

## The Ultimate Polymer Application: Resin-Bonded Cellulose Separators for Lead-Acid Batteries

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### Synopsis

Because it represents a polymer system routinely used in a highly corrosive environment, the resin-bonded cellulose separator is a paradigm of bad polymer application that succeeds. It succeeds because of the remarkable properties of cellulose itself, and through the formation of a highly modified structure that serves to protect both the resin and the cellulose in a reactive environment known to completely degrade both. X-ray diffraction analysis was used to determine the quality of retained cellulose in lead-acid battery separators made by impregnating thick cellulose matrixes with phenolic resins. The hydrolytic weight loss of separators stored in battery acid at 52°C was also measured and related to x-ray diffraction measurements of *intensive* degree of crystallinity and "qualitative perfection." The x-ray diffraction analyses and hydrolysis measurements are consistent with the formation of a copolymer between the cellulose and the impregnating resin. Treated and rewetted  $\alpha$ -cellulose displays a capability for reorganization, indicated by increases in *intensive* crystallinity and qualitative perfection that are absent in the resin-bonded cellulose separator matrix. Rewetting of the separator matrix actually decreased the "qualitative perfection" of the cellulose present. X-ray diffraction measurements indicate that *extensive* crystallinity of acid-treated separators increases, due probably to the higher reactivity of the "so-called" amorphous fraction of the cellulose present. The degree of crystallinity, an intensive measure, does not change significantly during acid treatment, but the "qualitative perfection" of the cellulose decreases with time of hydrolysis and increases in acid strength.

### INTRODUCTION

No polymer system in widespread use is required to perform well in as destructive an environment as the resin-bonded cellulose (RBC) battery separator. Cellulose is known to hydrolyze rapidly in mineral acids,<sup>1-6</sup> but the RBC separator must maintain its integrity in sulfuric acid media ranging from ~8% to ~40% (w/w), where it also encounters ranges in temperatures from -10°C to ~+70°C.

Despite these extremes, the RBC separator performs exceptionally well. In the most intense application, electric vehicle batteries with RBC separators frequently perform more than 250 full, 100% depth-of-discharge cycles. For automotive battery applications, where depth-of-discharge is shallow, such separators frequently cycle more than 5500 times (SAE J240a test schedule).

For separators, a good grade of  $\alpha$ -cellulose is used to make a thick paper sheet, usually 0.50 to 0.75 mm thick. The paper is treated, while swelled, with waterborne thermosetting resin of phenolic type, then partially dried. After curing,

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the phenolic resins provide binding for the cellulose fibers and very good resistance to nonoxidizing acids.<sup>7</sup> At the end of the cure ( $\sim 205^{\circ}\text{C}$ ), the composite matrix is quite rigid and has a porosity of  $\sim 65\text{--}70\%$ .

The thermal curing of the resin, however, may modify the cellulose somewhat. Ruznak and Tanczos<sup>8</sup> found a monotonic drop in degree of polymerization (D.P.) when cotton cellulose was thermally treated at  $190^{\circ}\text{C}$ . They also found a sharply defined rise in initial hydrolysis rate in dilute HCl as the cellulose was heated for increasing periods, indicating the formation of labile  $\text{—OH}$  groups.

In the battery industry, the stability and useful life of separators has long been a subject of study,<sup>9,10</sup> but only recently has the character of the matrix with respect to the effects of the acid medium been investigated. Campbell and Dafler measured stability of separators in dilute  $\text{H}_2\text{SO}_4$  using a quantitative or *extensive* measure of retained crystalline material.<sup>11</sup> They compared separators stored for long periods in battery acids to raw material cellulose, using a normalized comparison technique. They showed that there was a rapid initial loss of crystalline material, after which the matrix appears very stable in battery-grade acids ( $\text{H}_2\text{SO}_4$ , 6–10*N*).

Ray and Bandyopadhyay<sup>12</sup> pointed out that the index of crystallinity as defined by Hermans and Weidinger and Segal et al.<sup>13,14</sup> is insufficient to characterize cellulose in a hydrolytic medium, because the apparent degree of order may increase while part of the material is being irreversibly degraded.<sup>15</sup> They suggested that a measure of "qualitative perfection" was required to rationalize the two approaches. Viswanathan<sup>16</sup> used metallographic concepts to discuss fiber structures—particularly Ashmouni cotton—and we propose a measure used in the inorganic chemical industry to index the "qualitative perfection" of the retained cellulose in aged, hydrolyzed RBC separators.

In the acceptance of some inorganic oxides for use as battery-active materials or process raw materials, one of the material specifications (at ESB Inc.) is a maximum value for the ratio  $I(hkl)/W(hkl)$ , where  $I(hkl)$  and  $W(hkl)$  are the x-ray line intensity and width, respectively, of a specific x-ray diffraction line. For two samples of raw material of the same particle size distribution, that having the smallest value of the ratio is considered "to be preferred." In certain battery processes, small, average crystallite-size samples have proven most active due, undoubtedly, to a larger number of grain boundaries, dislocations, and similar heterogeneous reaction sites.

