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THE EFFECT OF HUMIDIFICATION ON ARTIFICIALLY AGED TIN-WEIGHTED SILKS

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ABSTRACT

In the late nineteenth and early twentieth centuries a variety of weighting agents were applied to silk yarns and fabrics to increase their weight in an attempt to make a greater profit on their sale. In addition, the weighting process imparted a more desirable drape to silk, making it more popular with consumers. Consequently, weighting became an almost ubiquitous practice during this time until sanctions on the amount of acceptable weighting were enacted in the 1930s due to concerns around the rapid deterioration of heavily weighted silks.

However, many of these textiles have been accessioned by museums and other cultural institutions and are now in need of extensive conservation. Weighted silks, particularly those weighted with tin salts, present a unique problem in textile conservation in that the medium itself is compromised and subject to continued degradation. While treatments to physically stabilize or consolidate already damaged weighted silk are commonly used, research that has aimed to slow or reverse the effects of these metallic salts have been largely unsuccessful. However, hydration of unweighted historic silk has been shown to increase the tensile strength of treated samples. This research investigates the effect of moisture level on artificially aged tin weighted silk.

This study applied two of the most common tin-weighting procedures and then artificially aged samples of weighted silk habutae. Those samples were then subjected to a series of humidification treatments and complete submersion in water with the aim of increasing the weakened fiber's tensile strength without affecting the drape of

the fabric. Samples were evaluated for breaking strength and cantilever bending length (as a proxy for drape) before and after receiving treatments.

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CHAPTER 1

INTRODUCTION

Silks produced in the late nineteenth and early twentieth centuries were frequently treated with additives in an attempt to increase their weight before sale. This practice was particularly profitable when silk goods were sold by the pound, rather than by the yard. In addition to its economic benefits, weighting silk imparted a series of desirable qualities, including altering the drape of the fabric.

Weighting evolved somewhat by chance from coloration techniques that used metallic salts. These metallic salts were soon used independently of any dyeing process to increase the weight of both yarns and fabrics. Tin salts became the most popular, although a variety of other metallic salts and compounds were also utilized with varying degrees of success.

Unfortunately, the metallic salts, as well as the process used to apply them, created weakened fabrics prone to degradation. Although economic sanctions and regulations imposed in the 1930s curtailed the production of weighted silks, many garments and other objects made from these fabrics have been accessioned into the collections of museums and other cultural institutions.

The fragility and often advanced state of decay of weighted silks is a well known problem in textile conservation. However, very little progress has been made in attempting to stop or reverse the continued degradation of these textiles. Although physical stabilization with stitching and adhesives or the application of consolidants

are common practice, attempts to counteract the weighting agents themselves have thus far been unsuccessful.

A study on unweighted silk have suggested that re-hydrating silk fibers restores some of the objects' tensile strength.[1] How such a treatment would effect weighted silks was proposed as an area for further research by the authors, but at the time of this writing no further study on this matter has been conducted.

This study focuses on recreating two of the most common tin weighting methods, pink and dynamite, and artificially aging these samples. After aging, these modern samples were exposed to an extremely lowered relative humidity, a moderately increased relative humidity, and complete submersion in water to determine if rehydrating the weighted silk had a significant impact on the tensile strength of the fabric. The stiffness of the samples was also evaluated before and after treatments to determine if the treatments had a negative impact on one of the more desirable qualities imparted by weighting.

A review of the literature associated with weighted silks, both their commercial production and their conservation, and the degradation of weighted silks is provided in Chapter 2. The recreation of weighting methods, artificial aging of modern samples, and the application of various treatments to these samples are provided in Chapter 3. The results of this testing are reported in Chapter 4. The conclusion of this study is provided in Chapter 5.

1 Eric F. Hansen and Stan Derelian, "Conservation I: Effects of Wet Cleaning on Silk Tapestries," *Museum Management and Curatorship* 10 (1991): 95.

CHAPTER 2

REVIEW OF LITERATURE

Silk Production and Chemistry

Numerous species of insects and spiders produce silk. *Bombyx mori,* is the commercial source of silk fibers.[2] Silk fibers are produced by the silkworm to form the cocoon in which it transforms into a moth.[3] The fibers secreted by the silkworm are composed of two proteinaceous filaments of fibroin cemented together by the protein sericin.[4] This fiber is known as a bave, while the individual fibroin filaments, which average 7-12 μm in diameter,[5] are known as brins.[6]

Fibroin crystallizes into β-pleated sheets that form layers of lamellar-like microfilaments when secreted.[7] During the crystallization process, the evaporation of water from the fibroin to the atmosphere allows for the formation of micropores.[8] These micropores average 1.1 nm in size[9] and allow for water to remain bound to the fiber after secretion.[10] The micropores also account for the hygroscopic nature of silk;

2 Ruth Robson, "Silk: Composition, Structure, and Properties," in Handbook of Fiber Chemistry, ed. Menachem Lewin and Eli M. Pearce (New York: Marcel Dekker, 1998), 415.
3 J. Merrit Matthews, *The Textile Fibres: Their Physical, Microscopical and Chemical Properties* (New York: John Wiley & Sons, 1913), 106.
4 Matthews, *Textile Fibres*, 1913, 110.
5 Ágnes Tímár-Balázsy and Dinah Eastop, *Chemical Principles of Textile Conservation* (Oxford: Butterworth Heinemann, 1998), 44.
6 Robson, *Silk*, 417.
7 Robson, *Silk*, 420.
8 Robson, *Silk,* 422.
9 Zhantun Zhu, Decai Gon Liu Liu, and Yuson Wang, "Microstructure Elucidation of Historic Silk (*Bombyx mori*) by Nuclear Magnetic Resonance," *Analytical and Biochemical Chemistry* 406 (2014): 2717.
10 Zhu et al., *Microstructure Elucidation*, 2709.

silk is capable of absorbing up to 30 percent of the fibroin's weight without appearing wet.[11]

The fibroin protein is composed of two main components: the H-chain (heavy chain) and the small L- chain (light chain),[12] which are linked by disulfide bridges.[13] The earliest attempt to sequence the amino acids of the fibroin protein was in 1902,[14] but it was not until 1957 that the main hexapeptide repeat in the H-chain of Ser-Gly-Ala-Gly-Ala-Gly was sequenced.[15] This hexapeptide is believed to be responsible for the high crystalinity and strength of silk,[16] with Ser-Gly-Ala making up roughly 85% of fibroin.[17] The crystalinity of fibroin is further increased by the high number of small amino acids in the H-chain.[18] However, these regions of high crystalinity alternate with amorphous, hydrophillic regions of larger amino acids to create the turns of the β-pleated sheets of the protein's secondary structure.[19]

In contrast, sericin is composed primarily of serine, glycine, and aspartic acid.[20] The high number of amino acids with polar side chains in sericin contributes to the hydrophillic nature of the protein, allowing it to be dissolved in water.[21] Sericin also has a high water content (86%), giving it an amorphous, random coil structure[22] unlike the β-pleated sheets of fibroin.

11 Matthews, *Textile Fibres,* 1913, 123-124.
12 Robson, *Silk*, 426.
13 Caroline Solazzo, Jolon M. Dyer, Santanu Deb-Choudhury, Stefan Clerens, and Paul Wyeth, "Proteomic Profiling of the Photo-Oxidation of Silk Fibroin: Implications for Historic Tin-Weighted Silk," *Photochemistry and Photobiology* 88 (2012):1218.
14 F. Lucas, J.R.B. Shaw, and S.G. Smith, "The Amino Acid Sequence in a Fraction of the Fibroin of *Bombyx mori," Biochemical Journal* 66 (1957):468.
15 Lucas et. al., "Amino Acid Sequence," 478.
16 Sollazo et. al., "Proteomic Profiling*,"* 1218.
17 E.V. Truter, *Introduction to Natural Protein Fibres: Basic Chemistry* (London: Elek Science, 1973): 50.
18 Robson, *Silk*, 427.
19 Solazzo et al., "Proteomic Profiling," 1218.
20 Robson, *Silk*, 427.
21 Robson, *Silk*, 427.
22 Robson, *Silk,* 422.

For the bave to be unwound from the cocoon and reeled for textile production, the silk worm pupa must be killed to prevent it from emerging and damaging the filaments. This is frequently accomplished through steaming the cocoons, a process that also softens the water-soluble sericin enough for the silk to be reeled.[23] Although some 1,500 meters of fiber are present in each cocoon, only 500-800 meters of this are capable of being reeled.[24] The remaining broken, shorter filaments are frequently turned into spun silk, a somewhat less desirable product.[25]

Silk fabric with the gum-like sericin still present is referred to as "raw silk."[26] However, the sericin dulls the fiber, giving it a yellowed color, as well as stiffens it.[27] This frequently prompts the removal of the sericin both for aesthetic reasons and to improve the feel.[28] The process of removing the gum is known as "boiling-off" or "degumming" and is accomplished in a hot soap solution (typically 95°C, 5-7.5 g/L soap).[29] Although the process softens the silk and improves its luster, both desirable qualities for consumers, removing the gum also removes 20 to 30% of the weight of the silk.[30]

Silk Weighting

Despite some early attempts, American sericulture failed spectacularly after the 1839 mulberry tree market collapse.[31] However, a combination of increased

23 Matthews, *Textile Fibres*, 1913, 127.
24 Robson, *Silk,* 418-420.
25 Matthews, *Textile Fibres*, 1913, 128.
26 Matthews, *Application of Dyestuffs to Textiles, Paper, Leather and Other Materials* (New York: John Wiley & Sons, 1920), 94.
27 Matthews, *Application of Dyestuffs,* 94.
28 Matthews, *Application of Dyestuffs*, 94.
29 Matthews, *Application of Dyestuffs*, 96.
30 Matthews, *Textile Fibres,* 1913, 131.
31 Janice Fronko, "Jonathan Holmes Cobb and American Sericulture" (master's thesis, University of Rhode Island, 2007), 112.

mechanization, particularly following the incorporation of the power loom,[32] and a 60% tariff on imported finished silk goods imposed in 1862 and 1863 that made them prohibitively expensive,[33] encouraged the development of a domestic silk processing industry. Raw silk was imported, frequently from China and later Japan,[34] and then processed and woven domestically to avoid this tariff.

The value of the American silk industry doubled every decade form 1860 to the turn of the twentieth century[35] and by 1909 the United States silk industry was valued at $196,425,000,[36] the equivalent of more than 5 billion USD in 2017.[37] The United States became a major global importer of silk, consuming 70% of Japan's silk exports by the first decade of the twentieth century.[38] By the end of the 1920s, the United States consumed over 80% of the world's silk,[39] of which as much as 80 % of this was purported to be weighted.[40]

The practice of weighting silk restored some of the weight lost through degumming by the deposition of inorganic salts within the fiber. Silk could be weighted to par, in which enough salts are added to bring the degummed silk back to

32 Giovanni Federico, *An Economic History of the Silk Industry: 1830-1930*, (Cambridge: Cambridge University Press, 1954), 56.
33 Frank R. Mason, "The American Silk Industry and the Tariff," *American Silk Quarterly,* 3rd series, vol. 11, no. 4 (1910): 4.
34 Federico, *An Economic History,* 54.
35 Mason, "Industry and the Tariff," 5.
36 Matthews, *Textile Fibres,* 1913, 107.
37 Robert Sahr, "Inflation Conversion Factors for Dollars of Years 1774 to Estimated 2027," Oregon State University updated June 19, 2017, http://liberalarts.oregonstate.edu/spp/polisci/research/inflation-conversion-factors-convert-dollars-1774-estimated-2024-dollars-recent-year.
38 Federico, *An Economic History,* 61.
39 Federico, *An Economic History,* 62.
40 U.S. House of Representatives, Committee on Finance, *Tariff Act of 1924*, 71st Congress, 1st sess., 1929, 54.

its raw weight.[41] Adding more weight to the silk than had been lost in the degumming process was known as weighting above par.[42]

Weighting also increased the silk fabric's thickness[43] and even the diameter of the yarn itself.[44] This increased yarn thickness also decreased the number of threads required to make the same surface area as unweighted silk.[45] Weighting stiffened the fabric and gave it a more desirable drape,[46] increasing its scroop (the highly desirable rustling sound silk makes when rubbed against itself[47]) and even increasing the colorfastness of black dyed silk.[48] Weighting not only augmented profits for merchants and manufacturers, it imparted desirable qualities for consumers as well.

