

Rudolf A. V. Raff, R. Dale Ziegler,
and Mark F. Adams

Washington State University
Pullman, Washington

Archives Document Preservation II

We have shown in our first publication on this subject (Raff, Herrick, and Adams, 1966) that CMC, the sodium salt of carboxymethylcellulose, a water-soluble, film-forming, high-capacity buffering agent with moderate alkalinity, effectively increases the pH of paper by a neutralizing action, and thereby retards the deterioration of the paper as it ages. We have further shown that CMC, in itself a polymeric cellulose derivative, may require the presence of a nonvolatile plasticizer to maintain flexibility in the treated paper, and that certain wet-strength resins were suitable for this purpose. Paper treated with these CMC-resin combinations increased in strength to such an extent that the folding endurance after aging was in most cases equal, or even superior, to that of the original untreated and unaged paper. Furthermore, the presence of the resin gave wet-strength to the paper, which increased on heat-aging. Up to this point, the paper specimens were treated by hand, a procedure too slow and unwieldy for practical use. Consequently, we have developed several pieces of equipment which allow our process to be carried out mechanically. We are presently reporting confirmatory test results on recent and naturally aged papers obtained by these mechanical treatment steps.

As was previously shown, additional protection of paper stabilized by our impregnation process could be achieved by encapsulating the paper between sheets of polyethylene-coated mylar film. Air and moisture are excluded by the plastic film, and free or generated acid is neutralized by the CMC. Paper treated in this manner can be expected to be resistant to prolonged periods of aging. However, archivists still prefer the less protective cellulose acetate for encapsulation, because it does not bond to paper as does the polyethylene-coated mylar. We have now shown that the encapsulation of a paper sheet in polyethylene-coated mylar can also be carried out in such a manner that the paper will not adhere to the film; it easily can be removed intact from the protecting envelope.

Test Methods

Great care was taken to reduce the variation in the test results obtained on individual paper sheets. The sheets that were treated in any one run were chosen so that all specimens had about the same weight. The specimens thus selected were then cut into

two halves; one half was tested as such, the other after treatment. A comparison of the results obtained on the two halves after conditioning showed the effect of the treatment.

The folding endurance tests of the yellow bond paper were made with a tester of the MIT type under a load of 0.7 kg.; on the newsprint specimens, a load of 0.5 kg. was applied. In all tests, the specimen length was cut in the machine direction of the paper. On some specimens, bursting strength (Mullen) tests were made following Tappi Standard T403 ts-63.

Otherwise, testing and aging procedures were as described in the earlier publication. Artificial aging at 100°C. for three days is assumed to correspond to a natural aging period of 25 years.

Impregnation Process

The treating procedure consists of impregnating the specimens with an aqueous 1 per cent (by weight) solution of CMC-12HP (range of substitution, 1.20-1.40; viscosity in centipoises at 25°C., 100-300), and varying amounts of Kymene 557, an epichlorohydrine-amine-type, wet-strength resin. In all cases, the Kymene additions are reported in per cent by volume, and refer to the commercial 10 per cent solution. The impregnated paper is dried, then pressed in a laboratory press for three minutes at 212°F. and 100 psi. Formerly, the sheets were treated by a hand method. In the work of this report, the specimens were treated with mechanical equipment which included a modified mimeograph machine for applying the solution to the sheet; an electrically heated photographic print drier for drying the treated sheets; and an electrically heated laboratory platen press for pressing the sheets.

In order to adapt the mimeograph machine for use as an impregnator, it was equipped with an electric-motor drive and a variable-speed control. A sheet-metal pan filled with the treating solution was placed under the applicator roll on the underside of the machine so that this roll was submerged in the solution at all times. Further, the applicator roll was locked in such a way that it pressed at all times against the cloth-covered drum, turning with it, and keeping both the outside and inside supplied with treating solution. Thus, as the paper sample passes between the applicator roll and the drum, the treating solution is applied to both sides of the paper specimen. A second spring-loaded rubber pressroll is attached to the machine, in contact with the drum just above the applicator roll; and when the paper sheet passes between this roll and the drum, it forces the treating solution to penetrate into the paper, insuring a thorough treatment of the sheet.

With this impregnator, it was found that the best results are obtained if the specimen makes at least six passes through the machine to obtain repeated contacts with the applicator roll, pressroll, and drum. Specimens treated with only three revolutions show erratic strength improvement, while sheets treated for 12 revolutions have about the same improvement as achieved with six turns. The drum speed is not very critical in that sheets treated at three rpm have about the same strength improvement as those observed at one rpm. In all cases, the paper specimens adhere well to the drum during the entire operation, but can be lifted easily at the end of the cycle.

