COMPARATIVE STUDIES ON THE DYEING OF YAMAMAI AND DOMESTIC SILK

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CONTENTS

CHAPTER I INTRODUCTION

Yamamai silk has excellent charactertics as a fiber, but its bleaching and dyeing have been considered to be very difficult as plenty of greenish yellow matters are fixed on it.

Yamamai silk, therefore, has been used only for the textiles which may retain its natural colour.

In this paper, some studies are carried out on the base of the scouring, bleaching and dyeing of domestic silk. The chemical characteristics of *yamamai* silk are examined. The steaming process, which has been devised by the author, is applied to the scouring and bleaching of *yamamai* silk, and the silk is found to be bleached as white as domestic silk.

The souring process is found to be effective for the dyeing of *yamamai* silk.

The relations of the adsorption of dye to the desorption of dye to the condition of a dyebath are examined.

The dyeing properties of *yamamai* silk are compared with those of domestic silk.

The dyeing mechanism of *yamamai* silk is examined. By these studies new informations are obtained, and are described for the purpose of the improvement of the dyeing and finishing of *yamamai* silk, and they are also available for that of domestic silk.

CHAPTER II CHEMICAL CONSTITUTION OF *YAMAMAI* SILK

In order to study the dyeing properties of *yamamai* silk, it is essential to investigate into its chemical constitution. So the chemical constitution of *yamamai* silk is described in this chapter.

Section 1 Chemical Resistance

The resistance of *yamamai* silk and that of domestic silk to some of chemicals are shown in Table 1. It can be seen in Table 1 that *yamamai* silk is more resistant to some of chemicals than domestic silk.

Table 1 Chemical resistance of *Yamamai* and domestic silk

Chemicals	*Yamamai* silk	Domestic silk
10% caustic soda (at 40°C)	Soluble in 50 min.	Soluble in 12 min.
Conc. hydrochloric acid (sp. gr. 1.16)	Soluble partially	Soluble easily
Conc. nitric acid	Soluble in 10 min.	Soluble in 5 min.
Zinc chloride	Soluble very slowly	Soluble easily
Conc. chromic acid	Soluble very slowly	Soluble easily
Rate of hydrolysis with hydrochloric acid	15 hr.	6 hr.

Section 2 Elementary Constitution

Elementary constitution of *yamamai* silk is obtained as in Table 2.

Table 2 Elementary constitution of *Yamamai* silk

Element	Constitution (%)
Carbon	47.18
Oxygen	29.67
Nitrogen	16.85
Hydrogen	6.30

Yamamai silk is composed of carbon, oxygen, nitrogen and hydrogen. Among them, carbon is the highest in the silk, about 50%, and oxygen is 30%, nitrogen, 17% (one third of carbon) and hydrogen is the lowest, 6%.

As seen in this table, nitrogen contained in the silk is 16.48%. Soluble nitrogen in it is 15.79%. Nitrogen compounds other than monoamino nitrogen are various in kind and are contained in the fiber, but their contents are comparatively slight. Nitrogen compounds contained in the fiber less than 1% are amino nitrogen, histidine nitrogen, amide nitrogen and lysine nitrogen.

Table 3 Nitrogen compound in *Yamamai* silk

Nitrogen compounds	Contents
Total nitrogen	16.48%
Soluble nitrogen	15.79
Insoluble nitrogen	0.69
Humine nitrogen	2.28
Amide nitrogen	0.30
Arginine nitrogen	1.09
Hexone salt and cystine nitrogen	1.99
Histidine nitrogen	0.51
Lisine nitrogen	0.19
Monoamino nitrogen	11.70
Nitrogen except amino nitrogen	1.52
Amino nitrogen	0.59

Section 3 Ash in *Yamamai* Silk

In *yamamai* silk, many kinds of ash are contained, but studies on their contents and kinds in detail have not been found anywhere. It is, therefore, important to investigate into the contents and kinds of ash contained in *yamamai* silk for the study of its dyeing properties.

The total content of cationic ash as oxide in *yamamai* silk is about 4.87% of it. The ingredients are shown in Table 4.

Table 4 Composition of ash in *Yamamai* silk

Ash	Content (%)	Ash	Content (%)
CaO	70.01	P_2O_5	2.47
Na_2O	8.89	Si_2O_3	2.36
K_2O	8.43	Fe_2O_3	0.31
MgO	4.25	Cl_2	0.28
SO_2	2.86	Al_2O_3	0.14

As shown in Table 4, in *yamamai* silk is contained 70.01% (the largest quantity); the contents of Na_2O, K_2O and MgO are 8.89, 8.43 and 4.25% respectively; and SO_3, P_2O_5, SiO_2, Fe_2O_3, Cl_2 and Al_2O_3 are also contained in it. The sum of C_2O, Na_2O and K_2O is 87.33% of all oxides of the ash. It can be assumed that the ash contained in the fiber affect the dyeing properties of *yamamai* silk, but their effects will be discussed in the later part of this study.

CHAPTER III BLEACHING OF *YAMAMAI* SILK

Section 1 Bleaching Method of *Yamamai* Silk

As plenty of greenish yellow matters are fixed on the surface of *yamamai* cocoons, raw silk reeled off from these cocoons has also colour of greenish yellow. It has been known that this greenish yellow matters are dissolved with organic acid easily, especialy with acetic acid, but they are not dissolved completely. Bleaching of *yamamai* silk has been considered to be difficult owing to its coloured matters, and so dyeing the silk in brilliant colour has been considered to be impossible.

The author has succeeded in bleaching the *yamamai* silk completely and the scouring method of *yamamai* silk and the results obtained are described in this chapter.

Experiment

Scouring Method

The *yamamai* silk used in this experiment was given by Naganoken Sericultural Experimental Station. The silk is scoured in the solution prepared from 50 gr. of Marseilles soap, 16 gr. of crystal soda, 10 gr. of sodium silicate and 3 gr. of Scourol-100 in 1 litre. On keeping its solution at 80°C,. the sample is steeped in the scouring bath for 10 min. and then kept in a steaming box. After repeating this opration several times, the scoured silk is washed with 3 gr/1 solution of sodium carbonate and water, and then dried. Boiling-off loss of *yamamai* silk is 17.0 %.

Bleaching Method

In this experiment *yamamai* silk was bleached with sodium hydrosulphite, hydrogen peroxide and potassium permanganate respectively, and its bleaching methods are described in detail.

1) Sodium hydrosulphite bleaching : The scoured *yamamai* silk is steeped in sodium hydrosulphite solution for 10 min. and kept in a steaming box for 10 min. After repeating this treatment several times, the fiber is passed through in diluted sulphuric acid and then washed with water thoroughly.

2) Hydrogen peroxide bleaching : The scoured *yamamai* silk is treated in the same way as in the case of sodium hydrosulphite bleaching with hydrogen peroxide solution to which sodium silicate or sodium borate is added.

3) Potassium permanganate bleaching : The fiber is steeped in 0.2% K_2MnO_4 solution (liquor ratio is 1 : 20), and then is aged in the air for a while, and then is treated in the mixed solution of sodiumbisulphite and sulphuric acid (5 c.c. of 32° TW $NaHSO_3$ and 6 c.c. of 168° TW H_2SO_4 in 1 litre) until K_2MnO_4 on the fiber is decolorized.

Results and Discussion

Bleaching effects with sodium hydrosulhite, hydrogen peroxide and potassium permanganate are shown in Table 5. In this table, it is seen that the greenish

Table 5 Bleaching effect of sodium hydrosulphite, pottasium permanganate and hydrogen peroxide to *Yamamai* silk

Bleaching agents	Concentration	Scourol-100	Acid after-treatment	Bleaching effect	Strength g/d	Elongtation
Hydro-sulphite	3	+	+	b	3.50	46
	3	+	−	b	3.84	48
	3	−	+	b	3.70	47
	3	−	−	b	3.40	47
	10	+	+	a	3.50	45
	10	+	−	a	3.70	47
	10	−	+	a	4.00	51
	10	−	−	a	3.70	46
Hydrogen-peroxide	3	+	+	d	3.62	43
	3	+	−	d	3.32	45
	3	−	+	d	3.38	42
	3	−	−	c	2.94	43
	10	+	+	d	2.94	43
	10	+	−	c	3.10	36
	10	−	+	d	3.40	35
	10	−	−	c	3.20	35
Potassium permanganate	0.2	+	+	d	3.52	37
	0.2	−	−	d	3.20	36
Nontreated					3.84	47

Note : a……Silk bleached as white as domestic silk
b, c……Intermediates between a and d
d……Silk not bleached

yellow matters on the scoured *yamamai* silk is bleached completely as white as domestic silk through hydrosulphite bleaching process.

Yamamai silk appears to be not bleached with K_2MnO_4 or H_2O_2, oxidizing bleaching agent, and to be damaged remarkably.

Effect of Bleachig Agent on Strength and Elongation of *Yamamai* Silk

The effects of oxidizing bleaching agents and reducing bleaching agent on the strength and elongation of *yamamai* silk are shown in Table 6 and 7.

The strength and elongation of the bleached silk do not decrease with the reducing bleaching agent at all, but, using hydrogen peroxide, the silk is not

Table 6 Strength and elongation of bleached *Yamamai* silk

Bleaching agent	Strength	Elongation
Hydrosulphite	101.6	99.7
Hydrogen peroxide	85.6	86.4

Note: The number in this table is compared with non-bleached *yamamai* silk as 100.

Table 7 Relations between concentration of bleaching agents and mechanical property

Concentration	Bleaching time	Strength	Index	Elongation	Index	Degree of bleaching
1.0	10	3.12	82.2	48	101	b
	30	3.60	95.0	47	100	c
	50	3.63	95.6	46	98	a
5.0	10	3.56	94.0	46	98	b
	30	3.80	100.0	47	100	b
	50	3.80	100.0	49	102	a
10.0	10	3.80	100.0	47	100	b
	30	4.10	104.0	48	101	a
	50	3.95	102.0	50	103	a
20.0	10	3.56	93.8	43	93	d
	30	3.81	100.0	49	109	b
	50	3.80	100.0	49	102	a
Non treated	—	3.84	100.0	47.3	100	—

Index……the same as Table 6

bleached, but damaged remarkably. It is evident from Table 6 and7, that sodium hydrosulphite is the most suitable for bleaching of *yamamai* silk.

Section 2 Scouring of *Yamamai* Silk after Pretreatment with Several Kinds of Acid

The author does not always consider that the dyeing of *yamamai* silk is more difficult than that of domestic silk, but the feeling of the fibre is deteriorated by the above treatment. It may be difficult for practical use without improvement of the feeling of *yamamai* silk. So in this section the pretreatment and the after-treatment with several kinds of acid in scouring *yamamai* silk are studied to improve the feeling. The scouring method applied in this study is a general method which is used for domestic raw silk. In the scouring solution, 20% of Marseilles soap on the weight of fiber, 8% of sodium silicate, 3% of sodium hydrosulphite and 2% of Scourol-100 are contained.

Raw *yamamai* silk is scoured, and dyed after steeping for 1 hr. in 2.0% acid solution (hydrochloric, sulphuric, acetic, oxalic and formic acid).

The boiling-off loss is calculated and the amounts of adsorbed dye are obtained. The results obtained in this experiment are shown in Table 8.

The results shown in Table 8 are as follows:

(i) The loss of weight is the minimum in the scouring after the treatment with oxalic acid.

(ii) After the treatment with hydrochloric acid, the loss is the maximum, 5.76%.

Table 8 Weight loss, boiling-off loss and adsorption of dyes by treatment with acids

Acids	Weight-loss by acid treatment	Boiling-off loss (%)	Adsorption of dye (%)
2% hydrochloric acid	5.76	10.85	14.5
2% sulphuric acid	2.41	11.23	18.8
2% acetic acid	0.79	15.02	10.3
2% oxalic acid	0.62	16.35	17.8
2% formic acid	1.04	13.05	12.2

(iii) In the case of sulphuric acid, the loss is between (i) and (ii).

And it is evident in Table 8 that the boiling-off loss after hydrochloric and sulphuric acid treatment are less than that after organic acid.

The amounts of adsorbed dye by the scoured silk after the pretreatment with sulphuric acid and oxalic acid are the maximum. In this acid treatment greenish coloured matters contained in *yamamai* silk is dissolved out in the acid solution.

Section 3 Effect of Souring after Scouring

After scouring with a general method, *yamamai* silk is steeped in several kinds of 2% acid solution for 20 min. at a room temperature and dyed. Then the boiling-off loss and amounts of adsorbed dye are calculated. The results are shown in Table 9.