At its most extreme, weighting could extend a single pound of raw silk to more than twenty-five ounces,[49] a practice that was considerably profitable when silk was sold by weight, rather than the more modern yardage[50] and contributed to the booming American silk manufacturing industry. The swelling that resulted from the weighting process allowed manufacturers to use a lesser yarn count to create the same surface area as unweighted silk,[51] further lowering manufacturing costs and thereby increasing profits.[52] Some silks were weighted to such an extreme that they had to be passed

41 Matthews, *Application of Dyestuffs,* 200.
42 Matthews, *Application of Dyestuffs,* 200.
43 Janet E. Miller and Barbara M. Reagan, "Degradation in Weighted and Unweighted Historic Silks," *Journal of the American Institute for Conservation* 28, no. 2 (1989): 97.
44 Federico, *An Economic History,* 49.
45 Federico, *An Economic History,* 49.
46 J. T. Marsh, *An Introduction to Textile Finishing* (New York: John Wiley & Sons, 1951), 304.
47 Marei Hacke, "Weighted Silk: History, Analysis and Conservation," *Studies in Conservation* 53, sup. 2 (2008): 3.
48 Hacke, "*Weighted Silk,*" 5.
49 Jacqueline Field, Marjorie Senechal, and Madelyn Shaw, *American Silk: 1830-1930 Entrepreneurs and Artifacts*, (Lubock: Texas Tech University Press, 2007), 106.
50 R.V. Kuruppillai, S. P. Hersh, and P.A. Tucker, "Degradation of Silk by Heat and Light," in *Advances in Chemistry Series: Historic Textile and Paper,* ed. John C. William, 111-127. Vol. 212 of *Advances in Chemistry,* ed. Howard L. Needles and S. Haig Zeronian. (Washington D.C.: American Chemical Society, 1986), 112.
51 Federico, *Economic History,* 49.
52 Field et al., *American Silk*, 105-106.

through a breaking machine to restore some of the handle lost by the stiffening of the fibers before being sold.[53] Consumers also benefited from the lower prices, with weighted silk costing a quarter of the cost of comparable unweighted silk.[54]

Weighting silk evolved alongside dyeing in the middle of the nineteenth century.[55] Mineral colorants like Prussian Blue provided a notable increase in weight to the silk.[56] The practice of weighting as a finishing technique in its own right soon evolved,[57] coinciding with the development of synthetic dyes in the mid nineteenth century which by themselves did not add significant weight. By 1910, some 80% of European silks were weighted,[58] with a similar percentage of all US silks weighted by 1924.[59]

Inorganic weighting practices began with combinations of iron salts with organic tannins to produce weighted black-dyed silks.[60] A similar increase in weight with substances that would not effect the final color of the silk was applied commercially using various forms of iron, tin, chromium, sulfates and chlorides of sodium, magnesium,[61] bismuth, tungsten, lead, antimony, and barium,[62] as well as with organics like glucose and gelatin.[63] Aluminum has also been identified on extant weighted silks.[64] A comprehensive list of organic weighting agents as well as various

53 Marsh, *Textile Finishing,* 304.
54 Federico, *An Economic History*, 50.
55 Marsh, *Textile Finishing,* 301.
56 Marsh, *Textile Finishing*, 301.
57 March, *Textile Finishing,* 301.
58 Hacke, "Weighted Silk," 6.
59 U.S. House of Representatives, Committee on Finance, *Tariff Act of 1924*, 71st Congress, 1st sess., 1929, 54.
60 Marsh, *Textile Finishing,* 301.
61 Matthews, *Textile Fibres*, 1913, 551.
62 H. Silberman, "Silk, The Weighting of, with Metallic Salts: The Theory and Practice of," *Journal of the Society of Chemical Industry* 16 (1897): 326.
63 Matthews, *Textile Fibres,* 1913, 551.
64 Miller and Reagan, "Degradation in Weighted and Unweighted Historic Silks," 101.

tannins and tin and iron compounds with their corresponding dates of popularity, can be found in Brooks et. al. (1996).[65] Some, including sugar and tannic acid, were used commercially in the 1820s,[66] but were quickly replaced by other additives. Most early weighting agents were abandoned by the twentieth century,[67] either due to their lack of economic viability as a result of the weighting agent's price or the damage they caused to fabrics.[68] However, iron and tannin compounds remained in use specifically for fabrics that would be dyed black, as these compounds imparted a dark color to the silk, regardless of later dyeing.[69]

Eventually, the commercial practice evolved into one based chiefly on salts of tin. Marsh suggests that chemical weighting became a commercially successful in the 1850s,[70] although Federico claims that the first successful experiments with synthetic rather than natural weighting only occurred in 1856, with commercial viability coming decades later in the 1870s.[71] Another anecdote claims the discovery of tin weighting as a viable method was completely by chance in a Germany dyehouse in the 1850s: a worker threw a skein with a tin mordant at another worker where it landed in a vat of tannin instead. When removed from the vat, this skein was determined to weigh far

65 M.M. Brooks, S. O'Connor, and J.G. McDonnell, "The Application of Low-Energy X-radiography in the Examination and Investigation of Degraded Historic Silk Textiles: Preliminary Report," in *ICOM Committee for Conservation: 11th Triennial Meeting, Edinburgh, Scotland, 1-6 September 1996.* (London: James & James, 1996), 673.
66 Federico, *An Economic History,* 49.
67 H.W. Smith, editor, "Technical Information for Alert Buyers," *American Silk Journal*, 31, no. 11 (1913): 42.
68 Silberman, "Silk, the Weighting of," 326.
69 Paolo Carboni, *Silk Biology, Chemistry Technology* (London: Chapman & Hall, 1952), 188.
70 Marsh, *Textile Finishing*, 17.
71 Federico, *An Economic History,* 49.

more than the other skeins without the tin mordant.[72] Regardless of precise origin, tin weighting soon became the most popular method, reaching its peak in the 1890s.[73]

Tin salts had the advantage of imparting far more weight with far less chemical input and effort on the finisher's part. A single cycle of tin and sodium phosphate baths could achieve the same extent of weighting as fifteen similar passes using iron compounds.[74] Other metals like aluminum could not approach the amount of weight imparted by tin compounds.[75] In spite of the expense of tin, even before the outbreak of World War I and the limits on its use created by wartime rationing, it was still considerably less expensive than alternatives that imparted the same weight gain like chromium salts.[76]

Tin was also preferred as it, unlike other weighting compounds like tannin, could be used on lighter-colored or even white fabrics.[77] The tin on the tin-weighting could also behave as a mordant when the silk was to be dyed.[78] However, if the weighting was uneven, the weighted silk could produce unlevel dyeings and the weighting even reduced the affinity of certain acid dyes for the fiber.[79] Tin also served as a base for additional weighting agents that would otherwise fail to adhere to the silk,[80] further increasing the amount of weight that could be imparted and lowering costs.

Technological advances improved the efficiency of the process and lowered the cost. New machines allowed for the recovery and reuse of tin left in the bath after

72 Thomas Waddle and J. Carter Bell, "On the Adulteration of Silk by Weighting," *Journal of the Society of the Chemical Industry,* 16 (1897): 300.
73 Federico, *An Economic History*, 49-50.
74 J. Merritt Matthews, *Textile Fibres: Their Physical Microscopical and Chemical Properties,* (New York: John Wiley & Sons, 1924), 309.
75 Matthews, *Textile Fibres,* 1924, 209.
76 Matthews, *Textile Fibres,* 1924, 209.
77 Brooks et. al., "*Low-Energy X-Radiography*," 673.
78 Matthews, *Textile Fibres,* 1924, 313.
79 Matthews, *Application of Dyestuffs*, 202.
80 Matthews, *Textile Fibres,* 1924, 309.

weighting.[81] Centrifuging and pressure were applied to the silk after the bath to recover even more of the unfixed tin for reuse,[82] and baths of different weighting agents could be combined to reduce the amount of labor and time required to treat the silk.[83] Weighting was initially confined to processing yarns, rather than piece goods,[84] with warps frequently weighted more heavily than wefts.[85] However, by 1897 weighting practices expanded to include whole yard goods[86] and machines for the continuous application of successive baths were patented.[87] Tin weighting was eventually expanded beyond silk, applied even to fabrics like rayon and cellulose acetate.[88]

Tin Weighting Processes

"Pink weighting" was an early and popular form of tin weighting. This relatively simple process repeated alternating baths of the ammonium salt of chlorostannic acid [$(SnCl_6)(NH_4)_2$], available commercially as *pink*, and sodium carbonate (Na_2CO_3) or disodium phosphate (Na_2HPO_4).[89] The silk absorbs stannic chloride ($SnCl_4$, tin(IV) chloride)[90] and this salt is then hydrolyzed when rinsed in water. The tin hydroxide ($Sn(OH)_4$) that results from this hydrolysis is then precipitated onto the silk[91] or forms a colloid with the amino groups on the silk.[92] By 1890, the original *pink* was replaced

81 Silberman, "Silk, The Weighting of," 326.
82 Matthews, *Textile Fibres,* 1924, 311.
83 Charles E. Mullin, "The New Clavel and Lindemeyer Silk Weighting Process- II," *Silk Journal and Rayon World* (December 1931): 28.
84 Marsh, *Textile Finishing,* 301.
85 George H. Johnson, *Textile Fabrics: Their Selection and Care from the Standpoint of Use, Wear, and Laundering* (New York: Harper & Brothers, 1927), 71.
86 Silberman, "Silk, on the Weighting of," 326.
87 Charles E. Mullin, "The New Clavel and Lindenmeyer Silk Weighting Processes. -II.," *Silk Journal and Rayon World,* (February 1932): 24.
88 Charles E. Mullin, "The New Clavel and Lindenmeyer Silk Weighting Processes. -II.," *Silk Journal and Rayon World,* (December 1931): 28.
89 Carboni, *Silk*, 189.
90 Tímár-Balázsy and Eastop, *Chemical Principles of Textile Conservation*, 105.
91 Carboni, *Silk*, 194.
92 Charles E. Mullin, "pH Control in the Silk Industry," *The Melliand* 1, 1 (1929): 73.

with the moderately less dangerous liquid stannic chloride,[93] although the original name persisted. While sodium carbonate was initially used, sodium hydrogen phosphate came to be the favored bath in America by the twentieth century.[94] This switch also had the desired effect of allowing the silk to "take up" more tin in successive baths.[95] After the sodium hydrogen phosphate bath, the silk was washed in water to remove any remaining sodium.[96] The cycles of pink and sodium hydrogen phosphate could be repeated as needed to reach the desired level of weighting of the silk, with each cycle increasing the weight by roughly 10%.[97]

A modification of this tin weighting method became popular by the turn of the century. "Dynamite weighting" built upon a method patented by H.J. Neuhaus in 1893. The Neuhaus method soon lost its protected status when it was determined that he was not the first to use the methodology.[98] The revocation of the patent allowed for the method's rapid adoption. The process began with the same sequence as pink weighting: tin(IV) chloride bath, wash, sodium phosphate bath, and wash.[99] However, following the final sodium phosphate bath, the silk was given a bath of sodium trisilicate ($Na_2Si_3O_7$) which had the effect of drastically increasing the final weight of the silk, sometimes up to 400% above par.[100] The silicate was believed to replace some of the phosphate to form tin phosphosilicate and sodium silicostannate

93 W.A. Vetterli, "Silk Dyeing," *CIBA Review,* 119 (Mar 1957): 24.
94 Mullin, "pH Control," 73.
95 Matthews, *Textile Fibres*, 1924, 310.
96 Mullin, "pH Control," 73.
97 Tímár-Balázsy and Eastop, *Chemical Principles*, 105.
98 Matthews, *Textile Fibres,* 1924, 310.
99 R. Geuhm and E. Bänziger, "On the Weighting of Silk," *Journal of the Society of Dyers and Colourists* 13 (1897): 40.
100 Tímár-Balázsy and Eastop, *Chemical Principles*, 105.