The impregnated paper samples are then transferred to a drum-type photographic print drier (drum diameter, 30"; drum width, 26"), which required no modification.

It was necessary to operate the drier at a lower temperature (120°F.), and at a speed of four minutes per revolution, to achieve the development of optimum properties in the subsequent pressing operation. Drying at a higher temperature (above 200°F.) does not give a consistently satisfactory product, which, moreover, will no longer be improved by the subsequent treatment in the press. It appears that the dried paper entering the press must still contain some moisture to act as a plasticizer for the CMC to be able to assume a coherent structure inside the sheet. Thus, paper sheets which are still slightly damp on leaving the drier will show a very good improvement in strength after pressing, as will air-dried samples. The time that is allowed to elapse after the sheets are dried and before they are being pressed does not affect the test results.

In spite of repeated attempts, no drying conditions could be established which would consistently result in paper sheets with maximum strength without pressing them. Thus, the dried paper samples must finally be pressed between thin sheets of Teflon of the desired surface texture. Optimum pressing conditions in a conventional platen press are three minutes at 212°F. and 100 psi. A pressing time of five minutes shows no advantage over three minutes, while one-minute pressing is not as effective. The use of lower pressures tends to be unsatisfactory. Any distortions in the sample are eliminated in the pressing operation, and perfect specimens are obtained. Also, pressing restores the thickness of the treated and dried paper close to that of the sheet before it was treated. This may be an important factor, when, for example, preserved pages of a book still must fit into the original cover.

It can easily be visualized that the first two steps, impregnation and drying, can be integrated into a synchronized operation. As to the third step, the plan is to replace the press by a system of heated rolls or drums, to duplicate the particular action of the press. There is even indication that a second print drier operated at a higher temperature (212°F.) might be sufficient. At any rate, a combination of these individual pieces of equipment will permit the construction of a single unit for the entirely automatic preservation treatment of documents.

The data obtained with the above-described mechanical equipment essentially confirmed the conclusions presented in our earlier paper in which the specimens were treated by hand; in addition, the data showed less spread and better reproducibility, including the treatment of additional paper grades.

Tests were made with recent papers: yellow bond paper (bleached sulphite pulp) and blank newsprint paper (high groundwood pulp content); and with naturally aged papers: the *N.Y. Times* of 1870 (free of groundwood pulp) and the *Buffalo Courier* of 1901 (containing groundwood).

The results obtained on yellow bond paper are given in Table 1 (folding endurance) and in Table 2 (bursting strength); those obtained on blank newsprint paper are shown in Table 3 (folding endurance) and in Table 4 (bursting strength). The data are also plotted in the corresponding Figures 1, 2, 3, and 4. The following conclusions were drawn:

1. Previously published results are confirmed that the CMC-Kymene treatment greatly increases the folding endurance as well as the bursting strength of the papers

Table 1. Folding endurance tests on untreated and treated yellow bond paper before and after artificial aging.

Kymene (% in CMC solution)	Not aged			Aged for 3 days at 212°F.			Aged for 9 days at 212°F.		
	Untreated	Treated	Increase in fold (%)	Untreated	Treated	Increase in fold (%)	Untreated	Treated	Increase in fold (%)
0		448	30		300	54		304	231
0.05	346	438	27	195	284	46	92	285	211
0.10		421	22		309	59		253	175
0.25		491	42		391	101		253	175

Note: The values shown for the untreated samples are averages of 50 individual tests, while the values shown for the treated samples are averages of 20 individual tests.

Table 2. Bursting strength tests on untreated and treated yellow bond paper before and after artificial aging.

Kymene (% in CMC solution)	Not aged			Aged for 3 days at 212°F.			Aged for 9 days at 212°F.		
	Untreated	Treated	Increase in mullen (%)	Untreated	Treated	Increase in mullen (%)	Untreated	Treated	Increase in mullen (%)
0		27	8		25	9		26	24
0.05	25	26	4	23	27	17	21	24	14
0.10		27	8		26	13		24	24
0.25		28	12		26	13		26	24

Note: The values shown for the untreated samples are averages of 40 individual tests, while the values shown for the treated samples are averages of 10 individual tests.

Table 3. Folding endurance tests on untreated and treated blank newsprint paper before and after artificial aging.

Kymene (% in CMC solution)	Not aged			Aged for 3 days at 212°F.			Aged for 9 days at 212°F.		
	Untreated	Treated	Increase in fold (%)	Untreated	Treated	Increase in fold (%)	Untreated	Treated	Increase in fold (%)
0		106	38		89	56		55	45
0.10	68	89	21	57	60	5	38	59	55
0.25		209	141		87	53		39	0

Note: The values shown for the untreated samples are averages of 60 individual tests, while the values shown for the treated samples are averages of 20 individual tests.

