# A Comparison of the Use of Sodium Metabisulfite and Sodium Dithionite for Removing Rust Stains from Paper

# ABSRACT

Rust stains in paper pose an interesting problem for paper conservation treatments. The rust may vary from covering the majority of a paper artifact to as small as a residual stain left by rusted paper clips or staples. Rust, Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O (or FeOOH), is difficult to remove chiefly due to its insolubility in water. Rust is traditionally removed from paper in a series of wet treatments by chemically reducing the insoluble ferric Iron (III) compound to a soluble ferrous Iron (II) compound. It can then be sequestered in water by adding a chelating agent such as EDTA, and repeating the process until the staining has been significantly reduced or eliminated.

Currently, the reduction agent most frequently mentioned in the literature for iron removal is Sodium Dithionite  $(Na_2S_2O_4)$ . It is also sometime called Sodium Hydrosulfite.

Sodium Dithionite has been proven to be effective for rust removal but can present significant practicality problems. MSDS standards label Sodium Dithionite as a hazardous substance: it is extremely flammable and prone to spontaneous combustion. Moreover, its use usually requires treatment to be conducted in a fume hood, which presents complications for oversize artifacts that won't fit in a fume hood. Since Sodium Dithionite is labeled a "Spontaneously Combustible Substance" by the Department of Transportation, it must be shipped by private carriers as hazardous materials freight, significantly increasing its cost.

On the other hand, the reducing agent Sodium Metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), having one more oxygen atom than Sodium Dithionate, is not labeled as a hazardous substance, according to its Material Safety Data Sheet (MSDS). Sodium Metabisulfite is not flammable, does not require hazardous material freight, and the chemical is also far less expensive than Sodium Dithionite. Sodium Metabisulfite combined with EDTA (Ethylenediaminetetraacetic acid) was

shown, in the experiment presented in this paper, to have significant success in removing rust from paper.

The intent of the experiment described in this paper was to compare both reducing agents' ability to reduce and eliminate rust stains from paper. Qualitative results derived from this experiment reveal the benefits and limitations of using each chemical for rust removal from paper. Sodium Dithionite, as expected, proved to be the more effective chemical for removing heavy rust deposits quickly, but its use was found to be significantly limited by cost and safety. Sodium Metabisulfite proved to be significantly safer, lower in cost, and easier to obtain, but was only effective treating light-to-medium rust deposits and required far more time for treatment.

# INTRODUCTION

#### Project History

In April of 2010, the author was brought to the Clausen Memorial Museum on the Island of Petersburg, Alaska as the second museum in a 14-month joint project involving twelve Alaskan museums. This project was organized by Alaska State Museum's Curator of Museum Services, Scott Carrlee, and Clausen Memorial Museum Director Sue McCallum. The project was funded by a generous grant from Alaska's Rasmuson Foundation.

One aim of this project was to conduct conservation treatments on paper artifacts that participating museums deemed high priority. The artifact requested for treatment at the Clausen Memorial Museum, was one of several sheets of paper recovered from a mountaintop along the border of British Columbia and Southeast Alaska called Devil's Thumb, or Boundary Peak 71 (fig. 1). The document contained several sheets, but due to the short time constraints only one sheet, chosen by the director, was selected for treatment.

These sheets were found in a metal can on the mountain, by a local mountain climber from Petersburg. They were part of a climbing log placed on the mountain in 1946 by a well-known mountain climber named Fred Beckey. Graphite inscriptions on the log not only recorded Beckey's first ascent,

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Fig. 1. Sheet of a climbing log recovered from Devil's Thumb Mountain along the border of Southeast Alaska and British Columbia. Graphite text on the paper reveals the inscription of well known mountain climber Fred Beckey dated 1946. Photographer: Dieter Klose. 20.1 cm x 14.8 cm. The Clausen Memorial Museum; Petersburg, Alaska



Fig. 2. Before treatment of the Devil's Thumb climbing log selected for treatment. Severe corrosion stains have penetrated the paper from the metal can the paper was stored in on the mountain. 21.1 cm x 24.9 cm. The Clausen Memorial Museum; Petersburg, Alaska

but also many others who had climbed Devil's Thumb since 1946. This log was therefore considered an important artifact by the museum and the community of Petersburg. Damage to the log was caused by severe iron corrosion staining from the metal can. So much rust had accumulated in the paper that sections of the paper had been replaced by thick deposits of rust (fig. 2).

