

# ON THE MECHANISM OF TIN-WEIGHTING OF SILK AND NYLON WITH STANNIC CHLORIDE

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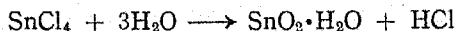
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## PART 1. THE RELATION BETWEEN MICRO-STRUCTURE OF FIBERS AND TIN-WEIGHTING.

### 1. INTRODUCTION

When silk is subjected to tin-weighting, it is thicker and heavier in feel and has higher draping quality than non-tin-weighted silk, and yet it does not lose its excellent character. Therefore silk has popularly been weighted with stannic chloride from ancient times.

The fundamental method of tin-weighting is based on the following processes: degummed silk is first immersed in an acid solution of stannic chloride, and is allowed to absorb the salt to saturation. Its excess solution is now removed by centrifugal hydro-extraction. The material is washed thoroughly with cold water, which hydrolyzes the stannic chloride into both gels of stannic oxide and hydrochloric acid. The gels of stannic oxide, being insoluble, remain precipitated in the fibers, while the hydrochloric acid is carried away by washing water. The gels-precipitated fibers are next treated with a hot solution of di-sodium phosphate. This series of such processes HOLTERHOFF [1] called a "pass", but in this experiment it is found that the process with di-sodium phosphate does not have directly much effect of weighting, and therefore the series excepting this process is called a "pass" here. In the author's one "pass", stannic chloride permeated into the fibers is hydrolyzed in the next chemical equation.



In this investigation, the following experiments were made:

1. Weighting of silk with various kinds of metallic salts and tin-weighting of fibers of many kinds.
2. The adsorption of stannic salts in silk fibers.
3. The relation between tin-weighting of fibers of many kinds and quantity of their absorbed water.
4. The relation between tin-weighting of nylon and its micro-spaces.
5. The relation between tin-weighting and tannin-weighting or saccharose-

weighting of silk.

6. The influence of swelling agents on tin-weighting of silk and nylon.
7. Extraction of adsorbed stannic chloride in silk and nylon with methyl alcohol or acetone.

The above experiments were performed, and the relation between tin-weighting and micro-structure of fibers was studied.

## 2. MATERIALS AND MEASUREMENTS OF WEIGHTING RATIO

### 2.1 Materials

#### 2.1.1 Silk and silk Habutai.

White raw silk of a size of 14 deniers which was manufactured by Yonago Factory of Nihon Rayon Co., Ltd., Japan, and whose grade was 3A was used as a material. The four yarns were twisted together, the number of twist was 550 times per meter and its measured size was 69.05 deniers. This silk yarn was degummed with distilled water, whose volume was 50 times the weight of the silk yarn. The material was first treated with that water in an autoclave at 110°C for 30 minutes and again with renewed water under the same condition, and then washed in hot water. Its loss of weight was 17.7%, and its size was 56.83 deniers. Hereafter in this study, the raw silk degummed directly, not twisted together, is called "the silk fiber", and that twisted together with four yarns and degummed by the method already described is called "the silk yarn".

Silk Habutai was degummed by the same method and used for this experiment. These samples contained 0.15-0.20% of ash.

#### 2.1.2 Nylon and nylon Taffeta.

Nylon and nylon Taffeta manufactured by Nihon Rayon Co., Ltd. was used. The nylon yarn was 6-nylon type and did not contained titanium oxide as a delustering agent. It was BR 210 d./24f., 300-H Type, A-grade and 25-22GE lot. These materials were extracted with Soxhlet's extractor for 8 hours with a mixed solution of methyl alcohol and benzene at a ratio of 4 : 6, and they contained. 0.10-0.12% of ash.

#### 2.1.3 Other materials

The wild silks such as Tussah silk (*Antheraea pernyi*), Yamamai silk (*Antheraea yamamai*) and Eria silk (*Philosamia cynthia ricini*) were degummed in the same way as the silk.

10 grams of greasy merino wool was taken and washed with water at 50°C. The soap solution required for cleansing it had to be of a volume of about 50 times the weight of the sample and was prepared by dissolving 2 grams of soap and 1 gram of  $\text{Na}_2\text{CO}_3$  in 500 ml. of water. The sample was first scoured with the soap solution at 50°C for half an hour, and again with renewed soap solution, then washed with water at 50°C, neutralised with 500 ml. of 1% acetic acid solution and lastly rinsed in hot water.

The absorbent cotton on the market was used.

Raw ramie was decorticated with 2% solution of caustic alkali in an autoclave at 100-105°C for half an hour, then treated with 0.2% soap solution at 100°C and washed in water.

Man-made fibers such as viscose rayon, vinylon, tetron (polyester) and cashmilon (polyacrylonitrile) were extracted in the same way as the nylon.

The filter paper (manufactured for paper chromatography No. 5 by Toyo Roshi Co., Ltd., Tokyo) was used.

The grains of clay plate prepared as follows: the clay plate (Tonplatte) was crushed up by an iron mortar and sifted out by sieves so that the fractions of grains with the diameter of about 1.0-1.5 mm. could be obtained, these grains were refined by the method of KOBAYASHI and YAMAMOTO [2], i. e. they were boiled for 2 hours with 6N hydrochloric acid and washed with distilled water until the reaction of chlorine to silver nitrate was not observed, and dried at 110°C.

The grains of glass were prepared in the same way as those of clay plate.

#### 2.1.4 Stannic chloride and its solution.

Stannic chloride was used for this study, in this case penta-hydrated stannic chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) in which the hydrate, as MEYERHOFFER [3] said, has a limitation of temperatures 19-56°C within which the penta-hydrate can exist. The hydrate stannic chloride is of guaranteed quality and on the market. Stannic chloride solution is prepared by dissolving it in water and its concentration is indicated by percentage of weight-to-volume (w/v%).

### 2.2 Measurements of weighting percentage.

#### 2.2.1 Gravimetric method

If  $A$  is the original dry sample of fibers and  $B$  is the dry weight of the sample of tin-weighted fibers, then the weighting percentage  $x$  will be below par.

$$x\% = \frac{B-A}{A} \times 100$$

#### 2.2.2 Ignition method

If  $A$  is the original dry sample of fibers and  $C$  is the ash of the tin-weighted sample of the fibers, they are ignited slowly in a crucible or ignited with 1-2 drops of strong nitric acid added. If  $D$  is percentage of the ash of the original dry sample (0.15-0.2% in silk and 0.10-0.12% in nylon), the weighting percentage  $x$  will be

$$x\% = \left( \frac{C}{A} \times 100 - D \right) \times 1.119$$

This factor 1.119 is obtained from the ratio of the molecular weight of  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  (mol. wt. 168.7) to that of  $\text{SnO}_2$  (mol. wt. 150.7), that is

$$168.7/150.7 = 1.119$$

It was ascertained by the author's other experiments that the  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  type of the stannic oxide (stannic acid gels) exists in the tin-weighted fibers, and the  $\text{SnO}_2$  type exists in the ash of the tin-weighted fibers ignited.

### 3. EXPERIMENTS AND DISCUSSION

#### 3.1 Loading of silk with metallic salts of many kinds and tin-weighting of fibers of many kinds with stannic chloride.

3.1.1 SILBERMANN [4] said in his book that silk can be weighted with not only stannic chloride but other metallic salts or mixed solution of these salts. Similarly, MATTHEWS [5] explained in his book that the salts of Pb, Bi, Ni, Cu, Mg, Sb, Fe, Cr and Al are used for weighting of silk. According to MIHARA [6], stannic salts and aluminium sulphate or zinc sulphate are used for weighting of silk. MARSH [7] describes in his new book that not only stannic chloride but also zinc acetate, lead acetate, aluminum sulphate and zirconium salt are used for silk weighting.

In order to know the difference in the ratio of weighting between stannic chloride and other metallic salts, silk Habutai (silk cloth) was weighted with many metallic salts. The metallic salts were chosen which are hydrolyzed with water into insoluble white hydroxide or oxide, or which had been used for weighting of silk from ancient times.

Each salt solution was prepared, its concentration being 1 mol. and the volume used of 50 times the weight of the sample. The silk Habutai were weighted with these metallic salt solutions. The specific gravity and hydrogen-ion concentration (pH) were measured for each solution.

These experimental results are shown in Table 1. In this Table, the salts of Pb, Sb, Ti, Bi and Sn show over 5% of weighting. Among the all weighting agents, stannic salts which have been used for silk weighting from old times, acquire higher tin-weighting of silk, especially stannic chloride has the largest effect on tin-weighting, but the luster and feeling of the tin-weighted silk are not changed so greatly for the original silk. Antimony tri-chloride gives high weighting to silk but the luster decreases greatly, and lead acetate decreases the luster. Bismuth tri-chloride is hydrolyzed easily into bismuth hydroxide with water, and therefore the weighting of silk is great but the luster decreases and the silk is gray-colored by sunlight. Titanium sulphate and titanium tetra-chloride give high weighting to silk but the weighted silk is reduced pale-yellow to brown by sunlight.

It is obvious that the effect of stannic salts on the weighting of silk is very large among the other metallic salts, and that the metallic salts are more easily hydrolyzed with water and pH of their solutions is generally very low and they give high weighting to silk.

3.1.2 If the silk weighting is made for the reasons that the stannic chloride solution is permeated into fibers, and that this stannic chloride is hydrolyzed into insoluble stannic oxide and deposited in fibers. The tin-weighting of fibers can be done, irrespective of the kinds of fibers, only if the stannic chloride solution is permeated into fibers.

Table 1. Silk weighting with water solution of metallic salts of various kinds, specific gravity and pH of the solution, (Conc. of all salts sol. were 1 mol.)

