〔報文〕 Experimental Treatment for Black-dyed Cotton Textiles Using Japanese Adhesives Funori and Nikawa

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1．Introduction

Iron mordanting has been part of the textile dyeing process for centuries. Iron, as a mordant salt, dates back as early as the sixteenth to thirteen century BC and has been discovered in Egyptian textiles[1)]. Iron mordant and tannins, combined to achieve dark colours (deep blacks, greys, and browns), have a long history together. During the sixteenth and seventeenth centuries, the use of iron salt as a mordant for black dyeing was prevalent in Europe, specifically in the Netherlands and Italy[2)]. Many recipes for black dyeing can be found in historical sources from that era. Examples of black-dyed textiles, particularly silk, dating from this period can be found in various European museum collections. During the early nineteenth century in Japan, black dyeing using a combination of galls, known as gobaishi or Japanese galls, and iron mordant was a widely used to achieve black and grey colours[3)]. The use of this technique was not restricted to clothing alone, as it was also utilised in the creation of ceremonial dolls known as Hina dolls. Silk was the primary material used to make the dolls' clothes, particularly for their hair, which was often dyed black using this method. Myriad Māori decorative textiles from New Zealand have been traditionally dyed black using iron-containing mud, called paru, combined with tannin dyes extracted from Manuka bark[4)].

Dyeing with iron-mordant (ferrous(Ⅱ) sulfate) in combination with tannins, dyes derived from plants and trees, naturally containing acids such as gallic acid, tannic acid, ellagic acid, represents an acidic process that causes hydrolytic degradation of protein in animal fibres, and cellulose in vegetable fibres. When environmental conditions are met, the iron-catalyst reaction decomposes the fibre, making it weak and brittle[3)5)]. Today this type of degradation represents a serious worldwide conservation matter.

Similar degradation to iron-tannate dye, caused by the iron catalyst, is found in paper manuscripts as gall ink corrosion. Investigative treatments for iron gall ink paper deterioration could be used for iron-tannate textile deterioration. Gelatin treatment has shown its potential and beneficial effect on iron gall ink corrosion[6)].

Potential treatments for iron-tannate dye textile deterioration include experimental consolidation on iron-tannate dyed experimental textile fibres. Polyethene glycol coating has proved effective on iron-mordanted silk fibres dyed black with tannic acid[7)]. Zn alginate[4)] and Na alginate have been tested and displayed beneficial properties on black-dyed Māori muka textiles fibres made from New Zealand flax[8)]. Furthermore, in the most recent study[9)],

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funori's propriety form TRI-Funori™ has been evaluated among other most used consolidants, Na alginate, Zn alginate (Na and Zn salts form of alginic acid derived from the cell walls of brown algae), alongside Paraloid® B-72, and Methocel® A4C, for the experimental conservation treatment of black-dyed Māori textile artefacts. Based on the evaluation of acidity, strength, and colour change, TRI-Funori™ and Methocel® A4C, with their beneficial properties, at 0.5% w/v, were found to be overall best-performing consolidants and showed potential as a treatment for deteriorated paru-dyed muka textiles.

This research aims to experiment with two Japanese traditional, natural conservation materials used in an entirely new application as a potential consolidation treatment for iron tannate dye textile deterioration.

In Japan, nikawa, a cowhide glue (a type B gelatin), has a long history as a conservation material, being employed as an adhesive, pigments binder and consolidant in the long tradition of Japanese painting restoration. A conservation material of 1000 years-long tradition and unique to Japan, funori (Gloiopeltis furcata), the seaweed has been used as the sizing or cleaning agent for textiles[10)11)12)] and also used in the conservation of Japanese painting and polychromy. Previous studies suggest funori's iron cation capturing ability[13)14)], potentially leading to the slowdown of fibre deterioration through its consolidation.

The present study employs experimental treatment with funori, which due to its genuine and unmodified properties in comparison to its propriety form TRI-Funori™, enables universal usefulness and allows versatility of use on various materials and at conservation sites.

To investigate the efficacy of treatment, previously mentioned studies[4)7)8)9)] employed artificially deteriorated iron-tannate dyed experimental textile fibres. The present study also uses experimental textiles, artificially aged cotton cloth[15)], rather than fibres, to test the potentiality of conservation treatment by evaluating samples' pH, tensile strength, and colour change in addition to iron(Ⅱ) ions presence. Therefore, this study aims to investigate the effect of funori and nikawa consolidation treatment on iron-tannate dyed and artificially aged cotton.

2. Experimentation

2－1. Iron-tannate dyed samples preparation

2－1－1. Material

Cotton cloth (Cotton Broad Mercer unprocessed, basis weight 122.5 g/m^2, Shikisensha, Co Ltd. - 色染社製綿ブロード 40 未シル ケット加工) was the material used for this study. The cloth was cut in 200×200 mm in 30 pieces by its warp direction.

2－1－2. Dyeing

In a myriad of dyeing technique recipes, multiplying the weight of the cloth by fifty enabled a sufficient and the most appropriate amount of dyeing liquid to dye the fabric evenly, that is, to facilitate uniform adherence of the dye to the textile. The total weight of all 30 samples was 141.2 g, and after adding a fiftyfold value (50 times the fabric's weight), it equalled 7060 (141.2×50 = 7060).

Based on the above calculation, the deionised water amount used in the dyeing and mordanting processes was 7060 mL. Tannic acid (Nacalai Tesque, Kyoto, extra pure reagent)

for dyeing was used at 1% w/v (70.6 g), and ferrous sulfate (Wako Pure Chemical Industries, Osaka, special grade reagent) at 2% w/v (141.2 g).

The samples were dyed at 70 ℃ for 60 minutes[1)16)17)] by fully submersing in the tannic acid solution whilst continuously stirring. After the dyeing solution's temperature decreased to 40 ℃, the samples were removed from the dyeing solution and thoroughly rinsed in deionised water. Mordanting was conducted at 40 ℃ for 30 minutes by fully submersing previously treated samples with tannic acid in the ferrous sulfate solution and continuously stirring. After mordanting, the samples were rinsed in deionised water. The process of dyeing/mordanting/rinsing was repeated 3 times. After the last mordanting (third), samples were thoroughly rinsed with deionised water to remove the excess ferrous sulfate. Samples were air dry for about 24 hours. Additional sample preparation included removing tangled threads from the edges and ironing.

