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Optical Studies on the Yellowing of Silk I

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Abstract

The author has studied the yellowing of silk by exposing it to light. Measurement has mainly been carried out by the colorimetrical method. It has been proved that the coloring of silk by light lies between the coloring of tryptophane and that of tyrosine and in the early stage of exposure it is closer to the former, while it is closer to the latter in the end.

The author has also obtained the empirical formula referring to the velocity of the yellowing.

1 Introduction

For a few years, NAKAMURA and the author have studied the yellowing of silk by exposing it to light.[1-5] Measurement has mainly been carried out by the optical methods, especially by application of colorimetrics.

Now, these studies on the coloring by light are fragmentary or not systematized and new results have been ascertained step by step since then. Therefore the author has unified the results obtained so far together with new measurements and discussions yet unpublished.

2 The Yellowing of Silk by White Light

In the past, many studies have been made concerning the yellowing of silk by white light and ultra-violet rays,[6,7] but the author applied colorimetrics for the first time, and obtained very accurate empirical formula on the coloring velocity.

(1) **Measurement**

(a) *Irradiating method of light*

Samples were irradiated by light from weather meter (W. M.), which is generally admitted to be similar to the sun light and used as white light source. As to experimental condition in W. M., there are two arc light lamps of 111 volts and the inner room temperature is 40° C and the humidity 41 %. Samples were exposed to light for various time intervals of 20, 40, 60, 100, 200 (hrs). The change of electro-carbon terminals and the cleaning of globe were conducted at proper time in the course of irradiation, and then experimental condition is noticed to be entirely equal for each sample.

(b) *Samples*

Heavy refined silk fabrics "omome habutae" were used as samples. Namely, after heavy plain-weave raw silk fabrics "omome hiraori kihabutae" were refined, these were whitened, washed, dehydrated, dried and stored in the desiccator in a dark place without variation of temperature.

(c) *The measurement of spectro-reflectance*

With a reflective-rate measuring equipment of spectro-photometer, the measurement was carried out for the same fourfold silk fabrics. The standard illuminant is C luminescent source (it has the same nature as the sun light which contains the light of blue sky).

The author measured percent reflectance of silk fabrics at intervals of 20 mμ within the range of wavelength 400~660 mμ, regarding the percent reflectance of $BaSO_4$ standard white plane as 100 %. And then the uniform samples of silk fabrics have been measured which were placed so that the length direction may be constantly vertical against progressive direction of monochromatic light. Spectral percent reflectance curves and their values which were obtained as above are represented in Fig. 1 and Table 1.

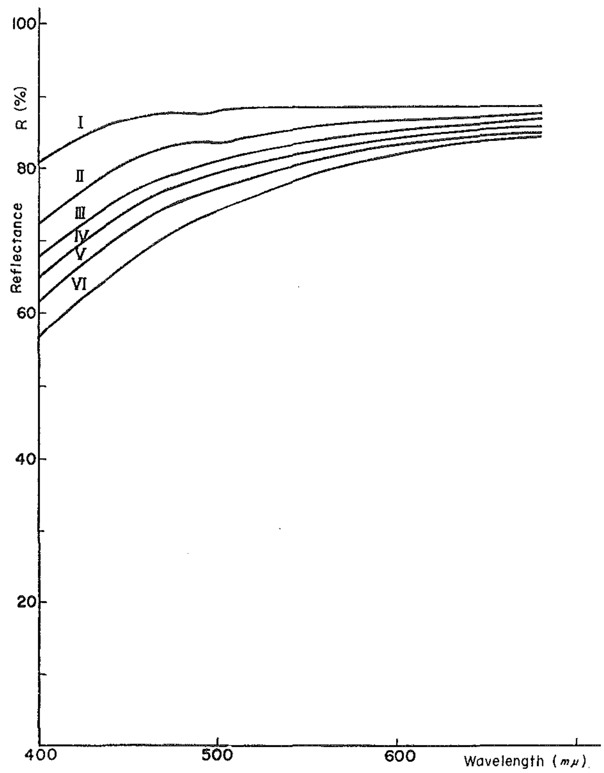

Fig. 1 Spectral percent reflectance curves for silk exposed by W. M. for various time intervals, i. e., 0 (I), 20 (II), 40 (III), 60 (IV), 100 (V) and 200 (VI) hrs.

