The Aging of Recycled Fibers

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by

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ABSTRACT

The object of this thesis is to study the aging of recycled paper, focusing on strength and optical properties. To observe the changes in these properties, the following experimental procedure was used. 100% softwood fibers were pulped, made into handsheets, tested, artificially aged, again tested, repulped and bleached before being made into handsheets once again. Because of cross-linking due to heating, the aging strength losses were masked.

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INTRODUCTION

While the aging of paper has been extensively studied, no studies have been made of the effect of recycling on aging. This is important becuase most papers are naturally aged for some time before they are recycled. Therefore, the purpose of this study is to study the aging of recycled fibers by following strength and color properties.

THEORY

The aging of paper depends on many of the physical conditions that it is subjected to. Some of these conditions will be discussed in this paper.

While a pH of 7 is most suitable for the preservation of paper (14), loss of permanence correlates with a decrease in paper pH (12). Paper, like most other substances, is highly degraded by acid. As the acid in the system increases, more damage is done. Therefore as the pH decreases, the strength of the cellulose and hemicellulose decreases.

The main part of cellulose is crystalline, and nearly all the hemicelluloses are amorphous. Partly for this reason, hemicelluloses hydrolyze much faster than celluloses, introducing acidic groups. These acidic groups tend to lower the pH still further and contribute to the premature breakdown of the more resistant carbohydrates (12).

Along with this acid hydrolysis of the hemicelluloses, the cellulose molecules are being oxidized and the glycosidic linkages broken. This oxidation decreases the size of the molecule (or chain) and decreases the mechanical strength (14).

The bleaching process also introduces acidic groups, which help to reduce the mechanical strength (12). Sodium hypochlorite bleach (NaClO) is not very stable and can easily decompose by either increasing concentration or temperature or by decreasing alkalinity. Despite careful control of these variables, some NaClO will react to form HClO on the cellulose chains. The resultant HClO will follow the following equation to give strong

acid groups which will degrade the pulp as mentioned earlier:

$2HClO \longrightarrow 2HCL + O_2$ (16)

Not only are the hemicelluloses and the celluloses attacked, but under accelerated aging conditions either the lignin or the extractives, or both, after bleaching give off hydrogen chloride, which causes color reversion and a loss of mechanical properties.

Also additives like optical brighteners and some pigments promote chemical degradation upon aging (12).

For these reasons the method of manufacture, the chemical additives, and the storage methods all help determine the rate of aging.

AGING METHODS USED

There are many methods for accelerated aging in literature. The three basic ones are: 1. dry oven aging, 2. moisture controlled aging, and 3. tube aging.

Most literature supports the dry aging methods (3-8, 10, 15); in fact, the TAPPI standards (1), ASTM (12), and the National Bureau of Standards (7, 11) involve only dry heat. This method calls for forced circulation of dry air during aging.

Aging in the presence of moisture gives a better simulation of natural aging since paper is not normally aged in the absence of humidity. It also allows for faster aging (12). This type of aging requires extremely accurate control of moisture and temperature since even a few degrees variance in temperature can greatly alter the physical properties during aging. Because of the difficulty in maintaining such close control necessary in order to get accurate results, this method will not be used in this study.

The tube method of accelerated aging is good in that it allows a large number of samples to be aged at once, and it retains the humidity during aging (2, 14). The main problem is that the air is not circulated and therefore any gases given off are trapped in with the sample. According to Philip Luner (12), during the accelerated aging process, chlorine in the form of hydrogen chloride is given off by either the lignin or extractives. Carbon dioxide, CO_2, is released from the cellulose and is also trapped in the tube (9). No studies were found during the literature search which would indicate any study of these gases and their effect on the samples. Mainly for this reason, the tube method was discarded in favor of the standard dry oven aging method.

Because it is the accepted method, because it has good agreement with naturally aged physical test values (8), especially in the range to be used, and because of its ease of operation and temperature control, the dry oven aging method will be used.