2－2. Artificial ageing

To monitor the efficacy of the consolidation treatment, samples were aged before (artificial ageing 1) and after (artificial ageing 2) the treatment.

Samples aged 1 day before the treatment were aged for 1 more day after the treatment. The same applied to the samples artificially aged for 3 days. ESPEC PDL-4J at conditions of 80 ℃ and 65% RH was used for accelerated ageing[15)18)].

Controls were samples with no consolidants but immersed only in deionised water. Consolidated and control samples' abbreviations are listed below (Table 1).

2－3. Analytical techniques

2－3－1. pH test

The pH of samples was measured by extracting 0.03 g of sample in 1 mL of Milli-Q® water. The samples were macerated for 24 hours at 25 ℃ and 50% RH. The pH meter (HORIBA LAQUAtwin pH-33) was used to measure the extract.

2－3－2. Bathophenanthroline test

The Bathophenanthroline test examined the presence of soluble iron(Ⅱ) ions. Developed for paper and parchment with iron gall ink deterioration[19)], it has proven its effectiveness in investigating iron(Ⅱ) ions on textile surfaces[20)]. Bathophenanthroline, by chemical composition 4, 7-diphenyl-1, 10-phenanthroline, a colourimetric reagent forms with iron(Ⅱ) ions, iron(Ⅱ)-bathophenanthroline complex. The appearance of a magenta colour visually manifests this reaction.

The test was conducted by wetting a piece (1×1 cm) of the Bathophenanthroline indicator paper (SUIGIT3000, CXD International) with deionised water. Using a piece of Melinex® foil as a protective covering layer, the wetted indicator paper was pressed against the sample surface for 30 seconds, enabling the iron(Ⅱ)-bathophenanthroline complex to develop.

2－3－3. Tensile strength test

The samples were prepared in 12×2 cm dimension strips, with the central 10 cm as the testing area (1 cm in both grips). The samples were measured following the direction of their vertical direction, the warp. For each sample, 5 strips were tested unless otherwise specified.

Table 1 Abbreviations of consolidated and control samples utilised throughout the experiment

Ageing period	Sample + treatment	Abbreviation
Unaged	Unaged (control)	[A0]
	Unaged + deionised water (control)	[A0 + W]
	Unaged + 0.2% funori extract	[A0 + F]
	Unaged + 1% nikawa solution	[A0 + N]
Artificial ageing 1 (1 day aged)	1 day aged (control)	[A1]
	1 day aged + deionised water (control)	[A1 + W]
	1 day aged + 0.2% funori extract	[A1 + F]
	1 day aged + 1% nikawa solution	[A1 + N]
Artificial ageing 2 (+ 1)	1 day aged + 1 day (control)	[A1 + A1]
	1 day aged + deionised water + 1 day (control)	[A1 + W + A1]
	1 day aged + 0.2% funori extract + 1 day	[A1 + F + A1]
	1 day aged + 1% nikawa solution + 1 day	[A1 + N + A1]
Artificial ageing 1 (3 days aged)	3 days aged (control)	[A3]
	3 days aged + deionised water (control)	[A3 + W]
	3 days aged + 0.2% funori extract	[A3 + F]
	3 days aged + 1% nikawa solution	[A3 + N]
Artificial ageing 2 (+ 3)	3 days aged + 3 days (control)	[A3 + A3]
	3 days aged + deionised water + 3 days (control)	[A3 + W + A3]
	3 days aged + 0.2% funori extract + 3 days	[A3 + F + A3]
	3 days aged + 1% nikawa solution + 3 days	[A3 + N + A3]

Before each test, the strips were placed in a conditioning chamber (Espec Walk-In Temperature & Humidity Chamber E Series) and left overnight at 23 ℃ and 50% RH. The tensile strength of samples was measured with Shimadzu Autograph AGS X Series, combined with Shimadzu TRAPEZIUM X testing software, with a force capacity of 5000 N at 20 mm/min speed. The tensile testing was conducted following JIS L 1096 (strip method).

2－3－4．Colorimetry

Colorimetry was conducted to evaluate the extent to which the ageing and consolidation treatment affected the colour change compared to the control samples (Table 2).

The colorimeter Konica Minolta CM-2600d Spectrophotometer and Konica Minolta Color Data Software SpectraMagic NX measured the colour change assessment. The measurement was assessed by D65 CIE standard illuminant and SCE measurement of reflectance. The measurement was taken from five different positions on each sample's surface. The average of ΔL^*, Δa^*, and Δb^* values were calculated for all 5 measurements. The standard for each sample is shown in Table 2.

2－4．Treatment with funori and nikawa

The respondent amount of consolidants had to be selected to maintain the textile's natural surface appearance, softness, and hand feel. For treatment with funori (ma-funori－H30 年製天菊久平布海苔，株式会社大脇萬蔵商店), the extract was selected and prepared at a ratio 2/1000 (funori/deionised water), while for nikawa treatment（播州膠はりま-3 寺脇産業株式会社）1% (w/v) was selected.

2 − 4 − 1 . Funori preparation and treatment

Before preparing funori extract, 2 g of dry funori was washed in deionised water. After a 30-minute soaking of funori, the solution was gradually heated to the boiling point and cooked for several minutes while constantly stirring. For this experiment, funori was chosen to be prepared by heating, rather than only extracting at the ambient temperature, due to better viscosity and enhanced consolidating properties of funori obtained at higher temperatures[21]. The prepared solution was filtered through two-layer cotton gauze and cooled to room temperature. The pH of the funori extract was measured at 7.42.

