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Comparative Degumming Effects of Detergents on Silk Twill

Yong Woo Lee, Anna Bianchi Svilokos* and Giuliano Freddi*
Sericultural Experiment Station, Rural Development Administration, Suwon, Korea
*Stazione Sperimentale per La Seta, Milano, Italy

絹織物에 대한 化學精練劑의 精練效果 比較研究

李龍雨 · A.B. Svilokos* · G. Freddi
農村振興廳蠶業試驗場 · *이태리 絹業 試驗場

摘 要

絹織物의 精練에 있어서 관행 精練劑인 비누와 이태리 絹織業界에서 사용되고 있는 3種의 화학정련제를 비교 시험하였다.

精練 견직물의 强伸度와 染色性은 비누 精練과 화학정련제 간에 차이가 없었으나 絹纖維質의 變性과 관련되는 粘度 및 아미노기(—NH_2) 함량은 비누정련견이 화학정련제 정련견에 비하여 약간 증가 및 감소되었으며 表面 微細構造에 있어서는 비누 精練絹이 비교적 불순물의 殘溜가 적었고 3종의 화학정련제 중에서는 정련제 "S"에 의한 精練絹에 불순물의 殘溜가 가장 적게 보였다.

Introduction

The minimizing of degradation of silk fibre is not to be too much emphasized in the processes of silk degumming, dyeing and finishing. It has been also an inevitable fact that silk fibre is subjected to be considerably degradaded by the degumming conditions, especially degumming agent. But, recently, soap as only one traditional degumming agent has been replaced by some chemical detergents for continuous degumming process in major silk industrial companies.

Concerning to the chemical detergents for silk degumming, a series of studies have already been done by the authors〔Freddi&Bragadin, Knott&Freddi and Bianchi&Previato〕

The degradation of degummed silk fibres was discussed through examining both tensile strength and intrinsic viscosity of the silk fibres which were degummed with several chemical detergents and an enzymatic agent〔Pancrirolli&Bianchi〕

It was disclosed that the silk fibre could be more degradaded by some chemical detergents, as compared with the traditional soap degumming. 〔Bianchi & Previato〕

In this works, the comparative effects of some chemical detergents in industrial use were studied about not only tensile strength and intrinsic viscosity but also the dyeability of degummed silk fabric and fine structures of it's surfaces.

Experimental

Materials

The sample fabric of silk was described as the following textures:

—fabric weight; 82 grams per m^2.

—number of yarns per width cm;

warp, 3plies(44.1 denier)×50

weft, 4plies(63.5 denier)×42

—number of twists per meter of yarn length;
warp S 130 t.p.m., weft Z 110 t.p.m.

Four kinds of degumming agents were examined; neutral soap made from olive oil fats as the control and three detrergents("I", "J", "S") commonly used in industry

Degumming Methods

For three detergents we followed the degumming conditions recommended, respectively, by the producers. The conditions for degumming the sample silk twill were summarized as follows;

—Detergent "I"
concentration of detergent: 8g/*l*,
sodium carbonate as auxiliary agent; 2g/*l*
temperature; 95~98°C, time; 45 minutes
bath ratio; 1:40

—Detergent "J"
concentration of detergent; 7g/*l*
sodium carbonate as auxiliary agent; 2g/*l*
temperature; 95°C, time; 60 minutes
bath ratio; 1:40

—Detergent "S"
concentration of detergent; 8g/*l*
temperature; 98°C, time; 40 minutes
bath ratio; 1:40

Test Procedures

—Degumming loss:

By measuring the conditioned weights of the fabric samples in pre and post degumming processes after leaving them in the air conditioned room(temperature 20±2°C, R.H. 65±2%) for longer than 48 hours

—Tensile strength:

Breaking load and elongation of warp and weft yarns taken from the sample fabrics with twenty replications each treatment were measured by Instron (High Wycombe 1122)

—Determination of intrinsic viscosity:

According to standard SNV 195595 with lithium bromide (LiBr) solution (Schweizerische Normen-Vereinigung)

—Determination of free amino groups:

Via Spectrophotometry using a UV-visible Spectrometer (Beckman DU-8): Nynhydrin method (Knott et al 1981)

—Dyeing

Fabric samples, weighing 8 to 9 grams, were dyed in liquors having the following composition (the values are referred to silk weight)