Table 9 Effect of souring after scouring on boiling-off loss and adsorption of dyes

Acid	Boiling-off loss	Adsorption of dye
2% hydrochloric acid	19.31%	97.64%
2% sulphuric acid	17.48	97.50
2% acetic acid	17.45	42.10
2% oxalic acid	15.38	97.64
2% formic acid	18.62	95.26

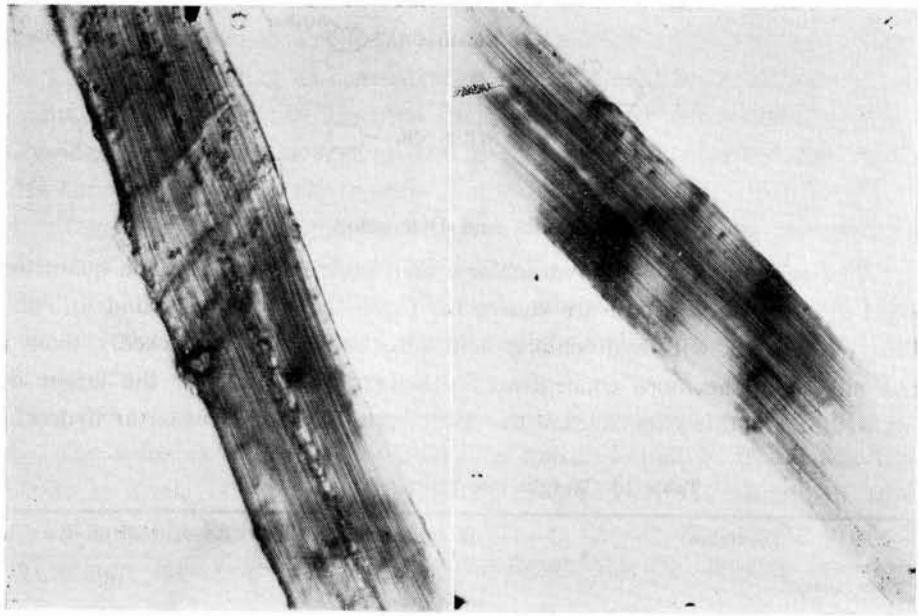
It can be seen from Table 9 that the exhaustion of dyebath is as high as 95-97% by souring after scouring (with the exception of acetic acid). By dyeing the soured silk, it rustles and the feeling and the luster of *yamamai* silk are improved. By souring the greenish yellow coloured matters are also removed a little. But it is observed that the dyed silk without souring has not the rustling of silk.

By microscopical observation on the surface of the *yamamai* silk treated with acid, sericin and crystals of calcium oxalate fixed on the fiber are obserbed to be removed remarkably.

From the abovementioned results in dyeing *yamamai* silk, a conclusion can be drawn that the souring is also a useful process for saving the acid used for dyeing.

CHPTER IV ON THE VARIOUS PRETREATMENT AND DYE ADSORPTION OF *YAMAMAI* SILK

Crytals of calcium oxalate fix on the surface of a *yamamai* cocoon (as indicated in photograph). It is difficult to decide that these crystals prevent the fiber from being dyed directly.



Yamamai silk, raw silk (left) and soured silk in hydrochloric acid (right).

R. N. SEN scoured raw tussar silk by a general method (in the bath of Marseilles soap and sodium carbonate) after souring with a dilute acid solution to remove mineral matters on the dyeing of tussar silk. A. MIHIRA reported that acid treatment after scouring is an effective process for the dyeing.

Section 1 The Relation between Acid Treatment before Dyeing and The Quantity of Adsorbed Dye

Experiment

Materials

Raw *yamamai* silk used is multiple-ends reeling of 42.1 d. and it is pretreated in acid solutions of various concentrations of hydrochloric acid, sulphuric acid, acetic acid, oxalic acid and formic acid, and in alkali solutions such as sodium carbonate, sodium silicate, and also in such a nonionic surface active agent as Scourol.

Conditions of treatment in this experiment are as follows;

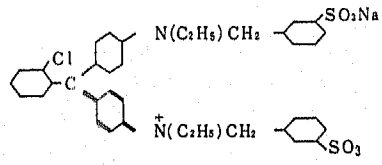
a. Steeping for 1 hr. at a room temperature.

b. Treatment at boiling point for 1 hr.

c. After treating for 1 hr. at a room temperature, scouring by a general method.

d. After scouring, steeping in various acid solutions at a room temperature for 20 min.

Yamamai silk treated by the above a~d methods is dyed with the following purified acid dye, Brilliant Milling Green B.



Results and Discussion

1. The relations between hydrochloric acid pretreatment and the quantities of adsorbed dye on *yamamai* silk are shown in Table 10. It can be found in Table 10 that the treated silk with hydrochloric acid adsorbs more dye markedly than non-treated silk, and the more concentrated the hydrochloric acid is, the larger is the loss in weight. In this experiment, the most suitable concentration of hydrochloric

Table 10 Weight loss and adsorption of dye

Treatment	Weight loss (%)	Adsorption of dye (%)
Non-treated	—	18.3
Distilled water a)	0.77	20.9
0.5% hydrochloric acid solution	0.97	86.4
0.7% 〃	2.38	88.9
1.0% 〃	3.29	94.5
1.5% 〃	4.40	95.4
2.0% 〃	5.76	96.5

a) Treatment in the distilled water for one hour at room temperature

Table 11 Weight loss and adsorption of dye by sulphuric acid treatment of *Yamamai* silk

Concentration of sulphuric acid	Weight loss (%)	Adsorption of dye (%)
0.2	0.64	91.1
0.5	0.78	92.8
0.7	1.06	93.5
1.0	1.21	94.5
1.3	1.48	95.9
1.5	1.79	95.9
1.7	2.11	96.4
2.0	2.41	96.4

acid for pretreatment before dyeing is 1%.

2. The relation between the amounts of adsorbed dye and the pretreatment using sulphuric acid are shown in Table 11. From Table 11, it can be seen that the more concentrated the sulphuric acid is, the larger are the loss in weight the amount of adsorbed dye. In this experiment, the suitable concentration for treatment is 1%.

3. The results in the case of using acetic acid solution for the pretreatment of *yamamai* silk are shown in Table 12.

In Table 12, according as concentration of acetic acid becomes higher, the loss in weight and the amount of adsorbed dye become larger remarkably.

Considering the loss in weight and the amounts of adsorbed dye, the most suitable concentration for acid treatment is about 0.5%.

4. The loss in weight and the amount of adsorbed dye on *yamamai* silk in treating with oxalic acid are shown in Table 13.

The amount of Brilliant Milling Green B adsorbed on *yamamai* silk does not vary in accordance with the acid concentration, and the loss in weight bcomes larger according as the acid concentration.

Thus the suitable concentration of acetic acid for treating *yamamai* silk is 0.5 %.

5. The amounts of adsorbed dye and the loss in weight by formic acid treating are shown in Table 14. In this table, it can be seen that the amount of adsorbed dye and the weight loss become larger according as the concentration of dye becomes higher, except some results. It can be concluded that the suitable concentration of formic acid for treating of *yamamai* silk is about 2.0~2.5%.

6. After boiling for 1 hr with nonionic surface active agent, Scourol-100 (Kao soap Co. Ltd.), *yamamai* silk is dyed with Brilliant Milling Green B and the loss in weight is calculated. The results are shown in Table 15.

In Table 15, the exhaustion of dyebath is very small, but the higher the concentration of Scourol-100 becomes the lager the weight loss becomes. It can be seen that steeping *yamamai* silk in the solution of Scourol-100 only is not suitable for acid dyeing.

7. As described in the preceding section, the pretreatment with only Scourol-100 is little effective for dyeing. It is better for *yamamai* silk to dyed after treating in the mixed solution of acid and Scourol-100. In this experiment, Scourol-100 on the weight of fiber of 1% is added to hydrochloric acid and the results obtained are shown in Table 16.

In this table, the amount of dye adsorbed on *yamamai* silk increases from 94.8 to 95.8% with the increase of the concentration of hydrochloric acid in Scourol-100 solution. In the dyeing in the dyebath containing Scourol-100 *yamamai* silk is dyed evenly.

Therefore, by using Scourol-100 and hydrochloric acid in the same bath, *yamamai*

Table 12 Weight loss and adsorption of dye by acetic acid treatment of *Yamamai* silk

Concentration of acetic acid solution	Weight loss (%)	Adsorption of dye (%)
0.5%	0.18	42.1
1.0	0.34	42.8
1.5	0.54	49.2
2.0	0.79	59.5
2.5	0.84	63.6

Table 13 Weight loss and adsorption of dye by oxalic acid treatment of *Yamamai* silk

Concentration of oxalic acid solution	Weight loss (%)	Adsorption of dye (%)
0.5	0.31	92.8
1.0	0.36	93.0
1.5	0.43	93.8
2.0	0.62	93.9

Table 14 Weight loss and adsorption of dye by treatment with formic acid

Concentration of formic acid solution	Weight loss (%)	Adsorption of dye (%)
0.2	0.13	50.2
0.5	0.12	59.4
0.7	0.48	67.7
1.0	0.26	71.5
1.3	0.92	78.4
1.5	0.85	80.3
1.7	0.97	82.6
2.0	1.04	89.0
2.5	1.34	88.6
3.0	2.32	80.8

Table 15 Weight loss and adsorption of dye by Scourol treatment of *Yamamai* silk

Treatment	Weight loss (%)	Adsorption of dye (%)
Distilled water a)	0.82	20.7
0.5 % Scourol-100	2.33	19.1
1.0 //	2.59	20.5
1.5 //	2.76	23.2
2.0 //	3.25	24.2

a) Treatment in the distilled water for 1 hr. at boiling point.

Table 16 Weight loss and adsorption of dye of *Yamamai* silk by using hydrochloric acid and Scourol-100

Concentration of hydrochloric acid solution (%)	Weight loss (%)	Adsorption of dye (%)
0.5	2.36	94.8
1.0	4.03	94.9
1.5	5.01	95.7
2.0	5.95	95.9

Table 17 Weight loss and adsorption of dye by sodium carbonate treatment of *Yamamai* silk

Concentration of crystal soda solution (%)	Weight loss (%)	Adsorption of dyes (%)
0.2	2.55	91.3
0.5	2.68	91.5
0.7	3.03	92.3
1.0	3.18	92.7
1.3	3.62	94.9
1.5	3.41	96.7
1.7	3.98	95.0
2.0	2.65	96.8

silk is able to be dyed more effectively.

8. In this experiment, *yamamai* silk is steeped in sodium carbonate solution, then soured in 1% hydrochloric acid solution, the silk is dyed, and the loss in weight is determined. The results obtained are shown in Table 17.

In Table 17, it is apparent that the weight loss of *yamamai* silk and the amount of adsorbed dye increase with the increase of concentration of hydrochloric acid.

By this pretreatment, the difference in amounts of adsorbed dye does not vary so greatly. The most suitable concentration of hydrochloric acid for the pretreatment is 2%. The residual solution after the treatment in this experiment is white and muddy. This is more remarkable than other pretreatments described in the preceding sections.

9. In the pretreatment with the sodium silicate, *yamamai* silk is treated in the sodium silicate solution of various concentrations and soured in hydrochloric acid in the same way as section 8. The results obtained in this experiment are shown in Table 18.

It can be seen in Table 18 that the weight loss of *yamamai* silk increases with the increse of sodium silicate concentration. But the amount of adsorbed dye is hardly made different by the concentration of hydrochloric acid. But the most suitable concentration of hydrochloric acid for the pretreatment is 0.2%.

Table 18 Weight loss and amounts of adsorbed dye in pretreatment with sodium silicate and hydrochloric acid

Concentration of sodium silicate	Weight loss (%)	Adsorption of dye (%)
0.2%	2.33	95.7
0.5	3.27	96.4
0.7	4.01	96.8
1.0	4.25	96.9
1.5	4.38	95.0
2.0	4.44	94.9
2.5	5.09	95.1
3.0	6.32	94.8

note : The weight loss of *yamamai* silk pretreated in only 1% sodium silicate is 1.56% and the exhaustion of a dyebath is 10.9%.

And in the sodium silicate pretreatment, a souring process is also available for improvement of dyeing property of *yamamai* silk.

As described in the above Sections 1-9, acid treatments (also in *yamamai* silk treated in alkali) increase affinity of acid dyes to the silk. It is considered that hydrogen ions of various acids which are adsorbed on *yamamai* silk by pretreatment make the sites for acid dye ions to be adsorbed.

