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EFFECT OF DRY CLEANING ON SILKS

A COMPARISON OF THE EFFECT OF DRY
CLEANING AND SOME SERVICE CON-
DITIONS ON THE STRENGTH OF SILK

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Bureau of Standards

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A COMPARISON OF THE EFFECT OF DRY CLEANING AND SOME SERVICE CONDITIONS ON THE STRENGTH OF SILK

By M. H. Goldman, C. C. Hubbard, and Charles W. Schoffstall

ABSTRACT

The study of tin-weighted and unweighted samples of silk after various treatments and exposures to sunlight and storage at standard conditions (of 65 per cent relative humidity at 70° F. temperature) permits the following conclusions: (1) No deterioration results from exposures to standard atmospheric conditions over a period of two and one-half months even when acid or alkaline perspirations are applied. (2) Sunlight exposure causes a marked deterioration in both unweighted (but dyed) and tin-weighted silks, the loss in strength in 100 hours exposure amounting to about 25 per cent for unweighted and about 50 to 75 per cent for weighted silks. (3) Acid and alkaline perspiration treatments increase the deterioration when sunlight exposures are given, so that the loss in strength in 100 hours' exposure is about 35 per cent for unweighted and about 65 to 100 per cent for weighted silk. (4) Dry-cleaning solvents in no case caused any appreciable deterioration of the silk fabrics.

CONTENTS

	Page
I. Introduction	606
1. Replacement of the sericin on raw silk	606
2. Process of weighting silk	607
II. Interest of dyeing and cleaning industry	608
1. Purpose of the study	608
2. Acknowledgments	612
III. Preliminary study	613
1. Literature on deterioration of silk	613
2. Theories of deterioration	614
3. Exposures	615
4. Treatment with perspiration	615
5. Ironing	616
6. Dry-cleaning	616
(a) Dry-cleaning practice	616
(b) Dry-cleaning solvents	617
(c) Dry-cleaning soaps	618
(d) Laboratory process for dry cleaning used during this study	618
7. First series of exposure tests	619
IV. Procedure for final study	620
V. Test results and discussion	622
VI. Summary and conclusions	633

I. INTRODUCTION

1. REPLACEMENT OF THE SERICIN ON RAW SILK

The silk fiber just as received from the cocoon has an almost transparent outer covering called sericin, which renders it harsh to the feel, stiff, coarse, and lusterless. This coating is permitted to remain through the reeling and throwing processes; thus it is a part of the raw silk of commerce as received by the manufacturer.

The soft lustrous silk materials with which the consumer is familiar are obtained by boiling the silk in a soap solution. In many cases this "boiling off" or "degumming" process is accomplished at a late stage in the manufacturing process of finished fabrics, for the silk is more easily handled in the gummed state.

This sericin is of importance to silk manufacturers for two reasons: First, it must be removed to bring forth the best qualities of the silk; and, second, it amounts to approximately one-quarter of the weight of raw silk. The latter is a serious consideration, for silk transactions are made on a weight basis. Of course, the price is adjusted depending on whether the material is degummed or not.

Experiments many years ago in the dyeing of silk brought out a very valuable fact; that is, that degummed silk that was dyed black by means of an iron-tannin mordant and logwood resulted in a finished material markedly heavier than the undyed material. In addition, it was found that successive treatments in the iron-tannin mordant further increased the weight of the silk.

Silk dyeing and finishing conditions changed decidedly with the advent of this new knowledge, for here was found a means of increasing the weight of the silk materials, which, of course, reflected in the price. Legal restrictions resulted, for the weighting was viewed as an adulteration, but later these were removed or ignored and silk weighting became an accepted practice.

The iron-tannin process was soon supplemented, and is now almost entirely supplanted by the use of tin salts. Other metallic salts were tried and are now in use to some extent. Tin salts, however, are used most, principally because of the great affinity silk has for them and because they do not discolor the silk, thus permitting the dyeing of all kinds of light shades.

The original idea of weighting as an adulteration has been greatly changed in view of the advantages of its use which might be set forth briefly as follows: First and most important is the price consideration, for by the introduction of silk weighting many more are enabled to purchase because of the resultant lower prices; second is the draping feature, a property rather difficult to describe, but in regard to

which claims are made by dress designers that weighted silk will permit the garment to drape the figure better than unweighted; third, the covering power, or the ability to cover more area with a given amount of silk (fiber), a property which permits, for instance, fewer threads per inch (with a consequent lowering of manufacturing costs) in a given material of weighted silk than of unweighted silk without lowering the actual covering value.

2. PROCESS OF WEIGHTING SILK

The process of weighting silk is briefly as follows: The silk is steeped in the bath, usually of stannic chloride (specific gravity between 1.25 and 1.265),¹ and after being rinsed in water the goods are agitated in a solution of sodium phosphate. The silk is then rinsed thoroughly. Additional cycles are used if it is desired to increase the weighting. Quite often the last treatments are with sodium silicate instead of sodium phosphate. Both of these are used in order to reduce any possible injurious effect of the stannic chloride, and because a higher percentage of weighting can be obtained by their use. Other metallic salts are sometimes used with the tin salts, especially for black silks that are to be dyed with logwood.

The per cent of weighting used differs widely. Originally, weighting only sufficient to replace the percentage of sericin was used, but not infrequently weighted silk goods have been found in which there was more weighting than silk. The present practice is not to exceed 25 or 30 per cent of the original weight of the raw silk, and large quantities of materials are produced with only sufficient weighting to equal the weight of the sericin.

The silk manufacturer, observing that some tendering action resulted from excessive weighting, was easily convinced of the necessity for a low percentage of weighting; otherwise losses by deterioration occurred, either during storage in his own mill or in the hands of the jobber, garment maker, or retailer. So long as this tendering was not too rapid, there was little danger of any complaint resulting from loss to the user of the material (especially a clothing material), because of the difficulty in tracing the deterioration to any of the multiplicity of service conditions that may have caused it. However, garments become soiled and must be cleaned, and it is at this point that the interest of the dry-cleaning industry starts.

¹ Hurst states that stannic chloride having a specific gravity higher than 1.35 is sufficient to first tender the silk, then dissolve it. Hurst, George H., *Silk dyeing*, November, 1925; and in *Printing and Finishing*, 1892.

II. INTEREST OF THE DYEING AND CLEANING INDUSTRY

1. PURPOSE OF THE STUDY

Silk materials form a large portion of the work handled by the dyeing and cleaning industry of this country. Notwithstanding efforts to avoid them, damaged materials result from time to time. The National Association of Dyers and Cleaners endeavor through a



FIG. 1.—*A fairly old dress badly deteriorated*

Analyses of deteriorated fabric showed presence of acid, and a strong test for chloride ions evidenced that the garment had been impregnated profusely with perspiration. The silk was tin-weighted.

research associateship established at the Bureau of Standards to study persistent troubles which occur throughout the industry. Occasionally in cleaning a lot of silk garments it has been found that one of them will be more or less tendered. The other silk fabrics although subjected to the identical dry-cleaning process at the same time, are unharmed.

Microscopical analyses of the damaged portions in each of the instances submitted by cleaners for study showed acid burns, and these were confirmed by chemical analyses, which gave an acid reaction and usually disclosed chloride ions. Tin weighting was found in each instance. Figures 1, 2, and 3 show several of the dresses received, which when analyzed gave the above results. Figure 4 is an enlargement of a portion of Figure 3.

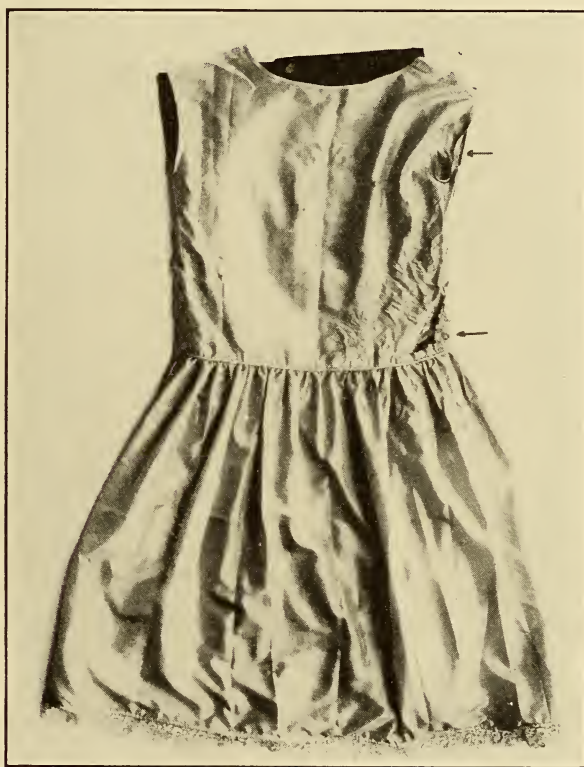


FIG. 2.—*A comparatively new dress showing deteriorations under arms, at left hip, and at the front of the waist*

Analyses of deteriorated fabric showed presence of acid and chloride ions. Microscopic analyses confirmed presence of acid. The silk was tin-weighted.

Another interesting case is illustrated in Figure 5, which shows silk draperies that had been received at the dry-cleaning plant apparently in good condition. No tests could be made for strength, even if it had been considered expedient, since these would necessarily have destroyed the usefulness of the fabric. The draperies were made of tussah or wild silk and were undyed and unweighted. These curtains had had one and one-half seasons' service.

