THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

OZONATION OF RECYCLED FIBER: PROCESS AND FIBER VARIABLES

Project 2697-53

Report Two

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

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SUMMARY

The research in Progress Report One indicated ozonation increases the strength potential of recycled fiber without significant loss of productivity or the introduction of pollution problems. Based on those encouraging results further work has been carried out to optimize the O_3 treatment in terms of fiber and process variables. The results of the research are briefly summarized below.

1. Six commercial OCC pulps were evaluated for comparison with the Institute model stock. The commercial pulps represented commercial "post-consumer waste" after undergoing a variety of cleaning operations including the asphalt dispersion (A/D) process. The evaluations indicated the commercially cleaned OCC pulps responded to ozonation in a similar manner to the Institute Model OCC. There was no evidence that the residual contaminants or the utilization of the A/D process interfered with ozonation.
2. Long and short fiber fractions viz., liner and medium, were ozonated separately and found to respond equally well to ozonation. There was some indication that certain strength properties are more highly dependent upon a given fraction of the furnish. Thus some "tailoring" of properties may be achieved by ozonating fractions independently. Process economies may also be achieved if only one fraction requires treatment.
3. Prerefined OCC responds to ozonation in a manner similar to unrefined stock. Thus, refining in combination with

ozonation may achieve strength levels beyond that reached by either process alone within reasonable operating parameters. At a given level of refining, however, the magnitude of the change in strength depends on the property being considered as well as the level of ozonation.

4. Post-refining of ozonated OCC with virgin kraft does not appear to be attractive as a means of improving strength. At a given freeness, strengths of the ozonated/refined stocks are similar to untreated/refined stocks. However, the ozonated pulp blends refine more readily, significantly reducing the refining energy required. It is hypothesized the fiber surface properties of ozonated fiber are significantly modified by any subsequent mechanical action.

5. Blending of ozonated OCC with prerefined virgin kraft is more attractive. Strength increases in most properties are observed which are roughly proportional to the degree of ozonation. However, the strength increases for the 60:40 virgin:OCC blend studied were more modest than obtained with the 100% OCC due to the large percentage of untreated virgin pulp in the blend.

6. Although OCC ozonated pulps show little or no reduction in freeness, wet pressing studies suggest the fiber's water holding capacity is increased. Some increases in wet pressing requirements may be expected.

7. All consistencies within the range 40-50% solids at the time of ozonation appear equally attractive. This range may be further increased if proper fluffing of the fiber can be maintained. Both the fluffed character and the consistency of the pulp appear to be

significant factors in achieving and maintaining high reaction efficiencies.

8. Very limited trials suggest low (1-3%) consistency ozonation may provide a processing alternative.

9. Limited trials suggest ozonation proceeds rapidly if sufficient ozone is present. On that basis a continuous process based on moving fibers or webs through an ozone reactor may be both feasible and more cost effective than a batch treatment process.

10. Scanning electron microscope (SEM) observations have shown good agreement with C stain studies in that low density softwood earlywood fibers and hardwood vessels respond to ozonation more rapidly than the higher density softwood latewood and hardwood fibers. Microcavitation, viz., pitting/erosion, is associated with the fiber wall microfibril winding. Optical studies have provided some information concerning depth of ozone reaction on the high density softwood latewood fibers. These observations have helped determine how ozone acts to improve bonding and should help in optimizing other processing, e.g., refining.

11. A processing engineering analysis is being carried out to develop current capital and operating costs. This will conclude all of the planned work.

INTRODUCTION

Results reported in Progress Report One indicated ozonation is a viable means of increasing the strength potential of recycled fiber without significant loss of productivity or the introduction of pollution problems. With that in mind, the studies were continued with a view toward optimizing the course of the treatment in terms of processing and process economics. Current work covers fractionation, blending, and refining of the ozonated recycled fiber both alone and with virgin kraft. In addition, ozonation of commercial OCC pulp was studied to determine if commercially cleaned post-consumer waste responded well to ozonation treatments.

Limited evaluations of various ozone processing variables such as consistency, fluffing, and rate of ozone application were undertaken because early trials were based upon a single ozonation processing condition. Microscopic studies were continued to provide a better understanding of the ozone/fiber reaction.

A review of the literature on ozonation treatments is contained in Progress Report One.

EXPERIMENTAL PROCEDURES

OCC SUPPLY

The "old corrugated" sample used in this work was obtained in the form of 200 lb test C-flute combined board sheets using selected linerboard and medium components. While the above sample is referred to as OCC in this report, it is recognized that it does not contain the residual contaminants present in post consumer old corrugated after cleaning. However, results obtained during the study indicated that its physical properties after repulping were comparable to commercial OCC pulps from a number of sources.

DEWATERING AND FLUFFING

The repulped OCC was dewatered and fluffed as follows:

1. Centrifugal dewatering to 25-30% consistency.
2. Fluffing and additional water removal to a consistency of 40% by repeatedly passing the dewatered pulp through a pulp shredder built at the Institute. This consists merely of a vertical rotating shaft with blunt horizontal bars protruding from the shaft.

OZONATION

The ozonation was carried out on a Welsbach ozonator at room temperature. The concentration of O_3 in the O_2 stream was about 2%. The gas stream from the ozonator was split into two parts in a ratio of 4:1. The smaller stream was passed into a double trap system containing potassium iodide to determine the ozone addition. The larger stream passed through a flask containing the pulp to be treated. The effluent gas from the flask was analyzed for residual ozone content, and the consumption was determined by difference.

Ozone concentrations were determined by absorption of ozone in potassium iodide solution, acidification, and titration of the liberated iodine with sodium thiosulfate solution to a starch end point. The pH of the pulp was determined before and after treatment and after washing the ozonated pulp in tap water.

HANDSHEET TESTING

Standard British handsheets were made from each pulp and the untreated fluffed control. Prior to handsheet preparation, the pulp was washed with tap water to raise the pH.

The following tests were performed.

		No. of Determinations per Condition
1.	Basis weight	10
2.	Caliper	10
3.	Apparent density	--
4.	Burst	10
5.	Elmendorf tear	4
6.	Modified ring compression	10
7.	Tensile	10
8.	Stretch	10
9.	Tensile stiffness (Et)	10
10.	Tensile energy absorption	10
11.	Concora flat crush[a]	6

[a]On 26 lb/M ft^2 sheets.

STUDY OF FIBER PROCESS VARIABLES — FRACTIONATION, BLENDING, AND REFINING

Initial ozonation trials covered in Progress Report One studied ozonation of composite OCC only. Data indicated ozonation was an effective means of improving the strength properties of the OCC. Therefore further studies were undertaken coupling ozonation with more conventional strength improvement methods in an effort to optimize strength improvement and/or overall cost effectiveness. Process variables included fractionation of the OCC into long and short fiber components prior to ozonation, blending of ozonated fiber with untreated stock, and pre- and post-refining of the ozonated fiber.

OZONATION OF LINER AND MEDIUM FRACTIONS

In previous studies the OCC composite was ozonated; however, it was hypothesized that ozonation of the long and short fiber fractions separately might be more effective in terms of overall strength improvements at reduced cost. For example, treatment of the medium fraction only could reduce ozonation costs by about two-thirds. Different pulp furnishes might also respond differently to ozonation. C-stain fiber studies suggested such possibilities could occur. Initial studies with these potentials in mind were therefore undertaken.

The liner and medium fractions of the IPC model OCC were separated by soaking, disintegrating, fluffing, and ozonating in accordance with procedures previously established for the OCC composite. This separation yielded a liner fraction which is essentially 100% softwood kraft and a medium fraction of approximately 80% hardwood NSSC and 20% softwood kraft. Single trials at ozonation levels of approximately 2.3% and 4.5% ozone consumed, based upon the pulp, were performed. The fractions were formed into handsheets and the usual physical tests were performed.

Physical test results are shown in Table I. Graphs of freeness, tensile, burst, tear and modified ring _vs_. O_3 consumption are shown in Fig. 1-3. Comparable results for the composite are also shown. The trends in percentage strength improvement for the liner and medium are very similar even though initial strength values for the liner and medium are quite divergent. This suggests that both furnishes respond about equally well to ozone treatment. However, it may still be desirable to fractionate and treat only one fraction for economic reasons and/or to avoid further fiber shortening and reduction of freeness. This would be particularly true for the hardwood furnish. Properties of the OCC composite generally are closer to the properties of the liner fraction, as might be expected, since approximately 70% of the composite is softwood kraft.

BLENDING OF OZONATED LINER AND MEDIUM FRACTIONS

OCC composite, the liner and the medium fractions were each ozonated and prepared into handsheets independently in previous experiments. In general, those studies indicated both fractions responded about equally well to ozone treatment when compared to the composite. However, for economic reasons it was suggested that ozonation of a single fraction such as the short fiber medium fraction would effect a cost saving while achieving substantial strength improvements. The short fiber fraction would also be least amenable to mechanical treatments for increasing strength due to the generation of fines. Thus it appeared to be the more attractive component of the OCC composite for consideration of alternative treatments. Studies were carred out in which both fractions were separately ozonated to various levels. The ozonated fraction was then blended with the untreated fraction in a 70% liner, 30% medium ratio prior to handsheet preparation. This ratio approximates the composition of the original OCC composite.

TABLE I

COMPARISON OF PROPERTIES OF HANDSHEETS PREPARED FROM OZONATED LINER AND MEDIUM FRACTIONS WITH COMPOSITE OCC

	Liner			Medium			Composite OCC[a]		
Ozonation time, min	0	15	30	0	15	30	0	15	60
Ozone applied, % of o.d. fiber	--	2.43	4.79	--	2.46	4.77	--	2.35	9.41
Ozone consumed, % of o.d. fiber	--	2.35	4.48	--	2.34	4.41	--	2.31	8.53
Reaction efficiency, %	--	96.7	93.5	--	95.1	92.5	--	98.3	90.7
C.S. freeness, mL	723	678	670	395	375	380	633	617	567
% Change	--	-6.2	-7.3	--	-5.1	-3.8	--	-2.5	-10.4
Basis weight, lb/M ft^2	13.6	13.3	13.4	13.4	13.5	12.8	13.2	13.2	13.5
Caliper, points	5.6	5.2	5.0	6.3	5.8	5.4	6.1	5.6	5.3
Apparent density	2.44	2.55	2.65	2.14	2.35	2.37	2.16	2.34	2.54
% Change	--	+4.5	+8.6	--	+9.8	+10.7	--	+8.3	+17.6
Bursting strength, psig	17.9	23.7	26.2	13.7	19.6	21.1	17.2	23.2	33.1
Factor[b]	1.32	1.79	1.96	1.02	1.46	1.65	1.30	1.76	2.45
% Change	--	+35.6	+48.5	--	+43.1	+61.8	--	+35.4	+88.5
Mod. ring compression, lb/inch	3.8	4.1	4.5	4.3	4.8	4.6	3.8	4.0	4.8
Factor[b]	0.278	0.309	0.336	0.332	0.358	0.359	0.284	0.307	0.353
% Change	--	+11.2	+20.9	--	+11.2	+11.5	--	+8.1	+24.3
Tear, grams	116.4	103.0	98.8	38.6	40.0	37.6	87.6	85.1	71.9
Factor[b]	8.59	7.75	7.38	2.89	2.97	2.94	6.64	6.45	5.31
% Change	--	-9.8	-14.1	--	+2.8	+1.7	--	-2.9	-20.0
Tensile, lb/inch	12.2	14.8	16.2	12.2	15.2	15.1	12.4	15.6	20.0
Factor[b]	0.90	1.12	1.21	0.91	1.13	1.18	0.94	1.19	1.48
% Change	--	+24.4	+34.4	--	+24.2	+29.7	--	+26.6	+57.4
Stretch, %	2.08	2.32	2.26	1.70	2.03	2.14	1.86	2.18	2.43
% Change	--	+11.5	+8.7	--	+19.4	+25.9	--	+17.2	+30.6
Et, lb/inch	1646	1899	2113	1675	1967	1989	1640	1946	2326
Factor[b]	121.4	142.9	157.9	125.5	145.9	155.3	124.2	147.8	172.0
% Change	--	+17.7	+30.1	--	+16.3	+23.7	--	+19.0	+38.5
TEA, ft-lb/ft^2	2.2	3.0	3.2	1.8	2.7	2.9	2.0	2.9	4.1
% Change	--	+36.4	+45.5	--	+50.0	+61.1	--	+45.0	+105.0
ZDT, psi	38.8	52.4	54.4	74.0	101.4	111.8	52.7	61.7	93.0
% Change	--	+35.1	+40.2	--	+37.0	+51.1	--	+17.1	+76.5
Brightness, %	14.4	17.9	23.6	22.2	26.6	28.8	16.6	20.2	33.4
% Change	--	+24.3	+63.9	--	+19.8	+20.7	--	+21.7	+101.2
Zero span factor, km	13.49	13.71	14.65	10.86	12.24	12.05	12.98	12.95	13.46
% Change	--	+1.6	+8.6	--	+12.7	+11.0	--	-0.2	+3.7

[a] Data obtained from Progress Report One, Project 2697-53, entitled "Effect of Ozonation on Recycled Fiber," dated September 24, 1978.

[b] Factors were determined by dividing the given property value, usually in English units, by the basis weight in lb/M ft^2.