Table 1 Spectral percent reflectance of silk yellowed by light

(mμ) \ t(hr)	0	20	40	60	100	200
400	80.6	72.2	67.0	65.0	61.3	56.5
420	84.0	76.2	71.7	69.2	66.1	61.2
440	86.0	79.2	74.8	72.8	70.1	65.2
460	86.8	81.8	77.4	75.3	73.1	68.7
480	87.0	82.3	79.3	77.4	75.2	71.8
500	87.8	83.3	80.7	79.1	77.2	74.0
520	88.0	84.2	81.9	80.2	78.9	75.8
540	88.1	84.9	82.9	81.5	80.1	77.8
560	88.2	85.4	84.0	82.5	81.3	78.7
580	88.2	86.0	84.6	83.2	82.0	80.2
600	88.2	86.2	85.2	84.0	83.2	81.0
620	88.2	86.4	85.6	84.5	83.7	82.0
640	88.6	86.8	86.0	84.9	84.3	83.0
660	88.3	86.7	86.0	85.0	84.5	83.4

(2) **Discussions**

(a) *The relations between reflectance, luminosity and exposure time*

Between percent reflectance R (%), luminosity (or luminous reflectance) Y (%) (Y is the collective percent reflectance determined by the standard luminosity and its center of wavelength is 555 mμ.) for each monochromatic light and exposure time t (hr), the following empirical formula is obtained with satisfactory accuracy.

$$R(\text{ or } Y) = a\,(t+18)^{-b}.$$

Some examples are given in Fig. 2 and Table 2.

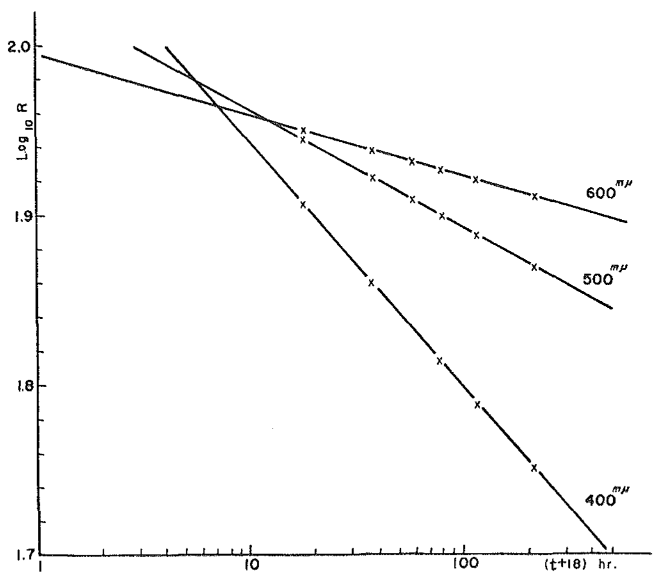

Fig. 2 Relations between reflectance R (%) and time of exposure t (hr).

Table 2 Constant values in some examples

Wavelength (mμ)	a	b	t_0(hr)	$-\frac{dR}{dt}$(%/hr)
400	124.0	0.148	−13.8	0.28
480	108.5	0.077	−15.1	0.17
500	106.6	0.068	−15.4	0.15
Y	100.9	0.047	−16.8	0.11
600	97.7	0.035	−17.5	0.08

The difference between measured values and calculated values by the above formula is less than 0.5 %. In the table, t_0 is the value of extrapolation of t

