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of Cotton Duck Before and After Weathering**

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# Phototenderization by Anthraquinone 2, 6-Disulfonic Acid of Cotton Duck Before and After Weathering

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## Introduction

Phototenderization of cellulosic and synthetic fabrics treated with some vat dyes has been recognized and investigated for many years [2, 3, 6, 7, 8, 9]. Venkataraman [13], in his discussion of photochemical degradation of cellulose, points out that energy resulting from photosensitization of an active vat dye is transferred from the site of absorption to another at which a chemical reaction occurs. He reviews the suggestion that the mechanism of activity of anthraquinone dyes involves the preliminary reduction of quinone to the leuco compound, followed by the reoxidation of the leuco compound to the parent vat dye by atmospheric oxygen with the formation of hydrogen peroxide. A dye-peroxide may also form. The reduction of anthraquinone to anthrahydroquinone may be accomplished by an equivalent dehydrogenation of cellulose, causing some oxycellulose to form at this stage. The work

of Lock, Bolland and Cooper, and others on the photosensitized oxidation of model compounds in the presence of sodium anthraquinone 2,6-disulfonate was reviewed recently [1]. Bolland and Cooper [5] found this anthraquinone dye to be particularly effective as a sensitizer in ethanol oxidation. Lock and others [1] showed two distinct processes for photo-oxidation based on their studies with glucosides and disaccharides; a break in the glycosidic linkage and oxidation of the sugar ring. This second process compared directly with photo-oxidation of alcohols studied first. Phototenderizing of cellulose appears to conform more closely to oxidation of ether linkages than does simple oxidation of  $-C-OH$  groups in alcohols. Anthraquinone sulfonic acid has been reported [12] to impart mildew resistance to cotton fiber by partial esterification of the fiber. Data obtained by this laboratory of field exposed fabrics treated with anthraquinone 2,6-disulfonic

acid for resistance to microbiological attack suggest that light could be the major factor affecting loss in breaking strength of the materials studied. This would be in accord with reports by other investigators for this and other anthraquinones.

Tenderization of the fabrics studied also could have been caused by hydrolysis of anthraquinone 2,6-disulfonic acid, resulting in the formation of sulfonic acid. The deterioration effects particularly associated with the formation of highly ionized acids by hydrolysis of organic fungicides containing halogen substituents were described by Rose et al. [11] for 2,2' dihydroxy 5,5' dichlorodiphenyl methane. Bayley [4] also showed that hydrolysis of copper naphthenate could account for loss in breaking strength of fabric so treated.

In addition to photolytic and hydrolytic causes for loss in breaking strength of fungicide treated materials, changes resulting from biolytic effects would also pertain when conditions of temperature and humidity are adequate for metabolic activity and growth of microflora.

The data relevant to the effects of anthraquinone 2,6-disulfonic acid presented herein were but a part of a broader program investigating the fungicidal efficacy of a variety of compounds applied to fabrics weathered for varying lengths of time at exposure sites in the Panama Canal Zone, at New Orleans, and in a tropical chamber.

## Experimental

### *Materials and Methods*

Square yard panels were prepared from 12.29-oz. cotton duck treated with 2.0 and 4.0% (nominal concentrations based on weight of fabric) anthraquinone 2,6-disulfonic acid. Aridex-L, a proprietary nondurable water repellent formulated as an emulsion of wax and an aluminum salt, was applied to all cloths. All test materials were dyed to OD-7 shade, but the composition of this dye is unknown. The control fabric was treated with water repellent and OD-7 shade dye only. Fabrics were weathered at all sites for 30 months. Every 3 months fabrics were removed from the site in the Panama Canal Zone (off ground, jungle shade) and from the Ft. Belvoir tropical chamber (intermittent incandescent illumination). Fabrics weathered at New Orleans (off ground, open field) were removed from exposure after 1, 2, 4, 8, 16, 24, and 30-month inter-

vals). Fabrics were also stored in an enclosed makeshift jungle warehouse. Samples of these fabrics were removed every 6 months during the 30 months of tests for determination of breaking strength.

Ten test strips, raveled to 1 × 6 in., were prepared from each of the weathered test fabric panels. The strips were sampled according to a predetermined pattern to assure different warp and fill threads in each of the test strips. Breaking strengths of the test strips, as the index of deterioration, were measured with the long dimension parallel to the warp on a Model J Scott Tester after conditioning for 24 hr. at 72° F. and 63% relative humidity.