In Figure 5 at A is shown a fairly even line across the curtain where the tendering ceases, resulting no doubt from the protection from the sun afforded by the casement of the window. Similarly, the top of the curtain, evidently protected by a window shade, showed this condition, but not quite so markedly. Only strips (partially tendered) remained, and they correspond to the protected folds



FIG. 3.—A dress that had never been worn, but was used for display purposes in a retail store

Note deterioration. See Figure 4.

resulting from the gathering of the fabric on the curtain rods. Figure 5 at B discloses a sharply defined watermark and partially fractured fabric resulting from the tendering effect of rain subsequently activated by sunlight. In this case no acidity was found, nor was there any metal weighting. The tendering evidently resulted from prolonged exposure (one and one-half seasons) to sunlight.

The members of the National Association of Dyers and Cleaners were desirous of obtaining adequate information of any effects which the process of dry cleaning would have on silks, especially weighted silks. Although primarily interested so that proper safeguards could

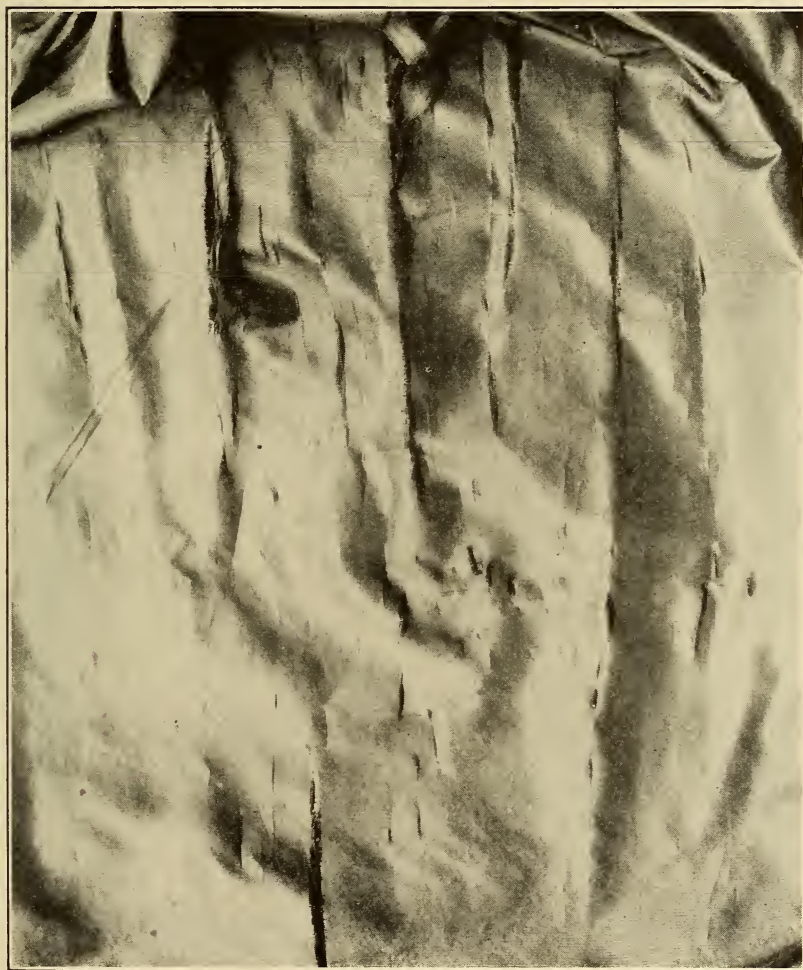


FIG. 4.—*Enlarged view of marked portion of dress shown in Figure 3*

Chemical analysis of the fabric disclosed the presence of acid and chloride ions with trace of sulphate ions.

be made against the numerous claims to which they were being subjected, they also were anxious to make such changes in the process as would be shown expedient if the research work disclosed that the dry-cleaning process was at fault.

Accordingly, a research was planned to study the effect of dry cleaning on weighted and unweighted silks after various conditions incident to service. This problem was carried on by the research associateship of this association established at the bureau.

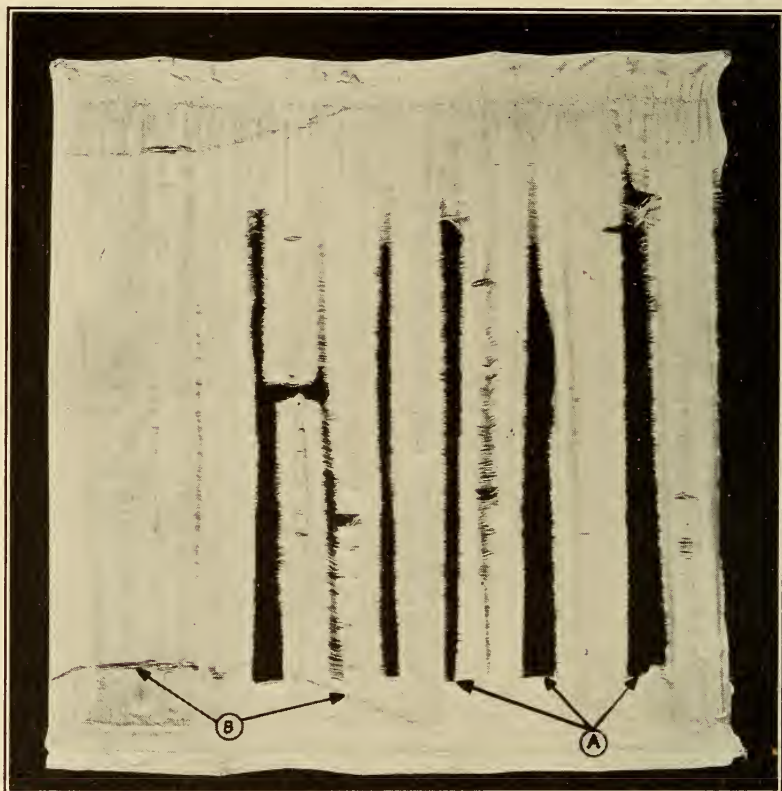


FIG. 5.—Draperies made from wild silk (*tussah*), after dry cleaning although apparently in good condition when received

Note absence of deterioration at top and bottom where protection from the sun was afforded by the curtain and casement of window. The strips correspond to folds in the drapes.

2. ACKNOWLEDGMENTS

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III. PRELIMINARY STUDY

1. LITERATURE ON DETERIORATION OF SILK

Technical literature discloses the fact that the deterioration of excessively weighted silks is well established.² The limitation of weighting which may be safely applied has been a much discussed

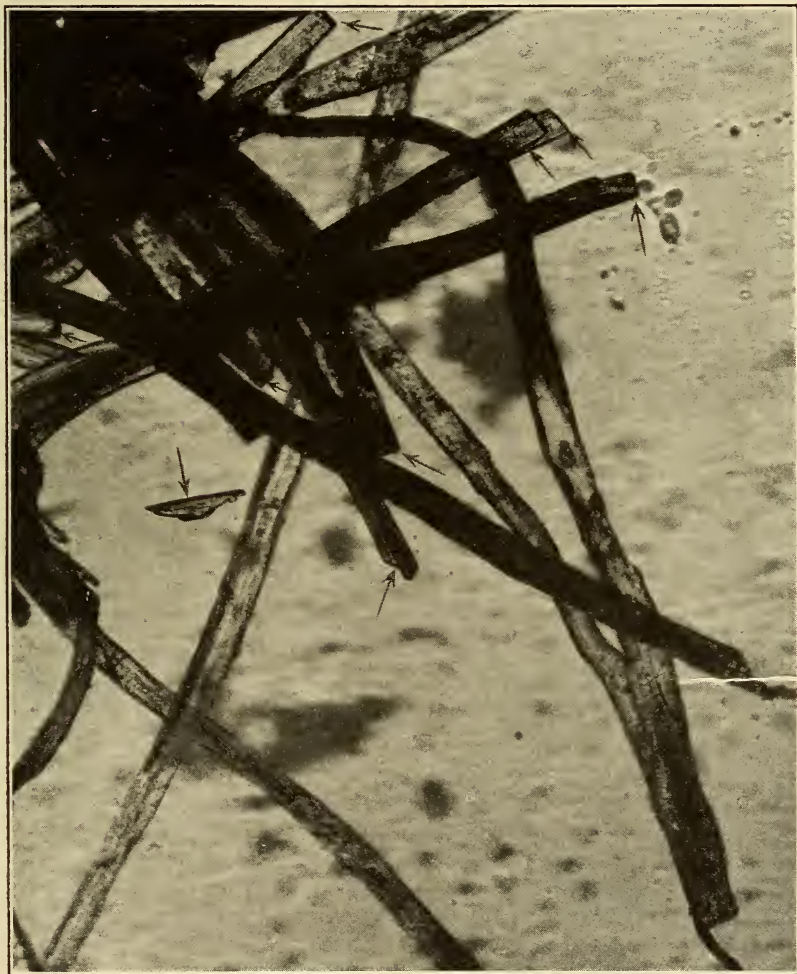


FIG. 6.—*Photomicrograph of portion of draperies shown in Figure 5*

Shows carbonization or sunlight burning resulting in brittle fibers. Crystalline fractures of the silk fibers are indicated by the arrows.

question. Matthews³ states that 18 ounces for warp yarn and 24 ounces for filling yarn is the safe limit; that is, every pound of raw

² Matthews, J. M., *Textile fibers*, p. 306; 1924. Farrell, W., *The practice and ethics of silk weighting*, *The Jour. of the Textile Inst.*, November, 1925. Tisdale, H. R., *Tin weighting skein silk and piece goods*, *Textile World*, June 23, 1924

³ Matthews, *loc. cit.*, p. 309.

silk after degumming and weighting should weigh less than these limits. Chittick's ⁴ safety limits in general agree with Matthews's.