This is proved by the fact that the untreated *yamamai* silk with acid indicates only 20% exhaustion of dyebath but the silk pretreated with only 2% hydrochloric acid adsorbs 94% exhaustion.

10. The weight loss and the amount of adsorbed dye on *yamamai* silk treated in a boiling condition for 1 hr. in 0.5% solutions of hydrochloric acid and nitric acid, and in 1.0% solution of acetic, oxalic and formic acid, are examined respectively. The results obtained in this experiment are shown in Table 19.

The loss in weight of the silk treated with formic acid is the minimum, but the amount of adsorbed dye hardly vary owing to the kinds of acids used. The hand feeling of *yamamai* silk after these treatments is the same with the one of the silk treated with acid without boiling after scouring. Also the silk treated in these process shows the same quality of fibroin with that of the silk scoured by a general

Table 19 Loss in weight and amount of adsorbed dye on *Yamamai* silk after treatment in boiling condition for 1 hr. with diluted acids

Acids	Weight loss (%)	Adsorption of dye (%)
0.5% hydrochloric acid	15.62	97.10
0.5% nitric acid	12.77	97.67
1.0% acetic acid	14.61	97.15
1.0% oxalic acid	10.25	98.14
1.0% formic acid	5.61	96.45

method. With this boiling treatment the *yamamai* silk is coloured remarkably in greenish yellow. And so it is interesting to use this principle for fabrics and decorations.

Section 2 The Relations between Amount of Adsorbed Dye on *Yamamai* Silk and Physical Condition of Dyebath

It is very important to study on the relations between the physical condition of dyebath and amount of adsorbed dye.

The Relations between Temperature and Amounts of Adsorbed Dye

The sample used in this experiment is *yamamai* silk soured with 2% solution of hydrochloric acid, oxalic and acetic acid after scouring.

Yamamai silk is dyed for 1 hr. at each temperature of 50°, 60°, 70°, 80° and 90°C, and liquor ratio of the dyebath is 50 times on the weight fibre. No dyeing assistant is used in this experiment.

Table 20 Temperature of dyebath and amount of adsorbed dye on *Yamamai* silk

Temperature (°C)	Acids	Adsorption of dye (%)
50	2% hydrochloric acid	98.98
	2% oxalic acid	96.60
	2% acetic acid	11.20
60	2% hydrochloric acid	100.00
	2% oxalic acid	98.78
	2% acetic acid	41.50
70	2% hydrochloric acid	100.00
	2% oxalic acid	99.34
	2% acetic acid	44.20
80	2% hydrochloric acid	100.00
	2% oxalic acid	99.93
	2% acetic acid	62.60
90	2% hydrochloric acid	100.00
	2% oxalic acid	99.45
	2% acetic acid	49.50

The results obtained in this experiment are shown in Table 20. In Table 20, it can be seen that the temperature at which maximum amount of dye is adsorbed on *yamamai* silk is 80°C, that is to say, it is the most suitable temperature for dyeing *yamamai* silk. *Yamamai* silk soured in a hydrochloric acid solution indicates higher exhaustion than the silk treated in acetic solution at all range of temperature.

In dyeing of *yamamai* silk soured with acetic acid, the amounts of adsorbed dye at 50°C is so small that it is better for silk to be dyed above 60°C.

This *yamamai* silk soured with acetic acid adsorbs the maximum dye on the fibre at 80°C. But, for the practical purposes, the dyeing must begin from 50°C, and continue fully for a while at 80°C because dyeing is apt to be unlevelling, if goods are dyed directly in the bath of high temperature from the the beginning.

The Relations between the Amounts of Adsorbed Dye and Liquor Ratio

As described above, the most suitable temperature for dyeing of *yamamai* silk is 80°C, and subsequently it is necessary to determine the suitable liquor ratio for dyeing of *yamamai* silk.

The experiment on the relation between liquor ratio and amount of adsorbed dye on *yamamai* silk is carried out with acid dye, Brilliant Milling Green B.

The results obtained in this experiment are shown in Table 21, in which the suitable liquor ratio for dyeing of *yamamai* silk is 30-40 times, especially 30 times on the weight of the silk. It is, therefore, better for *yamamai* silk to be dyed in the most suitable condition, that is at 80°C and in the dyebath of 30 times liquor.

In this experiment, Brilliant Milling Green B is used for the dyeing of *yamamai* silk, but individual members of acid dyes have different behaviour of adsorption on the fibre.

Table 21 Liquor ratios and amount of adsorbed dye on *Yamamai* silk

Liquor ratio (times)	Acid	Adsorption of dye (%)
15	2% hydrochloric acid	94.5
	2% oxalic acid	97.4
	2% acetic acid	33.1
20	2% hydrochloric acid	98.74
	2% oxalic acid	68.16
	2% acetic acid	36.90
25	2% hydrochloric acid	100.00
	2% oxalic acid	99.07
	2% acetic acid	70.19
30	2% hydrochloric acid	100.00
	2% oxalic acid	100.00
	2% acetic acid	74.10
35	2% hydrochloric acid	100.00
	2% oxalic acid	100.00
	2% acetic acid	68.7
40	2% hydrochloric acd	100.00
	2% oxalic acid	100.00
	2% acetic acid	64.80

CHAPTER V COMPARISON OF DYEING PROPERTIES OF *YAMAMAI* SILK WITH THOSE OF DOMESTIC SILK

As described in Chapter II, there are some differences in fine structure and composition of amino acids between *yamamai* silk and domestic silk.

Some of comparative studies between *yamamai* and domestic silk have been carried out by some scientists in the fields of composition of amino acids, chemical resistances and microscopical structures, but dyeing properties of these two kinds of silk have not been investigated in detail.

The author have studied dyeing properties of *yamamai* and domestic silk comparatively by dyeing them with direct, acid, basic, mordant, azoic and vat dyes, and obtained some of new informations.

The results obtained in these experiments are described in the following sections.

Section 1 Comparison of Dyeing Properties of *Yamamai* Silk with Domestic Silk when Using Direct Dyes

In this section, the differences of dyeing properties in direct affinity between *yamamai* and domestic silk are described comparatively.

As direct affinity varies remarkably with the auxochromes in a dye molecule, especially the number of sulphonic groups.

Experiment

Materials

Silk used in this experiment are raw and scoured silk of *yamamai* and domestic silk. Some of them are soured in such a hydrochloric acid solution as obtained good results in the preceding chapter.

Table 22 Exhaustion of dyebath by *Yamamai* and domestic silk

Dye	Raw d. s.	Scoured d. s.	Raw y. s.	Scoured y. s.	Scoured y. s. (soured)
Benzo Fast Scarlet 4BS (disazo)	69.85	41.70	69.50	38.25	100.00
Chrysophenine G (disazo)	80.83	72.80	69.99	43.01	100.00
Direct Deep Black RW extra (trisazo)	74.65	62.01	84.62	50.25	97.45
Direct Green B (trisazo)	86.22	48.95	89.97	40.55	100.00
Erie Fast Yellow WB (monoazo)	75.45	30.45	77.55	26.01	100.00
Diamine Fast Violet BBN (disazo)	68.3	53.05	57.25	35.50	100.00

note: d. s. ····· domestic silk, y. s. ·····*yamamai* silk

The dyes used in this experiment are indicated in Table 22. The dyes are applied to both the kinds of silk in the solution of 0.05% on the weight of fiber at 80°C for 1 hr. The amount of adsorbed dye are calculated colorimetrically with A. K. A. Type Photoelectric Colorimeter on the residual solution of the dyebath.

After washing and drying, dyed fibers are treated in a distilled water of 80°C for 30min. and the amounts of desorbed dye are determined colorimetrically.

Results and Discussion

The exhaustion of dyebath in the dyeing with direct dyes on *yamamai* and domestic silk are shown in Table 22.

In Table 22, generally speaking, trisazo direct dyes has higher direct affinity to *yamamai* silk than to domestic silk, and in the dyeing of raw silk, *yamamai* silk indicates higher exhaustion than domestic silk.

In the dyeing with Chrysophenine G and Diamine Fast Violet BBN, amounts of adsorbed dye on raw domestic silk is 11% higher in exhaustion than raw *yamamai* silk, but in the dyeing with Direct Green B, raw *yamamai* silk adsorbs 13% higher than raw domestic silk. In the dyeing of scoured silk, all dyes used show higher affinity in domestic silk than in *yamamai* silk, to the extent of 3-30% difference in exhaustion, and this trend of adsorption is not always so constant as in the case of raw silk.

In this experiment, it is found that in both the cases of silk raw silk adsorbs more quantity of dye than the scoured one, but amounts of adsorbed dye vary with the sorts of dye, and differences in the adsorbed amounts of each dye are smaller in *yamamai* silk than in other silk.

The ratio of the desorbed amount by boiling with water to the adsorbed amount of dye is shown in Table 23.

The dyes adsorbed on *yamamai* silk are desorbed more easily than others excepting Benzo Fast Scarlet 4 BS. It means that dyes are adsorbed more weakly on *yamamai* silk than on domestic silk.

The amount of desorbed dye on scoured *yamamai* silk soured in a hydrochloric acid is not varied with chemical structure of dye and the desorption by the treatment in boiling water is not observed. It means that acid adsorbed on the fiber by the souring in a hydrochloric acid solution is also effective for direct dyes to be adsorbed on the dye sites in the fiber, and the affinity of direct dyes to *yamamai* silk is increased by addition of such an assistant to dyebath as hydrochloric acid.

Table 23 Ratio of desorbed dye by treatment in boiling water to amount of adsorbed dye

Dye	Raw d.s.	Scoured d.s.	Raw y.s.	Scoured y.s.	Socured y.s (soured)
Benzo Fast Scarlet 4BS (disazo)	14.73	7.19	13.20	47.90	0.00
Chrysophenine G (disazo)	10.53	9.30	26.25	39.95	0.00
Erie Fast Yellow WB (monoazo)	8.24	9.29	10.79	54.25	0.00
Diamine Fast Violet BBN (disazo)	13.39	22.24	19.10	37.15	0.00

Section 2 Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk when using Acid Dyes

The dyeing properties of *yamamai* silk and domestic silk in dyeing with some acid dyes are compared in this section.

Experiment

Materials

The kinds of silk used in this experiment are same as those in Section 1.

The direct affinity of some of acid dyes to silk is examined in the same way as in Section 1. Acid dyes used in this experiment are classified on the chemical structure of dyes and shown in Table 24.

Table 24 Acid dyes used in Section 2

Dyes	CI. No.
Acid Fast Black 8B (disazo)	Acid Black 24
Acid Anthracene Red 3B (disazo)	Acid Red 89
Acid Brown G (disazo)	Acid Orange 24
Acid Violet 5BN (triphenylmethane)	Acid Violet 17
Brilliant Milling Green B (triphenylmethane)	Acid Green 9
Acid Fast Red 6B (monoazo)	Acid Violet 7
Tartrazine (hydroxy-pyrazole)	Acid Yellow 23

Results and Discussion

The amounts of adsorbed dye on silk and the ratios of the amounts of desorption to adsorption of dye are examined, and the results are shown in Table 25 and 26.

Considering the amounts of dye adsorbed on *yamamai* silk and domestic silk comparatively from the view point of chemical structure of dye molecule in Table 25, acid dyes are adsorbed on the fibers in the following order ;

disazo type > triphenyl methane type > hydroxy pirazole type and monoazo type, but monoazo and hydroxy pyrazole type acid dyes appear to have little direct affinity to both kinds of silk.

The differences of amounts of adsorbed dye between *yamamai* and domestic silk are hardly observed.

The ratio of amounts of desorption by the treatment in boiling water to those of adsorption are shown in Table 26. In the case of raw silk, almost equal amounts of adsorbed dye by *yamamai* and domestic silk are desorbed respectively by the treatment in boiling water.

Table 25 Exhaustion of dyebath

Dyes	Raw d.s.	Scoured d.s.	Raw y.s.	Scoured y.s.	Scoured y.s. (soured)
Acid Fast Black 8B	77.42%	57.09%	82.20%	43.80%	100.00%
Acid Anthracene Red 3B	60.89	41.75	57.55	36.50	100.00
Acid Brown G	64.62	38.15	67.51	41.17	100.00
Acid Violet 5BN	43.95	42.45	37.01	34.25	100.00
Brilliant Milling Green B	51.90	46.82	37.99	34.98	99.14
Acid Fast Red 6B	6.97	1.60	4.86	0.65	96.62
Tartrazine	0.54	0	0	0	100.00

Table 26 Desorption of dyes by treatment in boiling water

Dyes	Rae d.s.	Scoured d.s.	Raw y.s.	Scoured y.s.	Scoured y.s. (soured)
Acid Fast Black 8B	2.05%	1.61%	1.81%	68.55%	0.00%
Acid Anthracene Red 3B	5.40	4.03	8.96	76.60	0.00
Acid Brown G	10.32	9.71	7.31	40.28	0.00
Acid Violet 5BN	15.83	9.68	52.68	96.75	0.00
Tartrazine	—	—	—	—	0.00

In the case of scoured *yamamai* silk a large quantity of dye adsorbed is desorbed by the treatment. The results obtained vary with the individual member of acid dyes.