($3SiO_2.Na_2O.SnO_2$).[101] This step decreased the amount, and therefore cost, of tin salts needed to achieve the same weight.[102]

A modification of the Neuhaus method included a treatment of aluminum sulfate [$Al_2(SO_4)_3$] after the final phosphate and prior to the silicate bath. While aluminum is not fixed to the silk, the treatment allows for an increased amount of silica to be fixed to the silk.[103] The tin-phosphate-silicate method (with or without aluminum sulfate) became the most prevalent form of silk weighting.[104]

There is considerable variation in the proposed amount of weight gained by each pass of tin and phosphate. Carboni claims three passes of tin and phosphate should result in a weight gain of 20%, while three tin and phosphate passes, one aluminum pass, and one silicate pass should result in a weight gain of 60%.[105] Tímár-Balázsy and Eastop suggest that each pass of tin and phosphate can achieve a maximum of 10% weight gain,[106] while Matthews' claims that a single pass can impart a 25% weight increase,[107] and Silberman suggests a 25-30% weight increase.[108] Further, the amount of tin taken up by the silk with each pass is "not mathematically regular,"[109] complicating modeling the weight gain of multiple passes. Complete control of the amount of weight taken up by the silk is difficult to obtain, as slight variations in solution strength and the bath's temperatures can result in different weights.[110] Even

101Mullin, "pH Control," 74.
102Matthews, *Textile Fibres*, 1924, 311.
103Carboni, *Silk*, 197.
104Hacke, "Weighted Silk," 5.
105Carboni, *Silk*, 198.
106Tímár-Balázsy and Eastop, *Chemical Principles*, 105.
107Matthews, *Application of Dyestuffs,* 202.
108Silberman, "Silk, the Weighting of," 326.
109H. Ley, "The Weighting of Silk with Tin-phosphate," in *Journal of the Franklin Institute Devoted to Science and the Mechanical Arts Vol. CLXXV Nos. 1045-1050,* ed. R.B. Owens (Philadelphia: The Franklin Insititute, 1913), 442.
110Carboni, *Silk,* 198.

allowing the silk to dry between dips can affect the total weight gain.[111] Lack of precise control over the pH of the various baths in the process has also been blamed for the inconsistent application of weighting.[112]

Deterioration of Weighted Silk

Despite all the advantages of tin weighting, the inherent flaws it created were recognized as early as the turn of the twentieth century. The reduced tensile strength and generally increased rate of deterioration when compared to unweighted silk were well known.[113],[114] Weighting of 140% above par resulted in a loss of five-sixths of a fiber's strength when compared to unweighted silk.[115] The brittle and fragile fibers that resulted from the weighting process could lead to the silk's complete destruction with a few months of its manufacture,[116] often before the reaching the consumer.[117] The brittleness of degraded weighted silk result in what is known as shattering, in which a complete loss of extensibility in the fibers lead to their breakage when moved.[118] This breakage becomes so extreme that a textile can disintegrate completely over a relatively short time, even without handling. Perplexingly, not all heavily weighted silk has the same fragility, with the level of weighting often failing to correspond to the extensiveness of observed damage.[119]

The weighting process itself was frequently responsible for the damage seen. The hydrolysis of tin(IV) chloride releases hydrochloric acid that remains on the silk.

111Ikuzo Sakaguchi, "Cumulative Tin-Weighting of Silk with Stannic Chloride," *Textile Research Journal* 39, no. 11 (1969), 1054.
112Mullin, "pH Control," 74.
113Matthews, *Textile Fibres,* 1924, 306.
114T.L. Phipson, "Weighted Silk," *Chamber's Journal.* Sixth Series, Vol. 1 (1898): 44.
115Matthews, *Textile Fibres,* 1924, 306.
116Frank Warner, The British Silk Industry: Its Development Since 1903," *Journal of the Royal Society of Arts* 60, no. 3092 (1912): 402.
117Marsh, *Textile Finishing,* 301.
118Hacke, "Weighted Silk," 8.
119Matthews, *Textile Fibres,* 1924, 310.

Although the secondary bath of sodium carbonate or sodium phosphate, which was often alkaline, was used to neutralize the hydrochloric acid freed by the earlier hydrolysis,[120] silk dissolves completely in high enough concentrations like a 30ºTw solution of hydrochloric acid.[121] The hydrochloric acid formed during the weighting process was directly blamed for the damaged silk, even after "considerable" time had passed since the treatment.[122]

A variety of other problems were occur with weighted silks. In addition to decreasing the tensile strength, weighting often resulted in red spots, making the goods unsellable, and subsequent extreme tendering of these spot as copper or iron in wash water and sodium chloride from sweat enabled catalytic oxidation of the weighted silk.[123] These spots could occur within months of production.[124] Heavily weighted silks were also purported to be highly combustible,[125] although given the use of phosphorus compounds in flame retardant applications, this id doubtful. Perspiration, particularly when combined with heat, was also known to increase the rate of deterioration in weighted silk and decrease its tensile strength.[126]

Many of the defects seen in lightly colored weighted silks were only amplified in black weighted silks. Black silks were traditionally weighted to a greater degree than other silks, often through a combination of tannin and tin, increasing their degradation in comparison to less weighted silks.[127] However, black weighted silk that utilized a

120Carboni, *Silk*, 191.
121Matthews, *Textile Fibres,* 1913, 142-143.
122Matthews, *Application of Dyestuffs*, 38.
123Marsh, *Textile Finishing*, 305.
124Tímár-Balázsy and Eastop, *Chemical Principles*, 105.
125 Phipson, "Weighted Silk," 44.
126Julia Lurena Southard, "The Effect of Perspiration on the Breaking Strength of Selected Silk Fabrics," (master's thesis, Kansas State Agricultural College, 1930), 23.
127George H. Hurst, *Silk Dyeing, Printing, and Finishing,* Technological Handbooks, Vol. 9, ed. H. Trueman Wood, (London: George Bell & Sons, 1892), 39.

combination of iron, tannin, and logwood, rather than tin, showed no such deterioration,[128] suggesting that this deterioration was peculiar to tin compounds alone.

Silk fibers are highly sensitive to environmental factors including exposure to visible light and ultraviolet irradiation and extremes in acidity and temperature, which can lead to their rapid deterioration.[129] This sensitivity is greater in weighted silk. Electromagnetic radiation, both visible and ultraviolet, is particularly detrimental to the tensile strength of weighted silk[130] with much of this loss occurring within the first 10 hours of exposure.[131] High temperatures are also detrimental to weighted silk, presumably through a combination of dehydration[132] and oxidation[133] of the fibroin.

Despite these well-established effects, the exact mechanism for the degradation of weighted silks has yet to be satisfactorily determined. Metal ion catalyzed oxidation, hydrolytic breakdown, or mechanical shredding due to the physical presence of the metallic compounds themselves have been proposed as possible causes.[134] The metallic compounds are proposed to settle into the microvoids of silk, causing mechanical damage.[135] However, the proportion of weighting agent added does not always correspond to the amount of degradation seen, either historically during the active production of weighted silk[136] or in extant objects contemporary museum

128Marsh, *Textile Finishing*, 301.
129Francisco Vilaplaa, Johanna Nilsson, Dorte V.P. Sommer and Sigbritt Karlsson, "Analytical Markers for Silk Degradation: Comparing Historic Silk and Silk Artificially Aged In Different Environments," *Analytical and Bioanalytical Chemistry* 407 (2015): 1434.
130Nellie Meyers Roberts and Pauline Beery Mack, "A Study of the Effects of Light and Air on Unweighted and Tin Weighted Silk- Paper II," *Rayon and Melliand Textile Monthly* 17 (1936): 51.
131M. Tsukada and K. Hirabayashi, "Change of Silk Fibroin by Structure by Ultraviolet Radiation," *Journal of Polymer Science: Polymer Letters Edition* 18, no. 7 (1980): 507.
132Matthews, *Textile Fibres,*1924, 311.
133Julia Lorena Southard and E.L. Tague, "Changes in Solubility and Absorption Spectra of Silk Fibroin Caused by Tin Weighting," *Journal of Home Economics* 24, no. 11 (1932): 996.
134Hacke, "Weighted Silk," 9.
135Robson, "Silk," 455.
136Matthews, *Textile Fibres,* 1924, 310.

collections.[137] This has led to doubts over whether the metallic compounds are actually responsible for the damage seen in weighted silks.

The use of poor quality, and therefore already predisposed to damage, silk in weighting is one possible cause of this discrepancy.[138] In addition, the harsh conditions surrounding the weighting process, together with the fluctuations in pH that accompany bleaching, might be responsible for the observed damage.[139] However, due to the white color of degummed silk, bleaching was only deemed necessary when a "snow-white" color on the finished product was desired,[140] making the bleaching process unlikely to account for much of the damage seen in extant weighted silk.

Decline of Weighted Silk

The concerns over the rapid deterioration of tin-weighted silk led to early twentieth century attempts to counteract or limit the treatment's unfortunate effects. Recommendations for the composition of the tin baths that would impart the most weight without damaging the fiber were abundant even before the turn of the century.[141] Special care was taken to remove impurities present in water from the different baths in the process and remove any fatty acids from soaping the silk prior to weighting as they were purported to injure the fiber when combined with tin(IV) chloride.[142]

Various treatments were historically applied directly by manufacturers in the hope of slowing the silk's decay, but met with limited success. Ammonium sulphocyanide and sulfocarbamide were used to counteract the chlorides present in the

137Hacke, "Weighted Silk," 8.
138Garside et. al., "Understanding the Ageing Behavior," 79.
139Garside et. al., "Understanding the Ageing," 185.
140Matthews, *Application of Dyestuffs*, 113.
141O'Neil, "Weighting of Silk," *Scientific American* 62, no. 12 (1890): 184.
142Carboni, *Silk*, 191.

weighting process that were frequently blamed for the tendering.[143] Thiourea was used to lessen weighted silk's sensitivity to light,[144] while tannin was proposed to counteract the crystallization of tin-silicate colloids that supposedly resulted in the loss of tensile strength.[145] By the twentieth century an extensive number of patents were given for compounds that purportedly imparted some protective quality to weighted silk to prevent its deterioration.[146] 5 % hydrofluosilicic acid and hydrofluoric acid were also proposed as a means to strip inorganic weighting agents from silks with extreme weighting above par altogether to make them less brittle.[147]

Alternative processing methods to reduce the damage caused by the baths' conditions were explored as well. Foam weighting was developed as early as 1915 in an attempt to prevent damage to the silk by the alkaline nature of some of the baths by reducing the amount of time spent in damaging solutions[148],[149]

Social pressure and economic regulation eventually emerged. The so-called "pure dyes" of latter part of the nineteenth century professed to be silks that were not weighted above par.[150] Although discussion of imposing an upper limit on the amount of acceptable weighting began as early as 1897 in Europe,[151] American regulations were not implemented until decades later. A campaign against weighted silk, aptly titled "The Crusade," began in 1906.[152] The Silk Association of America complained

143Matthews, *Textile Fibres,* 1924, 311.
144Carboni, *Silk*, 199.
145Hacke, "Weighted Silk," 8.
146Merrill Horswill, "Research Report: Save the Silks! Protection for Weighted Silk Costumes," *Dress*, 14 (1988), 94.
147Matthews, *Textile Fibres,* 1913, 142.
148 Peter Schmid and Karl Gross, "Process for Weighting Silk," U.S. Patent 1,207,800, filed Oct. 7 1915, and issued Dec. 12 1916.
149Carboni, *Silk,* 197.
150Field et. al., *American Silk*, 105.
151Federico, *An Economic History*, 50.
152 "The Silk Crusade," *American Silk Journal,* 25, no. 9 (1906), 31.

about the "trash" silks being sold,[153] called for the abandonment of guarantees about the quality of weighted silks that were not always assured in favor of pure dyes that supposedly contained no weighting additives, and for legislation from Congress.[154] Some campaign supporters went so far as to blame weighted silks for "bringing the silk trade into disrepute"[155] and even called them the direct reason for the drop in market prices felt that year.[156]