Silk weighted by the tin-silico-phosphate method is often treated with thiourea and hydrosulphate compounds to decrease its tendency toward tendering. In addition to these, hydroquinone sulphonate and ammonium sulphocyanate are also employed.⁵

2. THEORIES OF DETERIORATION

The researches of previous investigators, including Sisley,⁶ Dreaper,⁷ Gianoli,⁸ have shown that deteriorated silks show the presence of chlorides and free acid, and that silks, weighted or unweighted, readily absorb and retain acids. This acid may not only be mechanically held but may be more or less firmly combined chemically with the fiber since the latter is a basic material.

Heermann ⁹ states that deterioration resulted from exposure to light in the case of both weighted and unweighted silks dyed with nitro colors (as picric acid, naphthol yellow S, and azoflavine FF). Nitric acid was found, and it was shown that the acid developed more quickly in the case of the weighted silk. Heermann believes that an unstable nitro compound is formed with the silk.

It is well established that paranitrotolueneorthosulphonic acid, an intermediate used in the preparation of dyestuffs, when treated in solution with sodium chloride, results in the formation of the sodium sulphonate which precipitates out, leaving a strong hydrochloric acid solution. The precipitation of the sodium salt may be attributed to the insolubility of it in strong chloride solution. Moreover, it is well known that many sulphonic acids are very strong acids.

Dyestuffs ¹⁰ are made by chemical treatment of intermediates introducing certain other groups of atoms (chromophores) with a resultant greater complexity of structure. This, in the case of many dyestuffs, is a union of two or more intermediates. Direct and acid dyestuffs, used to a large extent in dyeing silk, after dyeing may be present on the fiber in the form of the free dye acid, or as an acid salt, or as a normal salt, depending on the number of acid groups and their strength. Sulphuric acid or sodium acid sulphate, which is acid in character, may thus result from some chemical change brought about by sunlight, high humidity, etc. Also, the sodium chloride present in perspiration, sea air, etc., may combine with the sulphonic group to form the sodium salt thereof and free hydrochloric acid, or in the

⁴ Chittick, James, Concerning the weighting of silk piece goods, *Textile World*, Aug. 22, 1925.

⁵ See footnote 1, p. 607.

⁶ Sisley, P., Abstracts, *J. Soc. of Dyers and Colorists*, p. 83; 1909.

⁷ Dreaper, W. F., Abstracts, *J. Soc. of Chem. Ind.*, p. 25; 1912.

⁸ Gianoli, *Chemical Zeitung*, p. 105; 1910.

⁹ Heermann, *Chemical Zeitung*, 38, p. 1381-1382; 1918.

¹⁰ Green, Arthur G., *Analysis of dyestuffs*, p. 4 (2d ed.); 1916.

case of the salt of the sulphonic acid, there may occur a somewhat similar reaction.

The increased liability of metallic weighted silk to deterioration may result, especially in the presence of sodium chloride (in perspiration, sea air, etc.), from the action of the hydrochloric or sulphuric acids on the weighting itself, thus causing some reversal of the weighting process, which, if it forms stannic chloride of a sufficient concentration, will tender the silk.

3. EXPOSURES

The conditions most likely to effect some change in the fabric were exposure to sunlight, treatment with perspiration, ironing, and dry-cleaning solvents.

Sunlight exposures could be made by placing samples on the roof of the building with some precautions for removal during storms, etc. It is well known that the intensity of sunlight varies from month to month, from day to day, and throughout the day, but for the purposes of this study it was thought that exposures under these varying conditions would more nearly approximate the service conditions which the garment undergoes.

A conditioning room maintained at approximately 65 per cent relative humidity and 70° F. temperature was available for storing the portions of the samples used for check tests.

4. TREATMENT WITH PERSPIRATION

Procedures for testing resistance of fabric to fading resulting from perspiration had been outlined by the American Association of Textile Chemists and Colorists¹¹ and are in use in many laboratories, including the routine testing laboratories of the Bureau of Standards. Although essentially for testing fastness of dyestuffs, it was felt that they could be used advantageously in this study. It may be noted that although perspiration from the human body is generally acid when fresh, later, through decomposition, it becomes alkaline. The rate of decomposition depends largely on the health and race of the individual.

The formulas used are:

Acid perspiration—

10 grams sodium chloride	} per liter of solution.
1 gram lactic acid U. S. P	
1 gram monosodium orthophosphate	

Alkaline perspiration—

10 grams sodium chloride	} per liter of solution.
4 grams ammonium carbonate U. S. P.	
1 gram disodium orthophosphate	

¹¹ Year Book, p. 72; 1924.

5. IRONING

The temperature of the iron was measured by inserting a calibrated thermocouple into a hole drilled in the bottom of the iron. From observations of the temperature of the iron when used by an experienced operator, the temperature of 275° F. was selected. The procedure used was as follows. After the iron had reached 275° F. it was disconnected and the sample was ironed; it was then connected and brought up to 275° F. again for the next sample. Since the samples were small and only slightly dampened, the drop in temperature was not large.

6. DRY CLEANING

With the view toward formulating laboratory procedure for dry cleaning, the plant practice was studied and the following information was ascertained.

Solvents commonly used as dry-cleaning agents are gasoline, naphtha, benzol, chloroform, ether, carbon disulphide, turpentine, etc.

These solvents are chemically inert in contact with the fibers. Also, they do not alter the shaping; for example, a piece of pleated material retains the pleating in a dry solvent but loses it in water. An elaborately trimmed gown cleaned in a dry-cleaning solvent retains its form in every way, although the same article immersed in water becomes shapeless and must be shaped and ironed into form again.

(a) DRY-CLEANING PRACTICE.—Garments and other materials to be cleaned, in general practice, are usually sorted into three types—white materials, light-colored materials, and dark materials. Sometimes the light-colored materials and dark materials are sorted into woolsens and silks.

Silk garments are generally given extra care. Trimmings are protected, and generally the entire garment is fastened in a net bag to minimize friction, thus reducing wear and the danger of explosions caused by the generation of static electricity.

The common type of dry-cleaning machine has a slotted cylinder approximately 30 inches in diameter, which revolves within a steel or metal-lined wooden shell that holds the cleaning solvent. The staves of the cylinder are perforated to permit action of the solvent through the garments as they are gently lifted and dropped.

The cylinder is constructed with lifting staves that accelerate the cleaning action of the solvent by lifting the load of garments to an angle of about 45° and dropping it back into the solvent, providing the "drop and squeeze" necessary for good cleaning.

The quantity of dry-cleaning solvent used both for cleaning and rinsing garments is the same; that is, the depth of the solvent is about 8 or 10 inches from the bottom of the cylinder.

The quality of solvent differs for the addition of assisting agents to the gasoline or naphtha varies with the class of fabric to be treated. For example, soap soluble in the dry-cleaning solvent¹² may be added during the first 20 to 30 minute cleaning.

After the first cleaning the fabric is rinsed with clear and unadulterated cleaning solvent (silks are usually rinsed twice) in order to remove all traces of soaps and loose soil that may remain.

Following the rinsing process, the garments are drained of excess solvent, and further removal of the liquid is accomplished by placing the garments in a centrifugal extractor, where they remain for one to three minutes. They are then deodorized in a well-ventilated room at 120 to 150° F.

(b) DRY-CLEANING SOLVENTS.—Naphtha for dry-cleaning purposes is being purchased to a large extent to comply with Stoddard's specifications for solvent,¹³ although the more inflammable motor-fuel gasoline is still in use as a solvent. Solvent complying with Stoddard's specifications is a high flash-point petroleum product which has been adopted by the cleaning industry to lessen the loss of life and property by explosion and fire. It is sold under many proprietary names.

It was thought desirable in view of the fact that both types of solvents were used in the industry to include representative samples

¹² Standard practice is to use about 1 pound of concentrated "benzine soap" per 100 gallons.

¹³ Stoddard's specifications for heavy semionflammable dry-cleaning solvent are as follows:

1. The solvent shall be free from undissolved water and suspended matter.
 2. The color shall be water-white.
 3. Doctor test: The doctor test shall be negative.
 4. Unsaturated hydrocarbons: Not more than 2 per cent of the naphtha shall be soluble in concentrated sulphuric acid.
 5. Distillation range: The temperature limits for the distillation are as follows:
The initial boiling point shall not be less than 300° F.
The dry, or end point, shall be a temperature not greater than 400 to 410° F.
 6. Acidity: The residue remaining in the flask after the distillation is completed shall not show an acid reaction.
 7. Aromatic hydrocarbons: The naphtha shall not contain aromatic hydrocarbons, such as benzene, toluene, and others.
 8. The odor shall be sweet.
 9. Flash point: The flash point must not be below 105° F., closed-cup test.
- The tests mentioned in the specifications above shall be made and interpreted in accordance with Bulletin No. 5, Report of Committee on Standardization of Petroleum Specifications, published by the U. S. Bureau of Mines.

of each in this study. Accordingly, solvents were obtained which analyses showed to be as follows:

TABLE 1.—*Analyses of dry-cleaning solvents used in this study*

Tests	Solvent		
	Motor gasoline	Heavy cleaning solvent	Stoddard's specifications
	Color		
	Darker than No. 16 Saybolt	Water white	Water white
Distillation:			
Initial boiling point.....°F..	131.0	293.0	300 min.
10 per cent.....do.....		316.4	
20 per cent.....do.....	226.4	320.0	
50 per cent.....do.....	278.6	334.4	
90 per cent.....do.....	373.4	372.2	
Dry point.....do.....	428.0	406.4	400 to 410 max.
Recovered.....per cent.....	97.5	98.0	
Residue.....do.....	1.1	1.1	
Loss.....do.....	1.4	.9	
Doctor test.....	Negative.	Negative.	Negative.
Unsaturated hydrocarbons.....per cent.....	12.0	1.25	2 max.
Flash point, closed cup.....°F..	56.0	107.0	105 min.

