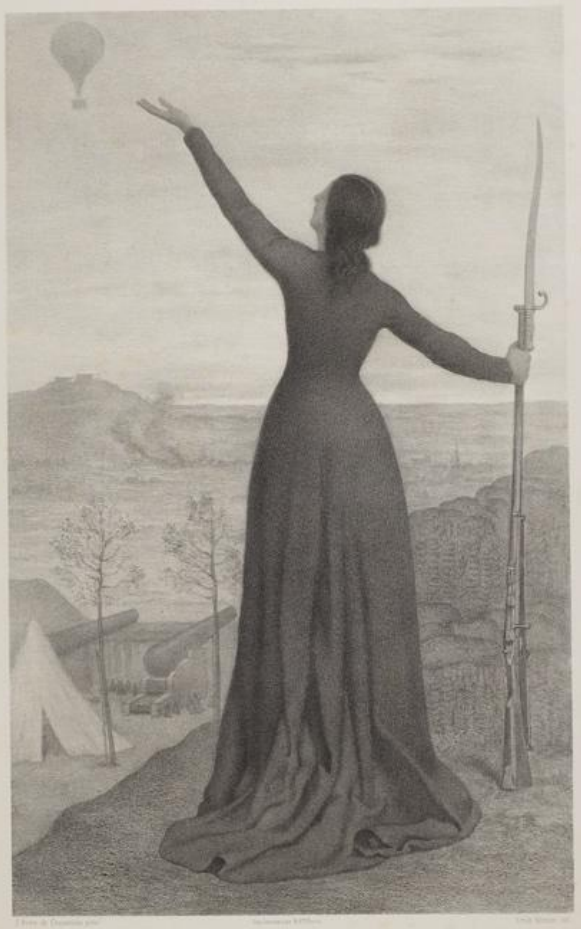
TEK-WIPE

- Longer total treatment time
- Conservator is active only for bath changes
- Gel functions as a poultice
- Weight of gel alone
- Each rinse solution application limited to amount needed to saturate TEK-Wipe