Standard deviations of the mean breaking strengths were computed for each treatment weathered for each designated interval at each test site. The average breaking strength obtained and the parameters of two standard deviations are shown graphically (Figures 1, 2, 3). The curves were fitted visually to the data as close as possible within the 95% probability limits indicated by two standard deviations.

## Results

### *Breaking Strengths of Treated Unweathered Fabric*

Anthraquinone 2,6-disulfonic acid was found to have a statistically significant effect on the breaking strength of the test material prior to weathering (Table I). The standard deviation and coefficients of variation computed for each of the test materials (Table II) were small, indicating a uniform effect resulting from homogeneous application of both concentrations of the test compound to the fabric. The significant reduction in breaking strength of the fabric upon treatment with anthraquinone 2,6-disulfonic acid is in accord with the report of Scholefield and Patel (1928, 1929) reviewed by Landolt [10] that tendering occurs with vat dyes even during the dyeing process if light is incident upon the material being dyed. The possibility exists that loss in tensile strength may be due to direct interaction of the compound with the fabric.

The mean break strength of the fabric treated with 4.0% anthraquinone 2,6-disulfonic acid is slightly higher than that of fabric treated with 2.0%. One would expect a more direct proportionality between concentration and effect. The apparent discrepancy in these data may be attributed to different amounts

of light incident upon these fabrics during processing and preparation for test. In any event, the least significant difference of 14.1 lb./sq. in. at the 1% level makes the difference between the two treatments nonsignificant and that of either fabric compared to the control significant.

*Breaking Strength of Fabrics Weathered in the Jungle Shade, Panama Canal Zone*

Tensile strengths of fabrics treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid are related to time weathered (Figure 1) as quadratic curves established by visual best fit to the data. The curves for the two concentrations of the test compound curve downward, showing rapid loss in breaking strength at an essentially parallel rate, during the entire course of weathering. The change in breaking strength for the control versus time weathered was fitted also by a quadratic curve. Visual examination of the data for this control suggests curves other than the one given in Figure 1. The quadratic curve shown conforms to the calculation made for these data; viz.,  $y_c = 180.5 + 0.172x_1 - 0.098x_1^2$ , significant at the 1% level. The initial rate of breaking strength loss for the control, accordingly, is slow compared to

the rate of loss after 9–12 months. The scatter of the data in this instance makes difficult a visual fit of a curve to the data. However, the scatter due to variation is not unusual for a biological substrate undergoing biological degradation.

*Breaking Strength of Fabrics Weathered in Open Field, New Orleans*

Cotton duck treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid showed rapid loss in breaking strength for the first month of weathering (Figure 2). The rate of change of breaking strength thereafter is very slow. In contrast to this, the control fabric lost breaking strength more slowly than either of the treated fabrics for the first 8 months of weathering. During the interval between 8 and 24 months of weathering the breaking strength was lost slowly. At 30 months the control retained but 22.8 lb./sq.in. breaking strength.

*Breaking Strength of Fabrics Retained in Tropical Chamber, Unweathered*

Rate of breaking strength loss of anthraquinone 2,6-disulfonic acid treated cotton duck compared to the control fabric shows a striking similarity when exposed in a tropical chamber (Figure 3). The initial breaking strength of the treated fabrics were significantly lower than that of the control, as was

TABLE I. Analysis of Variance for Breaking Strengths Measured for Anthraquinone 2,6-Disulfonic Acid Treated 12.29-oz. Cotton Duck, Unweathered

Concentration applied to fabric, %	Mean breaking strength, lb./sq. in.
2.0	164.1
4.0	171.4
0 (Control)	189.7
*L.S.D. 1%	14.1

Source of variation	Degrees of freedom	Sums of squares	Mean variance	F†
Between treatments	2	3478.47	1739.29	13.28
Error	27	3397.40	125.83	
Total	29	6875.87		

\* Least significant difference (L.S.D.) at 1% =  $2.771 \times 5.10 = 14.1$  lb./sq. in.

† F required for 27 degrees of freedom for error and 2 degrees of freedom for lesser mean square at 5% = 3.35; at 1% = 5.49. Calculated  $F = 13.82$ ,  $P = .01$ . Standard error of difference between 2 means =  $\pm \frac{125.83 \times 2}{10} = \pm 5.10$ .  $t_{.01} = 2.771$ .