NOTE—The heavy cleaning solvent complies essentially with Stoddard's specifications.

(c) DRY-CLEANING SOAPS.—Analogous to wet washing, a soap is added to aid the solvent in cleaning the materials. This soap, commonly called benzine soap, is soluble in the solvent, causes greater penetration, and acts as a vehicle in the removal of oil and stains.

In benzine soaps only a portion of the fatty acid (usually oleic acid)—that is, about 70 to 90 per cent—is neutralized with caustic alkali, thus differing from water-soluble soaps, in which all the fatty acid is saponified or neutralized.

The benzine soap used in this investigation was prepared according to the following formula: Part 1, 40 quarts of gasoline and 30 quarts of oleic acid; part 2, dissolve 5 pounds of caustic soda in 10 quarts of soft water. Add part 2 slowly to part 1 in a small stream, stirring constantly and continue stirring 15 minutes after all of part 2 has been added.

(d) LABORATORY PROCESS FOR DRY CLEANING USED DURING THIS STUDY.—*Step 1.*—Silk specimens were placed in glass jars containing dry-cleaning solvent to which benzine soap was added (70 grains to the gallon of stock solvent) and agitated mechanically for 45 minutes by slowly rotating the jars.

Step 2.—The specimens were removed from the soapy solvent and placed in new cleaning solvent for five minutes and rinsed free of soap.

Step 3.—The specimens were then centrifuged to remove excess cleaning solvent.

Step 4.—The specimens were then deodorized by placing in a current of air from an electric fan.

7. FIRST SERIES OF EXPOSURE TESTS

Having available the necessary information relative to the process to be used, it was desirable to obtain some data in a preliminary way which would aid in fixing the duration of exposure and intervals at which tests should be made. For this purpose there were purchased 6 silk materials, 5 unweighted and 1 tin-weighted, to which were added samples from 6 other silk fabrics, which had been submitted by an interested manufacturer, 5 of which were weighted.

Specimens were subjected to 9 treatments and exposures as listed in Table 2. All were exposed to direct sunlight for a period totaling 60 hours.¹⁴ Breaking-strength tests were made before and after the various treatments. An additional 40 hours of sunlight exposure was then made and strength results obtained.

TABLE 2.—Treatments and exposures of weighted and unweighted silk fabrics

No.	Treatment	Exposure
1	None	Sunlight.
2	Heavy solvent ¹	Do.
3	Motor gasoline ¹	Do.
4	Acid perspiration ²	Do.
5	Acid perspiration, then heavy solvent	Do.
6	Acid perspiration, then motor gasoline	Do.
7	Alkaline perspiration ²	Do.
8	Alkaline perspiration, then heavy solvent	Do.
9	Alkaline perspiration, then motor gasoline	Do.

¹ See Table 1 for analysis. ² See p. 615 for formula for acid perspiration, p. 615 for alkaline perspiration.

TABLE 3.—Deterioration in strength of silk fabrics, first series

[Per cent of original breaking strength ^a]

Type	Code No.	Treatment ^b																	
		1		2		3		4		5		6		7		8		9	
		60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours	60 hours	100 hours
Satin	I	95	94	103	93	103	88	98	76	97	79	95	80	88	81	88	70	93	78
Do	II	95	93	99	94	97	91	98	74	89	84	93	84	95	87	91	75	90	79
Do	III	93	78	100	75	104	74	81	52	80	63	83	53	81	65	81	66	79	66
Chiffon taffeta	IV	86	81	105	84	103	82	73	61	70	54	70	55	68	58	71	48	71	56
Crêpe	V	85	93	96	90	100	90	84	50	84	40	83	56	78	59	82	49	79	57
Taffeta (weighted)	VI	72	55	72	52	69	41	53	18	54	18	52	29	50	33	54	24	50	27
Crêpe	A	90	84	92	84	89	87	77	61	78	61	79	58	77	57	79	60	80	59
Crêpe (weighted)	B	69	19	73	17	72	17	48	4	45	4	46	4	47	5	49	3	48	5
Do	C	67	23	66	22	65	27	46	4	47	3	48	4	45	3	47	1	44	3
Do	D	40	18	40	18	37	14	25	4	24	3	26	2	29	3	31	3	30	2
Do	E	29	4	31	7	31	0	22	0	22	0	22	0	19	0	18	0	19	0
Taffeta (weighted)	F	55	15	61	21	50	16	45	4	34	3	35	4	33	3	36	4	34	2

^a Average of warp and filling results.

^b Numbers refer to treatments listed in Table 2.

¹⁴ During summer months.

^c Hours exposure to sunlight.

In this series of tests it was found that the weighted silk fabrics decreased in strength from 25 to 100 per cent; the unweighted silk decreased in some cases as much as 40 per cent, but, in general, the deterioration was of the order of 10 to 25 per cent. No loss in strength can be attributed to the dry-cleaning process.

It was noted that five hours' exposure to sunlight could be obtained on the average day, and since outer garments worn outdoors would be subjected to a similar exposure, this made a useful time subdivision for the major investigation. This period was started each day at 10.30 a. m. A total of 100 hours was thought to be a sufficient length of time for the purposes of this study.

It may be desirable to call attention to the fact that this length of exposure (100 hours) for the average garment would require in actual service a period of time aggregating six months to several years. Few garments are worn steadily day after day, and even when this is done their exposure to direct sunlight is generally of short duration.

IV. PROCEDURE FOR FINAL STUDY

The physical tests were made in accordance with standard methods as outlined in Circular 293 of the Bureau of Standards, United States Government General Specification for Textile Materials (Methods of Physical and Chemical Tests). The strip method of measuring the breaking strength was used, using an inclination balance type of machine of 150 pounds capacity, specimens 1 inch wide, distance between jaws 3 inches, and rate of speed of pulling jaw 12 inches per minute.

The weighting was determined by two different methods. Allen's¹⁵ method was used first as follows: (1) Extract with ether in soxhlet apparatus for four hours, dry; (2) extract with alcohol for four hours, dry; (3) extract with boiling distilled water, dry and weigh; then (4) ignite the material and weigh the ash. The first three treatments extracted the nonmetallic weighting, such as oil, sugar, paraffin, soap; the ash ignition was used to determine the metallic weighting.

These determinations were then checked by the method given by Matthews,¹⁶ as follows:

A—1. Dry sample for two hours at 105° C. and weigh. (Bone-dry weight of sample should be between 1 and 2 g.)

2. Boil sample in 250 cc distilled water for at least 30 minutes. (This step removes water-soluble finishing materials.)

3. Dry sample at 105° C. to constant weight. The loss in weight represents the amount of water-soluble finishing materials. (The above preliminary process is essential for practically all commercial samples, which usually contain 2 to 10 per cent of finishing materials.)

¹⁵ Allen, *Commercial organic analysis*, 8 (4th ed.), p. 655.

¹⁶ Matthews, J. M., *loc. cit.*, p. 971.

B—1. Warm 100 cc hydrofluoric acid solution (approximately 2 per cent) to 60° C. Immerse sample and work it in the bath for 20 minutes, not allowing the temperature to exceed 75° C. at any time. (It is safer to keep the temperature between 60 and 70° C. for the entire time of stripping.)

2. After rinsing the acid-treated sample in water, immerse it in a bath of soda ash (approximately 2 per cent) held at 60 to 65° C. Work sample as before and remove at end of 20 minutes.

3. Sample is thoroughly rinsed and dried to constant weight at 105° C. The loss by this operation represents the amount of tin weighting in the sample.

C—1. Determine the amount of residual mineral matter in the silk after the preceding treatment, by the usual ash method; that is, burning off all organic matter. (This final step should be carried out in all cases to check up the completeness of the stripping operations.)

The results of the two methods checked within 1 per cent. Tests were made separately on the warp and the filling, and the greatest difference was found to be under 2 per cent of weighting.

It was noted early in this study that a confusion of terminology existed in the literature as to the basis for calculating percentage of weighting. Some authorities use the weight of the raw silk as a basis, which it will be remembered is made up of about one-quarter sericin; the remainder silk fiber. Other authorities use as a basis the weight of the fiber after all extraneous material is removed.

For the purposes of this study it was decided to use the latter basis; that is, the weight of the fiber alone, the percentage of weighting then being the amount of weighting material divided by the weight of the fiber (after the removal of all extraneous material).

The percentage of soluble material is given separately. This is in the nature of finishing or filling material, similar to those found on some cotton fabrics. Attention is directed to the fact that the metallic weighting is not removable by either wet or dry cleaning methods.

The analyses of the silk samples used during the second series are given in Table 4.

TABLE 4.—Test data on silk fabrics used in second series

Code assigned	Type	Tin weighting	Soluble weighting	Thread count		Breaking strength (strip method)	
				Warp	Filling	Warp	Filling
		<i>Per cent</i>	<i>Per cent</i>			<i>Pounds</i>	<i>Pounds</i>
A-----	Crêpe-----	None	5.0	143	80	37	12
B-----	do-----	41.8	3.2	148	82	36	14.5
C-----	do-----	55.6	2.4	146	83	39	17
D-----	do-----	59.2	3.8	147	84	41.5	20.5
E-----	do-----	62.4	2.6	208	90	48	28.5
F-----	Taffeta-----	55.6	11.4	172	88	31.5	25

All the crêpes had alternate two picks right and left twist.

The taffeta was plain woven.

Per cent of tin weighting calculated on basis of fiber alone (and not fiber plus sericin).

All were dyed except E.