Limits were imposed on the extent of weighting in 1929 by the Silk Association of America,[157] although the Association had little legal ability to actually enforce these regulations. Federal legislation from the Federal Trade Commission followed in June of 1932 and was expanded in 1938.[158] These regulations defined "Pure Dye Silk" and restricted the total weighting to 10% above par, with the exception of black silks that could be weighted to 15%.[159] This law also required disclosure of metallic weighting and its corresponding percentage above par on all silks.[160] Eventually, weighting methods that involved metal ions were abandoned altogether to be replaced, when required, by synthetic polymers (acrylic emulsion polymers, also referred to as "hand builders") in the 1960s.[161] Although largely an abandoned practice, polymer weighted silk does appear in rare instances the twentieth and twenty-first centuries. Commercial polymer-weighted silk continued to be produced well into the twentieth century,[162]

153"Continuation of the Crusade," *American Silk Journal,* 25, no. 6 (1906), 36.
154"Continuation of the Crusade," 38.
155"Continuation of the Crusade," 38.
156"Continuation of the Crusade," 40-41.
157Ralph T. Mease, "Analysis of Weighted Silk," *Bureau of Standards Journal of Research*, 9 (1932), 669.
158 U.S. Federal Trade Commission, *Trade Practice Rules: September 1, 1935- June 30, 1945,* (Washington, D.C.; United States Government Printing Office, 1946): 151-152.
159U.S. Federal Trade Commission, *Trade Practice Rules,* 154.
160U.S. Federal Trade Commission,*Trade Practice Rules,* 155-156.
161Hacke, "Weighted Silk," 6.
162Marsh, *Textile Finishing*, 302.

examples of which are seen in extant garments like Patricia Nixon's 1973 inaugural gown.[163] While tin weighting has largely been abandoned, research into weighting silk in the twenty-first century has explored the use of rare earth metals like cerium.[164]

Conservation of Weighted Silk

Although no longer manufactured and sold, innumerable examples of shattered, stained, and powdered weighted silk textiles exist. Weighted silk is commonly found in a variety of museum textiles, from inexpensive undergarments from from the early 1910s[165] to the inaugural gowns of seven First Ladies across two centuries.[166] Frequently these late nineteenth and early twentieth century textiles are far more deteriorated than unweighted silks from previous centuries[167] and require extensive conservation before display.[168] Heavily weighted silk's proliferation in collections and its advanced deterioration creates an enormous problem with no clear solution for conservation.

Current conservation treatments for degrading, weighted silk are somewhat limited, with most research into conserving weighted silk ceasing before the twenty first century. These treatments focus on the physical stabilization of a shattering textile rather than counteracting the effects of weighting treatment. Weighted silk has been

163Mary A. Becker, Polly Willman, and Norleen C. Tuross, "The U.S. First Ladies Gowns: A Biochemical Study of Silk Preservation," *Journal of the American Institution for Conservation* 34, no. 2 (1995):145.

164Jun Wei, Jun Qui, and Rong Lu, "Novel Serecin-Fixing Agent Containing Rare-Earth Ion for Weighting Silk Fiber," *Journal of the Textile Institute,* 102, no. 9 (2011): 779.

165Shawna Lynne Lemiski, "Weighted Silk: Identification, Characterization, and Photodegradation," (PhD diss., University of Alberta, 1996): 76.

166Becker et. al. "The U.S. First Ladies Gowns," 145.

167Horswill "Save the Silks!," 93.

168"What Happens Behind Closed Doors? The Preparation of Caroline Harrison's Inaugural Gown," Smithsonian National Museum of American History, 2008, accessed November 12 2017, http://americanhistory.si.edu/press/fact-sheets/what-happens-behind-closed-doors-preparation-caroline-harrisons-inaugural-gown

treated with an underlay and overlay sewn around it or, if in the lining of a garment, completely removed and discarded.[169]

Alternatively, when the silk is too damaged to withstand a needle, adhesive backing fabrics or consolidants can be used to provide physical support. A variety of adhesives can be applied to a support fabric, allowed to dry, and then attached to the fragile textile by softening the dried adhesive with heat. [170] However, adhesive backed fabrics can alter the stiffness of treated fabrics,[171] while the reversibility and light stability of these treatments has also been called into question.[172] Consolidants like Parylene-C, a poly-paraxylylene, that impregnate deteriorating yarns in an attempt to stabilize individual fibers are less than desirable given the yellowing and embrittling these consolidants undergo when exposed to light.[173] Consolidation of the textile is often considered an extreme action and subject to some debate about its place in conservation[174] due primarily to concerns about questionable reversibility and long term stability.[175]

Attempts to chemically counteract weighted silks' decay have been less than satisfactory. Artificially aged, modern silk samples that were exposed to light for long periods have been used in conjunction with a variety of treatments including

169Karen DePauw, "The Heartbreak that Is Weighted Silk," Connecticut Historical Society, last modified July 31, 2014, accessed November 12 2017, https://chs.org/2014/07/the-heartbreak-that-is-weighted-silk/.

170Tímár-Balázsy and Eastop, *Chemical Principles*, 304.

171Tímár-Balázsy and Eastop, *Chemical Principles*, 317-318.

172Irene F. Karsten and Nancy Kerr, "The Properties of Light Stability of Silk Adhered to Sheer Silk and Polyester Support Fabrics with Poly(Vinyl Acetate) Copolymer Adhesives," *Studies in Conservation* 47 (2002), 194.

173 Bonnie G. Halvorson and Nancy Kerr, "Effect of Light on the Properties of Silk Fabrics Coated with Parylene-C," *Studies in Conservation* 39, no. 1 (1994): 54.

174Agnès Geijer, "Dangerous Methods for the Conservation of Textiles," in *Changing Perspectives in Textile Conservation,* ed. Mary M. Brooks and Dinah D. Eastop, (Los Angeles: The Getty Conservation Institute, 2011), 141.

175Tímár-Balázsy and Eastop, *Chemical Principles*, 305.

antioxidants and deacidifiers in an attempt to counteract deterioration in both weighted[176] and unweighted silk.[177] Unfortunately, none of the proposed treatments have produced the desired results in stabilizing silk. While some of these treatment have resulted improved tensile strength,[178] some have caused yellowing of the samples.[179]

Research in the twenty first century has focused on non-destructive identification of weighting agents on extant silks, determining the aging process of weighted silks, and creating a model for the progression of the effects of weighting agents on historic silks.

Neutron activation analysis (NAA) can successfully identify weighting agents, but the technique requires the complete destruction of a relatively large sample (2.5 cm x 5.0 cm).[180] Tannin, silicon, and other weighting agents can be identified using Raman spectroscopy.[181] Alternatively, the atomic ratio of the elements present as determined by scanning electron microscopy (SEM) in weighted silk can be used to a similar end.[182] These analyses in turn can help identify the weighting process used to apply the weighting agent, i.e. silicone is indicative of the dynamite weighting process. Near-Infrared (NIR) spectroscopy has also been used to not only identify the presence of weighting agents, but the relative amount that was applied to silks all

176Merrill Taber Horswill, "Characterization and Preservation of Weighted Silk," (PhD diss., University of Wisconsin, 1992), 76.
177Kuruppillai te. al., "Degradation of Silk," 14-115.
178Horswill, "Characterization and Preservation," 153.
179Horswill, "Characterization and Preservation," 149.
180Janet E. Miller and Barbara M. Regan, "Degradation in Weighted and Unweighted Historic Silks," *Journal of the American Institute for Conservation*, 28 (1998): 99.
181Tomás Aguayo, M. Carolina Araya, Mónic Icaza, and Marcelo Campos-Vallette, "A Vibrational Approach for the Study of Historical Weighted and Dyed Silks," *Journal of Molecular Structure,* 1075 (2014): 447.
182Paul Garside, Paul Wyeth, and Xiaomei Zhang, "Understanding the Ageing Behavior of Nineteenth and Twentieth Century Tin-Weighted Silks," *Journal of the Institute of Conservation* 33, no. 2 (2010): 182-183.

without the destruction of samples.[183] Other researchers have focused on measuring the crystallinity of samples with known weighting agents through polarized attenuated total reflectance Fourier transform infrared spectrsoscopy (Pol-ATR), and by extension the strength, of extant weighted silks to determine the impact of different weighting agents on the deterioration of extant silks.[184] Identification and analysis methods that require small samples or are even non-invasive are particularly useful for conservation research where extant textiles are irreplaceable.

Others have explored how silks weighted with different processes are aging. Pink and dynamite samples appear to age differently. Pink weighted samples are far more sensitive to UV irradiation than dynamite weighted silks, supposedly due to the presence of tin(IV) oxohydroxide compounds.[185] In contrast, pink-weighted silks are less affected by increased relative humidity than dynamite-weighted silks.[186]

Some research has attempted to create a framework for classifying the progression of degradation of weighted silks. A classification scheme was developed similar to the numerical scale originally proposed by book conservators and based on visual inspection of the textile and attempts to identify the stages of degradation.[187] Unfortunately, weighted silk is not always easily identified visually unless in advanced stages of degradation in which obvious shattering and powdering are

183Paul Garside, Paul Wyeth, and Xiaomei Zhang, "Categorizing Tin Phosphate/Silicate-Weighted Silks on Site by Near-Infrared Spectroscopy," *Journal of the Institute of Conservation* 35, no. 1 (2012): 48.

184Paul Garside, Sophia Lahlil, and Paul Wyeth, "Characterization of Historic Silk by Polarized Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy for Informed Conservation," *Applied Spectroscopy,* 50, no. 10 (2005): 1243.

185Solazzo et. al., "Proteomic Profiling," 1224.

186Paul Garside, Paul Wyeth, and Ziaomei Zhang, "Understanding the Ageing Behavior of Nineteenth and Twentieth Century Tin-Weighted Silks," *Journal of the Institute of Conservation,* 33, no. 2 (2010):190.

187Horswill, "Characterization and Preservation," 66.

present. Unweighted silks can display shattering similar to that seen in weighted silk, further complicating an attempt to create a visual classification scheme.[188]

Other attempts at identifying the stages of degradation of weighted silk involve chemical markers. The presence of free carbonyl groups that indicate oxidation on unweighted silk[189] and modification of amino acids, particularly a decrease in identifiable peptides,[190] in weighted silk have been identified as outcomes of artificial and natural aging. The orientation of the β-sheets of fibroin has also been used to classify the degradation state of the fiber. Although the ratio of crystalline β-sheets to amorphous regions does not change as silk ages, the β-sheets loose their orientation along the fiber as the amorphous regions degrade.[191] This ratio correlates with the loss of physical strength and eventual shattering seen in silk fabric.[192] The loss of a tyrosine band in IR spectra that corresponds with the loss of amorphous regions in weighted silk has also been observed in aged samples.[193]

More readily measurable markers like the pH of historic silks have been rejected as a basis for monitoring degradation as, particularly for tin-weighted silks, the pH fails to correlate with the physical condition of the silk.[194] This lack of correlation is most likely the result of the tin complex found on weighted silk acting as a buffer, maintaining a pH between 6.75 and 7.05 and potentially resulting in the surprisingly good condition of historic weighted silks that have avoided light exposure.[195]

188Lemiski, "Weighted Silk," 3.
189Vilaplana et. al., "Analytical Markers," 1438.
190Solazzo et. al., "Proteomic Profiling," 1219.
191Paul Garside and Paul Wyeth, "Crystallinity and Degradation of Silk: Correlations Between Analytical Signatures and Physical Condition on Ageing," *Applied Physics A* 89 (2007): 873.
192Garside and Wyeth, "Crystallinity and Degradation," 871.
193Aguayo et. al., "A Vibrational Approach," 477.
194Paul Garside, Paul Wyeth, and Xiaomei Zhang, "The Inherent Acidic Characteristics of Silk, Part II- Weighted Silks," *e-Preservation Science* 7 (2010): 129.
195Garside et. al., "Inherent Acidic Characteristics," 130.