# Treatment Options for Rust Removal from the Log

The method for rust remediation in paper mentioned most often in the literature is the combination of the reduction agent, Sodium Dithionite ( $Na_2S_2O_4$ ) with the chelating agent EDTA. Sodium Dithionite (S.D.) has been shown mentioned many times in conservation literature to be very effective for removing rust stains. However, S.D.'s acquisition and use could present serious practical challenges for treatment of the log.

The first and most significant obstacle was the cost of S.D.. Many chemical supply companies require a minimum order of 500 grams, which averaged about one third of The Clausen Memorial Museum's annual budget for supplies. Further, The US Department of Transportation (DOT) lists S.D. as a 'Spontaneously Combustible Substance' and assigns it a Hazard Class for transportation of 4.2 (Fisher Scientific Inc. 2011; DOT 2000). Transportation of 'Spontaneously Combustible Solids' by domestic air mail is prohibited (DOT 2011). Since all mail into Petersburg arrives by air transport, getting S.D. would have required a private shipping carrier. This would add even more cost for the chemical. Finally, since sulfur fumes are released by S.D., a fume hood would be required for its use, which was not available at the museum. After exhaustive review, the decision was made to find an alternative approach to remediation of the Devil's Thumb log.

# An Alternative Approach for Rust Removal from Paper Using Sodium Metabisulfite

A new approach to rust removal from paper was suggested to the author by Dana Sullivan, Lab Manager for Bostick and Sullivan<sup>®</sup>, a historic photographic chemical supply company located in Santa Fe, NM.

Addition of one oxygen atom to Sodium Dithionite, yields the chemical, Sodium Metabisulfite  $(Na_2S_2O_5)$ , or S.M.. When S.M. is dissolved in water in separates into sodium bisulfite. S.M. has been used as a reducing agent for many years in the photographic industry to create large quantities of sodium bisulfite for print and film developers. S.M. is also a very popular agent for clearing ferric (Iron II) oxilate developer from historic photographic printing process platinum palladium printing (Boeringa 2010).

Federal regulations classify S. M. as a Hazard Class 8, a chemical defined as a "corrosive with no danger of flammability". Therefore, it is allowed to be shipped through standard mail (Fisher Scientific 2008 Sodium Metabisulfite; DOT 2011). This was also advantageous, because in Petersburg Alaska, shipments by the US postal service tend to arrive faster than shipments by private carriers.

S.M. is much cheaper than S.D., and once dissolved in solution, does not appear to require the use a fume hood. It was also found to be a much safer chemical than S.D (Fisher Scientific 2008, Sodium Metabisulfite). Thus, time, expense, and safety considerations led to S.M. being considered the best option for treatment of the Devil's Thumb Log.

## Treatment of the Devil's Thumb Log

Treatment of the log was carried out over several days with several consecutive baths of 10% S.M. (weight to volume) mixed equally with EDTA (Ethylenediaminetetraacetic acid) to chelate the Iron (II), in purified water. The treatment was observed to have removed most of the rust staining from the paper, and was considered a success by the Clausen Memorial Museum (fig. 3).



Fig. 3. Devil's Thumb climbing log after being treated in several consecutive solutions of equal concentrations of 10% Sodium Metabisulfite to EDTA. 21.1 cm x 24.9 cm. The Clausen Memorial Museum; Petersburg, Alaska

# *Experiment to Compare S.D. Vs. S.M. for Rust Remediation in Paper and the Science of Rust by Reduction and Chelation*

The success of The Devil's Thumb Log treatment with S.M., and the limitations discovered for the use of S.D. motivated further investigation into options for rust remediation in paper artifacts. Once the log was completed an experiment was planned to conduct a side-by-side evaluation of the use of S.D. and S.M. for rust remediation from paper artifacts.

