Weathering of paperboard used in consumer packaging applications: a litter simulation study

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ABSTRACT *The disintegration of selected varieties of paperboard used in consumer packaging was studied, under outdoor and laboratory-accelerated exposure conditions. The tensile index of the paperboard samples generally decreased logarithmically with the duration of exposure. Rate parameters based on the data were used to rank the different samples in terms of their weatherability.*

Laminated or coated paperboard samples showed faster rates of degradation than other paperboard materials. This acceleration was attributed mainly to pre-photodegradation of the laminating film, which acts to initiate the photodegradation of the underlying ligno-cellulose layers. The entrapment of moisture by the coating, leading to longer durations of wetness, may also have contributed to the faster degradation rates.

KEYWORDS
Environmental control
Packaging
Paperboard
Tensile strength
Waste management

Paper and paperboard constitute about a third of the over 160 million tons of municipal solid waste generated annually in the United States (*1, 2*). Paperboard used in packaging is the major constituent of this fraction and is a particularly visible component in municipal solid waste. Landfilling is now and will remain for some time the preferred method for disposing of most municipal solid waste in the United States (*2*). Landfill capacity is shrinking rapidly, however, and attention is turning to the lifetimes of packaging materials after the consumer disposes of them and they become part of the solid-waste stream. The persistence of paperboard under landfill conditions (*3*) and its impact from a solid-waste management standpoint have been reported.

Discussions on the subject center on two key concerns: the fate of paper products under landfill environments where over 80% of municipal solid waste is disposed, and the fate of paper and paperboard that invariably end up as urban litter. The latter fraction is also an important, highly visible component of the waste stream (*4*). Recent statistics based on beach surveys show that an average 16% of the waste items encountered on the nation's beaches consists of paper-based debris. Concerns as to the litter fraction of municipal solid waste essentially raise the question of biodegradability and environmental photodegradability of paper products. In spite of its importance, information on the ability of paperboard to withstand weather, especially those paperboards used in consumer packaging, is quite limited in the scientific literature.

The disintegration of paper under library storage is conventionally described in terms of the permanence and durability of the paper. Permanence essentially refers to the chemical stability of paper during aging, while durability refers to stability in physical and mechanical properties (*5, 6*). Weathering of paper under outdoor or laboratory exposure results in marked changes in paper chemistry and consequently affects both the permanence and durability of the material. The term "degradation" as used in this study denotes loss of durability caused by chemical changes (loss of permanence).*

Our purpose was to study the extent of environmental degradability of selected paperboard products used in packaging under outdoor and laboratory-accelerated exposure conditions. Consequently, the findings are directly relevant to the fate of

*"Degradation" is used here to mean a disintegration (a loss in integrity, an embrittlement, or breakdown) during environmental exposure, caused predominantly by chemical processes taking place in the material. As such, degradation does not include strength decreases caused by extraction of soluble material, swelling and deswelling, and physical damage to the exposed paper. These changes are classified as "deteriorations" instead.

I. Characteristics of paper and paperboard materials

Code	Material	Gram-mage,[a] g/m²	Coating[b] Inner	Coating[b] Outer	Print-ing	Paper, tensile index (TAPPI method) MD N•m/g	MD Std. dev.	CD N•m/g	CD Std. dev.	Plastic, tensile strength (ASTM method) kg/cm²	Std. dev.
A	Paper cups (cold beverage)	270.0	Wax	Wax	yes	30.3	1.6[c]	...	...	...	...
B	Paper cups (hot beverage)	285.0	PE	...	yes	21.2	0.5[c]	...	...	...	...
C	Milk cartons (1/2 gallons)	510.0	PE	PE	yes	31.7	1.3[c]	...	...	...	...
D	Plain card stock	250.0	...	...	no	49.2	3.7	29.5	2.3	...	...
E	Plain plates	290.0	...	...	no	34.2	2.8	26.4	2.9	...	...
F	Clay-coated paper plates	285.0	Nitro-cell	...	no	39.8	2.4	30.1	2.4	...	...
G	Frozen food package	320.0	PE	PE	yes	42.4	3.4	25.1	3.9	...	...
H	Canned drink cartons	320.0	...	...	yes	70.9	2.3	30.3	1.6	...	...
I	Plastic Control 1 (1/2-gal HDPE milk jug)	...	n.a.	n.a.	n.a.	...	...	...	...	295.4	17.5
J	Plastic Control 2 (LDPE six-pack ring)	...	n.a.	n.a.	n.a.	...	...	...	...	158.2	11.3
K	Paper control (blotting paper)	260.0	...	...	...	33.2	18.6	2.4	1.1	...	...

[a]Measured according to TAPPI 410 om-88. [b]Coating on inner and outer surfaces. [c]No direction. n.a. = not applicable. PE = polyethylene.

paperboard materials exposed as litter.

Breakdown of paper and its assessment

Paperboard in the litter fraction of the municipal solid waste is mainly broken down by the action of sunlight, moisture, and, to a lesser extent, microbial processes. Since the material is often not in close contact with the soil and since it remains dry for the most part, biological factors would play a minor role at best in the disintegration of paperboard litter.