C.I. Acid Blue 90 : 3%
(Cianina SandolanN-G)
Na_2SO_4 : 5%
dispersant(LyogenMS) : 1%
pH value : 5-6 (adjusted with 80% acetic acid)

The sample fabrics were immersed in the liguor at 40°C and the treatment was conducted as follows:

- at 40°C for 15 minutes
- from 40°C to 85°C in 30 minutes
- at 85°C for 55 minutes

At the end treatment, the samples were rinsed and left to dry at room temperature. All the sample fabrics were conditioned at 20±2°C and R.H.65±2% before the following conditions

—Determination of dye content

The absorption optical density curve of C.I. Aid Blue 90 liquor was drawn by using Spectrophotometer (Beckman Du-8). The optical absorption was peak at the point of 608.9 nm, as shown in Fig. 1. The linear equation between dye content of liquor [μg/ml] and the optical density at the peak point of absorption was made in Fig. 2 for calibrating the dye content of each sample. Small dyed silk samples weighing 20 mg were dissolved with 0.04ml of LiSCN(60%) per mg of silk (W/V, titration accoring to Volhard's method). After about 20 minutes at room temperature

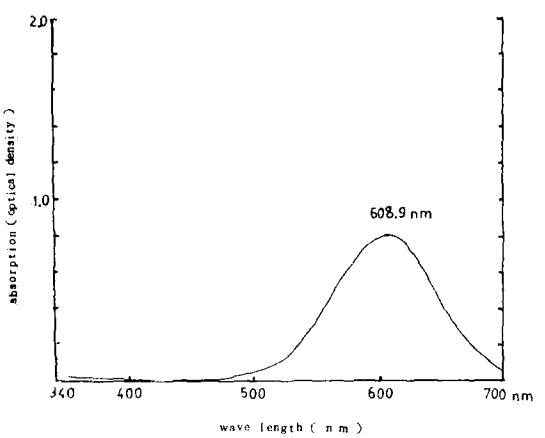

Fig. 1. Absorption curve of C.I. Acid Blue 90 solution at visible range of wavelength.

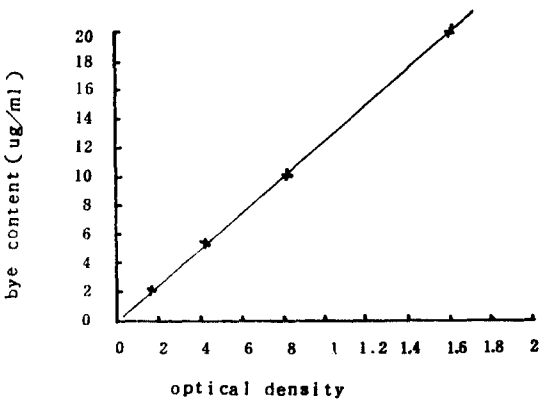

Fig. 2. Linear relation between dye content and absorption optical density at 608.9nm.

the solution was diluted with water (0.02ml per mg of silk). 10ml of ethyl alcohol(95%) were then added, which caused fibroin to precipitate keeping the dye in solution. After 30 minutes at room temperature fibroin was centrifuged at 12,000g for 5 minutes (Beckman centrifuge, model J 2-21)

The supernatant containing the extracted dye was taken out and the precipitate washed twice with ethyl alcohol every time subjected to centrifugation. The initial supernatant, added to the washing liquid(final volume : 25ml) was subjected to spectrophotometric analysis.

—Printing

Three kind of dyeing pastes were prepared as the following combination [Sandoz 1981]

· Direct printing

Red GN for silk discharge printng[Sandoz]	:	25g
urea	:	50g
thioethylene glycol	:	20g
hot water	:	*x*g
thickening(Indalca PA/3)	:	500g
antifoamer(NofomeC)	:	10g
ammonium tartrate 1:2	:	30g
		1,000g

· White discharge printing

Rongalite C(BASF)	:	200g
thickening(Indalca PA/3)	:	600g
antifoamer(Nofome C)	:	10g
water	:	*x*g
		1,000g

· Colour put-in discharge printing

the same dye paste as above direct printing	:	500g
Rongalite H(ASF)	:	80g
		580g

Sample fabrics, sizing 35×45cm each, were printed with the above dyeing pastes, respectively, and then dried. The silk prints were fixed in a steamer for 40 minute at 102°C in direct printing but in case of white and colour put-in discharge printing for 10 minutes at 102°C. The discharge printings were applicated onto the sample fabric shaded with C.I. Acid Blue 90. After steaming, the printed sample fabrics were well rinsed in cold water and then dried at room temperature.

