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Study on Removal of Iron Rust from Paper Objects with Thiourea Dioxide

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Abstract. There are many paper-based documents, archives and books contaminated by iron rust beacuse they were fixed with iron staples or clips. Iron rust not only disfigures the paper, covers the writtings or images of paper, but also makes paper brittle. Iron rust is very difficult to remove due to its insolubility in water and organic solvents. Thiourea dioxide(TDO), an agent with strong reducibility, easy accessibility, stability and safety was applied to remove iron rust in this work. The concentration of TDO solution, iron rust removal effect and removal rate were studied. The results showed that TDO was an effective and safe agents to remove iron rust from paper documents. The concentration was higher, the removal speed was faster. But to get high concentration, TDO need to be dissolved at higher temperature which is damage to paper. In view of the above facts, the proper treatment bath was 5% at 40℃. Results also showed that the combination of 5% TDO and EDTA can remove iron rust from paper completely in 4 hours.

1. Introduction

There are many paper-based documents, archives and books fixed with staples or clips. The composition of these staples and clips are iron usually. So the paper is easy to be rusted under high humidity (Fig. 1). The iron rust not only disfigures the paper, but also makes paper become brittle.

Therefore, the effect removal of the iron rust is always an interesting problem for the paper conservators.

Iron rust, $Fe_2O_3 \cdot H_2O$ (or FeOOH), is difficult to remove due to its insolubility in water and organic solvents. As reported in literatures[1-3], the effective way to remove it from paper is using the reducing agents to reduce the insoluble ferric iron (III) compound to a soluble ferrous iron (II) compound. Then the colorless ferrous iron is washed away with chelating agent in case it be reoxidized by atmospheric oxygen back to the colored ferric compounds. And it also mybe catalyze oxidation of cellulose, which has been mentioned in many literatures about the iron gall ink corrosion [4-6].

Fig. 1 The documents contaminated with iron rust

The reduction agent most frequently mentioned in the literatures for iron rust removal is Sodium Dithionite ($Na_2S_2O_4$), also called Sodium Hydrosulfite. It has been proven to be effective for iron rust removal but has significant practicality problems. It is extremely flammable and prone to spontaneous combustion. According to the problems of Sodium Dithionite, another reducing agent, Sodium Metabisulfite ($Na_2S_2O_5$), was brought forward to remove the rust from paper [7]. Sodium Metabisulfite has three advantages than Sodium Dithionate (1) one more oxygen atom,(2) not labeled as a hazardous substance according to Material Safety Data Sheet (MSDS), and (3) more cheaper than Sodium Dithionate. It was observed to be effective at removing rust stains especially for light-to-medium stains, but it took a long time from 24 to 48 hours because of its weak reducibility. So the reducing agent with strong reducing and safety to the environment is an urgent need for the paper conservator.Thiourea dioxide (TDO, $CH_4N_2O_2S$), due to its strong reducibility, easy accessibility and stability, has been widely used in the field of textile printing, paper, photographic and leather processing industries. The reduction process generates sodium sulfite and urea which are easy to manage since these are common commercial wastes. Although TDO has been widely used as strong inducing and environmentally friendly regent in industry, it has never been reported to be applied in paper restoration. This paper will study on the effect of TDO on removal iron rust from paper.

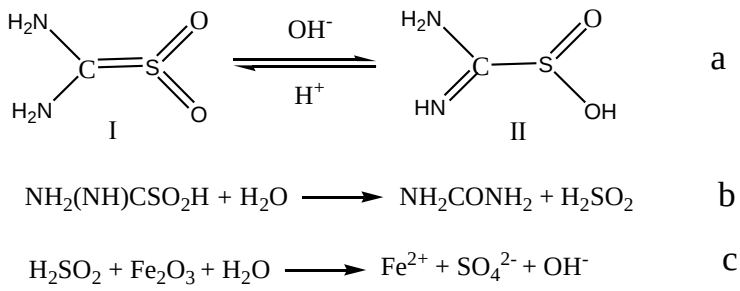

Fig. 2 Thiourea dioxide reaction at alkali or high temperature (a,b) and reaction with iron rust (c)

TDO has two kinds of tautomers in the experimental solution (Fig. 2 a). Under acidic conditions, TDO mainly exists in the form of isomeri. Under basic conditions or at high temperatures, TDO exists in the form of isomer II [8]. In fact, TDO appears terrifically stable at 20–30°C in solution. However, when it is heated or catalyzed by alkali, it decomposes rapidly to produce sulfoxylic acid and urea（Fig . 2 b). Sulfoxylic acid, act as a strong reductant, can react with iron rust-Fe_2O_3 to reduce the insoluble ferrici iron (III) to soluble ferrous iron (II) (Fig.2 c). This paper will try to find the effect of TDO removing iron rust from paper, and the proper concentration to be used.

