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The effects of aging on textiles that contain metal: implications for analyses

Abstract

Factors which affect the general condition of historic textiles containing metal are listed and discussed. Specific elements of structure for textiles which contain metal (metal, organic substrate, adhesive, fiber) are discussed according to physical and chemical deterioration processes with emphasis on what a careful observer might expect to see on an historic textile containing metal. The effects of common textile conservation practices on textiles containing metal are described.

Introduction

Recently five categories describing the inclusion of metal in textiles have been defined [41-43, 46, 47].

Table 1 *The Five Categories*

I.	Metal applied (with adhesive) to already woven fabrics.
II.	Metal wire or flattened strips.
III.	Metal wire or strips wound around fiber core.
IV.	Metallic surface applied (with adhesive) to organic wrapping wound around fiber core. a. Organic = cellulosic. b. Organic = proteinaceous.
V.	Metallic surface applied (with adhesive) to organic strips. a. Organic = cellulosic. b. Organic = proteinaceous.

These categories exclude metallic salts or oxides used as mordants or pigments. Reasons for assigning these categories are: 1) to provide a convenient way of describing textiles containing metal; 2) to survey the historic and geographic implications of such categorization; 3) to provide a pedagogic introduction to this aspect of textile technology. Other studies defining similar categories have been noted [8, 14, 25, 35, 54, 55, 90, 97, 109].

Textiles that contain metal stand out from other textiles. In surveying examples of textiles with metal some observations concerning the condition of historic textiles reflect both on their art historical significance and their fragility:

a) Textiles containing metal are generally in poorer condition than those which do not contain metal if comparable conditions of material quality and survival have been provided. Special stresses from the high mass of material and the multiplicity of degradation processes tend to undermine the integrity of the fabric containing metal on aging. Sometimes, because of their artistic, symbolic, or economic value, textiles with metal have been so treasured that special care and treatment has been provided while comparably old unadorned textiles have been treated as disposable.

b) In a textile that contains metal the areas that contain metal will tend to be more degraded than other areas. Not only are the fabric and thread systems which have metal more sensitive to natural aging processes, but they are more susceptible to degradation from the general practises such as cleaning and washing wich are intended to maintain the integtity and beauty of the material.

c) Historic textiles that contain metal and appear to be in good condition (superficially) invariably show considerable evidence of degradation and loss specifically associated with the metallic inclusion upon close (microscopic) inspection.

d) Archaeological and lexicographic evidence point to significant loss of textiles containing metal. Some excavations have unearthed beaten metal strips that appear to have been associated with textiles although no trace of attendant textile remains [33, 73, 79, 85, 109]. It is interesting that several languages retain words for the act of, or the person, reclaiming metal from textiles that are remnants of the tailoring process, have become worn, or lost favor [45, 48, 78, 111].

Aging

The condition of historic textiles may be seen as depending on two large factors: the quality and the peculiarities of the manufacturing processes; and the circumstances and uses to which the textile has been subjected.

a) Manufacture

i. The longevity of a textile material will depend heavily on the skill, patience, and intentions of the craftsmen involved. For example the tightness of weave, the ply of the thread, the fineness of the fibers have a profound effect on the aging behavior of any textile.

ii. The aging characteristics of a textile will also depend heavily on the quality of the materials employed. For example the quality of fibers available, seasonal variations in raw materials, alloy composition of metallic materials, may profoundly affect the aging behavior of the textile.

iii. Regional or workshop practices which may have little to do with skill or material quality but more to do with tradition, aesthetics, or individual experimentation may profoundly affect the aging of textiles. For one example iron mordants, used in a number of dying recipes, seem to be particularly corrosive to fibers. Other examples are the extremely fine Moghul silks of the seventeenth century, so fine because the raw silk may have been subjected to exhaustive degumming, producing a fine filament, initially of very high tensile strength, but which experiences serious embrittlement sooner than courser materials of a comparable age (e.g. Turkish, Persian) owing to the loss of sericin during the degumming.

b) History

Those textiles which were adorned with metal were generally devised for sumptuous or symbolic effect. Usually, but not always, the textile served a function in addition to its decorative value. Beyond its era of functionality the textile may be stored, displayed, or studied in a collection. Because of their portability and sumptuousness many textiles containing metal are known to have travelled great distances (gifts of emissaries, explorers' hoards, war booty, trade goods, heirlooms) undergoing climatic and environmental changes that would tend to place considerable strain on the textile. The following list attempts to take into account the many possibilities that a textile may experience in its history.

