THE EFFECT OF pH ON THE PHOTOCHEMICAL DECOMPOSITION OF SILK

By Milton Harris and Daniel A. Jessup

ABSTRACT

The extent to which silk is weakened by light depends upon its "pH" (as defined by its extract), other factors remaining constant. The maximum stability is found at about pH 10. Above pH 11 and below pH 3 the stability decreases rapidly. In the neutral region, pH 6 to pH 8, silk is less resistant to light than when it is more acid or alkaline. Silk treated with tenth normal sodium hydroxide solution is more stable to the action of light than either the untreated silk or silk treated with tenth normal sulphuric-acid solution. The acid-treated silk is least stable. These facts have an important bearing on practical silk finishing as well as on the nature of the action of light on silk.

CONTENTS

		Page
I.	Introduction	1179
II.	Experimental methods	1180
III.	Experimental results	1181
IV.	Conclusions and practical significance	1183

I. INTRODUCTION

Although silk is one of the strongest fibers known, its susceptibility to attack by light has been the source of considerable trouble, especially where the fabric has been exposed for any length of time. Formerly many investigators believed that only silk containing metallic weighting was attacked by light, but recent work has shown that the purest silk is affected.

Concerning the nature and mechanism of the breakdown, there are many and diversified opinions substantiated by little experimental work. Doree [1] states that the breakdown is caused by ultra-violet rays, acting either alone or in conjunction with the ozone produced by them. K. Homolka [2] and P. M. Grempe [3] state that the weakening of silk fibers by radiation is caused by the short ultra-violet rays from the sun. However, it should be noted that the sun's rays do not contain much short wave length ultra-violet and that this radiation does not pass through ordinary glass. (Radiation which passes through ordinary glass weakens silk.)

Herman [4] studied the effect of radiation on silk, using the mercury arc lamp. His results indicate that the radiation acts directly on the silk and that the deterioration is not a secondary reaction due to the ozone produced by the radiation.

[1] Doree, Charles and Dyer, Joseph W. W., Some Effects of the Action of Ultra-Violet Light on Cotton Fabrics, J. Soc. Dyers and Colourists, vol. 33, pp. 17–19; January, 1917.

[2] Homolka, Karl, Behandlung der Seide um ihre Widerstandskraft gegen die Einwirkung des Lichtes zur erholen, Melliand's Textilber. vol 5, p. 584; 1925.

[3] Grempe, P. Max, Bewahrung von Kunstseide und Seide bei Sonnenlicht und Wetter, Kunstseide vol. 9, pp. 462–463; 1927.

[4] Hermann, P., Ueber die Einwirkung der ultravioletten Strahlen auf Farb und Faserstoffsysteme, Melliand's Textilber. vol. 5, pp. 745–749; 1924.

While the experimental worker in textile fields has limited his studies largely to the effect of light exposure on tensile strength, the protein chemist has studied the chemical changes produced by light. Schanz [5] has shown that heat and light effect chemical changes in egg and serum proteins in acid and alkaline solutions and that the action is increased by the presence of oxygen. By exposure to sunlight, Effront [6] decomposed amino acids and protein matter in alkaline solution with the formation of ammonia and volatile acids. He found that sterile solutions of peptones exposed to sunlight decompose with formation of peroxide, nitrates, ammonia, and volatile acids. He concluded that the active agent was hydrogen peroxide, as this substance is known to decompose peptones and amino acids.

II. EXPERIMENTAL METHODS

A suitable and reproducible accelerated aging test was obtained by exposure to the light of a glass inclosed carbon arc, the external physical conditions being held constant. This was accomplished by placing the samples in a cabinet (15 by 15 by 15 inches) having a window of a special glass which is more transparent than window glass to the shorter wave lengths. The total radiation at a distance of 15 inches from the center, at right angles to the arc, operated on a current of 12.6 amperes, is 0.075 watts per cm^2. The temperature of the box was kept at 70° C. by a small fan for circulation and a thermostat control, most of the heat being supplied by radiation from the arc and the remaining heat from a carbon filament lamp bulb. A relative humidity of about 75 per cent was maintained by a saturated solution of sodium chloride.