The overall approach to the experiment was to put rust into a series of sample papers. Each sample would then be treated with varying concentrations of S.D. and S.M.. Sideby-side results would be observed and recommendations made for the preferred use of each chemical.

The experiment was designed to observe how effective each chemical is in removing rust from paper and the optimal procedure for its use. Every attempt would be made to conduct the experiment in a manner that could be replicated by/ for conservators. Key results were expected to be: (1) effectiveness in removing rust, (2) amount of chemicals required, (3) amount of time required, and (4) while producing little or no damage to the paper.

Rust stains on paper have always been a difficult problem for conservators for a variety of reasons. Rust, i.e., iron-oxide, is iron existing in a ferric state (Iron III). Ferric iron is not readily soluble in water, and cannot be removed by solvents or by washing with pure water (Selwyn 2008). Consequently, the most effective treatment for removing rust from paper requires a two-step process.

The first step involves reducing the ferric iron (Iron III) to its ferrous (Iron II) state by means of a reducing agent. In a ferrous state Iron (II) is readily soluble in water and can be washed out of paper (Selwyn 2008). This process can be demonstrated by observing how many laundry detergent boosters remove rust stains from clothing. Examination of the MSDS sheets from some of these products shows that they contain both S.M. and S.D. in their ingredients (Summit Brands 2008). Once the Iron (III) has been reduced to Iron (II) it must be removed. The removal of the Iron (II) can often be accomplished by simple washing. Laundry detergents do this by using high volumes of water created by a washing machine to remove the soluble Iron (II). On the other hand, paper treatments are generally conducted in trays of still water. A high-volume wash using large quantities of water can be used to remove residual Iron (II) from the water, but the process is slow and this runs the risk of residual Iron (II) being left in the water (AIC 1992 13-22).

Therefore, an alternative method of removing the soluble Iron (II) is needed, because any Iron (II) left over in the water will eventually oxidize back into Iron (III), potentially producing a new stain (AIC 1992 13–22). This is where the use of a chelating agent becomes essential to the process. Chelating agents serve to complex or sequester Iron (II) molecules in water so that those molecules can be washed away

more easily. In conservation literature, one of the more popularly recommended combinations for this process uses S.D. as the reducing agent and EDTA as the chelating agent (AIC 1992 13–22).

The chemical reaction that occurs when S.D. is used in this manner is essentially a two-part reaction. First, Sodium Dithionite (S.D.) dissolves fairly easily in water. When this happens the S.D. disassociates into Sodium Bisulfite (Na2S2O5), and Sodium Bisulfate (NaHSO3). The Sodium Bisulfite will then cause the ferric Iron (III) from the ironoxide to reduce to a soluble ferrous Iron (II) state. The Iron (II), then in a soluble form, can be sequestered by the EDTA and washed away (Shurvell 2011) (fig. 4).

S.M. [Sodium Metabisulfite  $(Na_2S_2O_5)$ ] also dissolves fairly easily in water. When it dissolves, it disassociates into sodium bisulfite. During this process a small amount of sulfur dioxide is released. Some of the sulfur dioxide will then combine with water molecules to create Sulphurous acid  $(H_2SO_3)$  which then disassociates, yielding hydrogen ions. The sodium bisulfite initially created from the disassociation of the S.M. causes the reduction of ferric Iron (III) from the iron-oxide to a soluble ferrous Iron (II). The soluble ferrous Iron (II) can then be sequestered by the EDTA and washed away (Shurvell 2011) (fig. 5).

# SODIUM DITHIONITE

- $1) \underbrace{Na_2S_2O_4 + 3H_2O}_{\text{(sodium diffionte)}} \rightarrow \underbrace{NaHSO_4 + NaHSO_3}_{\text{(sodium disulfate)}} + 4H^+$
- 2) NaHSO<sub>3</sub> + Fe<sup>3</sup>  $\rightarrow$  NaHSO<sub>4</sub> + Fe<sup>2+</sup> sodium bisulfite will react with insoluble ferric iron (fe<sup>2</sup>) in the iron oxide and reduce it to a soluble ferrous iron (fe<sup>2+</sup>)