i. Wear, abrasion, use, affects the aging of the textile. This kind of deterioration consists of a set of physical phenomena [32] describable in terms of frictional forces interacting, stresses, strains, folding, tearing, bending, compression, twisting, etc.

ii. If the textile is clothing, in addition to the above set of physical phenomena, the cloth may have come into contact with body fluids. The interaction of aqueous material with textiles may produce a wide array of chemical (hydrolytic) and physical (fluid absorption, salt deposition) changes, profoundly affecting the aging of the textile.

iii. The interaction of atmospheric gases – oxygen, ozone, oxides of nitrogen and sulfur, particulate matter, may affect the condition of any textile. Chemical reactions may degrade fibers, organic substrates, adhesives, and metals to form corrosion products.

iv. Archaeological textiles may have had direct contact with earth, decaying animal matter, moisture, ground water and minerals, as well as conflagration.

v. Biological attack – fungal, insect, rodent, ect. may come at any time in the life of a textile, archaeological or not. In addition to producing physical damage owing to loss of material, sometimes biological attack weakens the fabric chemically, so that further biological attack is facilitated. Generally the mechanisms of biological degradation are both oxidative and hydrolytic[84]. Although metallic elements are not susceptible to biological attack the textile system that supports the metal (adhesive, organic substrate, fiber) is not immune.

vi. Display and storage are benign for textiles compared to wear, use or burial, but prolonged exposure to high light levels, cycles of changing temperature and relative humidity, biological attack as well as exposure to atmospheric pollution may have profound effects on the aging behavior of textiles. Some of these hazzards are likely to be visited upon textiles (especially for transported collections of foreign origin) unless storage conditions accomodate these changes. Environmental changes can exascerbate problematic interactions among fibers, metal, adhesive, substrate. Adhesive, for example, used in a particular climate can alter substantially when placed in a different environment.

vii. Conservation treatments have experienced extensive revision and local idiocyncracies at various times. (The germ theory of disease must have given license to wash textiles that were made with the clear recognition that water would never be used on them: cf. paper, membrane, parchment, substrates for metal threads.) Technical training and technological advances enhance consciousness of the structure of matter and deterioration mechanisms as well as our ability to control environments. Connoisseurship and historical acumen tend more and more to enter into the decision making processes of what must be preserved for the cultural heritage. There is a general assumption that treatment, study, maintanance, storage of museum materials constantly improves, and that at least some of the deleterious effects of aging among museum textiles is ameliorated. Conservation treatment requiring any kind of handling is damaging to a textile. Treatment involving liquid agents, aqueous or non-aqueous, will produce irreversible changes in the textile. Of course no treatment or alternative treatments may be worse. Various forms of aqueous treatment – bleaching, soaping, lubricating, wetting, swabbing, humidifying, especially accompanied by agitation may be unsafe. In the first three cases chemicals are used which may be difficult to remove suggesting long term implications for the aging of the textile. In all cases, especially for old or embrittled examples material will be lost. Nonaqueous solvents can produce even greater loss, weakening of metal interfaces, and visual effects that may be unacceptable. Most treatments are performed to remove soils and stains (sometimes consolidants {glues, tapes, etc.} from earlier conservation treatments), to free the textile from undesirable wrinkles and folds, and to reveal and clarify design elements – color, weave patterns, metallic luster, etc. For this reason localized treatments specific to the area of damage and tailored to the type of damage are often the most appropriate. Sometimes the curatorial impulse to display a readable specimen imposes a costly conservatorial intervention, which the textile carries along as its legacy.

Deterioration mechanisms and methods of observation of the individual parts of metal-containing textiles

a) Metals

i. Gold, silver, and combinations of gold and silver, [8, 11, 17, 24, 34, 37, 41-43, 54-57, 73-77, 87, 97, 101, 109, 112] have been used most frequently as textile adornment, although examples of alloys of baser metals have also been observed. Table 1 indicates the various kinds of metal inclusions in textiles. Categories **I**, **IV**, and **V** involve adhesives; Categories **II** and **III** do not.

ii. Table 2 emphasizes the various physical forms by which metal is incorporated into textiles, along with