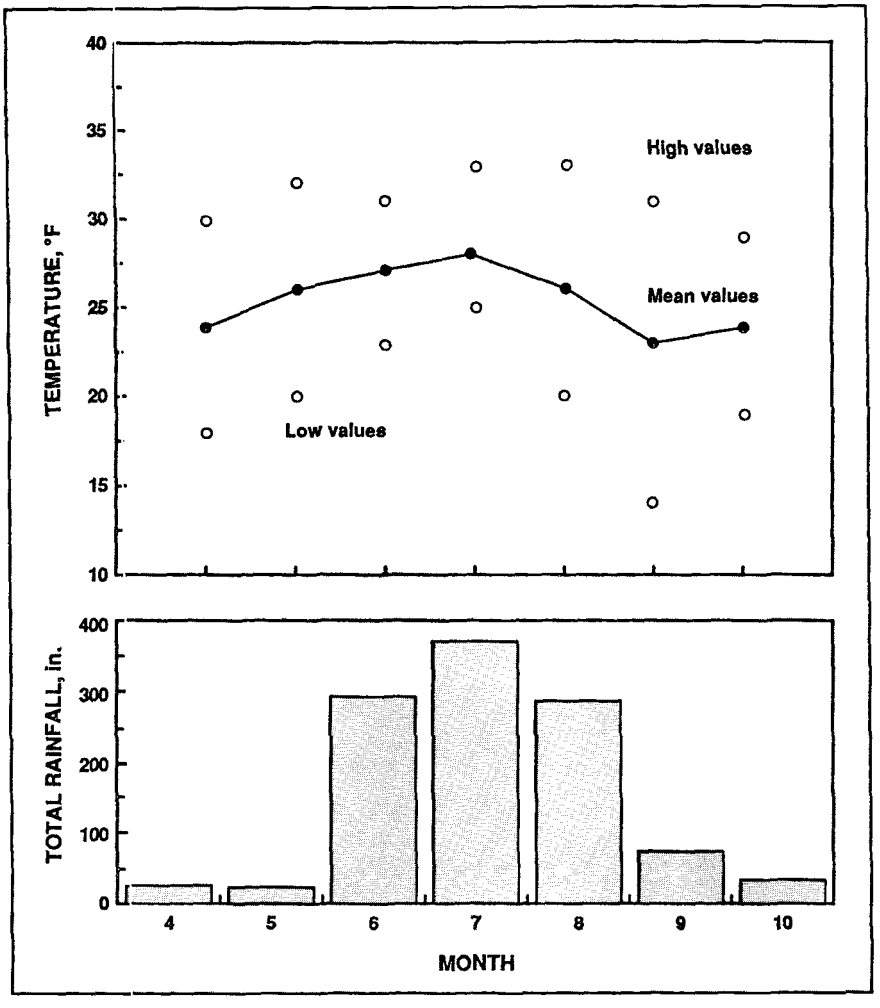
Pulp has sufficient chromophores, specially in the lignin fraction (*7–9*) to absorb sufficient sunlight to initiate photodegradation. Both the holocellulose and lignin fractions in the pulp undergo photodegradation, which enhances the free radical degradation reaction of cellulose. While the detailed mechanism of photodegradation of pulp is not entirely clear, it is believed to involve absorption of radiation by the α-carbonyl groups in lignin (*10*), which leads to the formation of adjacent phenoxy radicals in a free radical process. Extensive degradation of lignin eventually results in the formation of soluble products, including carboxylic acids and yellow quinanoid chromophoric structures (*11*). Holocellulose breaks down into a mix of mono-, di- and oligosaccharides that are water extractable (*12, 13*).

Exposure to moisture causes anisotropic swelling of wood fibers and may lead to the weakening of fiber-to-fiber bonds. The cyclic wetting and drying of paper, as in the case of litter exposed outdoors, is likely to weaken the paper and extract the soluble fraction in the sample. Water may also enhance the deleterious effect of light on paper (*14*). Generally, light-induced damage to paper is mostly a surface reaction. Free radicals produced at the surface of paper during photodegradation, however, are likely to be afforded greater mobility in the presence of moisture.

Environmental degradation, or weathering, of paperboard will result in marked changes in almost all properties of the material to varying extents. The kinetics of the breakdown process will thus depend on the particular set of tests used to monitor the weathering process. For this study, we selected criteria for assessing the disintegration of paperboard on the basis of relevance to litter and on the basis of practicability.

The tensile strength of paper reflects the structure of the fiber mat as well as the structures of individual fibers and is well suited for monitoring degradation. The extent of interfiber bonding primarily determines the strength of paper (*15*), and the theoretical basis of the test has been discussed (*16*). Monitoring the changes in tensile properties of paper is a well-established procedure that yields data easily amenable to interpretation. Furthermore, the tensile properties of paper are not as sensitive

1. Climate conditions at outdoor exposure site during the period of exposure



to small variations in relative humidity as some other mechanical tests (*17*) such as folding endurance (*18*) and tear resistance (*19*), a factor that may affect the precision of the data. While folding endurance is a sensitive measure of degradation, it is difficult to get meaningful results with paper of high basis weight. In previous studies on the weathering and the degradability of paper (*20–24*), wood (*25–28*), and synthetic polymers (*29–30*), tensile strength has been used as a principal measure of degradability. From a practical standpoint, a decrease in the strength of paperboard is directly related to the ease of mechanical compaction or embrittlement of the material, which in turn might be relevant to reducing the volume of the litter under exposure.

The change in the pH of paper is also a useful measure of permanence (*31*). Barrow (*32*) and others (*33*) reported data suggesting that the change in the pH of the paper might be a good indicator of early degradation. Wilson *et al.* (*34*) studied the accelerated and natural weathering of paper and found the generation of acidic materials to be associated with aging. The variation in acidity, however, was not sufficiently large to obtain a correlation between acidity and the stability of the paper.

Experimental procedures

The paperboard samples were commercial consumer packaging materials provided by manufacturers. Plain uncoated bleached board and blotting paper samples obtained from a commercial source were also included in the study. Blotting paper served as a readily degradable reference sample. Plastic reference samples, the low-density polyethylene (LDPE) six-pack ring material, and the high-density polyethylene (HDPE) milk jugs were obtained from a retail outlet. All materials were stored under ambient conditions away from light, until exposure.

Table I describes the different types of paperboard employed in the study.