Table 4. Bursting strength tests on untreated and treated blank newsprint paper before and after artificial aging.

Kymene (% in CMC solution)	Not aged			Aged for 3 days at 212°F.			Aged for 9 days at 212°F.		
	Untreated	Treated	Increase in mullen (%)	Untreated	Treated	Increase in mullen (%)	Untreated	Treated	Increase in mullen (%)
0		13.7	47		12.6	38		12.1	28
0.10	9.3	12.9	39	9.1	13.5	48	9.4	12.7	35
0.25		15.2	63		13.0	43		14.3	52

Note: The values shown for the untreated samples are averages of 15 individual tests, while the values shown for the treated samples are averages of 5 individual tests.

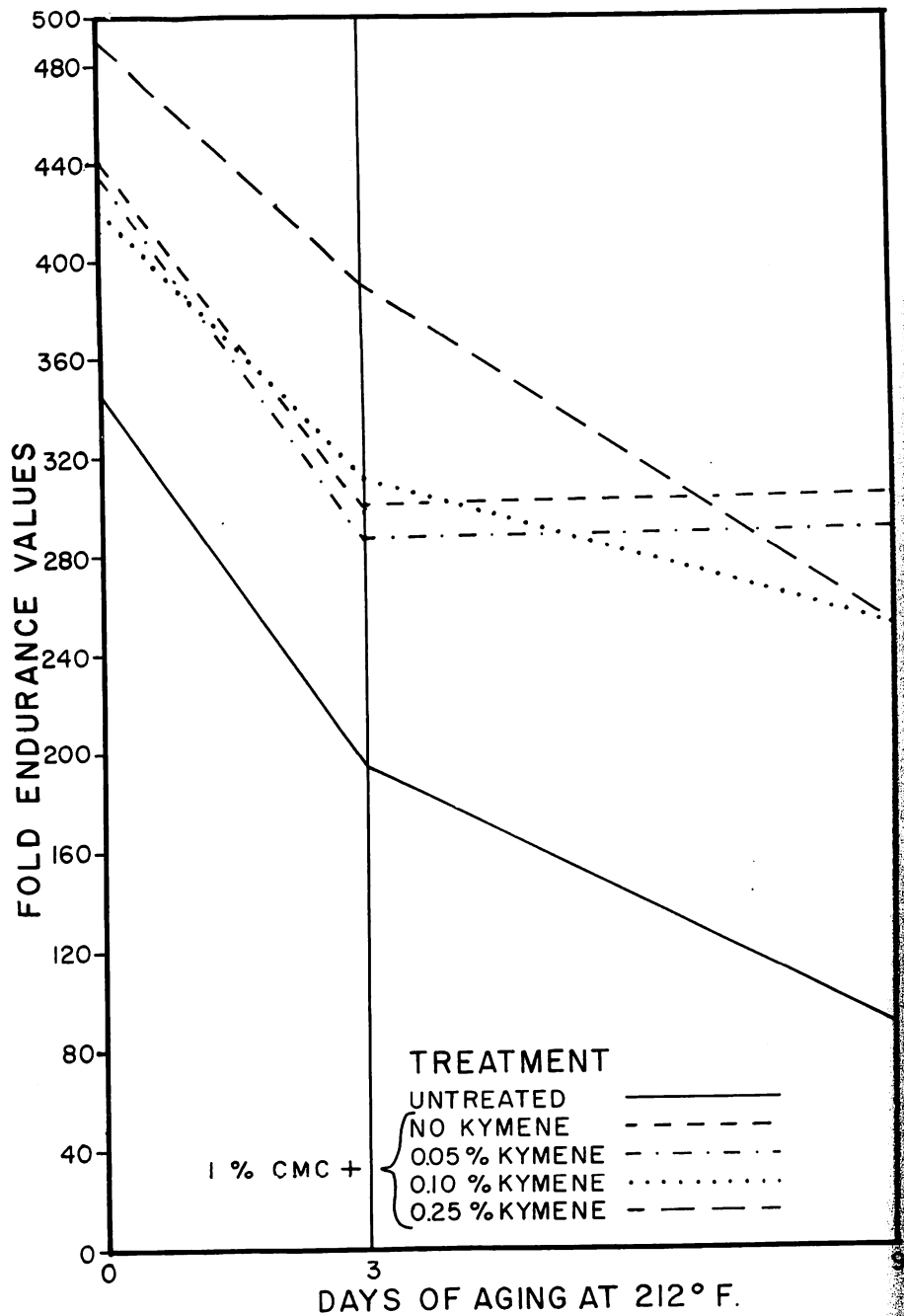


Figure 1. Folding endurance tests on untreated and treated yellow bond paper before and after artificial aging.