Table 2 *Incorporation of metal in textiles*

Category	Metal	Cloth	Examples
	Application of Metal with Adhesive to Textile		
I	Leaf	Silk, cotton, linen	Chinese, Japanese, Indian, Indonesian, Medieval Banners
	Dust	Silk, cotton,	Indian, Indonesian
	Paint/Leaf (with other woven embroidered, or printed features)	Silk	Banners, [Fortuny gowns], Chinese
	Paint/Leaf (as part of a painted cloth)	Cotton ,linen	Tibetan Tangkas, Indian Pichawais, Easel Paintings.
	Metal [Thread] without Core	Cloth	
II.	Wire (Woven as weft. Laid and couched in embroidery, sometimes sewn)	Silk Silk, cotton	Turkish velvets Turkish embroideries
	Flattened Wire or Strip (Woven as weft. Laid and couched in embroidery, sometimes sewn.)	Silk Silk	Persian brocades Eur. Stumpwork
	Sequins, Mirrors, Ornaments (embroidered appliqued)	Silk, cotton, linen wool	Eur., No. Afr., Indian, Turkish, Indonesian embroideries.
	Metal Thread with Core*	Core	
III.	Wire (Woven usually as weft. Laid and couched in embroidery, sometimes sewn.)	Silk, cotton Silk, cotton,linen	Indian, Persian Brocades Ecclesiastical Embroideries
	Flattened Wire or Strip (Woven usually as weft. Laid and couched in embroidery, sometimes sewn.)	Silk, cotton Silk, cotton, linen Silk, cotton ,linen	Indian, Persian Brocades Eur. tapestries, Bizarre Silks Ecclesiastical Embroideries
	*Reindeer sinew in some Scandinav.textiles [24,25]; animal hair in core of few early exmpls.[9, 91, 109]		
	Metal Applied to Organic Substrates[a,b]; Wrapped on Core	Core	
IVa	Metal leaf applied to one side.Woven into silk cotton or bast fiber fabrics. Embroidery, Applique	Silk	Chinese, Japanese, Indonesian, Central Asian
IVb	Metal leaf applied to one side. Woven into silk fabrics	Silk, cotton, linen	Chinese, Medieval Eur. Western Asiatic
	Metal applied to Organic Substrates[a,b]; No Core	Cloth	
Va.	Metal leaf applied to one side. Woven Embroidered, Appliqued	Silk, cotton, bast	Chinese, Japanese Indonesian, Central Asian
Vb.	Metal leaf applied to one side. Woven, Embroidered, Appliqued	Silk	Chinese

a = Cellulosic substrate; **b** = Proteinaceous substrate typical illustrative examples. See Table 4 for appropriate references.

The identification of metal composition and attendant corrosion products is best achieved by X-ray probe techniques on microsamples which provide elemental analyses and/or identification of inorganic materials. Some instrumentation [15, 35, 38, 41-44, 46, 47, 54-57, 65, 67, 97, 101, 110] which has been used: X-Ray Fluorescence (XRF), Proton Induced X-Ray Emmision (PIXE), Energy Dispersive X-Ray Spectrometry (EDS), which provide elemental analyses; and X-Ray Diffraction (XRD) which identifies inorganic compounds. Sometimes analyses have indicated nearly pure gold or silver, other examples have been found with baser metals, or thinly gilded or silvered copper. Some brass samples have also been found. Later metallic threads are known to contain aluminium and other metallic elements incorporated in synthetic polymers [8, 111].

iii. Deterioration mechanisms for metals surfaces may be both physical (friction, abrasion, stress, etc.) and chemical (reactions with oxygen, water, oxides of sulfur and nitrogen, minerals and salts, etc.) processes. While gold is the metal least susceptible to corrosion, traces of baser metal corrosion can cause severe pitting and displacement of gold surfaces. Gold is most often found as a thin layer over silver; the microscopic appearance of gilded silver often shows a surface on which it is possible to see both gold and silver (corresponding to beating or drawing together a small amount of gold with silver, rather than alloying gold and silver with heat). All the usual corrosion products (oxides, chlorides, sulfides) may be found on silver surfaces, "tarnished" or blackened on most historic samples. Metal threads rich in copper have the potential for producing all the corrosion products generally associated with copper, including bronze disease. The nature of the corrosion products may be heavily influenced by the attendant substrate, adhesive, or fiber.

b) Substrates (paper, parchment, vellum, membrane, leather)

i. Categories **IV [a,b]** and **V [a,b]**, Table 1. Some metallic threads are made by adhesion of a metallic surface (leaf, powder, paint) to an organic substrate [18, 24, 25, 42, 43, 46, 54, 55, 67, 81, 83, 97, 101, 104, 105, 107, 109]. The organic substrate is cut into narrow strips and either wound about a core fiber (**IV**) or incorporated into a textile as a woven, embroidered, or appliqued feature as a flat strip without a fiber core (**V**). The identification of the substrate is best achieved by microscopy at ca. 50-250x magnification. Distinguishing characteristics [46, 83] of these materials are presented in Table 3.