RESULTS

"Le Ballon," DT after bathing

TEK-Wipe

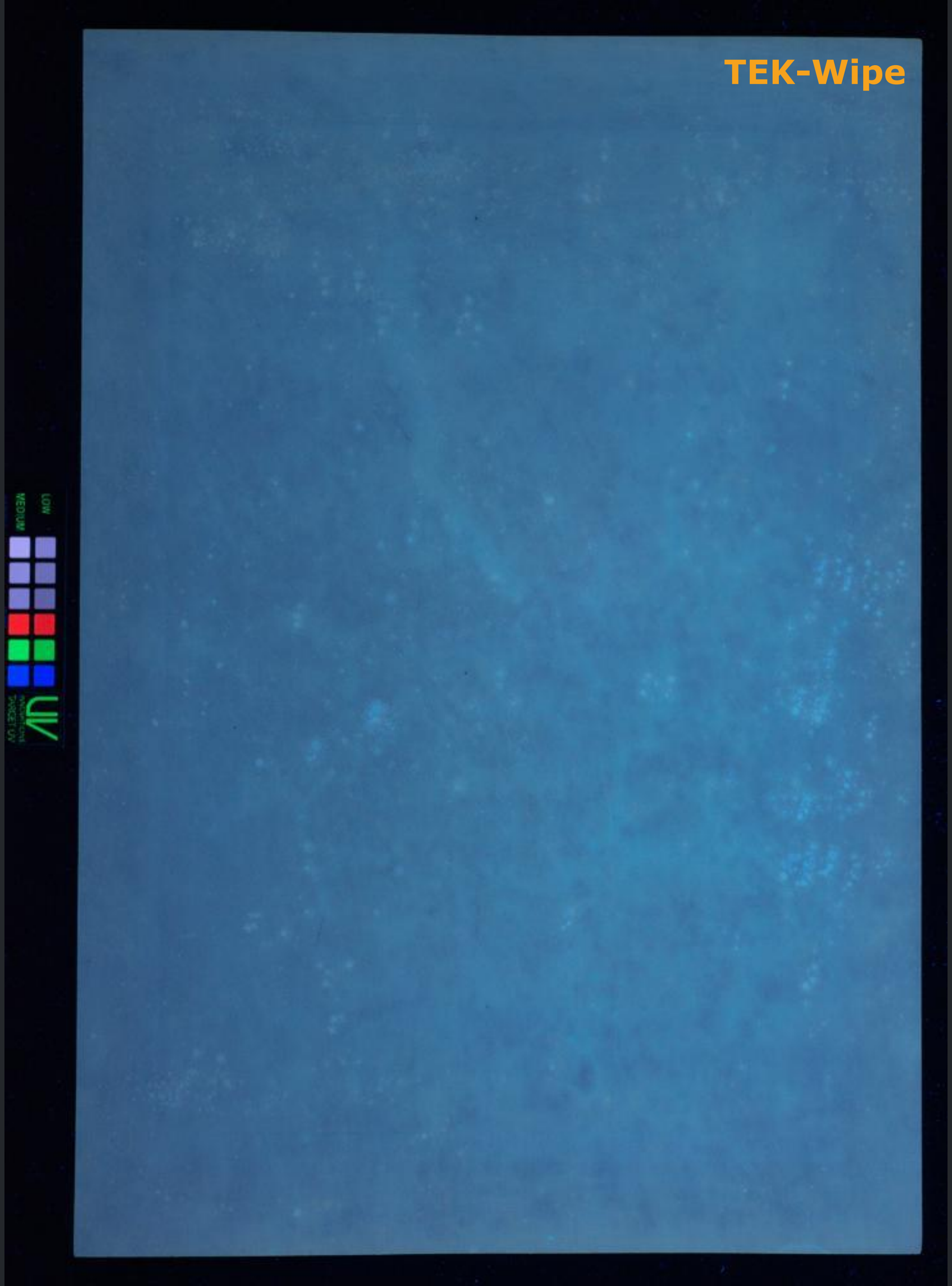


"Le Pigeon," DT after bathing

Suction Table

UV

"Le Ballon," DT



"Le Pigeon," DT

DELIVERY METHOD COMPARISON

SUCTION TABLE

- Quicker total treatment time
- Conservator is active through the entire treatment
- Gel functions as a reservoir
- Weight of gel and pull from suction
- Potential for more rinse solution to be delivered in spray form
- Potential for uneven spray applications

TIME

INTENSITY

MOISTURE CONTROL

PRESSURE

DEGREE OF RINSING

UNIFORMITY

TEK-WIPE

- Longer total treatment time
- Conservator is active only for bath changes
- Gel functions as a poultice
- Weight of gel alone
- Each rinse solution application limited to amount needed to saturate TEK-Wipe
- Saturated TEK-Wipe provides more even wetting

PRACTICALITY COMPARISON

SUCTION TABLE		TEK-WIPE
	INSTITUTIONS	
	PRIVATE PRACTICE	

PRACTICALITY COMPARISON

SUCTION TABLE

- Requires investment in large, expensive equipment

EQUIPMENT

TEK-WIPE

- Requires smaller, more easily available supplies

PRACTICALITY COMPARISON

SUCTION TABLE

- Requires investment in large, expensive equipment
- Greater physical restraint and control of moisture

EQUIPMENT

OBJECT NEEDS

TEK-WIPE

- Requires smaller, more easily available supplies
- Gentler to delicate objects or those with dimensionality

PRACTICALITY COMPARISON

SUCTION TABLE

- Requires investment in large, expensive equipment
- Greater physical restraint and control of moisture
- Conservator must act quickly and know the object can withstand the pull of suction

EQUIPMENT

OBJECT NEEDS

CONFIDENCE

TEK-WIPE

- Requires smaller, more easily available supplies
- Gentler to delicate objects or those with dimensionality
- Conservator has more time to monitor treatment and can safely treat delicate objects

PRACTICALITY COMPARISON

SUCTION TABLE

- Requires investment in large, expensive equipment
- Greater physical restraint and control of moisture
- Conservator must act quickly and know the object can withstand the pull of suction
- Requires electricity. TEK-Wipe can be used instead of blotter.