No current research addresses the treatment of extant weighted silks with the explicit goal of conservation in historic textile and costume collections. However, research on unweighted silk has suggested that re-hydrating the fibers can have marked effects on their physical state. Wet cleaning of eighteenth century, unweighted silk tapestries has resulted in a surprising increase in tensile strength.[196] As of the time of writing, no similar research on the effects of humidification and tensile strength has been applied to weighted silk, despite a call for it.[197],[198]

Wet cleaning is seen as a somewhat extreme step that should be avoided if at all possible due to the potential for damage to a textile that can occur during treatment.[199] However, early twentieth century research found that, when wet, weighted silk is less brittle than when dry.[200] While complete submersion in water to rehydrate fibers is not often possible or advisable for compound objects like the historic costumes found in museum collections, humidification is. This research aims to investigate the effect of complete wetting and humidification on weighted silk with regards to the possible benefits to tensile strength of the weighted silk fibers and how such a treatment will affect the drape of the textile. Hydrating the fibers will hopefully restore some of the physical strength of weakened weighted silks, therefore increasing this prevalent textile's lifespan and lessening the need for intensive treatment by a conservator at a later date.

196 Hansen and Derelian, "Conservation I," 95.
197Hansen and Derelian, "Conservation I," 96.
198 Miller and Reagan, "Degradation of Weighted and Unweighted Silks," 113.
199Hacke, "Weighted Silk," 11.
200Jeanette E. Ross, Ruth L. Johnson, and Rachel Edgar, "Degradation of Weighted Silk Fibroin by Acid and Alkali," *Textile Research* 6 no. 4 (1936), 213.

CHAPTER 3

METHODOLOGY

Materials and Apparatus

Materials:
Silk Habutae, TestFabrics (West Pitston, PA) No. 609
Silk Twill, Test Fabrics No. 611
Tin (IV) chloride
Disodium phosphate
Aluminum sulfate
Sodium trisilicate
Hydrochloric acid

Apparatus:
H.W. Butterworth & Sons padder, Model No. M9634
J.A. King Manual Sample Cutter, Model No. SASD-688
Weatherometer (Q-Sun Xenon Test Chamber, Model XE-3-HS)
Conditioning Chamber (Datacolor Conditioner with controller RP1)
Psychrometer
Tensile Testing Machine (MTS QTest 1 and TestWorks® 4 software)
Security Friction Tape, United States Rubber Company
Valve Grinding Compound, Permatex
"Shirley" Stiffness Tester

This chapter describes the weighting and aging procedures involved in sample preparation. A detailed description of the humidity and wetting treatments applied to the samples follows. It finally explains how these treatments are analyzed and estimated.

Preparation of Samples:

Application

Instead of expressing chemical concentrations directly, textile processors of the nineteenth and twentieth centuries would refer to the density of the solution using the

Baumé (ºBe) or Twaddell (ºTw) scales rather than g/mL. Baumé and Twaddell values are readily converted to g/mL and can be converted to concentrations (as g/L or % concentration) via tables specific to each particular chemical. Published tables exist for commonly used compounds like hydrochloric acid,[201] acetic acid,[202] sodium hydroxide.[203] However, tables for the four main chemicals used in the experiments were not available and had to be experimentally determined.

Solutions of tin (IV) chloride, disodium phosphate, aluminum sulfate, and sodium trisilicate of known concentration were prepared and their density measured to allow conversion of recipes in which solution strength is expressed as density (°Bé) into a direct measure of concentration. 40 cm (warp) x 15 cm (weft) of silk habutae (Test Fabrics No. 609) was prepared according to the methods described by Silbermann in 1897 and Garside and Wyeth in 2002. Samples were immersed in a tin (IV) chloride solution of 27.6°Bé (26% solution) for 4 hours at 23 ±2 °C. 250 mL of tin (IV) chloride was used to completely submerge each sample. The bath was agitated occasionally to ensure level application. At the end of 4 hours, samples were rinsed in 2 L of deionized water for one minute with constant agitation. Wet samples were then immersed in 250 mL of sodium hydrogen phosphate solution of 6.7° Bé (6.15% solution) at 60 ±2 °C for one hour before being rinsed in deionized water again for one minute with constant agitation. Samples were allowed to dry at 21°C and 60 % RH overnight between each cycle of tin-phosphate. Three cycles of pink and phosphate were repeated.

201Norbert Adolph Lange, *Handbook of Chemistry* (Sandusky, Ohio: Handbook Publishers, Inc.; 1941): 1117-1118.
202Lange, *Handbook of Chemistry*, 1092.
203Lange, *Handbook of Chemistry*, 1142-1143.

A second dipped samples (40 cm (warp) x 15 cm (weft)) was prepared using the dynamite weighting method described in Carboni (1952). The alternating cycles of pink and sodium hydrogen phosphate used in pink weighting were conducted three times. After the final bath of sodium hydrogen phosphate and subsequent overnight drying, the samples was immersed in a bath of 250 mL of aluminum sulfate at 7.0° Bé (9.54% solution) that was weakly acidified with sulfuric acid to achieve a pH of 4±0.5 for one hour at 60 ±2 °C before being rinsed in deionized water for one minute with constant agitation. Finally, wet samples were immersed in a bath of 250 mL of 4.1° Bé (4.158% solution) of sodium trisilicate at for one hour at 50 ±2 °C. After this hour, the samples were rinsed again in deionized water for one minute with constant agitation.

The same sequence and concentration of baths described above were applied for both pink- and dynamite- weighted samples using a pad-batch method (i.e. dip and squeeze) method in an attempt to improve the evenness of application. Rather than immerse the silk in baths of each solution for the desired time and agitate them, these samples were run through a laboratory padder at two different pressures: 15 psi and 50 psi. 150 cm (warp) x 15 cm (weft) of silk habutae was immersed in each solution before being run between pneumatic squeeze rollers. The rollers and troughs were rinsed thoroughly with deionized water following each padding. Following each bath of tin (IV) chloride, the samples were sealed in a plastic bag with the air removed and stored in the dark for 4 hours at 23 ±2 °C. The samples were then rinsed in deionized water before being padded in a sodium hydrogen phosphate solution. The samples were again sealed in a plastic bag with the air removed. The bag was then submerged in a beaker of water heated to 60 ±2 °C for one hour. The samples were then rinsed

again in deionized water and allowed to air dry before repeating the pink-phosphate process two more times. 150 cm (warp) x 15 cm (weft) of silk habutae was padded to produce dynamite-weighted samples similarly, with the addition of a padding of aluminum sulphate, sealed in a bag and submerged in 60 ±2 °C water for one hour and a padding of sodium trisilicate, sealed in a bag and submerged in 50 ±2 °C for one hour.

After padding, samples were stored in the dark, at 60 % RH and 21 ºC. Padding at 50 psi was adopted as the application process for the remainder of the experiment and is the methodology that the conclusions of this study are based on.

Weighting

To determine the weight gain of silk samples at each stage of the weighting process, a circular die was used to cut samples and the samples were then weighed. These samples were then weighed and compared to one another. Larger samples were cut with a 2.7 inch diameter die, and ,when less material was available, a 0.5 inch diameter die. See Discussion for further details.

Aging

Samples of pink- and dynamite-weighted silk were aged using light or heat to determine conditions to achieve a strength decrease of approximately 50 %. Too little loss of strength is too much like the original silk, while excessive aging would render the material too fragile. Pretests were conducted with light at 10, 20, 30, and 40 hours in a Q-Sun Xenon Test Chamber, model XE-3-HS, under AATCC 16.3 (2014) conditions of a chamber temperature of 43±2ºC, 30±5% RH, and irradiance of 420 nm of 1.10±0.03 $W/m^2/nm$ and 300-400 nm of 48±1 $W/m^2/nm$. Samples were secured to

the tray with masking tape to prevent movement from air circulation in the instrument. Areas of the sample that were direct contact with the tape were discarded. Samples were also aged in an oven at 80 ºC 24, 72, 96, and 120 hours. Samples were suspended between two wooden blocks with finishing nails to allow air flow around the samples. Areas of the samples that were in contact with the wood were discarded. 10 hours in the Q-Sun weatherometer was eventually chosen as the aging condition for the experiment.

Humidification and Wetting

A control group of aged samples of both pink- and dynamite-weighted silk was retained with no further treatment and stored at 21ºC and 60% RH. Aged samples were exposed to either complete submersion in a bath of deionized water or an altered humidity. Complete submersion was conducted at 21ºC for 30 minutes. Samples exposed to altered humidity were placed in the Datacolor Conditioner with controller RP1 for 90 minutes until equilibrium was reached where no further weight was gained or lost. A slightly elevated humidity of 70% RH was applied to one group to simulate the standard testing conditions of ASTM D1776 of 21±2ºC and 65± 5% RH. A final group was exposed to a lowered humidity of 30% RH before being stored in a silica desiccation chamber.

Stiffness

The stiffness in the weft direction of the unweighted habutae, unaged pink- and dynamite-weighted habutae, aged pink- and dynamite-weighted habutae, and aged and treated pink- and dynamite-weighted habutae was evaluated using a "Shirley" Stiffness Tester according to ASTM D1388. Samples that received a treatment of

complete submersion in water were evaluated both wet and after they had been allowed to recondition overnight. Pink-weighted samples that were completely submerged in water were blotted to 0.48±02 grams (approximately twice the dry weight) before being evaluated while dynamite-weighted samples were blotted to 0.50±0.02 grams (approximately twice the dry weight). Neither groups conditioned at 30% RH or 70% RH was allowed to return to storage conditions, but rather were tested immediately upon conditioning.

Tensile Strength

Samples were evaluated for tensile strength using a modified version of ASTM D5035 (2011). A MTS QTest 1 using TestWorks® 4 software was fitted with a 25 lb loadcell and the gage length set to 1 cm. Samples were held in jaws with 25 x 13 cm faces. A variety of methods were attempted to prevent slipage (see Discussion) with Security Friction Tape chosen for the experiment. Each face was covered with Security Friction Tape (¾ inches wide, less than 1 mm thick, manufactured by United States Rubber Company) to prevent slipping. Samples were cut to 1 x 5 cm with the weft as the long direction. Unweighted habutae, unaged pink- and dynamite-weighted habutae, aged pink- and dynamite-weighted habutae, and aged pink- and dynamite-weighted silk habutae with modified moisture content were tested.

Samples that were completely wetted were evaluated both while wet and after they had been allowed to return to storage conditions overnight. Pink- and dynamite-weighted samples that were completely wetted in water were blotted to 0.040±0.002 grams (approximately twice the dry weight) before being evaluated. Groups exposed

to altered humidities were not allowed to return to storage conditions, but rather were tested immediately after conditioning.

CHAPTER 4

FINDINGS

This chapter presents observations related to sample preparation. These finding helped to ensure that samples were properly weighted and aged before the main experiment was conducted. This section also reports how samples' stiffness and tensile strength were impacted by the various treatments.

Weighting Recipes

Sodium hydrogen phosphate (Table 1) and aluminum sulfate (Table 2) were simply weighed out and mixed, often with the addition of low heat (less than 60ºC). Sodium trisilicate, however, required the addition of a small amount of sodium hydroxide (NaOH) and the application of heat to solubilize it in water (Table 3).