Tests were made on pure silk which had been carefully boiled off and kept in the dark. Warpwise strips 48 inches long and about 1¼ inches wide were cut into 6-inch lengths. Enough warp threads were then removed to make each strip 1 inch wide. Each sample was allowed to remain in a solution of known pH for 10 minutes after which the excess liquor was removed by centrifuging for three minutes and subsequent drying in the dark.

The pH of the solutions was determined with the quinhydrone and hydrogen electrodes. The "pH" of the cloth (as defined by its extract) before and after exposure was obtained by extracting a standard sample for one hour with 50 cc of water, using an Underwriter extraction cup. The pH of the resulting solution was taken to be that of the cloth.

The tensile strength of the samples was measured on a pendulum type of testing machine. All samples were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 per cent and a temperature of 70° F. The average strength of three to five samples is reported.

---

[5] Schanz, Fritz, Die Lichtreaktion der Eiweisskörper Arch. ges. Physiol., vol. 164, pp. 445–456; 1916.

[6] Effront, Jean, Action de la lumière et de l'eau oxygénée sur les matieres albuminoides et acides amidés, Compt. rend, vol. 154, pp. 1111–1114; 1912.

III. EXPERIMENTAL RESULTS

In order to determine the relative effects of the chemical treatment, light, and heat, three sets of samples were prepared. Each set was treated with solutions of sodium hydroxide or sulphuric acid ranging in pH from 1 to 13. The first set was allowed to stand in the dark at room temperature, the second set was exposed to a temperature of 70° C., and a relative humidity of 75 per cent without light, and the third set was treated as the second except that it was exposed to the light of the carbon arc. All exposures were for 30 hours. The breaking strengths of the samples are given in Table 1.

TABLE 1.—*Relative effects of pH, heat and light on the breaking strength of silk cloth*

pH (±0.1)	In dark, room temperature	Breaking strength in dark, 70° C. and 75 per cent R. H.	Exposed to carbon arc radiation, 70° C. and 75 per cent R. H.
	Lbs. per in.	*Lbs. per in.*	*Lbs. per in.*
1	35	19	5
3	50	51	40
5	48	52	41
7	51	51	40
9	55	50	44
10	49	46	46
13	52	36	32

It is apparent from the results that in all cases, with the exception of pH 10 the breakdown obtained was accelerated by the action of the light. However, it is known that proteins in general are very susceptible to acid or alkali concentrations of 0.1 normal or greater. Even under these extreme conditions, the tendering was increased by exposure to the light.

Three sets of samples were prepared and treated so that the pH of the cloth ranged from 1 to 13. These were all given a 30-hour exposure and the average strength at each pH was taken. The following results were obtained:

TABLE 2.—*Effect of light on the breaking strength of silk cloth*[1] *at varying pH values*

pH (±0.1)	Breaking strength	pH (±0.1)	Breaking strength
	Lbs. per inch		*Lbs. per inch*
1	0	7	75
2	38	8	81
3	72	9	86
4	77	10	96
5	81	11	89
6	78	13	22

[1] Silk used here was of a heavier quality than that used in Table 1.

Several interesting points are portrayed here. As is evident from Figure 1, there is a definite region of maximum stability at about pH 10. The strength falls off rapidly below pH 3 and above pH 11. In the intervening range, there appears to be a minimum in the neutral region. Assuming that the protein material unites with small amounts of acid or alkali to form protein salts, the evidence indicates that the salts thus formed are more stable toward photochemical decomposition than the pure protein. Protein salts are probably also formed above pH 11 and below pH 3, but in these cases excessive