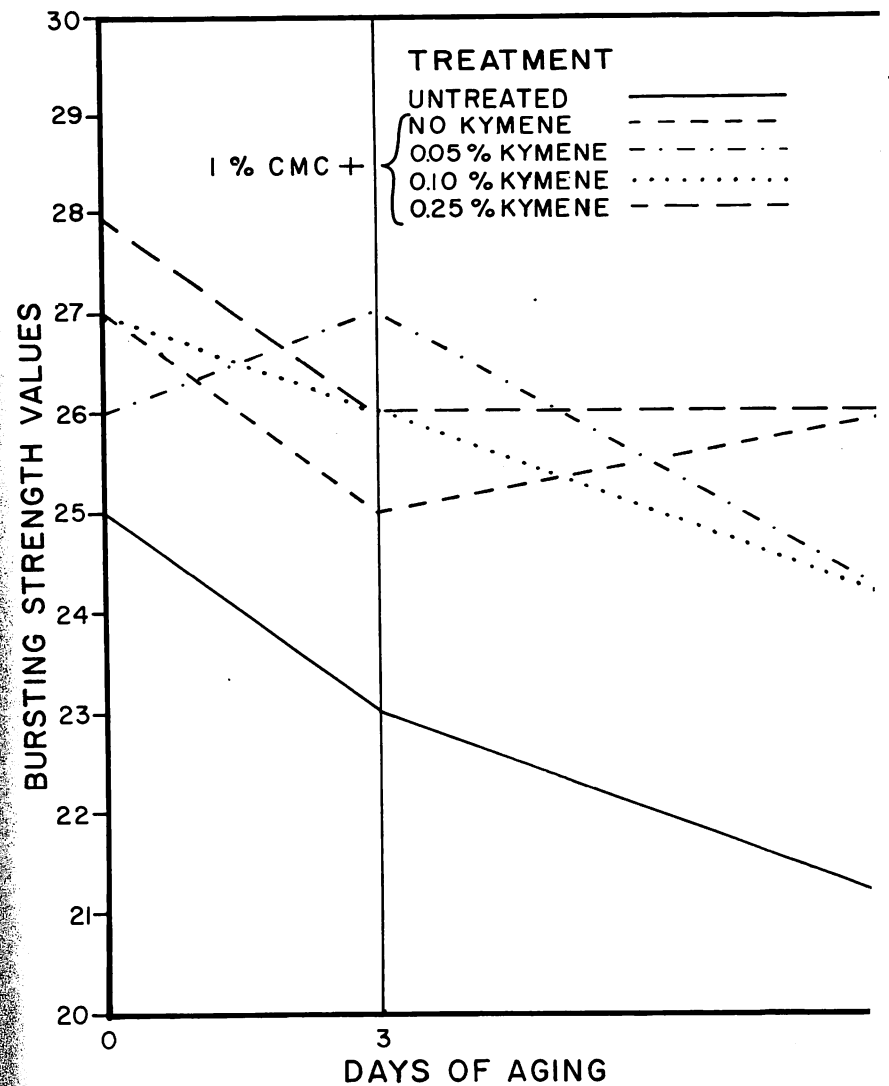


Figure 2. Bursting strength tests on untreated and treated yellow bond paper before and after artificial aging.

before they are aged. Other data indicate that the tearing strength remains essentially unchanged.

2. The strength data obtained after nine days of artificial aging (corresponding to 75 years of natural aging) demonstrate, even more than those observed after three days of artificial aging, the effectiveness of the CMC-Kymene treatment in retaining or preventing the age deterioration of paper. For example, at the end of the nine-day aging period, the folding endurance of the treated yellow bond paper was three times as great as that of the aged untreated paper. The folding strength of the treated