Considering the all results obtained in this experiment, it can be found that acid dye has little direct affinity to fibroin of *yamamai* silk. In the dyeing of *yamamai* and domestic silk, generally, the raw silk adsorbs more dye than the scoured silk does. The differences of amounts of dye adsorbed on *yamamai* silk from those on domestic silk are larger in an azoic acid dyes than in a triphenyl methane type dyes.

It can be assumed that the affinity of azoic type acid dyes to sericin is larger than it of triphenyl methane type acid dyes.

Exhaustion of dyebath by scoured *yamamai* silk increases remarkably by treatment in a hydrochloric acid solution as shown in Table 25.

The desorption of dye from the soured *yamamai* silk by treatment in boiling water is not observed as shown in Table 26.

As seen in the above results, adsorption of acid dyes on the scoured *yamamai* silk is able to be done firmly on the sites by souring process, by which also hand feeling and lustre of the silk are improved.

Section 3 Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk when using Basic Dyes

The comparative studies on dyeing properties of *yamamai* and domestic silk to some of basic dyes are described in this section, and some informations are obtained.

Experiment

Materials

Silk used in this experiment is prepared in the same way as in Section 1.

Some of basic dyes classified from chemical structure of dyes are examined on substantivity to *yamamai* and domestic silk. The dyes used in this experiment are shown in Table 27.

Table 27 Basic dyes used in Section 2

Dyes	CI.
Chrysoidine (monoazo)	Basic Orange 2
Bismark Brown Y extra (disazo)	Basic Brown 1
Malachite Green (triarylmethane)	Basic Green 4
Victoria Blue B conc (triarylmethane)	Basic Blue 24
Rhodamine G (xanthene)	Basic Red 8
Safranine T (azine)	Basic Red 2
Basic Blue GO (thiazine)	Basic Blue 25

Results and Discussion

The exhaustion of dyebath is shown in Table 28.

In Table 28, the relations between exhaustion of dyebath and chemical structure of basic dye are examined. It is found that triphenylmethane type, triazine type and xanthene types are adsorbed more easily than azoic type dyes, such as Chrysoidine, Bismark Brown B, but these differences are not so remarkable as those of direct and acid dyes. In the dyeing with Safranine, *yamamai* silk exhausts dyebath more easily than domestic silk.

Though domestic silk, in general, has larger affinity to basic dyes than *yamamai* silk, the difference of affinity of domestic silk from *yamamai* silk is not so large in basic dyes as in direct and acid dyes.

The ratios of desorption of adsorbed dye to adsorption are shown in Table 29.

Considering the treatment of the dyed silk in boiling water, basic dyes appear to be adsorbed a little more firmly on the silk than direct and acid dyes are adsorbed.

The differences in quantity of adsorbed dyes on raw silk from scoured silk in the dyeing with acid dyes and basic dyes have the same trends, but in the dyeing of direct dyes the trend is found to be various. These are due to the fact that the adsorption of acid and basic dyes are on the specific sites on *yamamai* silk and direct dyes are adsorbed by their substantivity.

The differences of affinity of basic dyes to silk owing to chemical structure of the dyes are not found, though the differences are observed in the dyeing with

Table 28 Exhaustion of dyebath

Dyes	Raw d.s.	Scoured d.s.	Raw y.s.	Scoured y.s.	Scoured y.s. (soured)
Chrysoidine	82.55%	80.51%	72.15%	71.45%	24.30%
Bismark Brown B & G	83.01	83.05	82.89	83.67	37.75
Malachite Green	93.28	97.31	87.25	97.16	40.01
Victoria Blue B conc	98.32	98.06	97.87	95.76	40.52
Rhodamine G	92.24	93.89	88.18	90.21	43.67
Safranine T	83.92	97.14	92.86	98.58	40.32
Basic Blue GO	90.08	95.05	89.25	96.31	28.25

Table 29 Ratio of desorption to adsorption of dye

Dyes	Raw d.s.	Scoured d.s.	Raw y.s.	Scoured y.s.	Scoured y.s. (soured)
Chrysoidine	11.90%	12.62%	19.78%	20.92%	47.25%
Bismark Brown B & G	4.25	3.41	4.96	3.62	25.64
Malachite Green	4.70	2.85	4.41	2.19	78.60
Safranine T	2.01	0.92	1.28	0.91	42.05
Basic Blue GO	4.72	2.51	5.13	2.15	83.25

direct and acid dyes.

It is natural that soured *yamamai* silk in a hydrochloric acid solution adsorbs basic dyes only a little, because hydrogen ions of acid prevent dyes from being adsorbed on *yamamai* silk.

Section 4 Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk when using Azoic Dyes

In order to study the dyeing properties of *yamamai* and domestic silk, the following experiment are examined.

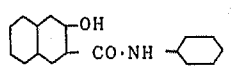
Experiment

Materials

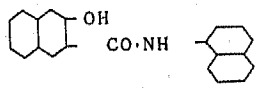
Yamamai silk and domestic silk used in this experiment are prepared by boiling in 0.5% ammonia solution for 3 hr., impurities are removed with warm water, washed completely with cold water and dried. The boiling-off losses of *yamamai* and domestic silk are 19 and 13% respectively.

Azoic dye consists of coupling component and diazo component, but the diazo component has not substantivity to the fiber. In this experiment, adsorption of only coupling component is examined.

Coupling components used in this experiment are Mitsui Naphthozol AS (CI. Azoic Coupling Component 2) and Sekanil AS-BO (CI. Azoic Coupling Component 4), and constitutional formulas are as follows ;



Azoic Coupling Component 2



Azoic Coupling Component 4

The water soluble impurities contained in these dyes are removed by washing several times in warm water.

These dyes are mixed well with Pelex NB and NaOH, and dissolved in hot water. Wetted goods are dyed in dyebath of 50 times on the weight of fiber. The quantity of the dyes adsorbed on the silk is determined colorimetrically with Reitz's Photoelectric Colorimeter.

Results and Discussion

Amounts of adsorbed dye by *yamamai* and domestic silk are shown in Table 30. It is apparent from Table 30 that 1 g of *yamamai* silk adsorbs 186. 7 mg. of Naphthozol AS and 280 mg of Sekanile AS-BO at the maximum, and 1 g. of domestic silk adsorbs 142. 5 mg. of Naththozol As and 240 mg. of Sekanile AS-BO at the maximum. So, *yamamai* silk has better dyeing properties than domestic silk. These results are similar to those of basic dye but differs from these of direct and acid dyes.

Table 30 Adsorption of azoic coupling component on silk (mg/g)

Silk	40°Bé NaOH	Adsorption of dye	
		Naphthoide AS	Naphthide AS-BO
Yamamai	1.50	187	220
	1.85	173	280
	2.10	170	200
Domestic	1.50	100	182
	1.85	120	240
	2.10	143	100

Section 5 Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk when using Chrome Mordant Dyes

In this section, the adsorption of mordant dyes by *yamamai* and domestic silk are examined and the following informations are obtained.

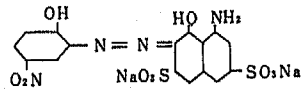
Experiment

Materials and Procedure

Silk used in this section is prepared by the same way as in the preceding section.

Silk is mordanted in a boiling chrome alum solution for 10 min. by Hishiyama-

Sekiguchi's method, after raising the tempreature of the solution to boiling point from 70°C in 20 min. The mordanted silk are steeped in a cold bath of Mitsui Chrome Green F (CI. Mordant Green 17) and the temperature of dyebath is raised to boiling point and silk is dyed at boiling point for 1 hr.



Chrome Green F

The adsorbed amounts of chrome alum and Chrome Green F on silk are determined colorimetrically on the residual solution.

Results and Discussion

The adsorption of alum and dye are examined at various pH and results are shown in Table 31. It is apparent that the amounts of chrome alum adsorbed on domestic silk are much less than those on *yamamai* silk.

Table 31 Adsorption of chrome alum and mordant dye at various pH

Silk	pH	Adsorption	
		Chrome alum (mg/g)	Dye (mg/g)
Yamamai	1.4	39	36
	2.0	79	34
	3.1	90	34
	4.4	77	37
	7.0	45	37
	10.0	90	34
Domestic	1.4	0	32
	2.0	11	29
	3.1	0	28
	4.4	11	27
	7.0	25	26
	10.0	11	25

Amounts of dye adsorbed on *yamamai* silk are more than those on domestic silk at all region of pH examined.

These results are similar to those of azoic dyes.

Section 6 Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk when using Vat Dyes

A. Comparison of Dyeing Properties When Using I N Process.

In the dyeing of silk with vat dyes, indigo and indigo type dyes (which are able to be reduced in a weak alkali solution) are applied to a silk in the same way as in cotton dyeing, but anthraquinone type vat dyes (which must be reduced with a strong alkali) are applied to silk by using surface active agents in the dye vat for the purpose of preventing the silk from damage with strong alkali.

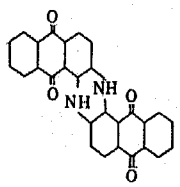
Experiment

Materials and Procedure

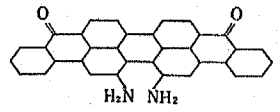
Silk used in this experiment is prepared in the same way as in Section 4.

Table 32 Vat dyes and their molecular formulae used in this experimint

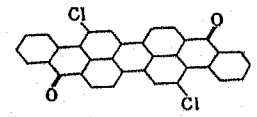
1. Mikethrene Blue RSN (CI. Vat Blue 4)



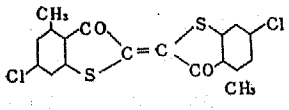
2. Mikethrene Black BBN (CI. Vat Green 9)



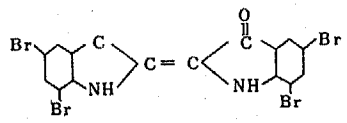
3. Mikethrene Brilliant Violet 2R (CI. Vat Violet 1)



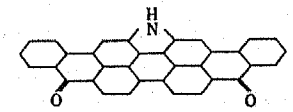
4. Mikethrene Brilliant Pink R (CI. Vat Red 1)



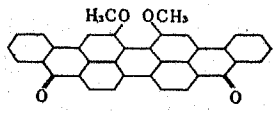
5. Mitsui Tsuya Indigo 2B (CI. Vat Blue 5)



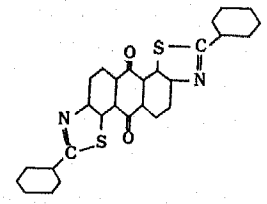
6. Mikethrene Grey 3B (CI. Vat Black 16)



7. Mikethrene Brilliant Green FFB (CI. Vat Green 1)



8. Mikethrene Yellow GCN (CI. Vat Yellow 2)



Vat dyes used in this experiment are shown in Table 32 and water soluble impurities contained in commercial vat dyes are removed by washing them several times in warm water. The dye of 5% (owf) is made into paste with a small quantity of ethanol and glycerine, and sodium hydroxide and water are added to the dye paste to the necessary quantity (liquor ratio is 1 : 50).

The dye is reduced at 60°C by adding sodium hydrosulphite.

Silk is dyed at 45–50°C for 30 min. Pelex NB and 80% (owf) of glaubers salt are added to the dyebath during the dyeing. After dyeing, the quantity of adsorbed dye is determined by the following procedure. A part of the residual solution is dispersed in a dispersing solution (consists of 500 parts of 5% white of egg, 10 parts of 30% hydroperoxide solution, 10 parts of 30° Bé sodium hydroxide and 10 parts of Pelex NB), and the amounts of adsorbed dye on silk are determined colorimetrically.

Results and discussion

The amounts of adsorbed dye by IN process of vat dyeing on *yamamai* and domestic silk are shown in Table 33.

