Foxing and Reverse Foxing: Condition Problems in Modern Papers and the Role of Inorganic Additives

ABSTRACT

Works of art on modern papers are known for their conservation treatment challenges. Many do not respond predictably to typical conservation treatment procedures. Stains and discoloration that have been successfully addressed will reappear, in some instances, almost immediately after treatment. An ideal, or successful, treatment begins with a knowledge of materials and the chemical reactions that cause condition problems. However, because of omissions in theory, paper conservators may lack accurate information about the complexity of the works of art in their care.

We may lack information in part because our field has adopted theory and terminology from the paper making and paper testing literature. Paper condition is described in terms of cellulose and carbohydrate chemistry. Tests designed to assess cellulose condition employ un-aged samples or specially-prepared test papers. Overall darkening or local disfiguring stains that may develop in paper over time are problems that are not explored by the paper manufacturing industry and its testing body. Paper conservators are in a unique position to observe and document the condition of modern papers over time.

When maintained in a stable museum environment, modern papers retain their original, neutral, off-white tone. Extreme condition problems are more likely to develop when works of art on modern papers have been in private hands. An alternative explanation of condition problems is suggested by the systematic examination and treatment of such late nineteenth- and early twentieth-century works of art. Observation and treatment over more than thirty years suggested that the instability of modern papers may be due to something other than cellulose degradation. The inorganic additives widely employed in modern paper manufacturing processes may be a source of discoloration in modern papers. Both foxing and reverse foxing may occur because inorganic additives in paper react. This alternate theory is suggested by the condition of works of art, among them, the examples illustrated below: (Fig. 1)

MODERN PAPERS OBSERVED

An extreme example of reddish-brown foxing stains on medium-weight, smooth-textured, off-white, wove paper is shown in Figure 1. The stains appear to be spreading and growing from a dense center, another characteristic of foxing. Under ultraviolet light (Fig. 2), the reddish-brown stains fluoresce white and yellowish-white. Organic hyphae of mold absorb ultraviolet light and do not fluoresce. When closely examined under ultraviolet light, the areas of foxing resemble dendrites or efflorescence. This example suggests that something other than mold growth has occurred.

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Fig. 1. Camille Pissarro, Rue, ca. 1890, lithograph, H. 14 1/4 x W. 10 13/16 inches, detail of foxing stains.

Fig. 2. Camille Pissarro, Rue, ca. 1890, lithograph, detail of foxing stains, ultraviolet light.
far the tone of modern papers will change from the neutral, off-white color originally intended.

Many European papers dating from the turn of the 20th century and up until the 1940’s change color when works of art are exposed to daylight. Colors include brown, orange-brown and even black. Generally, the verso is unchanged, the extent of the stain is not matched or a very different stain
pattern has developed. This condition problem is colloquially referred to as “light staining.” An extreme example is illustrated in figure 8. (Fig. 8) The extent of “light stains” on modern papers suggest that they are highly sensitive to unfiltered daylight. Later in the twentieth century, although paper tone does not change to such an extent, any portion of a modern paper that is covered by a mat will invariably age differently from the area within the window.

Stains in many modern papers appear to be extreme but are superficial. Changes in paper tone appear to occur as a result of precise contact rather than migration. Figures 9 and 10 show an example of a relatively thin paper. (Fig. 9) (Fig. 10) The margins had been folded under to fit its frame. The extensive, dark stains have not migrated through the sheet. Darkening has occurred only in the areas in direct contact with poor-quality framing materials. All of the discoloration has stayed at the surface.

Reverse foxing is most often observed on Van Gelder Zonen wove papers. In the example illustrated in figure eleven, the verso of the sheet was extensively darkened. (Fig. 11) It was also disfigured by large blotchy, white patches of “reverse foxing.” This is not a case of adhesive protecting paper tone from acid migration. No adhesive was applied to
the verso. Adhesive was applied only on the recto and does not correspond to the broad, amorphous shape of these white areas. The print had not undergone previous treatment but it had been drum mounted to its window mat.4

These and numerous additional examples examined by the author suggest that:

- Foxing “growth” may not be caused by mold.
- Aqueous treatments may not remove or rinse discoloration out of paper.
- Modern papers may contain something other than cellulose or metal inclusions that cause local discoloration.
- Overall discoloration in modern papers can be extreme, making it difficult to determine the intended paper tone.
- Modern papers are prone to extreme darkening with exposure to unfiltered daylight.
- Stains are superficial and appear to be due to direct contact at the surface rather than migration.
- Examination with ultraviolet light provides invaluable clues, both before and after treatment.

