13. FOXING

The term foxing is derived from the rusty red color of Reynard the fox and its use was first noted in 1848 [Meynell and Newsam 1979, 567; Carter 1980, 105]. Foxing is a descriptive term for scattered spots commonly reddish-brown in color, but also applied to spots of other coloration ranging from yellow to black. It should be distinguished from visible surface colonies of mold growth, which may result in paper stains of a wide range of colors, though both may be present concurrently. In Japan, foxing is known as *hoshi*, which literally means "stars" [Engelbrecht 1991, 62].

It may be easier to define what foxing stains (as identified by most conservators) are not. They are not the mold stains, with or without surface growth, which severely deteriorate the paper and cause a variety of colorations. They are not offset stains from contact with another paper or printing ink. They are not tide lines of liquid stains. They are not acid stains migrating from secondary material, although poor quality secondary materials may accelerate the foxing stain phenomenon.

13.1 Purpose

1. To provide criteria for differenting foxing problems from other stains in paper.

2. To ascertain, to the extent possible, the cause(s) of a foxing stain in paper.

3. To record established methods of identification used by both conservators and research scientists.

4. To identify areas needing further research.

5. To assemble treatments appropriate to various foxing stains.

13.2 Factors to Consider

13.2.1 Causes

Despite investigations spanning almost sixty years there remains confusion and uncertainty as to what causes foxing, whether there is a single cause or multiple ones, and whether there is more than one type of foxing. There are currently three major explanations for foxing which have been proposed most often: a) fungal activity, b) metal-induced degradation, and c) multiple causes. Recently, a fourth explanation has been proposed which attempts to explain foxing stains within the context of general discoloration of paper caused by the interaction of moisture and cellulose.

Unfortunately, most of the published research on foxing neglects to provide accurate and complete information

concerning size, shape, depth (within the sheet), or fluorescence pattern (or absence thereof) when describing foxing. In the future, it is hoped that investigators will use Cain's proposed classification system (see 13.2.3), making it easier to integrate disparate research. Although researchers claim their stains had the "typical coloration characteristic of foxing," this is fairly meaningless, as there is no way of judging the uniformity of this coloration. It is possible that researchers are finding different causes for foxing because the spots tested <u>are</u> different, even though they are all termed "foxing". Hey has even suggested removing metal induced foxing from the foxing category altogether as this is "metal induced degradation". Additionally, researchers proposing one cause over another often neglect to investigate both causes equally, lending an unstated bias to their findings of which the reader must be aware. Following is a summary of investigations and theories culled from conservation literature.

A. Fungal Activity

There are approximately 100 fungoid species designated as 'paper-attacking' though some specialists suggest that many more of the more than 30,000 species of fungi would attack paper [Gallo 1963, 57; RK]. Not all of these species are necessarily associated with foxing.

Some of the micro-organisms habitually associated with paper are found in the raw materials used to form the paper. These micro-organisms can remain latent for months or years awaiting the appropriate conditions for growth. Another likely means of infection of paper is through air-borne spores.

Certain fungi have been associated not just with paper generally but with foxing spots specifically. From old books and manuscripts showing the characteristic foxed discoloration, Beckwith et al. isolated fifty-five different fungi [Beckwith et al. 1940, 301]. These they sampled directly from foxed areas of the paper. From foxed spots Arai found twenty-five strains located specifically within the foxed areas of paper and, in fact, could not find evidence of the fungi in any unfoxed portions of the paper [Arai 1987, 1165]. Although these strains were all found in foxed spots, only seven were found to create browning stains in Arai's experiments.

1. Explanations
   The following explanations for formation mechanisms of foxing spots by fungi have been proposed.

   a. Color pigments are secreted by the mycelia, the vegetative branches of mold. These pigments have various chemical compositions but are mainly composed of carotenoids and anthraquinones [Gallo 1963, 58]. Beckwith et al. state that pigments may be only a minor cause of foxing because the chromogenic tints produced by various species of mold are not characteristic of foxing [Beckwith et al. 1940, 306]. Nol et al. believe fungi produce pigments and that coloration can be intensified within a foxed spot by certain combinations of fungi species which alone may not produce strong coloration [Nol et al. 1983, 22]. This explanation does not show a clear relationship between foxing and iron.

   b. According to one source, micro-organisms "develop at the expense of the glue materials forming hygroscopic areas on the paper in which the water soluble degradation products of the cellulose accumulate. They assume a red-brown color in damp surroundings" [Ambler and Finney 1957, 1141 as quoted in Gallo 1963, 26]. This theory is also consistent with Meynell and Newsam who found "foxed areas invariably showed fungal hyphae weaving around but not within individual cellulose fibers. The cellulose fibers within foxed lesions appeared normal. The lesions, however, wetted more easily than the rest of the paper and stained instantaneously with Coomassie blue, indicating the sizing was participating in the fungal growth [Meynell and Newsam 1979, 567]. This explanation is inconsistent with findings by Cain and Nol et al. who found evidence of cellulolytic activity and had to assume cellulose degradation was occurring [Cain 1983; Nol et al. 1983, 23]. This explanation shows no clear relationship between foxing and iron.

   c. Specific fungi tested to date have been found to produce foxing in laboratory experiments. They do this by secreting malic and other organic acids as well as amino acids. These acids are deposited on, and then attack the cellulose and/or sizing. This produces cello-oligosaccharides and glucose which in combination with amino acids produce a browning

reaction known as the Maillard reaction [Arai et al. 1988, 12]. Each ingredient alone will not induce a browning reaction, but they will in combination. This explanation does not demonstrate a clear relationship between foxing and iron.

d. Foxing is the visible sign, by production of color, of deterioration within paper. Although the breakdown of paper may result from many causes, fungi constitute a most important menace to the preservation of paper. Growth of fungi in paper and development of color are furthered by iron and by certain sizings and fillers [Beckwith et al. 1940, 305]. This explanation acknowledges foxing may have multiple causes requiring some iron content for fungi to create sufficiently strong coloration.

e. The fungi produces an enzyme or ferment which brings about a chemical change. This enzyme/ferment may be diffusible when moisture is present, explaining effects visible some distance from the site of the formation of the enzyme. The enzyme, in turn, may bring about its chemical change and the products of its activity may also diffuse some distance, causing local discoloration [Iiams and Beckwith 1935, 415].

   It is generally known that fungal growth breaks down its support by releasing enzymes. It may be that the circumstances that cause foxing also include some form of enzyme attack of cellulose. "Once growing, fungi cause damage in several ways. Actual damage to material is caused by the release of enzymes outside the organism (extracellular enzymes). These enzymes break down long-chain molecules such as cellulose or proteins into chemical units sufficiently small to be absorbed through the cell membrane into the cell. The action of extracellular enzymes is independent of the fungus; they can act even if the organism is killed or removed" [Allsop 1985, 532]. This explanation shows no relationship between foxing and iron.