A major difficulty arises in distinguishing these materials in a deteriorated state since identifying characteristics are often confounded by decomposition products.

The organic wrappings or strips used as substrates are gravely subject to the ravages of time. Paper, which

Table 3 *Appearance (Magnified) of Organic Wrapping Materials Found on Historic Textile Threads. Category IV and V.*

Wrapping Material	Chemical Composition	Appearance	Comments
Paper **IVa,Va**	Cellulose	White yellow brown. Opaque; no translucence No hair follicle pits.	Adhesive material usually visible between metal surface and paper. Silk core.
Membrane **IVb,Vb**	Collagen	Colorless offwhite pale brown. Translucent areas No hair follicle pits.	Adhesive material not uniformly visible. Dark areas of degraded adhesive. Silk, cotton, or linen core.
Parchment **IVb,Vb**	Collagen	White yellow. Generally opaque; sometimes nearly translucent areas. Hair follicle pits.	Adhesive material visible. Dark areas of degraded adhesive Silk, cotton, or linen core.
Vellum **IVb,Vb**	Collagen	Same as parchment. Hair follicle pits may be sparser and smaller than in parchment	Same as parchment
Leather **IVb,Vb**	Collagen	Brown. Hair follice pits larger than in parchment.	Same as parchment

is cellulosic, and the other organic substrates, which are collagenous are all known to deteriorate through a variety of mechanisms. [32, 84].

ii. Physical deterioration[32]. Tension, stress, abrasion, compression, and folding are prominently experienced by the textile during its period of use, all of which may have important effects on the substrate, in the form of losses, tears, unravelling, etc.

iii. Chemical deterioration[84]. Two general types of reaction tend to degrade the polymeric materials which form the basic polymer network: hydrolysis and oxidation. The hydrolytic reactions will tend to break (depolymerize) chains. The oxidative reactions will tend to produce cross-linking of the polymer chains, interact with functional groups that are present, form new functional groups, decompose to species that promote an autocatalytic effect on the oxidative processes. Both oxidative and hydrolytic processes may be catalysed be metallic species, always present in textile system that contain metal. Other types of chemical deterioration that can produce similar effects are: light damage, biological damage, fire damage, reaction with atmospheric pollutants, all of which are extreme examples of oxidative hydrolytic breakdown.

The appearance of aged substrates is usually quite different from new material, often reflecting the use the material has undergone or treatments that have caused both physical and chemical degradation. As might be expected, water damage or treatment may cause degradation and embrittlement of the substrate. Expansions and contractions of substrate from liquid absorption may result in detachment of the metallic surface and adhesive; oxidative processes tend to darken the material generally (cf the yellowing/browning of most organic materials on aging).

c) Adhesives

i. Adhesives are required for the inclusion of metal in textiles for examples of Category **I**, **IV**, and **V**, Table 1. Treatises and reports have indicated the use of a wide variety of materials used as adhesives [2, 3, 11, 19, 22, 28, 49, 57, 65, 92, 96]: bole, egg white, drying oils, gums, animal and fish glues, etc.

ii. These materials (except for bole) are difficult or impossible to distinguish microscopically. The analyses of these materials is similar to the problem of analysing media and varnishes on painted works [69], organic media used in studio patination of Medieval and later bronzes [97], or furniture finishes [69]. In all these, the original material is a complex organic mixture of high molecular weight substances. Upon aging, the chemical constitution of the material undergoes considerable (oxidative) change. A number of newer analytical procedures have been successfully used to identify organic materials of this kind even after considerable aging. Mass Spectrometry/Gas Chromatography (MS/GC) is an extremely sensitive tool for this analysis. Generally a small sample must be subjected to solvent extraction(s) and chemical derivatization(s) in order to produce material of low enough molecular weight to pass through the instrument. Pyrolysis Gas Chromatography (PyGC) [93, 94] in which samples are subjected to high temperature degradation and chromatographic collection of the fragments has been effective as an analytical fingerprint process especially when similar known samples or closely related materials are available for comparison. In a few studies Pyrolysis Gas Chromatography has been used with Mass Spectrometry (Py/GC/MS) [93, 94] to help identify the pyrolized fragments. Another chromatographic procedure is High Performance Liquid Chromatography (HPLC) [16, 34]. Fourier Transform Infrared Spectroscopy (FTIR) is a sensitive device that provides information on functional groups present in sample [64]. Amino acid analysis [34] should succeed for adhesives that contain egg white or glue. No systematic study attempting to analyse the adhesives specific to the inclusion of metal in textiles has been reported.