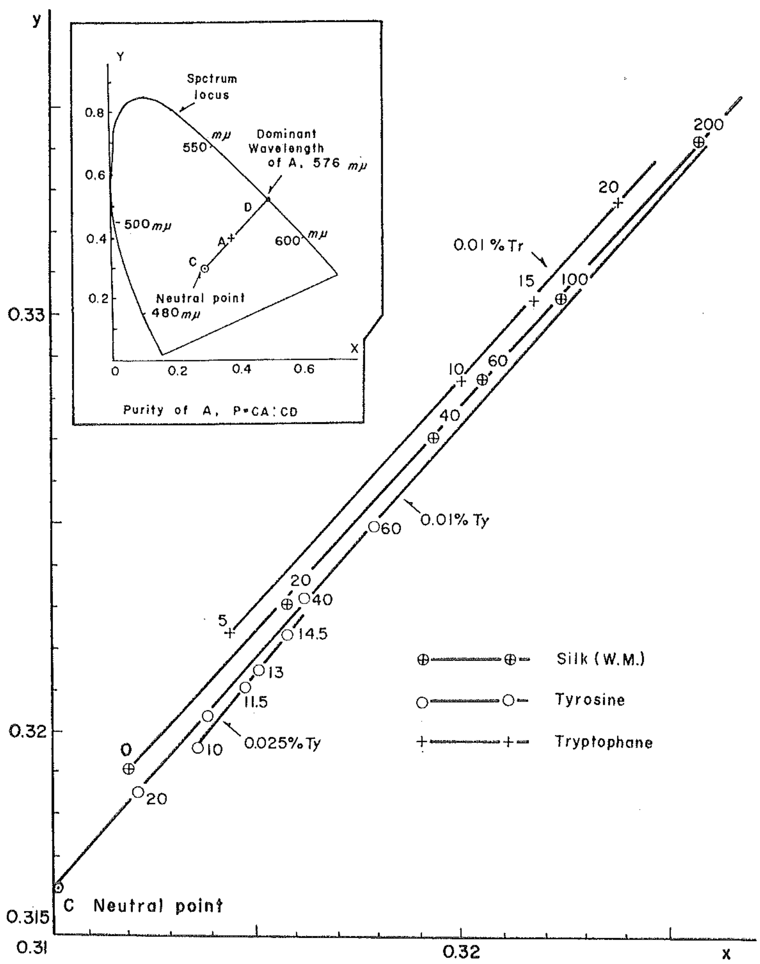

Fig. 3 Chromaticity diagram. Figures indicate the time of exposure (hr).

when R is 100 %.

Considering from this empirical formula it may be regarded that unexposed silk has been colored already when it was measured, and percent reflectance is the same as that of pure white silk fabrics which were exposed to light by W. M. for $|t_0|$ (hr). Constant b expresses the gradient of each line in Fig. 2.

(b) *The relation between chromaticity and exposing time*

According to spectral percent reflectance curves, chromaticity coordinates x, y, luminosity Y(%), dominant wavelength and excitation purity P (in the following will be written in brief as purity) of XYZ color system by C. I. E. are obtained through 30 selected ordinate method. And the results are in Table 3 and Fig. 3 by chromaticity diagram.

Table 3 Yellowing of silk by W. M.

Exposure time (hr)	Chromaticity coordinates		Luminosity (%)	Dominant wavelength (mμ)	Purity
	x	y			
0	0.3121	0.3191	88.1	572.7	0.013
20	0.3157	0.3232	85.1	574.5	0.035
40	0.3191	0.3273	83.5	574.7	0.054
60	0.3204	0.3284	82.1	575.3	0.060
100	0.3221	0.3302	80.8	575.6	0.069
200	0.3257	0.3340	78.3	575.9	0.088

In the figure, point C denotes the chromaticity point of C illuminating light, namely neutral point ($x=0.31006$, $y=0.31616$).

According to I. S. C. C. -N. B. S. color graph,[8] the sensuous hues vary within the domain of very pale orange which is near to orange pink but the dominant wavelengths are pure yellow and, in the early stage of exposure, these shift from 573 mμ to 576 mμ.

Here, the dominant wavelength is the wavelength of spectrum monochromatic light where the straight line joining neutral point with chromaticity point crosses spectrum locus, and it corresponds to hue. Purity P varies from 0 to 1 changing the saturation from pure white to spectrum light. (See Fig. 3)

Now it has been proved by many studies[9–13] till now that the coloring of silk by exposing it to light is caused by photo-autoxidation of tyrosine and tryptophane (henceforth abbreviated as Ty, Tr). It has not been established theoretically nor experimentally, however, which is the subject of this coloring and how is the relation of them.

To solve these problems, it will be the most effective method to expose both individual substances to light and compare these dominant wavelengths with that of the coloring of silk.

The author[3,4] has exposed aqueous solution of Ty and Tr of various concentrations to light with W. M. for various time intervals and obtained the degree of yellowing. The results are listed in Table 4 and Table 5.