2. Types
   The following fungi have been cultured specifically from foxing spots and create new browning stains when reinoculated into paper under laboratory conditions.

a. Beckwith et al. [1940, 301] list genus

1. *Alternaria*
2. *Aspergillus*
3. *Byssochlamys*
4. *Chaetomium*
5. *Fusarium*
6. *Hormodendrum*
7 *Monilia*
8. *Mucor*
9. *Penicillium*
10. *Stemphylium*

b. Arai [1987, 1166] lists species

1. *Aspergillus penicilloides*
2. *Eurotium herbariorum*

c. Nol et al. [1983, 22] lists species

1. *Aspergillus carneus*
2. *Aspergillus flavus Link (with Sclerotia)*
3. *Aspergillus flavus* Link (lacking Sclerotia)
4. *Aspergillus fumigatus* Thom
5. *Aspergillus niger van* Tieghem
6. *Aspergillus terreus var. aureus* Thom & Raper
7. *Aspergillus tamarii*
8. *Gliocladium roseum*(Link) Thom
9. *Penicillium funiculosum* Thom

d. Cain et al. [1987, 24] found species *Aspergillus repens*

3. Factors favoring growth and/or color formation

a. Relative Humidity (RH)
There is no minimum degree of RH for growth of all fungi as the level varies not only with the genus but with the species as well [Beckwith et al. 1940, 311-313]. The more hygroscopic the material (i.e. paper vs. leather) the lower the room RH can be in order to permit microbial growth [Gallo 1963, 59]. It is important to remember that a micro-climate, vastly different from the overall room RH, can exist within the paper's structure. Unsized tissues, for example, interleaved into books may absorb and retain water over a long period of time creating localized high humidity relative to atmosphere; this could enable fungus to develop even when surrounding RH is below 75%. Fungal hyphae may transport water from higher to lower areas of RH, perhaps centimeters away [RK].

Most research directed at microbial growth on paper shows that below 70-75% RH the chances of growth for many "paper-attacking species" of fungi is low. Arai found that below 75% RH, germination of mold spores of the type isolated from foxed spots is unlikely to occur. Interestingly Arai also found that 84% relative humidity induced growth better than 94% RH, though this is specific to the particular fungi he isolated [Arai et al. 1990, 805]. Beckwith et al. also found that below 75% they could not produce any fungal growth with the particular species they cultured [Beckwith et al.1940, 313]. In contrast to this, Nol et al. found three strains, previously isolated from foxed spots, which grew at 55% to 93.5-96% RH. Two of these strains also grew at 32.5% RH. However, foxing or coloration occurred only with one strain under RH conditions ranging from 32.5% to 96% [Nol et al. 1983, 24].

b. Temperature
Each species has its optimum temperature for growth. Generally, it has been found that growth increases with increasing temperature and decreases with decreasing temperature. Excessive heat kills most fungi and steam is a standard means of sterilizing cultures in lab procedures.

c. pH
All research has shown that foxing stains are more acidic than the surrounding paper [see, for example, Arai 1980; Hey 1983; Iiams and Beckwith 1935].

Arai's research suggests that the presence of amino acids is necessary when inducing foxing and that increasing the concentration the of amino acids results in darker brown spots [Arai et al. 1990].

d. Nutrients
Fungi may find nutrients in one or more of the following.

1. Cellulose
While some researchers insist that cellulose is not damaged in foxed areas [Meynell and Newsam 1979, 567], others have shown conclusively that fungi digest the cellulose [Cain 1983, 16 and Nol et al. 1983, 23].

2. Sizings and Adhesives
   Because they saw no damage to fibers, Meynell and Newsam claim foxing feeds on gelatin size, not on the cellulose [Meynell and Newsam 1978, 467]. However, observations have also been made that fungi prefer more hygroscopic, unsized papers to those that are sized [Meynell and Newsam 1978, 468; Gallo 1963, 58].

   Investigation into the influence of fillers and sizes on fungal growth and its production of acids found the following: gelatin, starch and dextrins promoted growth and color production [Beckwith et al. 1940, 3307]. There was less acid production by fungi feeding on casein and rosin than with starch or cellulose alone.

3. Oils
   Either from the medium of printing ink in a text or that transferred to paper by readers' or handlers' hands [Meynell and Newsam 1978, 467].

4. Micro-dust

e. Light Intensity
   Generally, the growth rates for most fungi are not sensitive to light intensity. However, no study has been made of the relationship of foxing stains to light.

   "Examination of a 1896 thirty-four volume set of Balzac's works on laid cotton paper found 'snowflake' fungal foxing in circulated volumes no different from that present in 1896 uncirculated, unopened volumes. Previously uncut pages were slit in the dark and examined in the first light exposure in nearly ninety years. Apparently dark storage produced the same pattern, color, and frequency of foxing as occasional exposure to light [Cain, Stanley and Roberts 1987, 24].

B. Metal-Induced Degradation

"Cellulose is directly oxidized catalytically in the presence of iron, copper, and cobalt compounds, and the reaction is most rapid at high humidities" [Tang 1978, 19]. Metal impurities in paper, specifically iron and copper, are believed to result from particles abraded from the metal equipment and/or from contaminated water used in the papermaking

process. Additionally, all wood-pulp paper may be expected to contain iron, as it is naturally present in wood [Beckwith et al. 1940, 302].

"In 'bullseye' copper- or iron-induced foxing the role of these two metals is probably that of oxidative catalyst. Both metals can undergo reversible oxidation-reduction. For example, they are both found playing such a role in metabolic biochemical reactions. Iron can alternately be oxidized from the +2 (ferrous) state to the +3 (ferric) state and then be reduced back to the +2 state as it plays the role of oxidizer. Copper can do the same between the +1 and +2 states. Thin-layer chromatographic studies show the extracts of 'bullseye' foxed and unfoxed paper to have all or most of the same bands. This further suggests iron and copper act to catalyze (accelerate) the oxidative degradation of paper" [Cain 1983, 15; Cain and Kalasinski 1987, 57]. In a tally of metal-induced foxing, analysis showed that twenty-seven were induced by copper and copper alloys to over 200 induced by iron [Cain and Miller 1982, 7].

1. Iron

a. Coloration
"The very color of foxing connotes the presence of iron" [Iiams and Beckwith 1935, 412]. Iron ions create yellow-brown spots and Tang found that "there is a trend for darkness of the foxing spot to increase with increasing iron content; the highest concentration of iron was noted in the center of the spots, with the metal concentration decreasing...as the distance increased from the center" [Tang 1978, 24, 26].

b. Occurrence
It would be very difficult to find any paper without some degree of iron [MH]. Numerous researchers have identified iron ions within foxing stains and found a significantly greater concentration of iron in the foxed areas compared to surrounding paper [Cain 1983, Cain 1988, Cain and Miller 1982, Cain and Miller 1984, Daniels 1988, Gallo and Hey 1988, Tang 1978, Tang and Troyer 1981]. One study, however, found no difference between foxed and unfoxed areas [Press 1976, 29]. This was corroborated by Tang, who found that in some foxed papers there was no difference in iron (or other metal ion) concentration [Tang 1978, 28]. While concentrations greater than 500 ppm

have been identified with undesirable spots, Hey suggests that "if iron is involved it is not its total concentration that is important but rather its availability to participate in reactions or its effective solubility" [Tang 1978, 28; Hey 1983, 341].

c. Form
Research indicates that iron in paper is found entirely in the ferric, rather than ferrous, form [Beckwith et al. 1940, 303].

d. Activation
Iron will not corrode below 70% RH, but in the presence of ions such as chloride, storage needs to be at 40% RH or lower to avoid corrosion. Hey suggests that "there is a strong chemical possibility that heavy metals present in the paper in a quiescent state will be activated by washing with an acid water, when this is not followed by deacidification" [Hey 1979, 68].