—Surface reflectance of dyed fabric

By making use of Spectrophtometer (Carl Zeizz PMQ Ⅱ), the surface reflectance of the fabric dyed with C.I. Acid Blue 90 was measured at the wavelengh of 450nm which showed the maximum reflectance, whereas that of the sample printed with Acid Red GN (Sandoz) at the peak point of 900nm. The whiteness of undyed and white discharge printed fabrics were measured at the wavelength of 457nm, respectively.

—Observation of fine structure

The fine structures of the surfaces of degummed silk fabrics and fibres were observed under the magnifications of 3,380 times for silk fabrics and 4,100 to 4,350 times for silk fibres by using Scanning Electron Microscope (Stereoscan 100, Cambridge)

Results and Discussion

1. Degumming loss and tensile strength

The weight loss by soap degumming was lower by around 1% than that of the detegents, however, there was no significant difference in the degumming losses among the detergents besides comparatively less losed weight of Detergent "I" (Table 1). These differences between soap and detergent's degummings or Detergent "I" and the other detergents were seemed to be related with the pH values of the degumming baths, that is, the pH value of soap degumming bath was lower than those of the detergents, while those of Detergent "J"

Table 1. Weight losses of degumming with soap, detergents carried out on silk twill.

Degumming agents	Soap	Detergent "I"	Detergent "J"	Detergent "S"
pH of bath				
—initial value at treatment temp.	8.78	9.64	9.97	10.23
—final value at treatment temp.	8.30	9.28	9.43	9.30
Degumming loss (%)	25.16	25.99	26.43	26.53

Table 2. Tenacity and elongation of degummed silk twill.

Degumming agents		Soap	Detergent "I"	Detergent "J"	Detergent "S"
Tenacity (grams per denier)	warp	3.53	3.63	3.45	3.54
	weft	3.42	3.75	3.53	3.70
	mean	3.48	3.69	3.49	3.62
Breaking elongation (%)	warp	9.07	10.31	9.43	9.86
	weft	12.19	12.31	11.93	12.69
	mean	10.63	11.31	10.68	11.28

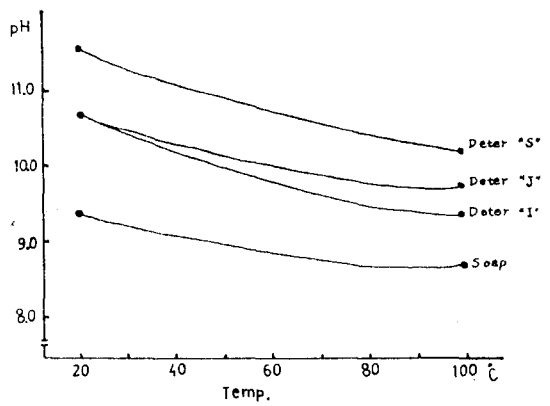

Fig. 3. Relation between temperature and pH variation of degumming baths.

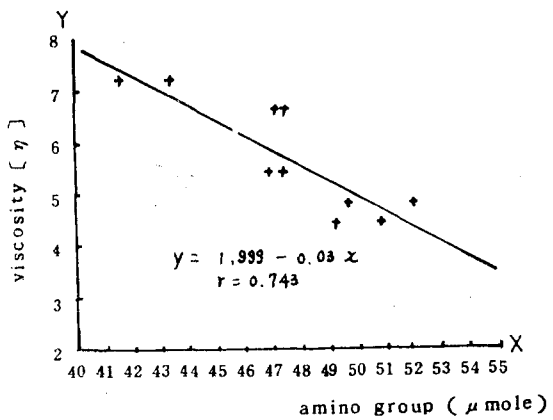

Fig. 4. Corelation between intrinsic viscosity and amino group content.

and "S" were higher than Detergent "I" (Fig. 3).