The value of  $W(hkl)$  can be used in the Scherrer equation<sup>17</sup> to calculate an average crystallite size, and the ratio  $I(hkl)/W(hkl)$  should be indicative of the distribution of crystallite sizes. The numerical determination of crystallite size distribution is a complex analytical procedure and was used by Warren and Averbach<sup>18</sup> to calculate the distribution of diffracting domains in strained alloys. Bienenstock<sup>19</sup> later generalized the procedure to calculate numerical distributions of crystallite sizes. In these methods, Fourier transform analysis is applied to the intrinsic broadening of the diffuse line. The distribution of diffracted x-ray power is seen to be proportional to the distribution of crystallite sizes. Buchanan and Miller<sup>20</sup> used these methods and other approximate methods to interpret the x-ray diffraction line broadening of isotactic polystyrene. The more primitive measure,  $I(hkl)/W(hkl)$ , is seen, therefore, as a rather simplified indicator of the distribution of crystallite sizes.

Morosoff<sup>21</sup> used the Scherrer equation to calculate what he called lower limits to the crystallite size of "never-dried cotton." He found significant differences

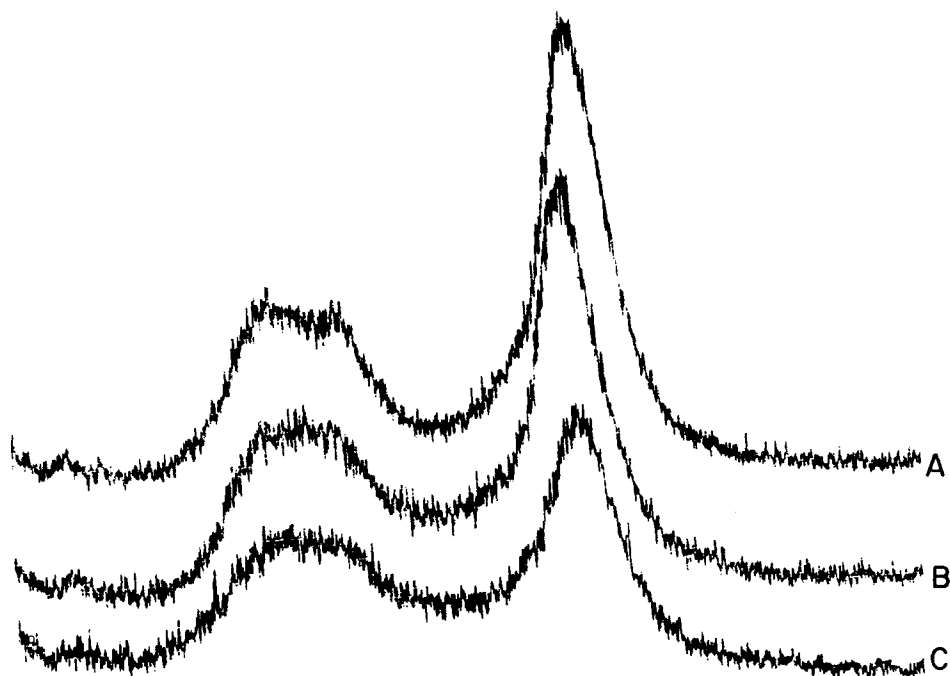


Fig. 1. X-ray diffraction profiles of  $\alpha$ -cellulose and RCB separators: (a)  $\alpha$ -cellulose stock before pulping; (b) RCB separator before use; (c) RCB separator after storage in 1.280 specific gravity  $H_2SO_4$  at  $52^\circ C$  for 3960 hr. This figure is reproduced from Campbell and Dafler<sup>11</sup> with the kind permission of The Electrochemical Society.

in line widths as function of the wetted history of the cotton fibers. In our studies, however, we found few and slight variations in line width *but* large changes in profile shape, as seen in Figure 1. The linewidths shown are in very close agreement, but intensities, indicative of the number of diffracting species of a given crystallite size, are quite different. Using only linewidths would limit us to "qualitative perfection" parameters that did not change with increased hydrolysis of separators. In the remainder of this discussion, we use the ratio  $I(hkl)/W(hkl)$  as an index of "qualitative perfection," and call it *CrA*. It is simple to measure experimentally and, being characteristic of the substance under study, it is not affected by variations in beam intensity or density of the sample. For a given sample, one calculates the same *CrA* value for any beam power that yields an acceptable signal/noise ratio. [If, for example, a fine nickel powder is diluted with another material, crystalline *or* amorphous, the resultant line, say, the Ni[111] line, is less intense than the line for the undiluted powder, but the ratio  $I(111)/W(111)$  remains the same.]

In this study, *CrA* is defined as  $I(002)/W(002)$ , where  $W(002)$  is the uncorrected line width. The parameter has proven to correlate well with direct hydrolysis measurements.

### CRYSTALLINITY

A characteristic index of crystallinity and quantitative ratio of crystallinity was measured for all acid-treated samples. No great pains were taken to ensure random orientation of fiber, but care was taken that samples had experimentally

