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FOURTH BIMONTHLY PROGRESS REPORT

Covering the Period

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TITLE: ACCELERATED DETERIORATION OF TEXTILES

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INTRODUCTION AND RELATIONSHIP TO PREVIOUS WORK

The previous reports of this series have been concerned, in part, with the photooxidative degradation of cellulose, catalyzed by ferric ion. It was demonstrated that cellophane is a valid model for cotton in these studies, and that accurate measurement of light absorbed could be made more easily in the cellophane than in cotton. Current experimentation, described herein, has been concerned with (1) accurately measuring the light absorbed by untreated cellophane and by cellophane containing ferric ion, and (2) relating the extent of degradation in the cellophane to the total amount of light absorbed. In these current studies degradation has been determined, not only as loss in breaking strength, the parameter used in preceding work, but also as reduction in the degree of polymerization. Increase in carboxyl content, a measure of the oxidation of the cellophane, has also now been determined for some of the photodegraded samples.

Uranyl oxalate actinometers have been used, as in the previous experiments, to measure the light intensities to which the cellophane samples were exposed. For comparison, a measurement of the intensity of sunlight has also now been made, using a uranyl oxalate actinometer.

Some experiments with photo-degradation catalysts other than ferric ion were described in the preceding report of this series. It was reported that ceric and cerous ions were about one-half as effective as ferric ion. The current report describes further experiments with these ions and with other compounds chosen as possible degradation accelerators.

SUMMARY

The amounts of light absorbed by untreated cellophane and by cellophane containing 0.2% ferric ion were determined for the range of wave lengths from 3600 to 6000 Angstroms. Highest absorbances, by both the treated and untreated

cellophane, occurred at 3600 A; the treated cellophane absorbed 26 percent of the light incident upon it and the untreated cellophane absorbed 12 percent of the incident light. At 6000 A the absorbances by the treated and untreated cellophane decreased to 8 percent and 2 percent, respectively. Over the range from 3600 to 5000 A the treated cellophane absorbed about two and one-half times as much light as the untreated.

Sheets of the cellophane containing 0.2% ferric ion and untreated cellophane were exposed to light in the Fadeometer for periods up to 150 hours. Degradation of the cellophane was measured as loss in breaking strength and also as reduction in degree of polymerization. The treated cellophane was degraded more than the untreated in every case where the samples were exposed for the same length of time. The number of scissions per cellulose chain in the treated and untreated cellophane were calculated from the data for reduction in D.P. after 150 hours Fadeometer exposure. There were two and one-half times as many chain scissions in the treated cellophane as in the untreated. Since the treated cellophane absorbed about two and one-half times as much light as the untreated, it appears that the ferric ion may have accelerated degradation mainly through an ability to absorb light energy and transfer it to the cotton. The validity of this hypothesis will be checked by employing catalysts, other than ferric ion, which have strong absorbances in the near ultra violet region (3600 to 4000 A), which are, themselves, stable to this irradiation, and are preferably not electron acceptors.

Some work was started on determining the changes in carboxyl content of cellophane upon exposure to light. It was found that the carboxyl content of untreated cellophane was increased from 2.4×10^{-5} mole per gram to 6.6×10^{-5} mole per gram by 150 hours exposure in the Fadeometer.

The intensity of sunlight, at noon, on a clear day was determined using a uranyl oxalate actinometer. The sunlight was found to be two-thirds as intense as the light in the Fadeometer to which the test samples are exposed.

Work was continued using degradation accelerators other than ferric ion on cotton. Those tested were: uranyl ion, ceric ion, cerous ion, ferrous ion, 2-anthraquinone sodium sulfonate, and 1-anthraquinone sodium sulfonate. None were as effective as ferric ion, our most effective catalyst. Ceric ion and cerous ion were about one-half as effective as ferric ion. The other compounds were somewhat less effective than this.

Two combinations of catalysts were also tested on cotton. These were: ferric ion plus ceric ion and ferric ion plus ferrocene. The strength loss caused by the ferric-ceric combination was not quite as high as the sum of the strength losses caused by these ions, individually. Although ferrocene, alone, has previously been found to cause no strength loss, the combination of 0.1% ferrocene plus 0.1% ferric ion caused a greater strength loss than that caused by 0.1% ferric ion, alone. However the combination was less effective than 0.2% ferric ion.

FUTURE WORK PLANNED

1. Studies of degradation accelerators, other than ferric ion, will be continued. Additional combinations of catalysts will be tried, especially combinations with compounds which might be conveyed to the cellulose substrate in vapor form.
2. Methods for accelerating the degradation of nylon and wool will be explored.