The treatments and exposures listed in Table 2 were then given. The sunlight exposure occurred during the period from September 9 to November 21, 1925, on the roof of the Industrial Building of the Bureau of Standards, Washington, D. C.

Duplicate samples were given similar treatments at the same time as those exposed to sunlight, but instead of exposure to sunlight they were hung in a conditioning room, which was maintained at approximately a relative humidity of 65 per cent at 70° F. These samples were exposed to light from an indirect lighting system about seven hours each day.

The sequence of treatments is shown in Figure 7. At the points indicated by B, the samples were ironed, using an electric iron at a temperature of 275° F. Then breaking-strength specimens were taken and tested, using the 1-inch strip method of test previously described. The remainder of the sample was then subjected to further treatments and exposures.

	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
①	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
②	H	B	B	H	B	B	H	B	B	H	B	B	H	B	B	H	B	B	H	B
③	M	B	B	M	B	B	M	B	B	M	B	B	M	B	B	M	B	B	M	B
④	A	B	B	A	B	B	A	B	B	A	B	B	A	B	B	A	B	B	A	B
⑤	A	H	B	A	H	B	A	H	B	A	H	B	A	H	B	A	H	B	A	H
⑥	A	M	B	A	M	B	A	M	B	A	M	B	A	M	B	A	M	B	A	M
⑦	L	B	B	L	B	B	L	B	B	L	B	B	L	B	B	L	B	B	L	B
⑧	L	H	B	L	H	B	L	H	B	L	H	B	L	H	B	L	H	B	L	H
⑨	L	M	B	L	M	B	L	M	B	L	M	B	L	M	B	L	M	B	L	M

FIG. 7.—Sequence of treatments

Each sample was divided into 18 parts, half of which were given sunlight exposures and the other half were kept in a conditioning room. The hours of exposure are given at the top of the chart, each rectangle denoting five hours. The numbers at the left denote the code number of the treatment (see Table 3). Reading from left to right will give the steps taken with each of these parts. The following symbols are used: B, breaking strength test; H, dry cleaning with heavy solvent; M, dry cleaning with motor gasoline; A, treatment with acid perspiration; L, treatment with alkaline perspiration. For instance HBA signifies that the material was dry cleaned with heavy solvent, then breaking strength specimens were taken from the sample and tested, then the remainder was treated with acid perspiration. In all cases the samples were ironed before taking the breaking strength specimens and in all cases these specimens were conditioned before testing.

V. TEST RESULTS AND DISCUSSION

The deterioration of the silk was measured in terms of breaking-strength values, and for convenience in evaluation these were calculated in terms of per cent of the original strength; that is, the strength before any treatments or exposures had been given. The warp and filling results were recorded separately. These results were then formed graphically in charts similar to the one shown in Figure 8, which shows a comparison of the unweighted sample A with a typical weighted sample D.

This chart (fig. 8) shows that no appreciable deterioration occurred as a result of exposures in the conditioning room, even when the treatments listed in Table 2 were given. This was to be expected, for it must be realized first that the age of the samples was unknown as far as date of manufacture was concerned, and second, that the data obtained in this phase amounted to a series of tests made over a period of two and one-half months on samples stored under almost ideal conditions. The variation from point to point in the results

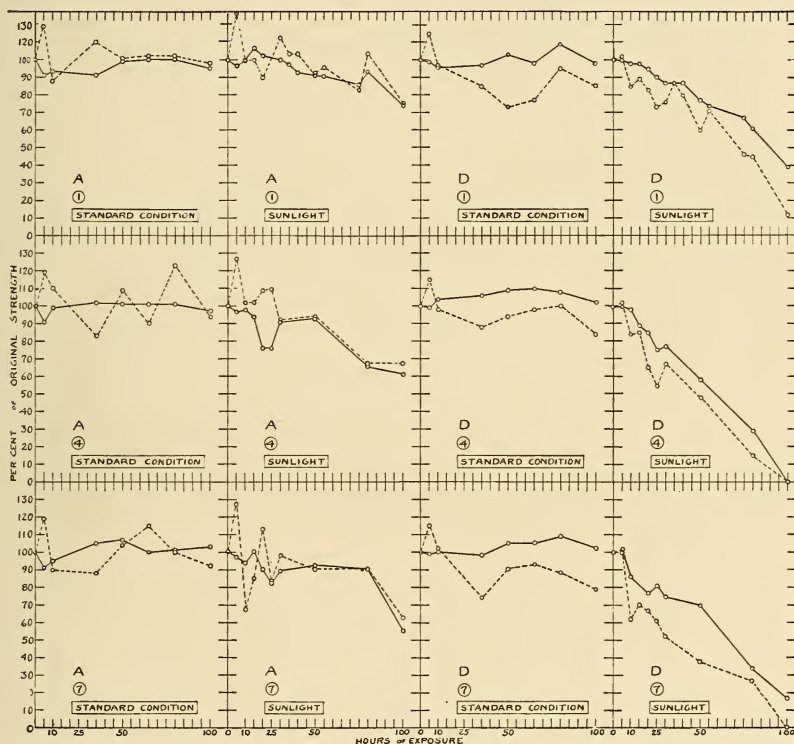


FIG. 8.—Comparison of two silk fabrics which have undergone various treatments as denoted by figures in circles (refer to fig. 7) and subjected to the exposures shown

Fabric A is a dyed unweighted silk; fabric D is a dyed tin-weighted silk.

of each sample in this phase was quite marked, and the interpretations should be based on the warp, which showed much less variations than the filling. The variations of the filling from point to point on the chart may be partly accounted for by the fact that the filling strength was quite low at the start and thus variations expressed as per cent appear large; for instance, filling breaking strength of D at start was 20.5 pounds, thus a 1-pound difference appears as 5 per cent. Also, there is a possibility of a lack of balance in the

filling on account of the crêpe weave, alternating two picks having right and left twist.

Figure 8 also shows that the exposures to sunlight cause deterioration even in the unweighted sample A and that this deterioration is more marked when the samples are treated with acid or alkaline perspiration.

Figure 9 shows deterioration resulting from sunlight alone and compares these results with those obtained on samples dry-cleaned at intervals. It is conclusively shown that neither the heavy solvent nor the motor gasoline added appreciably to the deterioration; in fact, there was some indication that the deterioration was retarded in the early stages as a result of the dry cleaning. The deterioration of the unweighted sample was in most cases less than half that of the weighted samples.

Figure 10 permits a comparison of treatments 1, 4, 5, 6, 7, 8, and 9 (see fig. 7), including standard condition, sunlight exposures alone, and sunlight exposure with acid or alkaline perspiration and two

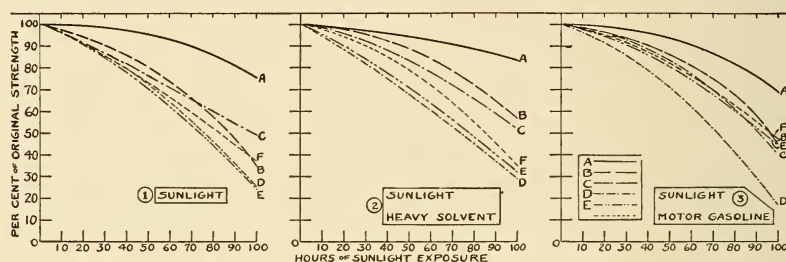


FIG. 9.—Comparison of the effect on the strength of silk fabrics exposed to sunlight, which have had no treatment, dry-cleaning treatment at intervals with heavy solvent, and the same but using motor gasoline

(See fig. 7 for sequence of treatments and Table 2 for code of fabrics.)

different dry-cleaning solvents. Confirming previous conclusions regarding deterioration resulting from sunlight exposures, it shows, in addition, that both alkaline and acid perspiration increase the deterioration, and that neither of the dry-cleaning solvents causes any additional deterioration.

Since all the samples were ironed before the breaking-strength test specimens were taken, it was thought that some attention should be given to this factor. Accordingly, samples were ironed 15 times, strength tests being taken after each five ironings. No appreciable loss was shown.

Some consideration was also given to determining what the result of covering the silk with a cotton material during the sun exposures would be. Samples of the weighted and unweighted fabrics were treated with acid perspiration and then sewed between two layers of bleached cotton sheeting. The treatment was repeated at 20-hour