PHYSICAL TESTS

According to Robertson (15) the tests most commonly used, listed in order of decreasing sensitivity to the aging mechanism, are: 1. fold, 2. tear, 3. breaking length, 4. burst or mullen, 5. breaking load, 6. elasticity, and 7. brightness. The tests used in this study are fold, burst, zero span tensile, tensile, brightness, and opacity.

FOLD TESTING

As is often true, the most sensitive tests are usually the most variable and controversial; the fold test is no exception (12,13). Because of this variability, a correction factor of 1.75% of the folding endurance is suggested for each gram that the basis weight differs from the standard (TAPPI, T205),(13). Since the folding endurance of naturally and artificially aged paper decreases much more rapidly than the tensile strength of the paper, it is fairly obvious that the loss in fold strength is due to a change occurring in the fiber structure (5).

Many variations of the TAPPI folding method are used when evaluating aging. Some (3, 10) use a 1/2 kg. load to give a better representation of the fold since folds below **ten** are suspect. Others (2, 13, 15) use a small fan to remove heat from the folding area. This has recently been accepted as the new TAPPI standard. Still another (7) suggests the use of a modified tester which only folds the sample 90° instead of the usual 270°. This is done to permit greater discrimination of the results on highly aged paper.

To reduce experimental error, the following recommendations

have been made (13):

1. Load. The load should not be set by means of the graduated scale and spring pointer as these are only used to show whether gross mistakes in loading have occurred. The load should be set using a dead weight and should be between 0.4 and 1.9 kg.

2. Plunger Friction. This can be reduced by lubricating the plunger and guide with a light mineral oil containing molybdenum disulfide.

3. Alignment. It is very important to put the samples in a vertical position. Non-vertical samples give higher results because the area folded is larger.

4. Orientation. All of the samples tested should have their felt sides against the fixed jaw. This is especially true with thick or highly two-sided paper.

5. Humidity. The relative humidity must lie within 50±2% since the fold test is more sensitive to humidity than temperature.

6. Heat at test site. This heat can be removed by directing a low velocity air stream at the jaws.

7. First Fold. Since the initial fold direction may influence the final test result, the fold tests should be started in the same direction.

There are four basic methods used to determine the loads used. They are: 1. testing all the samples at 1 kg load, 2. testing them at 0.5 kg load, 3. using a computed load to give 300 double folds and, 4. using a load equal to 20% of the tested breaking load (13).

Of these four methods to determine load, the last will be used in this study. It allows stronger unaged paper to be run at a higher load than the aged samples without jeopardizing their compatability (15).

TENSILE TESTING

Tensile failure can be promoted by one of two mechanisms (12). One is initiated by the failure of a fiber stressed beyond its breaking point. When this fiber fails, its load is immediately transferred to the fibers around it. The shock of the added load stresses the adjacent fibers beyond their breaking point, which eventually leads to failure of the sheet.

The other mechanism involves bond failure. This type of failure may either lead to bond or fiber failure (12).

BURSTING STRENGTH

The bursting strength or mullen has results paralleling the tensile test. This test shows a strength loss due to aging.

ZERO-SPAN TENSILE TESTING

Zero-span strength decreases more rapidly than the 4-inch span tensile because the cross linking which occurs with the 4-inch span tensile partially makes up for the loss of fiber strenght (15).

EXPERIMENTAL PROCEDURE

100% virgin softwood in the form of lap was pulped to a freeness between 300 and 350 in the Valley beater and made into handsheets on the Noble and Wood apparatus. The handsheets were tested for fold, burst, zero span, tensile, brightness, and opacity--then aged and retested. The aging procedure was carried out using dry oven aging at 100° C for 3 hours. Although the standards recommend 72 hours aging at 105°, which is equivalent to 25-28 years of natural aging, Wilson et al (8) have shown that every 12 hours accelerated aging at 100° C is equal to about 4 years natural aging. Three hours aging at 100° C would approximate 1 year of natural aging which is not unreasonable for the time before a paper is recycled.

Once the paper has been tested after aging, it was repulped to a freeness between 300 and 350 and underwent a mild hypochlorite bleaching before being made into handsheets again. The bleaching is 5% based on the oven dry weight of paper.