To measure the accurate concentration of funori extract used for consolidation, the calculation was as follows:

The weight of the funori extract, after filtration, was measured at 883.47 g. Subsequently, 3 g of funori extract was separated and placed into a drying chamber. Isuzu Kosumosu VTN-115 Drying oven, set at 105 ℃, was used. The residue was weighed and measured at 0.007 g. To calculate the total residue for 883.47 g of funori extract, the 883.47 was divided by 3 and multiplied by 0.007. The total residue for 883.47 g of extract was measured at 2.061 g. To calculate the concentration of funori extract, the formula was used:

$$\frac{Funori\ extract\ residue(g)}{Funori\ extract(g)} x\ 100$$

Thus, the funori extract concentration was calculated at 0.2%.

Funori consolidation treatment was conducted by submersing a sample into the extract for 30 minutes. After the treatment, the excess consolidation extract was removed from the samples. Horizontally positioned, samples were air dry for about 24 hours.

Table 2 Standard samples used for colour change measurement of consolidated and control samples

Standard:	For sample:
[A0]	[A1] [A1 + A1] [A3] [A3 + A3]
[A0 + W]	[A1 + W] [A1 + W + A1] [A3 + W] [A3 + W + A3]
[A0 + W]	[A1 + F] [A1 + F + A1] [A3 + F] [A3 + F + A3] [A1 + N] [A1 + N + A1] [A3 + N] [A3 + N + A3]
[A0 + F]	[A1 + F] [A1 + F + A1] [A3 + F] [A3 + F + A3]
[A0 + N]	[A1 + N] [A1 + N + A1] [A3 + N] [A3 + N + A3]
[A1 + W]	[A1 + W + A1]
[A1 + F]	[A1 + F + A1]
[A1 + N]	[A1 + N + A1]
[A3 + W]	[A3 + W + A3]
[A3 + F]	[A3 + F + A3]
[A3 + N]	[A3 + N + A3]

2 − 4 − 2 . Nikawa preparation and treatment

Nikawa granulate, weighted at 10 g, was soaked overnight in 1000 mL of deionised water. The nikawa solution was prepared in a water bath, heating the solution to 60 ℃ until complete dissolution and then lowering it to 40 ℃ to treat samples. The pH of the nikawa solution was measured at 7.27. Nikawa treatment was carried out by submersing a sample into the nikawa solution for 30 minutes. The excess solution was removed after the treatment duration ended, followed by horizontally air drying the samples for about 24 hours.

To summarise the experimental section, Fig. 1 shows a more comprehensive inspection of

the overall preparation of samples. As noted earlier, to prepare deteriorated samples, the samples were aged two times before (artificial ageing 1) and after (artificial ageing 2) the treatment. From each experimental phase, in addition to the focal consolidated samples, samples were excluded to be used as controls (unaged, only dyed/aged/deionised water).

3. Results

The analytical methods chosen for this study evaluated the impact of the consolidation of iron-tannate dyed, artificially aged cotton. All four tests indicated the beneficial effect of the consolidation in lowering pH and iron(Ⅱ) presence, increasing the tensile strength and not affecting the colour change no more than ageing alone would.

3－1. pH test

The pH value of the funori extract is 7.42, while that of the nikawa solution is 7.27. The neutral pH of the consolidations resulted in an increase in pH values of treated samples in comparison to the controls.

The pH test evaluated the pH value of consolidated and control samples, of which the effect is shown in Fig. 2. The pH changed from 4.08 and 4.50 in control samples [A0] and [A0 + W], respectively, to 5.35 and 5.76 in consolidated samples [A0 + F] and [A0 + N] respectively. The 4.08 of the [A0] sample indicates how the iron-tannate dye has the pH lowering effect, since the pH value of undyed and unaged cotton is 6.85. The same tendency of pH increase, in consolidated samples is evident in the other four groups of samples.

The pH increase in samples treated with consolidants is evident across all five groups: A0,

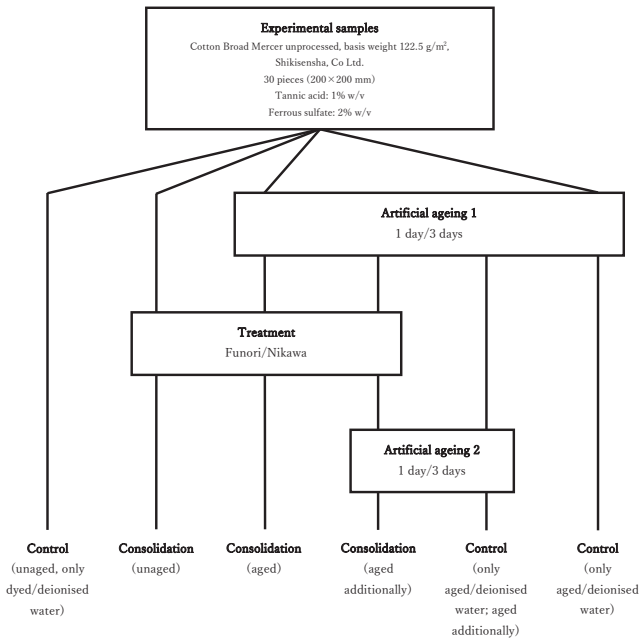

Figure 1 Chart showing the consolidation procedure and artificial ageing of experimental samples and type of samples (consolidated and controls) obtained accordingly

A1, A1 + A1, A3 and A3 + A3. In the 1 day aged group, the pH of [A1] increased from 4.11 to 5.08 after funori treatment [A1 + F] and to 5.73 after nikawa treatment [A1 + N]. Furthermore, ageing for an additional 24 hours after the consolidation, the same tendency of increasing in pH value is evident. The pH of the control sample [A1 + A1] increased from 3.95 to 4.58 in a sample with funori consolidation [A1 + F + A1] and 4.91 in the sample with nikawa consolidation in between two ageing periods of 24 hours [A1 + N + A1]. The inclination towards low pH value of only aged control samples is apparent in all five groups. In the samples aged for 3 days before the consolidation treatment, the pH of only the aged control sample [A3] increased its pH from 3.83 to 4.52 after funori consolidation in [A3 + F] and to 5.61 after nikawa consolidation in [A3 + N].