No.	Salts	Weighting %	s. g.	pH	Remarks	
					States of sol.	Weighted silk
1	$\text{Al}_2(\text{SO}_4)_3$	1.6	1.170	2.70		
2	$\text{AlCl}_3$	4.7	1.056	4.30	White turbidity	Decrease in luster
3	$\text{Al}(\text{CH}_3\text{CO}_2)_3$	3.4	1.070	4.35	"	"
4	$\text{BaCl}_2$	0.83	1.180	5.93		
5	$\text{BiCl}_3$	7.8	1.301		Dissolved in dil. HCl	Gray colored by sunlight
6	$\text{Bi}(\text{NO}_3)_3$	7.0	1.368		"	Decrease in luster
7	$\text{CaCl}_2$	0.86	1.088	6.95		
8	$\text{Ca}(\text{NO}_3)_2$	0.51	1.088	3.95		
9	$\text{Ca}(\text{SCN})_2$	0.86	1.088	6.98		
10	$\text{Pb}(\text{CH}_3\text{CO}_2)_2$	5.0	1.196	5.97	White turbidity	Decrease little in luster
11	$\text{Pb}(\text{NO}_3)_2$	2.4	1.272	3.10	"	
12	$\text{SbCl}_5^*$	9.9	1.166		Dissolved in dil. HCl	Decrease in luster. Fabrics were very dense.
13	$\text{SnCl}_4$	13.2	1.146	0.10		
14	$\text{SnCl}_2$	8.5	1.182	1.00	White turbidity	
15	$\text{SrCl}_2$	0.75	1.140	5.79		
16	$\text{Sr}(\text{NO}_3)_2$	0.65	1.162	5.80		
17	$\text{ZnCl}_2$	0.77	1.110	6.20		
18	$\text{Zn}(\text{NO}_3)_2$	1.72	1.152	5.28		
19	$\text{Zn}(\text{CH}_3\text{CO}_2)_2$	0.36	1.094	6.43		
20	$\text{Ti}(\text{SO}_4)_2$	4.1	1.282		Dissolved in dil. $\text{H}_2\text{SO}_4$	Decrease in luster
21	$\text{TiCl}_4$	5.0	1.112		Dissolved in dil. HCl	"

\*.....20%  $\text{SbCl}_3$  sol. (w/v%)

Sample was silk Habutai, it was first treated with each salt solution at 20°C for one hr. and then treated with s. g. 1.015 of disodium phosphate at 60°C for 20 min. and washed with water and dried. The percentage of weighting was measured by the gravimetric method. The specific gravity was determined at 20°C by the areometer and the pH was measured by the pH-meter (Tōa Denpa HM-5A) attached to the recorder.

In the U. S. A. patents [8] [9] [10], the tin-weighting of such textile materials as a derivatives of cellulose, cotton, regenerated cellulose, natural silk, wool and of other vegetable or animal fibers is made. The weighting of casein fibers is made with the solution of salts of tin, lead, titanium, zinc, antimony, aluminium, bismuth and tungsten. By this treatment a full and heavy hand can be imparted to the materials, and the results are in the raising of the temperature required to scorch the materials. The synthetic linear polyamide filaments of textile materials are weighted by impregnating the materials with a solution of a compound of a weighting metal, especially, stannic chloride solution, and then fixing the weighting metal on the material

as an insoluble compound. By such a treatment it is possible to increase the elongation of the material in both wet and dry state, and to increase the affinity of the material for dyes. Further, it is possible to render the hand of the material fuller and more silky than that of the untreated material. Usually the weighting treatment subdues slightly the luster. MINAGAWA [11] [12] studied the tin-weighting of wild silk fibroin and wool with stannic chloride.

As mentioned above, the tin-weighting is made of many fibers and its excellent effects are obtained. In this experiment, the tin-weighting of fibers of many kinds and other materials was investigated. The conditions of tin-weighting are as follows: the fibers and the materials are immersed in 40% solution of stannic chloride at 20°C for one hour, and washed with water for one hour. The percentage of weighting was measured by the gravimetric method. These experimental results are shown in Fig. 1. From these results, the following were found out: the rate of tin-weighting in the kinds of silks is large and that in wool is the largest of all materials. In cellulose

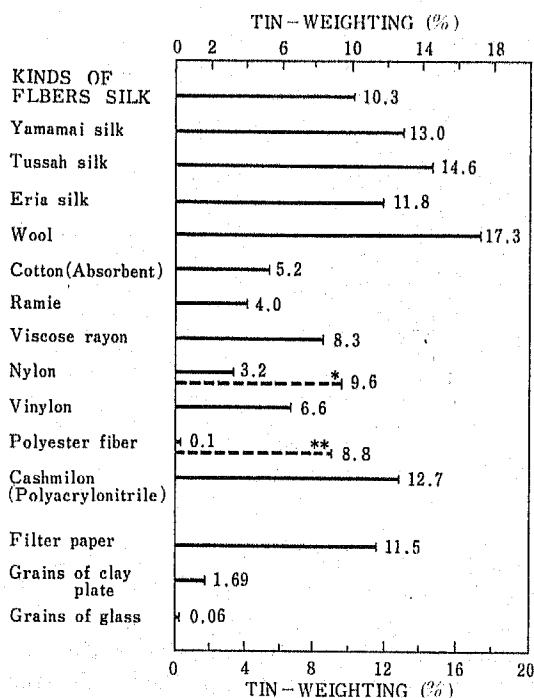


Fig. 1 Tin-weighting of fibers of various kinds with stannic chloride.

All fibers were treated with 40 % solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%) at 20°C for one hr. and washed with water for one hr. Percentage of weighting was measured by the gravimetric method.

\*.....21%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  sol. at 60°C for 20 min.

\*\*.....50%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  sol. of strong nitric acid at 20°C for 24 hr.

fibers, the rate of tin-weighting in viscose rayon, cotton and ramie is on the gradual decrease one after another. In synthetic fibers, in the order of acrylonitrile fibers, vinylon, nylon and polyester fibers, the rate of tin-weighting decreases little by little, the rate in polyester fibers is the smallest, but when these fibers are weighted with 50% stannic chloride in strong nitric acid solution, the rate increases. Also in the case of nylon, when the temperature of treatment with stannic chloride solution is raised from 20°C to 60°C, the rate increases. Filter paper and the grains of clay plate can be tin-weighted with stannic chloride solution in the same way as fibers.

From former days, the tin-weighting has been made of silk which has higher price than other fibers. The tin-weighting, however, is not only unique to silk but also it can be made for natural fibers, synthetic fibers and other porous materials such as the grains of clay plate which have a great deal of micro-voids.

### 3.2 On the adsorption of stannic salts in silk fibers.

According to PFEIFFER [13], the stannic chloride reacts with aldehyde, ketone, carboxylic acid, ester and acid amide in ether, benzene and chloroform or only stannic chloride. Among stannic chloride and these substances, the compounds of  $\text{SnCl}_4 \cdot 2\text{RCOA}$  ( $\text{A} = -\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{OH}$ ,  $-\text{OC}_2\text{H}_5$ , and  $-\text{NH}_2$ ) are made, and  $\text{RCOA}$  is in the form of  $\text{R}_\text{A} > \text{C} = \text{O}$ , and the coordination compounds can be made among O and Sn, and this coordination number is six.

In order to know whether the chemical combinations are made with amino group, carboxyl group, peptid-bond and other groups or not, the next experiments were performed. The silk was treated with various concentrations of stannic chloride solution. Before and after treatment, the concentrations of the solutions were measured by the method of alkali fusion [14] and by

Table 2. Adsorption of stannic chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) in silk

No.	Conc. of stannic chloride in original sol. (w/v%)	Conc. of stannic chloride in remaining sol. (w/v%)	Difference between Conc. of original sol. and that of remaining sol. (%)
1	2.935	2.937	+0.002
2	5.605	5.605	0.00
3	7.714	7.755	+0.041
4	14.965	14.995	+0.030
5	28.571	28.430	-0.141
6	56.477	56.075	-0.402

+ is the increase, - is the decrease.

0.5 grams of silk fibers were treated with 25 ml. of stannic chloride sol. at 20°C for 7 days. Before and after treatment, the concentrations of the solutions were measured and the differences of these solutions were determined. The quantitative analysis of tin was made by the next method: samples were fused together with sodium hydroxide in a nickel crucible, by Kashima's method the samples of alkali fusion were dissolved in hydrochloric acid solution, and  $\text{Sn}^{4+}$  was reduced to  $\text{Sn}^{2+}$  by the reductant of Pb and Sn was measured by the iodometry. The quantity of obtained Sn was converted into the weight of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , of which the concentrations are shown in the percentage of weight to volume (w/v%).

the iodo-metric titration [15]. The experimental results are shown in Table 2. The concentration of each stannic chloride solution before treatment is almost consistent with that of the solution after treatment within the limits of experimental error. Therefore, when silk fibers are immersed in the stannic chloride solution, it was known that the selective adsorption of only the stannic chloride from the solution does not take place in silk fibers. Silk fibers were treated with various concentrations of stannic chloride solutions, and excess solutions on the surface of the fibers, were wiped off by putting them between the leaves of filter paper. The weight of solution which permeated into fibers was measured, and from the concentrations of these permeated solutions, the quantity of stannic acid gels ( $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ) was calculated and shown in Fig. 2 as marks of multiplication ( $\times$ ). The silk fibers were treated with the stannic chloride solution for one hour, and washed with water, and dried and then the rate of tin-weighting was measured by the gravimetric method. These results are shown as full points ( $\bullet$ ) in Fig. 2. On the other hand, the rates of tin-weighting of these samples were measured by the iodo-metry, that is, the measured quantity of tin was calculated in the weight of  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  and shown as small circles ( $\circ$ ) in Fig. 2. Each value of tin-weighting measured by the above three methods, that is, the weighting of the stannic chloride solution permeated in fibers, the gravimetric method and the iodo-metry, is generally on the same straight line. Therefore each value measured is almost equal. It is presumed that the stannic chloride solution permeated in fibers turns completely with wash-water into the stannic acid gels ( $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ) and all of them are deposited in fibers. In the case of

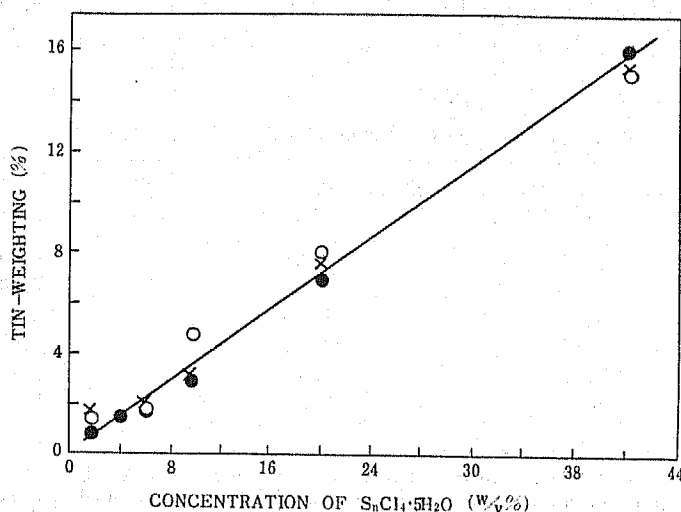


Fig. 2 Relation between concentration of adsorbed stannic chloride solution in silk fibers and rate of tin-weighting.