Mass of Na_2HP0_4 (g)	Volume of Solution (mL)	Mass of Solution (g)	Solution Density (g/mL)	Percent Solution	° Baumé
1.50	50.00	51.18	1.02	2.93	3.34
2.00	50.00	51.44	1.03	3.89	4.06
16.10	250.00	262.21	1.05	6.14	6.75
16.14	250.00	262.53	1.05	6.15	6.92
3.50	50.00	52.98	1.06	6.61	8.16

Table 1. Relationship Between Density, ºBaumé, and Concentration of Na_2HPO_4

Mass of $Al_2(SO_4)_3$ (g)	Volume of Solution (mL)	Mass of Solution	Density of Solution (g/mL)	Percent Solution	°Baume
1.00	50.00	50.39	1.01	1.98	1.12
1.51	50.00	50.38	1.01	3.00	1.09
2.50	50.00	51.17	1.02	4.89	3.32
1.51	25.00	25.76	1.03	5.86	4.28
2.00	25.00	26.02	1.04	7.69	5.68
2.25	25.00	26.19	1.05	8.59	6.59
2.40	25.00	26.38	1.06	9.10	7.59
2.50	25.00	26.24	1.05	9.53	6.85
5.01	50.00	52.52	1.05	9.54	6.96
25.05	250.00	262.64	1.05	9.54	6.98

Table 2. Relationship Between Density, ºBaumé, and Concentration of $Al_2(SO_4)_3$

Mass of $Na_20_7Si_3$	Mass of NaOH (g)	Volume of Solution (mL)	Mass of Solution (g)	Density (g/mL)	Percent Solution	°Baume
1.00	0.21	50.00	48.98	0.980	2.04	NA
2.51	0.20	50.00	46.57	0.931	3.24	NA
1.00	0.21	25.00	25.78	1.031	3.88	4.387
12.50	0.20	250.00	257.38	1.030	4.24	4.158
1.25	0.19	25.00	25.94	1.038	4.81	5.254
2.51	0.20	25.00	25.23	1.009	5.98	1.322

Table 3. Relationship Between Density, ºBaumé, and Concentration of $Na_2Si_30_7$

Determination of the density of tin (IV) chloride required more care, given the exothermic dilution and the offgassing of HCl. A balance was set up under the fume hood and the entire bottle of tin (IV) chloride was weighed. A small amount of tin (IV) chloride was poured into a beaker of deionized water and the weight lost from the stock bottle recorded. The diluted solution was allowed to cool before transfer to a volumetric flask and the appropriate amount of deionized water was added. The density of these solutions was then calculated to determine how much tin (IV) chloride was necessary to achieve the required solution density. The results can be found in

Table 4. The results were less precise than with other solutions: air movement caused variability of approximately 0.10g in the balance reading.

Mass of $SnCl_4$ (g)*	Volume of Solution (mL)	Mass of Solution (g)	Solution Density (g/mL)	Percent Solution of	° Baumé
53.36	250	285.32	1.14	18.3	17.95
79.64	250	301.71	1.21	25.9	24.85
81.34	250	306.93	1.23	26.0	26.89
82.50	250	308.76	1.24	26.2	27.59
82.73	250	307.73	1.23	26.3	27.20
82.61	250	306.38	1.23	26.4	26.68
36.42	100	123.02	1.23	29.0	27.13
53.36	100	136.32	1.36	38.4	38.63

Table 4. Relationship Between Density, ºBaumé, and Concentration of $SnCl_4$
* Based on 98% solution of $SnCl_4$ commercially available

Weighting

The J.A. King Sample Cutter is a standard device (ASTM D3776) to determine fabric weight, and was used when sufficient material was available. The large size of these samples and the need to take multiple specimens required that a more efficient means be used.

A set of gasket cutting dies was purchased to perform the same measurements on a smaller scale. A 0.5 inch diameter hollow punch die was purchased. This die (intended for rubber) was not sharp enough to cut through fabric. It was sharpened by hand using 320 and 220 grit sandpaper and mineral oil as a lubricant. The average weights of the 0.5 inch diameter circles at various stages in the weighting process can be found in Table 5.

Application Method*	1	2	3	4	5	6
Dipped Test	14.29	32.65	71.43	122.45	181.63	134.69
Padded- 15 psi Test	14.29	26.53	38.78	N/A	44.90	N/A
Padded- 50 psi Test	N/A	1189.80	44.90	N/A	44.90	238.78
Padded- 50 psi Final	22.45	30.61	42.86	N/A	55.10	N/A

Table 5. Average Percent Weight Gain of 0.5 in. Circles
* Method 1: One Tin/Phosphate
Method 2: Two Tin/Phosphate
Method 3: Three Tin/Phosphate
Method 4: Four Tin/Phosphate
Method 5: Three Tin/Phosphate, One Aluminum Sulfate, One Sodium Silicate
Method 6: Four Tin Phosphate, One Aluminum Sulfate, One Sodium Silicate

Many of the difficulties in achieving a level and consistent commercial application reported by historical sources were experienced in early attempts at weighting. Unused tin baths often had an opalescent sheen due to the presence of metastannic acid (H_2O_3Sn), also known as dihydroxy(oxo)tin, in the bath. The concentration of metastannic acid is inversely related to concentration of stannic chloride and can correspondingly effect the amount of tin that the silk picks up.[204] Recovered phosphate baths frequently had white precipitate in the bottom of the bath, suggesting that some of the tin did not penetrate the fiber and was instead precipitated out of the solution.

Dipped samples had the greatest weight gain, with padded samples gaining less. Within the dipped samples, those that received a fourth pass of tin-phosphate gained the most weight. However, this extra pass was abandoned as it made samples so stiff they became difficult to cut to the proper size for tensile testing. The pressure with

204 Matthews, Textile Fibres, 1924, 311.

which the samples were padded also affected the weight gain, with samples padded at a lower pressure gaining less weight overall than those padded at a higher pressure. Surprisingly, the average weight gain differed between the initial batch at 50 psi and the final batch of samples padded at the same pressure used in the experiment.

Patents for the continuous application of the weighting process existed by 1928.[205] Adapting this technique to a pad-batch methodology would decrease the amount of labor expended agitating the various baths as well as reduce the variation in weight gain across a given piece by ensuring that the contents of the baths are evenly distributed. This application would also reduce the amount of bath lost in each pass, as the excess is easily recovered from the troughs. In this work, rather than run the samples in a continuous process as described in the 1928 patent, a semi-continuous method was used due to space and equipment limitations. The semi-continuous method also allowed the amount of time dipped samples were in solution to be mirrored in the padded samples. However, neither the pink-weighted nor dynamite-weighted samples prepared in this manner achieved even remotely the same weight gain as seen in the dipped samples. In addition, a white precipitate in the sodium phosphate bath after samples were padded suggesed that the unfixed stannic chloride was reacting in the padding tray rather than on the fabric. Padding was initially abandoned as a potential application method for this experiment as a result.

However, a considerable amount of strength variation was seen among the pink- and dynamite-weighted samples produced by dipping (Table 6). This variation was deemed too large to provide reliable data to asses the potential effect of any humidification treatment. Even though the padded samples did not achieve the same

205 Mullin, "The New Clavel and Lindenmeyer Silk Weighting Process. -II," (January 1932): 23.

weight gain as the dipped samples, they did not display this same strength variability (Table 6). Therefore, padding was revisited as a potential application method. Initial tests used silk twill (Test Fabrics No. 611) padded with water and assessed for liquid pick up using the 2.7 inch diameter die. The pressure between the rollers was varied with each padding, ranging from 55 to 10 psi. The percent weight gain of the 2.7 inch diameter circles can be found in Table 7. The initial weighting tests described earlier had been conducted using 50 psi. A pressure of 25 psi gave a higher pickup and should thus allow more of the weighting solutions to remain on the fabric and correspondingly increase the weight pick up in an initial test run with a single pass of tin-phosphate.

	Dipped Pink	Dipped Dynamite	Padded Pink (50 psi)	Padded Dynamite (50 psi)	Padded Pink (15 psi)	Padded Dynamite (15 psi)
Average Breaking Strength (N)	51.819	56.996	41.868	68.182	61.475	69.367
Standard Deviation	4.341	23.590	10.006	0.446	2.292	2.090

Table 6. Average Breaking Strength (N) and Standard Deviation of Different Application Methods for Pink- and Dynamite-Weighted Habutae

	55 psi	40 psi	35 psi	25 psi	10 psi
Percent Weight Gain	64.03	64.73	68.12	72.56	97.25

Table 7. Percent Weight Gain of Silk Twill Circles Padded with Water at Different Pressures

A single pass of tin and phosphate was conducted at 25 psi. The weight gained in this test suggested that samples padded at 15 psi should gain more weight than those padded at 50 psi. However, when a test run of both pink- and dynamite-weighted

samples (both with three tin-phosphate passes) was completed at 25 psi, the total weight gained in both the pink- and dynamite-weighted samples was lower than that gained by the earlier samples padded at 50 psi (Table 5). Despite the lowered weight gain, the samples padded at 25 psi had similar cantilever results as the higher psi counterparts (Table 8). As a result, the initial 50 psi of the earlier samples was used for the main experiment.

	Untreated	Dipped Pink	Padded (50 psi) Pink	Padded (15 psi) Pink	Dipped Dynamite	Padded (50 psi) Dynamite	Padded (15 psi) Dynamite
Average Bending (cm)	2.31	2.13	2.08	2.02	2.74	2.23	2.19
Standard Deviation	0.06	0.10	0.07	0.08	0.20	0.11	0.06

Table 8. Preliminary Bending Length (cm) of Dipped, Padded (50 psi), and Padded (15 psi) Unaged Habutae Samples

Aging

High humidity, drastic pH environments, and long term UV exposure have been rejected as accurate mimics for natural aging as they fail to replicate the same analytical markers seen in analytical aging on unweighted silks.[206] Therefore, heating in air was initially chosen as it has been shown to achieve a similar reduction of chain length and decrease in tyrosine present seen in naturally aged silk.[207] 80ºC was chosen as the temperature for aging based on a previous study.[208] However, preliminary testing indicated that heat aging would take far too long to be a feasible method. After 120 hours only a small reduction (approximately 20%) in tensile strength was seen. In

206 Vilaplana et. al., "Analytical Markers," 1447.
207Vilaplana et. al., "Analytical Markers," 1442.
208 Garside et. al., "Understanding the Ageing Behaviour," 186.

contrast, light aging readily produced extreme results, creating fragile samples that became difficult to handle and began to powder after 30 hours. 10 hours was chosen as the amount of time for aging as it created a sizable decrease in tensile strength, but samples retained enough strength to be handled with ease. The results of the thermal preliminary tests when compared to the unaged pink- and dynamite-weighted samples can be found in Table 9 and the light preliminary tests in Table 10.

Pink/Dynamite	Hours of Exposure	% Strength Lost
Pink	72	4.953
Pink	96	-0.329
Pink	120	-4.844
Pink	336	47.694
Dynamite	72	-7.199
Dynamite	96	-3.185
Dynamite	120	3.690
Dynamite	336	25.983

Table 9. Percentage Strength Lost of Padded (50 psi) Preliminary Samples Aged for Various Hours of Exposure at 80ºC

Pink/Dynamite	Hours of Exposure	% Strength Lost
Pink	10	12.556
Pink	20	86.668
Pink	30	89.082
Pink	40	89.393
Dynamite	10	48.278
Dynamite	20	83.965
Dynamite	30	86.600
Dynamite	40	87.925

Table 10. Percentage Strength Lost of Padded (50 psi) Preliminary Samples Aged for Various Hours of Exposure at Under AATTCC 16.3 (2014) Conditions

The main experiment applied different humidity and moisture treatments to pink- and dynamite-weighted silk habutae. The silk was padded at 50 psi as a result of the above preliminary experiments. The weighted samples were then evaluated with cantilever bending length and peak load. The results and discussion of this experiment follow.

Stiffness

A two-sided independent t-test with a significance level of 0.05 was used to evaluate the change of mean cantilever bending length of pink- and dynamite-weighted samples after treatment. Each group consisted of 10 samples. Although some dependent variables did not fall within the acceptable range of skewness and Kurtosis values (Table 11), normality was assumed as the conditions of normality are frequently difficult to meet and a sufficient sample size was taken.[209] No outliers were observed in the data.