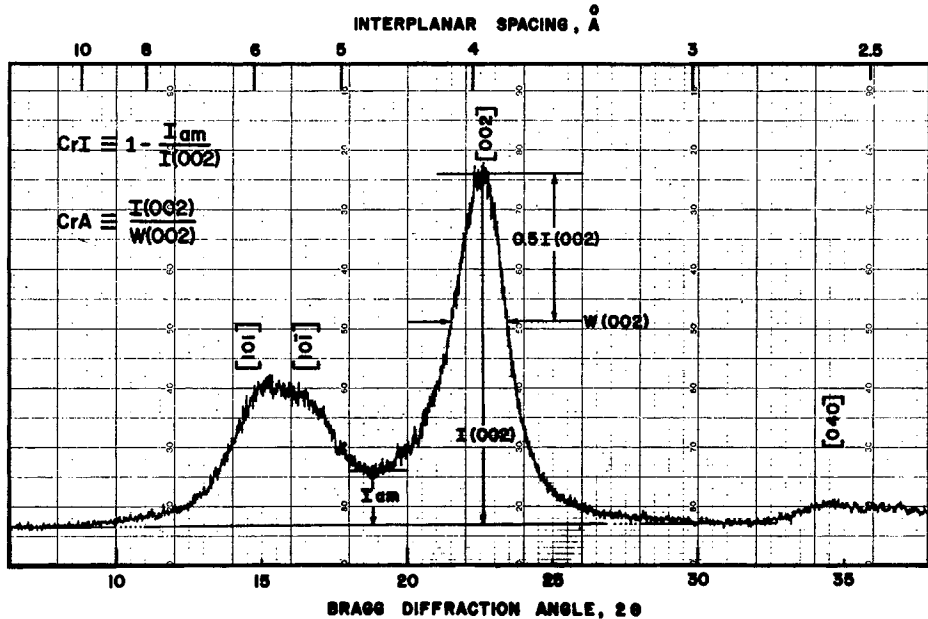


Fig. 2. Method of Segal et al.<sup>14</sup> for determining the *intensive* degree of crystallinity,  $CrI$ , and current method for determining the degree of "qualitative perfection,"  $CrA$ .

identical access to the x-ray beam. Ordinary wide-angle, powder diffraction techniques were used,<sup>22</sup> and the familiar crystallinity index of Segal et al.,  $CrI$ , was used to calculate the index of crystallinity,<sup>14</sup> a material characteristic. Segal's method has found wide acceptance.<sup>22,23</sup> The essence of Segal's method is shown in Figure 2, as is the method for calculating  $CrA$ .

The *extensive* crystallinity was measured by a comparative normalized x-ray technique.<sup>11</sup> Integrated [002]-line intensities were compared directly to the integrated [002]-line intensities of virgin RBC separators, and the ratio normalized with respect to density of the material. The value for the integrated intensity was approximated by triangulation, defining the integrated intensity as

$$A(002) = I(002) \times W(002) \quad (1)$$

where  $W(002)$  is the [002]-linewidth [the operational linewidth at  $0.5 I(002)$ ]. Because of the nature of beam collimation, we can assume that, for any measured line of finite width,

$$A_x = A_t N_x \quad (2)$$

where  $N_x$  is the number of diffractors present, and  $A_t$ , the x-ray beam target area, is an instrumental standard. The value of  $N_x$  is proportional to the density  $\rho_x$  of the analyzed material and a constant  $k_x$  related to the crystalline nature of the sample. For the comparison standard, we also have  $A_{std} = A_t k_{std} \rho_{std}$ . Equating target areas and rearranging, a crystallinity ratio  $CrR$  is resolved:

$$CrR = (k_x/k_{std}) = (\rho_{std}/\rho_x)(A_x/A_{std}) \quad (3)$$

and since intercepted volumes are the same, this simplifies to

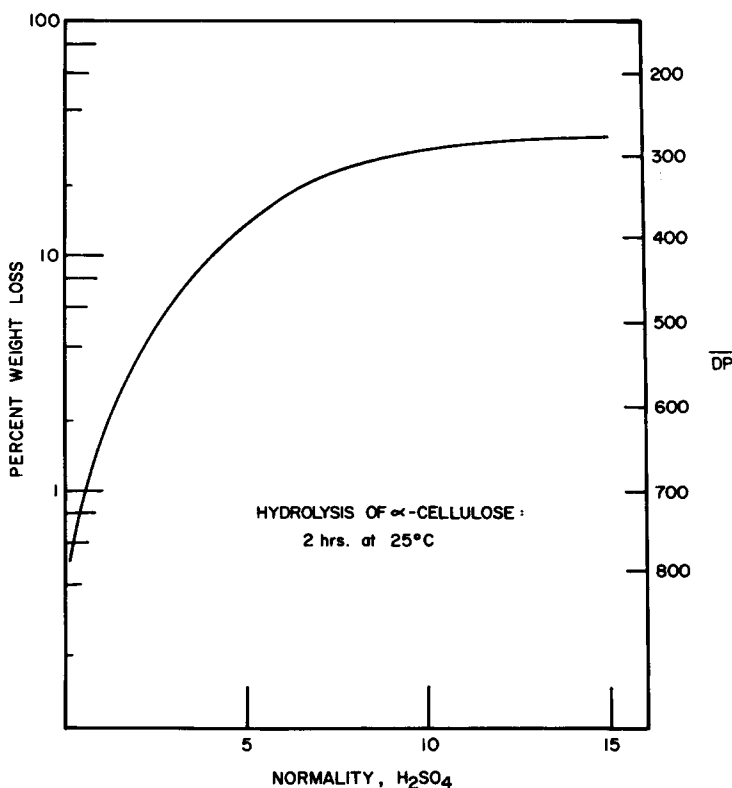


Fig. 3. Ant-Wuorinen and Visapaa's hydrolysis data for  $\alpha$ -cellulose in  $H_2SO_4$ . Data from Ant-Wuorinen and Visapaa.<sup>26</sup>

$$CrR = (M_{std}/M_x)(A_x/A_{std}) \quad (4)$$

where  $M_{std}$  and  $M_x$  are weights of materials in the beam. Because direct comparisons were made to standards, no corrections for absorption were made.<sup>22</sup> Segal's method for  $CrI$  is an example of what Miller<sup>24</sup> calls an internal x-ray method, as is  $CrA$ . The quantity  $CrR$ , in distinction, Miller would call an external method, because it involves a normalization and reference to another substance.