EQUIPMENT

OBJECT NEEDS

CONFIDENCE

MATERIALS AND SUSTAINABILITY

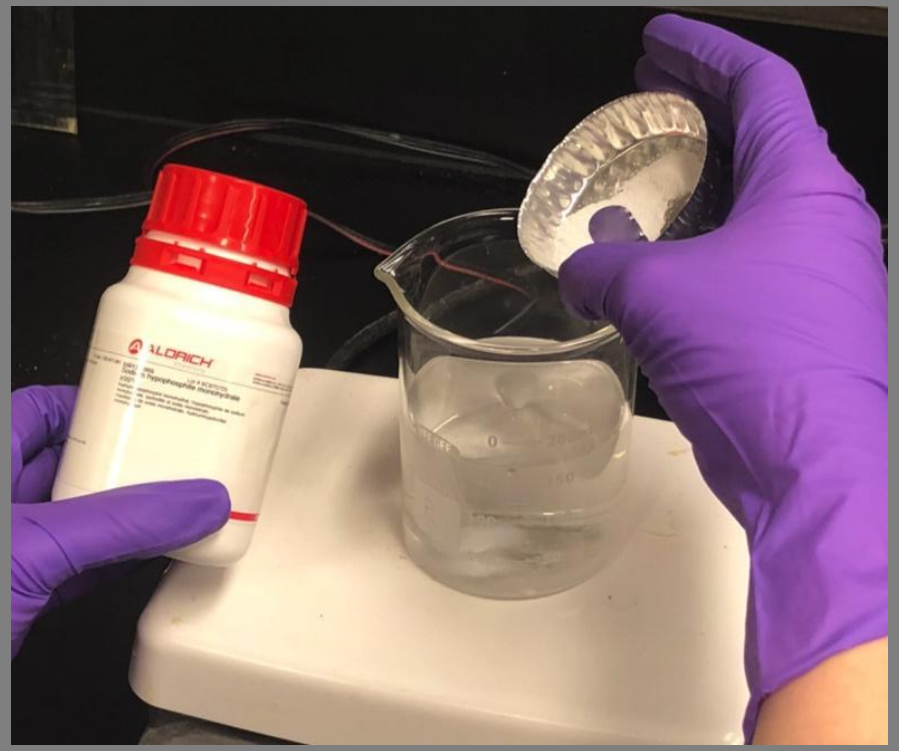
TEK-WIPE

- Requires smaller, more easily available supplies
- Gentler to delicate objects or those with dimensionality
- Conservator has more time to monitor treatment and can safely treat delicate objects
- TEK-Wipe is reusable and thus less expensive than blotter