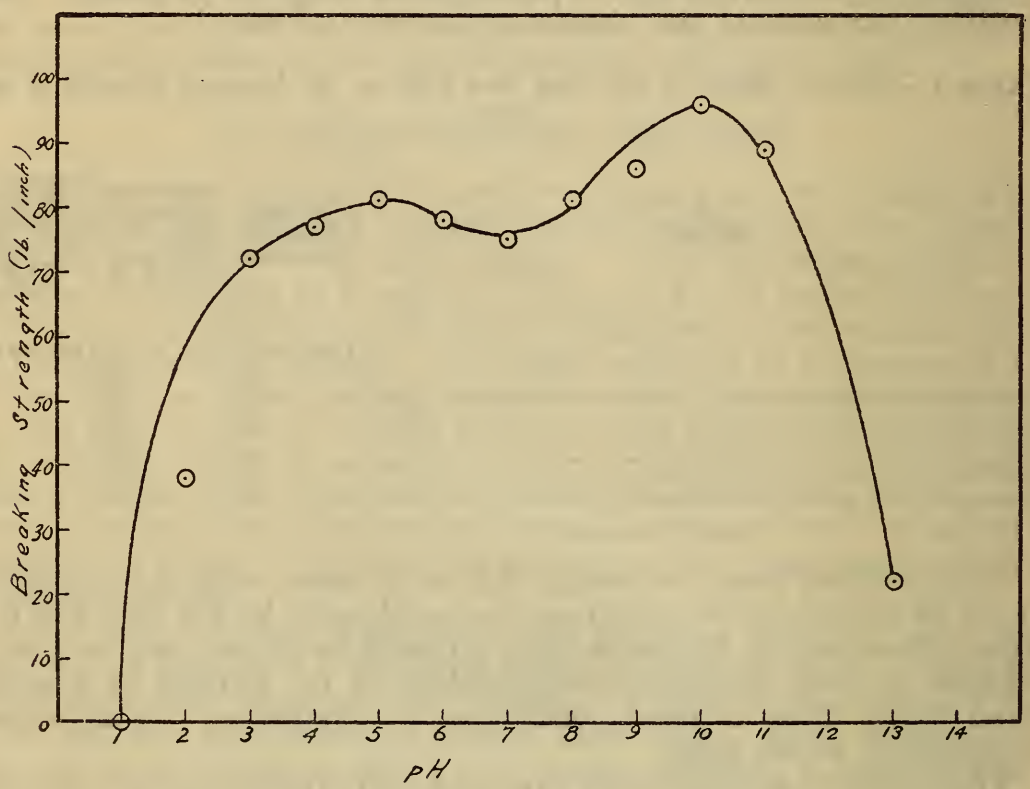

FIGURE 1.—*Effect of light on the breaking strength of silk cloth at varying pH values*

deterioration is more than likely caused by direct action of the excess acid and alkali.

An analogous reaction takes place in the photochemical oxidation of adrenaline. Vacek [7] found that light accelerates the reaction considerably. He observed that aqueous solutions of adrenaline decompose much more rapidly than solutions of adrenaline in dilute hydrochloric acid in which adrenaline hydrochloride is formed. Preliminary experimental work indicates that the decomposition of silk by light is a photooxidation reaction.

The relative rates of deterioration were determined by the following scheme: The first set of samples was treated with a solution of 0.1 *N* sodium hydroxide, the second with a solution of 0.1 *N* sulphuric acid, and the third was untreated.

[7] Vacek, Tomas, Oxidation of Adrenaline, Biochem. J., vol. 21, p. 457; 1927.