Outdoor exposure

Outdoor exposures were conducted at a test site in Miami, Fla. Test pieces of paperboard approximately 8 × 10 in. were exposed on racks with wood panel backing, at an angle of 45° facing south, during the period of April 5 to Aug. 25, 1989. Samples were exposed to sunlight and the elements during this period, and sampling was carried out on a weekly basis for the first 10 weeks and on a biweekly basis thereafter. The weather conditions at the exposure site are summarized in **Fig. 1.**

Weather-O-Meter and laboratory exposure

The samples were exposed to a borosilicate-filtered xenon light source in an Atlas Ci 65 Weather-O-Meter. The exposure cycle used was selected to obtain data that may correlate with exposure under Florida outdoor conditions. The cycle consisted of a light period of 1.5 h followed by 0.5 h of water spray with light. The black panel temperature at the sample position was 70±3°C, and the relative humidity was 55±5%. Samples were removed at specified intervals and were saved for testing.

Laboratory exposure of samples to white light was carried out using a 1-kW borosilicate-filtered xenon source yielding radiation similar to terrestrial sunlight at unit air mass. Samples were maintained at ambient temperature during exposure using a water-cooled metal backing plate.

Conditioning and tensile testing

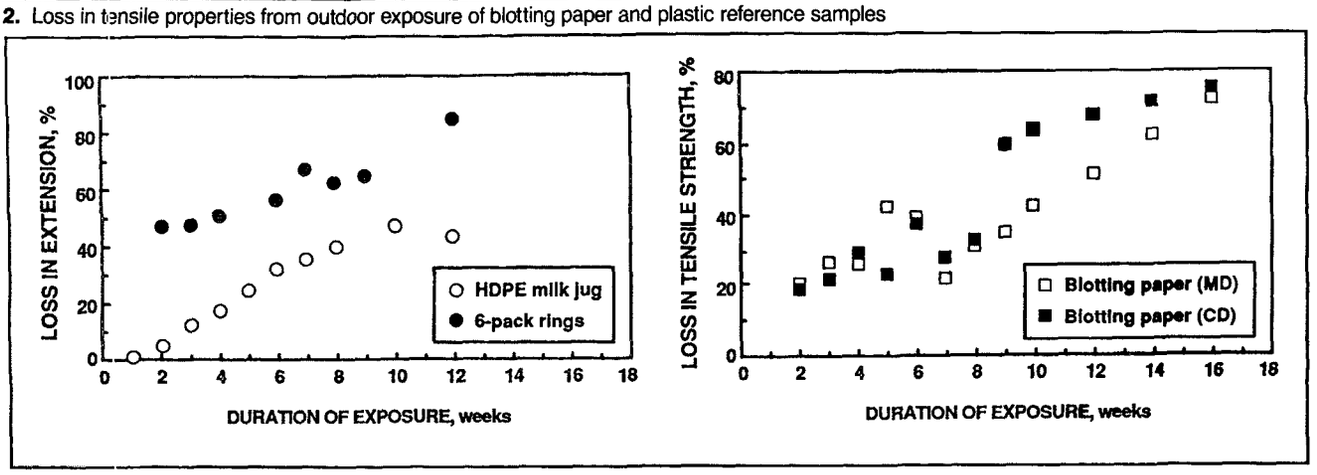
Samples collected after exposure were wrapped in black paper during storage. Conditioning was carried out on pre-cut test strips of paperboard as soon as they were received, according to TAPPI T 402 om-88. After conditioning at 50% RH for 48 h, the tensile properties of the samples were determined using an Instron 1122 testing machine. Tensile testing was carried out according to T 494 om-88 for paper samples and according to ASTM D 638-72 for plastic materials. Because of the shape of the 6-pack rings, it was not possible to obtain a standard test strip for testing 6-pack rings. The values given in the table are therefore only approximate.