DETAILS

The cellophane and cotton used in these studies were the Avisco Type 300 cellophane and the 80 x 80 print cloth described in the previous reports of this series. Samples were exposed to light in the Fadeometer at an ambient air temperature of $44 \pm 3^{\circ}$ C. as described in the Third Bimonthly Progress Report. Uranyl oxalate actinometers, described in the Second Bimonthly Report, were used to measure the light intensity in the Fadeometer. For all of the

experiments described below the light intensity was $1.85 \pm 0.20 \times 10^{-4}$ mole of light per hour per square centimeter, at the distance from the carbon arc where the test samples were mounted.

The amount of light absorbed by untreated cellophane and by cellophane containing 0.2% of ferric ion (present as ferric nitrate) were calculated from data for transmittances, and reflectances over the range of wave lengths from 3600 to 6000 A. The transmittances were measured directly with a Beckman DU spectrophotometer. Reflectances were measured, also employing the Beckman DU spectrophotometer, by the technique of Launer (Ref. 1). In this technique the transmittances through a single sheet of cellophane and through two sheets of the cellophane, held together, are measured directly. The reflectance from a single sheet is then given by the equation:

$$R_a = 1 - (T_a)^2/T_{2a}$$

where R_a = reflectance

T_a = transmittance through one sheets

T_{2a} = transmittance through two sheets

These calculated reflectances and the measured transmittances, expressed as percent, for untreated cellophane and for the cellophane containing 0.2% ferric ion are plotted in Figure 1 for the range of wave lengths from 3600 to 6000 A. Also plotted in Figure 1 are the absorbances, calculated from the relationship: % Absorbance = $100 - \% \text{ transmittance} - \% \text{ reflectance}$. Over the range from 3600 to 5000 A, the treated cellophane absorbs about $2\frac{1}{2}$ times as much light as the untreated.

Sheets of the treated and untreated cellophane were exposed in the Fadeometer for periods of 30 hours, 100 hours, and 150 hours. Losses in breaking strength for these samples and for unexposed controls are given in Table 1. Also given in Table 1 are the D.P.'s determined from the viscosities of cupraethylenediamine (CUENE) solutions of the cellophane, using the relationship:

$$\frac{N_{sp}}{c} = K_M M_w$$

where M_w = the weight-average molecular weight of the cellulose
 N_{sp} = specific viscosity of the CUENE solution
 c = concentration of cellulose, based on the base molar concentration
 K_M = 8.0×10^{-4} (Ref. 2)

$$\text{and D.P.} = \frac{M_w}{162}$$

The ferric ion was extracted from the treated cellophane with 0.1N HCl before the cellophane was dissolved in CUENE. It is probable that a slight decrease in D.P. of the exposed samples was caused by the HCl extraction. As shown in Table 1, untreated cellophane, exposed for 30 hours in the Fadeometer, had a D.P. of 348. A portion of this sample was extracted with HCl before it was dissolved in CUENE. The D.P. of this extracted cellophane was 317. HCl extraction of untreated cellophane, which had not been exposed in the Fadeometer, caused no measurable decrease in D.P. It is evident from the data in Table 1 that some "dark" reaction of ferric ion with cellophane occurs. Whether this "dark" reaction is hydrolysis, or oxidation, or both, remains to be checked.

The number of chain scissions per chain, s , was determined for the untreated and the treated cellophane, exposed for 150 hours, using the equation of Sakurada and Okamura (Ref. 3):

$$\frac{\text{D.P. final}}{\text{D.P. initial}} = \frac{2}{S^2} (S-1 + \frac{1}{e^S})$$

Initial and final D.P.'s for the untreated cellophane were taken as 362 and 268. For the treated cellophane D.P.'s of 288 and 148 were used. The calculated values of s for the untreated and treated cellophane are 1.0 and 2.4, respectively.

The carboxyl contents of the untreated cellophane samples were determined using the Methylene Blue Absorption Method of Davidson (Ref. 4). It was found that the carboxyl content increased from 0.024 mmole per g for unexposed cellophane to 0.066 mmole per g after 150 hours Fadeometer exposure. This increase of 0.042 mmole per gram is equivalent to one carboxyl group formed

per 147 glucose units. This is very nearly equal to two carboxyl groups per chain in the degraded cellulose (D.P. equals 267). It was found that the HCl extraction, used to remove the ferric ion from the treated samples, decreased the carboxyl content considerably. This was verified by determining the carboxyl content of untreated cellophane, which had been exposed 100 hours in the Fadeometer, before, and after, extraction with HCl. The carboxyl content was 0.046 mmole per g before extraction, and 0.011 mmole per g after extraction. Preliminary investigations of the possibility of measuring the carboxyl content of ferric treated cellophane by infrared absorption spectroscopy have been started.