This entire process of making handsheets, testing, aging, retesting, repulping, and bleaching was carried out three times per run to determine the interaction of recycling and aging. Three such runs were made.

RESULTS

The results of the individual runs are shown in Tables 1, 2, and 3. Table 4 shows the combined result from the three runs.

TABLE 1. RESULTS FROM THE INITIAL RUN

	Aged		Recycled		Aged		Recycled		Aged			
Test	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Fold	405	90.5	334	103	168	80	157	44	32	6	37	11
Brightness	79.0	0.7	77.4	1.1	76.3	0.7	75.4	0.4	67.2	0.6	65.1	1.7
Opacity	68.0	1.6	70.4	2.8	73.5	1.4	73.7	1.0	78.5	1.2	78.0	1.2
Tensile	4.69	0.36	5.14	0.57	4.55	0.24	4.40	0.31	--	--	--	--
Burst	37.3	3.4	37.9	4.3	28.3	2.9	29.2	2.4	--	--	--	--
Zero-span	31.4	2.0	32.3	2.6	31.8	2.1	33.5	2.2	33.5	2.3	34.8	2.2
Basis weight	2.50	0.07	2.50	0.07	2.50	0.08	2.50	0.08	2.50	0.05	2.50	0.05

After the final recycling period, the yield was quite low. For this reason tensile and burst were not run.

TABLE 2. RESULTS FROM RUN NUMBER 2

	Aged		Recycled		Aged		Recycled		Aged			
Test	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Fold	211	79	244	88	68	22	65	25	25	3	28	10
Brightness	77.2	1.3	75.8	0.1	69.8	1.7	68.7	1.1	65.9	1.8	63.4	1.7
Opacity	69.2	1.8	68.7	0.2	72.7	0.9	72.7	0.9	77.4	1.5	76.9	1.8
Tensile	5.04	0.43	5.06	0.33	4.14	0.37	4.34	0.19	3.11	0.32	3.50	0.39
Burst	34.3	3.2	33.7	4.0	24.8	2.2	26.1	2.2	18.2	2.0	21.4	1.9
Zero-span	37.5	2.7	34.2	4.8	33.0	2.2	33.8	2.4	30.3	2.7	31.5	2.8
Basis weight	2.50	0.06	2.50	0.06	2.47	0.07	2.48	0.06	2.52	0.08	2.51	0.09

TABLE 3. RESULTS FROM THE FINAL RUN

Test	Aged Mean	Aged S.D.	Recycled Mean	Recycled S.D.	Aged Mean	Aged S.D.	Recycled Mean	Recycled S.D.	Aged Mean	Aged S.D.	Mean	S.D.
Fold	319	139	242	85	82	40	67	25	39	12	52	18
Brightness	79.9	0.8	78.6	1.3	75.0	1.0	74.2	1.0	68.8	0.8	68.7	1.1
Opacity	69.0	1.5	69.3	1.3	74.4	1.1	73.7	1.0	76.7	1.2	77.7	2.6
Tensile	4.98	0.57	5.42	0.87	3.97	0.40	4.18	0.54	3.66	0.55	4.01	1.12
Burst	35.5	3.8	37.6	10.6	26.3	2.3	27.0	2.1	22.2	4.0	21.8	2.8
Zero-span	36.5	3.8	--	--	--	--	--	--	--	--	--	--
Basis weight	2.50	0.06	2.50	0.06	2.48	0.07	2.48	0.06	2.49	0.07	2.49	0.08

Most of the zero-span tensile strength data for the third run is missing due to a data breakdown in the testing apparatus.

TABLE 4. COMBINED RESULTS OF ALL 3 RUNS

Test		Aged	Recycled	Aged	Recycled	Aged
Fold	311	242	106	96	32	39
Brightness	78.7	77.3	74.5	73.1	67.3	65.7
Opacity	68.7	69.5	73.5	73.4	77.5	77.5
Tensile	4.90	5.21	4.22	4.31	3.39	3.76
Burst	35.7	36.4	26.5	27.4	20.2	21.6
Zero-span	35.1	33.3	32.4	33.7	31.9	33.2
Basis wt.	2.50	2.50	2.48	2.48	2.50	2.50

DISCUSSION OF RESULTS

BRIGHTNESS AND OPACITY

Figure 1 shows the trends observed by brightness and opacity. The opacity does not vary appreciably during aging, but increases steadily upon recycling due to the more refined fibers.