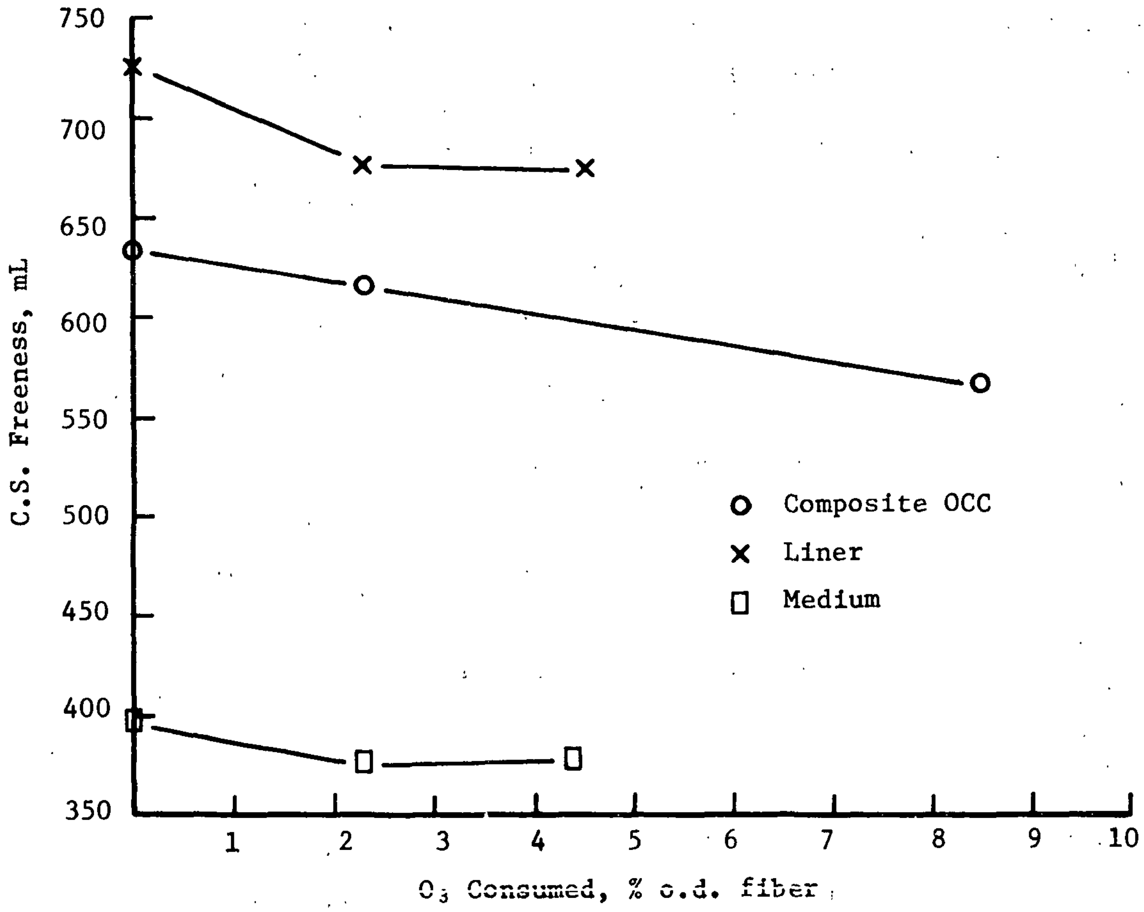


Figure 1. Freeness Trends of Ozonated Liner, Medium, and Composite OCC

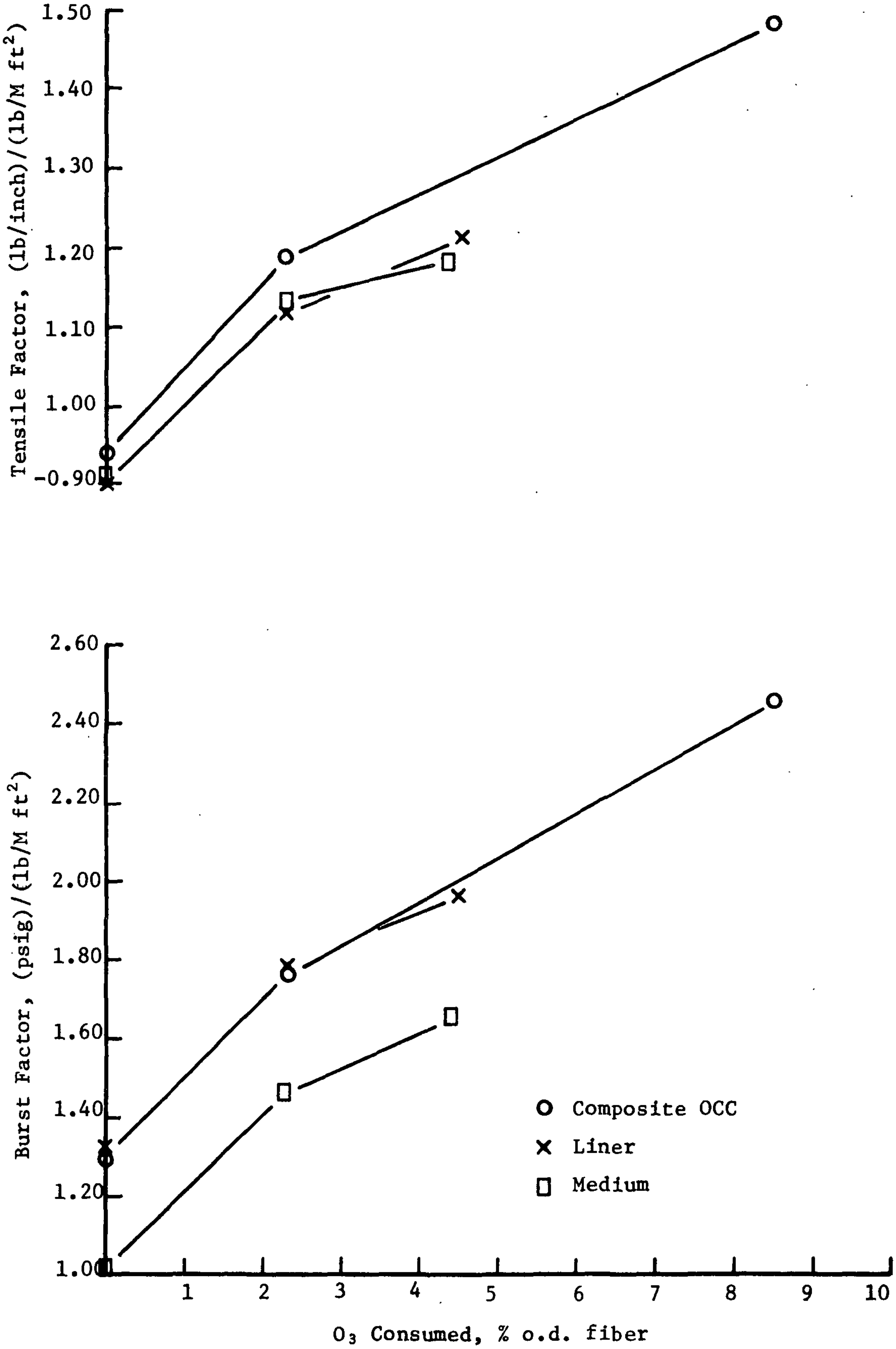


Figure 2. Tensile and Burst Trends of Ozonated Liner, Medium, and Composite OCC

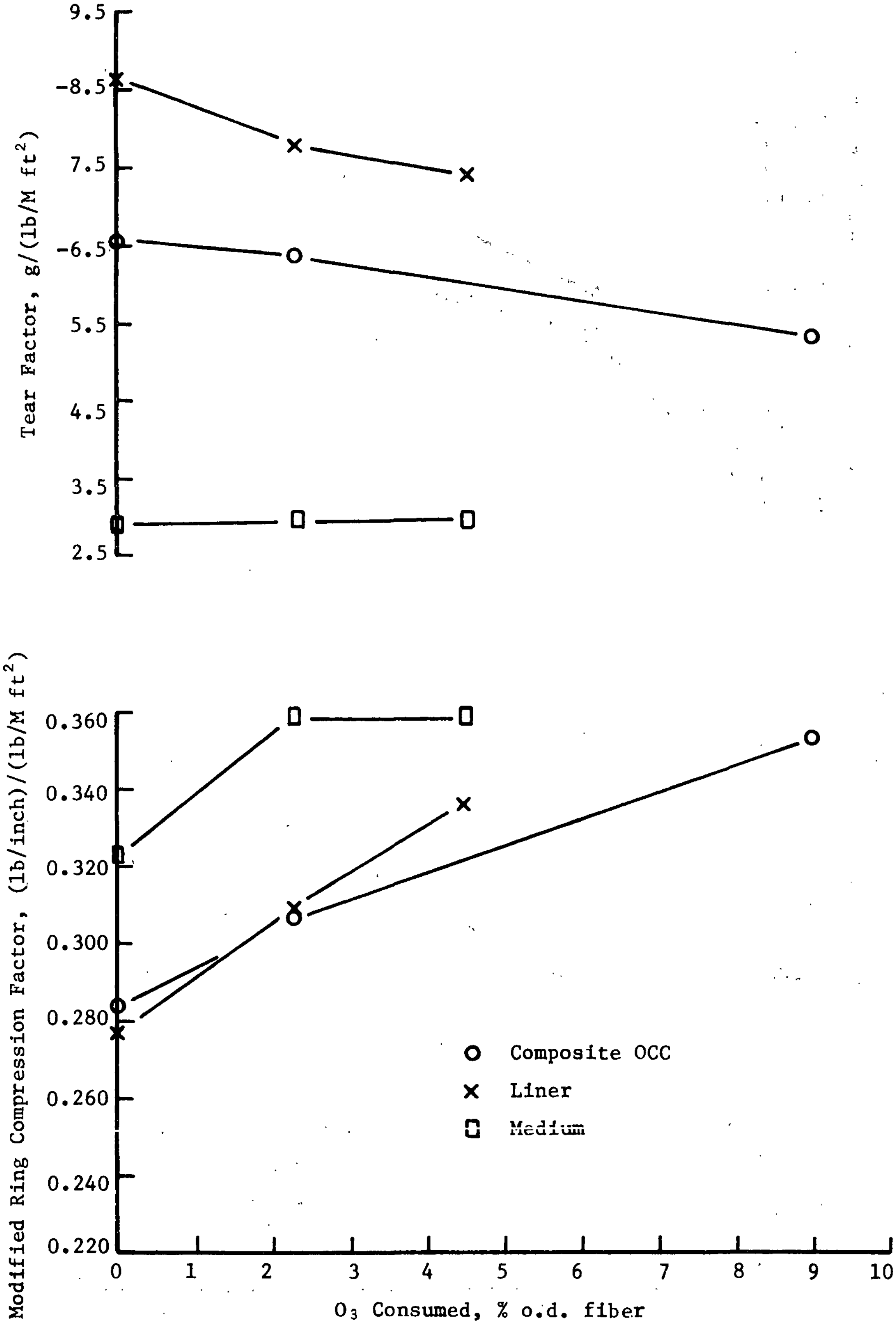


Figure 3. Tear and Modified Ring Compression Trends of Ozonated Liner, Medium, and Composite OCC

The liner and medium fractions of the Institute model OCC were separated by soaking, disintegrating, fluffing, and ozonating in accordance with procedures previously established. Single trials at ozonation levels of approximately 0, 2.5, 4.8, and 8.8% ozone consumed, based the o.d. liner weight, were performed on the liner fraction. These ozonated fractions were blended with untreated medium in a 70% liner, 30% medium ratio. Ozone consumption levels of 0, 1.7, 3.3, and 6.2%, based upon the o.d. fiber weight of the final blend, resulted.

The medium fractions were ozonated to levels of 0, 4.4, 8.3, and 11.8% ozone consumed based upon o.d. weight. The ozonated medium fractions were then blended with untreated liner at the 70:30 liner:medium ratio to provide ozone consumption levels in the final blend of 0, 1.3, 2.5, and 3.5% based on the o.d. fiber weight of the final blend. The higher ozonation levels for the medium were chosen because the medium provides the smaller fraction of the total composite.

Table II shows the strength properties of handsheets from the above blends.

Graphs of freeness, tensile, burst, tear, and modified ring compression _vs_. O_3, based upon total o.d. fiber weight, are shown in Fig. 4-6. The results suggest that separate ozonation of the medium fraction is effective in achieving significant increases in certain physical properties, particularly burst and tensile, at low levels of O_3 consumption based on total fiber weight. At the 1.3% O_3 consumed level (4.4% O_3 consumed on the medium only) increases of 25+% are noted for both burst and tensile. This is achieved with a nominal increase in tear as well. Although loss of tear strength has never been serious, increases in other strength properties without a loss of tear strength is desirable. Increases in modified ring were about equal regardless of which fraction of the blend was ozonated.

TABLE II

PROPERTIES OF HANDSHEETS FROM BLENDS OF
70% LINER AND 30% MEDIUM

	Blend Combination						
Ozone consumed, liner, % o.d. fiber	0	0	0	0	2.46	4.78	8.81
Ozone consumed, medium, % o.d. fiber	0	4.39	8.26	11.74	0	0	0
Ozone consumed, % total fiber	0	1.31	2.48	3.52	1.72	3.34	6.17
C.S. freeness, mL	655	615	590	590	630	630	590
% Change	--	-6.1	-9.9	-9.9	-3.8	-3.8	-9.9
Basis weight, lb/M ft^2	13.7	13.6	13.5	13.6	13.6	13.2	13.6
Caliper, points	5.5	5.4	5.3	5.2	5.2	5.0	5.0
Apparent density	2.49	2.53	2.53	2.63	2.60	2.64	2.74
% Change	--	+1.6	+1.6	+5.6	+4.4	+6.0	+10.0
Bursting strength, psig	17.1	21.4	23.2	24.0	19.0	20.1	23.6
Factor[a]	1.25	1.58	1.72	1.76	1.40	1.52	1.74
% Change	--	+26.4	+37.6	+40.8	+12.0	+21.6	+39.2
Modified ring compression, lb/inch	3.3	3.6	3.9	3.9	3.7	3.8	3.6
Factor[a]	0.245	0.268	0.292	0.286	0.273	0.287	0.268
% Change	--	+9.4	+19.2	+16.7	+11.4	+17.1	+9.4
Tear, grams	87.8	95.2	94.0	92.0	85.2	82.8	72.4
Factor[a]	6.41	7.00	6.95	6.74	6.28	6.26	5.32
% Change	--	+9.0	+8.4	+5.1	-2.0	-2.3	-17.0
Tensile, lb/inch	12.6	15.9	16.6	17.2	13.2	12.9	15.5
Factor[a]	0.92	1.17	1.23	1.26	0.97	0.98	1.14
% Change	--	+27.2	+33.7	+37.0	+5.4	+6.5	+23.9
Stretch, %	1.90	1.84	1.84	1.96	2.13	2.06	2.19
% Change	--	-3.2	-3.2	+3.2	+12.1	+8.4	+15.3
Et, lb/inch	1580	1568	1643	1726	1754	1766	2039
Factor[a]	115.6	115.3	121.5	126.5	129.2	133.6	149.8
% Change	--	-0.3	+5.1	+9.4	+11.8	+15.6	+29.6
TEA, ft-lb/ft^2	2.1	2.2	2.2	2.5	2.4	2.3	3.0
% Change	--	+4.8	+4.8	+19.0	+14.3	+9.5	+42.9

[a]Factors were determined by dividing the given property value, usually in English units, by basis weight in lb/M ft^2.

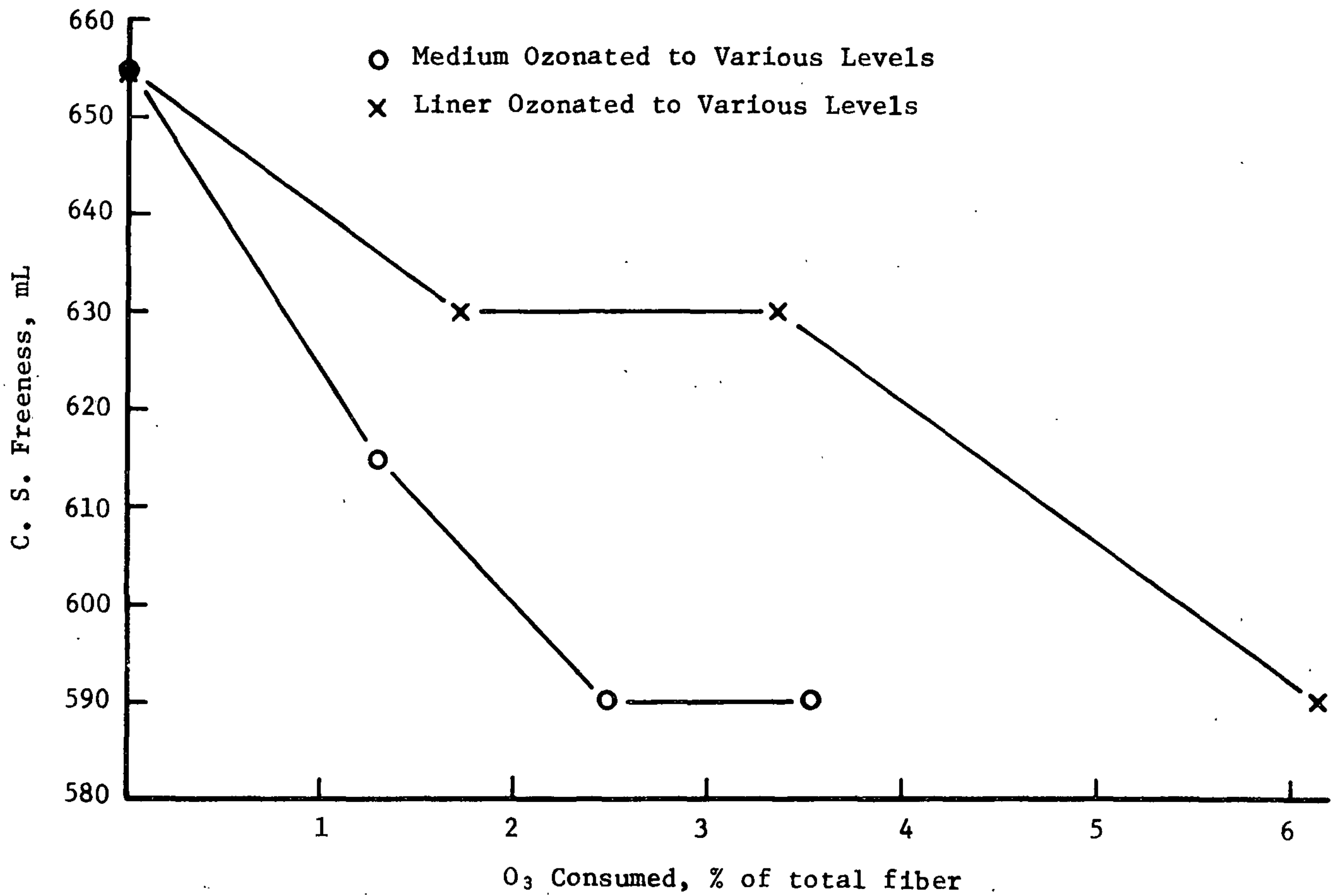


Figure 4. Freeness Trends of 70:30 Liner:Medium Blends When One Fraction of the Blend is Ozonated

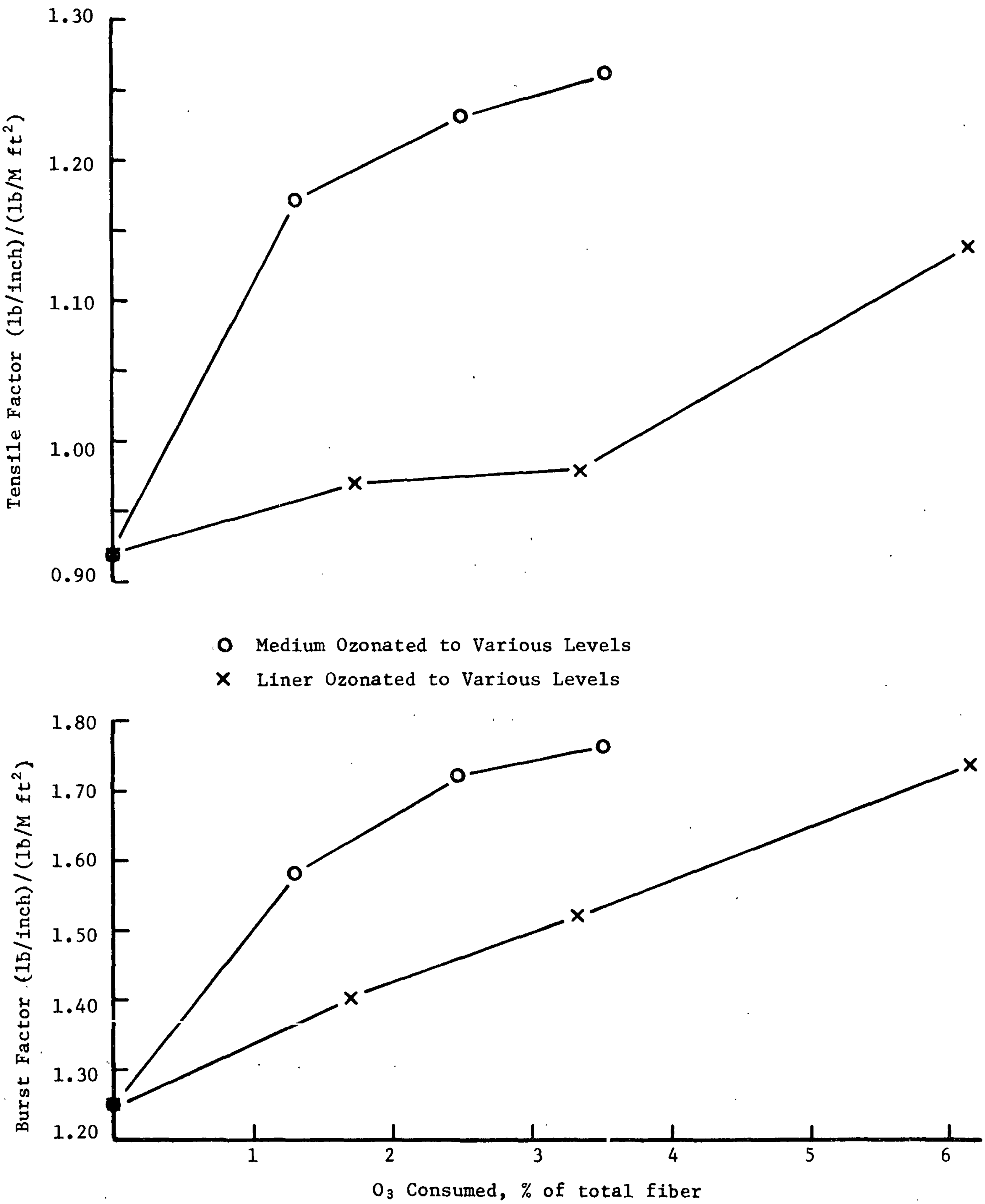


Figure 5. Tensile and Burst Trends of 70:30 Liner:Medium Blends When One Fraction of the Blend is Ozonated