- $\circ$ .....Measured by iodo-metry.
- $\bullet$ .....Measured by adsorbed stannic chloride solution.
- $\times$ .....Measured by gravimetric method.



the same concentration of stannic chloride solution, the difference in the quantity of tin-weighting depends on the quantity of permeated stannic chloride solution.

### 3.3 The relation between tin-weighting and quantity of absorbed water in fibers of many kinds.

According to FREY-WYSSLING [16], there are micro-spaces of various volumes and micro capillaries in fibers. At the early stage of hygroscopicity in fibers, the state of water is in mono-molecular membrane [17] which is adsorbed on the inner surfaces of these micro-spaces and capillaries, but when water is adsorbed still more, the water extends in micellar spaces and comes to the equilibrium of swelling. Therefore, it is thought that the hygroscopicity is related to the adsorption of stannic chloride solution in fibers. According to DAVISON [18], the highest swelling of regenerated cellulose fibers is related not to the carboxyl groups of the cellulose molecular-ends but to their structure of network. BULL [19] said that the quantity of adsorbed water in the state of mono-molecular membrane is 4.07% in silk, 6.58% in wool and 1.76% in nylon. The quantity of absorbed water in 100% of relative humidity represents the value of the total micro-capillary volume near the highest swelling of fibers.

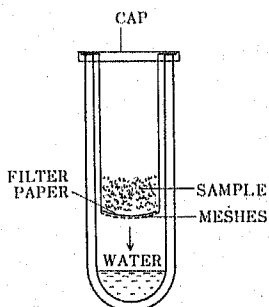


Fig. 3 Centrifugal cylinder

In the above experiments of 3.2 the fibers of high tin-weighting are wool, wild silk, cultivated silk and filter paper. In the case of cellulose fibers, the tin-weighting is increased in the order of ramie, cotton and viscose rayon. It is supposed therefore, that hygroscopicity is deeply related to the tin-weighting. The relation between the tin-weighting and the quantity of absorbed water was measured, i. e. the quantity of absorbed water was determined under the following conditions: the materials were immersed in water at 25°C for 30 minutes and then under a reduced pressure (2mm. Hg.) for 10 minutes. The excess solution was removed with a centrifugal separator equipped with centrifugal cylinders by KANETSUNA's method

[20]. In each of cylinders a tube is hanged with many small holes bored in its bottom, see Fig. 3. The centrifugal separator worked for 10 minutes at a speed of 3000 r.p.m. and these materials were weighed and the rate of absorbed water was calculated from the increase in weight to the original dry materials. The tin-weighting of fibers of many kinds was done in the same way as the experiments of 3.1.2, and the relation between the absorbed water and the tin-weighting is shown in Fig. 4. The coefficient of correlation between the absorbed water and the tin-weighting, was calculated, with the result that its value is +0.93, and so it is known that there is high positive correlation between the absorption of water and the tin-weighting.

### 3.4 The relation between tin-weighting and micro-spaces of nylon.

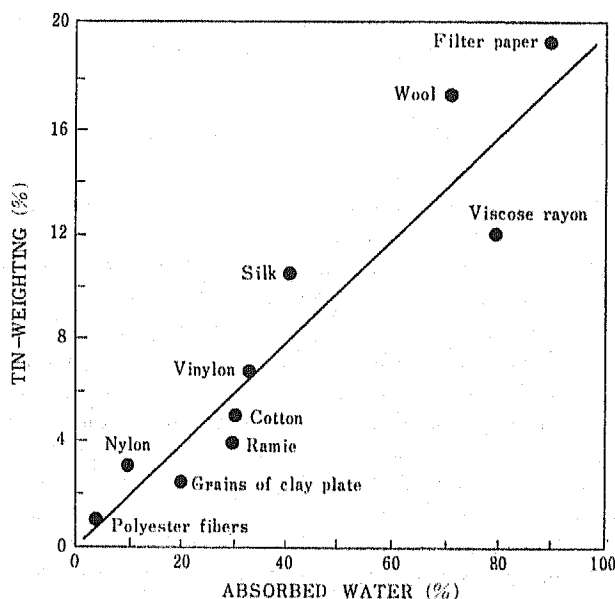


Fig. 4 Relation between tin-weighting and rate of absorbed water in fibers of various kinds.

In the tin-weighting of fibers with stannic chloride, it is important to know the mechanism of tin-weighting, that is, whether the radicals of fibers, for example nylon has amino and carboxyl groups, play a chief role in the tin-weighting or the micro-spaces of fibers are greatly related to the tin-weighting.

The non-stretched nylon and nylon gut, the samples of No. 1 and No. 2, are each shown in Table 3.2. These non-stretched samples were stretched with the stretcher (Koa & Co. Kyoto, Japan) to 4 times of the original length and treated at 60°C for 20 minutes. Their properties such as degree of stretch, diameter, degree of absorbed water, n-end groups, refractive index and degree of orientation are shown in Table 3.2.

The sample No. 1 was immersed in 25% stannic chloride solution at 60°C for one hour, and washed with water for 30 minutes. The sample No. 2 was immersed in the same stannic chloride solution at 60°C for 3 days and washed with water for 16 hours. These results are shown in Table 3.1. Even if non-stretched nylon and nylon gut are stretched, the quantities of the n-end groups of both non-stretched and stretched fibers are unchanged but the tin-weighting in the stretched fibers is decreased. The cross-sections of both the tin-weighted non-stretched and stretched nylon fibers are shown in Fig. 5. From Fig. 5, it is known that stannic acid gels are deposited in the outer layers of nylon fibers. Then the surface area per unit weight of nylon fibers was obtained and the rates of tin-weighting per unit surface area were calculated and the rates of tin-weighting in both non-stretched and stretched nylon were compared. A great difference between the tin-weighting in non-

Table 3.1. Changes in tin-weighting by stretching nylon

Samples	Percentage of tin-weighting	
	Per unit weight (%)	Per unit surface area *(gr.)
No. 1 Non-stretch	5.38	$6.12 \times 10^{-4}$
Stretch	4.38	$2.00 \times 10^{-4}$
No. 2 Non-stretch	8.29	$2.32 \times 10^{-3}$
Stretch	6.79	$1.03 \times 10^{-3}$

Conditions of weighting ; sample No. 1 was treated with 25% sol. of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%) at 60°C for one hr. and washed with water for 30 min. Sample No. 2 was treated with 25% sol. of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%) at 60°C for 3 days and washed with water for 16 hours.

\*.....The calculations of surface area of fibers were made as follows ; By using the specific gravity of nylon 1.14, the volume of fibers was first obtained from the weight of these fibers, and the diameter of fibers was measured under the microscope, and then the surface area was obtained by the next equation

$$\text{Surface area of fibers} = \frac{\pi}{4} x^2 + \pi x l$$

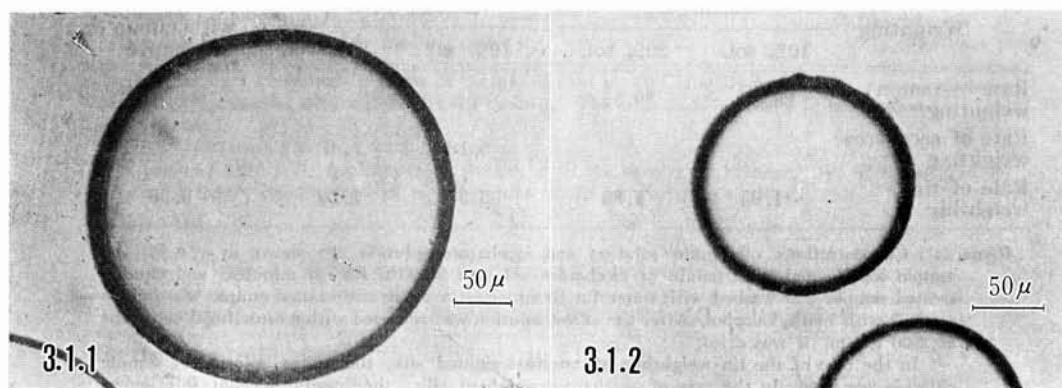
Here provided that x is the diameter of fibers, l is the length of fibers.

Table 3.2. Properties of non-stretched and stretched nylon in Table 3.1

Samples	Rate of stretching (times)	Diameter (mm.)	Rate of absorbed water (%)	Quantity of n-end groups (mol./gr.)	Refractive index			Degree of orientation (f × 100)
					$n_H$	$n_V$	$n_H - n_V$	
No. 1 Non-stretch	0	0.33	12.82	$2.11 \times 10^{-5}$	1.539	1.534	0.005	8.19
Stretch	4	0.148	10.50	$2.30 \times 10^{-5}$	1.578 <sub>5</sub>	1.523	0.055 <sub>5</sub>	90.89
No. 2 Non-stretch	0	1.06	12.79	$2.01 \times 10^{-5}$	1.540	1.534	0.006	9.82
Stretch	4	0.52	9.40	$1.99 \times 10^{-5}$	1.565	1.521 <sub>7</sub>	0.043 <sub>3</sub>	70.91

Refractive indices were measured by the Becke Line Method, a Na-lamp was used as a source of light.

Degree of orientation =  $f \times 100$ ,  $f = \frac{n_H - n_V}{n_H + n_V}$ , The value of  $n_H - n_V$  was obtained by the X ray method and  $n_H - n_V = 0.0610_6$  was used.