In his work on heterogeneous hydrolysis in strong acids, Ant-Wuorinen<sup>25</sup> used a somewhat different approach. His method used a measure related to the [002]-linewidth to calculate the *amorphous* character, and he then characterized crystallinity from that quantity.

Ant-Wuorinen and Visapaa (26) steeped cotton linters (presumably cellulose I) in  $H_2SO_4$  at concentrations from 0.1N to 15N. They measured  $CrI$  at the beginning and end of the series of hydrolyses. The degree of polymerization was also measured. The data are plotted in Figure 3. It is interesting to note that while the D.P. falls from  $\sim 790$  to 280 during hydrolysis, the  $CrI$  values were all but unchanged, decreasing slightly from 0.73 before treatment to 0.71 after hydrolysis in 15N  $H_2SO_4$ . None of the x-ray data used to calculate  $CrI$  was reported, so that the effect of extreme hydrolysis on the shape of the diffraction maxima is unknown and the [002]-linewidth changes unknown.

Somewhat later, Ant-Wuorinen and Visapaa<sup>27</sup> established what they refer to as an index of order, *IO*. Assuming the crystalline/amorphous concept inadequate, they argued against using the term "crystallinity." The parameter they used, *IO*, was in all essentials the same as Segal's *CrI*. Statton (28) concluded that "order" and "crystallinity" were probably articulations of the same basic idea or notion, and in this paper we continue the use of "crystallinity" as a useful term.

In this laboratory, a simple experiment in hydrolysis of  $\alpha$ -cellulose was done. Hydrolysis in 14.4*N* H<sub>2</sub>SO<sub>4</sub> was carried out at 52°C for 36 hr. The material was entirely denatured, the liquor becoming brown to black in color. The retained material was thoroughly washed by repeated centrifugation to obtain a white, viscous suspension that appeared to be a dispersion of very small, translucent crystals when diluted. A small sheet was made by filtration and dried in air at 52°C. After equilibration with dry silica gel, the small sheet was subjected to x-ray diffraction analysis and to direct x-ray comparison to the starting material. The resultant x-ray diffraction patterns are shown in Figure 4.

As in the work of McKeown and Lyness,<sup>15</sup> the diffraction patterns are exceptionally like one another. Their "peptized" solids were produced in 2.5*N* H<sub>2</sub>SO<sub>4</sub> by boiling and retained a considerable fiber-like character. The peptized solids prepared in this laboratory had no fiber-like character. The small sheet was brittle and horny in appearance, but it is, quite evidently, to be identified as cellulose I. The degree of crystallinity for the hydrocellulose was the same as for the raw material  $\alpha$ -cellulose, the only difference being in [002]-linewidth and a "smearing-out" of [101]- and [10 $\bar{1}$ ]-lines. If we assume that [002]-linewidth signifies "qualitative perfection,"<sup>12</sup> this experimental hydrocellulose is *more* crystalline than the  $\alpha$ -cellulose raw material.

In a series of papers, Ant-Wuorinen and Visapaa (29) have attempted to show conclusively that order, or "crystallinity" as used here, dictates the essential reactivity of cellulose undergoing acid hydrolysis.

What is clear is not simply that strong hydrolytic agents appear to increase the intensive crystallinity of cellulose, but that hydrolysis residues retain their capacity for forming supermolecular structures of considerable integrity. It may be this integrity which gives long life to RBC separators in acid media.

## EXPERIMENTAL

Resin-bonded cellulose separators were obtained from the Texon Corporation of South Hadley, Massachusetts. These materials were regular stock materials, ordinarily used in assembly of ESB, Incorporated, automotive batteries. They are thick paper stocks blended with very small amounts of synthetic fiber and impregnated, while wet, with water-borne phenol-formaldehyde resins. These are later cured by thermal treatment at temperatures of the order of 200°C. The  $\alpha$ -cellulose used in this work was also obtained from Texon. Simple experiments using polymerized films of phenolic on crystalline materials indicated that their presence on cellulose fibers would not interfere with the x-ray diffraction spectrum. The phenolic crystallites are, apparently, too small to produce a coherent signal and do no more than slightly reduce the S/N ratio of the diffractometer output.

A large number of randomly selected separators were cut into 30 mm  $\times$  30 mm