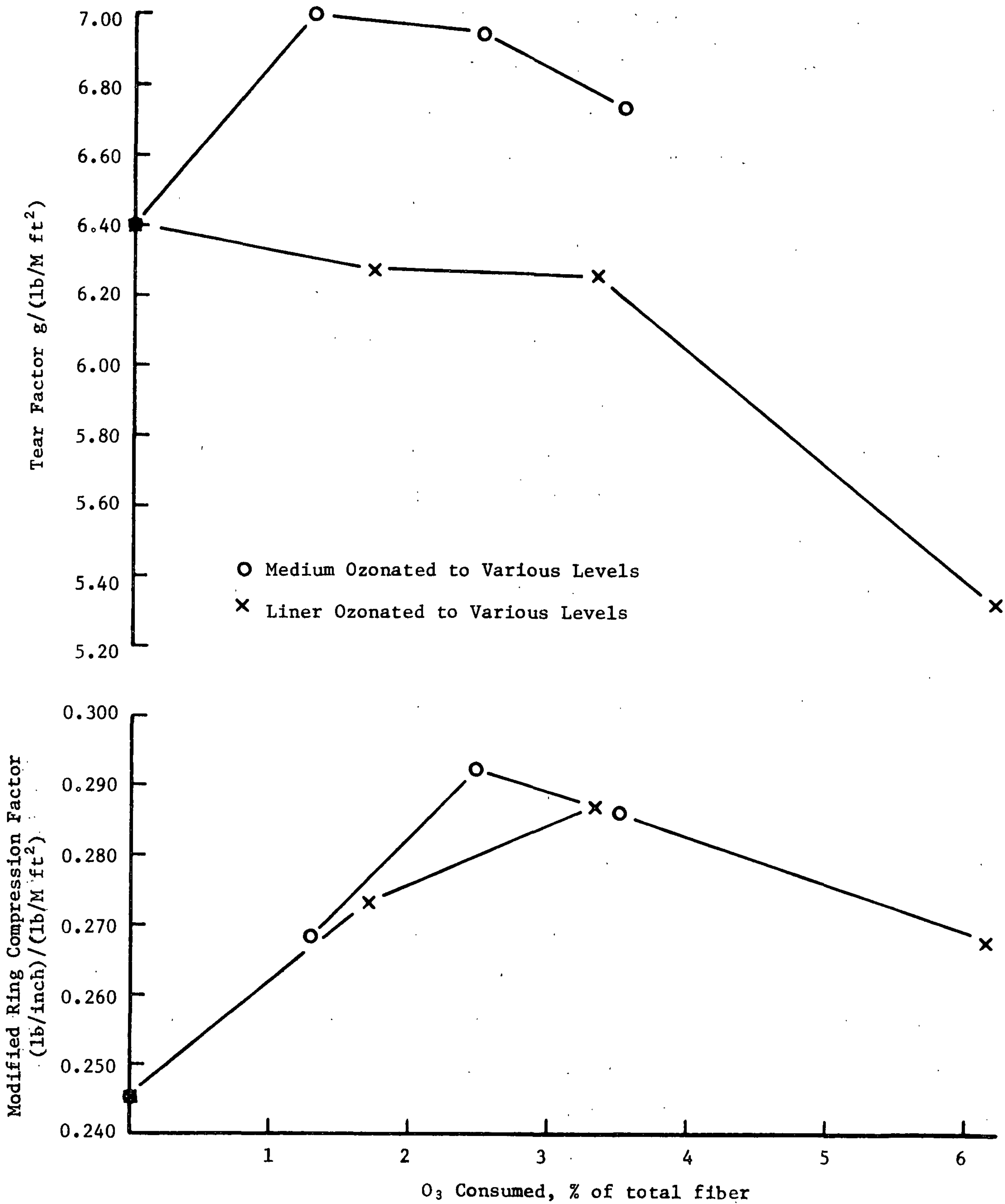


Figure 6. Tear and Modified King Compression Trends of 70:30 Liner:Medium Blends When One Fraction of the Blend is Ozonated

An important feature of this work relates to previous results which have suggested that ozonation levels of approximately 2.5% O_3 consumed are necessary to achieve significant strength increases in the final paper. The current results suggest that ozonating a fraction of the furnish to a level above the critical 2.5% O_3 level and blending it with the untreated remainder will result in strength increases at ozonation levels below the 2.5% O_3 level based upon the total fiber. Treatment of the medium fraction, viz., the hardwood NSSC, also appears to be the most efficient way to achieve the strength improvements.

The cost savings could be substantial. Treatment of only a third of the total OCC could significantly reduce the capital costs or alternately increase the production for a given O_3 plant size based on total board production. There would be some added cost for fractionating equipment to separate long and short fibers. However, it is believed this cost would be less than the capital saving for ozonation.

There is also some indication that certain strength properties are more highly dependent upon a given fraction of the furnish. Thus, some "tailoring" of properties might be achieved by ozonating the fractions independently.

OZONATION OF OCC PREREFINED TO VARIOUS FREENESS LEVELS

In order to determine the best ways to combine ozonation with refining of the stock, studies were undertaken to evaluate the effects of refining before and after ozonation. Initially, the effects of prerefining on ozonation treatment results were determined. For this purpose, OCC was refined to C.S. freeness levels of 650 mL (unbeaten), 595, 520, and 340 mL. The stock at each freeness level was then treated with ozone to give O_3 consumption levels of about 0, 2.5, and 4.7% based on the o.d. weight of the fiber.

The physical test results on the handsheets are summarized in Table III. Figure 7 shows that substantial improvements in bursting strength were obtained on the ozone treated sheets at each level of prerefining. The increases in burst were approximately proportional to the ozone consumption level except at the lowest initial freeness of 340 mL. Figure 8 shows the burst results graphed vs. freeness at the three ozonation levels. At equal freeness, the ozonated sheets generally exhibit higher bursting strength than the untreated control. Figure 9 indicates that the ozonation of OCC generally produces sheets with higher densities and bursting strength than the untreated prerefined OCC. Thus, ozonation after prerefining appears to increase bursting strength a greater amount than would be expected on the basis of mechanical refining alone.

The modified ring compression results in Fig. 10 show that ozonation after prerefining effected modest increase in strength. Similar results were obtained in previous work. When the ring results are plotted vs. freeness, it appears that the ozonated sheets exhibit about the same strength levels as the untreated refined control down to about 450-500 mL C.S. freeness (see Fig. 11). At lower freenesses, the ozonated sheets tended to exhibit higher ring compression strengths than the refined control.

In terms of linerboard, bursting strength is important from a regulatory standpoint; but edgewise compression strength is one of the basic factors governing box compression strength. Figures 12 and 13 show burst and edgewise compression results with freeness as a third factor. For a given edgewise compression strength, ozonation of OCC produces a sheet with higher burst than by mechanical refining alone. The amount of burst improvement increases with the level of ozonation.

TABLE III (Continued)

EFFECT OF PREREFINING AND OZONATION ON HANDSHEET PROPERTIES

Ozone Consumed, %	Tear, g	Tear Factor g/(lb/M ft^2)	Tensile, lb/inch	Tensile Factor, (lb/inch)/(lb/M ft^2)	Stretch, %	Tensile Stiffness Et, lb/inch	Et Factor, (lb/inch)/(lb/M ft^2)	TEA, ft-lb/ft^2	Concora, psi[a]
650 mL Initial Freeness									
0.00	87.2	6.42	12.3	0.91	1.59	1498	110.4	1.6	13.8
2.56	91.2	7.00	13.5	1.03	2.15	1576	114.7	2.4	20.1
4.75	94.8	6.90	15.5	1.13	2.27	1858	142.5	2.9	24.6
595 mL Initial Freeness									
0.00	86.0	6.22	18.2	1.32	2.03	2030	146.7	2.9	25.2
2.44	82.0	6.22	17.3	1.31	2.50	1969	149.4	3.7	28.9
4.58	73.6	5.69	18.4	1.42	2.68	2040	157.7	4.2	32.9
520 mL Initial Freeness									
0.00	77.6	5.87	18.1	1.37	2.24	1996	150.9	3.2	28.3
2.53	77.2	5.89	18.2	1.39	2.56	2017	153.9	4.0	30.0
4.86	72.0	5.47	20.0	1.52	2.62	2214	168.3	4.5	31.9
340 mL Initial Freeness									
0.00	68.4	5.11	19.5	1.46	2.68	2173	162.2	4.4	34.7
2.34	69.6	5.20	20.9	1.56	3.03	2327	173.9	5.5	37.2
4.54	63.6	4.78	21.9	1.65	3.09	2447	183.8	5.9	39.5

[a]Concora tests made on special 26 lb/M ft^2 sheets.