In tenacity and elongation of the degummed silk fabrics, there was no meaningful difference between soap and detergent's, as shown in Table 2.

2. Intrinsic viscosity and amino group content

The viscosity values showed a good accordance with the $(\alpha+\epsilon)$ amino group content of fibroins. There was some negative corelation ($r=-0.74$) between viscosity and amino group content, as shown in Fig. 4. In fact, the viscosity values are closely related with the molecular weight which is apt to be less decreased in the less degraded protein. In general, the viscosity of soap degummed fibroin was higher than those of degummed by the detergents, but Detergent "S" was the highest among three detergents (Table 3).

In the amino group contents, soap and Detergent

Table 3. Intrinsic viscosity and amino group content of degummed silk.

Degumming agents	Soap	Detergent "I"	Detergent "J"	Detergent "S"
Intrinsic viscosity [η]	0.662	0.442	0.479	0.543
Amino group content [NH_2 μ mole]	47.39	50.10	50.88	47.15

Table 4. Dye absorption of degummed silk twill by C.I. Acid Blue 90.

Degumming agents	Soap	Detergent "I"	Detergent "J"	Detergent "S"
Dye absorption [μg/mg silk]	22.76	23.06	24.05	23.86
△	reference	+1.32	+5.67	+4.83

Table 5. Surface reflectance of dyed silk twill by C.I. Acid Blue 90.

Degumming agents	Soap	Detergent "I"	Detergent "J"	Detergent "S"
White degree of undyed fabric (at 457nm)	78.81±0.31	76.00±0.32	74.75±0.63	78.19±0.22
Reflectance of dyed fabric (at 450nm)	33.69±0.69	34.19±0.37	33.10±0.50	33.60±0.50

"S" degummed fibroins were comparatively lower than degummed ones by Detergent "I" and "J". Therefore, this can be said that the silk fibroin is less degraded by soap and Detergent "S" than the other detergents.

3. Dye content and surface reflectance of dyed fabric

The dye absorption amount of soap degummed silk fabric by C.I. Acid Blue 90 was apt to be lower than that of the detergents degummed ones, in this case, the dye absorption amount was proportional to the amino group content of degummed fiberes which could provide the sites for combination with dyes.