MODERN PAPERS—THE PAPER CONSERVATION LITERATURE

When a paper conservator consults the literature, theory contradicts experience:

- Condition problems in modern papers are generally attributed to poor-quality fiber but significant condition problems occur on papers composed of linen, cotton and Asian bast fibers.
- Paper condition and discoloration are explained in terms of carbohydrate chemistry. Both oxidation and acidity cause cellulose degradation and paper darkening. In practice, modern papers do not respond predictably to conservation treatment procedures that, in theory, address cellulose degradation. Often, stains reappear.
- Conservation treatment improves the condition of cellulose by removing water-soluble by-products of cellulose degradation. In practice, examination under ultraviolet light reveals that, after many typical conservation treatment procedures, formerly discolored areas remain distinct and have not been “rinsed away.”
- Acids migrate into cellulose. However, numerous examples suggest that stains are superficial and may be caused by contact rather than migration. The surface of a modern paper can react as a kind of litmus test of contact with both acidic and alkaline housing materials.
- Alum rosin is most frequently blamed for unusual colors. In practice, the papers that exhibit the most extreme orange-beige or pink tones are hand-made papers manufactured before alum-rosin size came into use for machine paper making. Alum-rosin size is unlikely to be present in papers manufactured for fine art printing.
- Metal content in paper is always accidental and repeatedly attributed to bits of paper-making machinery that inadvertently find their way into the pulp slurry. Empirically, non-destructive analysis detects iron content throughout modern papers.
- Foxing is defined as reddish-brown, round stains that occur in a random pattern throughout a sheet. The debate has never been resolved as to whether foxing stains are due to mold or caused by metal-induced degradation of cellulose. Again, metal content is always there by accident. In practice, the appearance of “foxing” under ultraviolet light contradicts that of organic mold growth.6
- Reverse foxing is rarely seen. It is undefined and the cause is not known. It is discussed almost exclusively with regard to Van Gelder Zonen wove papers. Uneven deposition of size is mentioned in the literature but this isn’t a very likely explanation for printmaking papers that are lightly sized or unsized. Empirically, reverse foxing is also observed on other modern papers. Areas of reverse foxing appear as a paper dries or after a paper has fully dried after typical aqueous conservation treatment procedures.

INORGANIC ADDITIVES—THE TECHNICAL AND HISTORICAL LITERATURE

Apart from the aluminum sulfate in alum-rosin sizing, the role that inorganic additives may play in the condition of works of art is not acknowledged in the paper conservation literature.7 Although almost entirely absent from the paper conservation literature, the technical literature and periodicals of the paper industry are filled with references to inorganic additives. In the paper testing literature, inorganic additives are acknowledged but their potential to effect condition is generally dismissed. In small percentages, inorganic additives do not interfere with inter-fibril bonding and are non-damaging to cellulose fiber. Inorganic additives are reported in the forensic analytical literature where they are useful for paper dating.

Beginning in the nineteenth century, and inherent to the science of paper making today, non-fibrous, inorganic additives were routinely and selectively added to fiber stock to increase opacity, modify texture and absorption, fill gaps and determine paper tone. Long before the end of the 19th century, paper had evolved from craft to science. As the uses of paper multiplied, inorganic additives were found to modify fiber stock to suit many purposes. Inorganic additives act as fillers, brighteners and opacifiers. They aid in drying and improve ink retention. Additives increase bulk and are cost-effective. Finely-divided inorganic particles tend to settle at the surfaces where the newly-formed sheet dries first. Thus, physics puts them where the paper manufacturers want them. Paper conservators are familiar with many of the paper
additives listed below and acknowledge their use as coatings for commercial printing rather than fine art papers. However, inorganic additives were also mixed into fiber stock.