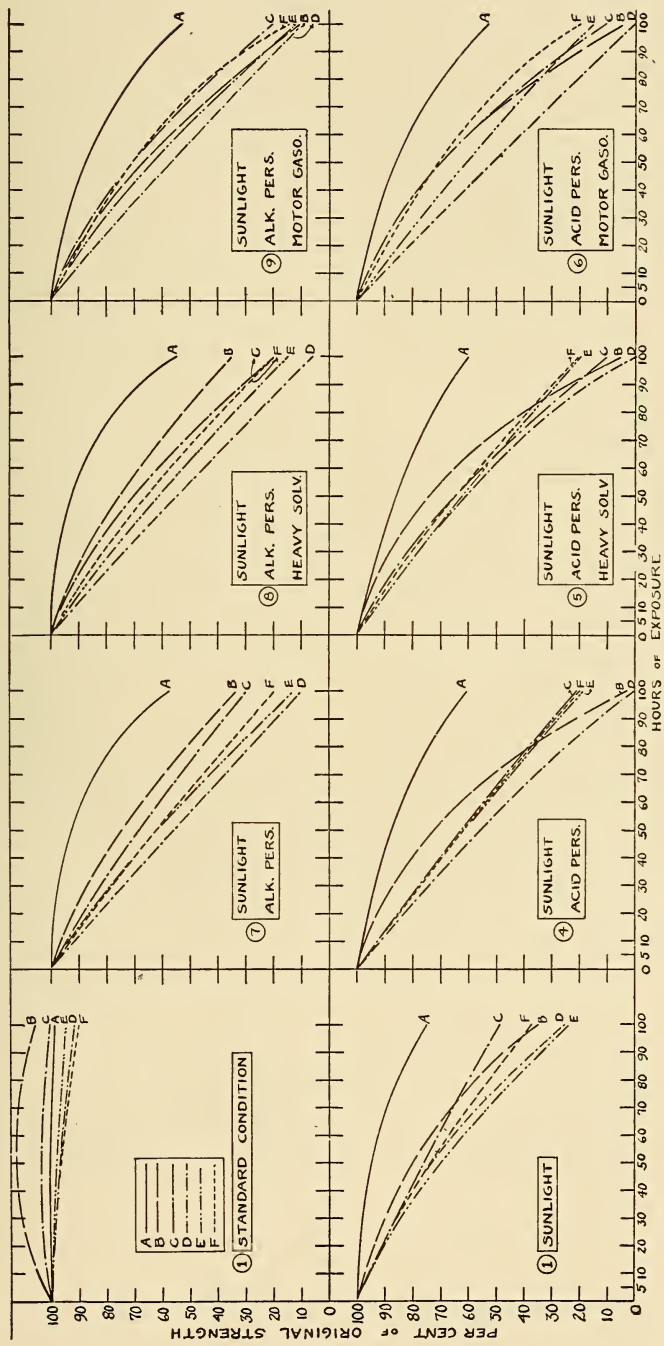


FIG. 10.—Comparison of the effect of sunlight exposures on the strength of silk fabrics treated as shown
The figures in circles are references to Figure 7, and for color of letters opposite curves see Table 2. "A" is an unweighted dyed silk; all others are tin-weighted.

intervals. These were exposed to sunlight for 100 hours and then tested. It was found that the unweighted samples decreased in strength about 35 per cent, and the weighted samples showed de-

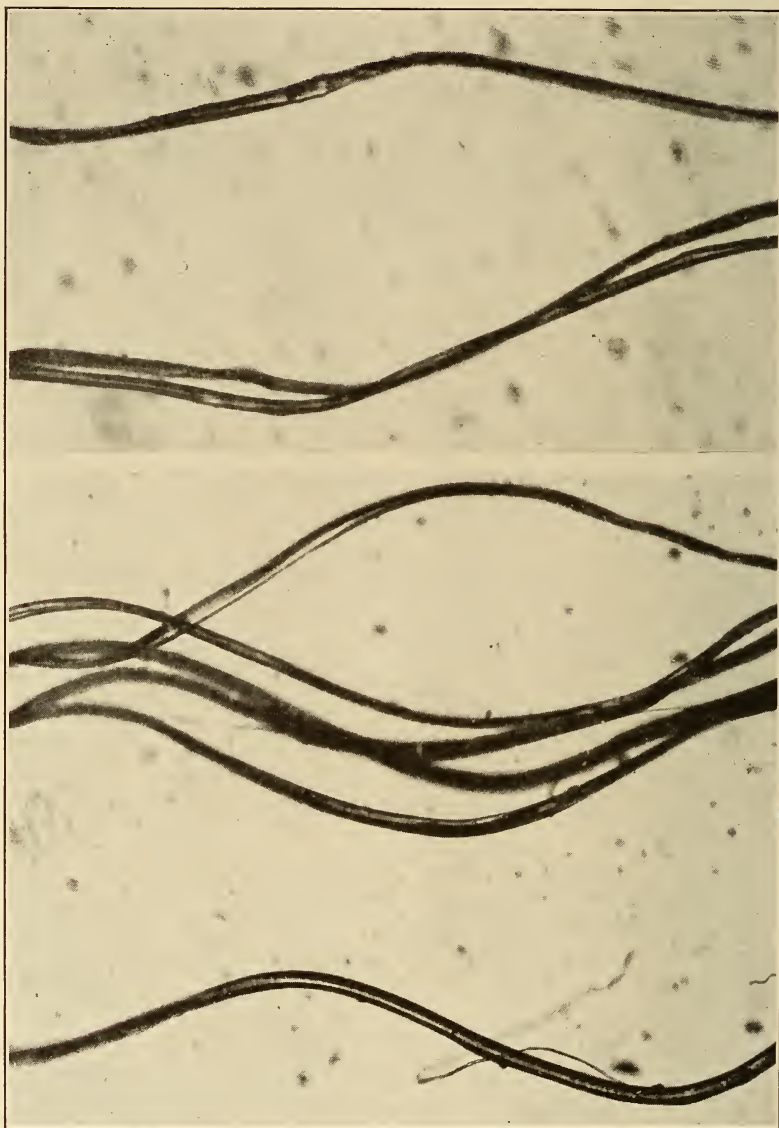


FIG. 11.—Upper. Fibers from sample A (unweighted silk), no treatment and no exposure. Lower. Fibers from sample D (weighted silk), no treatment and no exposure.

creases in strength ranging from 60 to 90 per cent. The rays of the sun which caused the deterioration evidently penetrated freely through the cotton sheeting.

The tendered or deteriorated silk in each case gave an acid reaction when analyzed, and examination under the microscope showed crystallization, carbonization (partial decomposition), or acid burns. The crystalline form appears as a result of the disintegration of the fiber into minute fibrils, caused by the brittleness resulting from deterioration or the actual shearing of the fiber by the crystals from the acid or alkaline treatments. A series of photomicrographs were

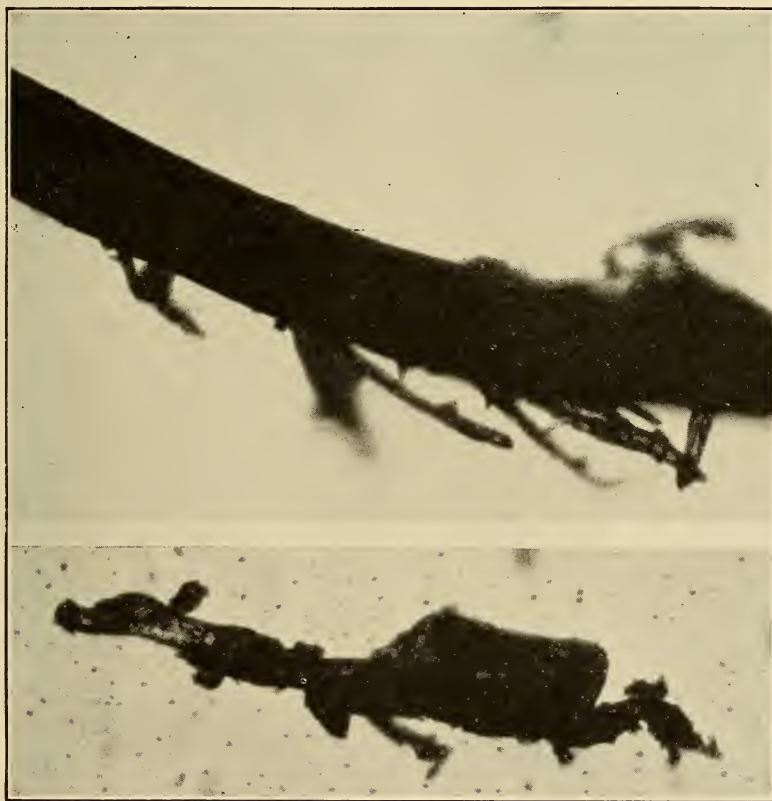


FIG. 12.—Upper. A filling yarn from sample C (weighted silk). Lower. A specimen of powder which fell while fraying sample C

Upper. A filling yarn from sample C which had been exposed to sunlight for 55 hours. (Refer to fig. 7.) Crystalline formations on the tightly twisted yarn are evident. Lower. A specimen of the powder which fell while fraying sample D (weighted silk) after it has been exposed to sunlight for 100 hours. (Refer to fig. 7.) Evidence of the crystalline coating on the tin weighting and carbonizing of the silk is apparent.

made showing some of the typical cases. These are given in Figures 11 to 16, together with explanatory titles.

The tendered silk, even though it had deteriorated to a point where the slightest strain broke or tore it, appeared to be in good condition, although somewhat faded (see fig. 17); in fact, it had the same characteristic appearance as weighted silk which has been ignited.