2. Copper
Daniels and Meeks describe copper-related foxing as varying in size "from small spots with no apparent nucleus and only a brown diffuse discolouration, to large spots of about 5 mm diameter with black dendritic patterns or green corrosion products; these spots include an outer ring of brown discoloured paper" [Daniels and Meeks nd., 2]. Analysis by EDX revealed that the foxed areas contained copper, zinc, sulfur, and chlorine, while the unfoxed areas "did not have detectable amounts of these elements" [Daniels and Meeks nd., 5; see 13.2.4.E.2]. It was concluded that chloride ions, from original or subsequent bleaching residues, accelerated the corrosion of brass (a copper/zinc alloy) inclusions in the paper. The soluble copper compound was then able to react with hydrogen sulfide generated in the paper or absorbed from the atmosphere. The stain was due to a combination of black copper sulfide and brown copper catalyzed degraded cellulose [Daniels and Meeks nd., 8]. Tang linked copper concentrations greater than 50 ppm with formation of undesirable spots [Tang 1978, 28].

C. Condensation
A modification of the cellulose, often visually evident by browning, which takes place at the interface between wet and dry parts of fibrous materials and which is not the result of degradation products being carried and deposited by a spreading

liquid. "Experiments suggest that the interaction of air, water and cellulose is responsible for the formation of browning" [Hutchins 1983, 58]. This interaction could occur at sites of temporary moisture accumulation in the paper. "Depending on the moisture content of a book, [for example,] it would be possible for uniform discolouration of zones, as well as smaller or larger stains, to develop. All the possible factors that influence condensation and evaporation would play a role in this: humidity, temperature, air pressure, paper porosity, and any irregularities in the paper which could include folds, tears, and dirt particles; even the presence of concentrations of iron or fungus could likewise induce condensation" [Ligterink et al. 1991, 51].

The above authors speculate on the relationship between foxing and other forms of discoloration (text block areas, leaf margins). The link is based on observations of both types of staining (foxing and zonal) appearing together on the same page in many books.

The condensation explanation for browning is a broad view ascribing moisture and cellulose and possibly oxygen as the only necessary ingredients to achieve staining. The presence of fungi and/or metals would act only as attractive sites for moisture and consequent browning.

D. Multiple Causes

Given the ubiquitous nature of both iron and fungi in paper it is quite possible they often act in tandem. Research appears divided (fungal infection vs. metal-induced degradation), and one must keep in mind, when reviewing each study, whether the presence of a dual cause was fully investigated. Often researchers did not adequately test for iron when they found fungi and vice versa.

A good example of this is the use of the SEM. Where Cain and Miller did not, in one study, find an iron core using SEM and EDX, they successfully located it using narrow beam x-ray fluorescence [see 13.2.4.F.1-3]. Other research, however, has relied on SEM alone to determine that there was no iron (or other metals) present without using other methods to check their results.

As early as 1935, Iiams and Beckwith proposed a dual cause of spot formation: organic acids secreted by the metabolizing fungi react with iron present (even in trace amounts) in the paper to form unstable

organic iron salts (organo-ferro compounds) which decompose to form iron oxides and hydroxides i.e. brown/rust coloration [Iiams and Beckwith 1935, 414].

Iiams and Beckwith also found that adding a 1:1,000 solution of iron caused fungal growth which "greatly exceeded any that had been produced in the laboratory without the presence of iron in the culture papers" [Iiams and Beckwith 1935, 414]. Their later research confirmed this as well as showing that iron increases the degree and intensity of the discoloration which accompanies fungal proliferation [Beckwith et al. 1940, 303-306]. The resulting brown tint had the color of ferric oxide. The presence of casein, gelatin, and starch add to the discoloring effects of iron.

Hey concurred with Iiams and Beckwith and proposed these dual mechanisms:

1. damp -> mold acid -> activation of iron -> increased acid -> mold death

2. damp -> activation of iron -> increased acidity -> local encouragement of mold -> increased acidity -> death of mold [Hey 1983, 341]

These models suggest that one reason why foxing stains do not cover an entire page might be that the acids secreted by the fungi collect, eventually reducing the pH enough to curtail further fungal growth.

Cain and Miller found that "snowflake" foxing contained a higher iron concentration than the surrounding paper [Cain and Miller 1982, 61]. A later study found hyphae and occasional fruiting bodies in all snowflake fungal foxed areas examined [Cain, Stanley and Roberts 1987, 24]. This suggests a dual cause.

Fungi use iron and copper as co-enzymes. This means that they are essential elements. After use, the excess may be secreted (perhaps as an altered or activated ion) [RK].

13.2.2 Origin/Occurrence

A. Related to the Manufacture of Paper

The extent of foxing appears to be in direct proportion to methods used in the manufacture of paper [Iiams and Beckwith 1935, 413]. It is possible that the potential for foxing is created when the sheet is first made - the foxing only becomes visible

later when storage conditions encourage it. Factors include the poor preparation of fibers, impurities in the pulp and the water added to it, and poor bleaching with chlorine. On the other hand, papers manufactured with a high magnesium or calcium carbonate content are less likely to be foxed. It has also been noted that woolen or rayon felts are damaged continually by microbial attack as shown by Sharpely and King. Two species of fungi located in damaged felt fibers are *Aspergillus niger* and *Aspergillus fumigatus*, both associated with foxing and noted for their cellulolytic capabilities [EM].

B. Causes Related to Storage

Ligterink et al. proved that foxing stains found in one particular book arose during storage of the loose sheets prior to binding. They noted that the stain patterns which were not repeated on an adjacent page were sometimes repeated on another page later in the book. By reconstructing the original unfolded, uncut quires it was discovered "that the stain patterns of successive quires matched up if the unfolded sheets were laid on top of each other, and could often be followed down through many sheets in the stack. The storage of these unfolded sheets obviously determined the form of the stains observed which must have therefore arisen before binding" [Literink et al. 1991, 49]. Interestingly, the stains were probably not visible at the time of binding as the discolorations are so great in some sheets they would probably have been discarded by the binder [see also 13.4.7.E]. By the same reasoning, book papers which show the same foxing pattern through several adjacent pages indicate the foxing began and became visible after the pages were bound.

C. Causes Related to Dampness

Research indicates that the internal moisture content of the paper must be at least 10% for fungal growth to occur [Allsop 1985, 59]. At 80% RH, paper in general absorbs 9-14% water, with more hygroscopic paper, a lower RH will permit mold growth. Iron alone will not corrode below 70% RH but in the presence of ions such as chloride, papers must be stored at 40% RH or lower to avoid iron corrosion.

13.2.3 Classification of Foxing

In an attempt to describe the various stains called "foxing" Cain and Miller have developed a classification of types by shape, color and UV fluorescence examination [Cain and Miller 1982, 1984]. Cain and Miller found that foxing was a three-dimensional phenomenon. In their investigation of foxing in books, Ligterink et al. found that "All foxing stains are part of three-

dimensional stain-structures, which are generated in stacks of paper either during the production process or in the book itself...many series of stains begin on one page and end several pages later, forming sharply delineated, or sometimes rounded, spatial entities" [Ligterink et al. 1991, 50].

A. "Bullseye"

These spots are small and round, with a dark center and concentric rings. They are red/brown to yellow in color with rings of a paler color. Bullseye foxing can be further subdivided by UV examination.