II. Tensile index of paperboard subjected to outdoor exposure and Weather-O-Meter exposure

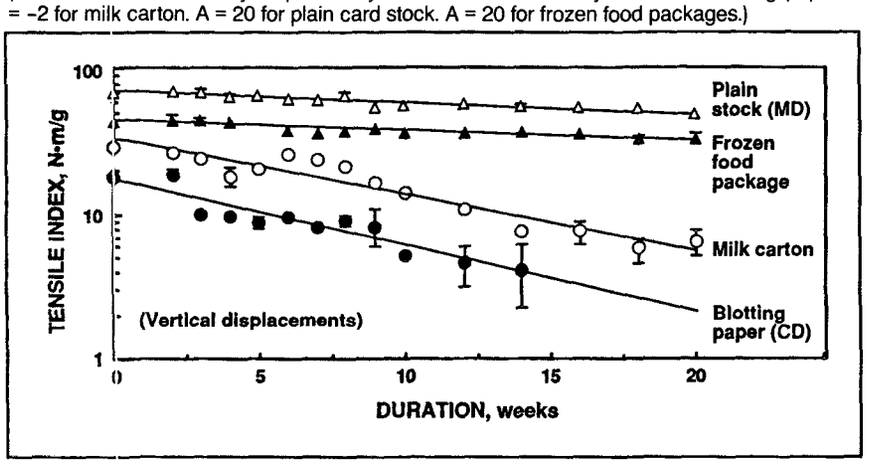
Time	Paper cups: Cold bev.	Paper cups: Hot bev.	Milk cartons	Plain card stock: MD	Plain card stock: CD	Paper plates: Plain	Paper plates: Coated	Frozen food package: MD	Frozen food package: CD	Canned drink package: MD	Canned drink package: CD	Blotting paper: MD	Blotting paper: CD	Plastic controls: Milk jugs	Plastic controls: 6-pack rings
Outdoor exposure															
Control	30.3	21.2	31.7	49.2	29.5	34.2	39.8	42.4	25.1	70.9	30.3	33.2	18.6	295.4	158.20
	1.6	0.5	1.3	3.7	2.3	2.8	2.4	3.4	3.9	2.3	1.6	2.4	1.1	17.5	11.30
2 weeks	24.9	18.9	28.7	48.7	...	34.9	...	...	24.9	60.1	0	17.5	9.9	282.3	150.50
	1.6	0.6	0.7	2.1	...	0.7	...	...	1.9	1.0	0	1.6	0.3	31.5	30.90
3	23.7	20.3	26.0	48.3	29.9	33.8	35.3	41.1	24.5	64.9	27.8	16.1	9.7	290.5	128.90
	0.9	...	0.2	3.4	0.8	2.0	1.4	3.2	...	3.0	1.3	0.8	0.4	23.1	17.80
4	18.3	18.6	20.2	44.9	21.2	31.6	...	36.3	22.7	60.1	27.2	16.4	8.8	284.3	128.90
	1.5	1.5	2.5	2.8	0.2	2.3	...	2.2	...	1.9	0.8	0.6	0.7	0.3	...
5	17.5	18.6	22.4	44.1	30.2	33.9	31.2	40.4	...	59.5	25.6	12.8	9.5	309.3	132.10
	0.4	0.3	1.6	0.8	2.3	1.9	1.8	2.0	...	1.8	2.1	2.0	0.5	19.0	1.32
6	16.0	15.2	27.5	41.4	21.8	33.0	30.2	...	17.6	46.6	22.5	13.3	7.8	347.5	139.20
	1.0	1.5	1.0	3.5	3.9	...	0.8	...	2.2	1.6	2.6	0.5	...	24.3	2.80
7	12.9	11.4	25.4	40.0	22.1	28.4	27.1	...	16.1	45.7	19.7	17.8	8.9	311.8	143.20
	0.6	2.5	1.1	0.8	1.3	1.2	2.2	...	1.1	1.5	1.3	0.7	0.7	31.2	1.23
8	12.7	15.5	22.8	42.4	24.3	29.1	22.0	26.8	16.5	41.9	19.6	15.2	8.3	283.9	143.20
	0.3	0.6	0.8	1.6	0.7	...	0.6	2.0	...	0.3	1.2	...	2.4	14.2	1.23
9	12.4	14.0	17.8	33.0	16.1	25.4	22.2	29.4	17.2	38.8	16.3	...	5.0	272.9	132.80
	0.7	0.4	0.2	...	2.3	3.0	2.2	...	...	1.1	1.3	...	...	5.4	9.30
10	12.6	15.0	15.8	34.8	21.8	24.5	...	21.7	15.9	36.8	16.8	12.8	4.5	280.7	137.40
	0.4	0.8	0.4	2.7	0.5	0.7	...	2.3	...	8.1	1.8	1.4	1.4	...	2.74
12	11.9	15.0	12.6	33.7	20.1	21.9	22.2	19.4	15.9	36.5	16.2	...	4.0	279.4	149.20
	2.2	2.1	...	0.8	0.5	0.9	0.4	1.0	1.0	1.3	...	...	1.8	2.3	...
14	11.2	13.6	9.3	32.3	18.8	19.6	21.9	...	15.0	33.3	15.9	8.4	...	276.6	...
	0.7	0.7	0.6	0.3	0.3	0.3	0.4	...	1.0	...	...	1.4	...	11.2	...
16	10.5	12.0	9.2	31.3	17.9	...	20.6	...	14.3	29.4	15.3	6.3	...	...	...
	1.0	0.9	1.4	0.9	0.8	...	...	...	1.8	...	...	1.4	...	...	...
18	8.0	8.0	7.5	30.6	17.6	17.7	19.7	...	11.3	27.8	12.0	...	...	...	142.90
	2.5	2.3	1.0	2.2	1.4	1.8	1.0	...	2.2	1.5	0.9	...	...	...	11.40
20	...	...	8.1	25.4	14.6	...	...	...	11.6	29.1	11.6	...	...	...	...
	...	...	1.2	2.5	0.5	...	...	...	1.3	1.1	1.3	...	...	...	...
Weather-O-Meter exposure															
50 h	20.9	18.1	14.4	...	25.9	33.6	31.1	40.1	24.5	62.3	26.7	26.0	14.0	291.2	...
	10.4	0.9	...	...	2.3	2.5	3.2	3.4	...	1.0	1.1	3.7	0.4	4.1	...
75	...	...	6.5	...	...	...	...	36.8	21.5	...	...	...	...	...	...
	...	...	...	...	...	...	...	...	2.5	...	...	...	...	...	...
100	16.4	16.6	6.1	...	23.5	31.5	26.4	37.0	...	57.5	24.0	22.6	13.2	309.1	129.10
	1.4	0.3	...	...	...	3.9	2.6	1.4	...	1.7	1.0	...	0.3	...	5.00
125	...	...	6.5	...	21.3	...	...	...	...	...	...	...	...	...	...
	...	...	...	...	1.3	...	...	...	...	...	...	...	...	...	...
150	12.9	12.8	5.4	37.4	...	26.8	24.3	...	19.2	53.5	...	22.8	12.1	274.8	...
	0.8	0.4	...	2.0	...	2.8	2.8	...	3.3	6.8	...	0.6	...	7.0	...
175	...	...	...	...	...	...	...	...	16.8	...	...	...	...	...	...
	...	...	...	...	...	...	...	...	2.7	...	...	...	...	...	...
200	12.6	12.1	7.5	35.6	20.7	21.0	27.1	...	...	45.5	...	21.9	11.3	260.3	149.40
	0.7	0.7	0.4	1.0	1.8	1.6	...	...	...	2.2	...	...	0.8	11.9	7.00
225	...	...	...	...	...	...	...	...	16.3	...	...	...	...	...	127.90
	...	...	...	...	...	...	...	...	0.7	...	...	...	...	...	13.00
250	...	...	...	...	...	24.4	24.8	...	16.3	...	...	...	...	216.2	...
	...	...	...	...	...	...	...	...	...	...	...	...	...	26.8	...
275	10.8	10.3	...	32.2	17.1	21.0	19.9	...	12.3	38.6	15.7	...	...	...	147.10
	0.9	0.8	...	0.7	0.9	...	...	...	2.1	1.8	1.0	...	...	...	3.80
300	9.5	9.2	4.1	...	...	23.2	20.6	...	...	35.8	20.0	16.6	10.6	156.4	...
	0.4	0.1	0.1	...	...	0.3	...	...	...	1.0	0.7	0.2	...	47.1	...
350	...	...	...	31.9	16.1	22.1	17.9	...	8.5	37.1	15.9	14.0	8.7	...	...
	...	...	...	0.8	0.9	1.2	...	...	...	2.0	0.9	0.3	0.8	...	...
375	...	...	...	30.7	15.7	...	...	12.7	...	...	...	...	...	...	...
	...	...	...	1.0	...	...	...	...	...	...	...	...	...	...	...
400	9.4	8.5	...	28.2	13.4	21.6	13.6	...	...	34.1	16.9	...	...	...	158.40
	0.5	0.6	...	1.6	0.8	1.4	...	...	...	1.5	0.4	...	...	...	5.60

Number listed below the mean value is the standard deviation.