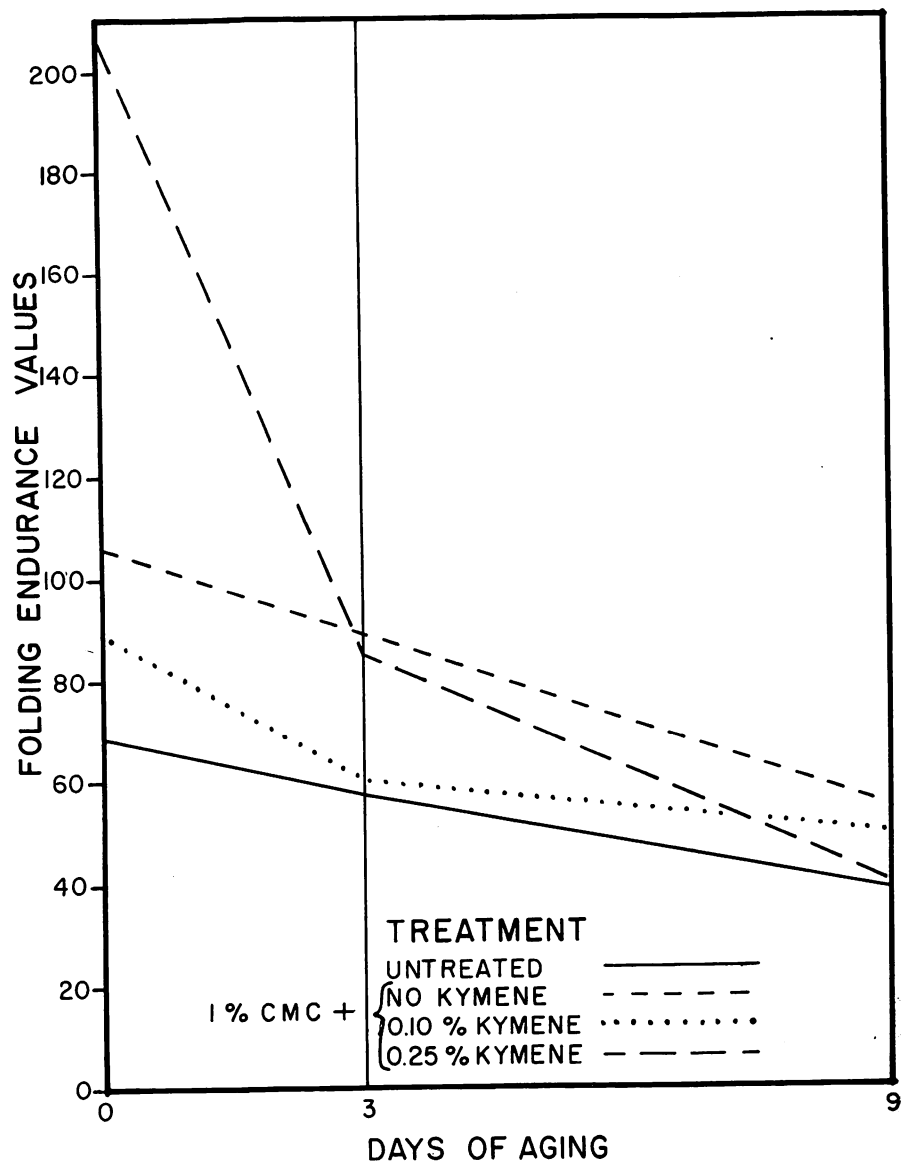


Figure 3. Folding endurance tests on untreated and treated blank newspaper paper before and after artificial aging.

newspaper was also greater than that of the aged untreated paper after the nine-day aging period, but the improvement was smaller than that shown by the yellow bond paper. The results of the bursting strength tests follow a similar pattern.