1. Centers do not fluoresce (appear dark blue/black), rings fluoresce yellow/orange and pale yellow.

2. Centers and rings do not fluoresce (appear dark blue/black).

This type of foxing always has metal cores, which do not fluoresce and appear dark blue/black.

B. "Snowflake"

These are spots with scalloped edges and/or irregular shapes which can measure inches across. They are red/brown to yellow in color but sometimes are not visible in normal light. It is theorized that the advanced stage of foxing causes coloration while the younger or dormant stage may not be visible in normal light [Press 1976, 29]. This type of foxing gets its name from its white fluorescence and snowflake-like appearance under UV. Snowflake foxing apparently has a higher iron concentration than the surrounding paper, but concentration may vary within areas of the foxing.

While only one iron particle of twelve found in "bullseye" foxing showed any presence of fungal hyphae, extensive examination of Balzac volumes showed no evidence of fungus, either hyphae or sporangia, in unfoxed areas, but hyphae and occasional fruiting bodies in all "snowflake" foxing examined [Cain, Stanley and Roberts 1987, 24]. These spots appear to occur in association with fungal activity.

C. Stains Confused with Foxing: Offset or Migration

The following discoloration are seen by conservators to be staining rather than foxing. These discolorations are often found in books and correspond in shape to a print or images within a print from the facing page (offset), or they conform to the shape of the body of the printed text (shadows). They usually appear yellowish in visible

light but differ under UV. Offsets fluoresce pale blue-white to white; shadows fluoresce yellow-orange around the body of the text. The condensation explanation for browning proposes the same causes for these types of staining as for foxing i.e. moisture.

13.2.4 Methods of Identification

A. Visual Examination in Normal Light
To determine shape, color, and quantity. To determine if foxing spots correspond on recto and verso.

B. Transmitted Light
To identify if there is a core or bullseye. To determine location and quantity of other spots or cores not visible in normal light viewing.

C. Microscopic Examination
Will help identify smaller iron cores and determine their exact location in the paper matrix.

D. Ultra-violet Fluorescence (360 nm)
This is probably the most useful tool conservators have at hand to examine foxing as it will identify the presence of metal (bullseye) when this is not necessarily clear with microscopic or visible light viewing. Fluorescence is an indicator of permanent change in the cellulose and may indicate degradation by metal-induced oxidation or fungal digestion.

1. Yellowish-White Fluorescence: Areas which fluoresce under UV but show no visible light foxing may indicate the early stages of growth. Brown staining develops later, spreading out from the center. More advanced foxing was described by Press as brown spots visible by white light surrounded by a clear rim of florescence. Scanning with a spectrofluorometer showed "two clear florescence peaks, on each side of the brown spot, which lay exactly in the valley between them" [Press 1976, 28].

   Areas which fluoresce under UV but show no visible-light foxing also may indicate a previous bleaching treatment. "After any browning has been removed by oxidizing bleaches...the lesions still differed in color under ultraviolet light and usually had fluorescent patches" [Meynell and Newsam 1978, 467].

2. No Florescence: Iron particles do not fluoresece and appear much darker than surrounding areas. See PCC 6.4.4.

E. Spot Tests

Stain tests used in research permanently stain cellulose and are therefore inappropriate for works of art or archival collection material on paper. In spot testing, the paper conservator is limited to those cases where a sample can be removed from the work without detracting from the appearance and integrity of the work of art or artifact.

1. Acidity
   pH can be tested with indicator strips or, more accurately, with a pH meter.

2. Sampling of bullseye to perform iron test:

   a. Potassium Ferrocyanide
      Saturate the sample with dilute hydrochloric acid and then add a 1% solution of the reagent. A blue color indicates the presence of iron. This test is extremely sensitive and one can get a positive result with Whatman filter paper or plain blotters [RD]. See PCC 10.4.12.A.2.b.

   b. Potassium Sulfocyanide
      The sample is allowed to absorb dilute hydrochloric acid almost to saturation. A dilute aqueous solution of the reagent is then applied with a dropper. A pink color shows the presence of iron. This test for ferric iron is sensitive to 1 ppm [Iiams and Beckwith, 1935, 412]. This test is more sensitive than SEM-EDS (~1000 ppm) or XRF (~100 ppm) [RK].

   c. Potassium Thiocyanate
      The sample is tested with a 5% solution of the reagent to which one drop of 10N hydrochloric acid was added. A brown color, easily distinguishable from the color of foxing, indicates the presence of iron [Iiams and Beckwith 1935, 412]. This test is sensitive to 1 ppm.

3. Fungal Activity
   Cotton blue-lactophenol can be used for identification of living tissue in paper samples using transmitted light microscopy. It may be purchased ready-made from biology suppliers [RK].

F. Analytic Instrumentation

Employed in research to identify fungal presence and/or metal ions.

1. Scanning Electron Microscopy (SEM)
   Used by Cain and Miller to examine iron and copper cores in sampled foxing. They found that while some particles had irregular, bumpy surfaces, others had "nearly smooth surfaces and their shapes suggested chips or flakes, perhaps from wear in the paper-making machinery" [Cain and Miller 1982, 56-7]. Arai employed this technique for identification of fungi; it readily shows hyphae and conidia of fungi, if present [Arai et al. 1988, 11].

2. Energy Dispersive X-ray Spectral Analysis (EDX or EDS)
   Using this technique, Cain and Miller identified cores of either iron or copper in all sampled foxing [Cain and Miller 1982, 56]. As this instrument is not sensitive to lighter elements like hydrogen and oxygen, it would not indicate if the iron was present in the form of hydrated iron oxides/hydroxides. Daniels and Meeks used EDX to identify copper and related elements in foxing [Daniels and Meeks nd.,7]. Also used by Arai [1987, 1165].

3. X-Ray Fluorescence (XRF)
   Press used XRF and concluded that there was no difference in iron concentration between foxed and unfoxed areas [Press 1976, 29]. Cain and Miller used a more sophisticated XRF set-up to locate an iron core in a foxing sample where SEM and EDX were unsuccessful [Cain and Miller 1982, 57].

4. Flameless Atomic Absorption Spectroscopy
   Tang found this to be a "simple, rapid, and extremely sensitive method of determining metals in cellulosic materials directly on the solid sample." Most areas of foxing analyzed showed higher iron or copper concentration than surrounding unfoxed areas [Tang 1978, 28, 31].

5. X-radiography
   Using x-rays generated at a 10kV potential, metal particles were visible on a radiography plate as white specs on a black background. Daniels and Meeks found that all visible foxing they examined "displayed a nucleus of a small particle of radiographically dense material, but there were more particles detected on the x-ray plate than were visible in the paper" [Daniels and Meeks nd., 5].

6. Thin Layer Chromatography (TLC)
   Employed to detect oligosaccharides and amino acids from foxed spots [Arai et al. 1988, 12]. Also used to show that foxing contained many of the same degradation products as found in normal cellulose [Cain 1983, 16]. A later study by Cain used TLC separation of extracts of foxed spots and of cultures of the isolated fungus, *A. repens*, showed certain unique bands in addition to those characteristic bands produced by extracts of unfoxed areas of the same paper [Cain, Stanley and Roberts 1987, 24].