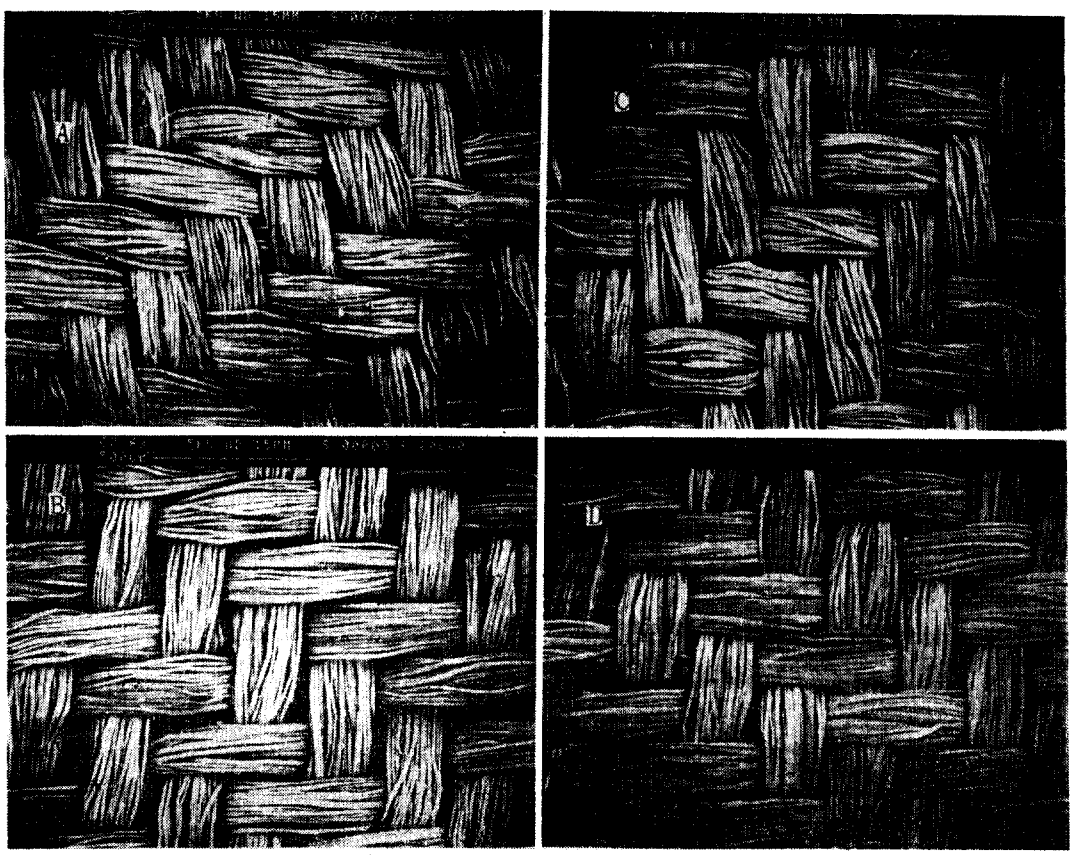

Fig. 5. Surfaces of degummed silk twill by Scanning Electron Microscope.

A : Degummed by Soap
B : Degummed by Detergent "J"
C : Degummed by Detergent "I"
D : Degummed by Detergent "S"

Table 6. Surface reflectance of printed silk twills

Degumming agents	Soap	Detergent "I"	Detergent "J"	Detergent "S"
*Printing I	90.4	91.2	90.9	90.2
**Printing II	65.6	64.5	64.4	64.6
***Printing III	85.6	87.5	86.8	87.2

* : direct printed with "Sandolan Red" for application printing of silk (reflectance at 900nm)
** : white discharge printed on the fabric shaded with C.I. Acid Blue 90 (reflectance at 457nm)
*** : "Sandolan Red" put-in discharge printed on the fabric shaded with C.I. Acid Blue 90 (reflectance at 900nm)