3.1.1 Tin-weighting of non-stretched nylon.

3.1.2 Tin-weighting of stretched nylon.

Fig. 5 Tin-weighting of non-stretched and stretched nylon, (Stained with hematoxylin).

stretched nylon and that in stretched nylon appeared. According to MINAGAWA [21], in the case that silk gut (*Bombyx mori*) is made from silk gland, if the stretch ratios of silk gland are variously changed, their tin-weighting decreases in inverse proportion to the degree of stretch. From the above results, the tin-weighting is greatly related to the micro-spaces of fibers.

### 3.5 The relation between the tin-weighting and the tannin-weighting or saccharose-weighting of silk.

MATTHEWS [22] said in his book that silk absorbs sugar to a considerable degree and this substance may be employed as a weighting material for light-colored silks on this account. It is also already known that repeated metallic baths give an increased weighting, and silk becomes quickly saturated with tannin and therefore unsusceptible to any further action.

In the above experiments of 3.4, it was well known that the tin-weighting is related to the quantity of micro-spaces in fibers. In this experiment, in the first place, the silk was weighted with tannin or saccharose and its micro-spaces were filled with this tannin or saccharose, and then these weighted silks were loaded again with stannic chloride solution. In addition, in the case of the tin-weighting of the saccharose-weighted silk, the methyl alcohol solution of stannic chloride was used. These experimental results are shown in Table 4.

Namely, when the silks were weighted beforehand with tannin or saccharose, their tin-weighting decreases. That is to say, because the micro-spaces in silk are filled with tannin or saccharose, only a small quantity of stannic chloride solution permeates into the micro-spaces in the fibers.

Table 4. Relation between tin-weighting and tannin-weighted silk or saccharose-weighted silk (Rate of weighting %)

Weighting	Tannin sol.		Saccharose sol.		Non-weighting with tannin or saccharose
	10% sol.	20% sol.	10% sol.	20% sol.	
Rate of tannin weighting	26.85	29.55			
Rate of saccharose weighting			5.18	7.47	
Rate of tin-weighting	1.95	1.85	3.37	1.20	9.38

Remarks : Concentrations of tannin solution and saccharose solution are shown in w/v %, the sample was treated with tannin or saccharose solution at 98°C for 30 minutes, and tannin-treated sample was washed with water for 10 minutes, or saccharose-treated sample was lightly washed with methyl alcohol. After the excess solution was removed with a centrifugal separator at 2500 r. p. m. it was dried.

In the case of the tin-weighting of tannin-weighted silk, the water solution of stannic chloride was used. In the case of saccharose-weighted silk, the methyl alcohol solution of stannic chloride was used. The concentrations of both stannic chloride solutions were 40% (w/v %). Tannin-weighted or saccharose-weighted silk was immersed in these solutions at 20°C under the reduced pressure (2~3mm. Hg.) excess solution was removed with a centrifugal separator, and washed with water.

The rate of tin-weighting was measured by the ignition method.

### 3.6 The influence of swelling agents on tin-weighting of silk and nylon.

It is supposed naturally that if the fibers are first treated with swelling agents and then treated with stannic chloride solution or they are treated with the mixture of these solutions, their tin-weighting will be increased.

The degree of swelling of silk and nylon in water and methyl alcohol was measured, and these results are shown in Table 5. The swelling of silk with water was larger than with methyl alcohol, but the swelling of nylon was opposite to that of silk. Nylon Taffeta was first immersed in phenol solution at 40-50°C for 5 minutes and washed with water and then weighted with 40% stannic chloride solution at 20°C for 10 minutes and washed with water for 30 minutes. These results are shown in Table 6. From these results, if the nylon Taffeta was swelled with phenol, the tin-weighting in nylon Taffeta increased. The solvents of the various ratios of methyl alcohol to water were prepared and the stannic chloride was dissolved in these solvents and the concentration of each solution was 20%. Silk was treated with these solutions at 20°C for 20 minutes, and nylon was treated with these solutions at 55°C for 20 minutes. Then the both samples were treated with 1% ammonium water solution and washed with water. The rate of tin-weighting was measured by the gravimetric method and these results are shown in Table 7. The tin-weighting in silk fibers increased according to the increasing rate of water, but as nylon fibers are opposite to silk fibers, the tin-weighting in nylon fibers increased, according to the increasing rate of methyl alcohol. Namely, when the fibers are swelled with swelling agents, the tin-weighting can increase.

Table 5. Degree of swelling in silk and nylon with water and methyl alcohol (%)

Swelling	Silk	Nylon
Degree of swelling with water	48.66	11.34
Degree of swelling with methyl alcohol	39.77	15.35

Samples were immersed in water or methyl alcohol at 20°C for 24 hours, the excess solution was centrifugalized at 3000 r. p. m. for 10 minutes. The degree of swelling  $Q$  is expressed in the next equation,

$$Q(\%) = (w - w_0) \rho_s / w_0 \rho_t \times 100$$

Here provided that  $\rho_t$  is the density of sample,  $\rho_s$  is the density of solution,  $W_0$  is the weight of the sample before swelling and  $W$  is the weight of the sample after swelling.

Table 6. Tin-weighting of nylon with phenol as a swelling agent

Treatment	Rate of absorbed water (%)	Rate of tin-weighting (%)
Untreatment with phenol	10.9	1.9
Treatment with 3% phenol	—	2.1
Treatment with 5% phenol	13.7	12.6

Table 7. Tin-weighting of silk and nylon with stannic chloride dissolved in mixed solution of water and methyl alcohol

Mixing rate of water and methyl alcohol	Water	0	10	20	30	40	50	60	70	80	90	100
	Methanol	100	90	80	70	60	50	40	30	20	10	0
Rate of tin-weighting of silk (%)		9.31	9.55	9.55	9.27	9.27	9.27	9.49	9.90	11.33	10.0	10.0
Rate of tin-weighting of nylon (%)		20.61	19.35	18.00	16.34	16.18	17.99	18.05	18.10	17.13	15.80	14.83

### 3.7 Extraction of adsorbed stannic chloride in silk and nylon with methyl alcohol or acetone.

In order to know whether the adsorbed stannic chloride in silk and nylon is combined directly to these fibers or not, when they are treated with stannic chloride, these samples were extracted with methyl alcohol or acetone with Soxhlet's extractor. These results are shown in Table 8. By when the fibers are treated with stannic chloride, the stannic chloride is once adsorbed in them, but this stannic chloride can be almost extracted with methyl alcohol or acetone from these fibers. Therefore, it is supposed that the adsorbed stannic chloride in fibers is not combined with these fibers.

MATTHEWS [23] said in his book that silk is dissolved with 70% Tw of strong stannic chloride solution. The writer thinks that the maximum quantity of tin-weighting can be attained in the case that silk is dissolved with stannic chloride solution. The sample of No. 1 in Table 8, is the silk powder manufactured in the way in which silk fibers were immersed in the mixed solution of stannic chloride, water and methyl alcohol at the ratio of 1:8:2 mol. and dissolved in this hot solution by heating on a water bath, and one part of this silk solution was dialysed with water by using dialysing collodion membrane, the other part was immediately extracted with methyl alcohol without dialysing with water. The nylon fibers are dissolved more easily than silk fibers with stannic chloride solution. The sample of No. 2, is the nylon powder manufactured in the way in which nylon fibers were immersed in the mixed solution of stannic chloride, water and methyl alcohol at the ratio of 0.1:1.3:1.0 mol. and dissolved, and one part of this nylon solution was dialysed with water in the same way as the silk powder, the other part was immediately extracted with methyl alcohol in the same way as the silk powder. Perhaps, the obtained 225.4% and 54.18% of the rate of tin-weighting may be about the maximum rate in the silk and the nylon respectively. In other experiments, the silk tin-weighting was made under 320 times of the "pass" with the conditions of one "pass" that follow: the silk fibers were immersed in 57.7% solution of stannic chloride at 20°C for one hour and washed with water for 30 minutes. The obtained rate of the tin-weighting in silk was 223%. The nylon tin-weighting was made under 120 times of the "pass" with the conditions of one "pass" that follow: the nylon fibers were immersed in 21% solution of stannic chloride at 60°C for 20 minutes and washed with water for 30 minutes. The rate of tin-weighting in nylon was

Table 8. Extraction of adsorbed stannic chloride in silk and nylon with methyl alcohol or acetone.

No.	Samples	Rate of remaining tin-weighting (%)			Remarks
		Washing with water	Extraction with methanol	Extraction with acetone	
No. 1	Silk powder	225.40	2.45	—	5 gr. of silk was dissolved by heating with mixed solution of stannic chloride, water and methyl alcohol at the ratio of 1:8:2 mol. The section washing with water : the solution was dialysed with water by using the collodion membrane for 23 days. The section extraction : the solution was extracted for 60 hr. by Soxhlet's extractor.
No. 2	Nylon powder	54.18	0.78	—	5 gr. of nylon was dissolved in mixed solution of stannic chloride, water and methyl alcohol at the ratio of 0.1:1.3:1.0 mol. In the same way as No. 1, dialysing with water or extraction with methyl alcohol was done.
No. 3	Silk	9.88	2.16	1.17	0.3 gr. of silk was immersed in 10 ml. of 39.43 % (w/v %) solution of stannic chloride at 20°C for 2 hr. and washed with water for 18 hr. Extraction was made for 10 hr.
No. 4	Nylon	9.08	0.34	0.33	0.3 gr. of nylon was immersed in 10 ml. of 25.0 % (w/v %) solution of stannic chloride at 60°C for 10 min. and washed with water. Extraction was made in the same way as No. 3.
No. 5	Silk	10.38	3.51	—	12 gr. of silk was immersed in 100 ml. of 50% (w/v%) solution of stannic chloride at the room temp. for about one year, and washed with water for 18 hr. Extraction with methyl alcohol was made for 10 hr.

The rate of tin-weighting was measured by the ignition method.