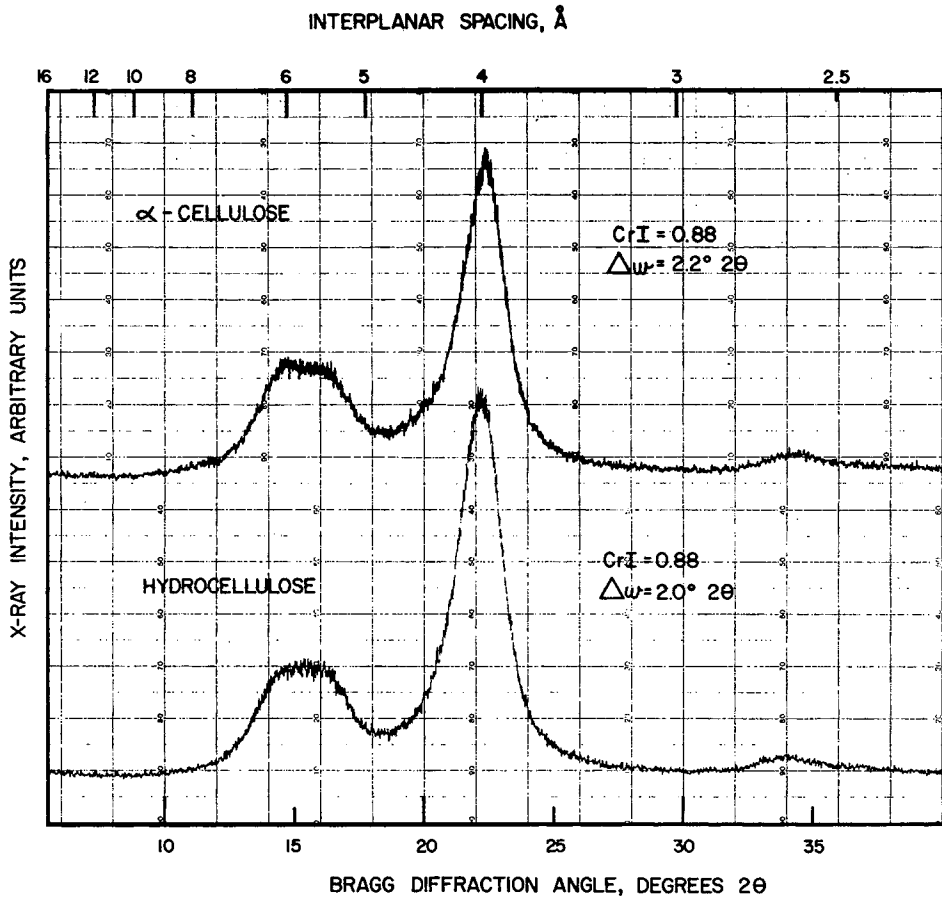


Fig. 4. X-ray diffraction spectra of  $\alpha$ -cellulose compared to the product of fully denatured  $\alpha$ -cellulose. This hydrocellulose was produced by 36 hr of hydrolysis in 1.400 specific gravity  $H_2SO_4$  at  $52^\circ C$ .

pieces and stored in battery-concentration  $H_2SO_4$ . A second group of very carefully cut pieces was dried and preweighed before storage in acid. The unweighed samples were used solely for x-ray diffraction measurements. The weighed samples were used to study hydrolytic weight loss in  $H_2SO_4$  of 1.265 specific gravity.

Approximately 40 to 60 chips were made up for each concentration of acid and shuffled before placing in the acid baths. The samples were put into 1-pound ointment jars of the solutions, and these were thermostated at  $52^\circ C$  ( $125^\circ F$ ) in an oil bath. At the end of specific storage times, four to seven samples were taken from each jar and rinsed in tap water, then in distilled water until free of sulfate. The chips were vacuum dried at  $40^\circ C$  and examined by x-ray diffraction. A Phillips Electronics Mark II X-Ray Diffractometer was used to obtain x-ray intensity data. All analyses were done at Cu-target parameters of 35–40 kVA and 15–20 mA x-ray current. Each series of measurements was concluded by analysis of a chip of virgin separator at the same x-ray parameters. These x-ray measurements were used to calculate both crystallinity and “qualitative perfection” of the separators after increasing periods of hydrolysis in acid.

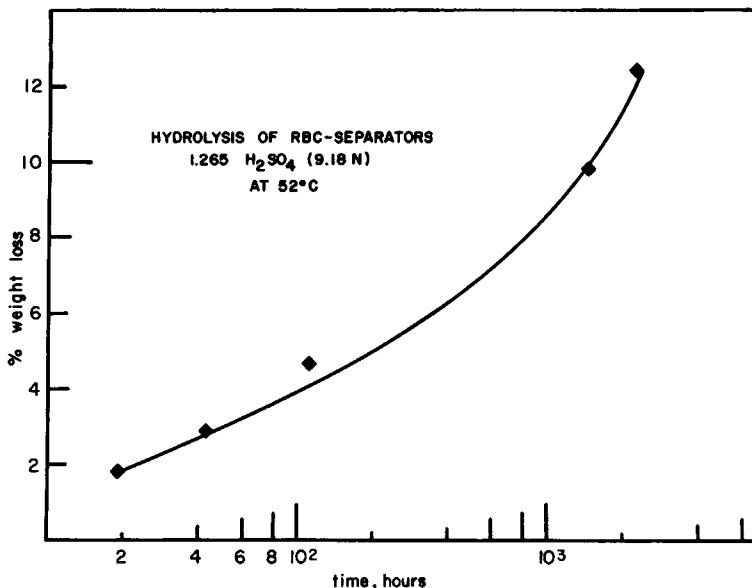


Fig. 5. Weight-loss data for RBC cellulose separators stored in 1.265 specific gravity H<sub>2</sub>SO<sub>4</sub> for increasing periods. Temperature of storage was 52°C.

The carefully preweighed chips were put into 1.265 H<sub>2</sub>SO<sub>4</sub> and hydrolyzed. Samples were withdrawn, in groups of five, at irregular intervals and washed and dried. The hydrolytic weight loss was calculated using these samples.

Reagent-grade chemicals were used throughout this work, and acid concentrations were determined by controlled-temperature hydrometry.

## RESULTS AND DISCUSSION

### Hydrolysis—Loss of Material

As in the case of unprotected  $\alpha$ -cellulose,<sup>1-6</sup> hydrolysis of the cellulose in RBC separators is initially rapid, becoming slower as the time of reaction is extended. Preweighed separator pieces, soaked in 9.14N H<sub>2</sub>SO<sub>4</sub> (specific gravity 1.265) showed fast initial reaction rates, losing 12.50% of their weight in 2410 hr at 52° ± 3°C. The weight loss data are shown in Figure 5 correlated using a polynomial curve-fitting equation.