7. Isotachophoresis
   Used to analyze organic acids [Arai et al. 1988, 1166].

8. High-powered Fluorescent Microscopy (160-1000x)
   Used to examine fungal mycelium and hyphae [Meynell and Newsam 1978, 467].

13.2.5 Effects of Foxing

A. Support

1. Sizing
   Meynell and Newsam observed that stained areas wet more easily than the rest of the sheet indicating fungi may grow, thrive on, and destroy the size [Meynell and Newsam 1978, 467]. It is possible that certain fungi prefer size to cellulose and will only attack cellulose when the available size is exhausted. The resulting uneven sizing in paper could cause uneven washing and bleaching during conservation treatments.

2. Cellulose
   Cain found that the degradation products of foxing spots are similar to the degradation products of cellulose and suggested that some cellulolytic activity is taking place, not simply a degradation of the size [Cain 1983, 15]. As by-products of digestion, fungi will excrete a variety of acids including malic, fumalic, lactic, and acetic, with resultant damage to cellulose [Arai 1987, 1166]. Iiams and Beckwith found the tensile strength of the foxed areas was considerably less than the unaffected parts of the same sheet, and that foxed areas were always more acidic than unfoxed areas [Iiams and Beckwith 1935, 409].

   Research shows that metal ions catalyze cellulose degradation, producing oxidized cellulose and large amounts of acid. The higher concentration

of acidity in foxed areas also contributes to cellulose deterioration.

B. Media

1. Pastel
   Gum binder is a good nutrient; some colors (dark rather than light) are preferred due to higher binder content [BF].

2. Color Prints
   Loss of color in patterns which approximate foxing areas have been observed in the blues. It may be acid attack of ultramarine by negative or reverse foxing [JCW].

3. Miniatures on Paper and Ivory
   Gum binder in watercolor may be attacked, possibly due to the high proportion of hygroscopic additives (glycerin, honey) [BF].

13.3 Materials and Equipment

13.3.1 Examination Equipment

A. Near Ultra Violet ("Black Light")
Radiant energy in the range of 320 to 400 nanometers.

B. Spot Test Reagents

C. Cultures
Ready made,sterile nutrient pad kits are available from Sybron/Nalge. They have a limited shelf life.

D. Stereomicroscope

13.3.2 Treatment Equipment

A. Chemical Reagents

1. Alkaline water
2. Bleaching reagents
3. Reducing agents
4. Chelating agents
5. Acids

B. Tools

1. Scalpel/Sampling blade

2. Microscope slides

3. Small brushes for localized work

4. Vacuum suction table for localized work

13.4 Treatment Variations

13.4.1 Environment

A. Housing
There is some experimental evidence that foxing will worsen over time if kept in a poor environment. As for any other damaged, brittle or inherently fragile materials, proper housing with non-acidic or buffered materials, non-damaging RH and temperatures and limited handling and exposure must be considered the first treatment step, which may mitigate further damage [Beckwith and Iiams 1935, 415-16].

B. Relative Humidity (RH)
Storing paper at a low RH is recommended as "the best precaution against foxing" [Daniels 1988, 93]. See 13.2.1.A.3.a and 13.2.1.B.1.d.

C. Temperature
Fungi generally prefer temperatures of 25°C to 35°C, dependent on species. There is no indication that iron corrosion is temperature dependent. Often temperature in storage or exhibition spaces is determined by comfort zones for people, and it is therefore easier to regulate RH to avoid conditions which may further damage paper.

D. Ventilation
Good circulation is often mentioned as a deterrent to mold and air borne fungi especially in articles relating to libraries [Allsop 1985, 533].

13.4.2 No Intervention

Walsh rightly notes that "foxing patterns do not always constitute a disfigurement to a work of art." She indicates a charcoal-and-ink wash drawing by Daumier in which the artist executed the work on a sheet of foxed paper and incorporated the snowflake pattern into his design [Walsh 1985, 8]. Some papermaking historians feel that metallic inclusions are part of the paper's history and should not be removed [RF].

Harding found that works of art on prepared paper (e.g. silverpoint) were "in general not susceptible to foxing, although one or two fox marks may occasionally be

evident. It would be very unwise to attempt removal of the spots, as this would normally involve the localised application of aqueous solutions... inevitably result[ing] in an unsightly spot with a surrounding halo, and disruption of the reflective properties of the surface of the drawing" [Harding 1986, 26].

13.4.3 Fungicides

Most conservators do not use fungicides. Though a variety of substances have been used as fungicidal fumigants (thymol, ortho-phenylphenol, etc.), none are actually fungicides as such (though one specialist maintains that ortho-phenylphenol is fungicidal [RK]). Rather, they are fungistatic, inhibiting fungal growth only while the toxin is present. Dissipation or evaporation of the substance will allow fungal growth to continue. A true fungicide would kill all fungi and spores on contact [Haines and Kohler 1986, 50].

13.4.4 Alkaline Washes

A. Neutralization of Acidity

As mentioned above, both fungal action and metal ion catalysis will result in acidic degradation products. To prevent further acid-catalyzed hydrolysis of paper these should be neutralized.

Beckwith et al. state that the intensity of color is greater in an acidic environment than when a sheet is alkaline. This indicates that imparting an alkaline reserve during sheet formation might reduce the severity of future discoloration [Beckwith et al. 1940, 311].

B. Reduction of Staining

Beckwith et al. determined that the content of material soluble in a weak base (4% aqueous solution of ammonium hydroxide) increased markedly in foxed areas as compared to unfoxed, and that this material is hygroscopic [Beckwith et al. 1940, 322]. This may in part explain why foxed areas in paper absorb moisture first and most completely when a sheet is moistened. Gallo and Hey found that washing with alkaline water can attenuate, if not completely remove, many foxing marks. Deacidification, with half-saturated calcium hydroxide solution, was even more satisfactory [Gallo and Hey 1988, 102]. However, many conservators would consider the pH of this solution too high [AK]. Percentages as high as the four percent used by Beckwith et al. are not recommended for treating works of art on paper, though less concentrated alkaline solutions have been found useful for reducing foxing.

C. Treatment of Metal Ions

It is believed that both calcium and magnesium compounds form stable complexes with the transition metals (eg. iron and copper) and by so doing "retard cellulose depolymerization by deactivating the transition metal catalysis", it should be noted that "magnesium [carbonate] is a more effective stabilizer than calcium carbonate" [Williams et al. 1977, 49; 57-58]. Hey believes this statement to be somewhat misleading and discusses reasons why calcium carbonate is the better choice for depositing and alkaline reserve [Hey 1979, 78-9]. It is believed that imparting an alkaline reserve in the paper will prevent metallic ions from catalyzing cellulose degradation, though this may not prevent degradation and discoloration of the metal itself [Tang and Troyer 1981,44]. When the reserve has been used up by the paper, metallic catalyzed deterioration of cellulose may resume [JK]. Tang and Troyer found both calcium hydroxide and magnesium bicarbonate ineffective in removing copper from handmade papers. Only ammonium carbonate significantly reduced the copper content.

D. Pre-Treatment for Bleaching

Conservators often find alkaline washing of foxing (either localized on the suction table or by immersion) a good pre-treatment for bleaching. Not only does this sufficiently diminish foxing stains in many cases, it may help to inactivate metal ions if present. Alkaline washes are also used to raise paper pH so that the bleach can be used in the least damaging pH range. If iron is present and hydrogen peroxide is the bleach of choice, this would be a prerequisite. Conservators have employed the following solutions for alkaline washing or deacidification: calcium or magnesium carbonate and bicarbonate, calcium or magnesium hydroxide, and ammonium hydroxide.