63%. The ratio of the maximum tin-weighting of 223% of the silk to that of 63% of the nylon is :

$$223\%/63\% = 3.5_4$$

In the above experiment of 3.5, the ratio of the rate of the absorbed water of 34.4% of the silk to that of 9.9% of the nylon is :

$$34.4\%/9.9\% = 3.4_7$$

The both values in these ratios are almost equal. It is presumed that the absorption of water and the volume of the micro-spaces are largely related to the tin-weighting in fibers.

The sample of No. 5 in Table 8, is the silk fibers which were immersed

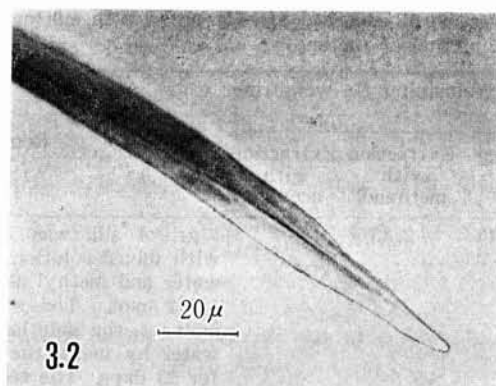


Fig. 6 (3.2) Silk fibers were immersed in 50%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%) solution at room temperature for about one year and extracted with methyl alcohol. Remaining tin-weighting was 3.51%. (Stained with hematoxylin).

in 50% stannic chloride solution at room temperature for about one year, and then hydrolyzed with stannic chloride solution, and became brown and broke up, some parts of the fibers dissolved in this solution. This sample of No. 5 is the remaining parts of the silk which must be saturated completely with stannic acid solution. This sample was extracted with methyl alcohol and the results are shown in Fig. 6. Because the remaining parts of the silk are saturated perfectly with stannic chloride for one year, it is supposed that the tin-weighting in these splinters of the silk will be great, but practically, the tin-weighting in them is almost equal to that in the silk that was treated with 50% solution of stannic chloride for 2 hours. Namely, it has been found that in the tin-weighting of silk with stannic chloride solution, the micro spaces of the silk become quickly saturated.

#### 4 SUMMARY

The relation between the micro-structure of fibers and the tin-weighting was studied. Silk and nylon as fibers were used mostly for the experiments. The contents of the experiments are as follows: weighting of silk with metallic salts of various kinds and tin-weighting of fibers of many kinds, the relation between the tin-weighting of fibers and the quantity of absorbed water, the relation between the tin-weighting and the micro-structure of nylon, the relation between the tin-weighting and the tannin-weighted or saccharose-weighted silk, the relation between the tin-weighting and the swelling agents, and the extraction of adsorbed stannic chloride in fibers with methyl alcohol or acetone. These experiments were performed and the results obtained are as follows:

1. It is obvious that the effects of stannic salts on the weighting of silk are very large among the other metallic salts, and that such metallic salts



have the properties that they are more easily hydrolyzed with water and the pH of their solutions are generally very low, resulting in high weighting in silk.

2. The tin-weighting is not only the unique quality for silk but also it can be made for natural fibers, synthetic fibers and other porous materials such as the grains of clay plate which have a great deal of micro-voids. Therefore, the tin-weighting is largely related to the micro-spaces (porosity) of materials.

3. The concentrations of stannic chloride solutions before treatment are almost consistent with those of the solutions after treatment. The selective absorption of stannic chloride only from its solution did not take place in fibers. In the case of the same concentration of stannic chloride solution, the difference in the quantity of the tin-weighting depends on the quantity of permeated stannic chloride solution. It is presumed that permeated stannic chloride solution in fibers turns completely with wash-water into inert stannic acid gels ( $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ), all of which are deposited in fibers and make little chemical combinations with chemical groups of fibers.

4. There is a high positive correlation between the absorption of water and the tin-weighting.

5. The non-stretched nylon has higher degree of tin-weighting than the stretched nylon. Because the quantity of the n-end groups of nylon is not changed by the stretch, the degree of tin-weighting is related to the physical micro-structure of fibers.

6. When the micro-spaces in silk are filled with tannin or saccharose, the permeated quantity of stannic chloride solution is decreased, and therefore the tin-weighting in the fibers are decreased. Namely, the degree of tin-weighting is related to the capacity of the micro-spaces in fibers; whether they have a large capacity or small one.

7. If the materials are either treated with swelling agents before they are tin-weighted with stannic chloride or treated with swelling agents and stannic chloride combined, the tin-weighting can be increased.

8. Silk and nylon are treated with the solution of stannic chloride and this solution is permeated into the fibers. If these permeated samples are extracted with methyl alcohol or acetone before they are washed with water, the greater part of the immersed stannic chloride can be extracted. Therefore it is presumed that stannic chloride does not make strong chemical combination with the fibers.

The degree of tin-weighting in the silk which was immersed in 50% solution of stannic chloride at room temperature for about one year, and that in the silk which was immersed in the same solution at 20°C for 2 hours, both of them are about 10%. Therefore it is clear that the micro-spaces in the fibers become quickly saturated with stannic chloride solution when the fibers are immersed in the solution.

Finally, the degree of tin-weighting is greatly related to the absorption of water and the micro-spaces in fibers. The tin-weighting of fibers depends

on the properties of stannic chloride : the stannic chloride solution sufficiently permeates into fibers because of its strong acidity, and this stannic chloride is easily hydrolyzed with wash-water into water-insoluble and inert stannic acid gels (stannic oxide). These gels have a large quantity of absorption water and are deposited in the micro-spaces of fibers as amorphous and very fine particles.

**PART 2. ON THE DEPOSITED LOCALITY OF STANNIC ACID GELS  
(STANNIC OXIDE) IN FIBERS  
OBSERVATIONS UNDER THE MICROSCOPE AND THE  
ELECTRON MICROSCOPE**

**1. INTRODUCTION**

The deposited locality of stannic acid gels in the tin-weighted fibers and the transformation of these fibers were studied. It is known that the tin-weighted silk is stained with an ammoniacal hematein solution, and forms a deep red-violet tin-lake [24]. After many tests, however, it has been found that hematoxylin has very sharp color reaction with tin, its color is deep reddish violet, and that, by this reaction, the purpose of observation under the microscope is accomplished enough. Tin-weighted fibers of various kinds were stained with hematoxylin solution, and observed under the microscope, but in the case of electron microscopic studies, the fibers were not stained.

**2. METHODS**

**2.1 Method of staining**

The method of staining tin-weighted fibers with hematoxylin : -0.1-0.5% solution of hematoxylin (dissolved in methyl alcohol-water in a ratio of 1:9) was prepared. The fibers were immersed in this solution, and heated in a boiling water bath for one hour, and then washed thoroughly in the boiling water which was renewed many times till it was not colored with dissolving hematoxylin, and thus the tin-weighted fibers were stained in deep red-violet color.

In the case of observation in the electron microscope, the tin-weighted fibers were not stained with hematoxylin.

**2.2 Section cutting**

Embedding methods : - For observation under the microscope, the embedding medium was prepared as follows : a very small quantity of styrene monomer, methyl-ethylketone peroxide (accelerator) and cobalt naphthenate (catalyser) were added to polyester CL-15 (manufactured by Konish Gisuke Co., Ltd., Japan). The tin-weighted fibers stained with hematoxylin were embedded in this resin, and left alone at 20°C till the resin was appropriate in hardness for cutting. The cross-sections of the sample fibers were made by cutting them with the "sledge" type microtome.

For the electron microscopic examination, the tin-weighted fibers were embedded in the mixed solution of methacrylate resin and epoxy resin. The cross-sections were made by cutting them with the ultra-microtome (JUM-5, Electron Optics Labo. Co., Ltd., Japan), and the thickness of the section was about 800 Å.

### 3. RESULTS AND DISCUSSION

(The collected figures of the results investigated are shown in the end of this report.)

#### 3.1 The cross-sections of tin-weighted silk fibers observed under the microscope

The cross-sections of tin-weighted silk fibers having various ratios of tin-weighting are shown in Figs. 10.1.1-10.1.5. According as the ratio of tin-weighting is increased, the cross-sectional area of the silk fibers is larger. Particularly, Fig. 10.1.5 the following phenomena are observed: when the tin-weighting of silk is repeated 160 times, the increase in weight amounts to 221.2%. Because a large quantity of stannic acid gels are deposited in the silk fibers, the fibers can swell no further, at last they are broken. In case the tin-weighting of silk fibers is too high, they are degraded and lose many of their wearing qualities. So the tin-weighting must be done in such a degree that the strength and elongation of fibers are not degraded. Fig. 10.1.6 shows the silk fibers tin-weighted with ammonium chlorostannate (Pink salt), with the obvious result that silk is weighted just the same with stannic chloride. Fig. 10.1.7 shows the cross-sections of the Italian tin-weighted silk.

#### 3.2 The cross-sections of tin-weighted nylon fibers observed under the microscope.

The cross-sections of tin-weighted nylon fibers are shown in Figs. 10.2.1-10.2.4, the state of stannic acid gels deposited in nylon fibers is very different from that of silk. Namely, the deposition of stannic acid gels is higher in the skin layer of nylon fibers, and the structure of their skin layer is changed. It is observed in Fig. 10.2.4 that the fibers adhere to each other, when the concentration and temperature of stannic chloride solution are both higher. From this fact, it is presumed that the skin layer of nylon fibers is much swelled and turned into some soluble state, when the solution of stannic chloride is permeated into nylon fibers.

#### 3.3 Observation under the microscope of the cross-sections of tin-weighted fibers of various kinds.

Many kinds of fibers were tin-weighted with stannic chloride, and their cross-sections were made. They are shown in Figs. 10.3-10.13. The cross-sections of tin-weighted Yamamai silk (*Antheraea yamamai*), Tussah silk (*Antheraea pernyi*) and Eria silk (*Philosamia cynthia ricini*) are each shown in Fig. 10.3, 10.4 and 10.5. All these wild silks have much volume of voids, and it is observed that a large quantity of stannic acid gels are deposited in these voids.

The cross-section of tin-weighted wool fibers is shown in Fig. 10.6. Stannic acid gels are deposited more in one half area from the central line (diameter) of the cross-section than in the other half area. It is well known that the cortex of wool fibers has "bilateral structure", i. e. ortho cortex and para cortex [25] [26]. The one half portion of the cortex is different from the other half portion in the quantity of deposited stannic acid gels. It is

presumed that this difference is based on the difference in the micro-structure between the two portions of the cortex.