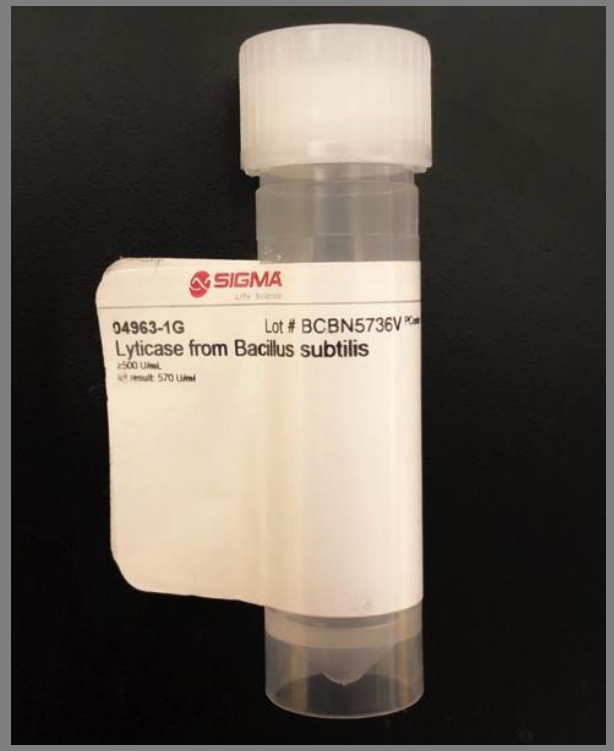
INNOVATIONS

Successful overall aqueous treatment of foxed chine collé

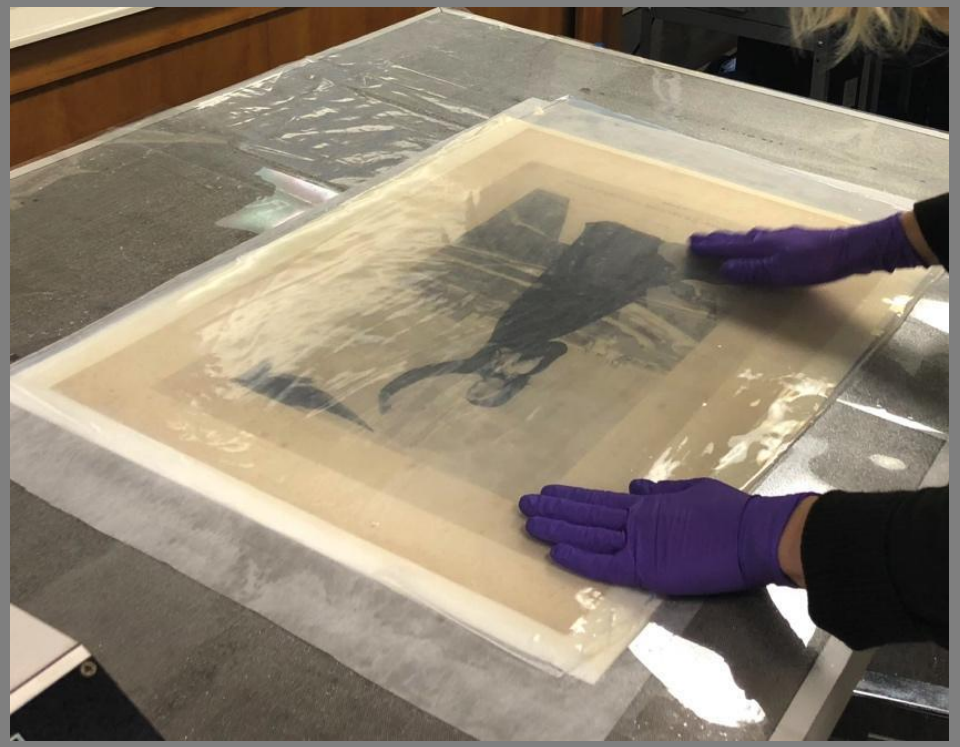
Sodium hypophosphite reducing agent



Lyticase enzyme to lyse fungal cell wall



Use of gel reservoir under suction



FUTURE RESEARCH & APPLICATIONS

Using XRF to detect iron presence

Characterization of Foxing

- XRF with small spot size
- Fluorescent stain for chitin on surrogate

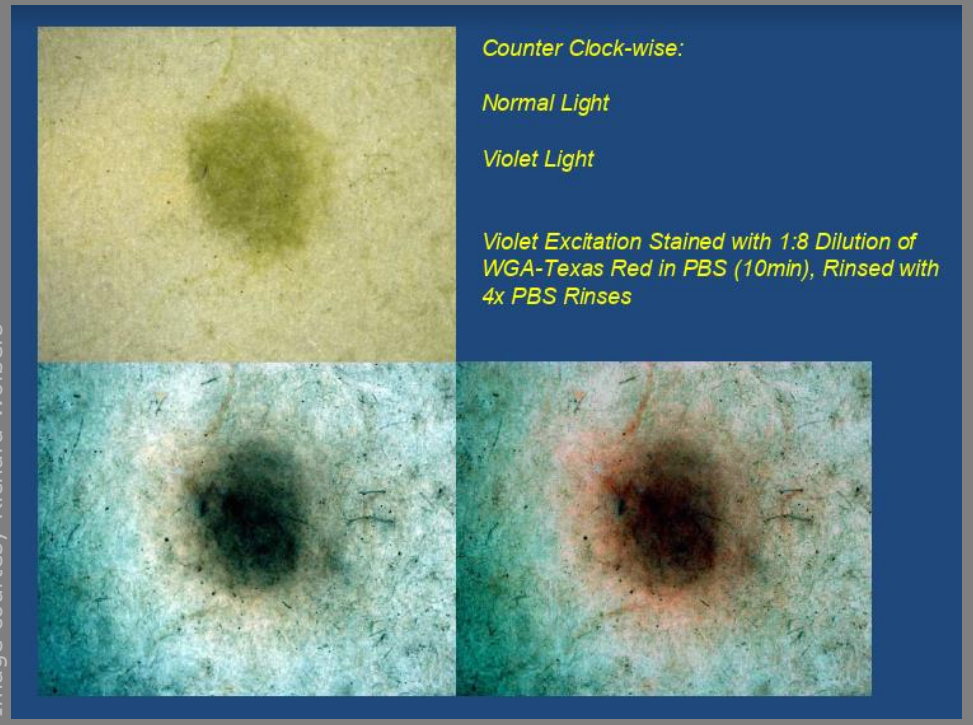
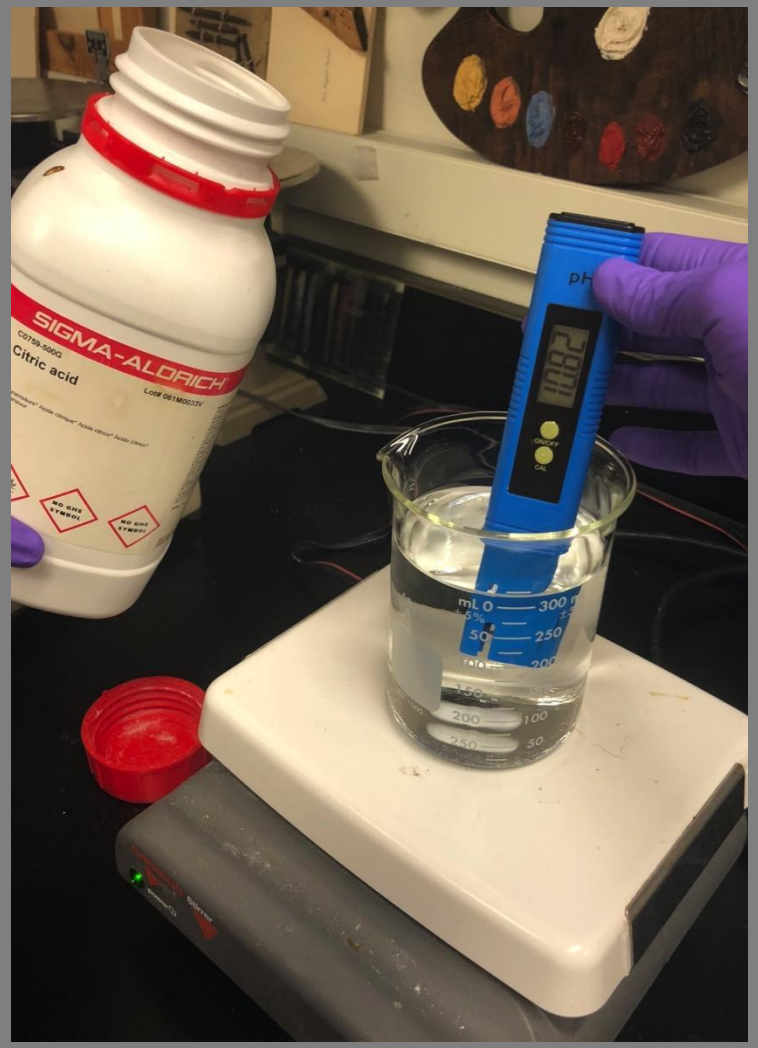


Image courtesy Richard Wolbers

Foxing with fluorescent stains

FUTURE RESEARCH & APPLICATIONS

Full immersion bathing



More materials prep for repeated steps

Treatment Protocol Modifications

- Full immersion bath
- Local gel application on suction table
- Blotter washing
- Use of enzymes with higher activity
- Repeated steps/applications
- Hybrid TEK-Wipe/suction table treatment

FUTURE RESEARCH & APPLICATIONS

Other Analysis

- Residue studies
- Chromatography
- Artificial aging
- Mechanical testing
- Conductivity tests

ACKNOWLEDGEMENTS

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Joan Irving – *Consultant, Major Supervisor*

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Debra Hess Norris – *Director, WUDPAC*

ANAGPIC selection committee

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Dr. Joelle Wickens

Lauren Fair

Lara Kaplan

Barbara Lemmen

Dr. Joyce Hill Stoner

Fran Wilkins

Theresa Slusser

Class of 2019

Amber Kehoe

Keara Teeter

Past Foxing Research

Jacklyn Chi ‘18

Kimi Taira ‘15

Michelle Sullivan ‘15

Yana Van Dyke ‘00

Gels Conference

James Black

Rachel Gallan

Cindy Lee Scott

All the “Gels Angels”

Getty Museum

Michelle Sullivan

ANAGPIC 2018

Queen’s University

All of you!

The Andrew W. Mellon Foundation
The National Endowment for the Humanities
Winterthur/University of Delaware Professional Development Fund