2. Experimental

2.1. Samples preparation

The paper from a modern notebook was selected for the preparation of paper samples with iron stain. The paper clips, bought from a local stationery shop (Fig. 3), were used to fix the paper. A desiccator with some water at the bottom was used to form high relative humidity (Fig.4 c).

The paper samples were divided in the size of 2.5cm to 7.5cm and fixed with the clips (Fig.4 a). Then they were put on the plate of the desiccator(Fig.4 b) and the desiccator was sealed(Fig.4 c). One month later. heavy iron rust were formed on the papre samples. Then the clips were removed away from the samples and the samples were dried in the atmosphere (Fig.4 c).

Fig. 3 Paper clips

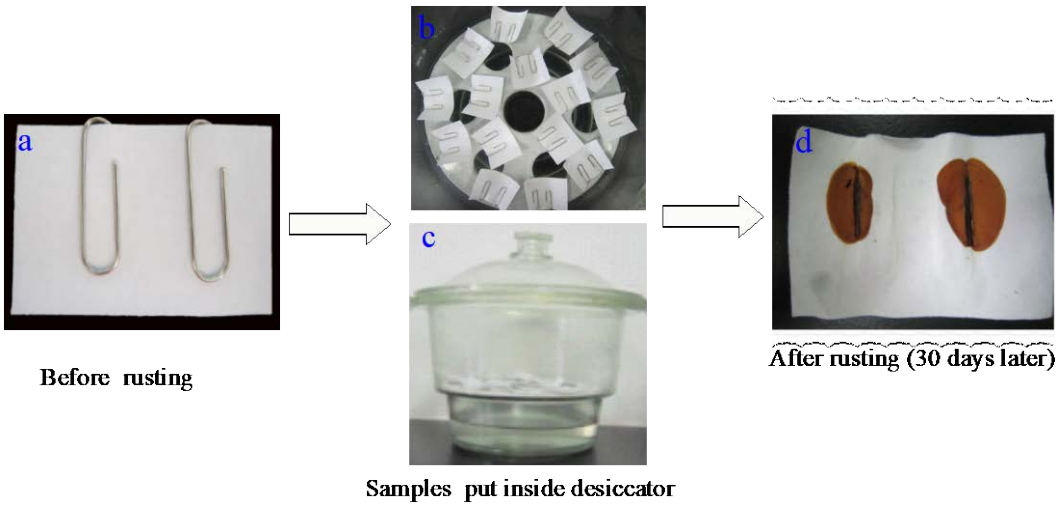

Fig.4 The process of samples rusted

2.2. TDO solutions preparation

The solubility of TDO in water is poor. At 20℃, the solubility is approximately 3%. But with the increasing of temperature, the solubility is increasing too. 2.5%, 5.0%, 7.5% and 10.0% TDO solutions were prepared at 25℃, 40℃, 60℃ and 70℃ separately.

2.3. EDTA+TDO solution preparation

2.5g EDTA was added in the 5.0% TDO solution.

2.4. Iron rust removal

The paper samples were kept in the above TDO solutions and TDO+EDTA solution at 40℃, to avoid the precipitation of TDO in high concentration. Then they were washed by water.

2.5. Determination of iron content

The Thermo Scientific Niton XL3t handheld X-ray fluorescence (XRF) analyzer was used to determine the amount of iron in the paper before and after treatment with TDO+EDTA solution.

2.6. The tensile strength of paper

The tensile strength of samples before and after with TDO+EDTA solution was tested by the tensile test machine.

3. Results and discussion

3.1. The influence of TDO concentration on the iron rust removal

Fig. 6 shows the process of samples treated with different concentration TDO solutions. Within10 mins, the iron rust removal speed of the samples immersed in the higher concentration was faster than the samples immersed in the lower concentration. But after 30 min, the above TDO solutions, except 2.5%, had almost the same effect on removal of iron rust. The removal speed of all the samples slowed down after 30 min. There are three possible reasons: (1) The unremoved iron rust after 30 mins was on the tightest touching part of clips and paper, so the amount of iron rust on which part was the highest. It was also the most difficult part to remove. (2) The concentration of TDO solutions was decreased after 30 mins due to their reaction with iron rust. (3) The high concentration of TDO solutions did not improve the removal speed because some amount of TDO was precipitated during the process due to low temperature.

So if the samples are immersed into the unused TDO solutions for several times, the removal consuming time will be shorten greatly. For example, it has been proved that it only took 1.5 hours to remove iron rust from the sample with 5% TDO bath when the TDO solution was changed every 30 minutes.

3.2. The influence of EDTA on the iron rust removal

Fig.7 shows the samples before and after treatment with EDTA+TDO solution. EDTA can chelate Fe^{2+}, which produced during the reaction of TDO and iron rust, and keep most of the Fe^{2+} retain in the solution. It also showed that EDTA can increase the removal speed. The iron rust can been removed completely in 4 hours with the combination of TDO and EDTA, which shorten the removal cosuming time greatly. The possible reason is that EDTA chelating with Fe^{2+} reduced the concentration of iron in the samples and promoted the reaction remove to right direction faster (Fig.4 c).