TABLE II. Standard Deviations and Coefficients of Variation for Breaking Strengths Measured for Anthraquinone 2,6-Disulfonic Acid Treated 12.29-oz. Cotton and Duck, Unweathered

Concentration applied to fabric, %	Mean,* lb./sq. in.	$\pm\sigma$ ,† lb./sq. in.	$\pm s$ ,‡ lb./sq. in.	C,** lb./sq. in.
2.0	164.1	4.2	13.2	8.0
4.0	171.4	3.7	11.8	6.9
0 (Control)	189.7	2.5	8.0	4.2

\* All values are averages of ten break strength measures.

†  $\sigma$  = standard deviation of mean =  $s/\sqrt{N}$  in which  $s$  is as defined in the next footnote and  $N$  is the number of break strengths measured for given sample.

‡  $s$  = standard deviation of any one break strength for a given sample =  $\sqrt{\Sigma d^2/N - 1}$  in which  $\Sigma d^2$  is the sum of the deviations squared and  $N - 1$  (degrees of freedom) for the number of values ( $N = 10$ ) used to compute the mean.

\*\*  $C$  = coefficient of variation =  $(s/\bar{X}) (100)$  in which  $s$  is as defined above and  $\bar{X}$  is the average break strength obtained for all samples of a given treatment.

established by statistical evaluation of the treated unweathered fabrics. The best fit curves for breaking strengths measured through 30 months under these conditions of reduced and intermittent artificial illumination in the chamber show deterioration progressing at essentially an equal rate for each of the test fabrics. Compared to the evident influence of photosensitive anthraquinone 2,6-disulfonic acid on rate of loss of breaking strength of treated cotton duck, particularly when weathered at New Orleans (Figure 2), it may be deduced that fabrics maintained in a tropical chamber showed no phototenderization during the course of exposure. All fabrics

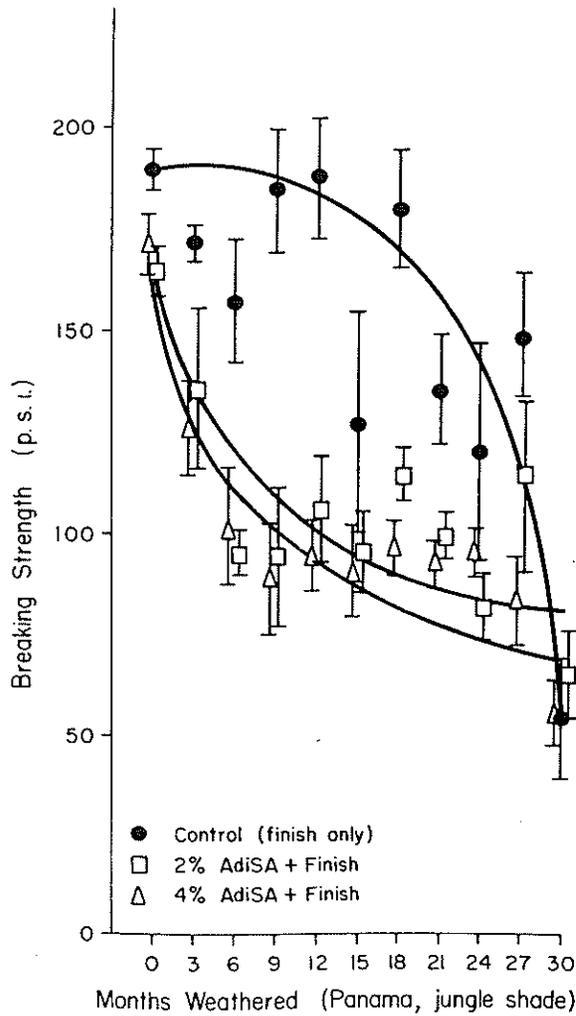


Fig. 1. Mean breaking strengths  $\pm 2$  standard deviations and visually fitted curves for breaking strengths of cotton duck (12.29 oz.) treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid (AdiSA) and finish weathered in jungle shade, Panama.