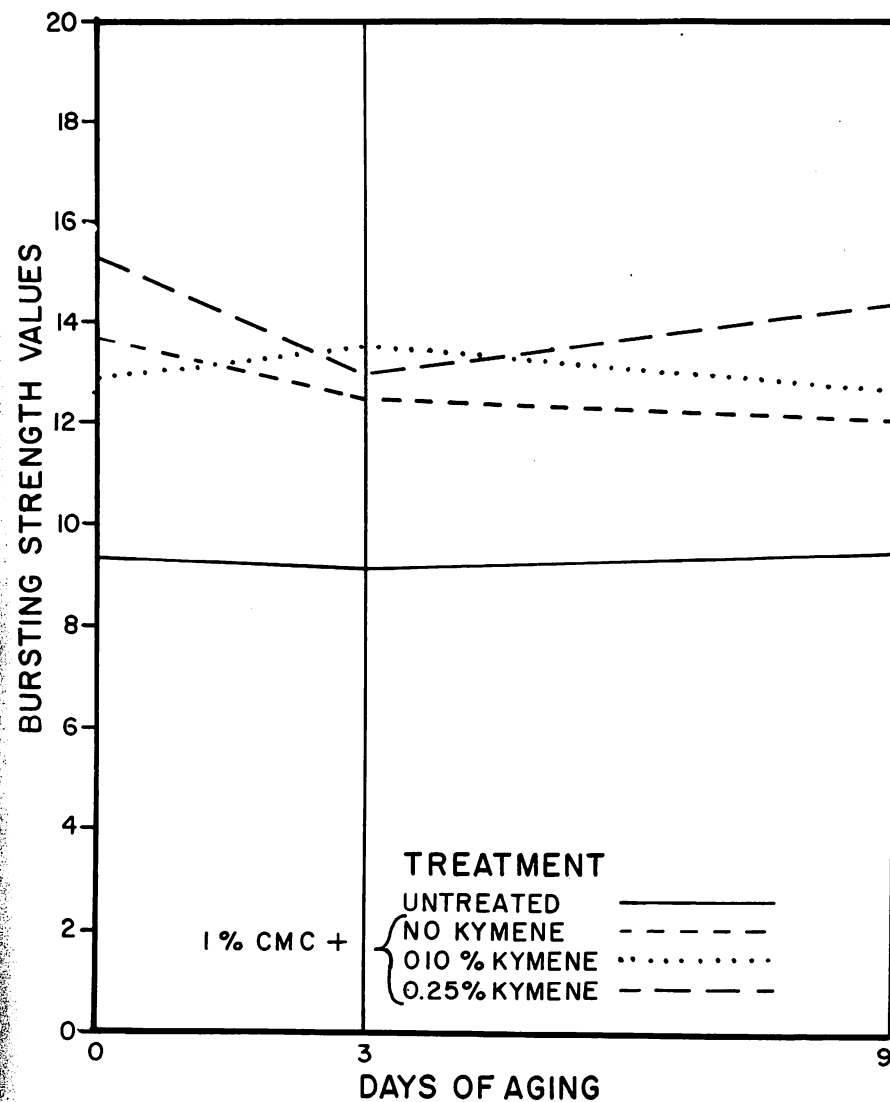


Figure 4. Bursting strength tests on untreated and treated blank newspaper paper before and after artificial aging.

3. While required in most cases, the presence of even a small amount of Kymene resin seemed unnecessary in some instances from the standpoints of increasing the strength and improving the aging properties of the paper. However, Kymene also imparts wet strength to the treated paper sheets, and, further, it prevents them from becoming tacky and from sticking together under abnormally high humidity conditions and/or pressure; therefore, the addition of Kymene to the system is required in all cases.

The results on naturally aged papers, the *N.Y. Times* of 1870, and the *Buffalo*