Fig. 4. Chemical reaction for Sodium Dithionite

# SODIUM METABISULFITE

- $\begin{array}{c} 1) \ Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \\ {}_{\text{SODIUM METABISULFITE}} \qquad \text{SODIUM BISULFITE} \end{array}$
- 2)  $2NaHSO_3 \rightarrow 2SO_2 + H_2O + 2Na^+$ some so<sub>2</sub> is released into the air
- 3)  $SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow HSO_3 + H^+$ some SO<sub>2</sub> will react with H<sub>2</sub>0 to produce sulphurous acid which dissocrates to give hydrogen ion
- 4)  $2NaHSO_3 + Fe_2O_3 + 2H^+ \rightarrow 2NaHSO_4 + H_2O + 2Fe^{2+}$ Sodium bisulfite will react with insoluble ferric iron (Fe<sup>3</sup>) in the iron oxide and reduce it to a soluble ferrous iron (Fe<sup>3</sup>)
- Fig. 5. Chemical reaction for Sodium Metabisulfite

EXPERIMENTAL EVALUATION OF THE EFFECTIVENESS OF REMOVING RUST FROM PAPER BY REDUCTION AND CHELATION

#### Paper Selection

Selection of sample papers for the experiment attempted to replicate the types of paper found in most libraries, archives, and museums. Fourteen samples were chosen for this experiment. Five samples were selected from a variety of modern papers; one paper was dated from the 1930's; one paper was dated from the 1940's; two papers were dated approximately twenty to forty years; and five were dated early- to mid-19th century.

The source of rusted metal used for this experiment had to come from a metal source that was commonly associated with paper, e.g., found in libraries, archives, and museums. It was assumed that the most common forms of metal found among this type of paper artifacts are paper-clips and staples.

Consequently, metal paper clips were selected to be used to create rust stains in this experiment. However, preliminary tests revealed that modern paper-clips do not rust easily. The appropriateness of testing modern paper clips with historic paper was also called into question. These problems were solved by purchasing several boxes of early 20th Century paper-clips from E-Bay<sup>®</sup> (fig. 6).

#### Sample Preparation

Each of the fourteen paper samples was prepared by dividing it into nine sections that were 1 inch by 3 inches in size. Two paper clips were placed on seven of the nine sections. One section was used as a control, and received no rust or wet treatment during the experiment. One section was to have rust put on it and left alone as an experimental control. To eliminate the variable of the lightening caused by the act of



Fig. 6. Gem No.1 vintage paper clips, estimated seventy to eighty years old, purchased on E-Bay® to be used for creating rust in paper samples



Fig. 7. Preparation of the sample section before rusting: Two vintage paper clips were placed on seven sections. One section was used as a 'Rust Control' and would also eventually also be used as a 'Rust/Wash Control'. Three sections were treated in 2.5%, 5%, and 10% solutions of equal percentages of Sodium Dithionite to EDTA, and three sections were treated in 2.5%, 5%, and 10% solutions of equal percentages of Sodium Metabisulfite to EDTA. Paper clips were not used on two sections. One of these sections was designated as a water-only 'Wash Control', and one was kept from all treatment as a 'Pure Control'



Fig. 8. To cause severe rust to occur on the paper-clips, all of the sections were hung on a rods suspended in plastic containers, and all of the sections were submerged twice a day in water for fourteen days



Fig. 9. Detail of a sample section after both rusted paper clips were removed

washing historic paper, one sample section was designated as a wash control.

Of the remaining six sections, three were to be treated with the same proportions of S.D. to EDTA at 2.5%, 5%, and 10% concentrations. The remaining three sections were treated with the same proportions, but with S.M. instead of S.D. (fig. 7).

It is important to note that for this experiment, each of the solutions of reducing agents contained EDTA. However, literature suggests that EDTA does not need to be in the solution with the reduction agent. Rather, the treatment in reduction solutions may be followed by a separate solution containing the same percentage of EDTA.

Once the samples were prepared, each of the sample sections was hung on rods by clips and placed into sealed plastic bins. Twice a day over a two-week period, the samples were placed into fresh water and re-hung. This procedure ensured that the paper-clips were thoroughly rusted (fig. 8).