Brightness is seen to decrease not only upon aging, but also upon recycling. This decrease during recycling despite a 5% hypochlorite bleach sequence, can only be explained by contaminants in the water used, such as iron.

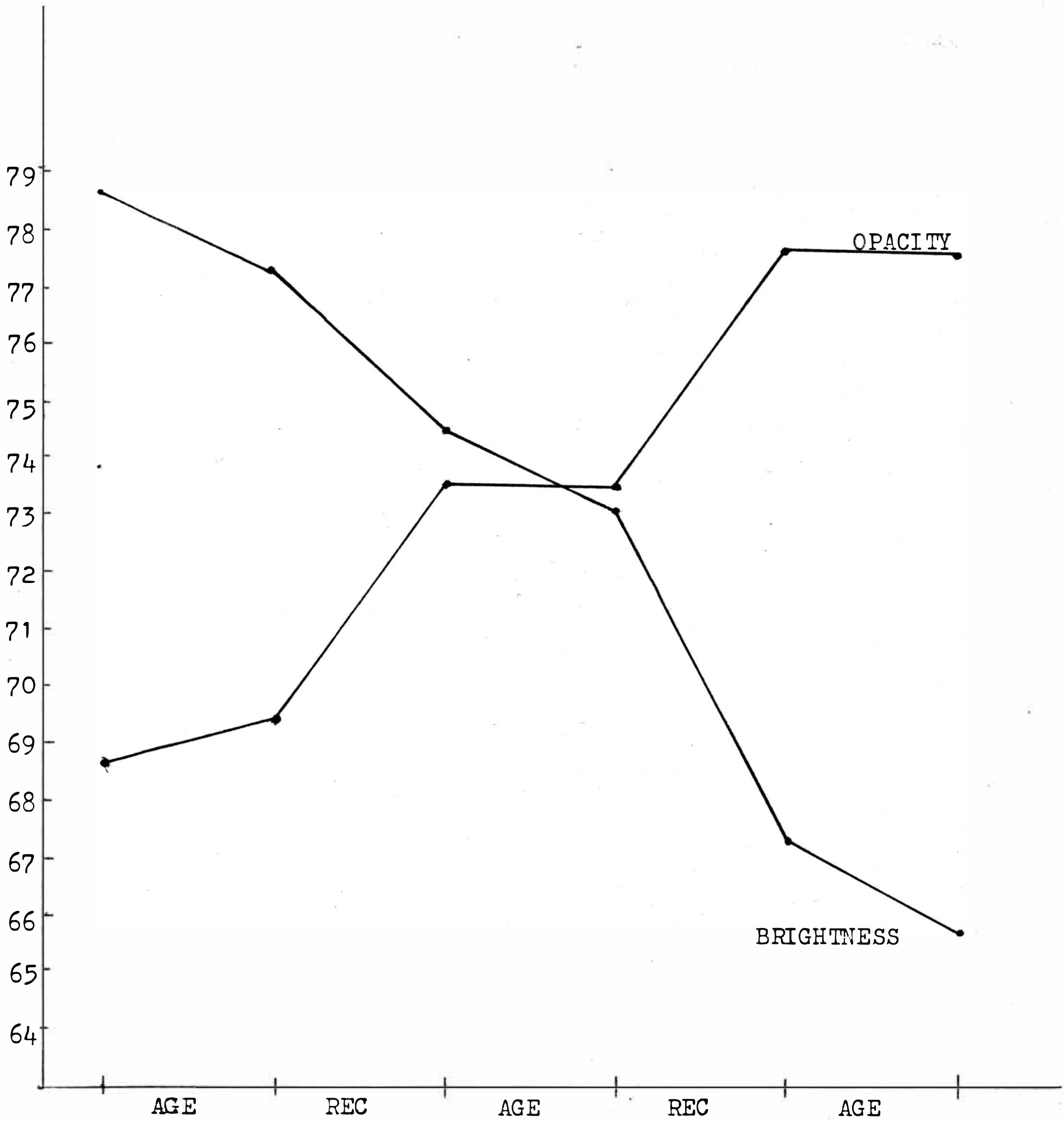
TENSILE

The tensile strength (Figure 2) decreased by fairly constant amounts during recycling and increased by fairly constant amounts during aging, instead of decreasing as was expected.

It appears that aging for such short periods of time (3 hours) at accelerated temperatures (100° C) strengthened the paper instead of weakening it. The only logical conclusion appears to be that the samples crosslinked within themselves when they were heated, giving higher strength characterisitics. This crosslinking between the fibers completely overshadows any strength loss due to aging.

FOLD

As seen on Figure 2 the fold test decreased nicely during recycling. The aging results, however, were quite interesting. During the first aging, the fold dropped by about 70 folds or 22%. After the second aging period, it dropped by only 10 folds or approximately 9.4%. The final aging time, the number of folds increased by 7 or about 22%.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OPACITY
BRIGHTNESS
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AGE