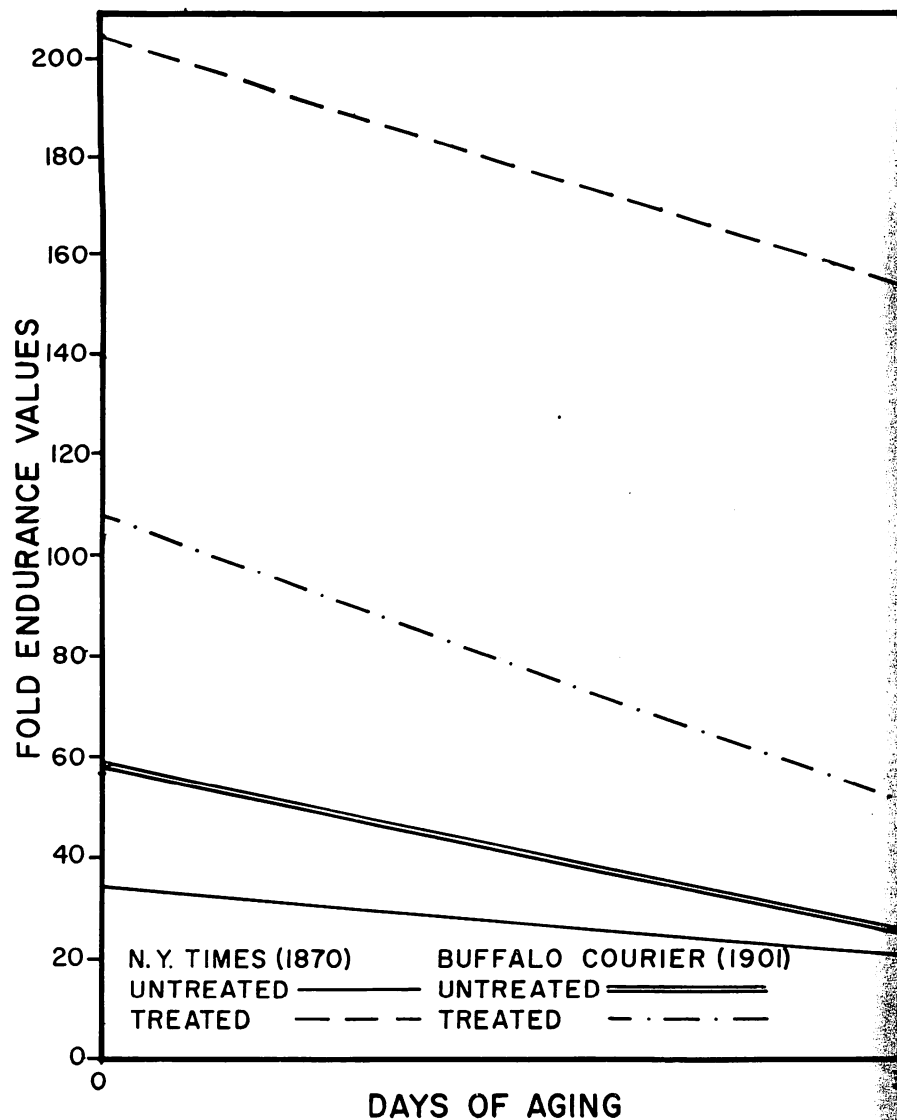


Figure 5. Folding endurance tests on untreated and treated old newspapers before and after artificial aging.

Courier of 1901, are summarized in Tables 5 and 6 and plotted in Figure 5. The following conclusions were drawn:

1. Before aging, sheets of the *N.Y. Times* treated with CMC and Kymene (0.1%) had about six times the folding endurance of the untreated sheets; with the *Buffalo Courier*, folding endurance was about doubled. The bursting strength of the papers was also improved by the treatment but to a lesser extent.

Table 5. Folding endurance tests on untreated and treated old newspapers before and after artificial aging.

Newspaper	Not aged			Aged for 3 days at 212°F.		
	Untreated	Treated	Increase in fold %	Untreated	Treated	Increase in fold %
N.Y. Times of 25 June 1870	35	205	485	22	154	600
Buffalo Courier of 8 September 1901	59	108	83	24	52	117

Note: The values shown for both untreated and treated samples are the averages of 20 individual tests.

Table 6. pH - values of untreated and treated old newspapers before and after artificial aging.

Newspaper	Not aged		Aged for 3 days at 212°F.	
	Untreated	Treated	Untreated	Treated
N.Y. Times of 25 June 1870	5.2	6.5	5.2	6.3
Buffalo Courier of 8 September 1901	4.6	6.1	4.6	5.8

Note: The data given are averages of two determinations.

2. After artificial aging for three days, the treated specimens of the *N.Y. Times* had more than seven times the folding endurance of the aged untreated sheets, so that treated specimens after artificial aging still had more than four times the folding endurance of the untreated and unaged sheets. The treated *Buffalo Courier* paper had about twice the folding endurance after aging as the untreated and artificially aged samples. Improvement in aging resistance in both cases is also evident in the bursting strength tests.

3. The pH tests reported in Table 6 show that the treatment reduces the acidity of the papers and that they then do not become more acidic during the artificial aging test.

4. The printing ink on these papers was not affected by the treatment.

Encapsulation Process

It was shown in our previous publication that paper stabilized by the CMC-Kymene impregnation process can be encapsulated for further protection between sheets of cellulose acetate or of polyethylene-coated mylar by the application of moderate heat and pressure, as is done in commercial automatic laminators. In this application, the polyethylene-coated mylar with its low permeabilities for water vapor and for oxygen gives a much better protection than cellulose acetate, which has a high permeability for oxygen and still more so for water vapor.

However, encapsulation of paper with polyethylene-coated mylar is irreversible in that a tight bond between film and paper does not allow the removal of the latter. As this result is unacceptable to archivists who demand that any encapsulation process of documents should be easily reversible, the use of the highly protective polyethylene-coated mylar film has so far been rejected in favor of the much less protective cellulose acetate.