After two weeks, the samples were removed from the bins and allowed to dry. The paper-clips were manually removed by prying them apart, and each of the sample sections were photographically documented (fig. 9). It was observed at this stage that every paper-clip created a different quantity of rust, even among paper-clips originating from the same box.

Quantifying the amount of rust created by each paper-clip would have required a precise analytical balance to measure the changes in weight created by the rust. Unfortunately, such a balance was not available for this experiment, and it was determined that visual results would have to suffice. RUST CONTROL

Fig. 10. In order to prove that rust cannot be removed by a water treatment alone, the 'Rust Control' was cut in half lengthwise. The bottom section shown in the image was kept in a continuous water bath for 48 hours. No change in the amount of rust was observed, after a water only treatment, in any of the fourteen samples

#### Sample Treatment and Measurement Control

To observe how much rust could be removed from the sample papers with just water, the section designated as the rust control was cut in half lengthwise across the two paper clips stains. One half of the rust control was placed in water for a 48 hour period (fig. 10). This step was essential to prove that the iron-oxide rust accumulated on the sample sections was not water-soluble and that the rust could not simply be washed away.

Following the treatment of the rust control, the remaining sample sections were treated in their appropriate solutions. The pH of each solution was monitored when it was freshly made and after each treatment was completed. The time required for each reducing agent to remove the rust from the paper, within the time allowed, was also logged. All samples were limited to a maximum treatment time of 48 hours.

# Test Results

The plan for this project included use of analytical methods that were easy to replicate, easy to understand, and available at low cost. For this reason, testing procedures were based chiefly on visual observations and use of a digital pH meter to monitor the changes in the solutions. Results were recorded from digital photographic images taken before the papers were exposed to rust, after the paper was exposed to rust, and after the rust was removed. Based on these results, each of the two reducing agents appeared to have had the effects discussed below.

Sodium Dithionite: Initial observations of iron removal/ reduction from the Sodium Dithionite solutions were the removal of all of the visually detectable rust deposits in every sample section treated. The 10% and 5% solutions of Sodium Dithionite removed all the rust in about 4 to 6 hours and only required one bath for complete removal of the rust from the paper. The 2.5% solutions took about 8 hours and required a second bath to completely remove all of the rust (figs. 11–12).

Sodium Metabisulfite: Sodium Metabisulfite solutions yielded different and significantly poorer iron removal results than was observed for Sodium Dithionite. Observations of all fourteen Sodium Metabisulfite sample sections revealed significant lessening of the rust staining, but complete rust removal occur did not occur in any of the fourteen sample sections. The Sodium Metabisulfite removed all but the thickest part of the rust deposits. The 10% solutions of Sodium Metabisulfite required three bath changes in a twenty-four hour period to achieve significant stain reduction. After twenty-four hours, the rate at which the reducing agents were dissolving the rust appeared to slow down or stop. The samples treated in the 5% and 2.5% solutions appeared to have the same results, but required a forty-eight hour period (figs. 13–14).

## ADDITIONAL OBSERVATIONS

Solutions of Sodium Metabisulfite appeared to be stable at room temperature with concentrations of 10% and lower. However, at solutions higher than 10%, a chemical change was observed that appeared to change the solution into a milky white substance resembling white glue. The rate at which this change occurred appeared to accelerate with an increase in the concentration of both the S.M. and the EDTA. No further testing was conducted on this phenomenon and the nature of the white substance was not identified (fig. 15).

Rust in the S.M. solution appeared to dissolve into the solution turning the solution a deep yellow, while the rust in the S.D. solutions appeared to separate from the paper resulting in small black pieces of metal at the bottom of the tray (fig. 16).

All of the non-modern paper samples showed significant lightening from both Sodium Dithionite and Sodium Metabisulfite chemicals, to a very similar degree. pH readings before and after treatment also revealed interesting results. The starting pH, measured by a digital pH meter, for all of the S.D. samples was about a 9.0. After the paper was removed from each bath the pH was found to be between 5.0 and 6.0.. This was common for all 14 samples tested with the S.D.. The starting pH for all S.M. sample sections was about a 6.5 when the solutions were made. After completion of each bath it was found that the pH appeared to drop by only about 0.3. For some samples it was less than 0.1.. None of pH readings for any of the S.M. samples dropped below 6.0.