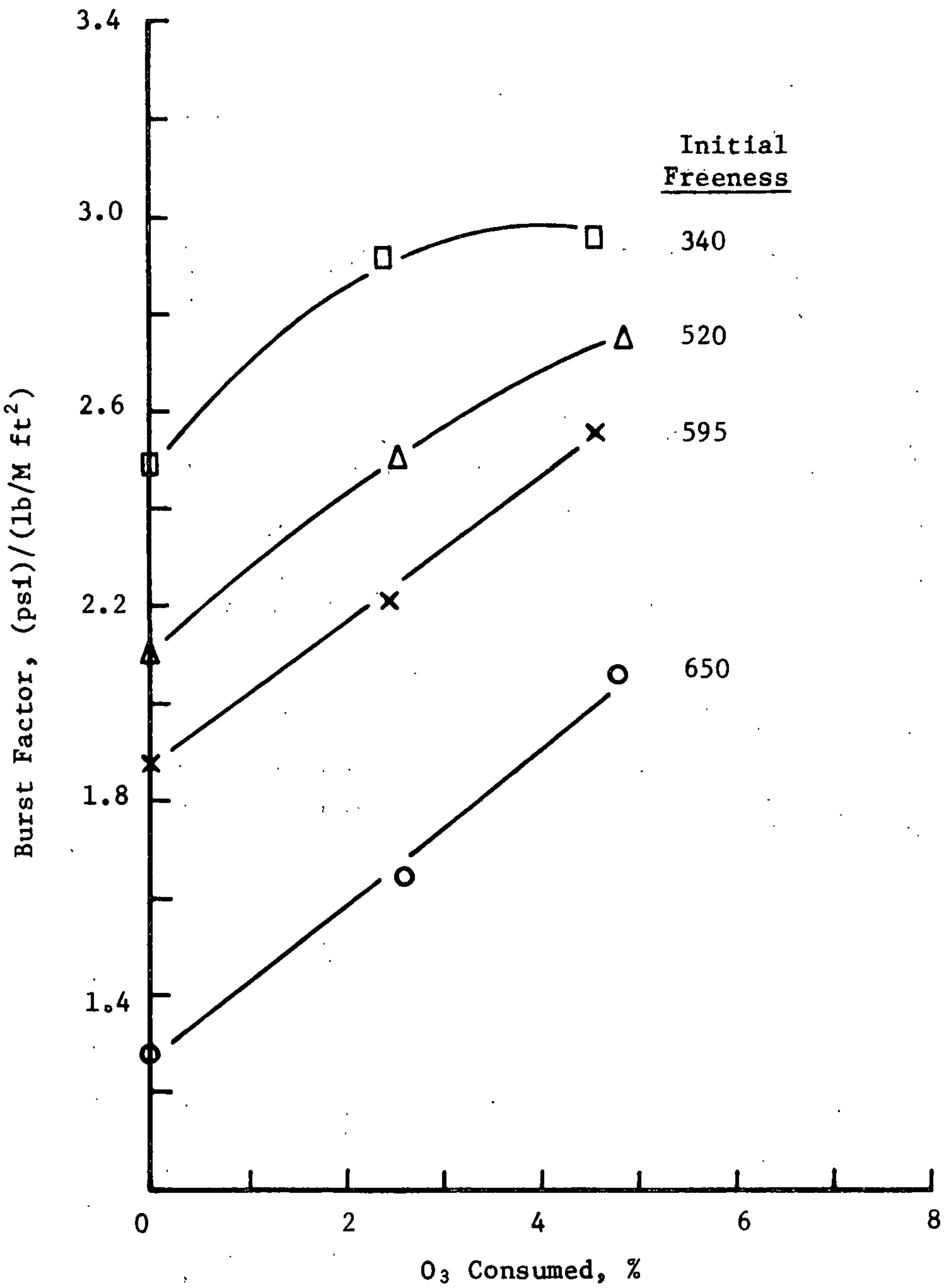


Figure 7. Effect of Prerefining and Ozonation on Burst Factor

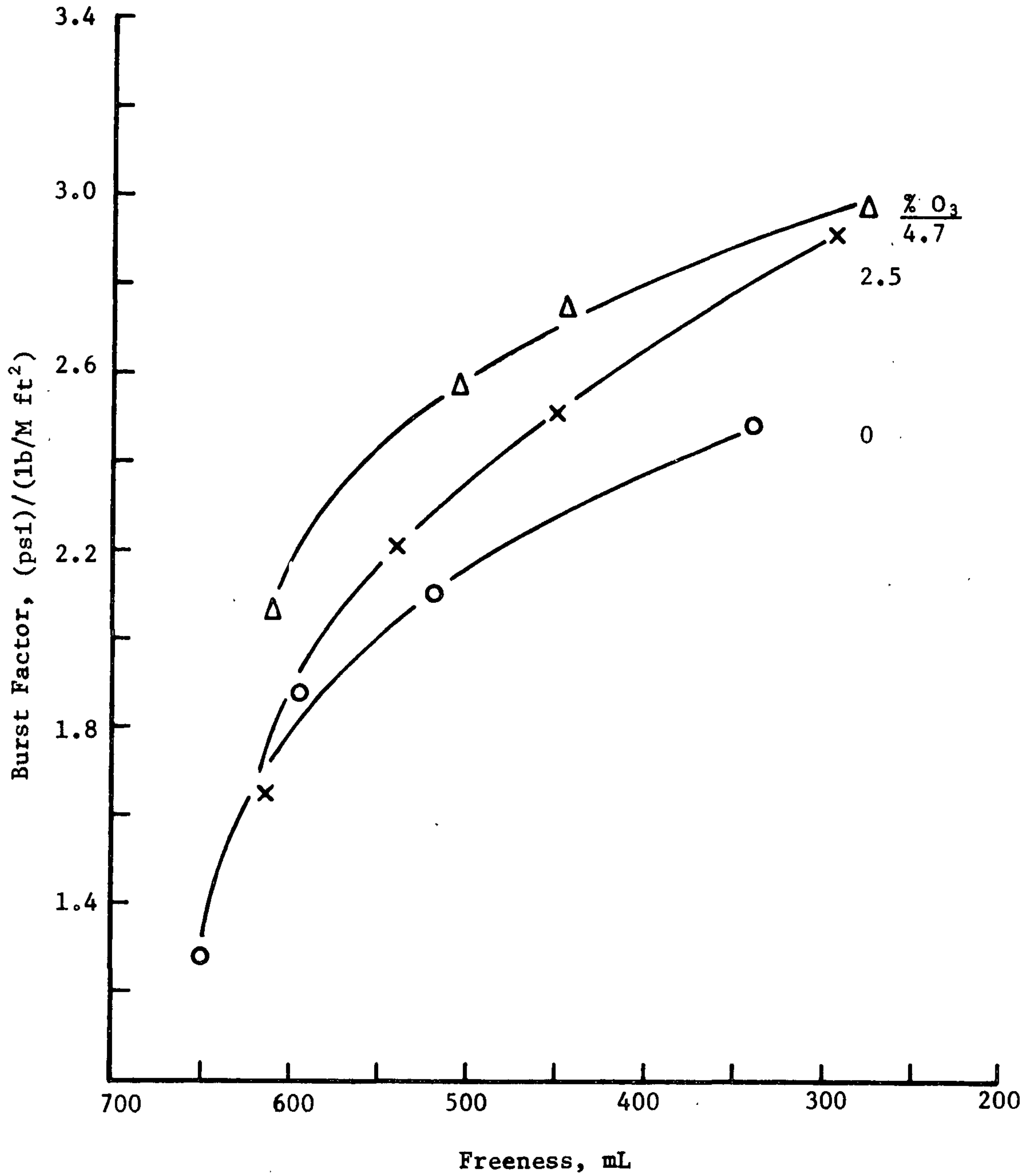


Figure 8. Burst Factor vs. Freeness at Various Prerefining and Ozonation Levels

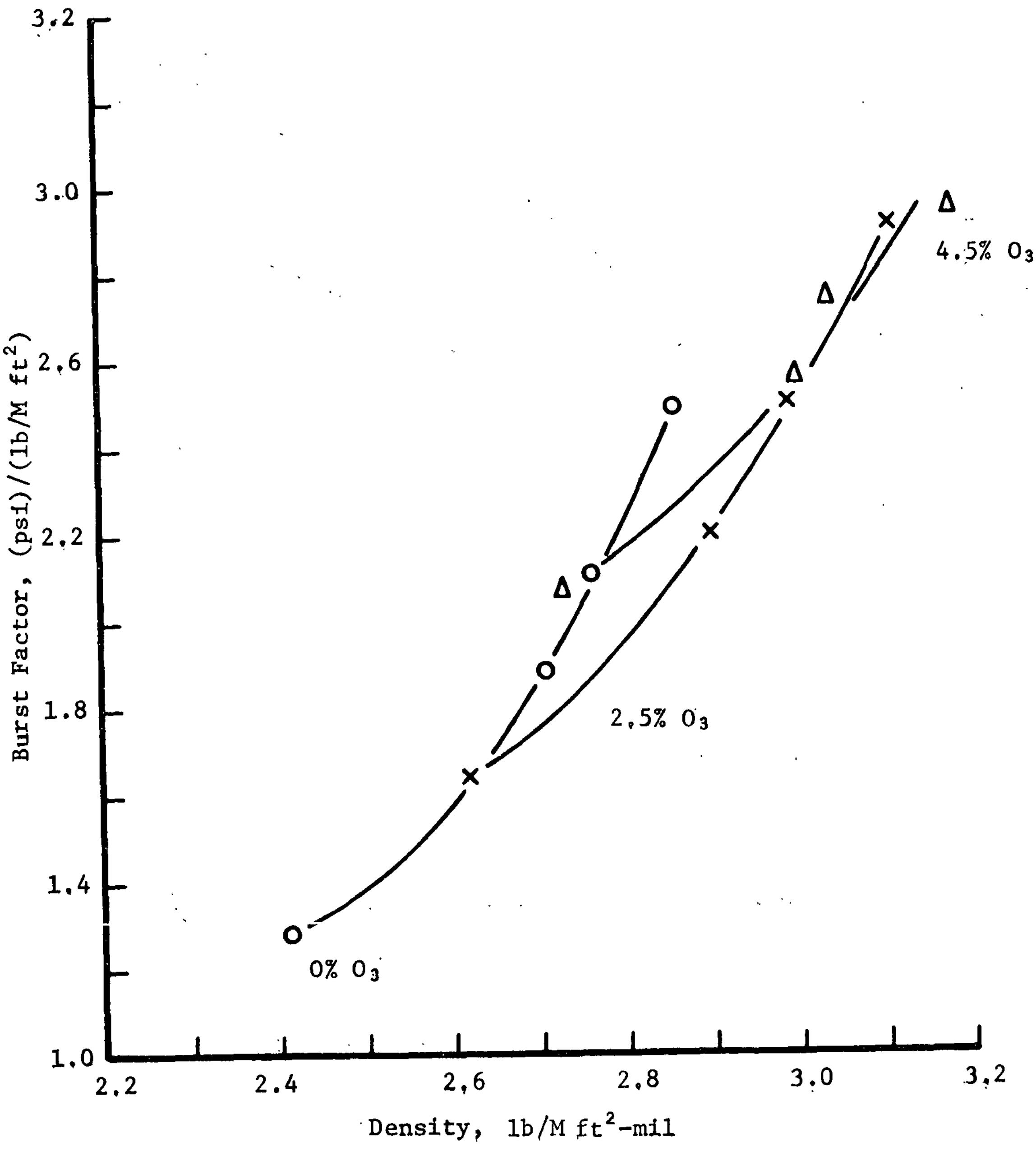


Figure 9. Burst Factor vs. Density at Various Ozonation and Prerefining Levels

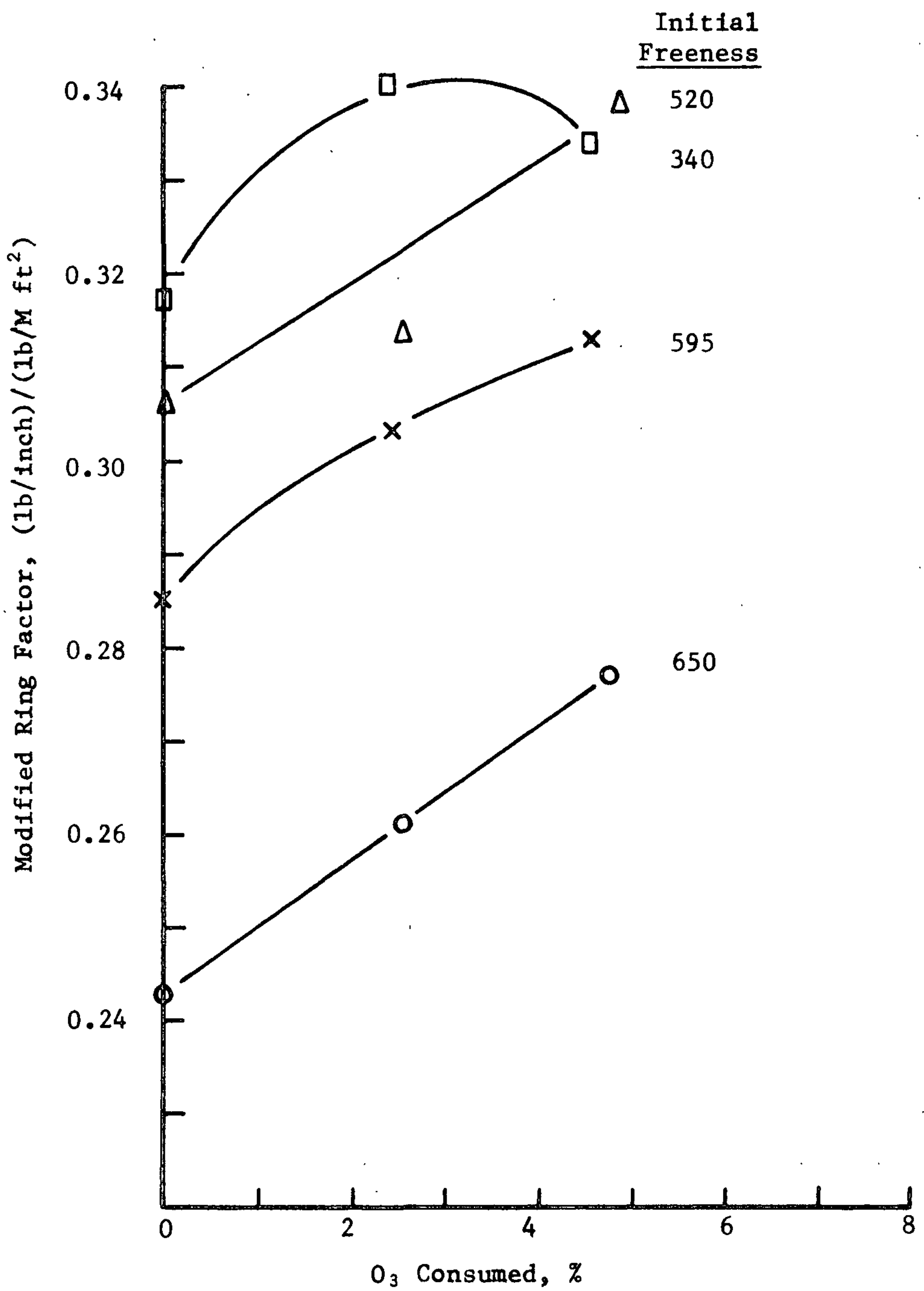


Figure 10. Effect of Prerefining and Ozonation on Modified Ring Compression

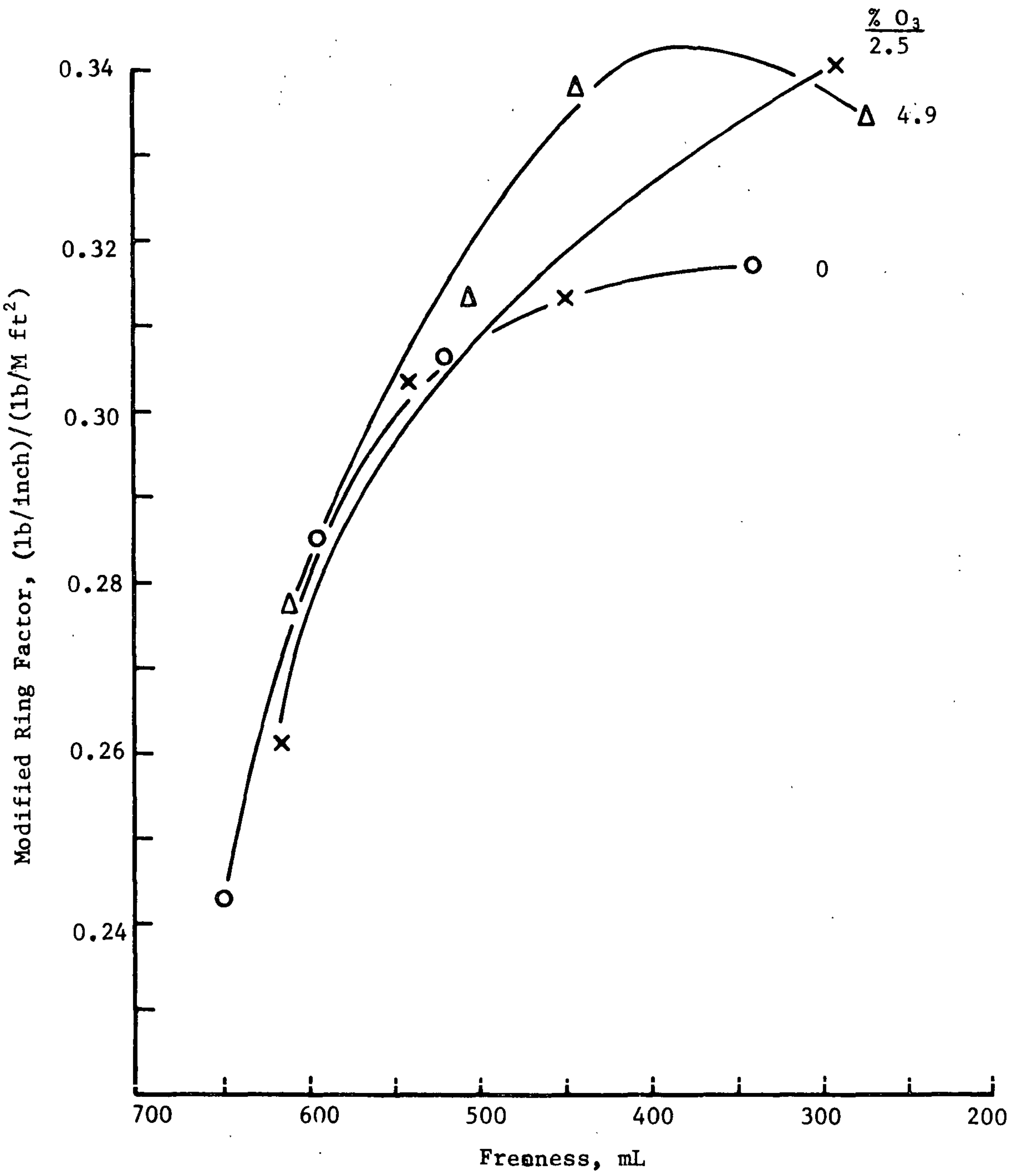


Figure 11. Modified Ring Compression vs. Freeness at Various Prerefining and Ozonation Levels