The pH-increasing effect of consolidation treatment is also displayed in the group of the most brittle samples, aged six days. The sample with the lowest pH value out of all twenty, the only aged control sample [A3 + A3], increased from 3.57 to 3.88 in the sample with the funori

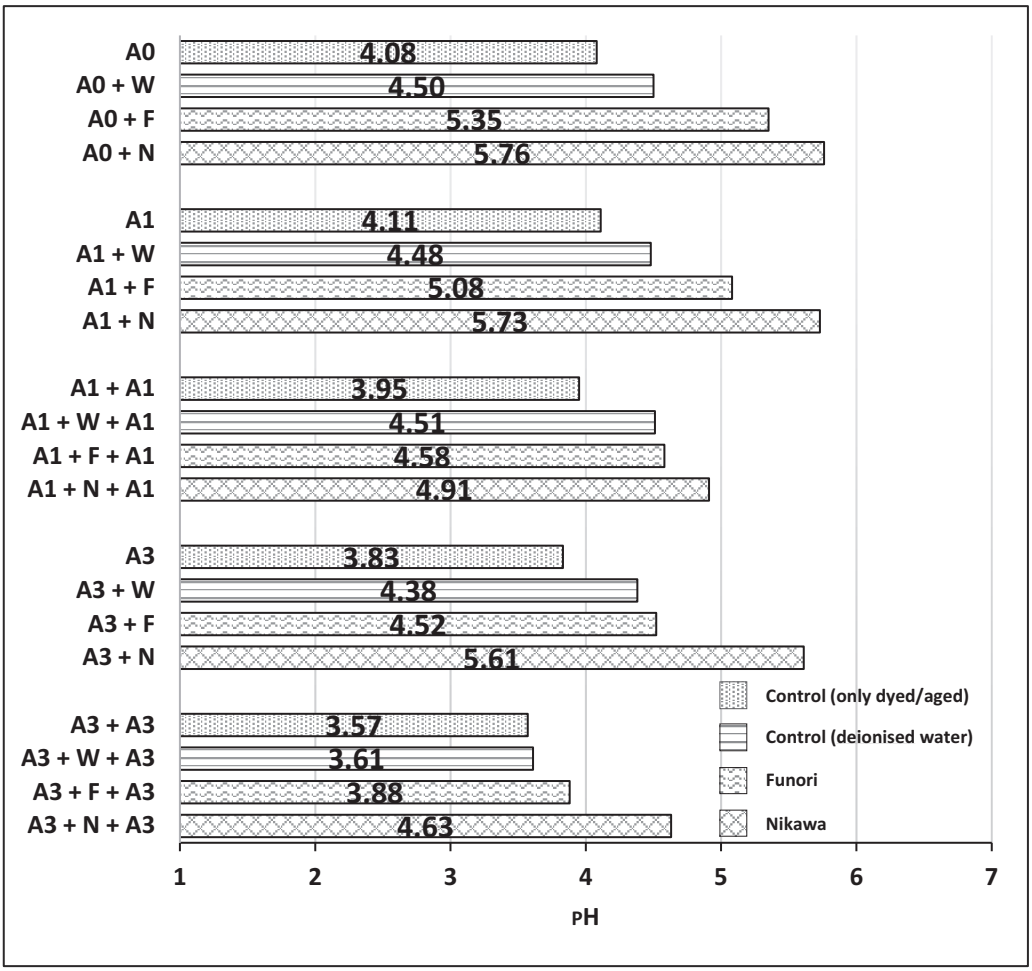

Figure 2 pH values of samples following the accelerated ageing period and before/after consolidation treatments

consolidation [A3 + F + A3], aged for additional 3 days after the consolidation, and to 4.63 after nikawa consolidation in [A3 + N + A3]. Fig. 3 shows the link between ageing and low pH. The less aged the sample was, the higher its pH value was. Thus, the pH in samples decreased with ageing. The highest decrease showed control samples. Compared to controls, consolidated samples increased in the pH value in all ageing periods. The effect of consolidation was not lessened even after additional ageing, where consolidated samples still had higher pH than controls at the same ageing conditions.

3－2. Bathophenanthroline test

The colour formation variability on test papers enabled comparing free iron(Ⅱ) ions' presence level for consolidated samples and controls. As a qualitative reference for the colour detected on the indicator test paper, the free iron(Ⅱ) ion test strip colour chart[1)] (Fig. 4) was used. The colour chart range: 1, 10, 25, and 50 + represents the intake of iron(Ⅱ) ions in units of parts per million (ppm); 1 and 10 on the colour chart are marked as mildly positive, while 25 and 50 + as very positive, thus the higher the number, the higher the presence of iron(Ⅱ) ions. No detection of iron(Ⅱ) ions was marked as negative.

Compared to the unaged samples, the presence of iron(Ⅱ) ions increased in the aged samples