LEFT TO RIGHT

Figs. 11–12. The left column shows each section at each percentage before the experiment began. The center column shows each and section after the paper-clips were rusted on the paper. The right column shows each of the sections after treatment with Fig. 12 the Sodium Dithionite. The visual results observed in all fourteen samples treated with Sodium Dithionite is the complete elimination of all of the rust from each sample at all three concentrations



LEFT TO RIGHT

Figs. 13–14. The left column shows each section at each percentage before the experiment began. The center column shows each and section after the paper-clips were rusted on the paper. The right column shows each of the sections after treatment with Fig. 14 the Sodium Metabisulfite. Observe in Fig. 11 and Fig. 12 the difference between the quantities of rust in each paper-clip stain. Results observed visually with samples treated with Sodium Metabisulfite, showed significant reduction in the light to medium rust stains



Fig. 15. Concentration of Sodium Metabisulfite and EDTA above 10% will change into a solution resembling white glue with a high viscosity. The rate of the change will depend on the concentration. The higher of the solution the faster the change occurs, ranging from several minutes to several hours

#### CONCLUSIONS

Rust stains in paper pose a difficult problem for conservators, as they cannot be removed using a simple washing procedure. To convert Iron (III) oxide (rust) into a soluble form, it must be reduced to a soluble Iron (II) state. Once this change has occurred the Iron (III) can then be sequestered by a chelating agent and washed away. Historically the chemical combination recommended for this was the use of Sodium Dithionite with EDTA. (Selwyn 2008) Sodium Dithionite has been proven throughout conservation literature to be effective for removing rust stains. However, its use presents significant hurdles related to cost, transit, and safety in use. This experiment dealt with the introduction of an alternative reducing agent called Sodium Metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>).

Sodium Metabisulfite does not have many of the handling and usage problems that Sodium Dithionite has. Sodium Metabisulfite is also significantly safer, lower in cost, and easier to obtain. The objective of this project was to compare the



Fig. 16. Small black pieces of metal appeared at the bottom of the tray with sections treated with Sodium Dithionite. This observation was contrary to the corresponding sections treated with the Sodium Metabisulfite where the reduction of the rust caused the treatment solutions to turn a deep yellow color

effectiveness of Sodium Metabisulfite vs. Sodium Dithionite in removal of rust from paper.

Based on visual results from the experiment, as well as the time required for each chemical to show maximum effectiveness, the author was able to make several recommendations as to when the use of each chemical would be most appropriate. Additional factors in the following recommendations are the cost of each chemical and safety issues.

As expected, Sodium Dithionite proved to be very effective in removing rust stains, successfully removing all visually observed rust from every sample tested. Sodium Dithionite might be the appropriate reducing agent for heavy rust deposits. Sodium Dithionite would also be the recommended reducing agent if treatment time is an important factor. Results of this experiment revealed that rust remediation with Sodium Dithionite will most likely be significantly faster than with Sodium Metabisulfite, saving from 18 hours to 24 hours of wet treatment time.

Sodium Metabisulfite was also observed to be effective at removing rust stains especially for light-to-medium stains. There are several circumstances where a conservator might favor Sodium Metabisulfite over Sodium Dithionite. One such occasion might be the cost of the chemicals. Sodium Metabisulfite currently costs about \$12 to \$15 for 1000 grams (Bostick and Sullivan® 2011), although smaller order quantities are possible. It might be a more logical choice for occasions where the cost of the chemistry would prevent the desired treatment from happening. This is especially the case if the stain was only a light to medium rust deposit. Based on current prices, the cost of Sodium Metabisulfite for a threebath treatment is approximately half the cost of the Sodium Dithionite for one bath (Bostick and Sullivan 2011; Fisher Scientific 2011). This does not include the additional cost of the hazmat shipping or the EDTA.