The cross-sections of tin-weighted cotton and flax fibers are each shown in Figs. 10.7 and 10.8. From these Figs., it is observed that stannic acid gels are deposited largely in the central canals and their neighborhoods of these fibers.

The cross-sections of tin-weighted viscose rayon and vinylon fibers are each shown in Figs. 10.9 and 10.10. Stannic acid gels are deposited more in the inner portion than in the skin layer of these fibers. The polynosic fibers (a kind of viscose rayon manufactured by Teijin Co., Ltd., Japan) have their skin layer of remarkable growth. Therefore it is seen that a small quantity of stannic acid gels are deposited in the central portion (Fig. 10.13).

The cross-sections of tin-weighted cellulose acetate fibers and nylon fibers are each shown in Figs. 10.11 and 10.12. Stannic acid gels are deposited more in the skin layer of these fibers.

From the results of the above observations, it is obvious that stannic acid gels are deposited in the voids and the portions of small density in these hydrophilic fibers, but as for the hydrophobic fibers such as acetate rayon and nylon, stannic acid gels are deposited in the skin layer.

### 3.4 The side view observation of tin-weighted silk and nylon fibers under the microscope.

Non-tin-weighted silk is shown in Fig. 10.13.1. The tin-weighted silk of which the weighting ratio is 70.6 % is shown in Fig. 10.13.2. In microscopic observation, it can not be found that there is a great difference between non-weighted and weighted silks. But in highly tin-weighted silk fibers, the fine fibrils in the form of filaments are separated from the fibroin.

Non-tin-weighted nylon is shown in Fig. 10.14.1. Nylon is treated with stannic chloride and without washing with water, immediately dried in a desiccator with phosphorus pentoxide. These fibers are shown in Fig. 10.14.2. The skin layer of these fibers is glassy and forms solid solution of nylon and stannic chloride. When these fibers are washed with water, the surface of the fibers is changed into irregularity (Fig. 10.14.3), and the stannic acid gels are segregated out in fibers.

### 3.5 Observation of the tin-weighted silk and nylon fibers in the electron microscope.

The stannic acid gels which are deposited in the central part of silk gut (*Bombyx mori*) are shown in Fig. 10.15. This silk gut used was prepared and tin-weighted by the following methods: the silk producing glands were taken out from mature silkworms at 5th age, and these glands were first immersed in 3 % solution of acetic acid for 10 minutes, and then the middle divisions of these glands were stretched out to 10 times of the original length, and the cells of the silk glands and the other impurities were removed by washing with water. The silk gut was made in this way from the silk glands. Its central portion was of smaller density than the outer layer, see Fig. 10.15.1. This silk gut was immersed in 35 % solution of stannic chloride at room

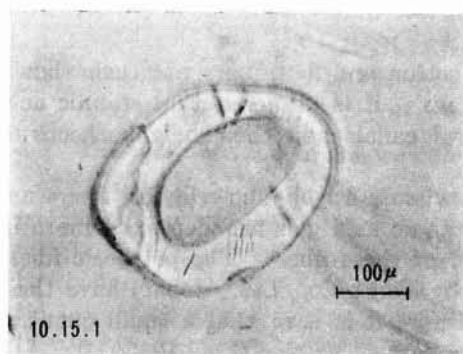


Fig. 10.15.1 The cross-section of the silk gut was made from the silk glands (*Bombyx mori*).

temperature for one hour and washed with water for one hour, and thus 4.9 % of tin-weighting of silk gut was obtained. The ultra-thin cross-sections of tin-weighted silk guts were made and observed in an electron microscope. The deposited stannic acid gels in the central portion of the silk gut are amorphous and its state of deposition is irregular. The ultra-thin cross-sections of non-tin-weighted and tin-weighted silk were each shown in Figs. 10.16.1-10.16.4. Because the particles of stannic acid gels are very fine and solid, part of the particles

are flown in the progressed direction of the ultra-microtome's knife-edge. When the tin-weighted silk fibers are observed under the microscope, the stannic acid gels are deposited largely in the voids but very little in the outer layer. The most part of the stannic acid gels are discharged by the treatment with hydrofluoric acid, but they still remain in the fissures of silk, see Fig. 10.16.4.

The ultra-thin cross-sections of non-tin-weighted and tin-weighted nylon are shown in Figs. 10.17.1-10.17.4. The stannic acid gels are deposited largely in outer layer of nylon fibers and these particles of gels are large. Nylon fibers were immersed in stannic chloride solution, which permeates into the outer layer. It is thought that when these samples are washed with water and stannic acid gels are produced, the gels are segregated out of the dissolved state of nylon and stannic chloride together.

From the above results, in the case of the tin-weighting of silk, the stannic acid gels are deposited largely in the inner portion of the fibers, but, in the case of nylon, these gels are deposited in the outer layer of the fibers. However heavily silk may be tin-weighted, therefore, its luster is not so much decreased, but even if the tin-weighting of nylon is slight, the structure of its outer layer is deformed and its luster is decreased and its whiteness is increased, as shown in Fig. 10.17.5.

Nylon was dissolved in a hot mixed solution of stannic chloride, water and methyl alcohol at the ratio of 0.1 : 1.3 : 1.0 mol. and this viscous solution of nylon was coated on some pieces of slide glass and some of these samples were washed at once with water, while the other samples were left alone for 7 days and washed with water. These results are each shown in Fig. 10.18.1 and 10.18.2. When this viscous solution of nylon coated on the slide glasses, was washed with water, the segregation of nylon was observed, and especially when this viscous solution was left alone for a long time, it was observed more clearly. It is conjectured, therefore, that when the tin-weighting of nylon is done practically with stannic chloride the similar transformation

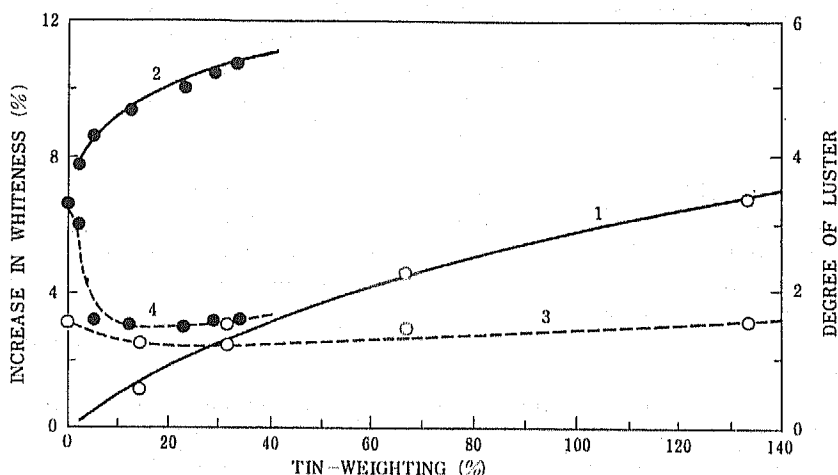


Fig.10.17.5 Relation between rates of tin-weighting in both silk Habutai and nylon Taffeta and degree of both whiteness and luster.

- 1.....○..... Degree of whiteness of silk Habutai.
- 2.....●..... Degree of whiteness of nylon Taffeta.
- 3.....○..... Degree of luster of silk Habutai.
- 4.....●..... Degree of luster of nylon Taffeta.

The degree of whiteness was measured by the spectrophotometer (Shimazu QB-50 Type), the degree of luster was measured by the recording type three dimensions-deformation photometer (Reflective light  $60^\circ$  was measured under  $60^\circ$  of incidence angle).

occurs in the outer layer of nylon.

Silk fibroin was dissolved with a hot mixed solution of calcium chloride, water and methyl alcohol at the ratio of 1 : 8 : 2 mol. by AJISAWA's method[27], and dialysed with water. Subsequently, colorless, transparent and viscous solution of fibroin was obtained. This viscous solution was coated on the slide glasses and dried very slowly, and then the spherical crystallisation of fibroin could be made. These crystals were observed in the polarising microscope between its crossed polarisers, see Fig. 10.19.

#### 4. SUMMARY

The deposited locality of stannic acid gels in the tin-weighting of silk, nylon and of many other kinds of fibers with stannic chloride was investigated under the microscope and in the electron microscope. The results are as follows :

1. The solution of hematoxylin can be used for staining the tin-weighted fibers, and the deposited localities of stannic acid gels (stannic oxide) were made clear in the tin-weighted fibers.
2. In the case of very heavily tin-weighted silk, it is observed that because a large quantity of stannic acid gels are deposited in the silk fibers, these fibers can swell no further, and finally they are broken.

3. When various kinds of hydrophilic fibers, such as silk, wild silks, wool, cotton, flax, viscose rayon and vinylon, are tin-weighted with stannic chloride, the stannic acid gels are deposited largely in the voids and the portions of small density in these fibers. But in the hydrophobic fibers, such as acetate rayon and nylon, the stannic acid gels are deposited largely in the skin layer.

4. In the silk fibers, the stannic acid gels are deposited largely in the inner portions, but in the nylon fibers, they are deposited largely in the skin layer. Consequently, the luster of silk is scarcely changed with heavy tin-weighting, but even if nylon is tin-weighted slightly, its luster is decreased and its whiteness is increased.

5. The stannic acid gels are amorphous and their state of deposition is irregular.

6. When the fibers are immersed in the stannic chloride solution, and this solution is permeated into the fibers, this stannic chloride is hydrolyzed with wash-water into insoluble stannic oxide and hydrochloric acid, and this oxide is segregated out in the voids and the amorphous portions of fibers.