13.4.5 Metal Removal or Inactivation

Metal related foxing, particularly that with a visible metal core, cannot be successfully inactivated by bleaching alone, though the staining may be reduced or eliminated. Conservation literature indicates that in order to prevent future metal-catalyzed oxidation of the cellulose, the metal should be mechanically and/or chemically removed, or rendered inactive. In practise, few conservators are currently using chelating agents to do this. Another suggested measure to render metals inactive is controlled environment (especially humidity) and proper housing.

A. Mechanical

Iron particles in the paper can be physically removed with a scalpel under a microscope. It has been recommended that such treatment should be followed by chemical treatment to remove any residual iron particles lodged in the fibers and to remove any staining that might have surrounded the particle. If any iron/metal is left in the fibers, it will eventually re-oxidize and the stain will reappear [Burgess 1988, 24].

B. Chemical

There have been several suggestions for decolorizing, complexing, or chelating metal impurities in paper.

1. Sodium Dithionite (Hydrosulfite)
   A 2-10% aqueous solution will convert the insoluble colored ferric ion (Fe^{+++}) to the more soluble colorless ferrous ion(Fe^{++}). Subsequent washing with a Fe^{++} specific chelating agent will remove the ferrous ions from the paper and should prevent color reversion [Burgess 1988, 24, See PCC 19.3.3.B.] Burgess also notes that the colorless ferrous iron can be removed by simple water washing, a chelating agent,however, would speed the process. If colorless ferrous salts are allowed to remain in the paper, they will "in time be oxidized by atmospheric oxygen back to the colored ferric compounds" [Burgess 1991, 33]. "Sodium hydrosulphite appears to be a relatively safe agent in that it does not substantially yellow paper, weaken it, or alter it's pH" [Hawlye, Kawai and Sergeant 1981, 21].

   See also PCC 19.3.3.B.

2. Chelating Agents: These have been used extensively in the paper industry and only recently has some research been directed towards their use in paper conservation [Burgess 1991].

   a. EDTA and Related Compounds
      Ferric or ferrous ion specific chelating agents have been successfully used to sequester and remove iron from paper, though generally in conjunction with a reducing agent. "Chelating reactions work fastest when both the chelating agent and the metal to be chelated are present in solution...An extremely good way to use chelating agents to remove iron is to couple them with another process which involves the reduction of the insoluble ferric ion to the more water soluble ferrous form. The conclusion is that chelation as a single

process will not always be an ideal way to approach removal of iron stains. Even in relatively concentrated solution,[chelating agents] do not seem to work very well...[due to] the low solubility of iron oxides and hydroxides" [Burgess 1991, 39]. Further research in the efficacy of ferric reagents such as Fe3 Specific (Dow Chemical Corp) would be beneficial.

b. Oxalic Acid
This was often recommended in the literature for removing iron stains, but it is highly acidic and its use is not advised. See Hawley, Kawai and Sergeant 1981.

3. Alkaline treatment of metal ions (See 13.4.3.C.).

4. Acid Solubilization
"Examples of acids which can solubilize iron are oxalic [see 13.4.4.B.2.b] or acetic acid. Home remedies such as vinegar or lemon juice have also been used in the past. Providing the acid is strong enough, iron removal will be relatively quick and complete. However, subjecting paper artefacts to pH between 0 and 4 can, and usually will, do considerable damage...Therefore, the use of acids to remove iron stains is now discouraged" [Burgess 1991, 39].

13.4.5 Bleaching

Bleaching would not remove metal impurities and may result in local metal-catalyzed degradation. This may explain the reappearance of metal-related foxing after bleaching treatment. The recurrence of stains after bleaching treatment may also be due to improper use of bleaching solutions, inadequate pre-treatment, or inadequate rinsing. While visible discoloration may disappear as a result of bleaching, florescence under UV will continue [Meynell and Newsam 1978, 467].

Special attention should be taken when bleaching foxed areas, as the cellulose in these areas is generally more degraded than in surrounding areas and will be further weakened by oxidative bleaches.

A. Chlorine Dioxide

Treatment can be either gaseous or aqueous. It has been found that this bleach will "often decolorize severe foxing without as much degradation or color reversion as the hypochlorites" [PCC 19.3.1.D]. Burgess emphasizes the importance of washing after treatment, whether gas phase or immersion bleaching has been employed, to remove bleaching residues and

solubilized discoloration products [Burgess 1988, 22]. This bleach is the least affected by trace metal elements in the paper.

Meynell found that ClO_2 was successful in reducing foxing, though he was often left with a "light biscuit-coloured patch" rather than a total disappearance of the stain [Meynell 1979, 31].

See also PCC 19.3.1.D.

B. Hydrogen Peroxide

The degradation of paper can be excessive if unstabilized hydrogen peroxide is used, particularly when metal-induced foxing is the cause of the staining being bleached. Stabilizers in the hydrogen peroxide will help prevent metal catalyzed breakdown of the bleach solution and therefore lessen cellulose degradation during the procedure. Stabilizers such as magnesium silicates and hydroxides used in hydrogen peroxide function similar to chelating agents in that they act to complex metals and prevent them from participating in chemical reactions [Burgess 1991, 42]. Probably even stabilized hydrogen peroxide should not be used on paper with conspicuous stains of heavy metals (e.g. iron, copper) or their salts or oxides unless complexing of these metals within the paper has also been undertaken.

This bleach is commonly used by conservators for foxing stains, though most do warn against it if they believe iron is present. Presumably, this assessment would be based solely on examination by visible or transmitted light, as most conservators reported that they rarely, if ever, used UV when examining foxing. The research has shown that all bullseye foxing is centered on iron particles, and that snowflake foxing generally shows higher iron concentration than surrounding areas [Cain and Miller 1982, 56; 60]. This would contraindicate the use of hydrogen peroxide unless it could be shown that specific foxing did not have a high iron concentration or if iron ions could be inactivated or removed prior to bleaching.

See also PCC 19.3.1.A.

C. Calcium Hypochlorite

Gallo and Hey found that 5% solution was more effective in removing foxing stains than were 5% solutions of Chloramine-T and hydrogen peroxide (though these concentrations were not recommended for

conservation use), and that reversion did not occur with sheets rinsed in alkaline water [Gallo and Hey 1988, 102]. Burgess suggests a much weaker bleaching solution (0.1 to 0.5%) and recommends that calcium hypocholorite only be used on severely stained artifacts in otherwise very good condition [Burgess 1988, 22].

Calcium hypochlorite is occasionally used by conservators for stubborn foxing stains and has been found to be especially effective. It has the added advantage of being a fungicide for some species of fungi.

See also PCC 19.3.1.B.1.

D. Chloramine-T
A 2% solution was recommended [Coleman et al. 1969, 197], though this bleach has generally fallen from favour due to the difficulty in removing residues from the paper [Burgess 1988, 22].

See also PCC 19.3.1.C.

E. Sodium Borohydride
This moderate to weak reducing bleach generally removes mild stains but is only capable of partially eliminating severe staining. It is commonly used by conservators in concentrations of .1 to 2%, sometimes in combination with hydrogen peroxide treatment [Burgess 1988, 22].