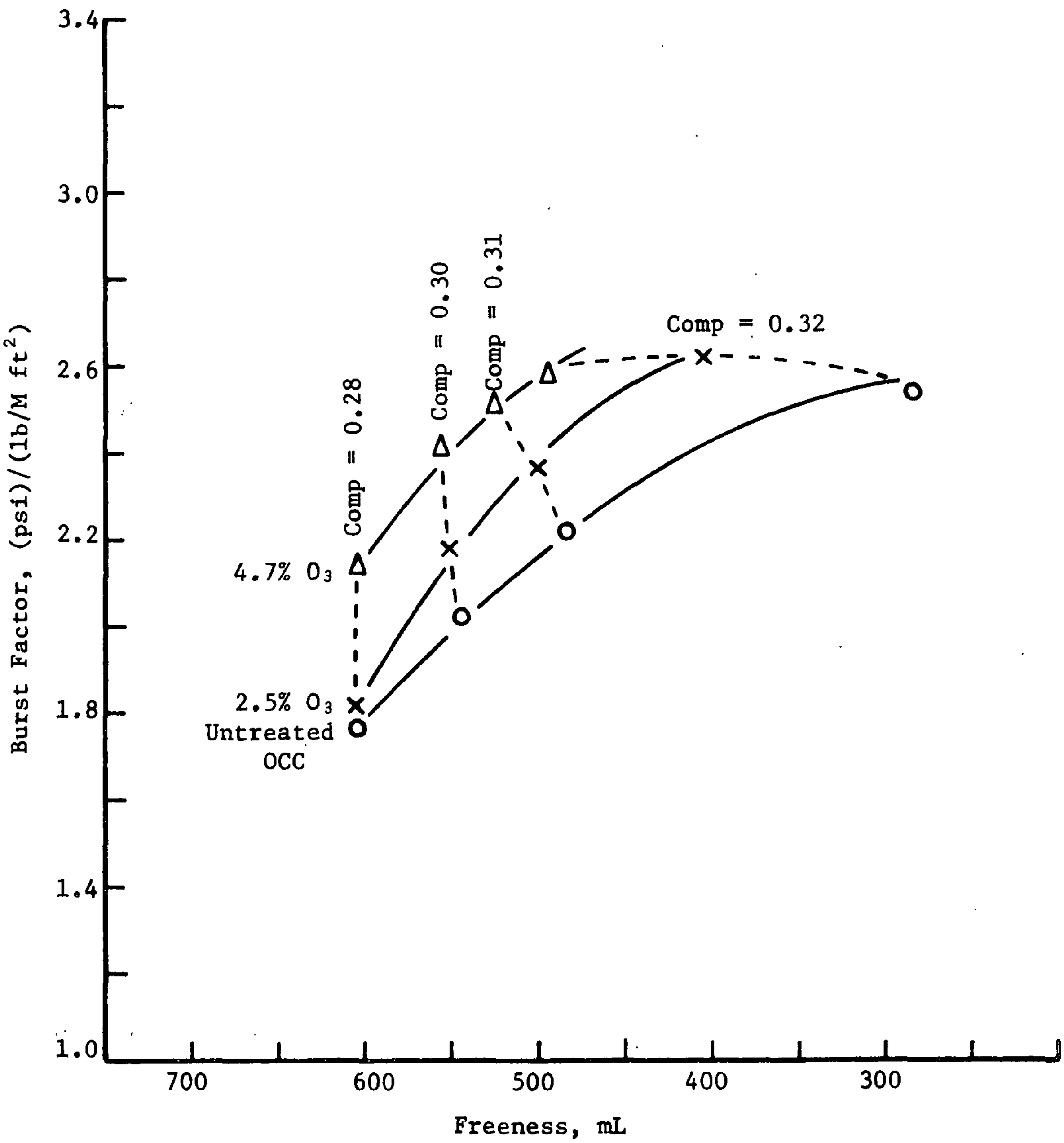


Figure 12. Burst vs. Freeness with Ring Compression as a Parameter

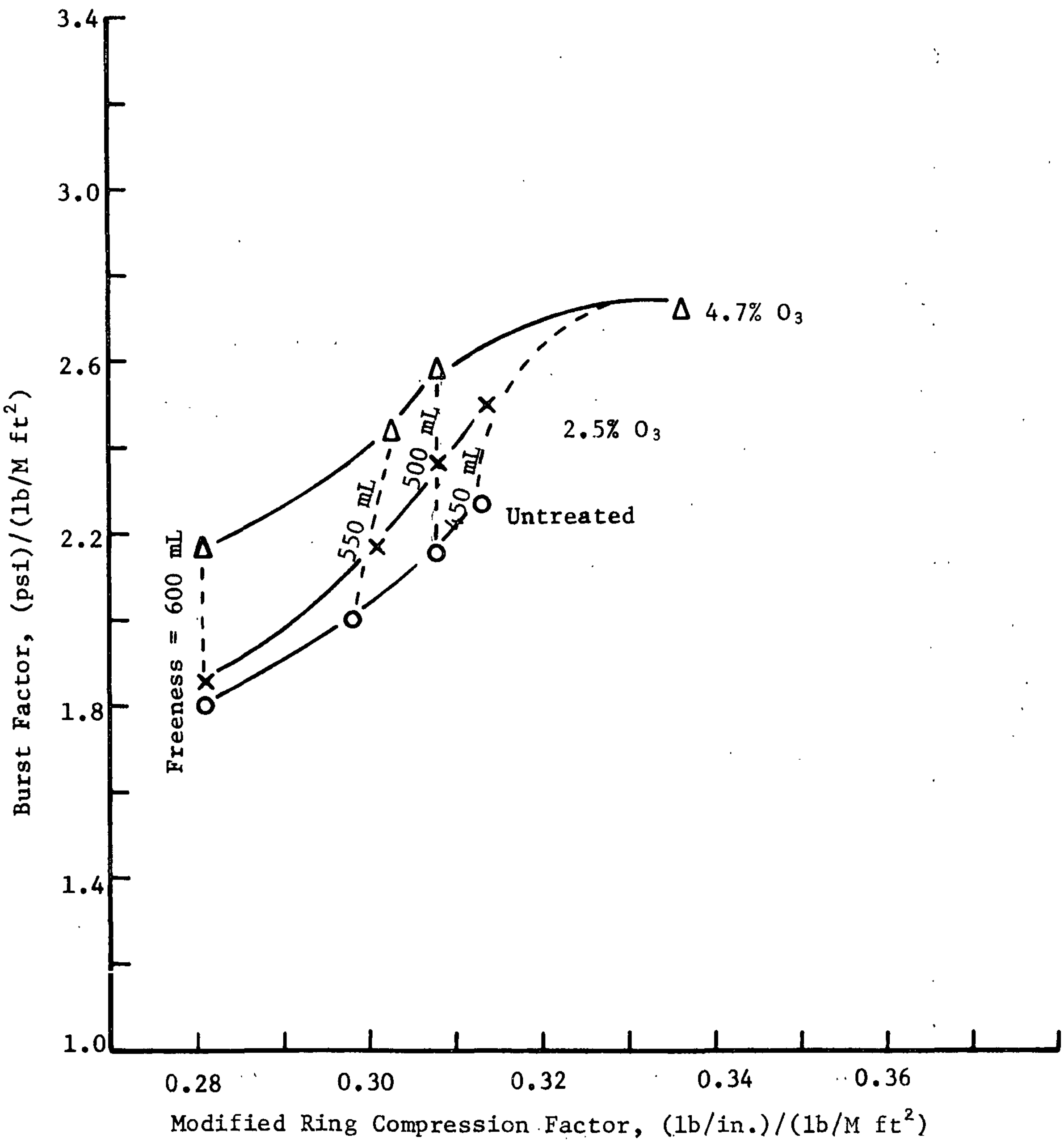


Figure 13. Burst vs. Ring Compression with Freeness as a Parameter

Figure 14 shows that ozonation substantially increased the Concora strength of the prerefined sheets, particularly on the stocks which were prerefined to 595 and 650 mL freeness. The increases in Concora strength were approximately proportional to the level of ozonation as in the case of bursting strength. Figure 15 shows the Concora results graphed vs. freeness. At equal freeness, the 4.9% ozonated sheets generally exhibit higher Concora strengths than the mechanically refined control. At the 2.5% O_3 level, the Concora strengths were about the same as obtained on the untreated refined control. Thus, as the degree of ozonation increases, the Concora strength at a given freeness is greater than achieved with mechanical refining.

The results in Fig. 16 show that ozonation generally increased tensile strength above that of the prerefined controls depending on the ozonation level. However, the changes in tensile strength were relatively small at the 2.5% O_3 for the stocks prerefined to 520 and 595 mL.

With regard to other properties, ozonation generally effected large changes in tensile energy adsorption (TEA) at all levels of prerefining. The effects of ozonation on tearing strength were generally small at all levels of prerefining.

Briefly summarizing, it appears that prerefined OCC responds to ozonation in a manner similar to the unrefined OCC treated in past work. However, at a given level of refining, the magnitude of the changes in strength depends on the property being considered as well as the level of ozonation. For example, the ozonated stocks generally exhibited large increases in burst at the various refining levels and modest increases in edgewise compression strength.

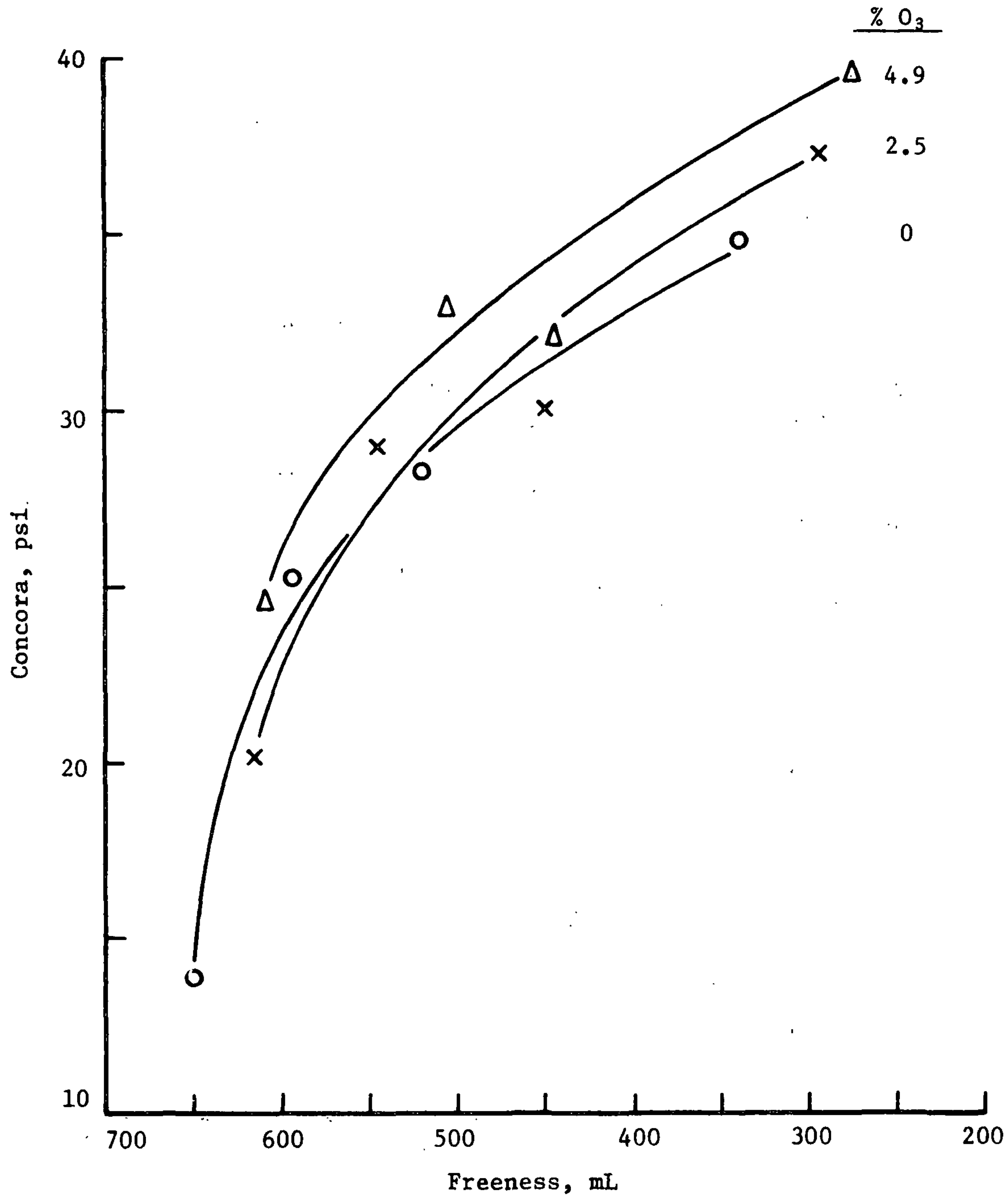


Figure 15. Concora Strength vs. Freeness at Various Prerefining and Ozonation Levels

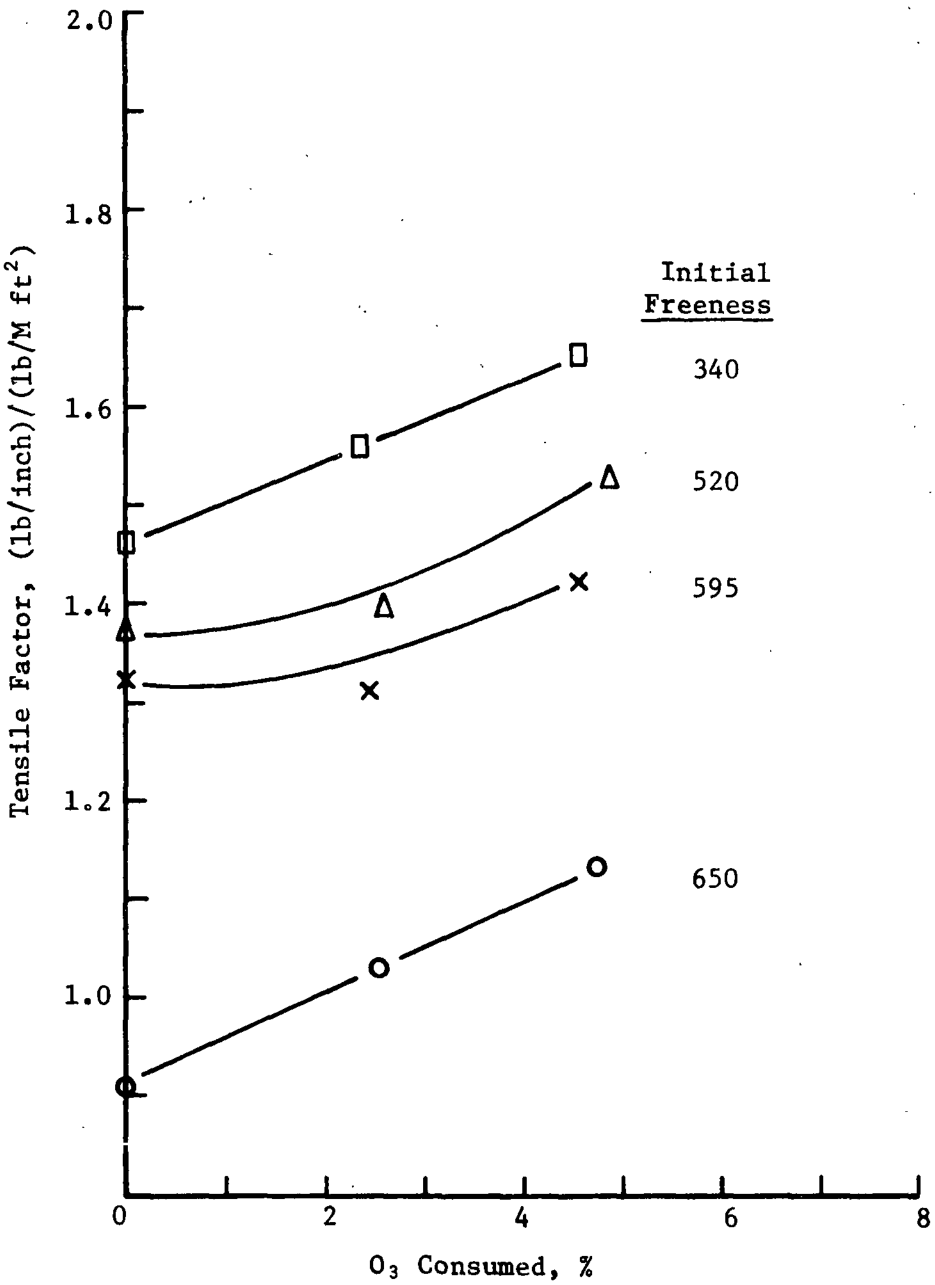


Figure 16. Effect of Prerefining and Ozonation on Tensile Strength

POST REFINING OF VIRGIN KRAFT/OZONATED OCC BLENDS

Based on limited exploratory work and the literature, it appeared that ozonated stocks would be expected to refine more quickly and possibly require gentler refining action than untreated fibers. Therefore, two ways of blending ozonated OCC with virgin fiber were considered, namely:

1. Blending of ozonated OCC with virgin kraft followed by refining of the blend.
2. Blending of ozonated OCC with prerefined virgin kraft.

The first approach involving post refining of the blend probably is more attractive from a mill processing standpoint. However, it appeared that savings on refining energy might result from either approach.

Therefore limited trials were carried out using both approaches. For the trials a blend level of 60:40 virgin:ozonated OCC was arbitrarily selected. While only a single blend level was used it was believed that the results would provide an indication of the merits of the two approaches and guide further work, if warranted. It was recognized that the amount of OCC in the blend was relatively high. The high blend ratio, however, serves to illustrate the problems involved as the OCC amount is increased.

With the above in mind the results obtained in the first approach involving post refining are discussed below. The results using blends of ozonated OCC with prerefined virgin kraft are discussed in the next section of the report.

For this phase OCC was disintegrated, fluffed, and ozonated to the 2.5% and 4.5% levels according to the previously established procedures. The ozonated OCC was blended with the virgin kraft in a 60:40 virgin:ozonated OCC ratio prior to refining. Ozonation levels based on total fiber corresponded to 1.0% and 1.9%, respectively. Standard beater runs were carried out.

Results are shown in Table IV. Graphs of burst, tensile, tear, and modified ring vs. freeness are shown in Fig. 17 through 20. In virtually all cases the untreated OCC/kraft blend developed strengths equal to or slightly better than the ozonated OCC/kraft blends at a given freeness level.

Figures 21 through 25 show the relationship of various physical properties to refining interval. One feature stands out, namely, beating interval. Therefore, presumably, the refining energy required to reach a given physical property level is substantially reduced. Because the kraft is comparable in each case it may be hypothesized that the ozonated OCC fiber is modified to an easier beating pulp. Thus beating of the blend becomes increasingly unattractive as a means for achieving the best overall strength.

A review of the SEM fiber surface studies provides an explanation for the refining effects. Microfibrillation originating from ozonation appears to be lightly bound to the parent fiber surface. Thus it is possible that intensive mechanical treatment could remove the microfibrils from the fiber surface. Fines generation could occur without necessarily any increase in strength properties. The pitting or erosion also observed on the fiber surface after ozonation suggests penetration of the fiber and swelling can more readily occur at least for some limited fiber wall depth. This potentially more porous wall would likely be more amenable to modification by both mechanical action, viz. the physical forces of refining, and penetration of fluids for initiation of swelling. Thus it is speculated that the initial surface generated by the ozone treatment is being destroyed by the Valley beater action. However, the ozonation treatment itself provided a limited fiber subsurface readily amenable to

TABLE IV

EFFECTS OF REFINING 60:40 KRAFT:OZONATED OCC BLENDS ON PHYSICAL PROPERTIES

Ozone Consumed, %		% C.S. Freeness, mL	Basis Wt., lb/M ft^2	Caliper, mils	Apparent Density	Burst Factor[a]	Mod. Ring Comp. Factor[a]	Tear Factor[a]	Tensile Factor[a]	Stretch, %	Et Factor[a]	TEA, ft-lb/ft^2	Concora, psi[b]
0 Minute Beating													
0.0	0.0	740	13.3	6.1	2.17	0.80	0.260	7.67	0.66	1.36	101.0	1.0	7.2
2.43	1.01	730	13.7	6.4	2.12	0.92	0.256	7.90	0.69	1.44	99.3	1.1	9.1
4.64	1.86	725	13.3	5.8	2.30	1.12	0.285	9.34	0.83	1.73	122.0	1.7	10.1
10 Minutes Beating													
0.0	0.0	710	13.2	5.3	2.50	1.77	0.308	8.30	1.16	1.93	143.7	2.5	13.7
2.43	1.01	660	13.3	5.1	2.59	2.09	0.308	8.85	1.28	2.03	152.9	2.9	19.2
4.64	1.86	645	13.4	5.2	2.59	2.24	0.325	8.12	1.35	2.10	156.9	3.3	21.0
20 Minutes Beating													
0.0	0.0	645	13.4	5.0	2.68	2.38	0.339	7.25	1.41	2.23	155.3	3.6	21.7
2.43	1.01	535	13.3	4.9	2.73	2.57	0.348	7.88	1.54	2.37	167.8	4.1	27.1
4.64	1.86	495	13.7	4.9	2.81	2.92	0.346	7.29	1.62	2.39	174.5	4.7	31.4
30 Minutes Beating													
0.0	0.0	520	13.4	4.6	2.87	2.75	0.341	6.92	1.62	2.45	170.7	4.5	29.4
2.43	1.01	330	13.5	4.6	2.91	3.10	0.352	7.23	1.76	2.63	180.4	5.3	30.1
4.64	1.86	320	13.3	4.6	2.91	3.07	0.350	6.19	1.76	2.61	182.1	5.3	30.8
45 Minutes Beating													
0.0	0.0	290	12.3	4.1	2.97	3.23	0.330	5.90	1.91	2.74	189.6	5.4	31.4
2.43	1.01	180	13.0	4.2	3.08	3.49	0.345	5.59	1.96	2.63	195.9	5.7	31.5
4.64	1.86	120	13.1	4.2	3.08	3.45	0.359	5.74	1.89	2.44	197.6	5.3	32.5
100% Virgin Kraft													
5 min beating		758	13.5	6.2	2.16	1.26	0.288	11.07	0.90	1.44	128.0	1.4	8.2
20 min beating		720	14.0	5.6	2.50	2.16	0.342	8.88	1.31	1.94	148.2	2.9	16.8
35 min beating		640	13.6	5.1	2.67	2.74	0.350	7.72	1.59	2.46	163.0	4.4	26.5
50 min beating		430	13.4	4.6	2.86	3.26	0.376	6.44	1.84	2.70	177.6	5.6	30.9
60 min beating		255	13.5	4.5	3.00	3.54	0.377	5.55	1.98	2.63	187.4	5.8	30.3

[a]Factors were determined by dividing the given property value by basis weight in lb/M ft^2.
[b]Concora test made on special 26 lb handsheets.