	Control (60% RH)		30% RH		70% RH		Wetted		Wetted then Reconditioned	
	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite
Variance	2.11E-003	1.36E-003	2.47E-003	1.67E-003	4.14E-003	1.36E-003	3.22E-003	3.78E-003	4.58E-003	8.78E-003
Kurtosis	-1.81	-0.73	-0.16	-1.39	-1.19	-0.73	-0.39	-1.46	-0.47	-1.24
Skewness	-0.47	-0.17	-0.61	2.04E-014	0.23	0.17	1.05	0.43	-0.50	0.49

Table 11. Normality Assumptions for the Stiffness of Pink- and Dynamite-Weighted Aged Silks

A statistically significant difference was found in all treatments on pink-weighted silk except the group conditioned to 70% RH (Table 11). The lack of statistically

209 Lincoln L. Chao, *Statistics: An Intuitive Approach* (Chicago: Science Research Associates, 1974), 150.

significant difference (p= 0.56) between this group and the control is unsurprising, given how little the treatment differed from storage conditions. All other treatments lowered the bending length of the aged samples. Water acts as a plasticizer, with humidity treatments used to increase historic textiles' flexibility,[210] and moisture can remain in the fabric, maintaining some of the newly imparted flexibility even after a humidity treatment.[211] This accounts for the decreased stiffness in the samples exposed to water as well as those wetted ($p=7.13x10^{-7}$) and later dried ($p=4.11x10^{-3}$). The decreased stiffness of the fabric while at a lower RH ($p=4.15x10^{-7)}$ is surprising, as silk is known to become more rigid with desiccation.[212]

	60% RH	30% RH	70% RH	Wetted	Wetted then Dried
Average Bending Length (cm)	2.11	1.95	2.10	1.64	2.03
Standard Deviation	0.05	0.05	0.06	0.06	0.07
p value		4.15E-007	0.56	7.13E-014	4.11E-003

Table 12. Statistical Analysis of the Average Bending Length (cm) of Aged Pink-Weighted Habutae

A similar effect was found in dynamite-weighted silks. Although not all data sets met the necessary values of Kurtosis and Skewness for normalcy, a two-sided independent t-test with a significance level of 0.05 was performed. Similarly, no outliers were observed in the data. A statistically significant difference was found in all treatments on dynamite-weighted silk except the group conditioned to 70% RH

210Boersma, *Unravelling Textiles,* 25.
211Boersma, *Unravelling Textiles,* 25.
212Tímár-Balázsy and Eastop, *Chemical Principles*, 45.

(Table 13). Again, the lack of statistically significant difference (p=0.55) between this group and the control is unsurprising, given how little the treatment differed from storage conditions. All other treatments lowered the bending length of the aged samples. Similar to the pink-weighted silk, the decrease in stiffness of the wetted ($p=8.44x10^{-16}$) and wetted then dried samples ($p=2.51x10^{-6}$) was expected. However, the significant decrease in the desiccated samples was unexpected ($p=4.15x10^{-7}$).

	60% RH	30% RH	70% RH	Wetted	Wetted then Dried
Average Bending Length (cm)	2.255	2.05	2.245	1.66	2.04
Standard Deviation	0.04	0.04	0.04	0.06	0.09
p Value		6.78E-010	0.55	8.44E-016	2.51E-006

Table 13. Statistical Analysis of the Average Bending Length (cm) of Aged Dynamite-Weighted Habutae

Tensile Strength

Although breaking a single yarn (ASTM D2256) was originally considered, as it would be the least destructive test method for historic silks, this method was abandoned for lack of sensitive enough equipment.

Silk habutae (Test Fabrics No. 609) was chosen as the fabric for the experiment as it closely resembles historic garment lining fabrics from the late nineteenth and early twentieth centuries, many of which were subsequently weighted. The thinness of the silk habutae, however, caused numerous problems while testing for tensile strength. Samples frequently slipped while being tested, invalidating the results generated. The slippage was visible when a camera was placed behind the jaw gap and used to record the trials.

Numerous attempts to prevent slippage were tried and abandoned as ineffective. These attempts included: cleaning the jaws with acetone, inserting a piece of double sided tape into the jaws to hold samples in place, attaching 320 and 220 grit sandpaper into the jaws, grinding the jaws themselves on 320 grit sandpaper with mineral oil lubricant to create a more level surface and even pressure on the samples, and attaching 1 mm thick rubber and Security Friction Tape (¾ inches wide, less than 1 mm thick), manufactured by United States Rubber Company, to the face of either one or both jaws. These methods either did not prevent slippage or resulted in samples that broke at the line of the jaw. Breaking at the line of the jaws also invalidates a sample's results.

Eventually the contact of the surface of the jaws was tested using the carbon and tissue paper method described in ASTM D5034 (2009). Incomplete contact of the jaw faces can allow samples to slip. However, no carbon whatsoever was transferred onto the tissue paper, suggesting a problem with the carbon paper. Contact was then assessed by holding a bright light behind the seam of clamped jaws. If light was visible through the seam, areas of the jaws were not making full contact. Unsurprisingly, numerous pockets of light were visible through the clamped jaws. Initial attempts to smooth the jaw surfaces and create full contact using 320 and 220 grit sandpaper and mineral oil were unsuccessful, with light still visible between the clamped jaws.

Permatex Valve Grinding Compound was then used to lap the jaws of machine to one another. A liberal coating of the grinding compound was applied to the inside face of one jaw and its mate was then rubbed against it in a random pattern for some

minutes. The grinding compound was removed from the jaws using acetone and the contact of the jaws retested. This process was repeated until the jaws were fully lapped to one another and no light was visible through the seam. This grinding was successful in preventing slippage of untreated habutae, but not for any samples that had been weighted with any application method or recipe. Eventually ¾ inch wide Security Friction Tape was inserted on the inner surface of each of the jaws. The combination of lapped jaws and Security Friction Tape provided the necessary contact and grip to eliminate slipping.

Once a method for ensuring samples did not slip from the jaws during testing was established, unweighted habutae, unaged pink- and dynamite-weighted habutae, aged pink- and dynamite-weighted habutae, and aged pink- and dynamite-weighted habutae with modified moisture content tested.

A two-sided independent t-test at a significance level of 0.05 was used to evaluate the change in mean tensile strength of pink- and dynamite-weighted samples after treatment. Each group consisted of 10 samples. Normality was assumed, despite some dependent variables not falling within the acceptable range of skewness and Kurtosis values (Table 14). Where possible, outliers were deleted and replaced with alternative data. This occurred in pink-weighted habutae at 70% RH, the control dynamite-weighted habutae, and dynamite-weighted habuate at 30% RH. However, outliers remained in the pink-weighted habutae at 30% RH.

	60% RH Aged Breaking Strength (N)		30% RH Breaking Strength (N)		70% RH Breaking Strength (N)		Wetted Breaking Strength (N)		Wetted and Dried Breaking Strength (N)	
	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite	Pink	Dynamite
Variance	5.35	5.77	7.57	9.56	11.85	30.82	2.53	1.09	15.13	9.30
Kurtosis	1.01	0.38	-0.11	0.10	6.25	0.64	-1.13	1.53	-0.62	0.03
Skewness	-0.59	0.71	-0.76	0.87	-2.22	1.00	-0.05	-1.50	-0.30	-1.18

Table 14. Normality Assumptions for the Breaking Strength of Pink- and Dynamite-Weighted Aged Silks

A statistically significant difference was found in all treatments on pink-weighted silk (Table 15). Similarly, statistically significant differences were observed on all groups of dynamite-weighted silk (Table 16).

	60% RH	30% RH	70% RH	Wetted	Wetted and Dried
Average Breaking Strength (N)	36.77	33.67	39.66	22.99	40.12
Standard Deviation	2.31	2.75	3.44	1.59	3.89
p Value		0.01	0.04	7.25E-012	0.03

Table 15. Statistical Analysis of the Average Breaking Strength (N) of Aged Pink-Weighted Habutae

	60% RH	30% RH	70% RH	Wetted	Wetted and Dried
Strength (N)	33.53	38.13	22.39	37.32	38.07
Standard Deviation	2.40	3.09	1.04	3.05	5.55
p Value		1.59E-003	7.81E-011	0.01	0.03

Table 16. Statistical Analysis of the Average Breaking Strength (N) of Aged, Dynamite-Weighted Habutae

The small standard deviations and variance observed in both wetted pink- and dynamite-weighted habutae is consistent with earlier studies that reveal the wet

breaking strength of weighted silks to be more uniform than dry breaking strength.[213] Likewise, the significant decrease in tensile strength seen in the completely wetted samples was expected, as observed in tensile testing of unweighted, wet silk.[214]

The significant difference observed between the control and humidification at 70% RH in both pink- and dynamite-weighted samples ($p=0.04$ and $p=8.81\times10^{-11}$, respectively) is surprising given the testing conditions' similarity to the control. Likewise, the increase in strength seen in the dynamite-weighted silk ($p=1.59\times10^{-3}$) at a lowered humidity is unexpected. Conventional preventative conservation holds that drastically decreased relative humidity can lead to embroilment of fibers.[215] A corresponding decrease in tensile strength would be expected, as seen in the pink-weighted samples. The difference between the pink- and dynamite-weighted samples at a lowered RH suggests that the different weighting processes have different sensitivities to humidity. Perhaps most surprising is the positive effect that wetting and allowing samples to dry had on the tensile strength of both pink- and dynamite-weighted silk ($p=0.03$ and $p=0.03$, respectively), supporting Hansen and Derelian's work on unweighted silk[216] and suggesting that complete wetting can increase the breaking strength of weighted silks.

213 Ross et. al., "Degradation of Weighted Silk," 213.
214Robson, "Silk,"449.
215 Foekje Boersma, Uravelling Textiles: A Handbook for the Preservation of Textile Conservation (London: Archetype Publications, 2007): 34.
216Hansen and Derelian, "Effects of Wet Cleaning," 95.

CHAPTER 5

CONCLUSION

Tin weighted silk was a common finishing technique in the late nineteenth and early twentieth centuries. What began as a method to compensate for weight loss in degrummed silk developed into weighting levels well above par. Silk that underwent such high levels of weighting is frequently fragile and prone to shattering. Although public outcry and federal regulations eventually led to its phasing out, objects that underwent this treatment are prolific in museum and other cultural institutions. The problems created by the weighting process not only led to dissatisfied consumers, it has led to considerable problems for its long term conservation.

This study developed a method for the even application of the two most common historical tin weighting methods. This enables future research on the conservation of weighted silk that does not utilize prized extant objects. Recreating weighted silk also eliminates any variation that might result from experimentation on objects that might have experienced different life histories that effect their aging process.

This research also suggests a potential future conservation treatment for increasing the tensile strength of tin weighted silks as well as suggesting how pink- and dynamite-weighted silks might have different sensitivities to humidity. Increasing the relative humidity by a mere 10% increased tensile strength, but did not impact the bending on both pink- and dynamite-weighted silks. However, maintaining an increased RH for extant objects is not recommended for well-established reasons.

Most intriguing was the effect of complete wetting and then reconditioning at an approximation of conditions more likely to be found in a museum. This treatment, although it altered the drape of the fabric, increased the tensile strength of both pink and dynamite-weighted silks. This suggests that weighted silks might benefit from wet cleaning or a similar process that results in complete submersion. However, this treatment did impact the drape of the fabric, as well as create a more fragile textile during the wetting process itself.

Pink-weighted samples had a reduced tensile strength at a lowered humidity, while dynamite-weighted samples had an increased tensile strength, suggesting that the manner in which an object was weighted, not simply the presence of weighting agents in general, effects silk's sensitivity to humidity. Particular care should be given to extant objects known to have undergone pink weighting to avoid a lowered humidity and the resulting loss of tensile strength.

Further research into how complete wetting effects extant objects with different life histories is necessary to confirm the applicability of this treatment to objects found in museum collections. In addition, care must be exercised when submerging weighted silk in water as, like unweighted silk, it becomes more fragile when wet. Further research into the long term effects of these treatments is also necessary. It is possible that the benefit seen by complete submersion is only temporary. Applying this treatment also requires a judgment evaluation of the benefits of increased tensile strength with the impact on drape.

APPENDICES

APPENDIX A: PRELIMINARY TESTING RAW DATA

The following tables provide the raw data from the various preliminary tests that informed the main experiment.