A Chronology of Inorganic Paper Additives:

<table>
<thead>
<tr>
<th>Additive</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Sulfate</td>
<td>1820</td>
</tr>
<tr>
<td>Calcium Sulfate (gypsum)</td>
<td>1823 (Europe)</td>
</tr>
<tr>
<td>Clay</td>
<td>(1807), mostly after 1870</td>
</tr>
<tr>
<td>Satin White (coatings)</td>
<td>1879-1880 (England, Germany)</td>
</tr>
<tr>
<td>Zinc Sulfide</td>
<td>After 1932</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>About 1925-1927</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>(1906) 1930</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>About 1933</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>About 1938</td>
</tr>
</tbody>
</table>

Browning, B.L. Analysis of Paper. Appendix XIX. New York, 1969

Paper manufacturers also added dry pigment to pulp. Paper conservators acknowledge that something called “bluing” is used by the industry to make papers appear less yellow. “Bluing” is not a benign organic dye. It’s usually synthetic ultramarine (sodium aluminosilicate), smalt (silica) or Prussian Blue (potassium ferrocyanide). Thus, modern European papers were further complicated by these unstable, inorganic pigments. It is less well-known that naturally occurring earth colors or synthetic iron oxide pigments were used in hand-made Dutch, French and English papers in the nineteenth century. This kind of mechanical coloring is traditional and requires no mordant. Dry pigment is simply dispersed in the pulp slurry. This practice has serious consequences for paper conservators because mechanically-toned papers were exactly the type of paper sought by artists for etchings.

Extensive information about inorganic additives is found in the paper making and paper testing literature. Paper manufacturers consider small amounts of inorganic additives non-damaging to cellulose fiber. However, impurities in mineral additives and the metal oxides employed by the paper industry are not inert in the conditions that are known to cause damage to works of art. When selected for a work of art, these complex substrates undergo rigorous, unpredictable and uncontrolled processes. Over a long lifetime, many works of art on paper reside in unstable environments with fluctuating temperature and humidity. Affixed to a wall, they may be exposed to acidic mats and unfiltered daylight for decades. These papers are also subject to intervention by restorers, framers and paper conservators. Over time, papers with additives may develop foxing or reverse foxing stains, become “light stained” within a window mat, “time stained” at a sheet’s edges or “burned” by acids exposed at the beveled edge of a poor-quality mat. Given the chemistry of the inorganic additives employed for modern paper making, it is possible that additives, rather than cellulose, have reacted under these uncontrolled conditions.

The inorganic additives employed by the paper industry are primarily naturally-occurring minerals and metal oxides. When naturally occurring minerals are added to papers, impurities such as iron, calcium, manganese and potassium are inevitably present. These impurities act as salts and readily undergo acid-base reactions. The earth colors or iron oxides used to tone papers are among the most reactive compounds on earth. As in nature, these additives are unstable in the very conditions that make paper into a work of art and in the conditions known to cause damage to works of art on paper over time - fluctuating humidity, daylight and low pH. The extreme and inevitable color changes that occur in modern papers in daylight may be due to the photo-catalytic properties of metal oxides. The naturally-occurring iron oxides (earth colors) and the synthetic iron oxides added to late nineteenth- and early twentieth-century papers may be the cause of foxing and reverse foxing. With pH changes, when the paper is wet, or in the presence of other elements in the paper, air or water, these additives undergo reactions and form new compounds that crystallize on the surface or within the fibrous web. Each time the paper is wet and dried as the art is made, and each time the paper undergoes humidity changes over its lifetime, conditions for crystal formation occur.

When the historical and paper conservation literature is searched, documentation of condition problems can be found. Papers from China were the preferred support for luxury print editions. We know from the historical literature that this paper tended to develop stains. Writing in 1874, the French bibliophile Alphonse Lemerre advised collectors that humidity hastened the development of little spots on Chinese paper, and that spots could develop within a year. One need only examine a clay-filled paper from China or Japan under ultraviolet light to see many brightly fluorescing impurities throughout. They are prone to discolor in uncontrolled conditions over time.