3.3. The effect of TDO removal iron rust

The iron content in the samples was detected by portal-XRF (Table 1). The results show that the content of the iron in the samples before treatment was about 90%. It decreased to around 30% after treatment with EDTA+TDO solution, which was about the same concentration of the iron in the samples without iron rust. This indicates that the iron rust has been removed completely.

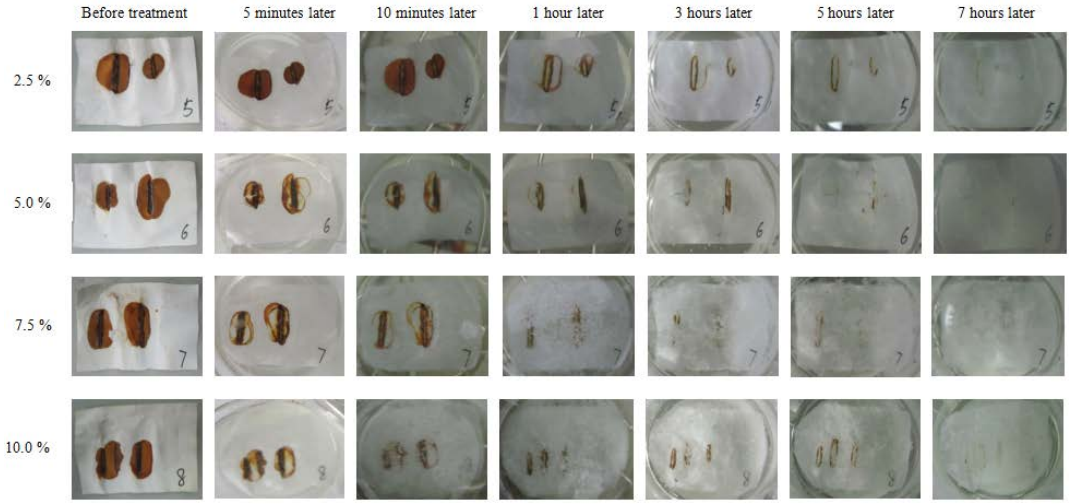

Fig. 5 The process of samples treated with different concentration TDO solutions(from up to down2.5%, 5.0%, 7.5%, 10.0%) in 7 hours (from left to right: before treatment, 5 minutes later, 10 minutes later, 1 hour later, 3 hours later, 5 hours later and 7 hour later)

Fig.6 The samples before and after treatment with EDTA+TDO solution

3.4. The tensile strength of paper treated with TDO+EDTA

Table 2 shows the tensile strength of samples before and after treated with EDAT+TDO solution. There was a slight decrease of the sample treated with EDAT+TDO compared with the untreated samples.

Table 1 The iron content in the samples before and after treatment

Sample	Before treatment(%)	After treatment (%)
Iron rust sample	89.388	31.706
Control sample	34.830	32.596

Table 2 The tensile strength of the samples before and after treatment

	Before treatment	After treatment
Tensile strength (kN/m)	1.036	1.014

4. Case study

The documents were written in 1949 by some famous artists from a private collection. Since these documemts were fixed with clips, iron rust was formed on the surface of the paper seriously (Fig. 7 a).

A small area of iron rust (Fig. 7 b) was treated with 5% TDO+EDTA solution. After treatment, the iron rust was removed completely (Fig. 7 c).

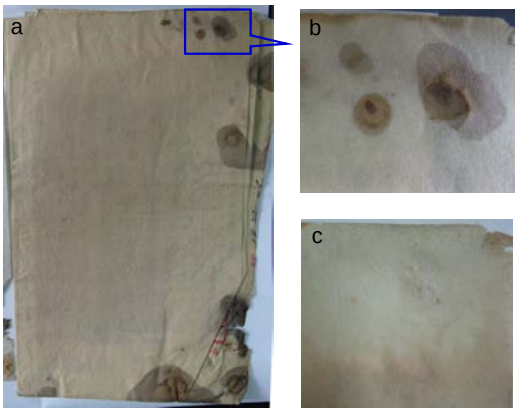

Fig. 7 (a) The original document, (b) before treatment, (c) after treatment

5. Conclusion

In this work, Thiourea dioxide has been employed to remove iron rust from paper objects.The results show that TDO was an effective and safe reducing agents to remove iron rust from paper documents. The TDO concentration was higher, and the removal speed was faster within 30 mins. But the higher concentration needs to be dissolved at higher temperature, which is damage to paper. Low temperature caused the precipitation of TDO and reduced the effect of removal. The low concentration of TDO solution (2.5%) could not remove the rust completely. So the proper TDO concentration solution was 5% at 40℃. The combination of TDO and EDTA improved the removal speed greatly. In addition, the tensile strength of sample treated with EDTA+TDO had a slight decrease, so the treatment of brittle paper with EDTA+TDO should to be very carefully.

Acknowledgements

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