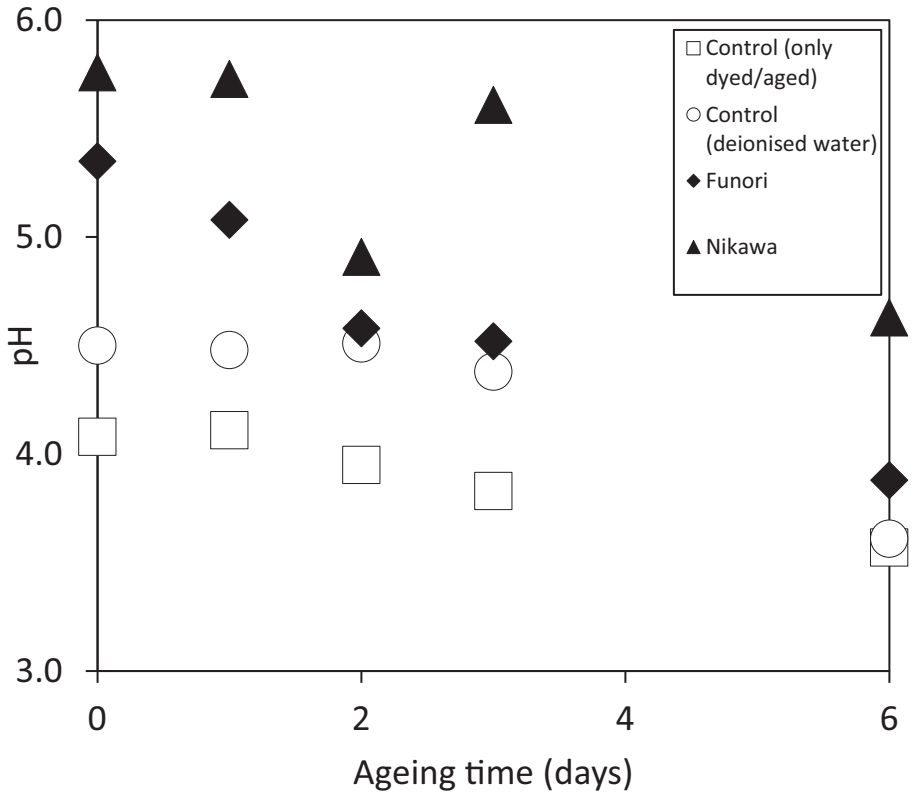

Figure 3 The correlation between the increase in the ageing period and decrease in pH (□ = Control (only dyed/aged); ○ = Control (deionised water); ◆ = Funori treatment; ▲ = Nikawa treatment)

with each increase in artificial ageing; iron (Ⅱ) ions also increased in the control samples, mainly only dyed, aged samples. In samples aged for lesser periods, the presence of iron (Ⅱ) ions was also decreased in control samples with deionised water, alongside the samples with consolidations. However, in the longer periods of ageing, before and after, the controls had higher iron (Ⅱ) presence when compared to consolidated samples, indicating the longer duration of consolidants' effectiveness even after the additional period of ageing after the consolidation.

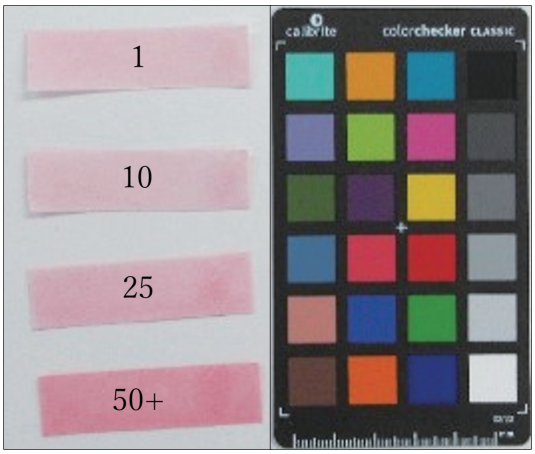

Figure 4 Iron (Ⅱ) ion presence reference strips made in accordance with CCI's Iron (Ⅱ) ion test strip colour chart[20)]

Although controls with deionised water had a lower presence of iron ions (iron (Ⅱ) ions are soluble in water), this did not have a lasting effect since, with the additional ageing, the reoccurrence of iron ions would happen.

All tested samples were referenced with the iron (Ⅱ) ion test colour chart, and the results are as follows (Table 3):

The presence of free iron (Ⅱ) ions increased with artificial ageing. This tendency is shown in control samples [A1], [A1 + A1], [A3], and [A3 + A3]. In the unaged samples, only in the control [A0] sample there was detection of iron (Ⅱ) ions, while in the control sample [A + W] and the consolidated sample [A0 + F] and [A0 + N], there was no detection. This is attributed to the removal of excess iron (Ⅱ) ions both in the control sample [A + W] (with exposure to deionised water) and in the consolidated samples [A0 + F] and [A0 + N] (with funori and nikawa consolidations).

Controls had the highest presence of iron (Ⅱ) ions since they had neither consolidants nor deionised water.

Compared to the unaged samples, the presence of iron (Ⅱ) ions is increased in the group of 1 day aged samples. The presence of iron (Ⅱ) ions increased in the control samples [A1] and [A1 + W], while the consolidated samples [A1 + F] and [A1 + N] had no detection presence. This could be prescribed again to funori and nikawa consolidation treatment and its removal of excess iron (Ⅱ) ions released by the ageing of 1 day. After additional ageing of 24 hours after the consolidation treatment, the presence of iron (Ⅱ) in the sample with funori consolidation [A1 + F + A1] was the same as in the control sample [A1 + W + A1]. At the same time, there was no presence in the sample with nikawa consolidation [A1 + N + A1]. The presence of free iron (Ⅱ) was determined to be very positive in the samples in control samples [A3] and [A3 + W], while negative detection was in samples with consolidation [A3 + F] and [A3 + N].

Iron (Ⅱ)ions reoccurrence happened on the samples after the additional ageing period (3 additional days after the consolidation). The highest detection showed a control sample aged six days in total [A3 + A3], with neither consolidation nor deionised water. The sample with

Table 3 Iron(Ⅱ) presence detection on consolidated and control samples

Sample	Detection
Unaged	
[A0]	Mildly positive
[A0 + W]	Negative
[A0 + F]	Negative
[A0 + N]	Negative
1 day aged (+ 1)	
[A1]	Very positive
[A1 + W]	Mildly positive
[A1 + F]	Negative
[A1 + N]	Negative
[A1 + A1]	Very positive
[A1 + W + A1]	Mildly positive
[A1 + F + A1]	Mildly positive
[A1 + N + A1]	Negative
3 days aged (+ 3)	
[A3]	Very positive
[A3 + W]	Very positive
[A3 + F]	Negative
[A3 + N]	Negative
[A3 + A3]	Very positive
[A3 + W + A3]	Mildly positive
[A3 + F + A3]	Mildly positive
[A3 + N + A3]	Negative

funori consolidation [A3 + F + A3], alongside the control sample [A3 + W + A3], was determined as mildly positive, while the sample with nikawa consolidation aged for 3 days before and after the consolidation [A3 + N + A3], had no iron(Ⅱ) ions presence, and was determined as negative.