Except for the very early work of Freudenberg and his colleagues,<sup>30</sup> hydrolysis in highly concentrated H<sub>2</sub>SO<sub>4</sub> ( $N > 5$ ) seems only to have been measured by Ant-Wuorinen and his co-workers.<sup>25-27</sup> They treated  $\alpha$ -cellulose in 5N and 8N H<sub>2</sub>SO<sub>4</sub> at a temperature of 100°C and used the data to investigate the order and kinetics of heterogeneous cellulose hydrolysis. Using the amorphous/crystalline hypothesis, they also calculated crystalline fractions in the material by assuming that the rates of hydrolysis of the amorphous fraction were different, in terms of order, than the rate for the crystalline fraction. Their data are plotted in Figure 6 and compared directly to the hydrolysis data for RBC separators. One can see that RBC separators are far more stable in hydrolytic media than the usually quite reactive cellulose.



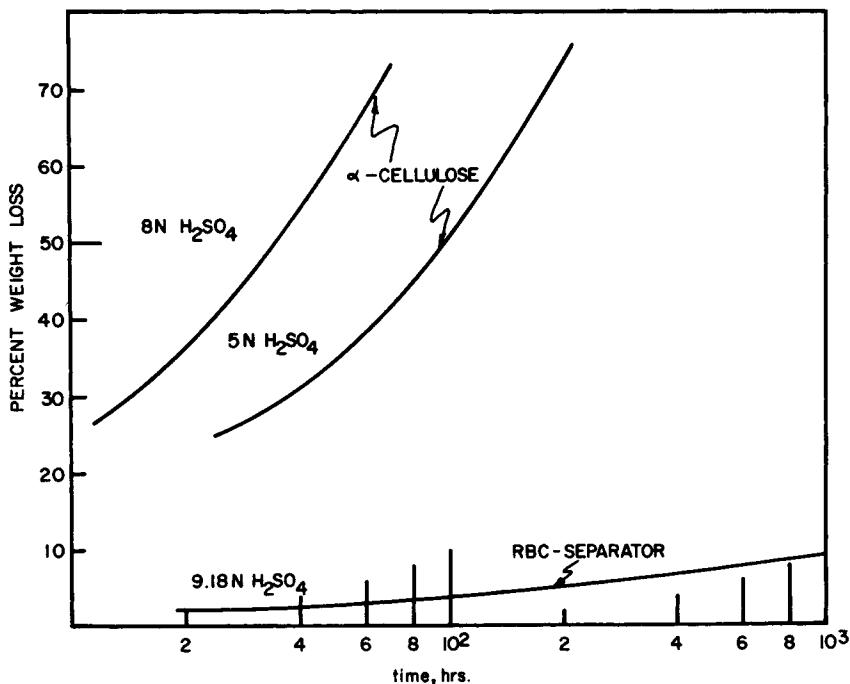


Fig. 6. Comparison of Ant-Wuorinen and Visapaa's data for  $\alpha$ -cellulose with those for RBC separators. Ant-Wuorinen's data were generated by serial fixed-period hydrolyses at 100°C. The serial periods for 5N acid were 24 hr, and the serial periods for 8N acid were 12 hr. The RBC separator data were generated by continuous hydrolysis in 9.18N H<sub>2</sub>SO<sub>4</sub> at 52°C. Ant-Wuorinen's data were abstracted from reference 26.

Conclusions from this particular comparison of hydrolysis data must be tempered. The present data were generated by stagnant hydrolysis at 52°C. Ant-Wuorinen's data, while generated at 100°C, were also done in a slowly flowing system and at lower H<sub>2</sub>SO<sub>4</sub> concentrations. The conclusion that the phenolic resin acts to protect the cellulose from extensive, high-rate hydrolysis is, nonetheless, inescapable.

Scanning electron microscopy (SEM) was used to attempt a textural characterization of the fiber matrix in separators and the starting material. Figure 7 shows 1000× and 3000× SEM photos of the two matrixes. The differences are worth remarking. In the case of the  $\alpha$ -cellulose, the fiber surfaces are rather sharply defined compared to RBC separator surfaces. In examination of separator SEM photos, there are also some characteristic "dimple-like" effects—absent on cellulose itself—that are probably due to a shrinking (surface free-energy minimization) of the polymerizing resin films. Except for those areas, the SEM pictures indicate the cellulose surfaces to be uniformly coated with the impregnating resins.

#### Crystallinity—Extensive and Intensive

The measure of  $CrR$ , the crystallinity ratio, indicates in an approximate sense the kinds of hydrolysis attack on the RBC separators. In this normalized scheme, the initial value is, by definition, 1.00, or 100%. What is interesting to note is