TABLE 3.—*Effect of light on the breaking strength of silk cloth treated with 0.1 N NaOH and with 0.1 N H_2SO_4*

Time (hours of exposure)	Breaking strength (pounds per inch)		
	No treatment	0.1 *N* NaOH	0.1 *N* H_2SO_4
0	98		
5		99	80
15		98	63
20		95	53
25		102	45
30	82	88	38
50		75	22
75	50	59	
100		56	
130	21	48	

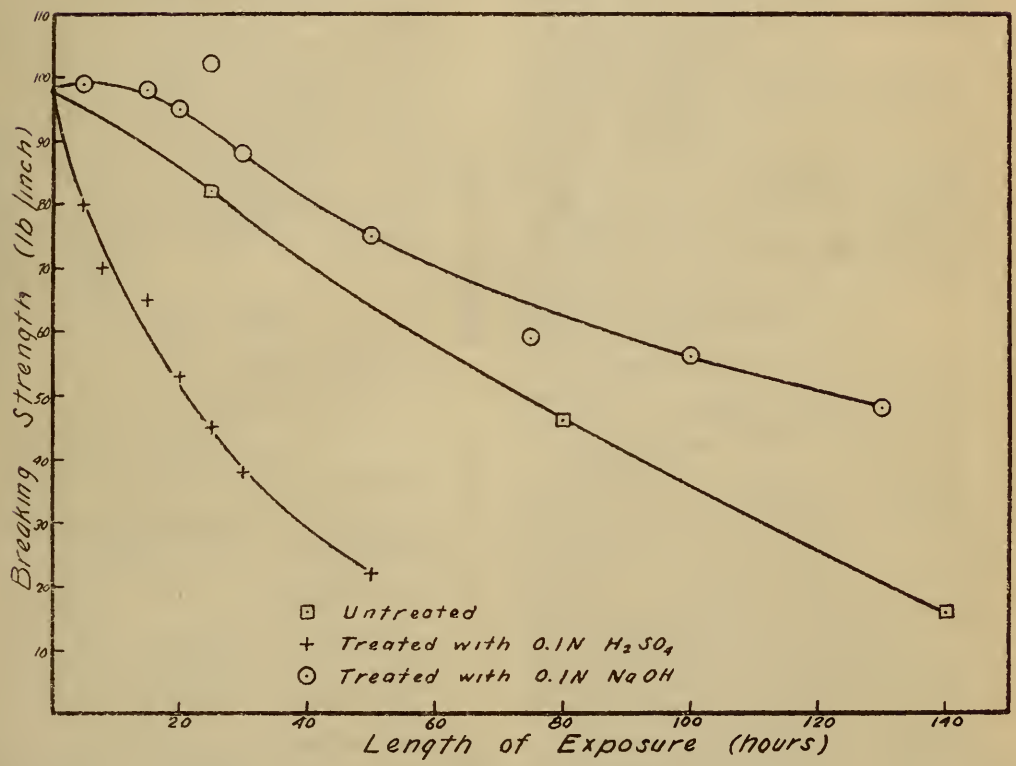

FIGURE 2.—*Effect of light on the breaking strength of silk cloth treated with 0.1 N NaOH and with 0.1 N H_2SO_4*

The results in Table 3 and also in Figure 2 show the relative stability of neutral, acid, and alkali treated silk to light. After a 50-hour exposure the acid-treated sample had lost 67 per cent of its original strength while the alkali-treated sample had lost only 23 per cent.

IV. CONCLUSION AND PRACTICAL SIGNIFICANCE

These experiments show that silk decreases in strength on exposure to light and that the rate of deterioration depends upon the pH to which the silk has been finished. Contrary to what might be expected from the fact that alkalies hydrolyze proteins more rapidly than do acids, silk treated with 0.1 *N* NaOH is more stable in light

than silk treated with 0.1 N H_2SO_4. Silk whose water extract has a pH of about 10 shows maximum stability to light.

The stability decreases rapidly above pH 11 and below pH 3. From pH 6 to pH 8; that is, in the region of neutrality, silk is less resistant to light than when it is more acid or alkaline.

These observations lead at once to the very practical conclusion that commercial finishing should leave silk at a "pH" of about 10 if the maximum stability to light is desired. Whether other considerations will permit of such finishing must be decided for the materials to be processed.

WASHINGTON, October 9, 1931.