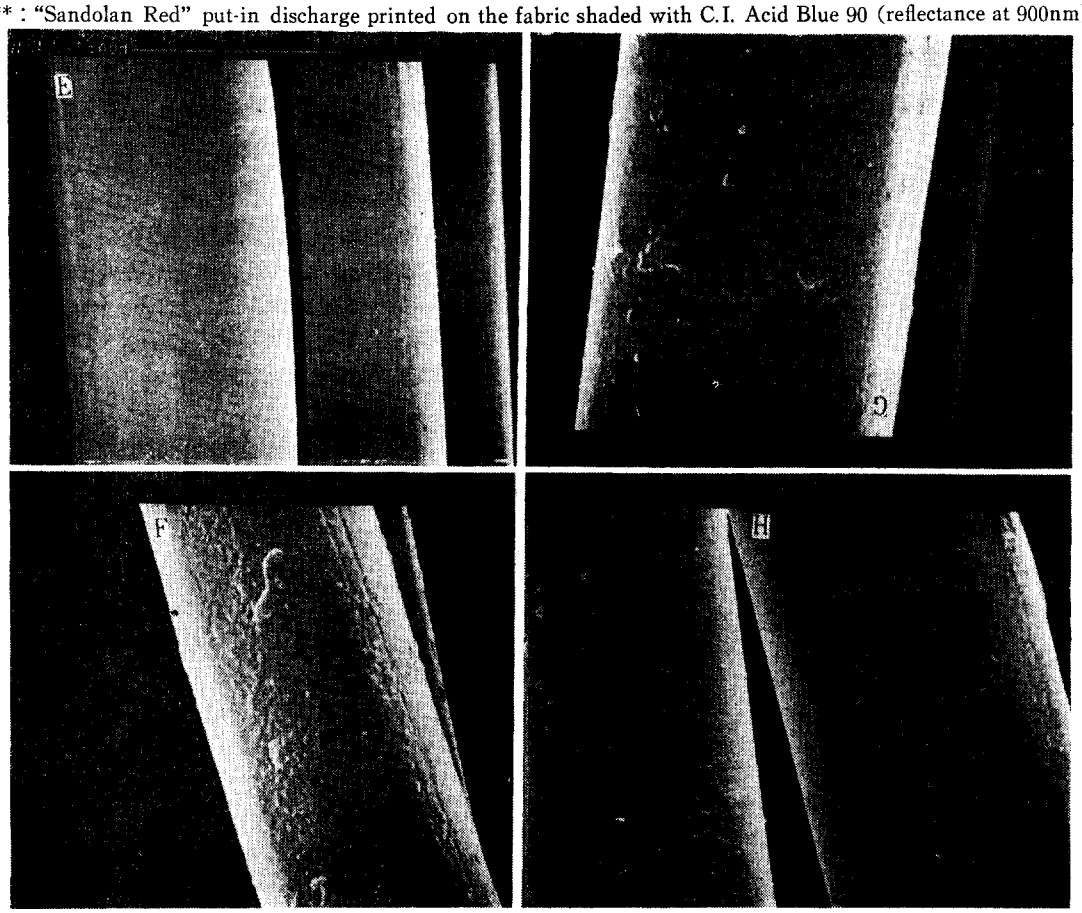

Fig. 6. Surfacial features of degummed silk fibres in magnification 4,100 to of 4,500 times by S.E.M.
E : Degummed by soap
F : Degummed by Detergent "J"
G : Degummed by Detergent "I"
H : Degummed by Detergent "S"

The white degree (surface reflectance at 457mm) of undyed fabric was the highest in both soap and Detergent "S", next in order, Detergent "I" and Detergent "J".

In the surface reflectance of dyed or printed silk twill by C.I. Acid 90, the considerable difference was no seen among the degumming agents (Table 5). This was little coincided with dye contents of the fabrics because the surface reflectance of dyed fabric was affected by not only dye content but also luster and the other factors. In the surface reflectance of printed fabrics, even though the soap degummed showed higher reflectance in Printing II and lower reflectance in Printing III than the other degummed ones, there was no noticable difference among the agents (Table 6).

4. Fine structures of surfaces

The fine surfaces of degummed silk twill were observed by Scanning Electron Microscope in Fig. 5.

The great differences were not found out in the superficial appearences of degummed fabrics among four kinds of degumming agents, but Detergent "S" fabric was comparatively cleaner than the others.

The morphological features of the degummed silk fibres under the magnifications of 4, 100 to 4, 350 times were shown in Fig. 6.

Generally, there was no noticable difference in the ultra fine structures of degummed fibres. However, partially, the features of the fine structures of fibre surface were differentiated among the degumming agents, that is, the surfaces of detergents degummed fibres were not much cleanner than that of soap degummed one.

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Conclusions

As the silk twills degummed by the detergents were compared with the degummed by soap, there was no significant difference in tensile strength and dyeability but a little decreased viscosity and slightly increased amino group content of degummed silk by the detergents which is closely related with the degradation of fibre. Even though the uneven spots were slightly observed in the ultra fine structures of detergents' degummed fibres by Scanning Electronic Microscope, without soap, Detergent "S" was most recommandable among three detergents in consideration of the results obtained.

References

Freddi, G., Bragadin, C. (1982) Studio Preliminare sul Controllo della degradazione della fibroina di *Bombyx mori* mediante determinazione dei gruppi Aminici primari con ninidrina, I.S.A. Report London, 1982, 20-24.

Freddi, G., Maifreni, T. (1985) Method of extraction and determination of dyes applied onto silk, LA SETA, 1985, 32-39.

Knott, J., Grandmaire, M. and J. Thelen (1981) Determination of the (α+ξ) Amino group content of wool by reaction with nynhydrin. J. Text. Inst., 1981(1), 19-25.

Knott, J., Freddi, G. and M. Belly (1983) Preliminary Study concerning the Degumming and Degradation of *B. mori* Silk, Melliand textilberichte, 1983(7), 481-483.

Pancirolli, F., Svilokos Bianchi A. (1973) La Purga enzimatica sella seta, La Seta, 1973, numero unico, 3-6.

Sandoz (1981) Dyeing and Printing 011/81, 14-22.

Schweigerische Normen-Vereinigung, Textilien (1968) Prüfung auf Faserveränderung und Faserschädigung Bestimmung der Viskositätszahl von Naturseide in Lithiumbromid-Lösung, SNV 195595.

Svilokos Bianchi A, Previato I (1983) Nuovi sistemi di sgommatura: Possibili cause della degradazione della fibroina da *Bombyx mori* e metodi di controllo La Seta 1983, 8-16.