Table 33 Adsorption of vat dyes by IN process (mg/g)

Dye	Adsorption	
	Yamamai silk	Domestic silk
Mikethrene Blue RSN	33.8	51.5
Mikethrene Black BBN	32.7	59.3
Mikethrene Brilliant Violet 2R	28.6	60.9
Mikethrene Brilliant Pink R	25.7	63.8
Mitsui Tsuya Indigo 2B	84.8	93.5
Mikethrene Grey 3B	44.5	56.5
Mikethrene Brilliant Green FFB	23.3	55.4
Mikethrene Yellow GCN	44.3	67.6

It is apparent in Table 33 that independently of the kinds of vat dyes the amounts of dye adsorbed on domestic silk are more than those on *yamamai* silk.

The amounts of adsorbed Tsuya Indigo on *yamamai* silk are very large. This dye, therefore, appears to be suitable for dyeing of *yamamai* silk.

B. Comparison of Dyeing Properties when using Vat Acid Process

In a general method of vat dyeing, dyes are reduced to leuco-compound by using caustic soda and sodium hydrosulphite, and this leuco-compound is used for dyeing. In a vat acid process, after vat dyes are reduced, organic acids such as acetic acid or formic acid are added to alkali leuco-compound in order to neutralize the solution, and free leuco-compound is prepared. But, in fact, a mixed solution of alkali leuco-compound and acid leuco-compound appears to be formed.

Because acid leuco-compound which is prepared in this process, has low intrinsic affinity to fiber and is slightly soluble in water, the leuco-compound must be dispersed in a fine colloidal state by a dispersing agent. This leuco-compound is used for dyeing.

In a vat acid process, vat anions are formed as follows.

$$\rangle C - OH \leftrightarrows > C - O^- + H^+$$

vat acid vat acid anion

Because a vat acid behaves as dye anion, the dye is adsorbed on positive sites on silk.

Experiment

Materials

Silk used in this experiment is prepared in the same way as in Section 5.

Dyes and assistant used in this experiment are shown in Table 34.

Dyes mixed well with ethanol and wetting agents are reduced with 30° Bé sodium hydroxide and sodium hydrosulphite. After dyes are reduced completely, 2.2 parts of glacial acetic acid are added to 10 parts of sodium hydroxide in order to neutralize the leuco-compound, and silk is dyed for 30 min. at 50°C, in a neutral region of pH.

Table 34 Dyes and composition of dyebath

Dye and agent	1	2	3	4
Mitsui Tsuya Indigo 2B (%)	5			
Mikethrene Grey 3B (%)		5		
Mikethrene Brilliant Pink R (%)			5	
Mikethrene Brilliant Green FFB (%)				5
Ethanol (%)	5	5	5	
Pelex NB (1:10) (%)	10	10	10	10
Emal-40 (1:10) (%)	20	20	20	20
NaOH (30° Bé) (%)	10	10	10	10
Hydrosulphite (g/l)	6	6	6	6
Water (times)	50	50	50	50
Reducing temperature (°C)	60	60	60	60

The residual solution after dyeing is oxidized with an oxidizing dispersing agent, and the amounts of adsorbed dye are obtained colorimetrically.

Results and Discussion

Amounts of adsorbed dye on *yamamai* and domestic silk by the vat acid process are shown in Table 35. It is apparent from Table 35 that exhaustion of dyebath on domestic silk is larger than that on *yamamai* silk. Especially, Mitsui Indigo 2B is adsorbed in a large quantity.

Mikethrene Grey 3B is adsorbed on *yamamai* silk comparatively easily. The exhaustion of dyebath varies with the individual member of dyes according to its property and degree of dispersion of the dye.

Table 35 Adsorption of dyes by vat acid process

Dye	Adsorption	
	Yamamai silk	Domestic silk
Mitsi Tsuya Indigo 2B	31.5%	72.4%
Mikethrene Grey 3B	45.1	37.3
Mikethrene Brilliant Pink R	15.2	36.6
Mikethrene Brilliant Green FFB	36.0	49.6

CHAPTER VI DYEING MECHANISM OF *YAMAMAI* SILK

As described above, the composition of protein and fine structure of *yamamai* silk differ markedly from those of domestic silk.

The author has indicated in Chapter V that the dyeing properties of *yamamai* silk also differ from those of domestic silk.

Up to the present, many an information on the dyeing of wool (protein fibre) is found, but reports on the dyeing properies of *yamamai* silk have not been found.

In this chapter, titration curve and amounts of acid to be bound on *yamamai* silk, dyeing mechanism of acid dyes, the effects of neutral salt on acid dyeing, variation of ion concentration in a dyebath, the change of mechanical properties of *yamamai* silk by dyeing, and the effects of ash contained in *yamamai* silk on dyeing properties are described.

Section 1 Titration Curve of *Yamamai* Silk and Amounts of Acid to be bound

It is apparent that the dyeing properties of *yamamai* silk correlate with amounts of acid and basic groups and the groups capable of forming hydrogen bonds contained in *yamamai* silk.

The titration curve of soluble protein and wool keratine have been determined by STEINHARDT et al., and dyeing properties of wool keratine also have been studied by him and many other authors. The titration curve of silk fibroin has been obtained by GLEYSTEEN, HARRIS and HOZYO.

In this section, the titration curve and acid-binding capacity of *yamamai* silk are described.

Experiment

Materials

Yamamai silk used in this experiment is scoured as described above and electrodialyzed in the following condition : scoured *yamamai* silk is electrodialyzed in the vessel with semipermeable membrane of commercial cellophane sheets, at 50 volts for seven days.

The ash content in *yamamai* silk thus purified is 0.16% of the fibre.

Procedure

The sample is steeped in the bath (liquor is 200 times on the weight of fibre) at various pH, and kept at 10–15°C. for 24 hr, and the final pH of the solution is determined.

The quantity of bound hydrochloric acid to *yamamai* silk is determined by titration.

Results and Discussion

The titration curve of *yamamai* silk obtained in this experiment is shown in Fig. 1.

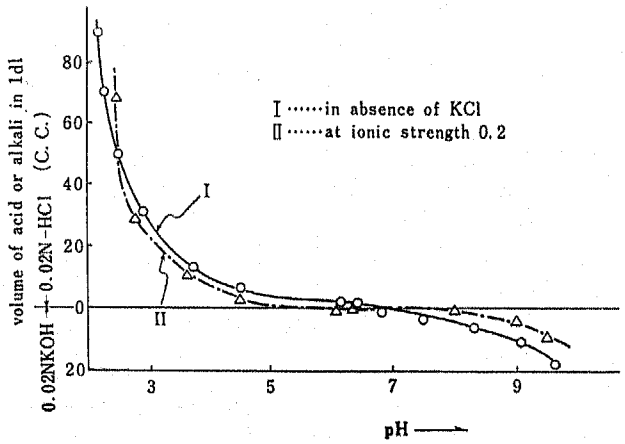


Fig. 1 Titration curve of *yamamai* silk

The ordinate shows the volumes of 0.02 N hydrochloric acid or potassium hydroxide in 100 ml. By curve 1 is indicated the titration curve at ionic strength 0.2, while curve 2 is the titration curve in absence of potassium chloride. A little difference between curve 1 and curve 2 is found at all regions of pH, and at the regions above pH 2.5, adsorptions of hydrogen ions and hydroxyl ions in absence of electrolyte are less than those in presence of electrolyte.

Table 36 Adsorption of hydrochloric acid by *Yamamai* silk

pH	Amounts of adsorption	
	Absence of KCl	Ionic strength 0.2
1.05	0.389	0.356
1.75	0.348	0.315
1.99	0.232	0.206
2.45	0.202	0.125
2.71	0.161	0.070
3.10	0.027	0.055
3.30	0.005	0.040

The quantity of hydrochloric acid adsorbed on *yamamai* silk is shown in Table 36.

It is apparent in Table 36 that the quantity of hydrochloric acid bounded on *yamamai* silk decreases with the decreasing hydrogen ion concentration both in presence and absence of salts.

Section 2 Acid Dyeing of *Yamamai* Silk

The great majority of acid dyes are alkali salts of aromatic sulphonic acids, but a few dyes contain only carboxyl groups and some only phenolic hydroxyl groups. The dyes are a very heterogeneous collection of chemical types and display a wide diversity of behaviour in dyeing. Apart from this, however, it is necessary to observe the phenomena of adsorption on *yamamai* silk of the dyes of simple construction.

This section explains the dyeing properties of *yamamai* silk with acid dyes in the dyebath in which acid and other assistants are cantained.

A. Adsorption of Acid Dyes in Buffer Solution

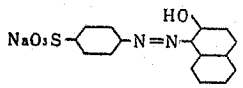
Experiment

Materials

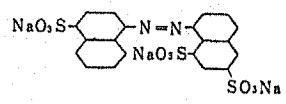
Yamamai silk used in this experiment is prepared in the same way as in Section 1, and the dyes are Orange II and Brilliant Scarlet 3R, shown in the fallowing formulae;

Table 37 Acid dyes used in this experiment

Orange II



Brilliant Scarlet 3R (C.I. Acid Red18)



Clark-Lubs' buffer solutions are prepared as shown in Table 37. *Yamamai* silk is dyed in the dyebath (liquor ratio is 50:1) at 80°C for 1 hr. The dye concentration in the dyebath is 10 m. mole in 1 litre and the quantity of the adsorbed dye is determined colorimetrically with Leitz's Photoelectric Colorimeter.

Results and Discussion

The quantity of the adsorbed dye on *yamamai* silk from the dyebath of buffer solution is shown in Fig. 2.

It is apparent in Fig. 2 that the adsorption of dyes from the buffer solution indicates the maximum at pH 2 in the dyeing with Brilliant Scarlet 3R and Orange II. respectively. In the region above pH 3 the adsorbed amount of the dye increases

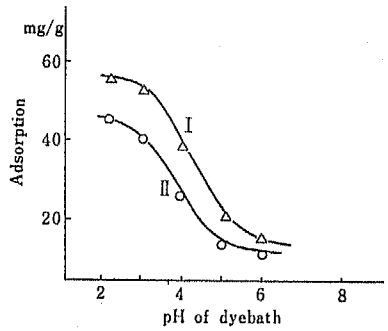


Fig. 2 Adsorption of acid dyes from buffered dyebath
I : Brilliant Scarlet 3R II : Orange II

Table 38 Clark-Lubs' buffer solution

0.1 M potassium biphthalate	0.1 M hydrochloric acid	0.1 M sodium hydroxide	Total volume	pH
50	46.70	—	100	2.0
50	20.32	—	100	3.0
50	—	0.40	100	4.0
50	—	23.85	100	5.0
50	—	45.45	100	6.0

sharply.

B. Adsorption of Acid Dyes in All Regions of pH

Experiment

Materials

Yamamai silk and dyes used in this experiment are the same as in A of this section.

Procedure

Yamamai silk is dyed in the dyebath (dye concentration of the dyebath is 10 m. mole in litre, liquor ratio is 1 : 250) at 60°C for 3 hr. In the acid regions, hydrochloric acid is added into the dyebath and in the alkali regions sodium hydroxide is used. Potassium chloride is used as a neutral salt in this acid dyeing (ionic strength is 0.2).

The quantity of the adsorbed dye on *yamamai* silk is determined colorimetrically on the desorbed solution from the dyed silk with ammonia water.

Results and Discussion

The amounts of the adsorbed dye on *yamamai* silk is shown graphically in Fig. 3. It is apparent from Fig. 3 that at lower pH the adsorption of the acid dyes are very large, at pH 1 1 gr of *yamamai* silk adsorbs 0.55 m. eq. of Orange II and 0.45

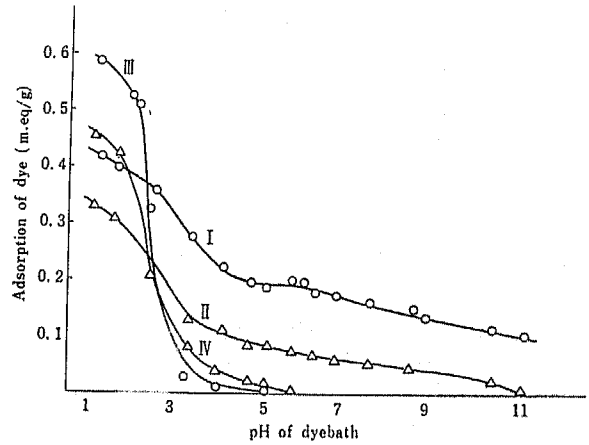


Fig. 3 Adsorption of acid dyes from all region of pH in dyebath
I: Orange II in the presence of electrolyte
II: Brilliant Scarlet 3R in the presence of electrolyte
III: Orange II in the absence of electrolyte
IV: Brilliant Scarlet 3R in the absence of electrolyte

m. eq. of Brilliant Scarlet 3R respectively.