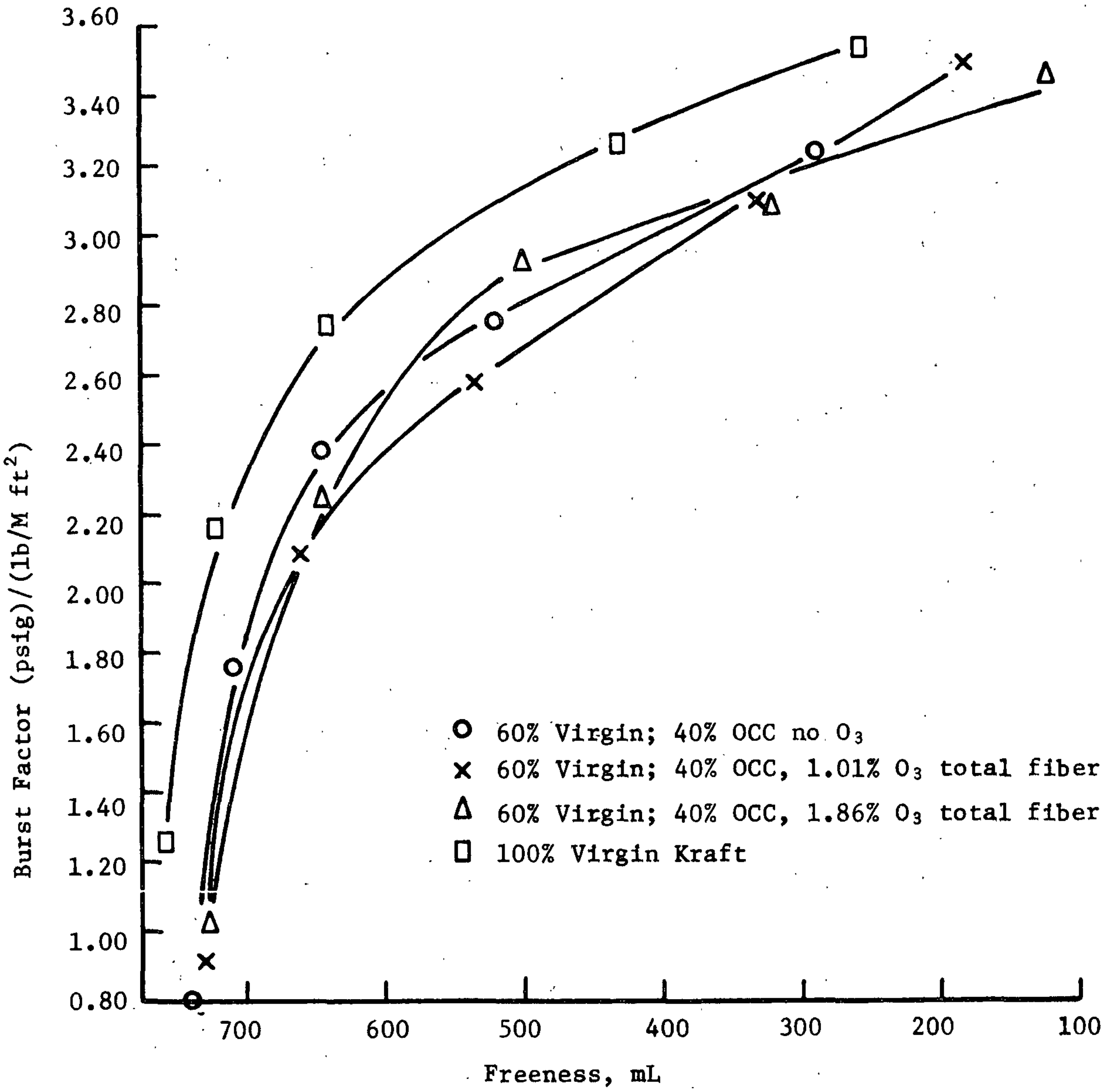


Figure 17. Burst Trends when Virgin Kraft/Ozonated OCC Blends are Refined Together

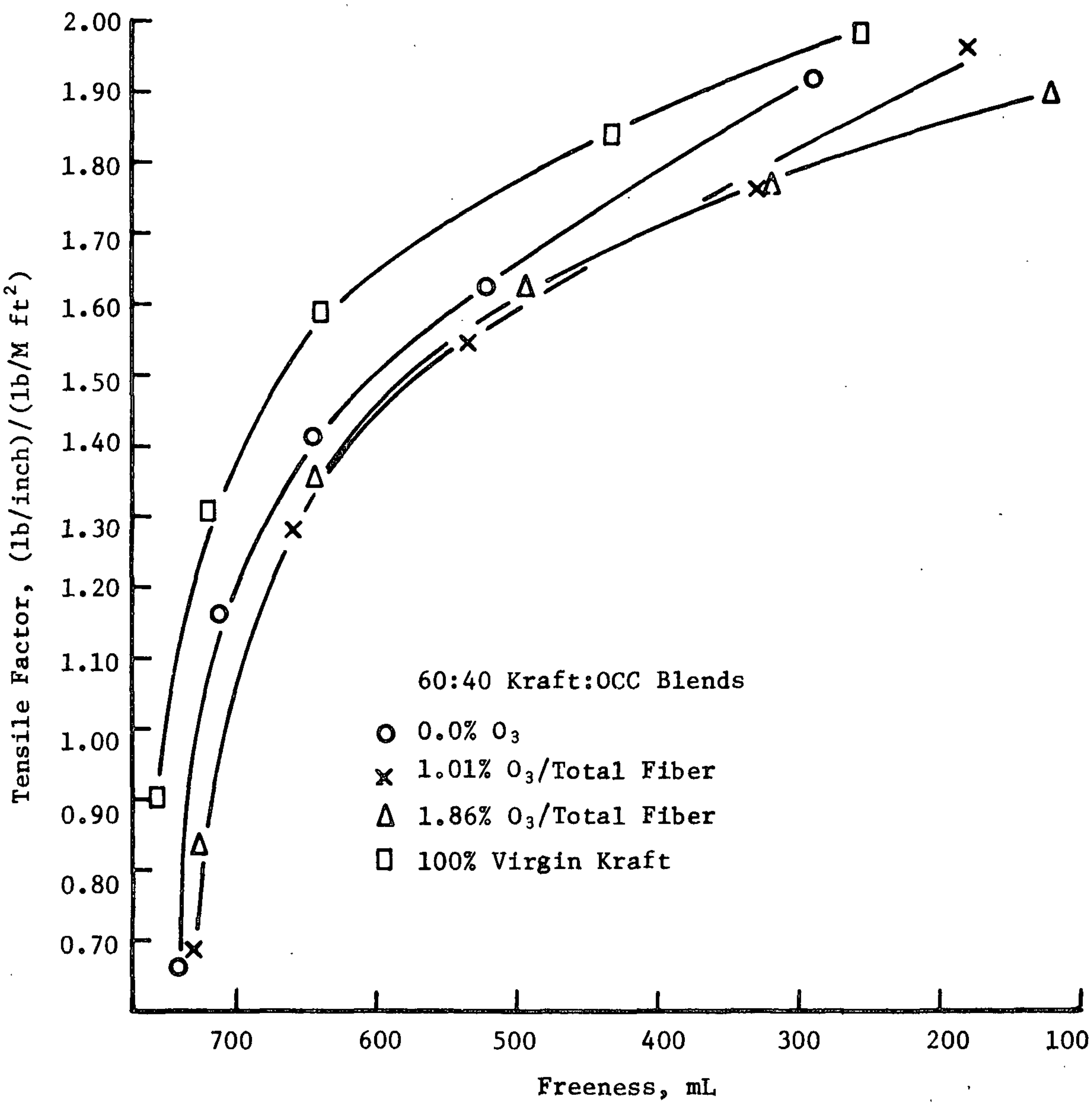


Figure 18. Tensile Trends when Virgin Kraft/Ozonated OCC Blends are Refined Together

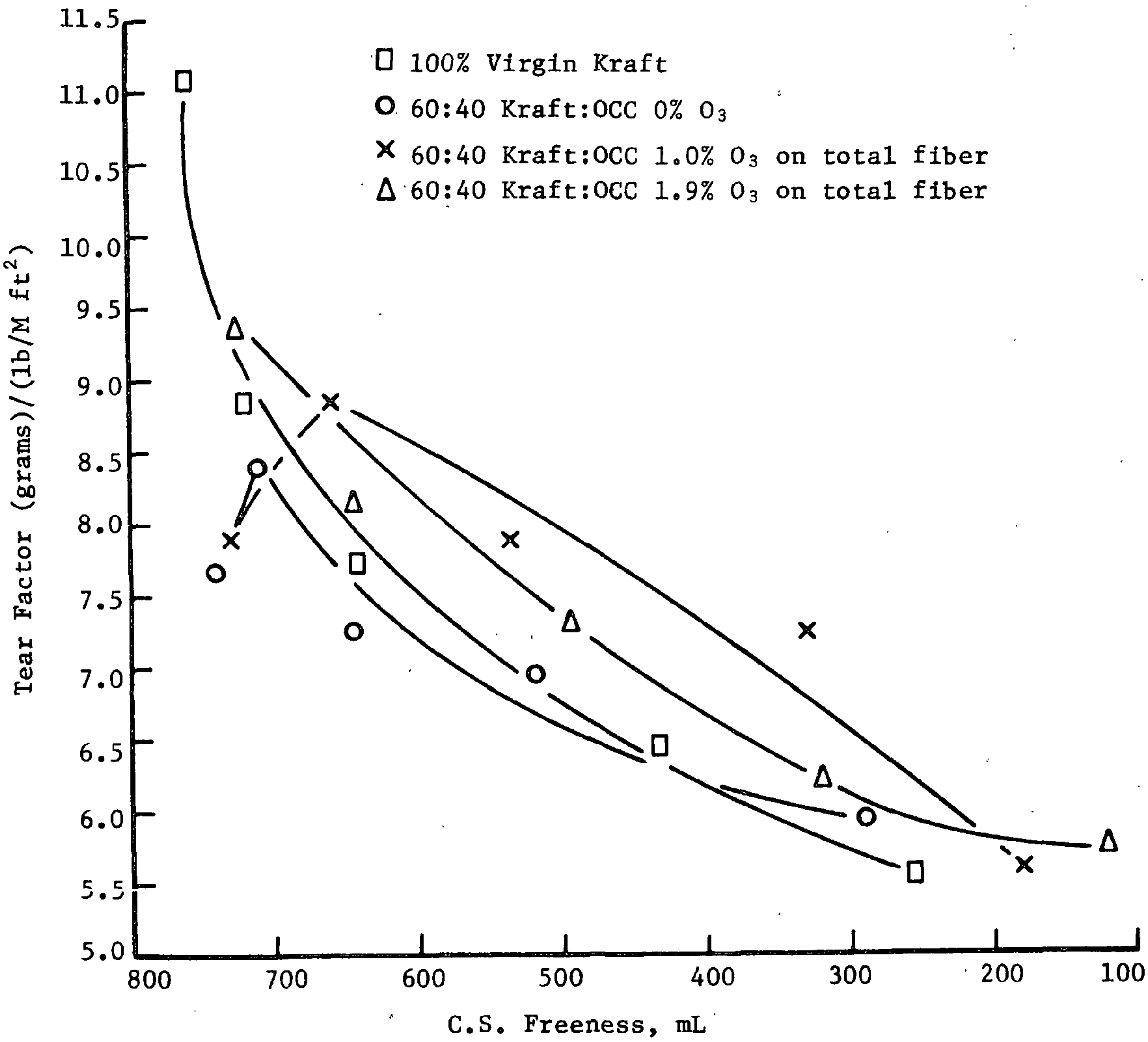


Figure 19. Tear Trends when Virgin Kraft/Ozonated OCC Blends are Refined Together

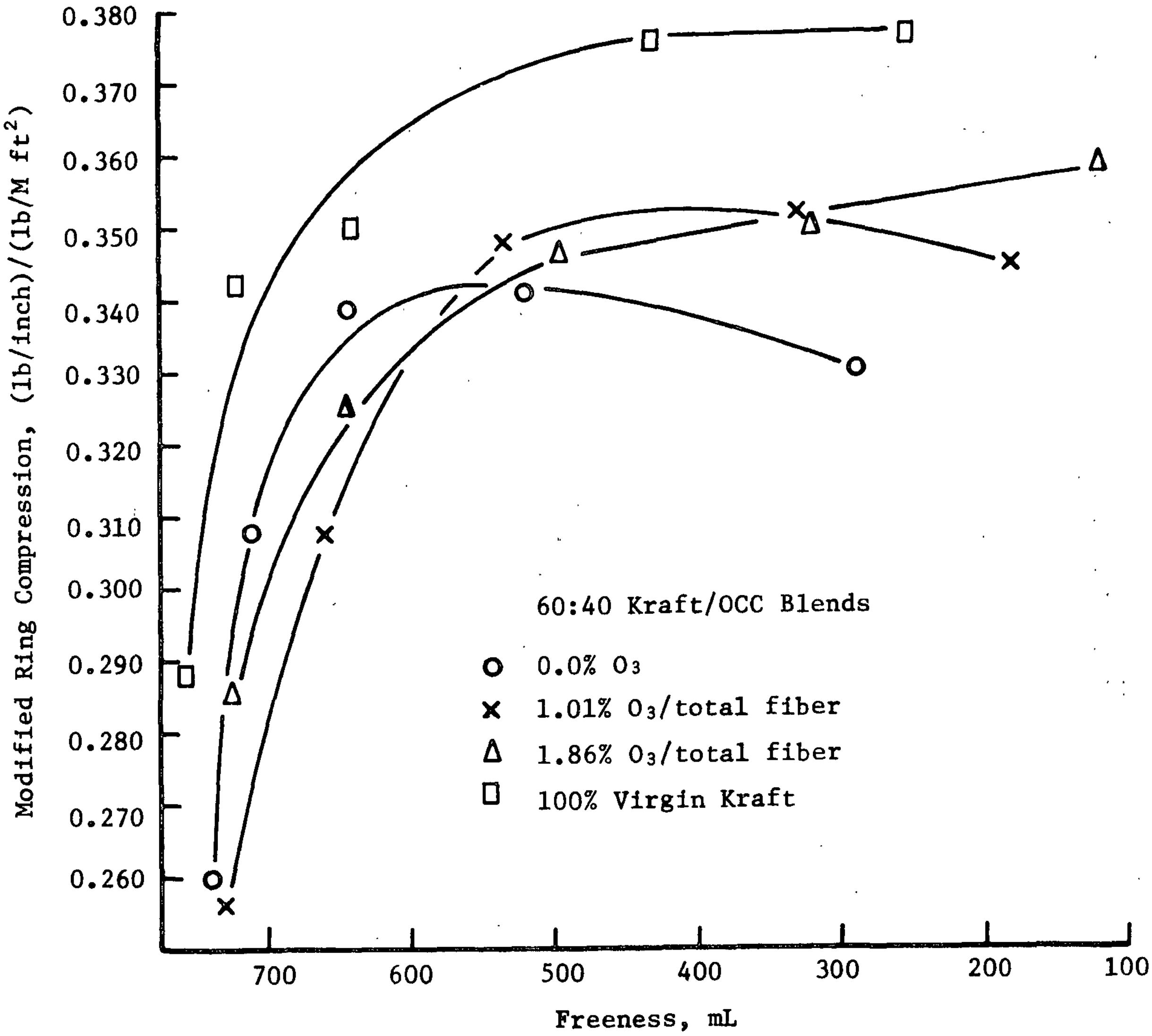


Figure 20. Modified Ring Compression Trends when Virgin Kraft/Ozonated OCC Blends are Refined Together