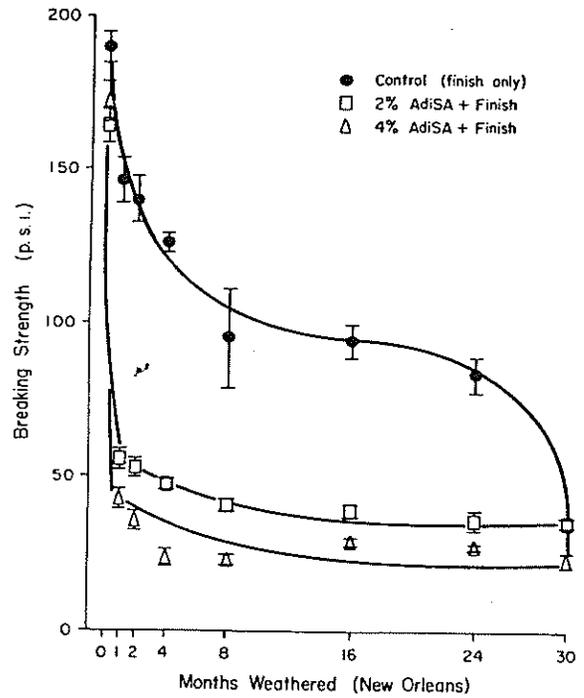


Fig. 2. Mean breaking strengths  $\pm 2$  standard deviations and visually fitted curves for breaking strengths of cotton duck (12.29 oz.) treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid (AdiSA) and finish weathered in open field, New Orleans.

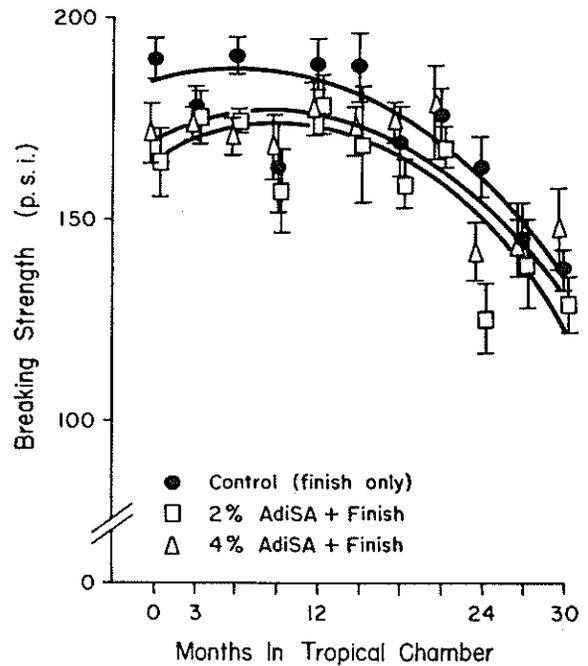


Fig. 3. Mean breaking strengths  $\pm 2$  standard deviations and visually fitted curves for breaking strengths of cotton duck (12.29 oz.) treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid (AdiSA) and finish exposed in tropical chamber.

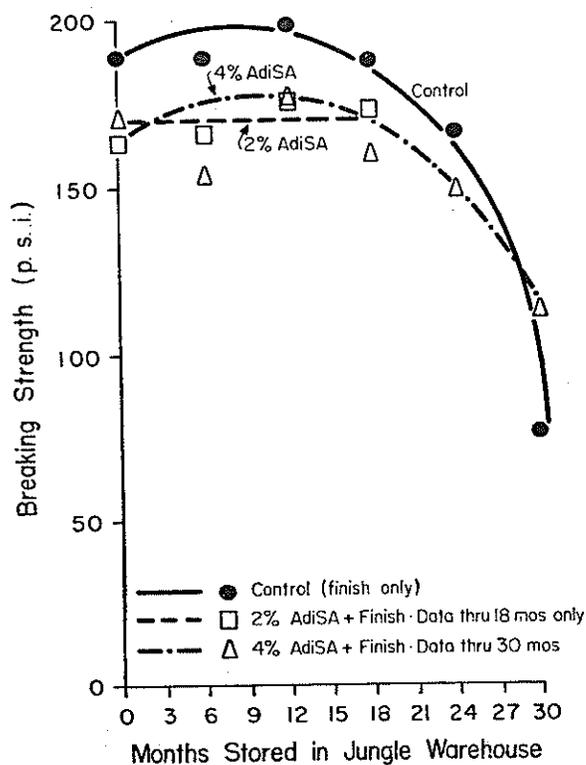


Fig. 4. Visually best fitted curves to mean breaking strengths of cotton duck (12.29 oz.) treated with 2.0 and 4.0% anthraquinone 2,6-disulfonic acid (AdiSA) and finish stored in an improvised jungle warehouse.

exposed in the tropical chamber and the breaking strength of the control in Panama jungle shade showed similar rates of loss. The effect obtained with 2.0% anthraquinone 2,6-disulfonic acid was less than that measured for fabrics treated with 4.0% of this compound. These differences are essentially small. Accordingly, the change in breaking strength obtained after tropical chamber exposure for which the 2.0% treatment exceeded the effect of the 4.0% application may not be truly significant. The relative positions of curves obtained with their respective data were established by visual fit. Calculated regressions may show these differences to be negligible. The important point, therefore, is that rates of deterioration for both treatments are the same, the small differences in position of the curves notwithstanding.