In the case of Curve I and II, the adsorption of the acid dye on *yamamai* silk is comparatively small, when the silk is immersed in an alkaline dyebath in which patassium chloride is contained.

At the regions of pH 5 and 7, constant adsorption of dye takes place, at lower pH than 5 adsorption of dye increases with decreasing pH. But at lower pH than 4 the adsorption increases sharply with decreasing pH. And the slope of curve in the part at lower pH is gentler than that in the part above pH 2.

The adsorption of the acid dyes in the absence of potassium chloride is shown with curve III and IV. In Fig. 3, at higher pH than 5, no adsorption of the acid dyes takes place, but at lower pH than 3 the adsorption of the acid dyes increases sharply.

Considering the types of adsorption curves it can be assumed that the adsorption of the acid dyes takes place not only on amino groups of the silk, but also on amide groups of polypeptide chains of the silk.

The adsorption phenomena of the acid dyes, as described above, is also observed in the case of nylon 66 by PETER, ELÖD and Mc GREW et al: the adsorption of the dye increases until all the end amino groups carry dye ion at comparatively lower pH, but in a strong acid region the adsorption of hydrogen ions takes place accompanied with a great increase in dye adsorption.

The affinity of Orange II to *yamamai* silk in the dyebath in which hydrochloric acid is contained is shown in Table 39.

Table 39 Adsorption of Orange II by *Yamamai* silk from acid dyebath

pH	Dye on fiber (eq/kg)	Dye in solution (eq/1)	Affinity (kg. cal)
1.05	0.586	8.41	10.07
1.75	0.526	1.131	8.89
2.00	0.521	1.151	8.33
2.45	0.508	1.211	8.36
2.71	0.327	2.071	6.98
3.10	0.108	3.141	5.44

The affinity ($-\Delta\mu^\circ$) is calculated by the following equation :

$$-\Delta\mu^\circ = RT\,ln\left[\frac{\theta_D}{1-\theta_D}\right]\left[\frac{\theta_{Na}}{1-\theta_{Na}}\right]^Z - RTln[Na]_\sigma^z[D]_\sigma$$

but, in the case of monobasic dyes, the following equation is used for calculation of affinity,

$$-\Delta\mu^\circ = RTln\left[\frac{\theta_D}{1-\theta_D}\right] - RTln[Na]\sigma$$

where, $\theta_D = n_D/N_D$ (when N_D is the total sites for dye in the fibre and n_D is those sites of N_D which have been occupied by the dye molecules), $[D]\sigma$ and $[Na]\sigma$ are dye ion concentration and sodium ion cnocentration in the dyebath respectively.

It is apparent from Table 39 that the higher affinity can be obtained in the dyebath of lower pH.

Section 3 Effect of Neutral Salts on Dyeing of *Yamamai* Silk

Neutral salts are added in a dyebath as an accelerating agent, a retarding agent, or a levelling agent according to a dyeing method.

In direct dyeing of cellulose fibre, neutral salts are active in depressing the surface potential and they are used as an accelerating agent. Retarding agent are generally used for levelling dyeing.

The author investigates into the effect of neutral salts on the acid dyeing of *yamamai* silk.

Experiment

Materials

Yamamai silk used in this experiment is prepared as in Section 1. Ash content in the silk is 0.16%.

Procedure

Dyed *yamamai* silk in the condition of Table 40 is immersed in ammonia water and the adsorbed dye is dissolved out and is determined colorimetrically with A. K. A. Type Photoelectric Colorimeter.

The constitutional formula of Alizarine Saphirol SE (CI. Acid Blue 43) is as follows.

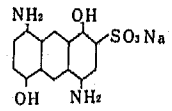


Table 40 Dyes and condition of dyeing

Dye	pH	Concentration of NaCl	Temp.	Time
Orange II	1.0, 2.0, 3.0	1.0, 0.5, 0.05, 0	60°C	3 hr
Brill. Scarlet 3R	2.0, 3.0, 4.0	〃	〃	3
Alizarine saphirol SE	〃	1.0, 0.4, 0.1, 0	70°C	2

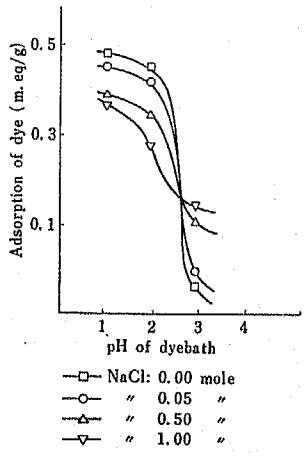


Fig. 4 Adsorption of Orange II in the presence of NaCl

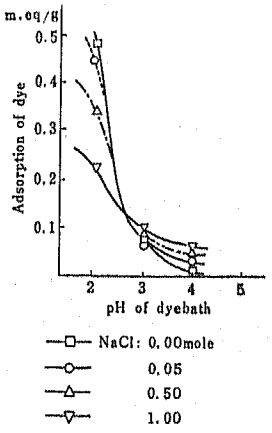


Fig. 5 Adsorption of Brilliant Scarlet 3R in the presence of NaCl

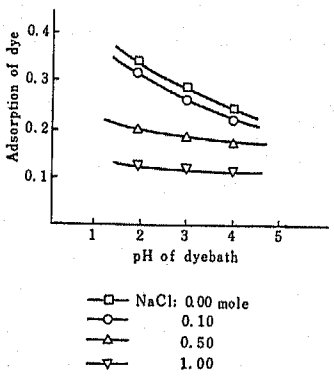


Fig. 6 Adsorption of Alizarine Saphirol SE in the presence of NaCl

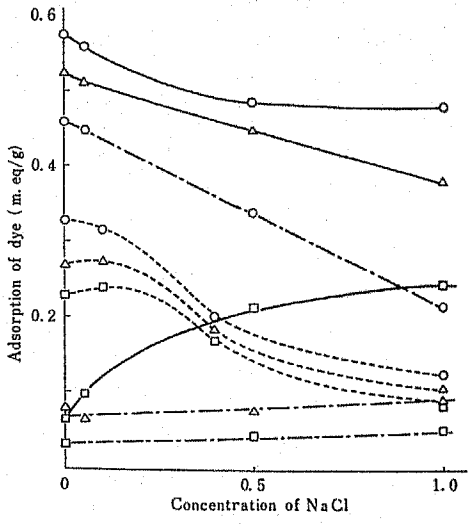


Fig. 7 Effect of electrolyte on adsorption of dyes

Results and Discussion

The effects of neutral salts on the dyeing properties of *yamami* silk are illustrated in Fig. 4, 5, 6, and 7.

Fig. 4, 5 and 6 suggest that marked differences in the effects of neutral salts are found in the behaviours of Orange II, Brill. Scarlet 3R and Alizarine Saphirol SE.

In dyeing of *yamamai* silk with Orange II and Brill. Scarlet 3R in the dyebath, in which neutral salts are contained, increasing electrolyte concentration produces considerable decreases of dye adsorption at a lower pH, but above a critical pH (2.5~3.0) the reverse effect takes place. However, in dyeing with Alizarine Saphirol SE, a critical pH is not found and increasing electrolyte concentration remarkably decreases in dye adsorption in all regions of pH.

The relations between up-take of acid dyes and concentration of electrolyte at each pH are illustrated in Fig. 7.

In the dyeing of protein fibre with acid dyes, when a neutral salt is added in the dyebath, concentration of anion in the dyebath increases with increasing electrolyte concentration. The increase of other anions than dye anions is considered to lead to the displacement of dye from the fibre.

The displacement of the dyeing equilibrium by the addition of salts is explained by ELÖD on the Donnan theory as being due to the reduction in the membrane potential and the consequent equalisation of the ionic concentrations inside and outside the fibre.

On the electrical theory this is attributed to the fact that the equilibrium position of the displacement reaction is governed not only by the concentration of the two competing ions but also by their relative affinities to the fibre.

By K. KANAMRO, ζ-potential of silk in an acid solution decreases sharply about pH 3, and at pH 4 ζ-potential indiciates negative. From this fact it is considered that the adsorption of acid dye anion on the silk decreases according as the decreasing of ζ-potential and no adsorption of dye anion may be produced in the region of negative potential.

However, adsorption of acid dye takes place due to hydrogen bonds or other binding power when neutral salts are added in the dyebath.

Section 4 Mechanism of Acid Dyeing Process of *Yamamai* Silk

In general dyeing various assistant are used in the dyebath. In acid dyeing of protein fiber, for example, acids, neutral salts and surface active agents are added in the dyebath.

It is considered to be important that the examination of the behaviour of each assistant contained in the dyebath is necessary to study on the adsorption mechanism of acid dyes.

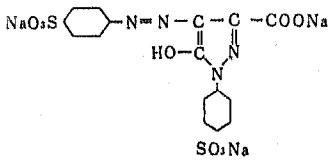
In this section, the changes of ionic concentrations of Cl', H^+, and dye anion in the dyebath during dyeing are examined and some informations obtained are described.

Experiment

Materials

Yamamai silk used in this experiment is purified in the same way as described in Section 1.

Dye applied on *yamamai* silk is Tartrazine NS conc. (C. I. Acid yellow 23) and its formula is as follows.



Procedure

Yamamai silk is immersed in the dyebath kept at 40±1°C. (liquor ratio is 250 times) in which hydrochloric acid (0.01 mole in 1 litre) and the dye (0.002 mole in 1 litre) are contained. The concentrations of H^+, Cl' and dye anion are determined at various times.

The concentration of chloride ion is determined by the titration method with silver nitrate (potassium chromate is used as an indicator). The hydrogen ion concentration is determined with potassium hydroxide (cresol purple is used as an indicator). The dye concentration is determined colorimetrically.

Results and Discussion

The ionic concentration of chloride, hydrogen and dye are shown in Fig. 8, from which it can be seen that the first change of the ionic concentrations consists in the almost simultaneous adsorption of hydrogen and chloride ions.

The chloride ions adsorbed on *yamamai* silk comparatively quickly, and after reaching the maximum adsorption in 30–40 min., they desorb slowly, and the chloride ion concentration is restored to the first stage of dyeing.

The hydrogen ions are adsorbed on *yamamai* silk until an equilibrium is preserved.

The dye ions are adsorbed very slowly on *yamamai* silk and the dye concentration in the dyebath decreases to 1/2 of the first dye concentration, and the dye ion concentrations on *yamamai* silk and in the dyebath attain an equilibruim in 5 hr.

From the results described above, in early stage of dyeing, chloride ions, which have faster rate of diffusion than dye ions, are adsorbed on positively charged

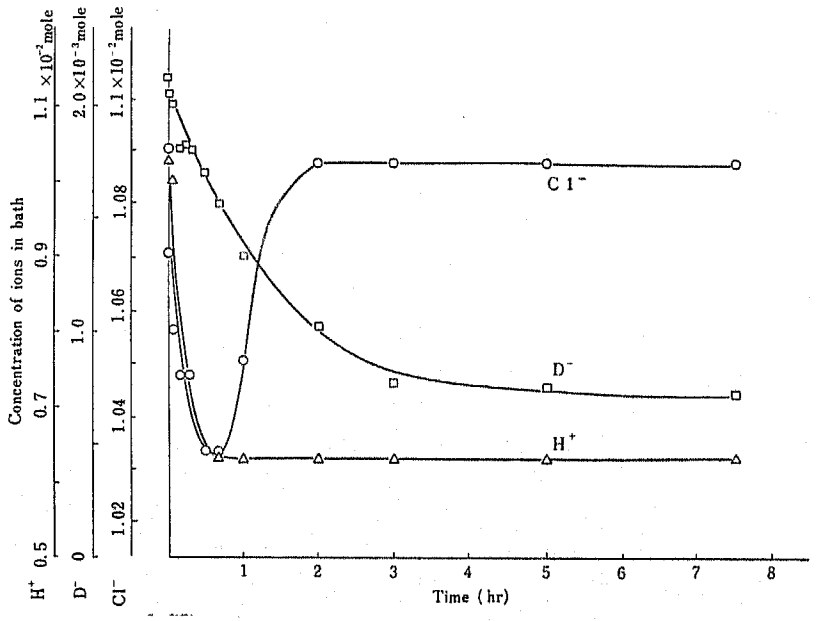


Fig. 8 Change of ionic concentration in dyebath

basic sites on *yamamai* silk, and the dye ions are able to displace chloride ions because the dye ions have a greater affinity to positively charged basic sites than chloride ions have.