iii. The organic adhesives are particularly sensitive to oxidative degradation. The mechanism of degradative processes has received considerable scientific attention [84]. It is similar to the degradative processes described above for the substrates, and similar degradative processes also apply to the fibers, but the adhesive material, among the various organic materials in the system is most sensitive to oxadation. Numerous examples of exposed adhesive on substrates show uneven darkening from yellow to quite black. Water damage or treatment may also produce disasterous effects on the system, weakening either the adhesive-substrate or the adhesive-metal bonding. Fiber, substrate, and adhesive each have different water absorption capacities so that changing cyles of temperature and humidity may produce mechanical stresses in the system.

d) Fibers.

i. The identification of fibers is a well documented subject [89] and is usually achieved with a high degree of success using 10-250x magnification with ordinary microscopy. Occasionally the deteriorated condition of a fiber can confuse an observation, but even severely degraded fibers usually contain enough of their fingerprint characteristics to be identified[89]. Among historic textiles wool has almost never been identified as part of the process of including metal in textiles. Most examples are silk, but cotton and linen are also found. (There are a few examples of gold stamped Cashmere wool; metal threads are also found in embroideries and carpets that also contain wool, but the core for the metal thread has never been identified as wool; a few archaeological ecclesiastical textiles are said to contain metallic threads with animal hair cores.)

ii. A number of general studies have described in detail oxidative, light and hydrolytic degradation of the polymeric materials comprising textile fibers [84].

iii. Occasionally textiles that are heavily laden with metallic threads deteriorate mechanically from the stresses within the system. Among the parts of the system, the fibers seem to resist degradation best. Uniformed treatment, such as washing or dry-cleaning of textiles with threads of Categories **IV** and **V** (Table 1 and 2) may damage metal threads grievously while doing far less damage to the fibers. It is not uncommon to see a historic textile with only a shadow of its original metallic component. Sometimes the cores of metal wrapped threads are almost all that survive of the original.

Conservation

Beyond the need for analysis and characterization of historic textiles comes its treatment in a museum environment which inevitably seeks to minimize the effects of natural aging and to optimize art historic and aesthetic importance. A list of published treatments include:

i. washing (aq/nonaq)
ii. swabbing(aq/nonaq)
iii. humidfying
iv bleaching
v. vacuuming
vi. mechanical cleaning
vii. sewing
viii. mounting
ix. consolidating
x. darning, reweaving
xi. biocides/fungicides
xii. storage
xiii. reuse
xiv. additives (UV screens, softening agts, anti-statics, fire retarders, stain-guards)
xv. no treatment

Some of these treatments (or variants of these procedures) are only historically interesting (consolidating, reuse) reflecting an obsolete sensitivity to the importance of the textile or ignorance of the consequences of treatment. A few of these treatments (bleaching, additives) are generally used in modern textiles in order to forstall the ravages of use or time.

Any treatment is best applied only after identification of the entire textile system. Even after identification is complete and problems clearly appreciated the choice of treatment cannot generally be relied upon by reference to the literature alone; but is best administered by an experienced conservator familiar with the behavior of comparable examples.

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Table 4 *References for Typical Textiles or Studies by Categories*

I.	3, 20–22, 26, 30, 49, 50, 57, 61, 63, 65, 92, 100,103, 108
II.	6, 7, 31, 66, 82, 97, 112,
III.	1, 4, 5, 6, 7, 10, 11, 13, 14, 15, 23, 27, 31, 35, 38–40, 44, 47, 51, 53, 55, 58, 59, 60, 62, 63, 66, 71, 82, 86–88, 91, 95, 97, 98, 102, 104, 106, 109, 112
IV.	18, 46, 52, 54, 55, 67, 68, 71, 72, 81, 97, 101, 104, 105, 107, 109,
V.	18, 36, 46, 52, 70, 72, 81, 101, 104, 107

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Three categories: A, narrow, 0,25 0,50 mm; medium 0,60–1,00mm; C, wide, 1,00. (A–B=0,40-0,60mm; B–C=0,75-1,00mm)
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