The quantity of rust is also a factor. Based on visual results from the experiment, Sodium Metabisulfite will only be effective on light-to-medium rust stains. If treatment time were not a concern and adequate ventilation was not possible, Sodium Metabisulfite might be the more appropriate chemical for the treatment. The conclusions would suggest that preliminary treatment with Sodium Metabisulfite might be beneficial. If any rust were still present after treating with the Sodium Metabisulfite, a follow up treatment with Sodium Dithionite may be used to remove any remain rust.

Finally, for Sodium Dithionite to be used properly proper ventilation is required due to the sulfur fumes the chemical releases. This means that treatments will need to be conducted in a fume hood. While most labs do have fume hoods, many smaller labs and private practices do not. This may present problems when larger artifacts won't fit in a fume hood. If an oversize treatment was being conducted that required filling a sink with Sodium Dithionite, the use of some form of 'oversink' extraction system would be strongly recommended. It was observed throughout this experiment that any fumes released by the Sodium Metabisulfite were barely detectable. According to current MSDS Sodium Metabisulfite carries no significant risk, and is not considered highly hazardous by OSHA (Fisher Scientific 2008 Sodium Metabisulfite).

The author's opinion is that Sodium Metabisulfite, as a powder should be handled with proper care and with good ventilation, but once in solution would not require the use of a fume hood. This would suggest that Sodium Metabisulfite might be a good starting point for attempting to remove rust from oversize material.

Finally, one benefit of Sodium Metabisulfite is its ability to be shipped as a 'non-hazardous' material. This would further decrease the cost of the chemical when compared to Sodium Dithionite by allowing shipment through standard mail.

This project was conducted with sample sections that were only 1 inch x 3 inches, and therefore only 100 milliliters was used for each solution in this experiment. This means that at the highest concentration of 10%, only 10 grams of each chemical were used per sample section. From a practical standpoint, most treatments require solutions of far greater quantity than 100 milliliters. To conduct a treatment on a normal scale would typically require at least one liter of solution to fill a tray. To put this in perspective, conducting a treatment with a 5% solution of Sodium Dithionite, for one liter, would require 50 grams of Sodium Dithionite. Based on the current cost of Sodium Dithionite this would be about \$8 for 1 liter of a 5% bath (Fisher Scientific 2011). This figure does not include the cost of the EDTA or the additional cost of the Haz-Mat shipping required to acquire the chemical. If a larger artifact required a solution of ten liters to fill a large tray or sink and using 500 grams of Sodium Dithionite, the cost of the Sodium Dithionite for one bath is now about \$80.

#### ADDITIONAL PRECAUTIONS

Both reducing agents react specifically with iron compounds which are present in many forms of media. Many pigments and inks, such as iron gall ink, contain iron in their composition. Testing before treatment is strongly recommended for ink solubility and for the paper's ability to handle extended washing times. It is very important to follow the treatment of either reducing agent with thorough washing to remove remaining any remaining chemicals. In addition, if EDTA was not added from the beginning, several baths of EDTA should follow either reduction bath. If any nonsequestered Iron (II) is left in the solution following the reduction bath, the Iron will re-oxidize back to its Iron (III) state somewhere else on the paper possibly producing a new stain (AIC 1992 13–22).

It should be stressed that Sodium Dithionite is very hazardous, and it absolutely must be used in either a fume hood or with some form of adequacy ventilation (Fisher Scientific 2008 Sodium Dithionite). Without proper ventilation Sodium Dithionite will create a severe safety hazard by making an entire room smell of sulfur in a short period of time. In addition, Sodium Dithionite dust is also very flammable (Fisher Scientific 2008 Sodium Dithionite). Proper safety gear should always be worn. As with all experiments more research is obviously required. Sodium Metabisulfite is a relatively unused and unknown chemical in paper conservation and this experiment was conducted under the limitations of minimal analytical equipment. It is possible that far more precise results may be possible with the repetition of this experiment with analytical equipment that could detect trace amounts of Iron. More research is required for a greater understand of its potential for conservation in the future.