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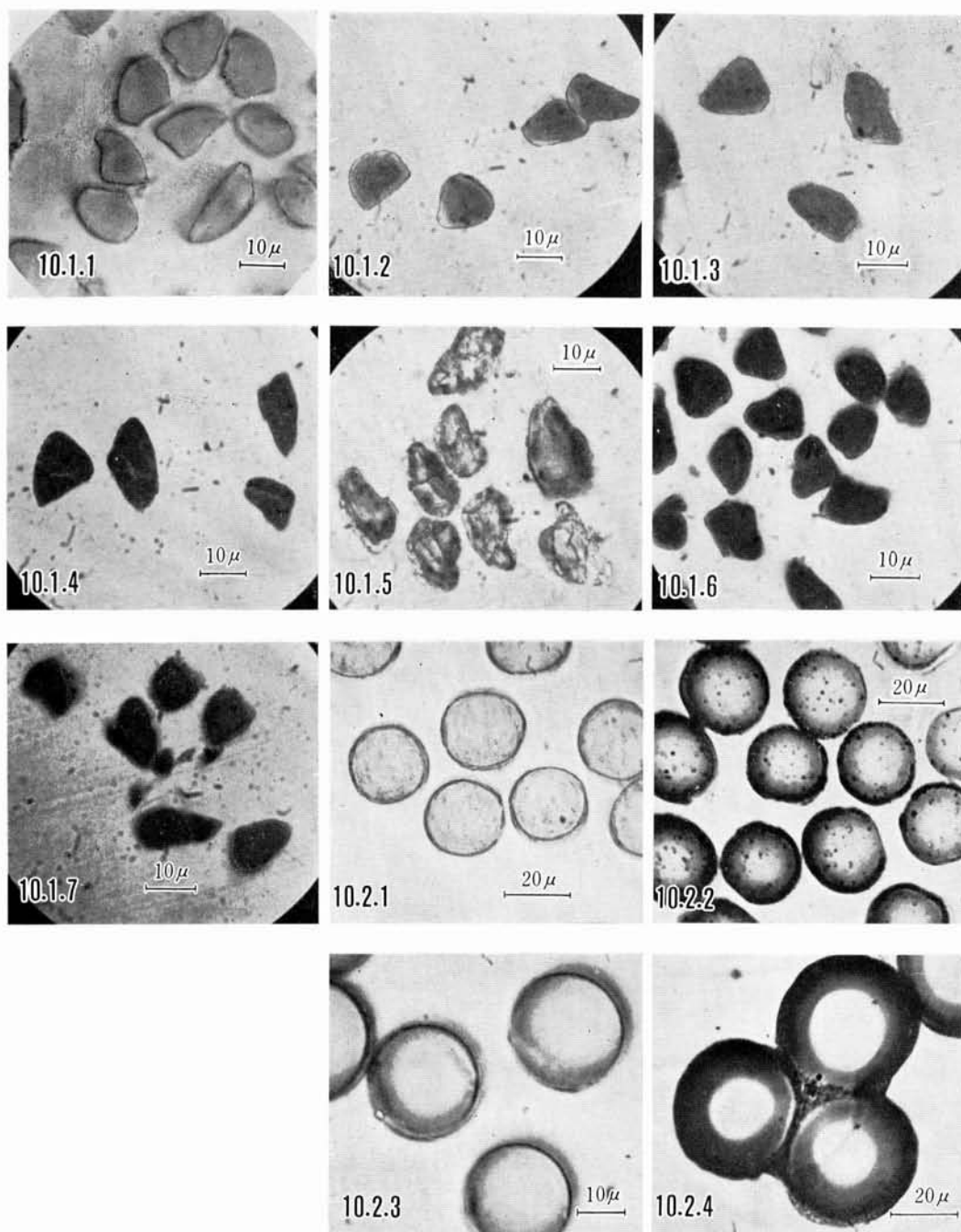
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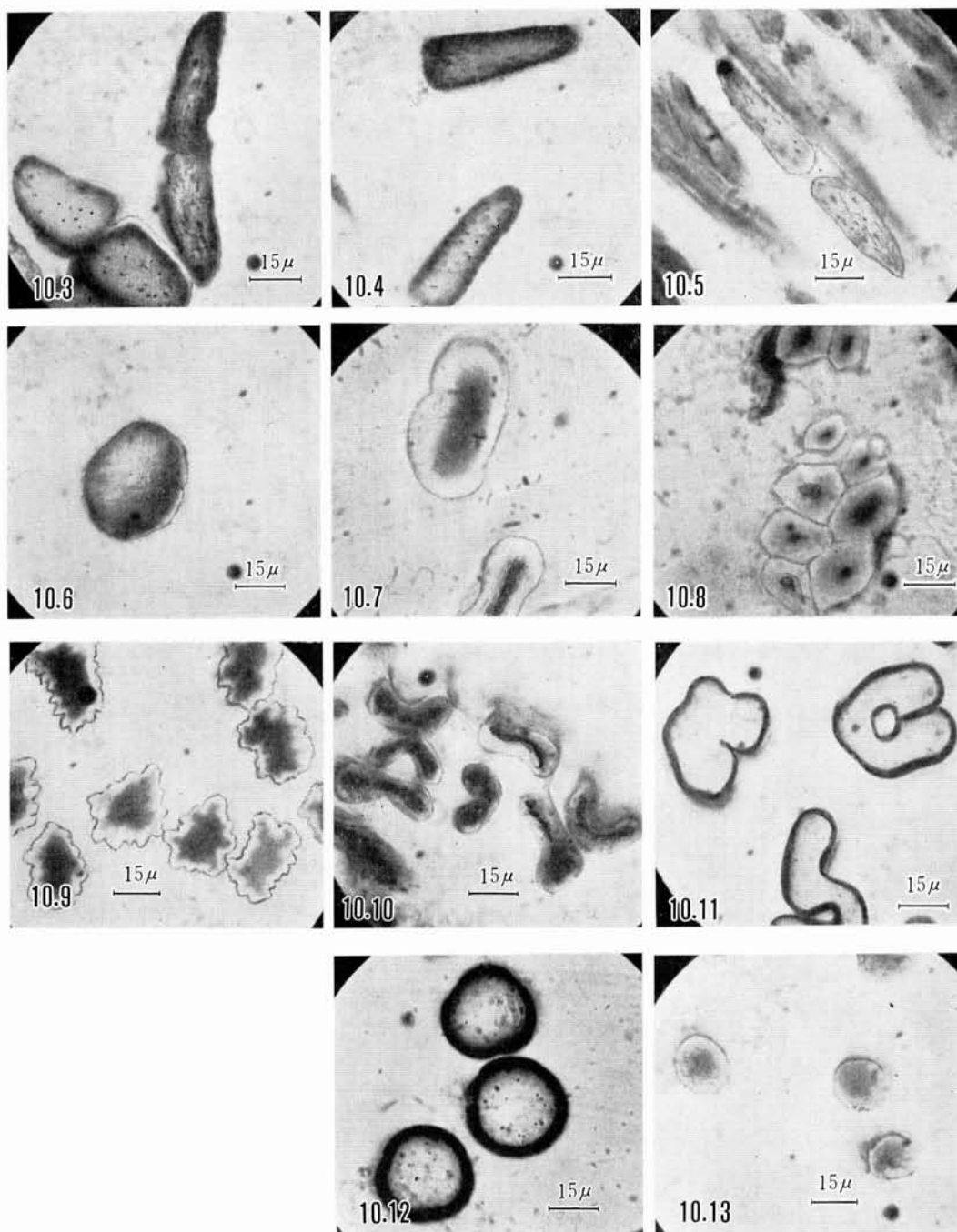
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- 10.1.1 Silk, non-tin-weighted.
- 10.1.2 Silk, rate of tin-weighting 18.3% (2"pass" times). 1 "pass" :-  
treated with 42 %  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%) 20°C, 60 min. washed  
with water, 60 min.
- 10.1.3 Silk, rate of tin-weighting 22.3% (5"pass" times).
- 10.1.4 Silk, rate of tin-weighting 54% (20"pass" times).
- 10.1.5 Silk, rate of tin-weighting 221.2% (160"pass" times).
- 10.1.6 Silk, weighted with Pink salt, rate of tin-weighting 14.6%.
- 10.1.7 Italian tin-weighted silk, rate of tin-weighting 24.6%.
- 10.2.1 Nylon, non-tin-weighted.
- 10.2.2 Nylon, rate of tin-weighting 3%, treated with 50%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$   
(w/v%), 40°C, 30 min., washed with water, 60 min.
- 10.2.3 Nylon, non-tin-weighted.
- 10.2.4 Nylon, rate of tin-weighting 26.6%, treated with 40%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  
60°C, 20 min., washed with water, 60 min.



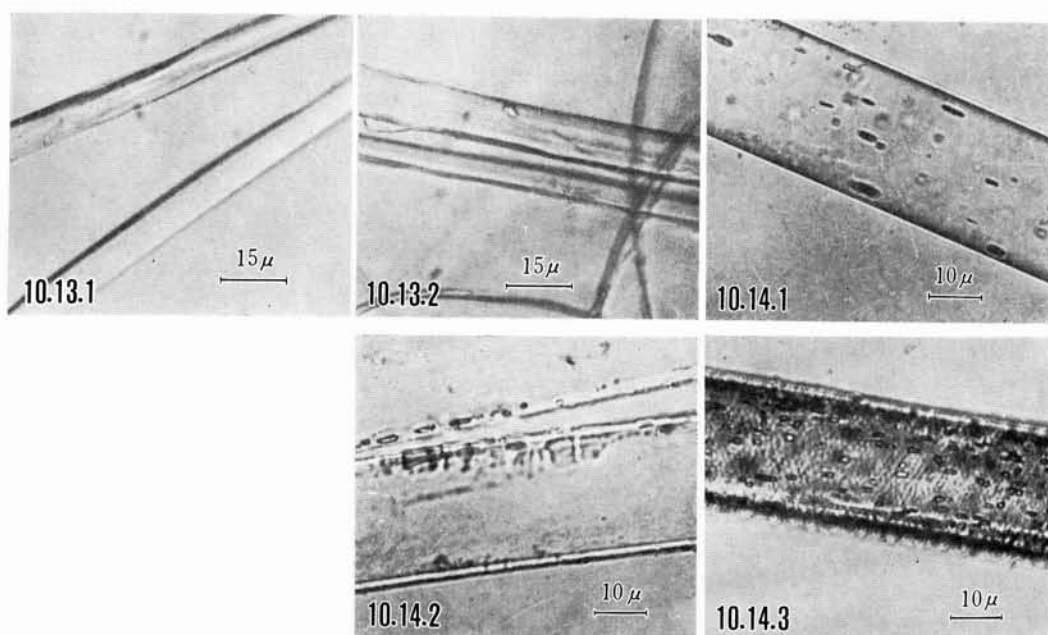
**Figs. 10.1.1-10.2.4 Microscopical pictures of tin-weighted silk and nylon**  
(Stained with hematoxylin. Black parts indicate deposited localities of stannic acid gels.)