FIGURE 1

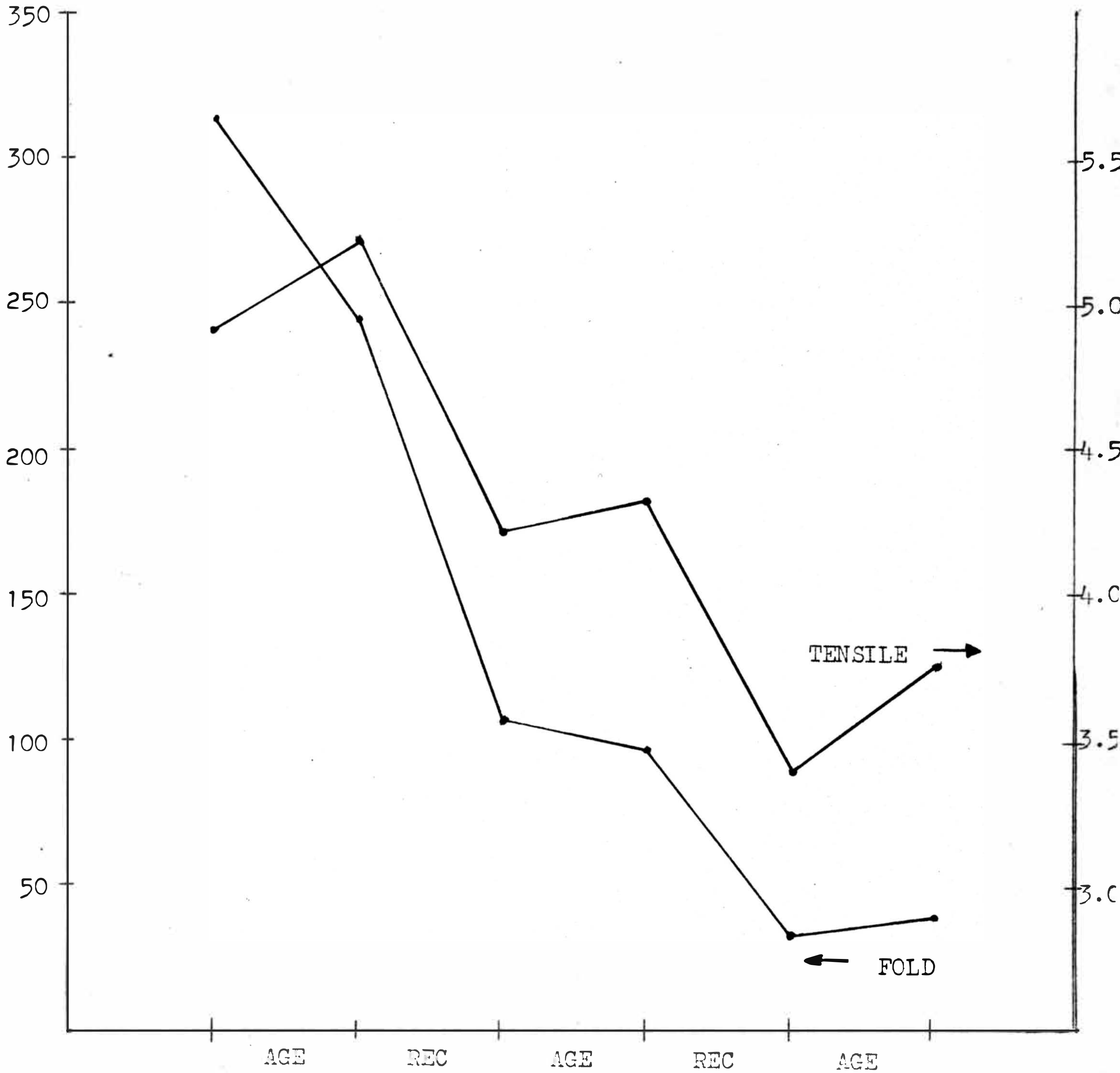


FIGURE 2

This decrease in the loss of fold strength can be explained by crosslinking within the sample. Because folding endurance is the most sensitive test, a decrease in strength is noticed upon aging. The more the sample is heated, the more effect the crosslinking has upon the strength loss until finally it overshadows the strength loss during aging completely.

BURST

The mullen or bursting strength results (Figure 3) were very similar to those of the tensile test. A large strength loss was observed during each recycling, and small strength gains were observed during aging. Again this strength gain would probably be due to crosslinking.