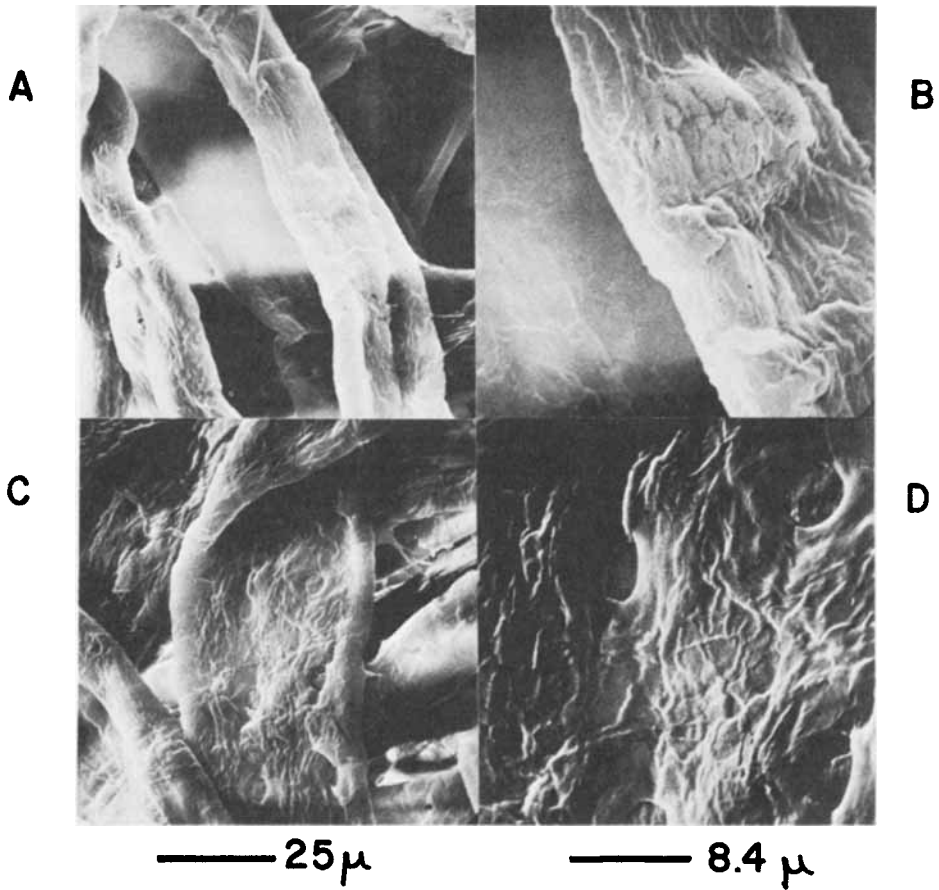


Fig. 7. Scanning electron micrographs of  $\alpha$ -cellulose and RBC separators. A and B are micrographs of  $\alpha$ -cellulose, and C and D are micrographs of RBC-separators. A and C and B and D are the same magnifications.

what happens to  $CrR$  as the hydrolysis time at  $52^{\circ}\text{C}$  becomes progressively longer. The data, derived from sample populations of five to seven numbers, are shown in Table I. The data show that only small changes occur in the retained cellulose material after extensive hydrolytic attack. In 3960 hr of hydrolysis in  $9.00N$   $\text{H}_2\text{SO}_4$ , RBC separators lose 15.7% of their weight, presumably cellulose only; yet after normalization by weight and direct comparison with virgin separators,

TABLE I  
Crystallinity Ratio C and R of Hydrolyzed Separators

Acid strength		CrR			
Sp. gr.	$N$	691 hr <sup>a</sup>	1360 hr	2400 hr	3960 hr
1.260	9.00	0.887	0.965	0.939	0.916
1.280	9.75	0.855	0.839	0.925	0.841
1.325	11.48	0.878	0.900	0.833	0.847

<sup>a</sup> Period of hydrolysis.

the retained material is *more* crystalline in character than after only 691 hr of hydrolysis.

In the acids of increasing strengths, the trends are similar. All samples indicated increases in  $CrR$  with time of hydrolysis, but with monotonic decreases, then, as hydrolysis proceeded. The largest gain in  $CrR$  occurred, as expected, in the most dilute acid, the worst degradation being associated with the most concentrated acid.

What may be remarkable about these data is the degree of resistance to hydrolysis displayed. The question that deserves answer by further experimentation is how the cellulose maintains itself in media that do attack it as strongly as shown here.

In agreement with Ant-Wuorinen<sup>29</sup> and others,<sup>15</sup> these data indicate, despite considerable hydrolytic weight loss in the matrix, that the most hydrolysis-resistant material is that which is highly ordered, or crystalline. But it is also intuitively clear that what Ray and Bandyopadhyay<sup>12</sup> called "qualitative perfection" changes considerably. Hermans and Weidinger<sup>13</sup> pictorialized this as a "splitting" of the fiber bundle parallel the fiber axis.<sup>13</sup> A broadening of the [002]-diffraction maxima would indicate the correctness of this picture, but what appears to happen is not simply a slight line broadening but a decrease in [002]-intensity (viz., fewer first-order [002]-diffractions). In the x-ray analysis done here, the [002]-linewidth changed less, relatively, than the [002]-line intensity.

### Crystallinity Index and Qualitative Perfection

The crystallinity index  $CrI$  and a measure of "qualitative perfection,"  $CrA$ , were calculated for the samples of RBC separators treated in  $H_2SO_4$ . The values for these measurements are shown in Table II. The datum levels for RBC separators before hydrolysis are  $CrI = 0.781$  and  $CrA = 6.55$ . Hydrolysis in acids of increasing strengths increases the *intensive* crystallinity as calculated from Segal's index,<sup>14</sup> but as we have defined it here, hydrolysis leads to large losses

TABLE II  
Intensive Crystallinity and "Qualitative Perfection"

Period of hydrolysis, hr	$CrI$	$CrA$
	1.260 $H_2SO_4$	
691	0.827	5.49
1300	0.801	4.40
2400	0.829	4.16
3960	0.784	3.54
	1.280 $H_2SO_4$	
691	0.828	5.07
1300	0.786	4.43
2400	0.817	4.42
3960	0.782	3.16
	1.325 $H_2SO_4$	
691	0.838	5.02
1300	0.779	4.08
2400	0.781	3.51
3960	0.767	2.77

of "qualitative perfection." (In all these measurements, the relative change in [002]-line intensity was as much as 50%, while the [002]-linewidth varied less than 16%.)