2. Loss in tensile properties from outdoor exposure of blotting paper and plastic reference samples



3. Typical plots of log(tensile index) vs. duration of outdoor exposure for selected samples. (The curves are vertically displaced by a constant A for clarity. A = 0 for blotting paper. A = -2 for milk carton. A = 20 for plain card stock. A = 20 for frozen food packages.)



Determination of sample pH

A 1.00-g sample of paperboard was cut in approximately 1/2-cm squares and placed in 70 mL of distilled water. After maceration and after allowing the sample to stand covered for 72 h, we measured the pH of the water. The test was carried out generally according to T 410 om-88, but a longer period of extraction was used to ensure complete removal of acidic compounds from coated and laminated paperboard.

Results and discussion

Effects of weathering on changes in tensile index

Outdoor exposure involves diurnal irradiation with sunlight, cyclic temperature changes, and intermittent soaking from rain and presents a harsh environment for paperboard. Photodegradation, physical deterioration from repeated swellings and drying, slight hydrolysis, and even some biodegradation may have occurred concurrently in the exposed samples. Most of the breakdown, however, may be attributed to photodegradation processes. Pulp itself absorbs in several regions of the sunlight spectrum. In the case of packaging materials, which are exposed to light on the outer surface of the package, the surface treatment and pigments may cause further absorption of sunlight.

In addition to being exposed outdoors, samples were also exposed to a filtered xenon source in a Weather-O-Meter, closely simulating the spectral characteristics of direct sunlight. Exposures were carried out for up to 400 h, under conditions as already specified.

As the data in **Table II** show, the loss in tensile strength is a consequence of both exposure to an outdoor environment and exposure in the Weather-O-Meter. With most paperboard materials tested, a change in the tensile index was observed within a single week of outdoor exposure. At the end of a 20-week period, all materials tested showed extensive losses in tensile strength, with values for most samples varying between those obtained for the plastic and blotting paper controls.

Figure 2 shows changes in tensile strength with exposure for the two types of control samples. The blotting paper control lost over 80% of its strength and was embrittled in about 16 weeks outdoors to such an extent as to preclude tensile testing. Polyethylene control samples also photodegraded, loosing about 10% of the initial tensile strength within the 18 weeks of outdoor exposure. For the plastics, however, the ultimate extension, or the elongation at break, is regarded as a better measure of the extent of degradation (*30, 35*). The HDPE and LDPE controls lost 43% and 85%, respectively, of their original ultimate extension during an exposure period of 12 weeks. Tensile stress for plastics is defined as the force per unit of undeformed cross-sectional area, whereas the tensile stress for paper is defined as the force per unit width [primarily because of difficulties in accurately measuring the thickness of paper (*36*)]. Therefore, a direct comparison of the tensile strengths for the two materials is not valid.

In the Weather-O-Meter exposure, the loss of tensile index of paperboard (and the ultimate extension in the case of plastics) occurred at a faster rate than for outdoor exposure. This result is not surprising because the exposure cycle entailed continuous exposure to

III. The values of "a" and "b" parameters for paperboard samples exposed outdoors and in Weather-O-Meter

Code	Sample type	Outdoor exposure			Weather-O-Meter exposure		
		a	$-b \times 10^3$	*r*	*a*	$-b \times 10^3$	*r*
A	Cold beverage cups	25.3	2.84	0.94	23.8	1.22	0.93
B	Hot beverage cups	21.2	1.80	0.85	20.2	1.04	0.98
C	Milk cartons	34.7	3.44	0.95	15.8	2.26	0.76
D	Plain paperboard						
	MD	50.7	1.41	0.96	47.0	0.53	0.98
	CD	28.8	1.38	0.83	28.3	0.75	0.99
E	Paper plate	38.4	1.88	0.96	37.9	0.26	0.95
F	Coated paper plate	36.7	1.71	0.92	33.5	0.57	0.89
G	Frozen food carton	48.4	3.05	0.93	46.8	1.47	0.99
	CD	25.0	1.75	0.95	27.7	1.23	0.95
H	Soft drink carton						
	MD	67.9	2.18	0.96	67.0	0.83	0.99
	CD	30.3	2.16	0.96	28.8	0.68	0.93
K	Blotting paper						
	MD	24.1	3.37	0.89	30.9	0.93	0.97
	CD	15.4	4.79	0.92	16.5	0.77	0.95

Note: Units of b are $weeks^{-1}$ and $hours^{-1}$ for outdoor and Weather-O-Meter exposures respectively.

light and included the exposure of water-sprayed paperboard to light at a temperature of 70°C. Factors such as high temperature, high humidity, and exposure to light are known to accelerate the deterioration of wood and paper (*37*). The tensile index of the blotting paper was reduced by 57% in 350 h of exposure. The LDPE material was embrittled and too weak for testing at 300 h of Weather-O-Meter exposure.

For the printed paperboard materials, the exposure was carried out with the printed surface facing sunlight (or the xenon light source in the Weather-O-Meter). The surface coloration of printed packaging progressively faded during exposure, resulting sometimes in changes in hue brought about by the preferential fading of some of the components in the color formulations. It is reasonable to expect that fading has some effect on resistance to weathering. An alteration of light absorption characteristics and the greater buildup of heat for the darker materials exposed to sunlight may enhance the photodegradation process. The phenomenon is well documented in the case of outdoor weathering of colored plastics (*38*). However, there was no clear relationship between surface color and the resistance to weathering in the paperboard materials tested.