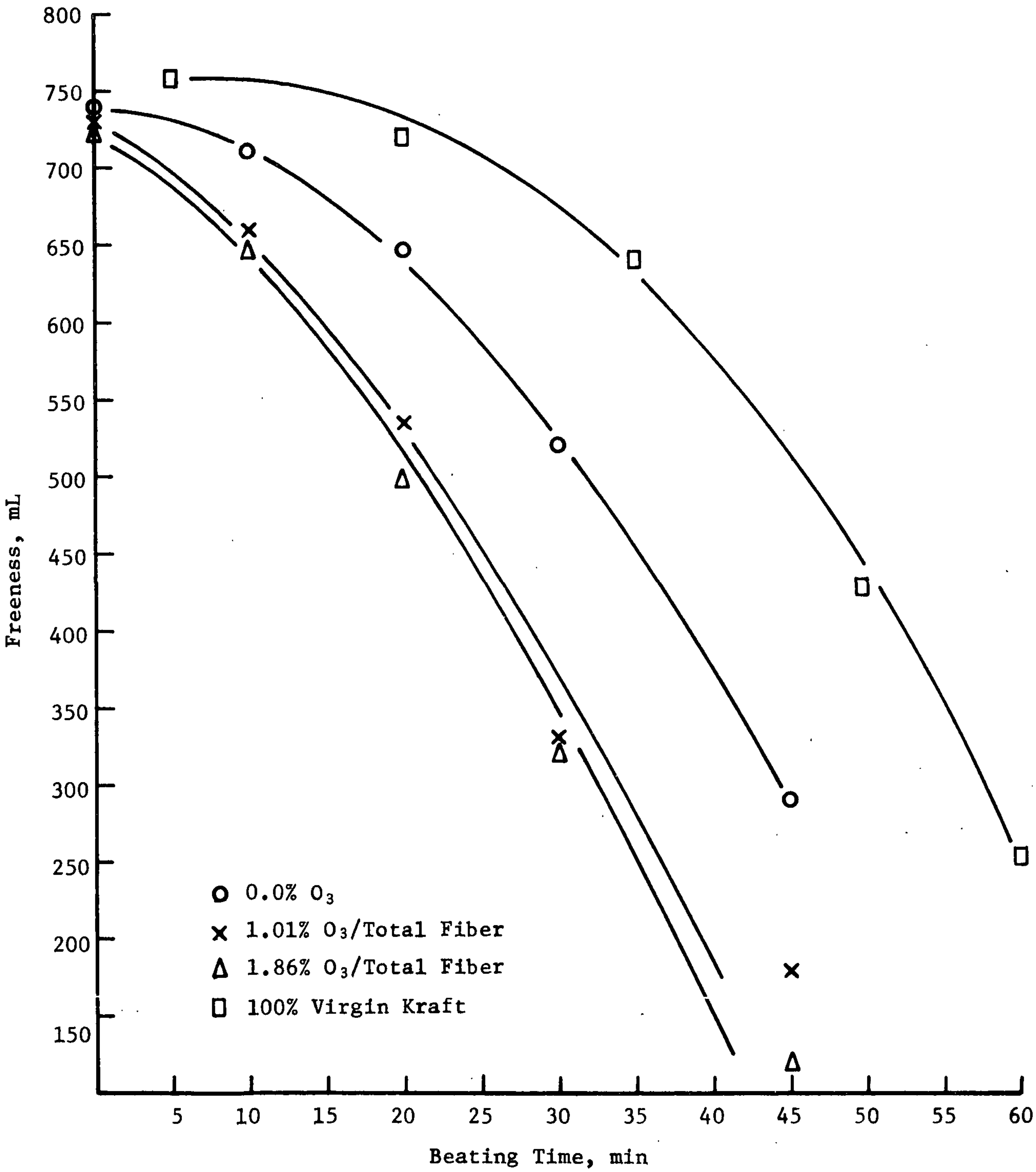


Figure 21. Freeness Trends vs. Refining Energy Consumed for Virgin Kraft/Ozonated OCC Blends

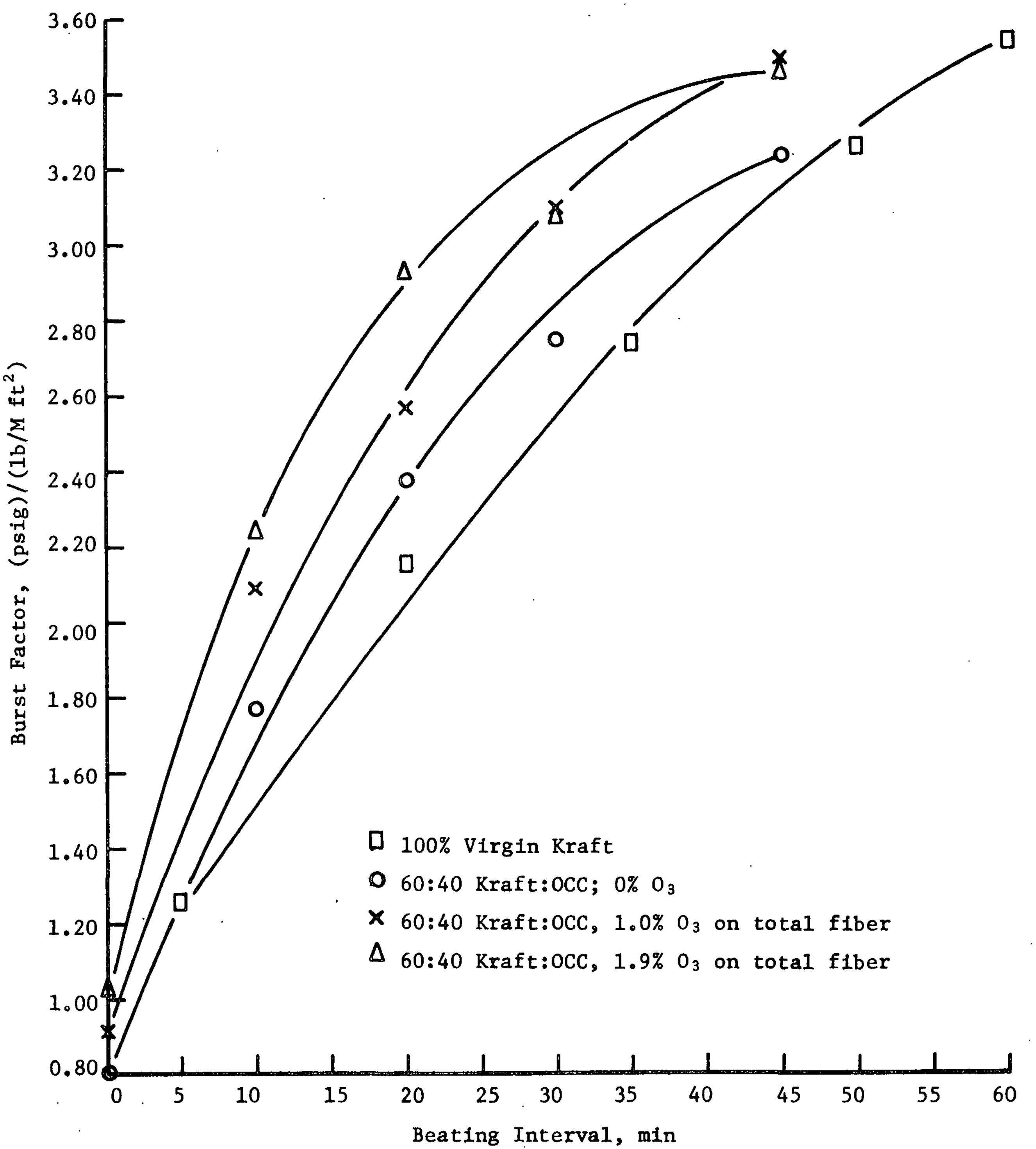


Figure 22. Burst Development vs. Refining Energy Consumed for Virgin Kraft/Ozonated OCC Blends

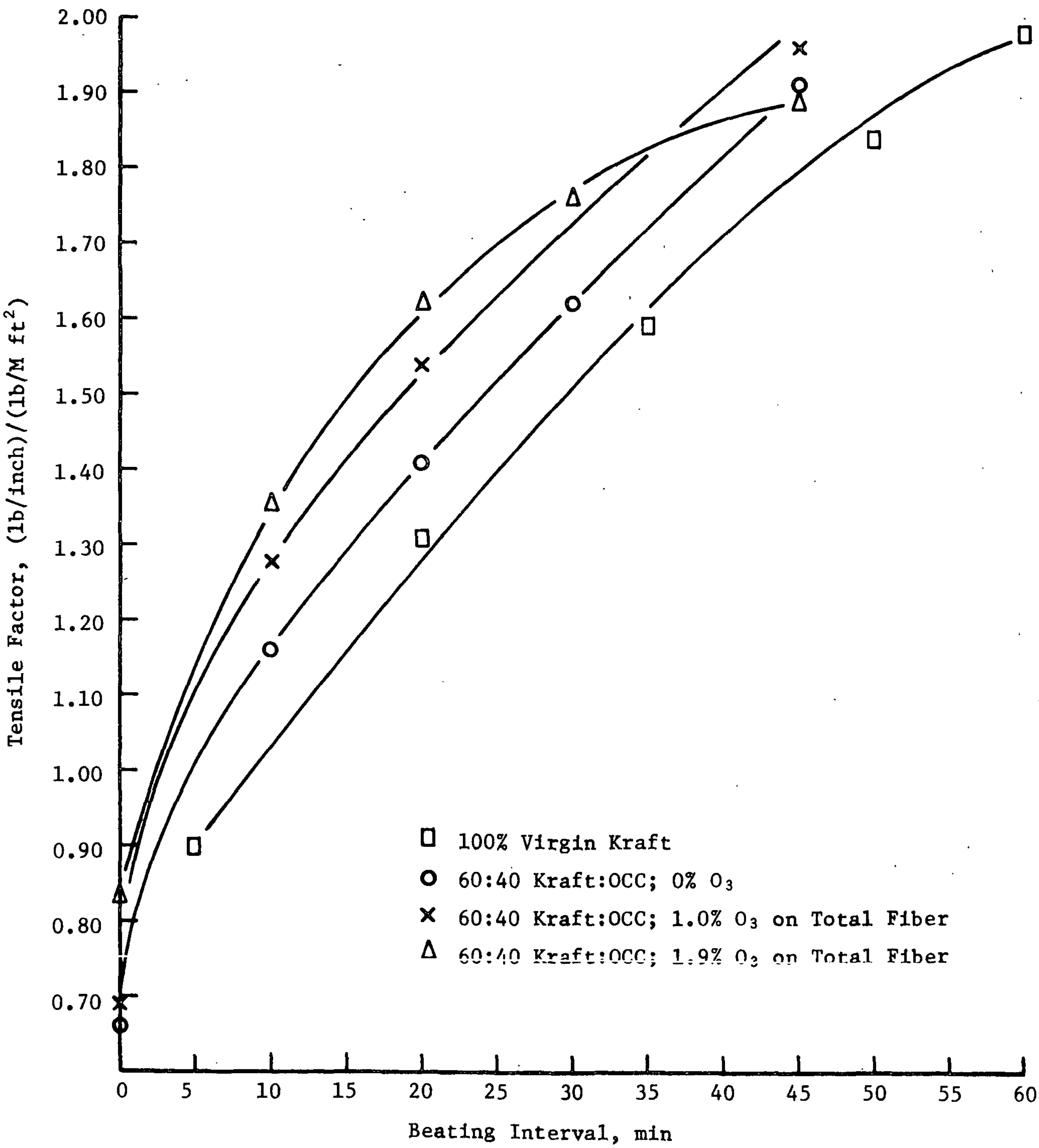


Figure 23. Tensile Trends vs. Refining Energy Consumed for Virgin Kraft/Ozonated OCC Blends

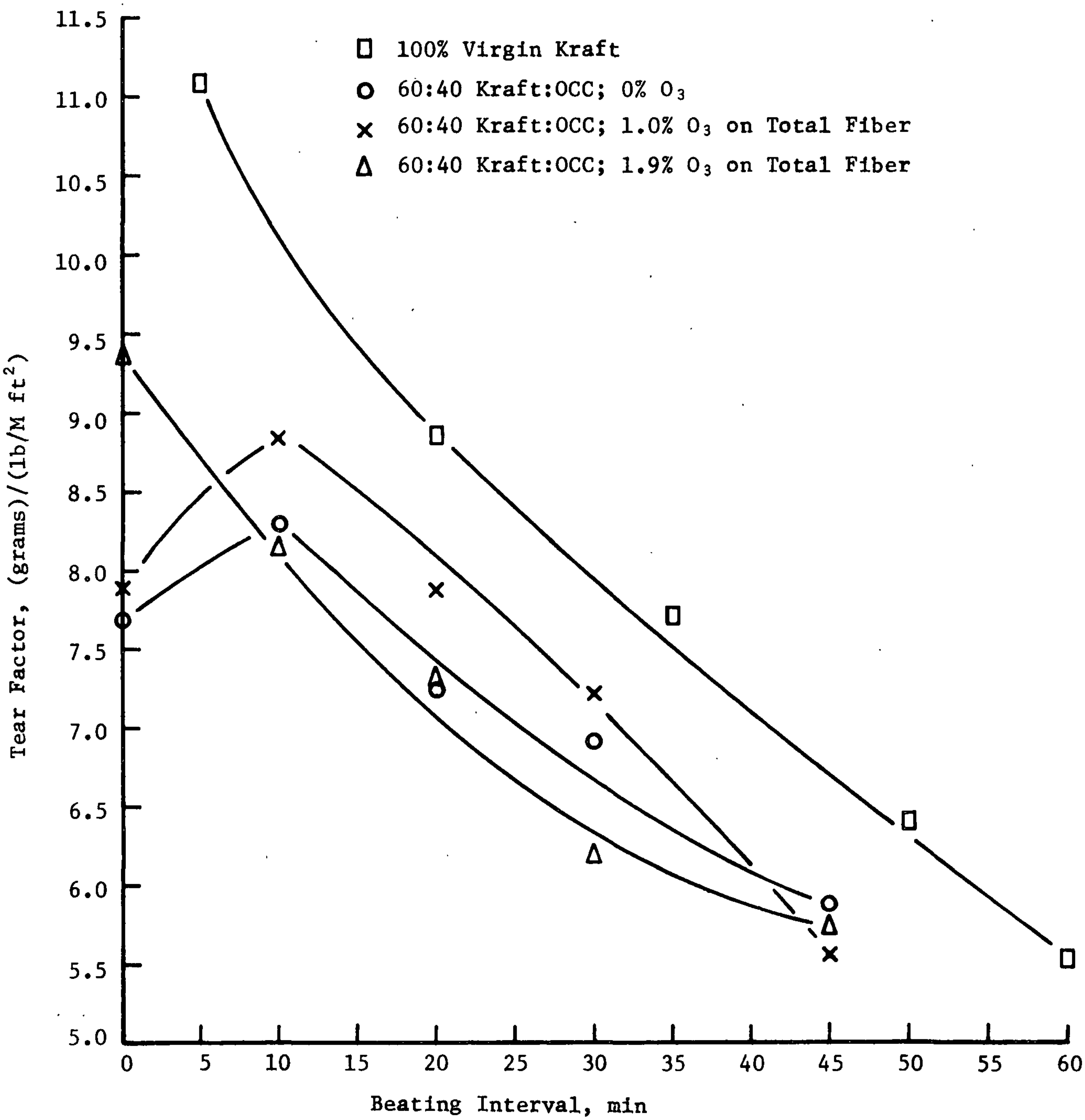


Figure 24. Tear Trends vs. Refining Energy Consumed for Virgin Kraft/Ozonated OCC Blends

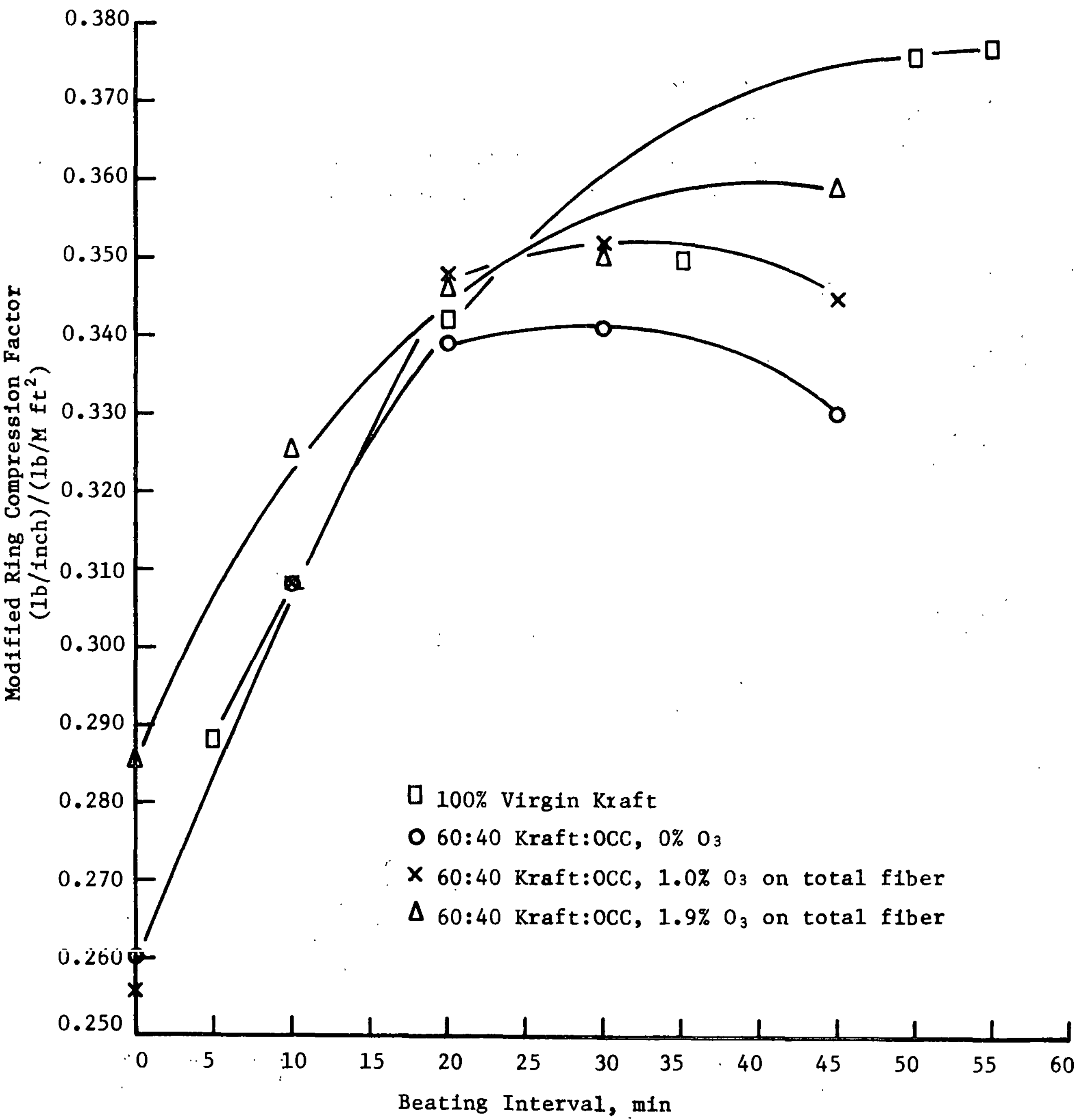


Figure 25. Modified Ring Trends vs. Refining Energy Consumed for Virgin Kraft/Ozonated OCC Blends

refining. The result is a trade off with physical properties and freeness similar to that expected by mechanical refining alone; but the refining energy required to achieve these conditions is very substantially reduced.