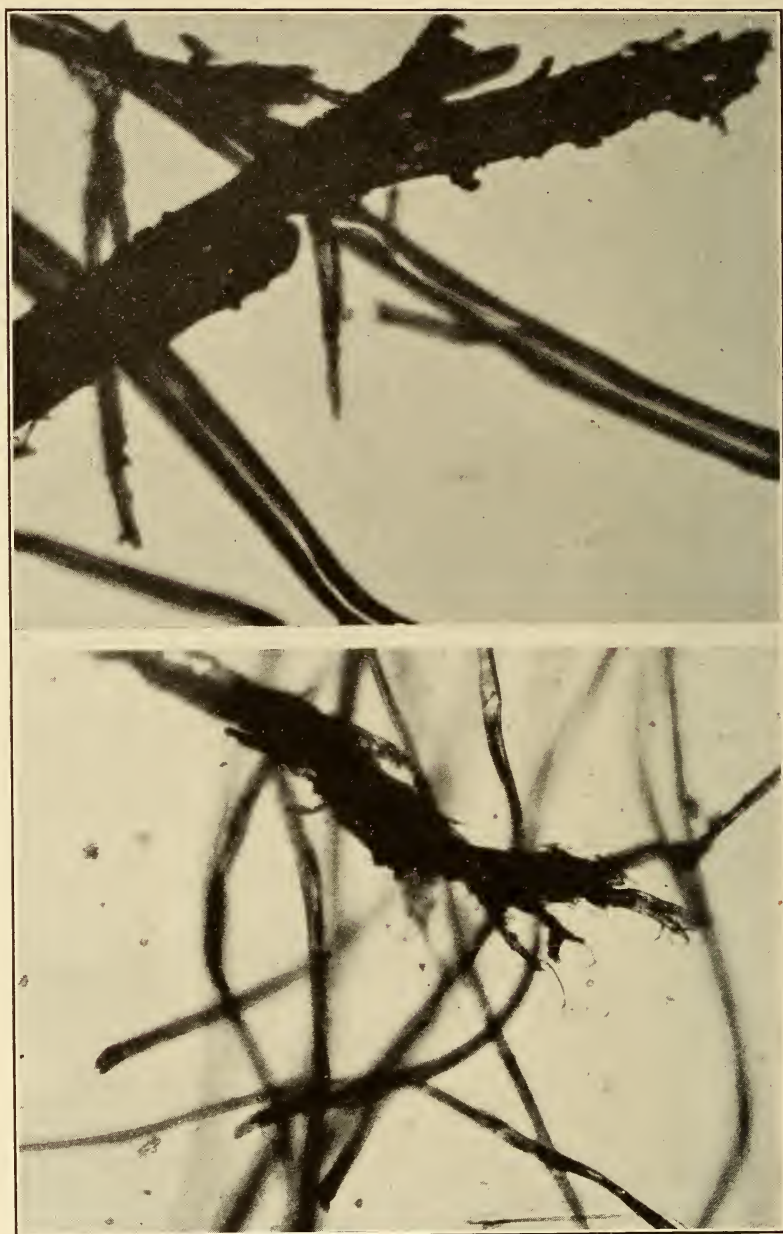


FIG. 13.—Upper. *Fibers from sample C (weighted silk).* Lower. *Samples from sample B (weighted silk)*

Sample C after treatment outlined in Figure 7, consisting of acid-perspiration treatments at intervals and sunlight exposure for 60 hours. Corrosive action on some of the fibers is evident. Fibers from sample B (weighted silk) after treatment as above for 100 hours. Ends of fibers show typical acid burns. Complete deterioration is shown in one place.

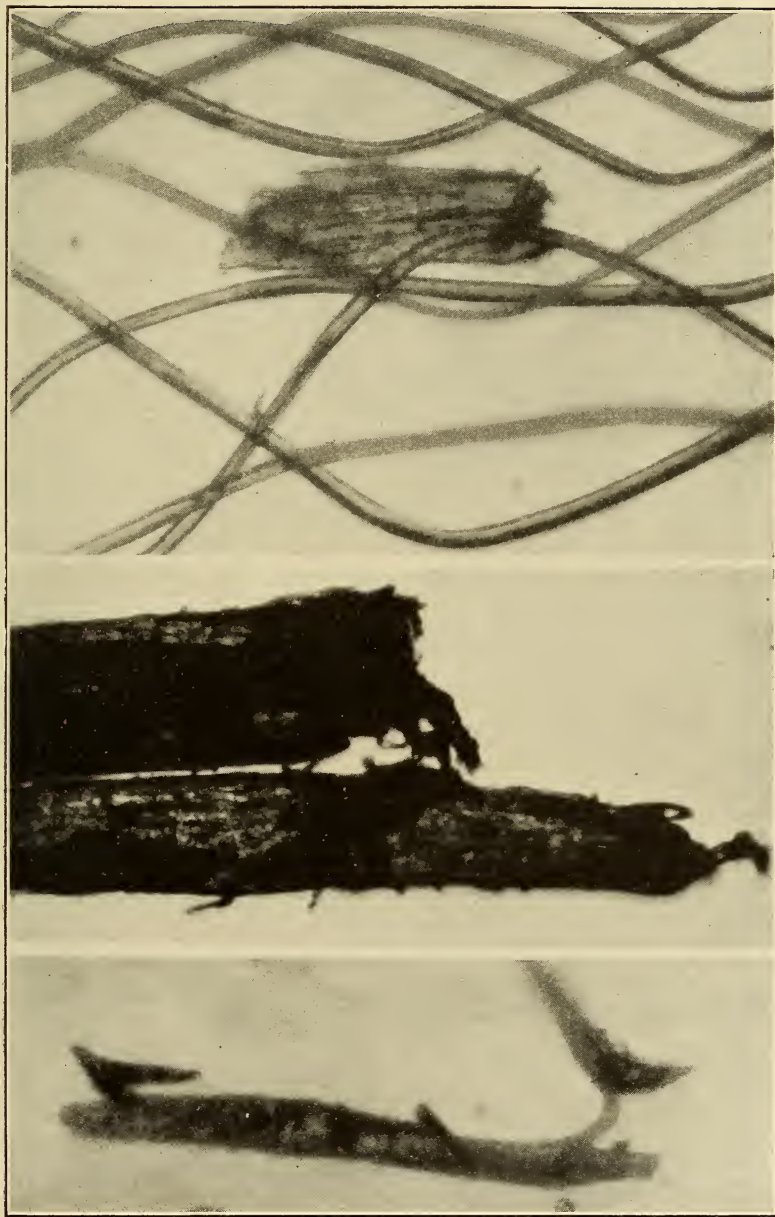


FIG. 14.—Top. Fibers from sample A (unweighted silk). Middle. Fibers from sample B (weighted silk). Bottom. Specimen of powder that fell during fraying of sample D

Fibers from sample A after treatment consisting of alkaline perspiration treatments at intervals and sunlight exposure for 60 hours. (See fig. 7 for sequence.) Little, if any, deterioration has occurred. A crystal structure from the alkaline solution is evident. Fibers from sample B (weighted silk) after similar treatment as above, showing marked deterioration and the typical crystalline effect. A specimen of the powder that fell during the fraying of sample D after treatment similar to above except that the exposure was for 80 hours instead of 60.

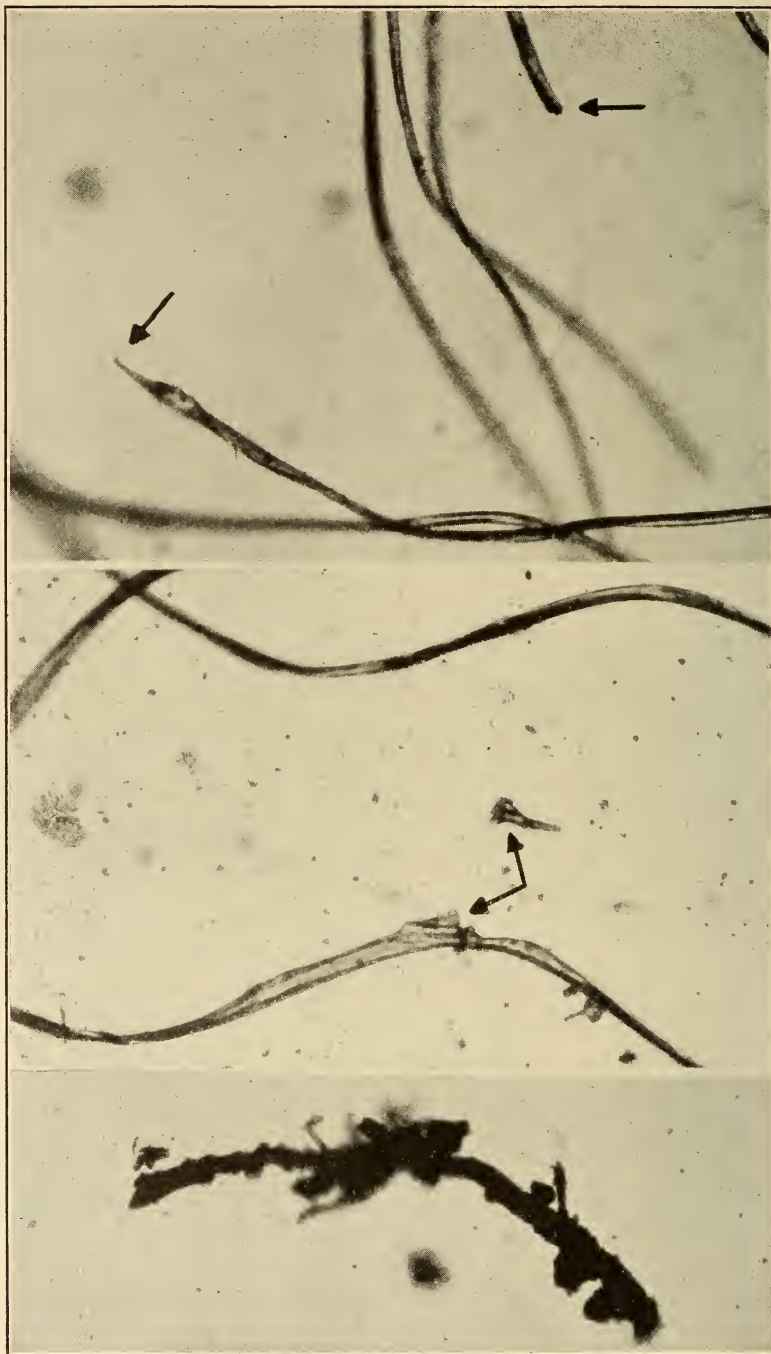


FIG. 15.—Fibers from deteriorated weighted silks

Top: Sample B after 60 hours of treatment 5 (fig. 7). Rounded ends and pigtail formations characteristic of acid burns are evident. Middle: Sample C after 60 hours of treatment 6. Note crystalline structure and brittle fragments indicated by arrow. Bottom: Dust particles from sample C when it was torn after 100 hours of treatment 6. The fabric had been completely deteriorated.