See also PCC 19.3.3.A.

F. Natural or Artificial Light
Ultraviolet radiation in the light source, combined with moisture in the paper, will produce peroxides which could then destroy mold (if present) and bleach discolorations [Hey 1983, 342]. This is best not used with papers with conspicuous stains of heavy metals (e.g. iron, copper) or their salts or oxides. This bleaching method is commonly used by conservators for foxing stains. Some work has been done with localized light bleaching using a fiber optic light source directed only at the foxing stain to be bleached.

See also PCC 19.3.4.A and B.

13.4.7 Conservators' Observations of Foxing

On particular papers or artists' work that show any unusual or consistent foxing patterns:

A. Early Papers and Artists

1. Many of Leonardo's and Durer's drawings and prints are foxed. In a Durer print, The Triumph of Maximillian, executed on a composite support of several pieces of paper joined together, foxing appears on only some of the papers. Foxing has been observed on old Chinese papers and incunables [MH]

2. Have not seen much foxing on papers earlier than 17th century, especially Italian [BF].

B. 17th and 18th Century Papers and Artists

1. Tiepolo used what appears to be good quality laid paper (watermarked with three crescents). Many are heavily foxed overall [HO].

2. Have often found that with 17th/18th century rag papers alkaline washing alone is sufficient to remove/reduce foxing so that bleaching is not necessary. This is generally not observed to the be case with 19th/20th century papers [RF].

3. Foxing of 18th and 19th century watercolors on good quality papers often migrates from poor quality backing boards [JD].

C. 19th Century Papers and Artists

1. Goya's complete set Disasters of War on antique laid [BF].

2. Mounted albumen prints foxed on photo but little on mounts, or not in area of solid printed border [BF].

3. Matisse Jazz suite: small scattered bullseye foxing [BF].

4. Arches wove [KGE].

5. White spots on VGZ papers, some late 19th century wove papers with lightly calendered surfaces [MS, see also 13.6 Special Considerations].

D. 20th Century Papers and Artists

1. Van Gelder Zonen - Picasso, Braque, Miro exhibit snowflake and reverse foxing [BF; see Special Considerations 13.6].

2. Iron introduced into paper in solution: water used in plein air watercolor painting. Dramatic occurrence of foxing only on the part of the sheet that was colored with wash. Artist unidentified, 20th century American [NR]. It is not certain that this is iron induced foxing or due to the paper being damp.

3. Very rare to see foxing in gelatin silver photos of the 20th century - perhaps they are protected by baryta layer or clay fillers in paper [BF].

E. Printing Papers

1. Printing papers which have been kept moist for long periods of time before actual printing often show foxing [PV].

2. Printmakers often observe fungal growth before printing if they have not kept damp papers carefully. The fungal activity shows up as spots which wet out differently from the rest of the sheet [SB].

3. Foxing seems more common in late 19th century American printing papers rather than drawing papers of the same time period. Snowflake foxing is often seen on unbound Audubon/Havell prints which are Whatman and Whatman Turkey Mill papers [RF].

F. Chine Collé papers

1. In many collé prints foxing is seen in area of adhesive, as the paste is a good nutrient. It would be interesting to see if contemporary collé prints using CMC will also become foxed where adhesive is used [BF].

2. Redon chine collé prints are often foxed [MHE].

3. Heavy foxing noted on plate papers of many chine collé prints where thin image bearing sheet has no stains [NH, SB].

4. The poor quality, hygroscopic plate paper often shows foxing [SB].

G. Japanese Papers

1. Have rarely seen foxing on Japanese prints. However, when observed the papers were often mounted to poor quality Western materials [JCW].

2. Have often seen foxing on Japanese prints, especially those kept in Japan. There are certain types of traditional handmade papers such as tengujo, which is force-dried on iron steam driers. These show tiny scattered brown spots believed (by Japanese) to be iron contamination [BF].

H. Effects of Light

1. Have observed foxing in paper in areas in contact with acidic poor quality window mats and none in exposed area. Uncertain whether this has to do with light inhibiting the formation or whether higher humidity/acidity levels in covered areas are favoring formation [KGE].

2. Exhibition under fluorescent light seems to have "bleached foxing in 2-3 known cases" [KDL].

3. Have observed snowflake foxing which was "negative" (or lighter than the paper) in the area beneath an acidic matboard window and "positive" (brown or darker) in the area exposed to light. Was its growth under the mat discouraged by alum rosin sizing in the mat? [JCW] Same phenomenon also noted in reverse foxing on Van Gelder Zonen papers where portion exposed to light by window mount is dark brown [DDM]. See also 13.6 Special Considerations.

13.4.8 Observations on Current Conservation Practices

The following summarizes responses to the foxing questionnaire as well as statements made by contributors.

A. Examination

1. Respondents are divided as to the cause of foxing, but many believe a combination of factors are responsible.

2. Respondents easily differentiated fuzzy mold growth from foxing stains.

3. Respondents usually did not describe foxing by shape, fluorescence (or lack thereof), color or size, although some did use the terms "bullseye" and "snowflake".

4. Respondents usually do not use ultra-violet radiation in the examination of foxing spots.

5. Respondents usually do not employ spot tests to confirm the presence of iron/metal.

B. Treatment

1. Respondents do not often mechanically or chemically attempt to remove metal from paper, although several respondents mentioned occasionally trying acids and chelating agents. The following are examples:

   a. On iron spots have excavated centers. Have also tried (without success) oxalic acid, hydrofluoric acid and titanium trichloride [BF].

   b. Very dilute oxalic acid used to remove pin-point foxing on the suction table. Also have reduced dark bullseye foxing stains with dilute citric acid [JCW].

   c. Have used oxalic acid and EDTA on iron stains/specks found in foxing. The results were questionable and the aesthetic improvement was minimal. Admittedly I have not tried these chemicals in some time and it would seem their application has merit [NH].

   d. If iron is present I'd perhaps try Versene FE3 Specific, <1% solution before considering a bleach [KGE].

2. Respondents usually employ an alkaline wash or apply it locally to foxing prior to bleaching. They do this for several reasons: to diminish foxing and possibly obviate the need for bleaching, to raise the pH of the foxed area to an acceptable pH range in preparation for oxidative bleaching, and/or to possibly inactivate metal ions in paper. The following are examples:

   a. Wash overall. Locally apply ammonium hydroxide solution pH 8.5 to foxed spots, blot dry to remove discoloration or contain any staining from spreading. If spots remain, local application of either hydrogen peroxide or sodium borohydride [ML].

   b. Wash overall. Remove any obvious metallic inclusions mechanically. Pre-treat stain areas locally with deionized water made alkaline (pH 8.5) by the addition of calcium hydroxide solution. Allow to dry and assess need to bleach [SB].

c. Wash art in alkaline water and bicarbonate solutions. Have used calcium hydroxide, magnesium carbonate, magnesium, bicarbonate, and ammonium hydroxide solutions. If further removal of foxing stains is needed, light bleaching in an alkaline bath is preferred method [NH].

d. Have reduce bullseye foxing spots on the sky of a watercolor on Whatman paper by locally washing with dilute ammonium hydroxide on the suction table [JCW].

e. It should be noted that significant improvement can be brought about with ammonium hydroxide and this pre-treatment makes bleaching with hydrogen peroxide and sodium borohydride more effective [MHE].

f. I have had some success in removing/reducing foxing with local application of ammonia using small cotton poultices soaked in ammonia and placed in the foxed areas. With many 17th and 18th century rag papers I have found alkaline washing is often sufficient to remove/reduce foxing so that bleaching in not necessary. Ammonia (pH 8.5) is also used as a pre-treatment when bleaching is necessary. The ammonia is applied locally with a brush and area partially dried before immersing in water for sun bleaching [RF].