3－3. Tensile strength test

Consolidations improved the tensile strength in aged samples, while control samples, specifically samples with deionised water, had a damaging effect and lowered the strength. Control samples with deionised water also had lower strength, suggesting a strength-decreasing effect on unaged and particularly aged samples.

Fig. 5 shows the damaging effects of artificial ageing on samples' tensile strength, additionally weakened due to 30-minute exposure to deionised water. This tendency is evident in all five groups of samples.

Samples treated with the 30-minute consolidation showed the opposite effect. In the group of unaged samples, although the average value shows the lower tensile strength of consolidated samples in comparison to the control, unaged sample [A0], standard deviation error bars

indicate that strips from among consolidated samples had the highest tensile strength in this group (A0 – unaged samples). The consolidated samples show higher tensile strength when compared to the control sample with deionised water [A0 + W].

In the group of samples aged for 1 day, the sample aged for 1 day [A1] and the sample with deionised water [A1 + W] displayed lower tensile strength when compared to the consolidated samples exhibiting the highest level of tensile strength in this group, particularly the sample consolidated with nikawa solution [A1 + N].

The same tendency is evident in the group of samples aged for two days (24 hours before and after the consolidation). Consolidated samples [A1 + F] and [A1 + N], artificially aged for 24 hours after the consolidation: [A1 + F + A1] and [A1 + N + A1] have increased the resistance in comparison to the sample that was only aged for a total of two days [A1 + A1] without the treatment between two ageing periods, and the sample with deionised water [A1 + W + A1]. The tensile strength of the sample with the nikawa treatment between two ageing periods [A1 + N + A1] showed higher tensile strength even than the sample from the previous group, aged

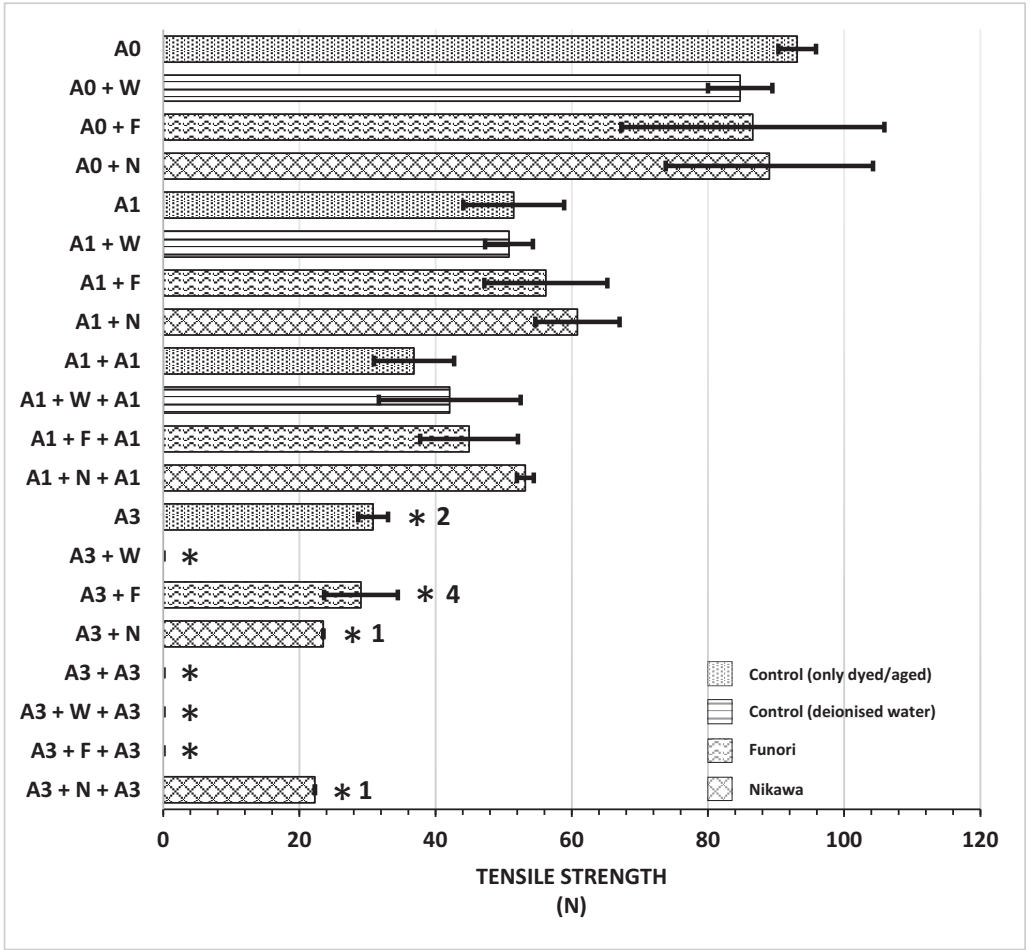

Figure 5 Tensile strength of samples (* = no detection; *1 = data from only 1 strip; *2 = data from 2 strips, *4 = data from 4 strips)

for only 1 day [A1].

In the group of fragile samples aged for 3 days, the sample with the funori consolidation [A3 + F] yielded the most detection out of all samples: 4 strips out of 5, and based on standard deviation, had the highest strength strips in this group. The sample with nikawa consolidation [A3 + N] yielded detection from 1 out of 5 strips tested.

Control samples, aged for 3 days [A3], yielded detection from only 2, while the sample with deionised water [A3 + W] was exceptionally fragile, and among the 5 strips tested, there was detection from none.

In the group of the most deteriorated samples, the samples aged for six days (3 days before and after the consolidation), mere preparation of strips for the tensile test indicated extreme fragileness. This was evident during the preparatory procedure for the test, whereby the slightest manual tense was sufficient for their edges to break.