Section 5 Relations between Amounts of Dye adsorbed on *Yamamai* Silk and Breaking Strength

As a fibre has a constant affinity to a particular dye, a limited amount of dye is adsorbed on the fiber independently of the type of bond between the dye and the fibre. In dyeing of silk fibroin with acid dye, dye ions are adsorbed on positively charged end amino groups of the fibroin, and the amount of dye which saturates all the amino groups is thought to be the saturation value of the fibre. In strong acid regions, however, hydrogen ions are adsorbed on weakly basic amide groups, and the sites for acid dyes are formed. In these conditions, acid dyes are adsorbed on the sites which are formed by adsorption of hydrogen ions, and the amount of adsorbed dye is larger than the amount of end amino groups in the silk, and these phenomena are defined as "over dyeing".

It may be natural that the physical properties of the silk which has been over dyed are affected by the dyes markedly. In this section, the effects of over dyeing on the tensile strength and elongation of *yamamai* silk are studied.

Experiment

Materials

Yamamai silk used in this experiment is prepared by the same way as in Section 1.

Procedure

Yamamai silk is dyed with Orange II at 70°C for 1 hr., and the amount of adsorbed dye on the silk is determined colorimetrically on the desorbed solution with ammonia water.

The tensile strength and the elongation of *yamamai* silk dyed with Orange II are determined with K. S. Type Senimeter.

The number of samples required for the determination can be decided by the following equation from the results of the preliminary experiment.

$$n = \frac{t^2 \cdot S^2}{(x-m)}$$

Where, m and $\bar{x}$ are the mean value of population and measured value respectively, and s is defined as the following equation,

$$s = \sqrt{\frac{1}{n-1}\sum(x_1-\bar{x})^2}$$

where, t is the quantity indicated in Student's Distribution. In this experiment, t is 2.033 at 95% of confidence coefficient.

Samples which are more than 32 are necessary to determine the breaking strength of the silk in order that the mean value of population is between +0.70 and −0.70 at 95% of confidence limit, and samples more than 25 are necessary to determine the elongation of *yamamai* silk. 40 samples of *yamamai* silk, therefore, are used to determine the breaking strength and the elongation of *yamamai* silk.

When it is assumed that the breaking strength and elongation obtained by using K. S. Type Senimeter indicate a normal distribution, the value of sample population is obtained presumably, with 95% of confidence limit, by the following equation,

$$m = \bar{x} + \left(\pm \frac{s}{\sqrt{n}} t\right)$$

Then the verification of significance is determined by the following equation.

$$t = \frac{\bar{x}-\bar{y}}{w}\sqrt{\frac{n}{2}}$$

where, w is the standard deviation of two values to be examined, $\bar{x}$ and $\bar{y}$ are mean values of the samples respectively.

Results and Discussion

The effects of dye concentration in *yamamai* silk on the breaking strength and on the elongation of *yamamai* silk are indicated in Table 41 and in Fig. 9.

Table 41 Effect of adsorbed dye on breaking load and elongation of *Yamamai* silk

Amount of adsorbed dye	Braking load	Elongation
0.085	14.59±0.59 g	21.3± 5.6
0.225	14.27±0.62	14.6± 5.9
0.326	14.73 0.51	18.7± 4.8
0.356	14.06 0.36	17.3± 6.2
0.382	13.75±0.42※	10.3± 4.8※※
0.402	13.27±0.57※※	4.0± 4.6※※
0.405	12.53±0.42※※	3.6± 3.8※※
0.405	11.98±0.49※※	1.0± 3.3※※
0.418	11.87±0.48※※	0.5± 3.2※※
0.0	14.62±0.53	21.6± 5.2

note: ※ and ※※ are sgnificant at 5% and 1% of level of significance

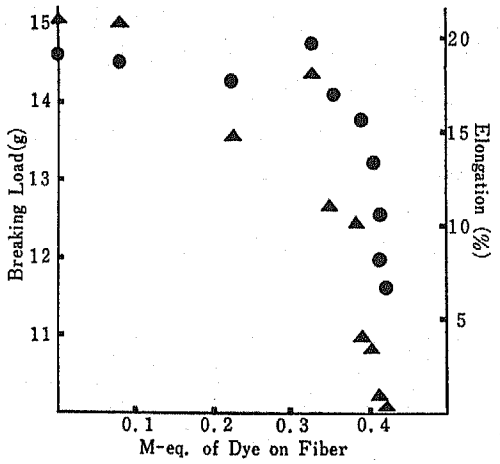


Fig. 9 Effect of dye concentration on *Yamamai* silk on breaking properties
● Breaking load, ▲ Elongation

From Tabb 41, and Fig. 9, it is apparent that the strength and the elongation of *yamamai* silk which has adsorbed more than 0.35 M-eq/g of dye drop sharply, and the fibre is damaged remarkably.

The dye concentration at which the fibre begins to be damaged is not always definite, but the concentration appears to be saturation concentration of end amino groups of the silk.

From these results, it is better for *yamamai* silk not to be dyed more than 0.35 M-eq/g.

Section 6 Effect of Ash in *Yamamai* Silk on Dying Properties

Generally, a large quantity of ash is contained in *yamamai* silk, and in these ashes calcium, potassium, natrium, magnesium etc. are contained.

The ash contained in *yamamai* silk appears to affect the dyeing properties of *yamamai* silk markedly. It has long been known that the ash contained in cotton affects the dyeing properties of the fibre.

In this section, *yamamai* silk, in which ash is removed by an electrodialysis method and by the treatment with hydrochloric acid, is dyed with acid and basic dyes, and the effects of ash on dyeing properties of the fiber are examined.

Experiment

Materials

Yamamai silk used in this experiment is scoured in 0.3% ammonia water (30 times on the weight of fibre), washed well in warm water and cold water. Sericin removed in this scouring is about 13% in weight. This silk is Sample III.

The purified silk by electrodialysis method is Sample I.

The silk of Sample II is prepared by the following method. *Yamamai* silk is steeped in 1/10000 N hydrochloric acid solution (pH=4.0) until pH of this solution is kept constant. Washing of acid treated silk is repeated until pH of distilled water after washing is kept constant and chloride ions are not detected in the waste water. In this procedure, it is expected that the matters soluble in a hydrochloric acid solution and exchangeable cation are removed in the solution. This is Sample II. Ash contents of Sample I, II and III are shown in Table 42.

Tabel 42 Ash contents of sample

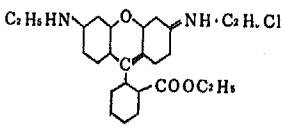
Sample	Ash content (%)
I	0.16
II	0.07
III	1.24

Procedure

In the buffered dyebath (liquor ratio is 1 :200) 200 mg of *yamamai* silk is dyed at 60°C for 1–1.5 hr. The concentration of dye adsorbed on the fibre is determined colorimetrically with Leitz's Photoelectric Colorimeter.

Dyes used in this experiment are Orange II, Brilliant Scarlet 3R, and Rhodamine 6GCP (CI. Basic Red 1 indicated as follows).

Rhodamine 6GCP



The composition and pH of Clark-Lubs' buffer solution is shown in Teble 43.

Table 43 Clark-Lubs' buffer solution

Composition	pH
0.2M-KCl 50ml+0.2M HCl 97.0ml·····200ml	1.0
0.2M-KCl 50ml+ 0.2M-HCl 10.6ml ·····200ml	2.0
0.1M-KH phthalate 50ml+0.1 m-HCl 20.32ml·····100ml	3.0
0.1M-KH phthalate 50ml+0.1 m-NaOH 0.40ml ·····100ml	4.0
0.1M-KH phthalate 50ml+0.1 m-NaOH 23.85ml ·····100ml	5.0
0.1M-KH_2PO_4 50ml+0.1M-NaOH 5.70ml·····100ml	6.0
0.1M-KH_2PO_4 50ml+0.1M-NaOH 29.63ml ·····100ml	7.0
0.1M-KH_2PO_4 50ml+0.1M-NaOH 46.80ml ·····100ml	8.0
0.1M-H_3BO_3 / 0.1M-KCl } 50ml+0.1M-NaOH 21.30ml·····100ml	9.0
0.1M-H_3BO_3 / 0.1M-KCl } 50ml+0.1M-NaOH 43.90ml·····100ml	10.0

Results and Discussion

The results obtained in this experiment is shown in Table 44, Fig. 10, Fig 11. and Fig. 12.

Adsorption of acid dye in the acid dyebath by protein fiber is presumed to take place as follows.

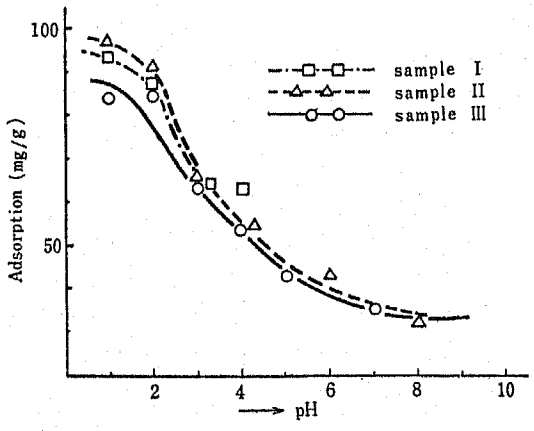


Fig. 10 Adsorption of Orange II

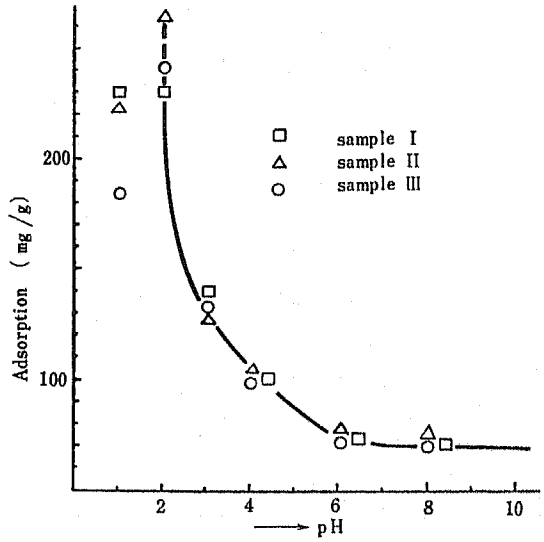


Fig. 11 Adsorption of Brilliant Scarlet 3R

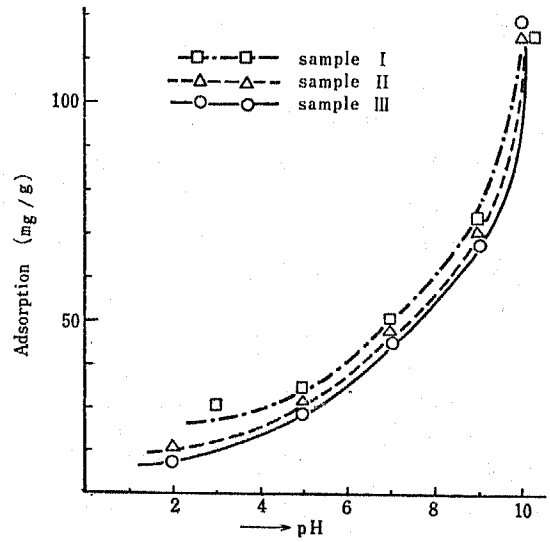


Fig. 12 Adsorption of Rhodamine 6GCP

$$\begin{array}{l} NH_3^+ \\ | \\ F \\ | \\ COO^- \end{array} + H^+ \rightarrow \begin{array}{l} NH_3^+ \\ | \\ F \\ | \\ COOH \end{array} + Cl' \rightarrow \begin{array}{l} NH_3Cl \\ | \\ F \\ | \\ COOH \end{array} + D^- \rightarrow \begin{array}{l} NH_3D \\ | \\ F \\ | \\ COOH \end{array} + Cl'$$

where, $^+H_3N\text{-}F\text{-}COO^-$ and D^- are charged protein fiber and dye ion respectively. Principally, acid dyes are adsorbed on basic groups in the fibre, such as amino and

Table 44 Adsorption of dye and ash content (mg/g)

	Orange II	Brill. Scarlet 3R	Rhodamine 6GCP
I	309.37	846.98	267.20
II	309.21	877.08	259.10
III	287.40	808.76	257.93
pH	1, 2, 3, 4	1, 2, 3, 4, 5, 6, 7, 8	5, 6, 7, 8, 9, 10

The quantity indicated above is the sum of the quantities of adsorbed dye at each pH

amide groups.