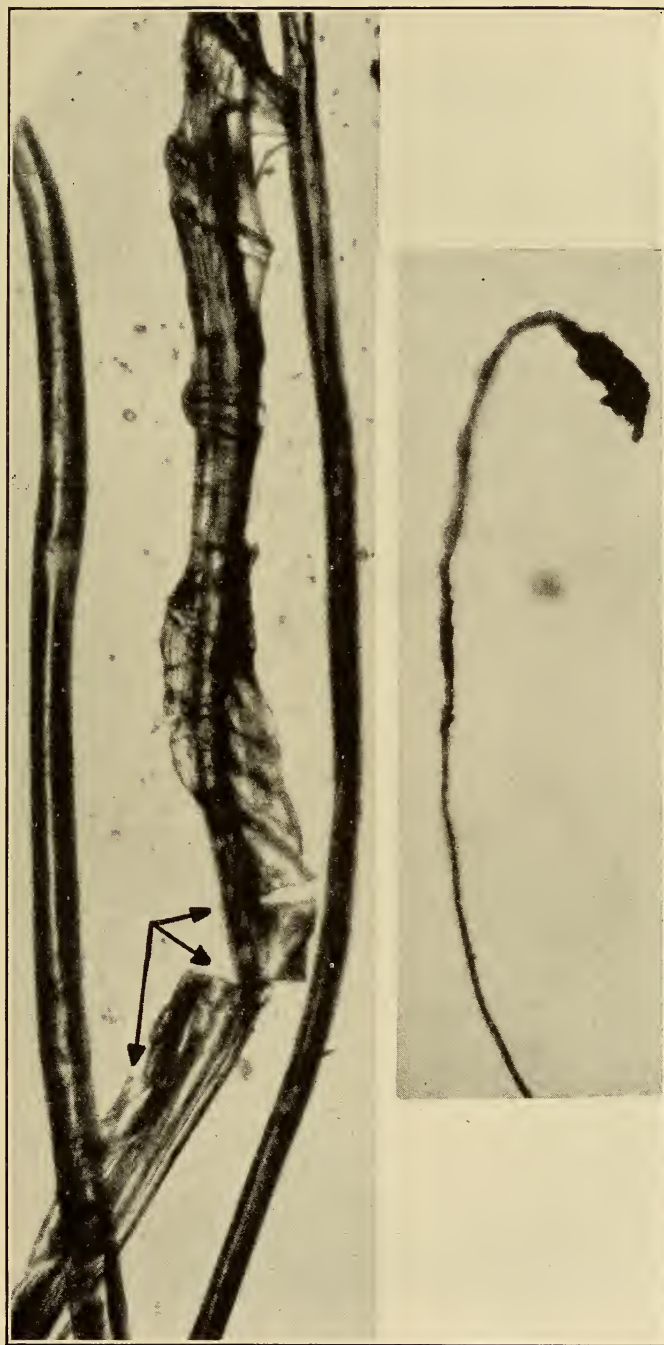


FIG. 16.—Upper. Fibers from sample A (unweighted silk) Lower. Fibers from sample C (weighted silk)
Sample A has undergone treatments with alkaline perspiration and dry cleaning with motor gasoline and had been exposed to sunlight for 60 hours (see treatment 4 in fig. 7). The arrows point to the breaks in the fiber caused by the brittleness and crystalline character of the silk resulting from the treatments and exposures. Sample C treated similarly. The corrosion of the entire fiber may be observed.

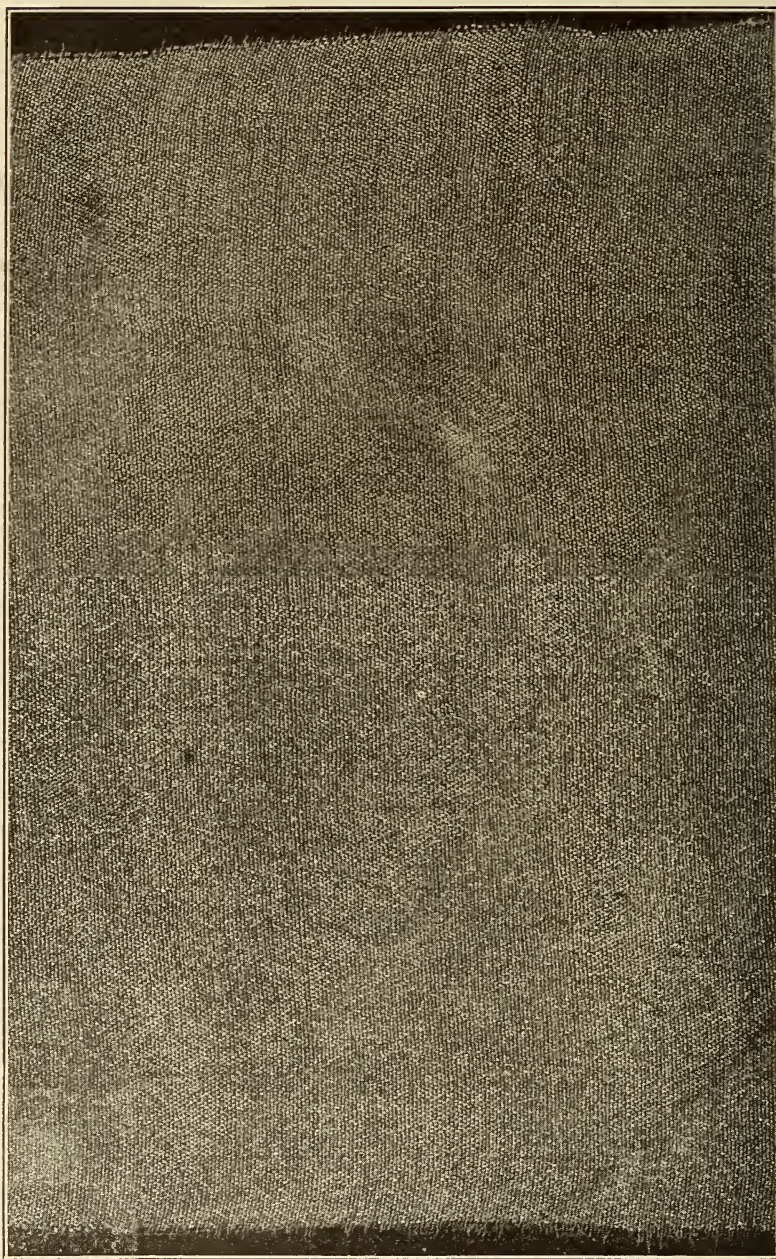


FIG. 17.—A portion of sample D (a weighted silk material) after exposure to sunlight for 100 hours. The fabric, except for some fading, appeared to be in excellent condition, and shows how the dry cleaner may be deceived by deteriorated material. Only a slight strain was necessary to tear the material; in fact, it could not support its weight when wet.

(Weighted silk when ignited leaves an ash retaining the same form as the original fabric; that is, the identity of the weave is not lost.) Even the slight whipping of the wind resulted in tearing in the latter stages of the tests, and the weight of the solvent on the fabric was at times sufficient to tear the sample when it was lifted from the liquid.

This fact is important, for dry cleaners are unable to judge the deterioration of a garment from its appearance, and to subject it to any kind of strength or tear test would destroy its usefulness. It can readily be observed that even the slight stresses and strains incident to careful dry cleaning may result in tears and holes.

However, the strength factor of the silk materials used for garments is fairly high considering the stresses incident to its normal use. Thus, although the deterioration of the sample A appears large when expressed as per cent of the original strength, there is little possibility that with normal care any tearing of the fabric will result. The fact, as previously stated, that the equivalent of the exposure given in this study may require six months to several years to equal it in actual usage, indicates that no particular alarm need be felt, for in all probability the garment will be out of service either because of style changes or actual abrasive wear before sufficient disintegration has taken place to impair its usefulness. Occasionally these deteriorated garments occur, however, and in the large number of garments handled by the dry-cleaning industry they provide a source of trouble and, generally, expense.

A careful study of these results shows that the dry-cleaning solvents did not affect the silk fabric; in fact, as pointed out previously, some retarding of the disintegration was evident in the early stages of the treatments. This may have resulted from a slight amount of benzine soap remaining on the fiber, which acted as a moisture repellent. From a chemical standpoint, none of the ingredients used in the dry-cleaning process contains any chlorides whatsoever, with the possible exception of a trace as an impurity in the caustic soda used in making the benzine soap, which impurity would be still further minimized because of the small amount of the soap used in the cleaning process.

Practical observations disclose the fact that vegetable and animal oil or fats and animal secretion as soil on silk weighted with tin salts, after short exposure or in the presence of heat becomes indelible.¹⁷

VI. SUMMARY AND CONCLUSIONS

The study of tin-weighted and unweighted samples of silk after various treatments and exposures to sunlight and storage at standard conditions (of 65 per cent relative humidity at 70° F. temperature) permits the following conclusions.

¹⁷ Note by C. C. Hubbard.

1. No deterioration results from exposures to standard atmospheric conditions over a period of two and one-half months, even when acid or alkaline perspirations are applied.

2. Sunlight exposure causes a marked deterioration in both unweighted (but dyed) and tin-weighted silks, the loss in strength in 100 hours' exposure amounting to about 25 per cent for unweighted and about 50 to 75 per cent for weighted silks.

3. Acid and alkaline perspiration treatments increase the deterioration when sunlight exposures are given, so that the loss in strength in 100 hours' exposure is about 35 per cent for unweighted and about 65 to 100 per cent for weighted silk.

4. One undyed weighted sample showed disintegration similar to the dyed samples.

5. Dry-cleaning solvents in no case caused any appreciable deterioration of the silk fabrics.

WASHINGTON, June 25, 1926.