Control samples [A3 + A3] and [A3 + W + A3] were too fragile to be detected. While there was no detection from the sample with funori consolidation [A3 + F + A3], the only sample that offered detection in this group of severely deteriorated samples, was the sample consolidated with nikawa solution [A3 + N + A3], giving detection from 1 out of 5 strips that were tested.

The tensile strength test data demonstrated that consolidated samples improved strength compared to control samples in aged sample groups. The tensile strength of aged and consolidated samples was higher than in controls, only dyed and samples with deionised water.

Table 4 Colour difference (ΔE^*) in samples based on comparison with standards (unaged control and unaged consolidated samples)

Reference	*Sample*	ΔE^*
[A0]	[A1]	0.93
	[A1 + A1]	1.21
	[A3]	1.96
	[A3 + A3]	4.83
[A0 + W]	[A1 + W]	1.16
	[A1 + F]	1.28
	[A1 + N]	1.99
	[A1 + W + A1]	2.08
	[A1 + F + A1]	1.52
	[A1 + N + A1]	2.85
	[A3 + W]	2.06
	[A3 + F]	2.03
	[A3 + N]	2.41
	[A3 + W + A3]	6.66
	[A3 + F + A3]	3.95
	[A3 + N + A3]	3.69
[A0 + F]	[A1 + F]	0.91
	[A1 + F + A1]	1.29
	[A3 + F]	2.07
	[A3 + F + A3]	4.10
[A0 + N]	[A1 + N]	0.62
	[A1 + N + A1]	1.12
	[A3 + N]	1.87
	[A3 + N + A3]	2.65

3－4．Colorimetry

To calculate the single value ΔE for samples' colour difference comparison, the formula $\Delta E^* = [(L^*_1-L^*_2)^2 + (a^*_1-a^*_2)^2 + (b^*_1-b^*_2)^2]^{1/2}$ was used and as standard, the control and consolidated samples. The colour measurement data is presented in Table 4 based on the calculations. In accordance with standard samples, the most colour change showed control samples: [A3 + A3] ($\Delta E^* = 4.83$) and [A3 + W + A3] ($\Delta E^* = 6.66$).

When using 1 day aged samples as standards for samples aged for 1 day before and after the consolidation, the most colour change showed the control sample with denoised water [A1 + W + A1] ($\Delta E^* = 2.43$). Table 5 shows the least colour change displayed in the samples with

consolidation [A1 + F + A1] (ΔE^* = 0.48) and [A1 + N + A1] (ΔE^* = 0.92).

The sample aged for 3 days, consolidated with nikawa solution [A3 + N], had the least colour change (ΔE^* = 1.36), followed by the sample with funori consolidation [A3 + F + A3] (ΔE^* = 2.09). Table 6. shows the most colour change among samples aged for 3 days had the control sample with deionised water [A3 + W + A3] (ΔE^* = 5.19).

Table 5 The colour difference for 1 day aged samples (before and after the consolidation). [A1] sample was used as a reference

Reference	*Sample*	ΔE^*
[A1 + W]	[A1 + W + A1]	2.43
[A1 + F]	[A1 + F + A1]	0.48
[A 1 + N]	[A1 + N + A1]	0.92

Table 6 The colour difference for 3 days aged samples (before and after the consolidation). [A3] sample was used as a reference

Reference	*Sample*	ΔE^*
[A3 + W]	[A3 + W + A3]	5.19
[A3 + F]	[A3 + F + A3]	2.09
[A3 + N]	[A3 + N + A3]	1.36

4. Discussion

4－1. pH test

The application of funori and nikawa consolidations with their neutral pH showed positive results in raising the pH of acidic iron-tannate dyed and aged samples. The impact of artificial ageing was observed in the reduction of pH levels in all samples, controls and consolidate. Even so, the consolidated samples continued to remain considerably less acidic when compared to controls in the same ageing groups. The controls, only dyed and treated with deionised water, were found to be the most acidic samples.

4－2. Bathophenanthroline test

Consolidated samples have been shown to be less susceptible to the effects of artificial ageing and the rise in iron(Ⅱ) ions when compared to control samples, for both ageing groups. This has been observed even when the consolidation is applied either before or after additional ageing and is particularly noticeable after the nikawa consolidation treatment. This is possibly attributed to the ability of gelatin to prevent iron migration because it acted as a form of fibre coating, as demonstrated in the study of gall ink deterioration[6]. Since the iron(Ⅱ) ions are highly water soluble, a possible cause would be that the nikawa treatment first solubilised the excess of iron(Ⅱ) ions, leaving them partially inside the treatment solution. When the consolidation cooled, it gelled and acted as a chelate with the iron ions that remained in the consolidation coating on the sample, preventing their migration on the surface. Once the consolidated samples were additionally aged, the artificial ageing had no effect on the nikawa coating, resulting in the negative detection of iron(Ⅱ) ions in both ageing periods.

Similarly, it is suggested that the same occurred in the aged samples with funori treatment. Intrinsically, funori extract does not gel, however its gelation is demonstrated to be enhanced in the presence of divalent metal ions[13]. It is suggested that the iron(Ⅱ) ions interacted with the funori extract, stimulating its gelation. This is particularly demonstrated in aged and consolidated samples, where, most likely, this interaction resulted in formed chelate, controlling the migration of ions to the surface, by capturing, demonstrated by negative detection on iron

(Ⅱ) ions in both ageing groups.