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# REFERENCES

- AIC, Book and Paper Group. 1992. *Paper Conservation Catalog.*9th ed. American Institute for Conservation Book and Paper Group. Washington, D.C.: AIC. Chapter 13. Pg 22
- Boeringa, M. Ware, M. 2010. The Longevity of Platinum and Palladium Prints, A Synopsis. Alternative Photography. http://www.alternativephotography.com/wp/post-printing /longevity-of-platinum-and-palladium-prints
- Bostick and Sullivan. 2011. Sodium Metabisulfite. Santa Fe, NM
- Department of Transportation. 2009. Hazardous Materials Table. Title 49 CFR 172.101. October 16.
- Department of Transportation. 2011. Domestic Mail Manual. US Postal Service. June 6
- Department of Transportation. Emergency Response Guidebook. 2000. Hazard Classification System. www .nh-tems.com/documents/.../HAZMAT\_Document\_2 .pdf (Accessed 26/06/2011)
- Fisher Scientific. 2008. Material Safety Data Sheet. Sodium Metabisulfite. ACC# 21001. September 16. Fairlawn, NJ http://fscimage/fishersci.com/msds/21001.htm (Accessed 26/06/2011)
- Fisher Scientific. 2008. Material Safety Data Sheet. Sodium Hydrosulfite. ACC# 01503. July 29. Fairlawn, NJ. http://fscimage/fishersci.com/msds/01503.htm (Accessed 26/06/2011)
- Fisher Scientific Inc. 2011. Sodium Dithionite. Price Sheet. Sugarland, Texas
- Hazardous Materials Transportation Guides. 1991. US Department of Transportation. February 1991. Chapter

1. Pg 4. http://ntl.bts.gov/DOCS/hmtg.html (Accessed 26/06/2011)

- Summit Brands. 2008. Material Safety Data Sheet. White Brite®, Yellow Out. #7845. August 22. Fort Wayne, IN
- Selwyn, S., and Tse, S.2008. 'The Chemistry of Sodium Dithionite and its Use in Conservation', IIC Reviews in Conservation Number 9 2008
- Shurvell, Gus. 2011. Personal Communication. Department of Art Conservation, Queen's University, Kingston, Ontario.
- Spectrum Chemical Inc. 2011. Sodium Dithionite. Price Sheet. New Brunswick, NJ

#### FURTHER READING

- AIC Book and Paper Group, 'Chapter 13: Foxing', in *Paper Conservation Catalog*, 9th edn, American Institute for conservation of Historic and Artistic Works, Washington, DC (1994)
- Cripps, C., A Comparison of Various Chelating Agents and their Effectiveness in Removing Iron Stains from Linen and Cotton, Art Conservation Program, Queens University, Kingston (1994)
- Gent, M., and Rees, J., 'A conservation treatment to remove residual iron from platinum prints', *The Paper Conservator* 18 (1994) 90–95.
- Hawley, J.K., Kawai, E.A., and Sergeant, C., 'The removal of rust stains from arctic tin can labels using sodium hydrosulfite', *Journal of the International Institute for Conservation Canadian Group* 6 (1981) 17–24.
- Lockwood, K., 'The effectiveness of selected chelate-reducing agent systems in the removal of iron stains from paper', in Art Conservation Training Programs Conference, Harvard University Art Museums, Cambridge (1984) 87–100.
- MacKay, A., The Effectiveness of Selected Chelating Agents and Sodium Dithionite in the Removal of Rust Stains from Cotton, Art Conservation Program, Queens University, Kingston (1992) unpublished report.
- Prytulak, G., Optimum Conditions for the Removal of Iron Stains from Marble, Paper and Wool Using the Sodium Dithionite: Sodium Tripolyphosphate System, Art Conservation Program, Queens University, Kingston (1985)
- Smith, B.L., A Study of Iron Stain Removal using Two Selected Chelating Agents (EDTA and STPP) and Sodium Dithionite, Art Conservation Program, Queens University, Kingston (1994)
- Suryawanshi, D.G., and Bisaria, S.K., 'Removing metallic stains from paper objects using chelating agent EDTA', *Restaurator* 26 (2005) 276–285.

SETH IRWIN

Paper conservator in private practice Houston, TX sethai@aol.com