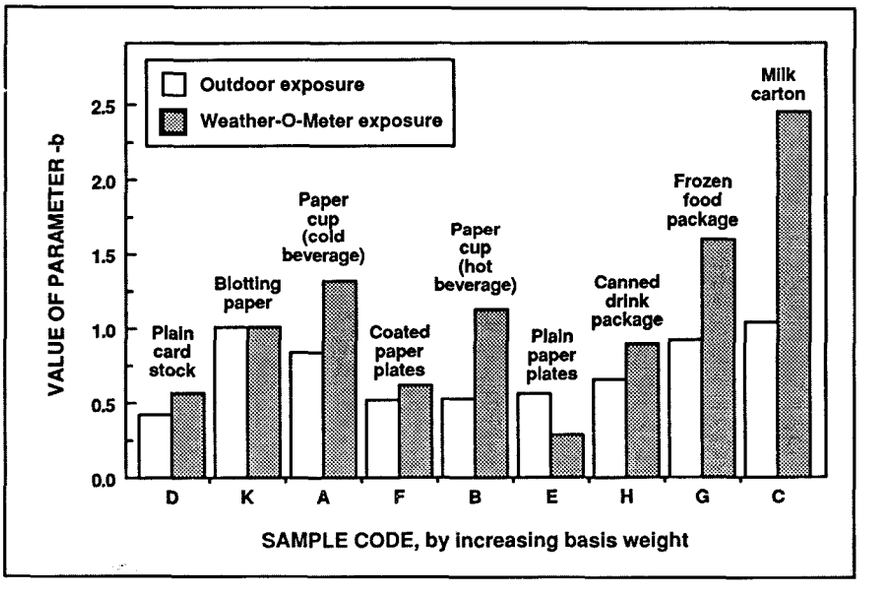
Data in Table II yielded tensile index vs. exposure time curves concave to the horizontal axis, as might be expected (*39*). Assuming that the loss in strength is directly related to chemical changes in the pulp, a kinetic approach might be adopted (*40*) for the interpretation of the data. The change in tensile index can be described by an empirical equation:

$$\text{Tensile index} = a + 10^{-b\,(\text{duration})} \qquad (1)$$

Figure 3 shows typical plots obtained with selected paperboard samples for outdoor exposure. As might be expected, the values of tensile index, and hence the gradient of the plot, were different when the testing was carried out in the machine direction (MD) instead of the cross direction (CD). (In the case of samples such as paper plates, the two directions cannot be readily distinguished.)

Table III lists the coefficients a and b from Eq. 1, as well as the correlation coefficient obtained for data on different types of paperboard. The moderate-to-high correlation coefficients associated with the fit of data to the equation in both outdoor and

4. Values of parameter b for different samples arranged in increasing order of basis weight



laboratory experiments suggest that the underlying mechanisms of disintegration are similar for the two exposures. Though the two sets of data yielded numerical values of the gradient b that were close to each other, the time scales and the exposure conditions were very different for the two exposure experiments. The relative values of b obtained in the outdoor experiment correlated well with those from the laboratory exposure, with a correlation coefficient of 0.76.

The gradient b of the plots given in Table III is a direct measure of the rate at which the tensile index of the paperboard material decreases with exposure time. This parameter allows us to rank the different paperboard materials tested as to their susceptibility to disintegration under the test conditions. In descending order of susceptibility, these rankings are:

- Outdoor exposure: C, K, G, A, H, E, B, F, D
- Weather-O-Meter: C, G, A, B, K, H, F, E, D.

The rankings obtained are not identical but there is some similarity. Samples C, G, and A consist of paperboard coated on both surfaces (plastic or wax). In both exposures, these samples have a high ranking, which indicates a fast breakdown. Samples D, E, and F are ranked lower in both exposures. Sample B (hot beverage cup) and Sample K (blotting paper) show a disparity in ranking that is difficult to explain. **Figure 4** is a plot of the values of b relative to that for the blotting paper control for different types of paperboard ordered according to increasing grammage. As the figure shows, the relative susceptibility of different types of paperboard to loss of strength is similar for outdoor and Weather-O-Meter exposures.

An exclusively light-induced degradation, being a predominantly surface reaction (*41–43*), might be expected to produce behavior dependent on grammage, with the thicker board being least affected by exposure. However, this result is not observed in Fig. 3. In fact, the trend is the reverse. It seems that the samples of higher basis weight lose strength faster than paperboard of lower basis weight.

Influence of coatings and laminations

The interesting unexpected feature of the data is the apparent high susceptibility of plastic and wax-coated paperboard materials to disintegration under outdoor exposure. Of particular interest is the milk carton (Sample C), coated paper cups (Sample B), and the frozen food carton (Sample G), which show particularly high rates of breakdown. The same items showed the highest activity in the Weather-O-Meter exposure as well. Surprisingly, some of these products were found to weaken faster than even the blotting paper reference sample. This interesting behavior might be attributed to the coating on paper rather than to differences in furnish characteristics.

One possibility is that the thermoplastic lamination undergoes photodegradation to produce chromophores such as unsaturated groups, carbonyl groups, and initiating species such as hydroperoxides during early exposure. Auto-oxidation of polyethylene is known (*44, 45*) to yield such functionalities, which provide a source of free radicals that can readily diffuse into the paperboard and initiate photo-oxidative reactions in a lignocellulosic substrate. The plastic lamination may thus enhance the photodegradation of the pulp.