As for the iron oxide pigments in European papers, references in the paper making and historical literature can also be found. Lumsden writes in his etching manual, “In nearly all modern paper, the pigment employed is too crudely yellow. For beauty of colour, one has to rely upon Japan.” George Plowman gave the following instructions in his treatise on etching. “Old account books of handmade French or Dutch paper are much sought after by etchers. Dry out any paper that may be left after printing before putting it away, as it is liable to mildew.” In 1880, when the results of an inquiry into the poor quality of nineteenth-century British papers was published, the authors stated that “the earth pigments employed in papers are reactive compounds” and “...there are few papers made which do not receive some addition of coloring matter.”

When evenly dispersed in a sheet and exposed to daylight, metal oxide additives sensitize paper to light. A clue to the light sensitivity of papers containing metal salts comes from...
and reverse foxing. In 1998, Ordonez and Twilley published a paper about salt crystals on the surfaces of paintings. The authors identify the multiple inorganic additives in modern media and suggest that salts from additives effloresce on painting surfaces. In 2007, Deborah La Camera published her findings on crystal formations within iron gall ink. It is interesting that many of her examples are not early ink formulations but inks used by nineteenth-century artists on contemporary papers. When we observe foxing and reverse foxing, we may be seeing efflorescence and crystal formation, the reactions of inorganic iron oxide pigments in paper.20

INORGANIC ADDITIVES—FOXING AND REVERSE FOXING

This paper is intended to suggest that paper conservators begin to consider foxing as crystal growth or polymerization. Frequently, crystals or salt efflorescence are observed inside a framed work of art. These are generally explained by weeping glass or off-gassing from acrylic glazing. However, such crystals may arise not from glazing or media but from inorganic components in paper. Crystals form under the same conditions as mold. On a surface, their fluffy appearance may suggest organic growth. In paper, they may form along cellulose fibers and resemble the spreading mycelia of mold. (Fig. 12)

A component in the handmade Dutch paper illustrated in figure 13 has reacted and darkened over time. (Fig. 13) This is especially visible in transmitted light. (Fig. 14) The Arches...
paper used for Matisse’s pochoir prints would have been repeatedly wet and dried during printing. In normal light, the detail of a Jazz print in figure 15 appears unstained. (Fig. 15) With transmitted light in figure 16, opaque areas in the paper are visible under the ink. (Fig. 16) Stains will predictably develop when this paper is kept in damp conditions. The beginnings of disfiguring local reactions are visible in a detail of an untreated Van Gelder Zonen wove paper. (Fig. 17) This paper was employed for the Saltimbanques series published by Vollard in 1905. In transmitted light, additional dense areas are revealed. (Fig. 18)

Reverse foxing may be related to a phenomenon often observed by paper conservators that may be termed “reverse media patterns.” The Jazz print illustrated in figure 19 was exposed to excessive light and framed against a corrugated
of other elements available in the paper, the air, the inks, the water used for printing or for later interventions. Each time the paper is wet out and dries, when it is dampened for mounting and with high or fluctuating humidity, conditions for crystal formation occur. A slow-drying paste is sufficient to initiate this reaction. In figure 21, the area under the hinge is distinct from the surrounding paper not because the paste cardboard backing. (Fig. 19) It may not be accurate to say, as paper conservators generally do, that the ink protected the paper from darkening. Rather, the white areas under the ink are not protected paper but areas where an inorganic reaction has taken place as a result of water introduced during printmaking and/or later interventions. In a close-up of the verso of the top right corner (Fig. 20), one sees that the white areas are bright white. These areas are hard, chalky and no longer wet out with water. This suggests that something other than cellulose is present and has proliferated in these areas. It could be an oxide, a hydroxide, an oxide-hydroxide or a compound oxide. Its composition would depend on pH, on the presence...
has protected the original paper tone but because a local reaction was initiated under the wet paste. (Fig. 21) This area no longer reacts as the rest of the sheet. Over time, the area appears more distinct from the surrounding paper because the photo-sensitized paper around it has darkened.

Figure 22 shows a detail of the most well-known print from the Saltimbanques series. (Fig. 22) It is also the most well-known example of reverse foxing problems. In this case there is a white area near the plate mark and in the forehead of the subject on the right. There is a “light stain,” indicating that the print has been exposed to some unfiltered daylight. The reverse foxing in the paper became visible over time, as the sensitized paper around it darkened. Under ultraviolet light, (Fig. 23) the areas reflect brightly and a somewhat larger area of an inorganic content is indicated. In transmitted light when the print was wet, (Fig. 24) a much larger area was affected, that begins to approach the extensive, blotchy white patches of the Van Gelder Zonen paper illustrated in Fig. 11.