3. In bleaching foxing, conservators will almost always apply bleach locally to spots first, followed either by an overall bleaching or by rinsing alone. The following are examples:

a. For local applications use sodium borohydride .5-2.0% with a couple drops calcium hydroxide added to maintain pH, pre-wet areas with ammonium hydroxide (pH 9) and local rinse with same. Does not cause halos. Do not use hydrogen peroxide if possibility of iron (bullseye) is apparent. Also, it tends to cause halos [BF].

b. Sodium borohydride .5% and .1% solutions were applied locally to foxed areas of a pre-washed pencil drawing on paper. As the foxed spots were already quite damaged a reducing bleach rather than an oxidizing bleach was preferred. Application of the the borohydride was restrained as it was anticipated the elevated pH of the borohydride solution would also swell

paper fibers locally and result in further release of color bodies in the rinse bath. Water rinsing resulted in further diminishing of foxed areas to a pale tan color which no longer competed with the visual impact of the drawing. Overall treatment of drawing in bleach was not considered appropriate, both because of the risk of paper delaminating in small blisters and because the unfoxed portions of the paper showed a tendency to lighten considerably when spot tested [KN].

c. Have seen red-brown foxing reduced with sodium borohydride go light gray-looking dirty. This could not be oxidized back to white with peroxide [RF].

d. If a hard sized paper is foxed, I will sometimes float the sheet on a bath of peroxide. The bleach comes up through the spots but not through the rest of the sheet [JCW].

e. Follow alkaline washing and drying of the sheet with local application to spots of either hydrogen peroxide (3%, pH raised to 9.0-9.5 with calcium hydroxide) or sodium borohydride (.5%). Allow to dry. Repeat as necessary. Minor rings which may form and remaining foxing marks tend to bleach out when followed by overall light bleaching. Rinse thoroughly in water baths [NH].

4. Respondents most often mentioned using hydrogen peroxide as bleach of choice on foxing. Sun bleaching in water with calcium hydroxide added was also frequently cited. Reducing the foxing with sodium borohydride was the third most mentioned bleach. One respondent mentioned using chlorine bleaches when hydrogen peroxide could not be used due to presence of metal in paper. The following are examples:

a. Use 2% hydrogen peroxide (pH 8.5 with ammonium hydroxide and calcium hydroxide added). Use 3-4 applications drying between each application. Use hydrogen peroxide only until slight bubbling begins, then discard and mix new solution if necessary [SB].

b. Sunlight or sunlamps are used rather than a fluorescent light bank. Adding a few drops of hydrogen peroxide to the tray seems to catalyze the effect of light [NH].

c. Have used hydrogen peroxide in water-ethanol mixes on the suction table for charcoal or white chalk drawings which were badly foxed. Have sun bleached a foxed intaglio image by Albers in 75% ethanol, then washed in the same mix to great effect [JCW].

d. For artwork which cannot be immersed, wash art as possible (suction table, disk, or by floating) and light bleach by local wetting of foxed areas and exposing to light source. Mask sensitive areas. Rinse thoroughly as above [NH]. One technique for shorter light bleaching time is to locally bleach foxed spots with hydrogen peroxide, rinse, then place in sunlight bath. Conservators sometimes add a few drops of hydrogen peroxide to the bath used in light bleaching.

5. Some respondents noted that in some cases foxing could not be completely diminished and that they accepted a pale ghost-image of the stain rather than continue bleaching.

6. Respondents generally have noted few incidences of color reversion. Some noted reversion with hydrogen peroxide, but often attributed this to poor rinsing.

7. Some respondents stated they believe that chlorine bleaches to be useful on fungal foxing.

8. Respondents generally do not use a fungicide for foxing.

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13.6 Special Considerations: Reverse Foxing

13.6.1 Definition

This is an informal term coined by conservators who noticed spots in paper which had a much lighter tone than the surrounding sheet. This is sometimes referred to as negative foxing. The phenomenon may not actually be foxing, i.e. it may not be related to metallic or biological causes. These spots do, however, have some of the characteristics described in Cain's classification of foxing and, for lack of a better term, at present these stains or spots will be referred to as reverse foxing. There has been little or no research on reverse foxing. Observations have been made of numerous reverse foxing spots on Van Gelder Zonen (VGZ) papers, in particular those used by Vollard to print Picasso's Saltimbanque series. These are on wove paper with VAN GLEDER ZONEN watermark. Reverse foxing is not isolated to VGZ papers but has been noted by conservators on Arches and Ingres papers as well.

There are several Van Gelder Zonen papers with different watermarks [DDM]. Those observed are:

A. Fleur-de-lys with VGZ/Z

B. VAN GELDER ZONEN/HOLLAND

C. VAN GELDER ZONEN

Works by Picasso, Braque, and Miro exhibit snowflake and reverse foxing [BF].

Works by Pennell, Zorn, and Shaw also exhibit snowflake and reverse foxing [DDM].

13.6.2 Description

There were three types of spots observed on the VGZ papers examined. Whether these spots are caused by uneven sizing or fillers in the sheet, or perhaps by a pH sensitive dyes is not known. Whether the three spots noted are different stages of the same thing is not known. For conservators VGZ papers, and perhaps others with reverse foxing, can often be problematic (see 13.6.3.) [TO].

A. Visible white splotches similar to "snowflake" which are lighter in tone than the sheet. They are of varying size but generally quite large, round, and have uneven diffuse edges. In some cases the white splotches have tiny whiter cores. They are located almost invariably within the plate mark area on the verso of the paper and are rarely seen on the recto, except sometimes as small pinpoint white spots which

correspond to centers of the splotches verso. These spots generally fluoresce a brighter white.

B. Visible white circular spots lighter in tone than the sheet. These are generally quite small, have a hard sharp edge and are distinctly round. These spots are not restricted in location and were found on the recto, verso, plate and in the margins. Often these spots seem to migrate through the paper. These fluoresce white.

C. Not visible, or only faintly visible, in normal light, these small greyish/brown spots or inclusion are noted in transmitted light and UV. They do not fluoresce, appearing blue/black under UV. They appear to have a core.

13.6.3 Treatment Warnings

Caution should be taken when attempting to bleach Van Gelder Zonen papers which have reverse foxing. Numerous conservators have found areas of the paper not previously white will turn stark white during bleaching. It is possible the areas which turn stark white during bleaching are the invisible brown inclusions found under UV examination. Some conservators have stated they got stark white spots with water washing alone! Bleaches reported to cause this to occur are: hydrogen peroxide, sun bleaching, sodium borohydride, Chloramine-T and calcium hypochlorite. One bleach which has been reported to have some success is chlorine dioxide, used at approximately .2% for only several minutes. This bleach can also cause white spots but the short bleach time seems to allow conservators to reduce stains as necessary and begin rinsing before the stark white spots can begin to appear [TO].

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