4－3. Tensile strength test

Artificial ageing periods enabled the assessment of consolidation treatments and the impact of the treatment on deteriorated fibres with the additional ageing period, the duration and the impact of the deterioration factor on the resistance of consolidation coating. The consolidations acted as coating film and reinforced the fibres, increasing their tensile strength. Since the same percentage of funori and nikawa, 0.2% and 1% w/v, respectively, was used throughout the testing of all four groups of aged samples, in the group of most fragile samples, only the sample consolidated with the nikawa treatment resisted the tensile force. Alongside controls which were too weak to be tested for tensile strength, and out of 5 strips, none could be tested, the sample with funori treatment, only in this group, exhibited no detection. This could be attributed to the lower percentage of funori (0.2%) compared to that of nikawa (1%). Previously mentioned study[9] which tested five consolidants for black-dyed Māori textile fibres implied the effectiveness of consolidation treatment on tensile strength in aged fibres that were consolidated with higher percentages. By the study's parameters, the strength of consolidated fibres, aged after the treatment, was improved in TRI-Funori™ (funori's propriety form) at 1.0% w/v. Na alginate and Zn alginate at 2.0% in addition to Paraloid B72 at 2.0% w/v, and Methocel® A4C at 1.0% w/v. The study also indicates that Zn alginate and Na alginate at 0.5% lost their impact on fibres' strength, aged after the treatment. A slight increase in the concentration of funori can help to improve the reinforcing coating properties of the consolidation treatment. The enhanced tensile strength of the consolidated samples, aged after the treatment is expected to be similar to that of the nikawa treatment, particularly the strength of most fragile samples, aged for 3 days before and after the consolidation treatment.

4－4. Colorimetry

During the artificial ageing process, the colour of controls experienced fading due to the effects of ageing in both ageing groups, 1 and 3 days aged. However, this phenomenon was not present in consolidated samples. The consolidation process enhanced the appearance of the samples, and after the consolidations dried and solidified, the additional artificial ageing had minimal impact on the colour change. The artificial ageing process led to a bleaching effect on the colour of the controls, especially for samples that were treated with deionised water and aged for the longest. In contrast, consolidants did not alter the colour of samples and instead, helped preserve the original colour, whether the samples were aged before or after consolidation.

5. Conclusion

This study experimented with iron-tannate dyed, artificially aged cotton, and detected a beneficial effect of funori and nikawa consolidation. It has been found that consolidations increased the pH, decreased the presence of iron(Ⅱ) ions and improved the tensile strength, with the addition of the least colour change (especially in samples aged for longer periods). This tendency was apparent in unaged and aged samples before and after consolidation

treatment, ascribed to the pH neutrality and chelating properties of funori and nikawa consolidation. Furthermore, consolidated samples, after additional ageing, displayed an increase in pH and decrease of soluble iron(Ⅱ) ions presence, particularly samples consolidated with nikawa solution, possibly due to a higher concentration of consolidant at 1% w/v. This shows that treatment was ongoing, even after the additional ageing period. Correspondingly, another finding is that consolidation concentration plays a significant role and should be employed depending on the state of the samples' deterioration. Funori consolidation at 0.2% w/v and nikawa consolidation at 1% w/v chosen for this study were most effective on samples aged for 1 day and samples aged for an additional 1 day after the treatment. In samples aged for 3 days, funori was still effective, more so than nikawa, while in the most fragile samples artificially aged for the longest period, 3 days before and after the treatment, detection yielded only sample with nikawa consolidation. The increase in the concentration of funori consolidation is also expected to affect highly fragile samples significantly. The use of funori and nikawa as consolidation treatments demonstrated no effect on the colour of samples, regardless of their ageing. On the contrary, the consolidants were found to effectively maintain the original colour of the samples even after additional ageing periods.

Regarding both consolidants' properties and their effect on artificially aged samples shown in this study, and assessed by selected analytical methods, both funori and nikawa consolidations suggest their potential as consolidation treatments for iron-tannate dyed deteriorated cotton textile.

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Experimental Treatment for Black-dyed Cotton Textiles Using Japanese Adhesives Funori and Nikawa

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For centuries, the dyeing technique that combines iron salts and tannins extracted from plants and trees as mordants has been utilised worldwide, including in Japan. However, this process can cause molecular degradation of textile fibres in the form of excessive soluble iron (Ⅱ) ions. Various studies have been conducted to find ultimate treatment methods for restoring the tensile strength of the affected fibres and preventing degradation. Despite the lack of a definitive treatment method, conservation scientists are continuously working towards finding effective solutions. This research aimed to use funori and nikawa, continually used in Japanese conservation and restoration sites, to capture iron(Ⅱ) ions and suppress their deterioration while restoring the tensile strength of weakened textile fibres.

Experimental samples dyed with iron-tannate dyed and artificially deteriorated have been prepared and treated with each consolidant and evaluated using pH measurement, confirmation of the presence of iron(Ⅱ) ions, tensile strength testing, and colorimetry. The findings confirmed that treatment with funori and nikawa increased pH, reduced the amount of excessive soluble iron(Ⅱ) ions, and restored tensile strength in artificially deteriorated samples. This effect was particularly noticeable for cotton textile samples with accelerated ageing for 1 day before and after both consolidation treatments. Furthermore, results suggest that nikawa consolidation treatment has the potential to restore the tensile strength of iron-tannate dyed highly deteriorated cotton textile samples, exhibited in samples with accelerated ageing of 3 days before and after the treatment.

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鉄媒染綿布に対するフノリと膠を使用した処置方法の検討

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植物や樹木から抽出されたタンニン酸と金属塩を媒染剤として使用する黒染め染色技法が，日本のみならず世界中において古くから使用されてきている。しかし，鉄媒染剤による染色は，可溶性の鉄(Ⅱ)イオンの形で使用されるため過剰に使用されると織物繊維の分子の分解を引き起こす。このような劣化の影響を受けた繊維を強化する方法について，検討が行われてきたが，決定的な処置方法は見つかっていない。本研究では，鉄(Ⅱ)イオンを捕捉し劣化を抑制した上で，繊維を強化する効果を持つような材料の適用を試みた。日本の保存修復現場で使用されているフノリと膠を用いた処置方法の可能性を検討した。タンニン酸鉄媒染で染色した上で加速劣化させた試料を作成し，それぞれの材料で処置し，pH 測定，鉄(Ⅱ)イオンの存在確認，引張強度試験，および測色により評価した。フノリと膠による処置により，酸性度の軽減，遊離鉄(Ⅱ)イオン量の低下，引張強度の上昇が確認された。この効果は，低および中程度加速劣化させた綿サンプルで最も効果的であった。また，膠については，劣化の激しいタンニン酸鉄で染色した綿への強化が可能なことを示唆している。

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