CONCLUSION

When maintained in an ideal environment, modern papers remain neutral and off-white. In high or fluctuating humidity, in contact with poor-quality housing and in unfiltered daylight, modern papers undergo changes that may be due to the chemistry of inorganic additives rather than cellulose chemistry. Foxing may be caused by inorganic additives as they polymerize in and on paper. Reverse foxing may not be due to uneven deposition of size but to reactions that create local deposits of inorganic compounds. This alternative explanation of condition problems in modern papers has significant consequences for treatment. It is sincerely hoped that paper conservators and conservation scientists will begin to analyze modern papers with their complexity in mind.

NOTES

1. This paper is a summary of a presentation given at the Book and Paper Group Session at the 43rd Annual Meeting, American Institute for Conservation of Historic and Artistic Works, May 13–16, 2015, Miami, FL. Many more examples of condition problems were illustrated in that presentation. The author intends to publish a more detailed and thoroughly referenced article on this topic in the near future. The author’s observations and findings are presented in abbreviated form here. Only a fraction of the many references consulted over the course of the author’s research are included here.

2. Under UV, the appearance of this area is distinct from the surrounding paper.

3. Such stains appear to be exacerbated by framing techniques, such as stretch mounting, where the paper is dampened overall before the edges are attached to a window mat or backing.

4. Often, prints provide the most extreme examples of condition problems but additives are certainly present in papers manufactured for drawing and other purposes.


7. See Bruckle, I. “Aspects of the use of Alum in Historical Papermaking,” Institute of Paper Conservation Conference Papers, Manchester (1992): 201–206. In this and subsequent publications, Irene Bruckle has drawn attention to aluminum sulfate. Present in trace amounts and evenly distributed throughout the fibrous cellulose web, that an inorganic additive may play an active role in local stains may be overlooked by non-destructive, qualitative analytical methods.


10. Our own conservation scientists have tended to overlook additives. The role of metals as catalysts for oxidative degradation of cellulose is acknowledged, however, metal content is invariably described as accidental.


12. Catalytic reactions are known to occur most rapidly in high humidity.

13. Many inorganic additives are also transition metals, which have received attention lately in connection with iron gall ink corrosion. The chemistry of transition metals merit further attention in this context as well.


15. Lemerre, A. “Le Livre du Bibliophile,” Paris, 1874, n.p. Clay and other naturally-occurring minerals would contain impurities that act as salts and react readily with humidity and changing pH. Such impurities would result in local stains. Iron, just one example, begins to react or rust at relative humidity levels of 50%.
17. Plowman, G. T. Etching and other Graphic Arts: An Illustrated Treatise. New York, 1914. I believe he is referring to papers containing iron oxide pigment additives.
19. Newhall, B. “The History of Photography,” Museum of Modern Art, New York (1982): 13–25. Over the course of the century, it appears that the use of iron oxides diminished, however, the compounds of zinc and titanium later used as brighteners and opacifiers are known to act as photo-catalysts. Many useful references have come to us from the textile industry. These properties are also discussed in compendia of artist’s pigments.
21. This is emphasized by Ordonez and Twilley, op. cit. Inorganic crystals form in the same conditions as mold - high humidity or as a paper dries after being wet.
22. Using polarizing light microscopy, Walter McCrone had identified yellow ochre along with linen fibers in a sample taken from the Kasimir print. None of the paper conservators or scientists I conferred with knew what to make of this finding, since we generally think about condition in terms of organic or cellulose chemistry.
23. The importance of preventive conservation measures to ensure the long-term preservation of modern papers cannot be overstated. However, when paper conservators see only well-preserved examples, important information may be understandably missed.
24. The scope of the presentation of this subject to the Book and Paper Group was preliminary. The presentation, and this summary in the Book and Paper Group Annual, are focused on sharing observations with fellow conservators and suggesting a new theory about condition problems inherent to modern papers. The author intends to pursue treatment implications elsewhere.

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