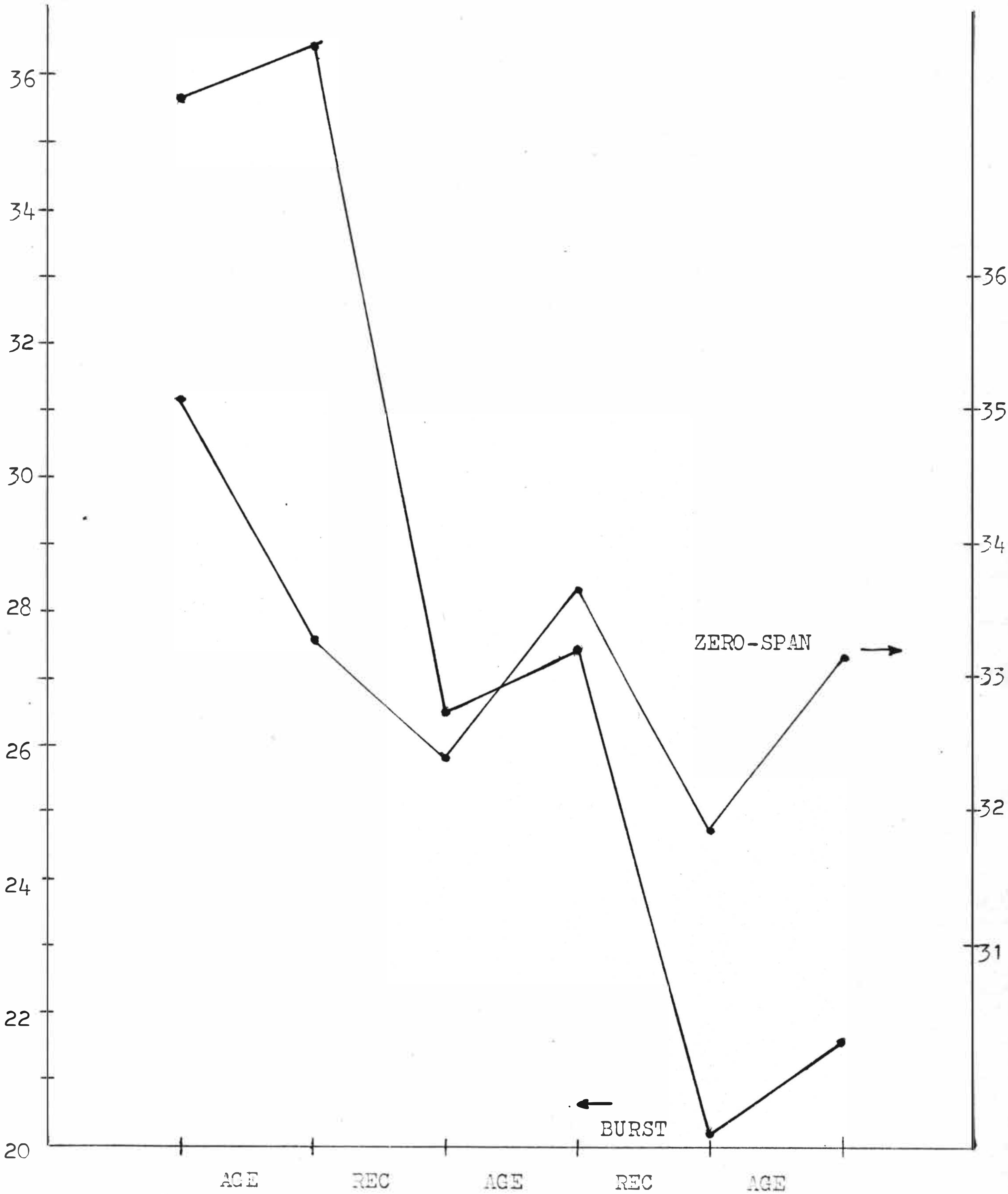
ZERO-SPAN TENSILE

The zero-span tensile results (Figure 3) do not show a very evident trend. The strength losses due to recycling are present, but the aging results are quite different. The change due to aging appears to be about the same magnitude but decreases during the first aging period and increases during the others. The increasing strength is due to crosslinking upon heating, but one would not expect the magnitudes of these changes to be so similar. This data is somewhat uncertain as to its accurateness since several samples could not be tested.

STRENGTH TESTS

Besides the aging effects on the various strength tests, recycling caused a major decrease in the strength. There are several reasons why this could have occured, discussed below.

1. Bleaching. Even a mild bleaching can cause degradation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ZERO-SPAN
BURST
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REC
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REC
AGE

FIGURE 3

to the fibers, reducing their strength and therefore the strength of the paper. Since each time the paper was recycled it was bleached, the resulting loss in strength can be due, at least in part, to the bleaching that occurred.

2. Broken bonds. The fibers in the handsheet were tightly bonded together. When the handsheets were pulped many of these bonds were completely destroyed. This reduced somewhat the capability of the fibers to form new strong bonds as they were weakened when the bonds were broken.