#### Discussion

The weathering of fungicide treated fabrics is an important consideration for judgment of the suitability of the compound as a textile preservative. The response of the treated textile to weathering in-

cludes the totality of such components of outdoor exposure as photosensitization, leaching, alternate wetting and drying, microbial activity, hydrolysis of chemical compounds applied, and abrasion resistance. These factors remain to be separately defined and collectively applied as to their role in the deterioration of fungicide treated fabrics upon weathering. Photosensitivity of fungicides as well as dyes applied to cotton textiles may be the prime factor relevant to the stability of these compounds. The stability of these compounds in the presence of light might further affect the breaking strength of the cloth insofar as light energization of the compound weakens the molecular structure of cellulose. The studies referenced previously afford a reasonable basis for understanding and appreciating phototenderization of fabrics by anthraquinone dyes. The comparative deterioration of anthraquinone 2,6-disulfonic acid treated cotton duck exposed at weathering sites of relatively different light intensities demonstrates the probable dependence of rate of breaking strength loss on the photosensitive oxidative changes influenced by the anthraquinone investigated. This phototenderization may well be in accord with the mechanism of oxidative change proposed by Lock [1], Bolland and Cooper [5], and others based on their studies of light energized sodium anthraquinone 2,6-disulfonate and simple sugars or alcohols; it may also be in accord with the mechanism of phototenderization summarized by Venkataraman [13].

The evidence obtained remains essentially presumptive in nature but coincides with the known light sensitivity of anthraquinones and their subsequent effect by oxidative change on the strength of fabrics to which they are applied.

Hydrolysis of fungicides and the activity of ionized acids released by this process is a possibility that must be considered. Unfortunately, circumstances prevented closer study to differentiate hydrolytic from photochemical effects. However, on the supposition that some hydrolytic changes might occur at all sites, it is interesting to note that treated fabrics stored in a dark makeshift jungle warehouse in Panama showed entirely different curves (Figure 4) from those stored in the jungle shade (Figure 1), where some light did penetrate. If hydrolysis were a prime factor, the curves in the jungle shade and in the jungle warehouse should be similar. In fact, only the curves for the untreated controls are similar.

Compared to the rate of loss of breaking strength

obtained at the New Orleans site (exposure in full light), which was most rapid during the first month, that of fabrics weathered in the jungle shade in Panama was less rapid. The rapidity of loss in breaking strength of the treated as well as the control fabric when weathered at New Orleans appears to indicate the degradative effect of light on the fabric tested. Curves fitted to data of breaking strength change in the jungle shade show a more rapid rate of loss than was obtained in the tropical chamber. Whereas the loss in breaking strength of the control at the New Orleans site may have been influenced by light primarily, similar control fabrics exposed in the jungle shade and in the tropical chamber showed rates of loss probably predominantly influenced by microbial factors.

### Summary

Cotton duck treated with anthraquinone 2,6-disulfonic acid appeared to deteriorate at rates directly related to the light intensities of the Panama jungle shade, New Orleans open field, and tropical chamber exposure sites. Treated fabrics showed a statistically significant reduction in breaking strength prior to weathering. This tenderization appears to be attributable to the effect of light incident upon the fabric during the time of treatment. The mechanism of the photo-oxidative changes may be that suggested by Bolland and Cooper [5] for ethanol in the presence of light energized sodium anthraquinone 2,6-disulfonate, or that reviewed by Venkataraman [13] for phototenderization effects of anthraquinone dyes. In strong light, rapid rates of breaking strength loss were obtained, to which linear functions best apply. In reduced light, breaking strength data were fitted best by quadratic functions. The former appears

consistent with phototenderization. The latter condition prevails when deterioration results primarily from microbial activity.

The possibility that heat induced hydrolytic breakdown products of the anthraquinone compound were responsible in part for the loss in tensile strength of the fabrics cannot be ruled out. The data presented, however, indicate that hydrolysis was not a prime deteriorative factor compared to the probability of photo-oxidative changes.

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