Table 4 Yellowing of aqueous solution of Tyrosine

Conc. (%)	Exposure time (hr)	Dominant wavelength (mμ)	Purity
0.025	10.0	577.4	0.018
〃	11.5	577.0	0.025
〃	13.0	577.0	0.027
〃	14.5	576.6	0.031
0.01	20.0	576.0	0.021
〃	40.0	576.0	0.034
〃	60.0	576.0	0.043

Table 5 Yellowing of aqueous solution of Tryptophane

Conc. (%)	Exposure time (hr)	Dominant wavelength (mμ)	Purity
0.05	3.5	572.1	0.033
〃	4.0	573.5	0.058
〃	4.5	574.3	0.068
0.01	5.0	572.7	0.028
〃	10.0	574.6	0.058
〃	15.0	574.9	0.068
〃	20.0	575.1	0.081

In the case of short time irradiation by light, the concentrations of solutions were increased from 0.01 % to 0.025 or 0.05 %. This is because the purities or coloring saturations of the 0.01 % solutions were exceedingly small and the dominant wavelengths were inaccurate.

In this way, as to the accuracy of dominant wavelength, the value below 1 mμ is relatively significant as reference value in these tables.

According to these tables, dominant wavelength of tyrosine decreases merely from 577 mμ to 576 mμ throughout the time of exposure, but on the contrary, that of tryptophane increases from 572 mμ to 575 mμ conspicuously in the beginning of irradiation. It is also to be noted that such a tendency is independent of the concentrations. There is a large difference in exposure time between the silk and each solution. This is due to the fact that the coloring of silk is by far slower than that of each solution, while the author has compared the dominant wavelengths when the degrees of purities are nearly the same.

Thus the author reaches the following conclusions: the dominant wavelength for coloring silk lies in the middle of those for tyrosine and tryptophane. To be more precise, it is closer to tryptophane in the early stage of exposure and shifts from short wavelength to long wavelength in the same manner as in the case of tryptophane, but it coincides with that of tyrosine in the end of irradiation.

More progressive studies as to this section will be published in the next report.

3 The Velocity of the Yellowing of Silk

(1) The yellowing of silk by ultra-violet rays

The author has exposed the scoured silk and unscoured silk through light emitted by mercury lamp (in the following will be written as ultra-violet rays in brief) for various time intervals within the range of 50 hours, measured "white content" W (%) and obtained the following empirical formula with errors less than 0.3 %:[2,14]

as to the scoured silk $W=96.3\ (t+2)^{-0.137}$,

as to the unscoured silk $W=74.9\ (t+6)^{-0.124}$.

Here "white content" means percent reflectance of irradiating light transmitted through a filter of 405∼517 mμ wavelength with its center at 472 mμ.

(2) **The velocity of yellowing**

Between reflectance R (%) and exposing time t (hr), the following relation is obtained in general.

$$R = a(t+k)^{-b}.$$

As some of the above formulae show, in the case of irradiation of ultra-violet rays, k is conspicuously small and b is large in comparison with the case of irradiation of white light by W. M.

This means that the decreasing rate of R or the velocity of yellowing is large.

$$-\frac{dR}{dt}=\frac{ab}{(t+k)^{b+1}},$$

where b is a positive number and quite smaller than 1, so it hardly effects denominator.

In the case of irradiation by white light, $k=18$ (const.) and $a \doteqdot 100$, so the velocity is in direct proportion to b and in inverse proportion to t. In Table 2, the decreasing rates of R when t is 20 (hr) are shown. And then in the case of exposing to ultra-violet rays, the unscoured silk has large k and small a and b in comparison with the scoured silk, so the decreasing rate of R is small. When t is 20 (hr), the latter is 0.39 (%/hr) and the former is 0.24 (%/hr). But in comparison with the decreasing rate against the monochromatic light of 480 mμ in the case of irradiation by white light, both are quite large.

Next, in the event of no irradiation, "white content" W equals 87.2 % (measured) or 87.4 % (calculated) in the scoured silk and 60.0 % (measured and calculated) in the unscoured silk. These results show that the latter is deeper in coloring before exposing. It is considered that this corresponds to the small constant a in the formulae and is due to coloring matter besides the coloring by light.

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