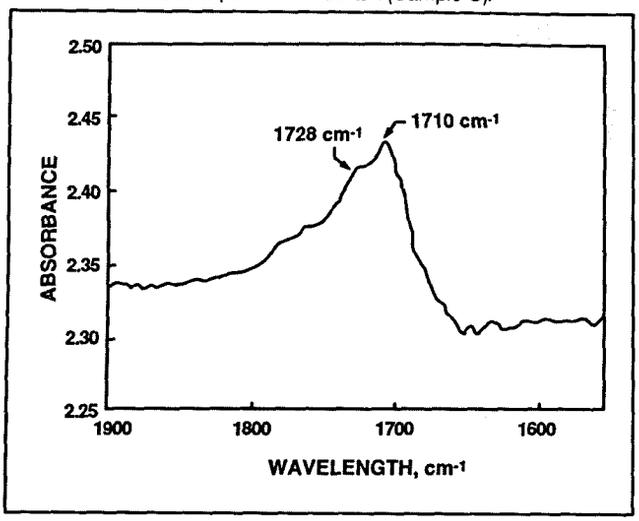
A sample of milk carton material exposed outdoors for eight weeks was studied to determine the extent of degradation of the polyethylene film. Careful soaking in water followed by delamination and cleaning allowed the plastic film to be separated from the paperboard for examination by Fourier transform infrared spectroscopy (FTIR). The reflectance FTIR spectrum of film from surfaces exposed to light showed a strong band at 1750 cm^{-1} characteristic of carbonyl absorption, while the film from the reverse side of the same paperboard sample (the surface not exposed to light) did not show such an absorption band. A difference spectrum obtained by subtracting the reflectance spectra, shown in **Fig. 5**, illustrates this absorption band. Carbonyl functionality is an efficient chromophore-absorbing functionality in the ultraviolet region of the spectrum, and it may initiate the photodegradation of the lignocellulose. [In fact, the introduction of carbonyl groups into the macromolecular main-chain of low-density polyethylene is a primary technique used in the design of rapidly photodegradable polyethylene used in products such as six-pack rings (*46*).]

It follows that in paperboard coated on only a single side with a plastic film, such as the hot beverage cup (Sample B), the rate of photodegradation will depend on the surface exposed to light. This hypothesis was studied in a laboratory experiment in which strips of paperboard from the hot beverage cups (Sample B) were exposed to a filtered xenon light source (radiation which closely simulates sunlight), for a period of 50 h with samples maintained at ambient temperature. The tensile properties of strips exposed with plastic-coated surface facing light indicated relatively more degradation than those exposed with an uncoated surface facing light. The latter samples were stronger by about 12%, and they showed a 27% higher strain at break and a 42% higher value for tensile energy absorption, even at this short duration of exposure. The observation is consistent with the possibility of plastic coating enhancing the photodegradation of the coated paperboard.

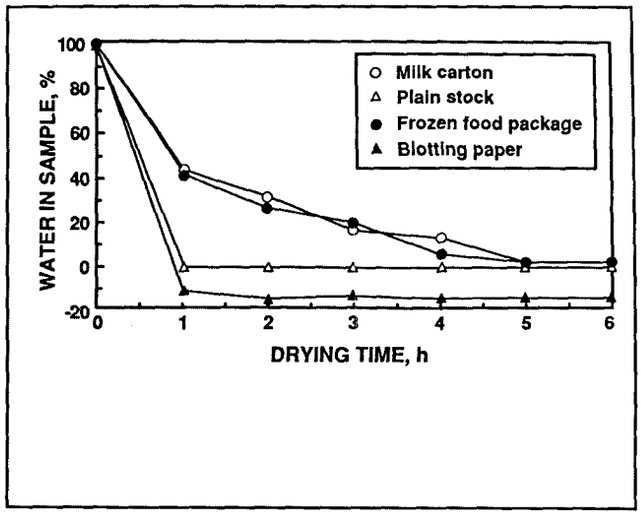
Transparent polymer coatings allow the passage of light, moisture, and oxygen into the bulk of the paperboard. However, once soaked by water on exposure to rain (or the water spray in the case of the Weather-O-Meter), the coating would impede the drying process, maintaining a high humidity level within the board for a longer period of time, compared to uncoated board of similar basis weight. The combination of trapped moisture with light irradiation and heat exposure is possibly another contributing cause of the higher susceptibility of coated paperboard to weathering. Peroxides and other initiating species formed during degradation tend to be more mobile when the paper contains substantial amounts of moisture. The moisture may facilitate faster, more extensive propagation of these radical species throughout the bulk of the substrate. Hon found that higher moisture contents of < 5–7% in cellulose increase the formation of free radicals on exposure to light (*47*).

The slower drying rate of the plastic-laminated paperboard samples was demonstrated by measuring the weight loss of selected samples of

5. A part of the difference spectrum showing a carbonyl absorption band. Difference between reflectance FTIR spectra of polymer coating from two surfaces of exposed milk carton (Sample C).



6. Drying curves for soaked paperboard showing slower rates of drying at 50°C for laminated paperboard types (milk carton and frozen food package)



paperboard soaked in water at ambient temperature for 48 h and allowed to dry at 50 ± 1° C in an air oven. The data showed that the paperboard samples fall into two classes: those that dried completely (attained constant weight) in 1 h of drying, and those that required 4-6 h of oven drying to reach constant weight. The rates of drying obtained under outdoor conditions will be much slower as a result of lower ambient temperatures and higher humidity. Paper milk cartons and frozen food containers were in the second class of paperboard samples, and this factor might have also caused the faster disintegration of the samples. **Figure 6** illustrates the data on the release of water by different saturated paperboard samples.

So far, we have assumed that the total change in tensile properties on exposure to light and humidity is due to chemical changes taking place in the paper. However, at least a part of the observed loss in strength of paperboard might be attributable to physical consequences of repeated wetting and drying cycles encountered as a result of intermittent rain outdoors or cyclic water spray in the Weather-O-Meter. Wetting swells the lignocellulosic fibers and extracts any water-soluble photodegradation products in the samples. Repeated swelling and deswelling of the fibers may play a role in bringing about the changes in strength obtained on exposure. It is important to establish at least the magnitude of this effect.