In Fig. 10, the relations between pH of dyebath and concentration of dye adsorbed on *yamamai* silk are indicated. It can be seen that the difference of adsorption among Sample I, II and III are smaller in the higher than pH3, but they are larger in the lower regions than pH3. Fig. 10 indicates that *yamamai* silk in which ash is removed by the electrodialysis method and the hydrochloric acid treatment, adsorbs more dye than the nontreated silk. The same results are seen in Fig. 11 in the case of Brilliant Scarlet 3R.

The adsorption of Rhodamine 6GCP in the all regions of pH is shown in Fig. 12. In the lower region than pH 7, adsorption of dye is smaller, but adsorption of Rhodamine 6 GCP increases with the increase of pH. The adsorptions of Rhodamine 6 GCP by Sample I and II are larger than the adsorption by Sample III.

The forms of cationic ash contained in *yamamai* silk are examined by the following two hypothesis : The first is that cationic ash combines with the end carboxyl groups of the protein, and the second is that cationic ash combines with an organic or inorganic acid in *yamamai* silk contained as impurities, and does not combine with protein itself.

The quantity of a levelling acid dye adsorbed on basic groups in the fiber is almost equivalent to the quantity of basic groups and is independent of the cationic ash which may combine with carboxyl groups of protein.

As already described, acid-binding capacity of *yamamai* silk is 0.23 m. eq/g, and almost the same quantity of carboxyl group is supposed to be contained in *yamamai* silk. About 70% of ash is CaO, and assuming that the carboxyl groups form salt with Ca, the quantity of contained calcium is much larger than the twofold quantity of carboxyl groups.

Some organic acids seperate from *yamamai* silk by electrodialysis, and these organic acids are supposed to be formed into some salts with cationic ash. It is not adquate, therefore, to consider that the cationic ash combines with only end carboxyl groups of protein.

As the second hypothesis, nearly all the portion of cationic ash in *yamamai* silk is assumed to be combined with organic or inorganic acid contained in the silk as

impurities. Now, assuming that the total quantity of cationic ash is calcium, and that the calcium is contained as calcium oxalate in the fiber, the contents of salts in the fibers of Sample I, II and III are 0.37, 0.16 and 2.83% respectively. Assuming that the levelling acid dye combines with only silk protein, the correct amounts of dye adsorbed on the fibers of Sample I, II and III are shown in Table 45.

Table 45 Correct adsorption of Orange II (mg/g)

pH \ Sample	I	II	III
1	94.20	97.66	86.67
2	86.64	91.08	87.42
3	65.06	66.33	65.26
4	64.62	54.62	56.42
Total	310.52	309.69	295.77

From Table 45, it is apparent that the difference of adsorptions between Sample I, II and III decreases very markedly.

According to MIMUROTA and SAKAGUCHI, however, Ca is the cationic ash which has the smallest atomic weight, and oxalic acid is the organic acid which is the smallest in molecular weight of the acids contained in *yamamai* silk.

Assuming that ash with average molecular weight of 200 is contained in *yamamai* silk, the contents of ash contained in Sample I, II and III are 0.57, 0.25 and 4.43% respectively.

The adsorption of Orange II, Brilliant Scarlet 3R and Rhodamine 6GCP by silk protein of Sample I, II and III are shown in Table 46.

Table 46 Correct adsorption of Orange II (mg/g)

Sample	Orange II	Brill. Scarlet 3R	Rhodamine 6GCP
I	311.53	851.00	268.47
II	310.10	876.90	259.83
III	300.63	846.39	269.93

From Table 46, the differerences among Sample I, II and III decrease markedly.

From these results described above, the great majority of cationic ash con tained in *yamamai* silk is supposed to be combined with an organic or inorganic acid contained in the silk as impurities and not to be combined with end carboxyl groups of the fibroin.

CHAPTER VII CONCLUSION

The bleaching of *yamamai* silk, the relation between the adsorption of dye and various pretreatment, the comparison of the dyeing properties of *yamamai* silk with those of domestic silk, and the mechanism of dyeing of *yamamai* silk have been studied. Summaries of these results are as follows.

Chemical Composition of *Yamamai* Silk

The results obtained are as follows :

(1) The chemical resistance of *yamamai* silk is larger than that of domestic silk.

(2) *Yamamai* silk is composed of 47.18% of carbon, 29.67% of oxygen, 16.85% of nitrogen and 6.30% of hydrogen.

The total nitrogen is 16.48%, and soluble nitrogen and insoluble nitrogen are 15.79 and 11.70% respectively.

(3) The constitution of the ash which is contained in *yamamai* silk is as follows: CaO, Na_2O, K_2O, MgO, SO_3, P_2O_5, SiO_2, Fe_2O_3, Cl and Al_2O_3 are 70.01, 8.89, 8.43, 4.25, 2.86, 2.47, 2.36, 0.31, 0.28 and 0.14%.

Bleaching of *Yamamai* Silk

(1) The greenish yellow matters can be bleached completely with sodium hydrosulphite as white as domestic silk.

The oxidizing bleaching agents cannot bleach *yamamai* silk, and damages the silk markedly.

(2) The scouring of *yamamai* silk is found to be possible with success by using a steaming method, and the boiling-off loss is 17% in weight.

(3) *Yamamai* silk scoured with the solution of 10% sodium hydrosulphite is not damaged at all in strength and elongation, but the hydrogen peroxide solution damages the silk markedly.

On Various Pretreatment and Dye Adsorption of *Yamamai* Silk

A. Effect of Acid Pretreatment

(1) Among the weight losses by the pretreatment with HCl, H_2SO_4, acetic acid, oxalic acid and formic acid are found to be variously different according to the concentration of each acid.

(2) The amount of dye adsorbed on the pretreated *yamamai* silk with acetic acid is smaller, but that of dye adsorbed on the pretreated *yamamai* silk with formic acid or hydrochloric acid is larger.

Yamamai silk, pretreated with Scourol-100 only, adsorbs only a little dye.

The most suitable concentration of acid for the pretreatment of *yamamai* silk is 0.5% acid.

The souring process of *yamamai* silk with a cold acid solution or a boiling acid solution is found to be effective for an increase of dye adsorption.

(3) The adsorption of dyes on *yamamai* silk is found to be increase markedly by the treatment with both of Scourol-100 and hydrochloric acid.

(4) The process of alkali pretreatment is ineffective for the improvement of dyeability of *yamamai* silk, but the adsorption of alkali-treated silk is increased markedly by the treatment in an acid solution.

(5) The souring process after scouring is an effective process for the adsorption dye on *yamamai* silk, and improves the hand feeling and the lustre of the silk, and the process produces the rustling of silk.

B. Relation between Adsorption of Dyes and Physico-chemical Conditions of Dyebath

(1) The most suitable temperature of the dyebath for the dyeing of *yamamai* silk with acid dye is found to be 80°C.

For practical purposes, the dyeing must be begun from 50°C, and continued fully for a while at 80°C because dyeing is apt to be unlevelling.

It is recommended that *yamamai* silk is dyed at the most suitable condition of 80°C, in the dyebath of 30 times on the weight of fibre.

Comparison of Dyeing Properties of *Yamamai* Silk with Those of Domestic Silk

(1) As the results of the studies with direct dyes, dye of trisazo type is more adsorbed on *yamamai* silk than that of disazo type.

It is found that raw *yamamai* silk has higher affinity to direct dyes than raw domestic silk, and the exhaustions of dyebath by raw *yamamai* silk and by raw domestic silk are larger than those of scoured of both kinds.

In the boiling water treatment, direct dyes adsorbed on *yamamai* silk are desorbed more easily than those adsorbed on domestic silk. This result means that the dyes adsorbed on domestic silk are combined more firmly with the dye sites than those adsorbed on *yamamai* silk.

The *yamamai* silk soured with hydrochloric acid adsorbs a large quantity of direct dyes, and no desorption are observed with the boiling water treatment.

(2) In the adsorption of acid dyes with direct dyeing on both *yamamai* and domestic silk, disazo type acid dyes indicate the greatest exhaustion of dyebath.

The direct affinities to the both kinds of silk are not found in monoazo and hydroxypirazole type acid dyes. The raw silk of both the kinds adsorbs more quantity of acid dyes than the scoured silk.

Little differences in the quantity of adsorbed dye with chemical structure are found in scoured *yamamai* silk, and the dyes adsorbed on soured *yamamai* silk do not desorb with hot water at all. The souring process is very useful process for practical purposes because of the improvement of the hand feeling and the lustre of the silk.

(3) As results of the comparison of the dyeing properties of *yamamai* silk with those of domestic silk with basic dyes, it is found that the differences in the adsorption of dyes owing to the differences in chemical structure of dyes are larger in triphenyl methane type than those in azo type basic dyes. But these differences are not so large as in direct and acid dyes.

Generally, the quantity of dye adsorbed on domestic silk is larger than that of adsorbed dye on *yamamai* silk.

The quantity of desorption of basic dyes adsorbed on *yamamai* silk by the treatment of boiling water is smaller than that of acid dyes.

Raw silk adsorbs more basic dyes than scoured silk. The soured *yamamai* silk in a hydrochloric acid solution adsorbs basic dyes only a little, because hydrogen ions of acid prevent dyes from being adsorbed on *yamamai* silk.

(4) In the dyeing with azoic dyes, Naphthoide AS and Naphthoide BO, *yamamai* silk adsorbs more dye than domestic silk.

(5) In the dyeing with chrome mordant dyes, the adsorption of chrome alum and dyes is independent of pH in the dyebath, and the quantity of adsorbed dyes on *yamamai* silk is larger than that on domestic silk in all region of pH. And it is found that chrome alum is adsorbed easily on *yamamai* silk. Chrome mordant dyes are excellent dyes for the dyeing of *yamamai* silk.

(6) As the results of the comparison of the dyeing properties of *yamamai* silk with those of domestic silk by the using IN process of vat dyes, it is found that domestic silk adsorbs more dye than *yamamai* silk does.

The quantity of adsorbed dye varies according as the kinds of vat dyes, the structure and the dispersibility of dyes.

(7) In the dyeing with vat acid process of vat dyes, the quantity of adsorbed dye on domestic silk is larger than that on *yamamai* silk.

Dyeing Mechanism of *Yamamai* Silk

The following results are obtained by studying the dyeing mechanism of *yamamai* silk.

(1) The quantities of acid bound on *yamamai* silk in all region of pH in the absence of electrolyte and ionic strength 0.2 are determind.

The acid bound on *yamamai* silk increases sharply according as the decreasing pH under 3.0, and the quantity of bound acid decreases in accordance with the increase of pH above pH 3.0.

(2) The adsorption of Orange II and Brilliant Scarlet 3R on *yamamai* silk in presence of acid and electrolyte is determined. In the dyeing of these dyes, the increase of electrolyte concentration produces a considerable decrease in the dye adsorption at lower pH values than pH 3, but above a critical pH 3.0, the reverse effect takes place. At pH 1.0, 1 gr of *yamamai* silk adsorbs 0.55 m.eq. of Orange

II and 0.45 m.eq. of Brilliant Scarlet 3R respectively. From these facts, levelling acid dyes are supposed to be adsorbed not only on the end amino groups in the silk, but also on other dye sites in the silk.

(3) Affinity of Orange II to *yamamai* silk is determined; affinity at pH 1.05 and at pH 3.10 are −10.07 and −5.44 Kg. Cal.

(4) A normal acid dyebath contains a mixture of hydrogen ions from the acid, sodium ions from both dye salt and some added electrolyte, and dye anions and other anonis from the added acid and electrolyte.

When silk is placed in the dyebath, all kinds of ions are adsorbed on *yamamai* silk by their intrinsic affinities to the silk.

From the above results it can be assumed that the first adsorption consists in almost simultaneous adsorption of hydrogen and chloride ions. An equilibrium of the hydrogen ions is quickly attained. After the chloride ions have reached the maximum adsorption, these ions leave the fibre owing to the adsorption of dye ions.

The chloride ions are considered to be substituted by the dye anions.

(5) The relations among the breaking load, the elongation and the amounts of adsorbed dye on *yamamai* silk are examined.

When *yamamai* silk adsorbs acid dye more than 0.35 m.eq/g the silk is damaged remarkably.

(6) The effects of ash, which is contained in *yamamai* silk, on the dyeing properties are examined. *Yamamai* silk, which contains less ash, adsorbs more dye than the silk which contains more ash.

From these facts the following important conclusion is drawn: the great majority of cationic ash contained in *yamamai* silk is considered to be combined with organic or inorganic acids contained in the silk as impurities and not to be combined with end carboxyl groups of the silk.

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