The intensity of sunlight was measured, actinometrically, over a one hour period, around noon, on a clear day. The window of the actinometer cell was aimed directly at the sun during the entire hour. Using the value of 0.6 for the quantum yield, analysis of the uranyl oxalate actinometer solution indicated that 1.2×10^{-4} mole of light had been absorbed in the one hour through the 1 sq. cm. window of the cell. This is about two-thirds of the value, 1.85×10^{-4} mole of light per sq. cm. per hour, reported above as the intensity in the Fadeometer.

Table 2 lists the degradation accelerators which were investigated on cotton. Breaking strength losses for samples exposed in the Fadeometer and for samples stored at 70° F., 65% R.H. under ordinary indoor illumination are given. The 2-anthraquinone sodium sulfonate was recommended by Dr. Edward Wulkow of the Army Chemical Research and Development Laboratories (CRDL), Army Chemical Center, as the most effective of a group of quinones studied in initial experiments at CRDL. As shown in Table 2, it was much less effective than ferric ion.

As shown in Table 2 ferric ion was equally effective, applied as either ferric chloride or as ferric nitrate. 0.2% ferric ion caused little more strength loss than 0.1% ferric ion. Similarly, cerous ion was equally

effective, applied either as cerous chloride or as cerous nitrate. 0.25% cerous ion was less than twice as effective as 0.1% cerous ion. It is significant that cerous and ceric ions are equally effective, but ferric ion is considerably more effective than ferrous ion. The cerium is apparently more easily raised to its higher oxidation state by atmospheric oxygen than is the iron.

REFERENCES

1. Launer, H. F., J. Research NBS 27, 429 (1941).
2. Staudinger, H., and Daumiller, G., Ber. 70B, 2508 (1937).
3. Sakurada and Okamura, Z. Physik. Chem. A187, 289 (1940).
4. Davidson, G. F., J. Textile Inst. 39, T65 (1948).

TABLE 1
PHOTODEGRADATION OF CELLOPHANE IN THE PRESENCE
AND ABSENCE OF FERRIC ION

<u>Hours Exposed in Fadeometer*</u>	<u>Ferric Ion Concentration, %</u>	<u>Loss in Breaking Strength, %</u>	<u>D.P. Before Extraction with HCl</u>	<u>D.P. after Extraction with HCl</u>
0	0	0	350 to 370 ^a	362
0	0.2	0	Not tested	288
30	0	0	348	317
30	0.2	14	Not tested	195
100	0	6	328	Not tested
100	0.2	17	Not tested	185
150	0	6	266, 268 ^b	Not tested
150	0.2	25	Not tested	148

* - Ambient air temperature was 44° C.

a - Range for 5 sheets, D.P.'s determined on different days.

b - Two separate sheets, exposed at different times.

TABLE 2

PHOTOCATALYTIC DEGRADATION OF COTTON

<u>Catalyst, %</u>	<u>How Applied</u>	<u>Percent Strength Loss</u>	
		<u>After 30 Hours Fadeometer Exposure</u>	<u>After 30 Hours at 70° F., 65% R.H.</u>
None	--	5	0
Ferric ion, 0.1%	Fe(NO ₃) ₃	58	14
Ferric ion, 0.1%	FeCl ₃	60	8
Ferric ion, 0.2%	Fe(NO ₃) ₃	75	26
Ferrous ion, 0.1%	FeCl ₂	26	0
Ceric ion, 0.1%	Ce(NO ₃) ₄	34	7
Cerous ion, 0.1%	Ce(NO ₃) ₃	30	9
Cerous ion, 0.1%	CeCl ₃	33	9
Cerous ion, 0.25%	CeCl ₃	46	0
Uranyl ion, 0.2%	UO ₂ (NO ₃) ₂	15	0
1-anthraquinone sodium sulfonate, 0.1%		12	0
1-anthraquinone sodium sulfonate, 0.2%		10	0
2-anthraquinone sodium sulfonate, 0.1%		17	0
2-anthraquinone sodium sulfonate, 0.2%		27	0
*ferrocene (0.2% iron equivalent)		0	0
ferrocene (0.2% iron equivalent) plus 0.1% ferric ion		70	12
ceric ion, 0.1% plus ferric ion, 0.1%		75	18

* taken from Table 4 of the Third Bimonthly Report

Figure 1. Percent Transmittances (T), Reflectances (R), and Absorbances (A), for Untreated Cellophane (U), and Cellophane Containing 0.2% Ferric Ion (F) at Wave Lengths Between 3600 and 6000 Angstroms.