IV. Loss in tensile index from cyclic wetting and drying, %

	Loss in tensile index by the number of cycles, %					
	1	*2*	*3*	*4*	*5*	*6*
Plain board	1.0	3.2	5.4	6.4	7.3	8.5
Milk carton						
MD	0.4	1.4	2.0	3.5	4.5	4.5
CD	0.0	1.7	2.7	3.1	5.1	6.0
Blotting paper						
MD	0.6	1.8	2.1	3.9	5.1	6.0
CD	2.2	3.2	3.2	4.3	5.9	7.5

Table IV shows the change in tensile index resulting merely from cyclic wetting (1 h under ambient conditions) and drying (4 h at 50°C) of paper milk cartons, plain paperboard, and blotting paper standard. Samples were dried at a temperature higher than that generally associated with outdoor exposure. Though somewhat harsher than conditions normally encountered outdoors, the test conditions for outdoor exposure were comparable with test conditions in the Weather-O-Meter exposure. Data relating to six cycles of wetting and drying show that less than 9% of the initial tensile index was reduced. The highest loss of 8.5% was obtained in the case of the milk carton material. Weight loss measurements on the samples (data not shown in the table) showed a 3-6% loss in weight from extractable losses. Thermal cycling of the moist samples might have generated soluble degradation products such as saccharides at a rate higher than that obtained under normal outdoor conditions, resulting in exaggerated weight losses. The determination of weight loss in the samples exposed outdoors was not practical because of errors arising from surface unevenness, fungal growths, and coating disruptions.

The actual number of wet-dry cycles the paperboard was subjected to during the outdoor exposure is not known, but we suspect that it was greater than six cycles.

Changes in pH as an indicator of degradation

Early photodegradation of paper is also marked by the generation of numerous acidic reaction products. In fact, it is reasonable to expect sharp changes in pH to precede any observable changes in the mechanical strength of paper undergoing degradation. These changes in strength will be apparent only after extensive breakdown of the fiber structure,

V. pH of paper products exposed in the Weather-O-Meter

Code	Product	Exposure time, h 0	50	100	150	200	250	275	300	350	400
	Paper cups										
A	Cold beverage	5.90	...	5.65	...	5.27	...	5.08	...	5.47	5.42
B	Hot beverage	5.73	...	5.17	5.55	...	...	5.58	...	...	5.39
C	Milk cartons (1/2 gallon)	7.09	7.07	6.85	5.91	6.57	...	...	4.46	...	...
D	Plain card stock	5.52	...	5.68	...	5.65	5.36	...	...	5.45	5.46
E	Clay coated paper plates	6.85	6.02	...	6.32	5.11	...	...	5.20	...	5.98
F	Coated paper plates	6.80	6.76	...	...	5.41	5.59	...	5.60	...	5.96
G	Frozen food package	5.34	5.05	...	4.78	5.01	4.80	...	...	5.53	...
H	Canned drink cartons	5.68	...	5.12	4.89	4.58	...	...	4.70	...	4.89
K	Blotting paper	6.44	5.10	5.12	...	4.74	...	...	5.33	5.25	...

whereas the first stages of chemical breakdown will lead to decreased pH.

We studied this change in pH using samples exposed in the Weather-O-Meter, where the exposure was better defined than in the samples exposed outdoors. Paperboard exposed outdoors may show erratic changes in pH brought about by the extraction by rain water of the low-molecular-weight degradation products such as acids. This effect is not expected in Weather-O-Meter exposure, in which a fine water spray was used. **Table V** gives the variation in pH for paperboard samples at selected exposure times.

In general, the data show that measurable changes in pH occurred early during weathering and can therefore be a useful early indicator of degradation. The change is often not monotonic, but the pH decreases during early weathering to reach a plateau, or it may even increase after the plateau after longer durations of exposure. This increase in pH is difficult to explain. Secondary reactions of the products of degradation are probably responsible.

Coated paperboard seems to yield a smaller decrease in pH during early weathering. This finding may be attributable to the restriction imposed by the laminate film in checking the diffusion of soluble acidic components out of the paperboard. Cold water extraction of paperboard for determining pH is diffusion controlled, and the data, especially for the thicker paperboard, may reflect the ease of diffusion of acidic components into water rather than the acidity of the matrix. After the coating or lamination has been degraded enough to allow the acidic materials to be extracted, the pH does drop sharply.

The preliminary data obtained here, however, confirm that a significant drop in acidity is a consequence of weathering and that it occurs in a much shorter time than do changes in mechanical properties.

Conclusions

The experimental results illustrate that paperboard packaging materials, even those which are processed, printed, and laminated, undergo considerable disintegration during outdoor exposure. The susceptibility of the laminated board to weathering is particularly surprising and interesting because these materials tend to be used as high-grammage paperboard and are generally perceived as being more difficult to disintegrate. The findings are relevant to the issue of urban litter and its degradability.

To translate these results into practical terms, the strength loss data need to be compared with the time scales and conditions of exposure that litter streams undergo. At least in some instances, the litter is exposed to sunlight only for a limited time and is then placed in an environment that is more conducive to biologically mediated breakdown. Even in these instances, the prior photodegradation, though limited, is likely to assist subsequent biological degradation.

This outcome is a common observation in the case of synthetic polymers and is likely to be so for lignocellulosic substrates as well, at the very least to the extent that the photodegradation changes the accessibility of the fibers to water. An increased polarity of the paper resulting from the presence of oxygenated functional groups and the availability of saccharide nutrients as degradation products may encourage subsequent biodegradation under appropriate biotic conditions.

This study establishes merely that a key mechanical property (tensile strength) of the paperboard changes on exposure to light and humidity under relevant exposure conditions. Neither the nature nor the extent of true chemical degradation of the pulp due to exposure has been studied. Demonstrating change in a mechanical property is not sufficient to establish degradation at a molecular level: it is also necessary to show an associated chemical process leading to the change in the property. Further work is needed to quantitatively relate the extent of chemical breakdown to loss in mechanical properties and to find a chemical explanation as to the ranking of the various samples.□

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