- 10.3 Yamamai silk, rate of tin-weighting 13.0%.
- 10.4 Tussah silk, rate of tin-weighting 14.6%.
- 10.5 Eria silk, rate of tin-weighting 11.8%.
- 10.6 Wool, rate of tin-weighting 17.3%.
- 10.7 Cotton, rate of tin-weighting 5.2%.
- 10.8 Flax, rate of tin-weighting 4.0%.
- 10.9 Viscose rayon, rate of tin-weighting 8.3%.
- 10.10 Vinylon, rate of tin-weighting 6.6%.
- 10.11 Acetate fibers, rate of tin-weighting 3.9%.
- 10.12 Nylon, rate of tin-weighting 16.6%.
- 10.13 Polynosic (a kind of viscose rayon), rate of tin-weighting 2.5%.

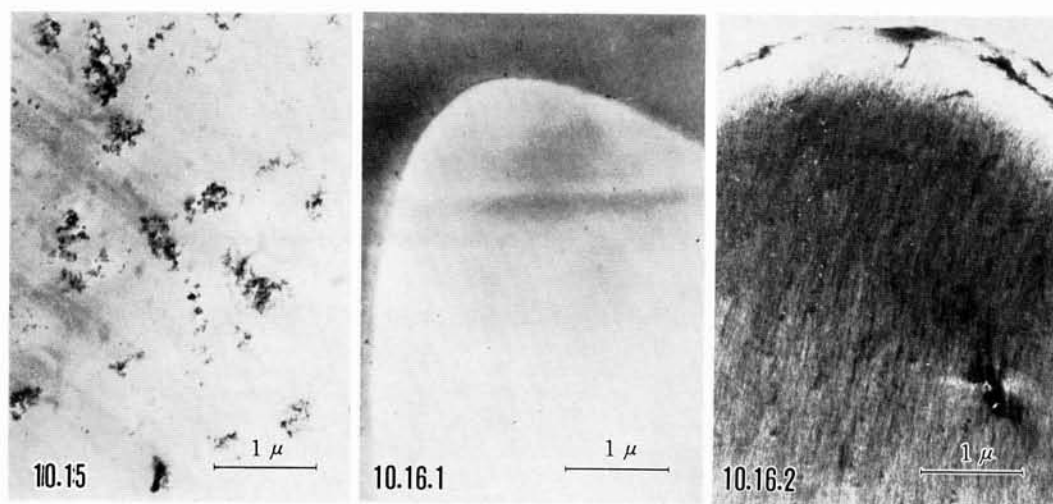


**Figs. 10.3-10.13** Microscopical pictures of tin-weighted fibers of various kinds  
(Stained with hematoxylin. Black parts indicate deposited localities of stannic acid gels.)

- 10.13.1 Silk, non-tin-weighted.
- 10.13.2 Silk, rate of tin-weighting 70.6%.
- 10.14.1 Nylon, non-tin-weighted.
- 10.14.2 Nylon was treated with 15.2%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%), 60°C, 5 min. not washed with water.
- 10.14.3 Nylon, rate of tin-weighting 29.6%. Sample was treated with 25%  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (w/v%), 60°C, 5 min. and washed with water for 60 min.
- 10.15 Particles of deposited stannic acid gels in central portion of silk gut (*Bombyx mori*). Rate of tin-Weighting 4.9%
- 10.16.1 Silk, non-tin-weighted.
- 10.16.2 Silk, rate of tin-weighting 39.7%.



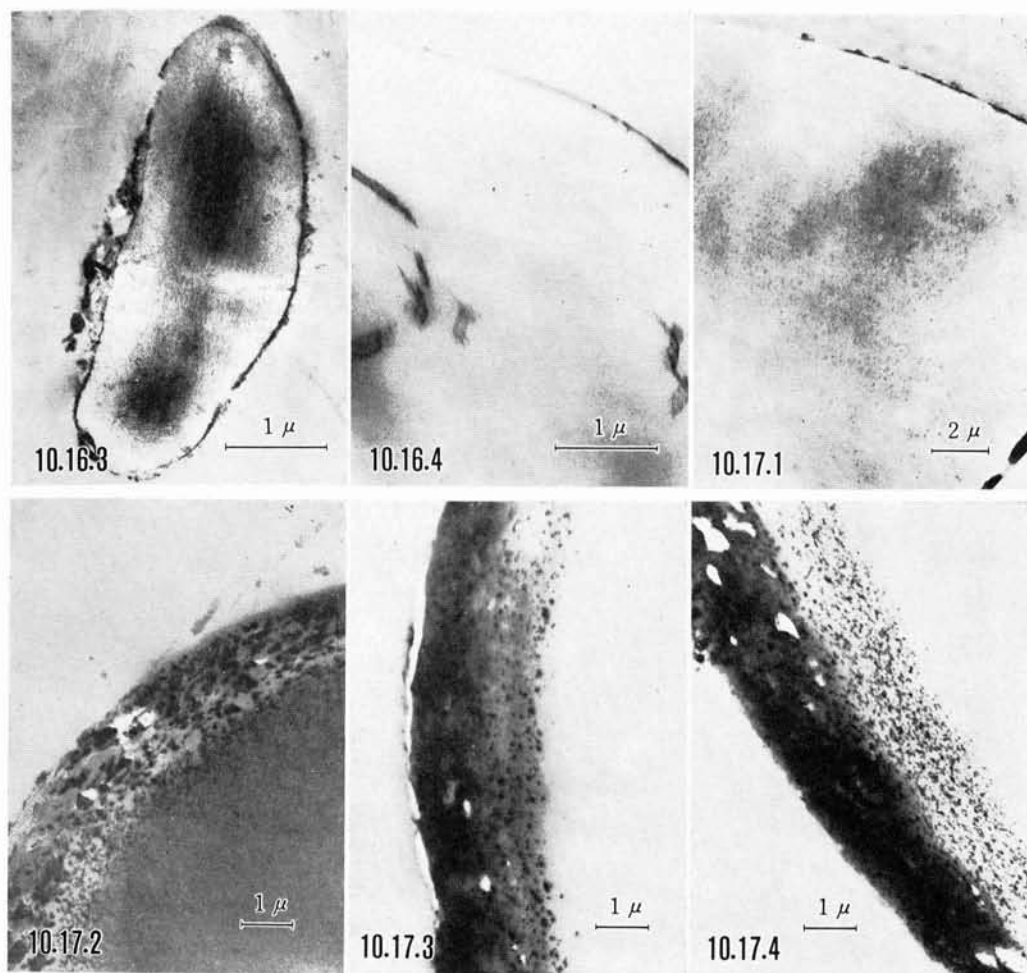
Figs. 10.13.1-10.14.3 Microscopical pictures of tin-weighted silk and nylon.



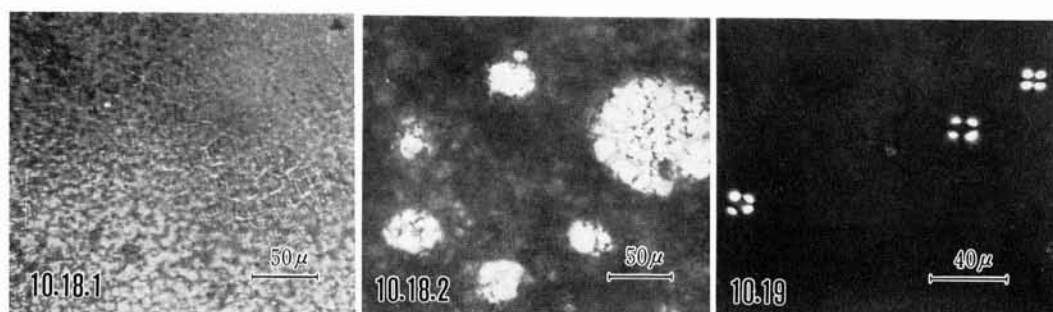
Figs. 10.15-10.16.2 Electron microscopical pictures of tin-weighted silk 1.

- 10.16.3 Split fibers of silk, rate of tin-weighting 39.7%.
- 10.16.4 Silk, discharged tin with HF. 1 gr. of tin-weighted sample was treated with 100 ml. of 4% HF, 60°C, 5hr., remaining tin-weighting 8.8 %.
- 10.17.1 Nylon, non-tin-weighted.
- 10.17.2 Nylon, rate of tin-weighting 26.6%.
- 10.17.3 Nylon, rate of tin-weighting 26.6%.
- 10.17.4 Nylon, discharged tin with HF, in the same way as 10.16.4, remaining tin-weighting 5.4%.
- 10.18.1 Nylon was dissolved in mixed solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O} : \text{H}_2\text{O} : \text{MeOH} = 0.1 : 1.3 : 1.0$  mol. by heating, and immediately washed with water.
- 10.18.2 Nylon was dissolved in the same way as 10.18.1 and left alone for 7 days, and washed with water.
- 10.19 Spherical crystals of silk fibroin. Silk was dissolved in mixed solution of  $\text{CaCl}_2 : \text{H}_2\text{O} : \text{MeOH} = 1 : 8 : 2$  mol. by heating, dialysed with water, and the fibroin solution was slowly dried. Between crossed polarisers.





Figs. 10.16.3-10.17.4 Electron microscopical pictures of tin-weighted silk and nylon 2.



Figs. 10.18.1-10.19 Regeneration of nylon from the nylon solution. Spherical crystals of silk fibroin regenerated from fibroin solution.  
(Figs. 10.18.1 and 10.18.2 were stained with hematoxylin. Black parts are stannic acid gels).