Pink-Weighted Weight (g) of 0.5 inch Circles- Dipped Method

Sample	Unweighted	1 Tin-Phosphate	2 Tin-Phosphate	3 Tin-Phosphate	4 Tin-Phosphate
1	0.0049	0.0055	0.0061	0.0083	0.0111
2	0.0050	0.0059	0.0065	0.0085	0.0110
3	0.0050	0.0053	0.0066	0.0087	0.0115
4	0.0045	0.0057	0.0066	0.0086	0.0105
5	0.0048		0.0066	0.0080	0.0105
6	0.0050			0.0082	
7	0.0046				
8	0.0049				
9	0.0050				

Dynamite-Weighted Weight (g) of 0.5 inch Circles- Dipped Method

Sample	Unweighted	Dynamite (1 Tin-Phosphate)	Dynamite (2 Tin-Phosphate)	Dynamite (3 Tin-Phosphate, 1 Aluminum Sulfate)	Dynamite (3 Tin-Phosphate, 1 Aluminum, 1 Silicate)
1	0.0049	0.0063	0.0079	0.0095	0.0142
2	0.0050	0.0060	0.0080	0.0095	0.0136
3	0.0050	0.0062	0.0078	0.0097	0.0138
4	0.0045	0.0064	0.0078	0.0103	0.0136
5	0.0048	0.0070	0.0074	0.0098	0.0139
6	0.0050	0.0064	0.0083	0.0093	
7	0.0046	0.0063			
8	0.0049				
9	0.0050				

Pink-Weighted Weight (g) of 0.5 inch Circles- Pad Method

		50 psi	50 psi	15 psi	15 psi	15 psi
Sample	Unweighted	2 Tin-Phosphate	3 Tin-Phosphate	1 Tin-Phosphate	2 Tin-Phosphate	3 Tin-Phosphate
1	0.0049	0.0066	0.0073	0.0056	0.0060	0.0066
2	0.0050	0.0063	0.0067	0.0059	0.0063	0.0067
3	0.0050	0.0062	0.0071	0.0055	0.0064	0.0067
4	0.0045	0.0065	0.0072	0.0055	0.0063	0.0069
5	0.0048	0.0062	0.0072	0.0057	0.0060	0.0069
6	0.0050	0.0061	0.0072	0.0055	0.0061	0.0069
7	0.0046			0.0054	0.0065	0.0068
8	0.0049			0.0055	0.0065	0.0070
9	0.0050			0.0056	0.0060	0.0069
10	0.0052			0.0054	0.0061	0.0068

Dynamite-Weighted Weight (g) of 0.5 inch Circles- Pad Method

		50 psi	50 psi	15 psi
Sample	Unweighted	3 Tin-Phosphate; 1 Aluminum, 1 Silicate	4 Tin-Phosphate; 1 Aluminum, 1 Silicate	3 Tin-Phosphate, 1 Aluminum, 1 Silicate
1	0.0049	0.0072	0.0166	0.0069
2	0.0050	0.0069	0.0172	0.0069
3	0.0050	0.0072	0.0160	0.0074
4	0.0045	0.0063	0.0165	0.0072
5	0.0048	0.0077	0.0169	0.0069
6	0.0050	0.0071	0.0161	0.0071
7	0.0046			0.0072
8	0.0049			0.0072
9	0.0050			0.0070
10	0.0052			0.0070

Weight (g) of 2.7 inch Circles of Twill Padded with Water at Different Pressures

Sample	Dry Weight	55 psi	40 psi	35 psi	25 psi	10 psi
1	0.1824	0.3080	0.3058	0.3079	0.3160	0.3632
2	0.1847	0.2934	0.2982	0.3085	0.3167	0.3600
3	0.1840					
4	0.1822					
5	0.1845					
6	0.1829					
7	0.1828					
8	0.1831					

Breaking Strength (N) of Unaged Samples

Sample Number	Unweighted	Unweighted, Wetted	Dipped Pink	Dipped Dynamite	Padded Pink (50 psi)	Padded Dynamite (50 psi)	Padded Pink (15 psi)	Padded Dynamite (15 psi)
1	62.191	50.704	60.030	77.984	65.844	66.537	71.570	68.348
2	65.425	55.345	62.934	62.942	69.235	69.131	68.877	72.043
3	63.882	52.275	60.560	49.206	68.306	62.598	67.966	72.618
4	65.268	52.938	62.103	67.758	62.127	64.162	66.408	69.651
5	61.937	50.156	62.870	62.671	64.789	68.956	68.572	72.528
6	64.947	48.470	68.231	77.864	70.982	63.633	68.184	71.006
7	64.233	51.899	70.184	72.321	66.617	59.579	67.311	71.654
8	66.267	48.813	60.379	66.853	67.670	65.892	67.692	70.550
9	65.162	46.826	62.725	39.429	68.176	63.036	70.520	70.853
10	60.400	53.926	66.041	40.346	68.631	59.544	69.826	74.845
11	61.019	54.704	59.294	21.851	67.740	64.909	70.293	71.168
12	60.759		67.821	40.277		59.944	72.086	70.300
13	71.890		74.153	48.422		58.684	69.804	66.562
14	62.286			46.920		63.252	66.447	69.278
15	65.886			34.828		60.953	66.591	73.736
16	65.870			34.570				72.644
17	63.000			42.877				
18	66.701			60.254				
19	63.439			50.772				
20	62.878			32.975				
21	65.724			72.436				
22	63.690			41.797				
23	66.401			69.934				
24	64.473							
25	62.111							
26	67.123							
27	63.540							

Breaking Strength (N) of Light Preliminary Testing

Pink/Dynamite	Number of Tin-Phosphate Passes	Application	Hours of Exposure	Breaking Strength (N)
Pink	4	Dipped	20	32.249
Pink	4	Dipped	30	13.649
Pink	4	Dipped	40	16.710
Dynamite	4	Dipped	20	11.456
Dynamite	4	Dipped	30	14.598
Dynamite	4	Dipped	40	3.750
Pink	3	Padded (50 psi)	10	57.199
Pink	3	Padded (50 psi)	10	60.471
Pink	3	Padded (50 psi)	20	8.970
Pink	3	Padded (50 psi)	30	7.346
Pink	3	Padded (50 psi)	40	7.137
Dynamite	3	Padded (50 psi)	10	30.704
Dynamite	3	Padded (50 psi)	10	34.629
Dynamite	3	Padded (50 psi)	10	33.023
Dynamite	3	Padded (50 psi)	20	10.164
Dynamite	3	Padded (50 psi)	30	8.494
Dynamite	3	Padded (50 psi)	40	7.654
Pink	3	Padded (15 psi)	10	42.502
Pink	3	Padded (15 psi)	10	44.235
Dynamite	3	Padded (15 psi)	10	30.614
Dynamite	3	Padded (15 psi)	10	35.645

Breaking Strength (N) of Heat Preliminary Testing

Pink/Dynamite	Hours of Exposure	eaking Strength (
Pink	72	58.586
Pink	72	66.805
Pink	72	66.460
Pink	96	68.047
Pink	96	66.962
Pink	120	74.945
Pink	120	68.391
Pink	120	68.290
Pink	336	35.193
Dynamite	72	74.524
Dynamite	72	63.828
Dynamite	72	65.499
Dynamite	96	70.922
Dynamite	96	59.890
Dynamite	120	60.753
Dynamite	120	59.078
Dynamite	120	63.313
Dynamite	336	46.917

Cantilever Bending Length (cm) of Unaged Samples

Sample Number	Untreated	Dipped Pink	Padded (50 psi) Pink	Padded (15 psi) Pink	Dipped Dynamite	Padded (50 psi) Dynamite	Padded (15 psi) Dynamite
1	2.25	2.05	1.95	2.00	2.85	2.10	2.15
2	2.25	2.25	2.05	2.00	2.90	2.35	2.20
3	2.35	2.30	2.10	1.95	2.80	2.15	2.20
4	2.35	2.20	2.10	2.05	2.90	2.25	2.15
5	2.30	2.15	2.20	2.05	2.65	2.20	2.20
6	2.35	2.10	2.10	2.10	3.05	2.35	2.05
7	2.35	2.00	2.15	1.95	2.45	2.10	2.25
8	2.30	2.00	2.00	2.15	2.50	2.40	2.25
9	2.40	2.10	2.10	2.05	2.70	2.20	2.15
10	2.23	2.10	2.05	1.90	2.55	2.20	2.25

APPENDIX B: MAIN EXPERIMENT RAW DATA

The following tables provide the raw data from the main experiment.

Weight of 0.5 inch Circles- Pad Method (50 psi)

Sample	1 Tin-Phosphate	2 Tin-Phosphate	3 Tin-Phosphate	3 Tin-Phosphate, 1 Aluminum, 1 Silicate
1	0.0060	0.0065	0.0072	0.0074
2	0.0059	0.0065	0.0068	0.0076
3	0.0063	0.0063	0.0071	0.0075
4	0.0058	0.0064	0.0073	0.0076
5	0.0061	0.0064	0.0070	0.0079
6	0.0054	0.0065	0.0068	0.0077
7	0.0060	0.0066	0.0069	0.0078
8	0.0061	0.0066	0.0070	0.0077
9	0.0060	0.0063	0.0070	0.0074
10	0.0059	0.0061	0.0071	0.0076
Average	0.0060	0.0064	0.0070	0.0076
Standard Deviation	0.0002	0.0002	0.0002	0.0002

Cantilever Bending Length (cm) of Aged Pink-Weighted Samples

Sample	Control (60% RH)	30% RH	70% RH	Wetted	Wetted then Dried
1	2.10	1.90	2.20	1.70	2.00
2	2.15	1.85	2.15	1.60	2.00
3	2.05	1.95	2.05	1.60	1.95
4	2.15	2.00	2.15	1.75	2.05
5	2.15	1.95	2.05	1.60	2.10
6	2.05	2.00	2.05	1.60	2.10
7	2.05	1.90	2.05	1.60	2.00
8	2.10	1.95	2.15	1.65	1.90
9	2.15	2.00	2.10	1.60	2.05
10	2.15	1.95	2.00	1.70	2.10

Cantilever Bending Length (cm) of Aged Dynamite-Weighted Samples

Sample	Control (60% RH)	30% RH	70% RH	Wetted	Wetted then Dried
1	2.20	2.10	2.20	1.60	1.95
2	2.25	2.00	2.25	1.70	2.10
3	2.20	2.05	2.25	1.70	2.15
4	2.30	2.05	2.25	1.75	2.10
5	2.30	2.05	2.25	1.60	2.00
6	2.25	2.05	2.30	1.65	2.20
7	2.25	2.10	2.20	1.60	1.95
8	2.25	2.10	2.30	1.65	2.05
9	2.25	2.00	2.20	1.60	1.95
10	2.30	2.00	2.25	1.75	1.95

Breaking Strength (N) of Aged Pink-Weighted Samples

(Outliers Highlighted)

Sample	Control (60% RH)	30% RH	Wetted	Wetted then Dried	70% RH
1	35.564	37.367	23.956	41.029	41.712
2	36.103	29.278	22.821	39.312	39.408
3	31.977	32.864	25.427	38.316	41.239
4	36.924	34.258	24.619	35.621	40.153
5	35.746	28.967	22.458	44.054	40.541
6	36.198	34.645	20.620	38.254	38.570
7	39.388	36.294	21.176	43.391	30.668
8	36.814	33.191	21.415	33.367	43.622
9	39.029	34.307	23.145	45.771	40.638
10	39.918	35.575	24.226	42.127	40.048
11	37.826	28.697	27.688	37.771	40.504
12		28.168	23.360	38.958	39.202
13					41.020
14					40.800
15					39.229
16					41.359
17					36.640
18					39.455

Breaking Strength (N) of Aged Dynamite-Weighted Samples

(Outliers Highlighted)

Sample	Control (60% RH)	30% RH	Wetted	Wetted then Dried	70% RH
1	33.190	37.720	20.064	32.746	32.457
2	31.084	36.771	23.089	39.892	40.592
3	35.652	36.343	23.007	38.094	32.235
4	33.196	38.782	21.408	38.623	33.429
5	32.556	43.804	21.531	38.869	44.066
6	33.537	42.787	23.144	31.506	39.191
7	30.214	38.687	22.888	35.421	34.427
8	38.304	37.172	23.165	38.258	37.551
9	32.004	34.980	22.586	40.019	37.195
10	35.567	34.214	22.985	39.751	49.579
11	34.494	34.813		33.734	48.766
12		36.579		37.589	

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