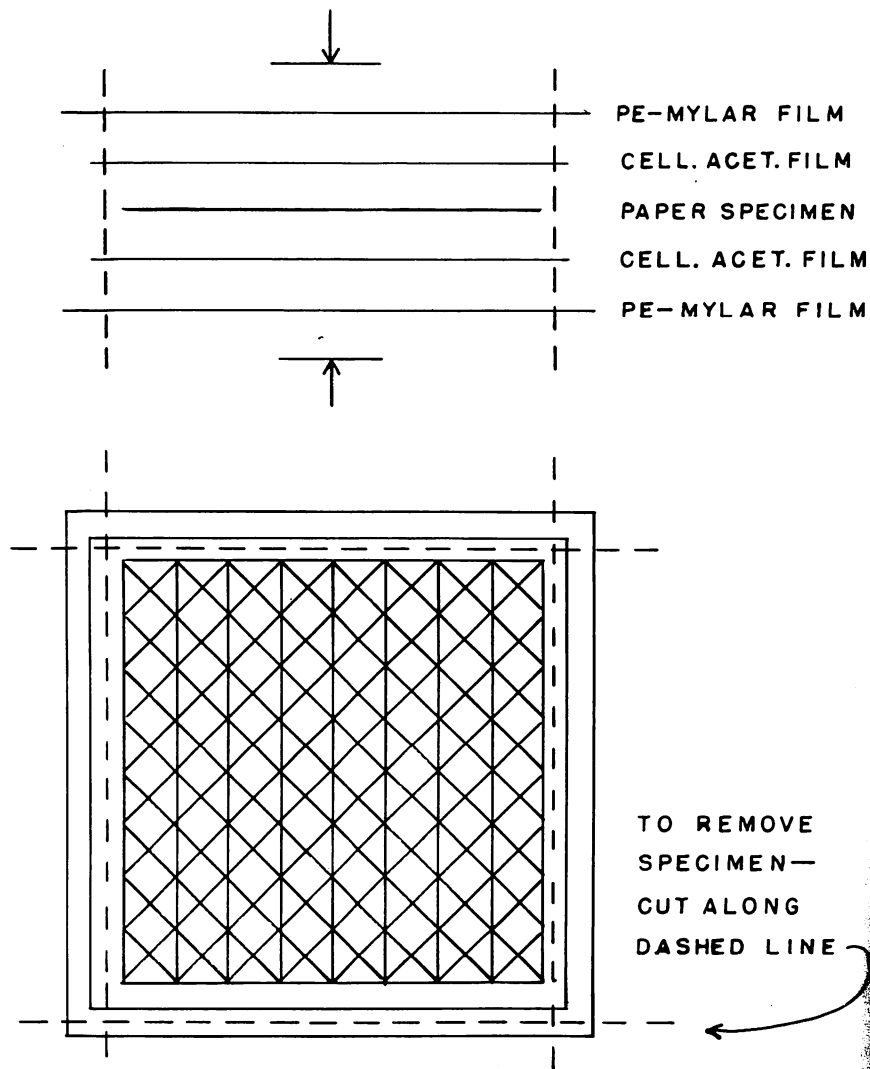


Figure 6. Removeably sealing a paper sheet in polyethylene-coated mylar film.

It has now been found, as illustrated in Figure 6, that polyethylene-coated mylar film can still be used in a reversible encapsulation process if the document is sandwiched between two slightly larger sheets of cellulose acetate film before being sealed between the still slightly larger sheets of the polyethylene-coated mylar. The encapsulated document then rests freely in the sealed envelope and can be readily removed by cutting along the edges, as shown in the figure.

Summary

We have shown in our previous publication that impregnation of paper with an aqueous solution of CMC (the sodium salt of carboxymethylcellulose) and Kymene (a commercial wet-strength resin) not only increases the strength of the paper but also destroys acids in the sheet by its buffering action, and, thereby, improves the resistance of the paper to degradation on aging. Frequently, the strength of the impregnated paper after heat-aging was still superior to that of the original untreated and unaged sheet.

In this previous work, the papers were treated by hand methods; in the present study, mechanical equipment was used, which included a redesigned mimeograph machine; a photographic print drier; and a laboratory platen press.

The present paper also gives confirmatory tests results on recent and on naturally aged papers subjected to the mechanical treatment steps. Most strikingly, the folding endurance of sheets from the *N.Y. Times* of the year of 1870 increased sixfold by the CMC-Kymene treatment. After artificial aging for three days at 100°C., corresponding to a natural additional aging period of 25 years, the treated specimens had more than seven times the folding endurance of the aged untreated sheets, so that the treated samples after aging still had more than four times the folding endurance of the untreated and unaged original paper. Improvement in aging resistance was also evident in the bursting strength tests.

Finally, it is shown that encapsulation of a document in polyethylene-coated mylar, excluding both moisture and air, can be carried out reversibly. Here the document is sandwiched between two slightly larger sheets of cellulose acetate film before being sealed between the sheets of the polyethylene-coated mylar in a commercial automatic laminator. The encapsulated document then rests freely in the sealed envelope and can be easily removed by cutting along the edges. This should allow archivists to use, for the encapsulation of documents, the highly protective polyethylene-coated mylar film in preference to cellulose acetate film, which is considerably permeable by air and moisture.

Acknowledgment

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