Immergut and Ranby<sup>31</sup> reported similar conclusions for native cotton, using D.P. measurements. They concluded that the *most ordered micelles* were proof to hydrolysis, except for the very strongest agents. These data would clearly support their conclusions, despite the interference of the impregnating phenolic resins used to protect the cellulose. In fact, these data fit very well into the amorphous/crystalline model *and* the fringed micelle model for cellulose.

The use of phenolic resins in battery technology has, however, lent us some additional insights into the possible synergistic action of cellulose and the phenolic impregnate. In large stationary battery use, phenolic resins of a similar kind are used to bind woven fiber-glass tubes used as active material supports and separators. In these batteries, the phenolic resin binding on the tubes is completely eroded after a few thousand hours of use.

The model that emerges is this: the phenolic coating is severely hydrolyzed in the absence of the chemical binding provided by the cellulose in the RBC separators. This means that both elements, cellulose and resin, cooperate in giving stability to the RBC separators. Recalling the work of Ruznak and Tanczos,<sup>8</sup> who pointed out that heating to  $\sim 190^\circ\text{C}$  provides easily hydrolyzed —OH linkages in cellulose, we reasoned that during the curing step ( $\sim 205^\circ\text{C}$ ) used in separator manufacturing, the cellulose linkages react with some labile resin linkages to form copolymers that both protect the cellulose linkages and afford the resin a more stable state with respect to acid hydrolysis.

We reasoned that, if this is correct, there should be a difference in degree of crystallinity, *CrI*, of heated  $\alpha$ -cellulose and RBC separators before and after exposure to water vapor. Manjurath, Venkataraman, and Stephen<sup>32</sup> showed conclusively that the x-ray diffraction order of wet or damp cellulose was higher than that of dry cellulose. Morosoff<sup>21</sup> produced similar findings for "never-dried cotton."

We treated  $\alpha$ -cellulose sheets to test temperatures in the order of  $190^\circ\text{C}$  and then equilibrated them with indicating silica gel. Samples of RBC separator material were also dried over silica gel.

Samples of both materials were also equilibrated with  $\text{H}_2\text{O}$  vapor at  $25^\circ\text{C}$ . When these samples were analyzed by x-ray diffraction, the degree of crystallinity of the RBC separators did not vary, within experimental error. However, the heated  $\alpha$ -cellulose showed a consistent increase in *CrI* from 0.843 in the dry state to 0.921 in the moisture-equilibrated state. This indicates that any linkages created thermally in the curing separator were probably reacted with the impregnating resin. It is clear from the immense literature of the fabric industry that we can clearly expect copolymerization between the resin impregnate and the cotton fibers, but this x-ray test gives a particularly elegant demonstration.

It is also useful to compare these qualitative findings with Ant-Wuorinen and Visapaa's hypotheses on cellulose reactivity.<sup>29</sup> If, as they indicate, the intermolecular hydrogen bonded, —OH linkages are equally susceptible to attack by acid, then copolymerization of cellulose and phenolic impregnate, through these linkages made labile during the high temperature curing step should lend exceptional stability to the whole structure. It means that degradation is mainly

through attack at the acetal linkages, and these are far less accessible because of the oriented fibrous character of the matrix.<sup>13</sup> This explanation agrees with the  $CrA$  data developed here. If  $I(002)$  decreases while  $W(002)$  changes little, then the average crystallite length has been decreased (parallel to the  $[002]$ -direction), while the crystallite size (perpendicular to the  $[002]$ -direction) is relatively unchanged. Attack at acetal linkages, followed by hydrolysis and weight loss, will lead to relatively fewer diffractors and necessarily to a reduction in  $I(002)$ . This means that the crystallite population, as time of hydrolysis continues, is made up of shorter crystallites, relatively unchanged in thickness.

In distinction, the fully hydrolyzed cellulose seen in Figure 4 indicates no change in  $CrA$ . While the ratio  $I(002)/W(002)$  is the same, we know the particle dimensions are smaller. This indicates, conclusively, that the unimpregnated cellulose is attacked very generally (all labile  $-OH$ 's and the acetal linkages), while the RBC separator is very selectively attacked.

## CONCLUSIONS

Lead-acid battery separators made of cellulose and impregnated with thermosetting, phenolic resins display unusual resistance to attack by sulfuric acid. The cellulose is attacked and the separator matrix loses substantial material on prolonged storage in battery acid, but the degree of crystallinity decreases only slightly, though the decrease in  $CrI$  is related to increasing acid strength.

The "qualitative perfection" of the retained cellulose decreases, and presumably the average crystallite length is reduced during long storage of RBC separators in acid. X-ray measurements indicate that dry separator matrixes do not undergo any reorganization, as does  $\alpha$ -cellulose, when the matrix is equilibrated with water. This is taken to indicate the intermolecular hydrogen-bonded  $-OH$  linkages enter into copolymerization reactions with the impregnating resin, and the cooperative, final structure has better acid resistance than either the cellulose or the phenolic impregnate.

X-ray diffraction measurements can be used to measure not only the *intensive* crystalline character of degraded RBC separators but also the degree of "qualitative perfection" and, with suitable, parallel chemical measurements, can quantify the *extensive* crystalline properties of the material.

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