3. Paper recycled. In order to have a yield which would allow for recycling, the scraps from the tests and the trimmings from the handsheets were repulped along with handsheets not meeting basis weight requirements. Because of the trimmings and scraps, many fibers were cut giving more fines when repulped and weaker fibers available for bonding.

4. Increased number of fines. Each time the handsheets and scraps were repulped there were a greater number of fines present. These extra fines lowered the freeness which was used to indicate the amount of refining done. With extra fines, more refining appeared to have been done on the fibers than actually occurred and with this lower refining, the strength decreased.

All of the above explanations for strength loss upon recycling are quite possible and I believe they were each responsible to some extent for the large strength loss observed.

CONCLUSIONS

It seems quite evident from the fold test that aging reduces strength; however, due to the short aging periods the strength loss for the majority of tests was not obvious since it was masked by the crosslinking due to heating.

The optical properties were as expected during aging; the brightness was steadily reduced and the opacity remained virtually unchanged.

RECOMMENDATIONS

The main recommendation to be made here is that much more research be done in this field.

Other recommendations are:

1. The water used should be fairly free from iron as this clouds the brightness results and interferes with the bleaching to some extent.

2. Blanks be run with each trial showing the result due to additional aging without recycling.

3. The tear test should also be run.

Once again more study needs to be done before we can get a clearer picture of aging and the aging of recycled fibers.

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