Figure 26 shows that the ozonated blends exhibit slightly lower densities at a given freeness than the untreated stock. It appears that the ozonated blends would require more pressing to obtain densities equal to the untreated blend. The burst results in Fig. 27 indicate that the ozonated blends tend to have a somewhat higher bursting strength than the untreated blend in the mid-density range. This effect is more evident at the higher ozonation level where the bursting strength results were about midway between the results for the untreated blend and the 100% virgin kraft.

Figure 28 shows that the ozonated blends exhibit higher tensile strengths than the untreated 60:40 blend at a given tearing strength. After the initial beating interval the tensile strengths achieved with the ozonated blends approached those obtained with the 100% virgin kraft at a given tearing strength.

The edgewise compression strengths of the ozonated blends were about the same as obtained with the untreated blend at constant density (Fig. 29). Figure 30 shows that the ozonated blend at the lower treatment level exhibited higher bursting strength at a given compression strength than the untreated blend or virgin kraft pulp over the initial portions of the burst range.

The above results suggest there may be trade-offs between burst and edgewise compression, tensile and tear using the ozonated blends. This may depend in part on the wet pressing or density target levels.

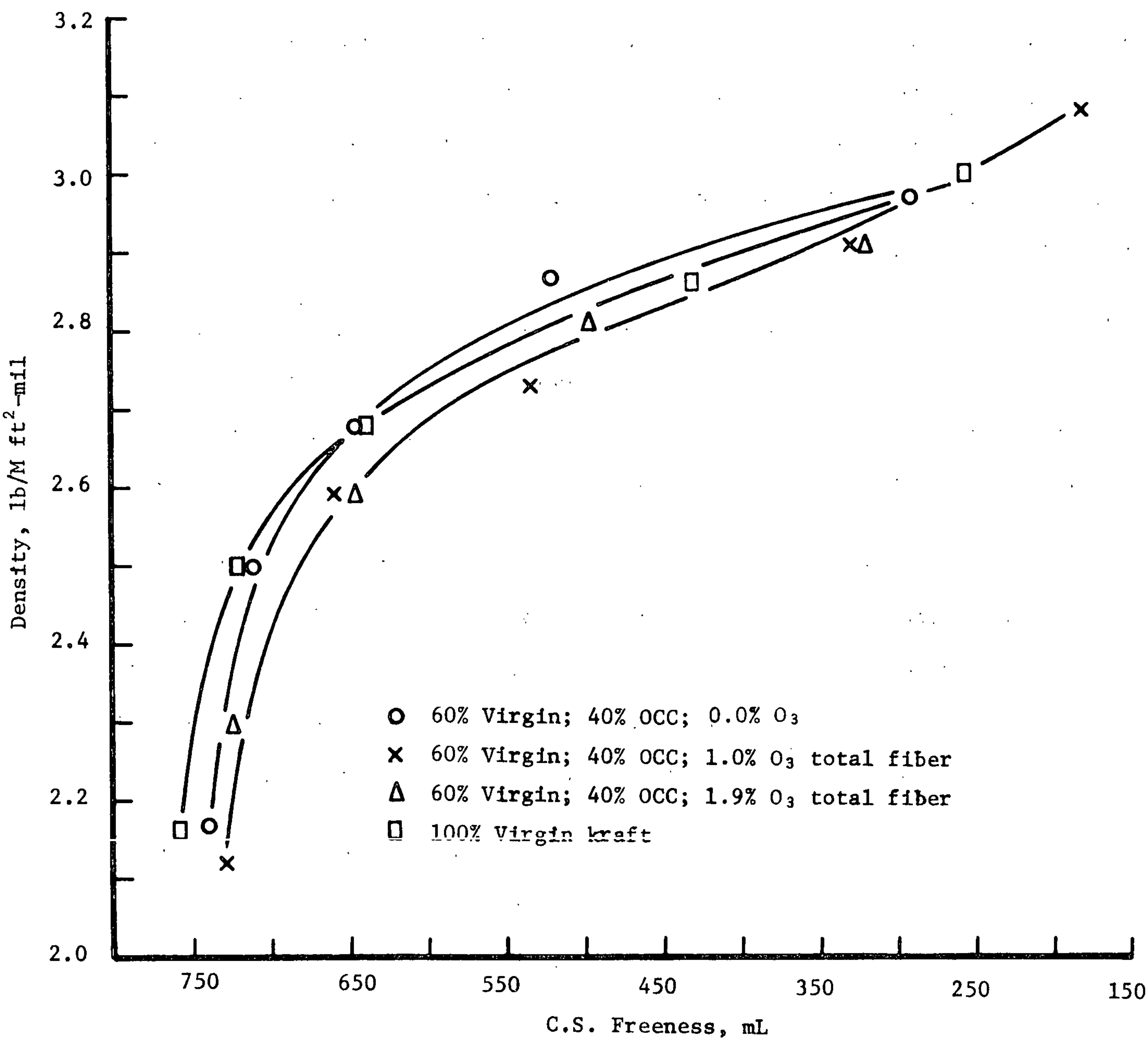


Figure 26. Density *vs.* Freeness for Post-Refined Blends

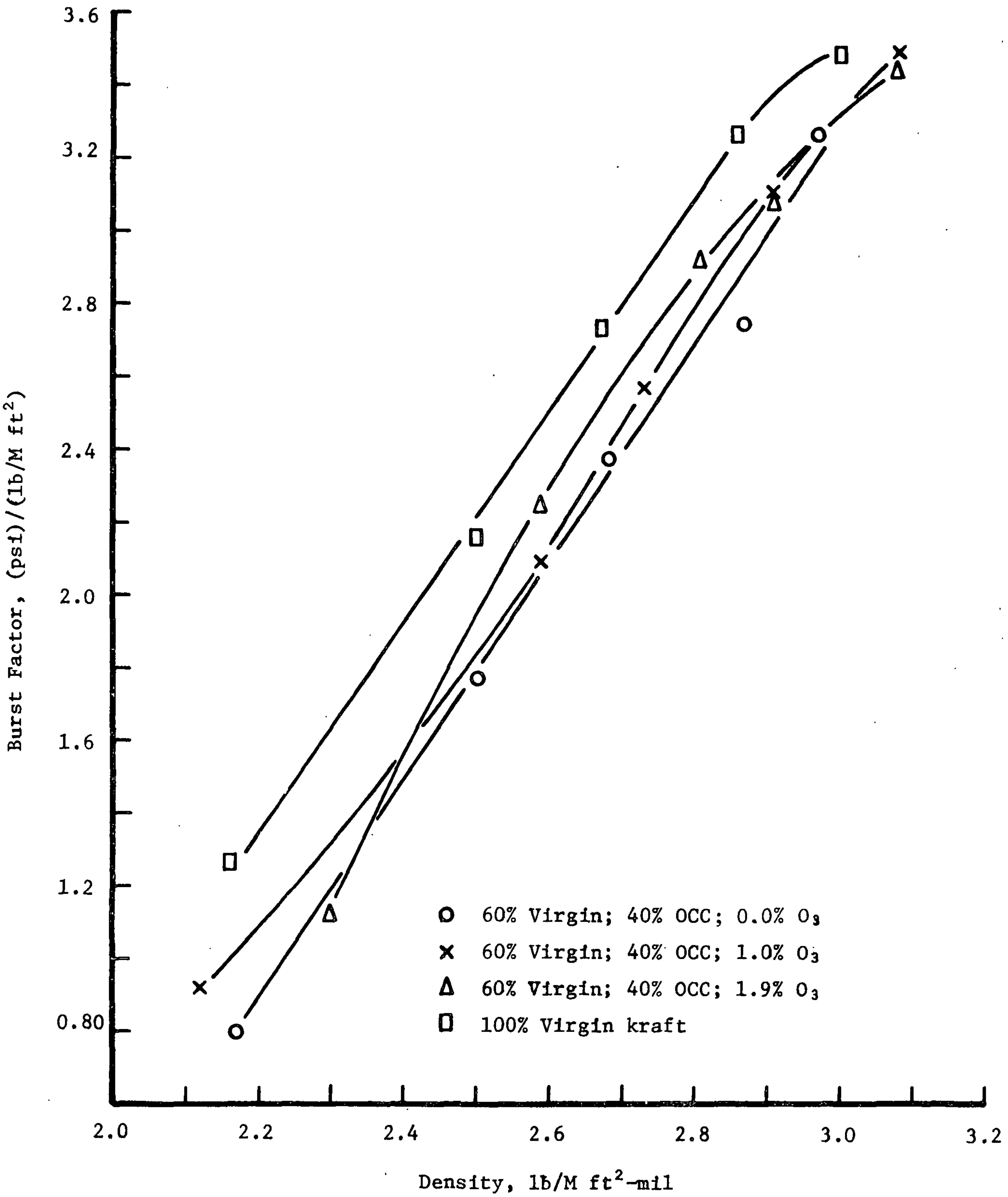


Figure 27. Burst *vs.* Density for Post-Refined Blends

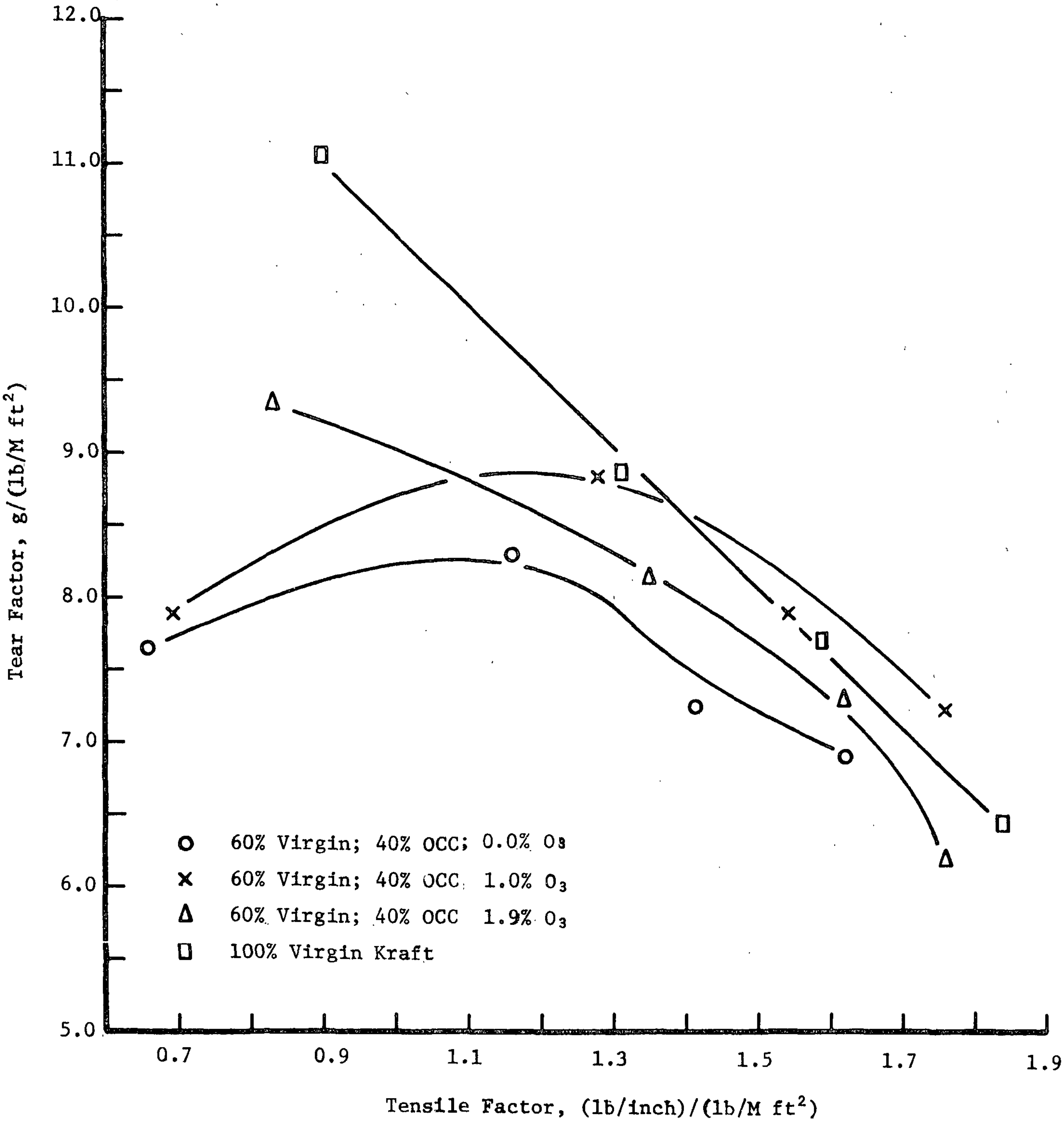


Figure 28. Tensile *vs*. Tear for Post-Refined Blends

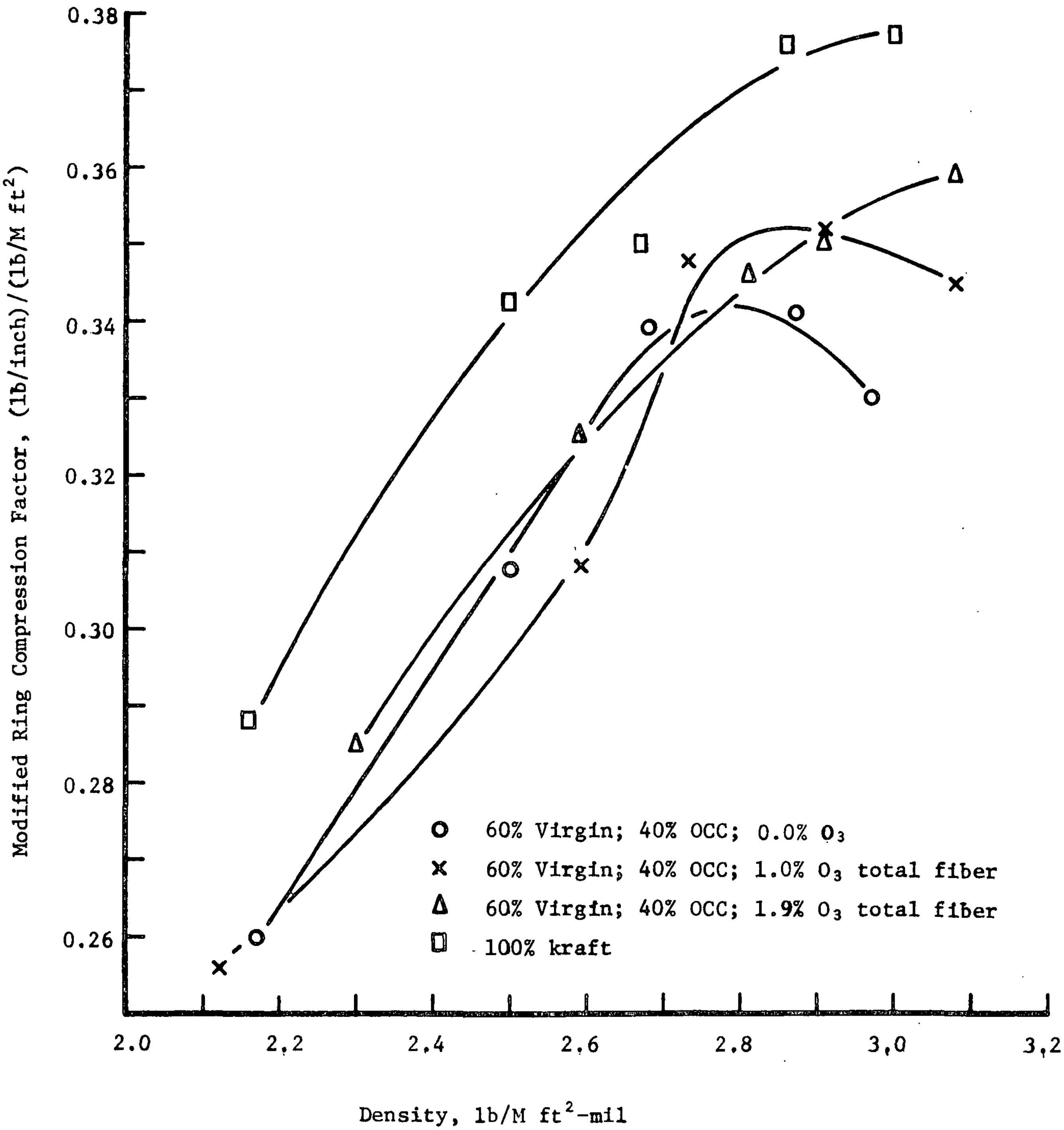


Figure 29. Edgewise Compression Strength *vs*. Density for Post-Refined Blends

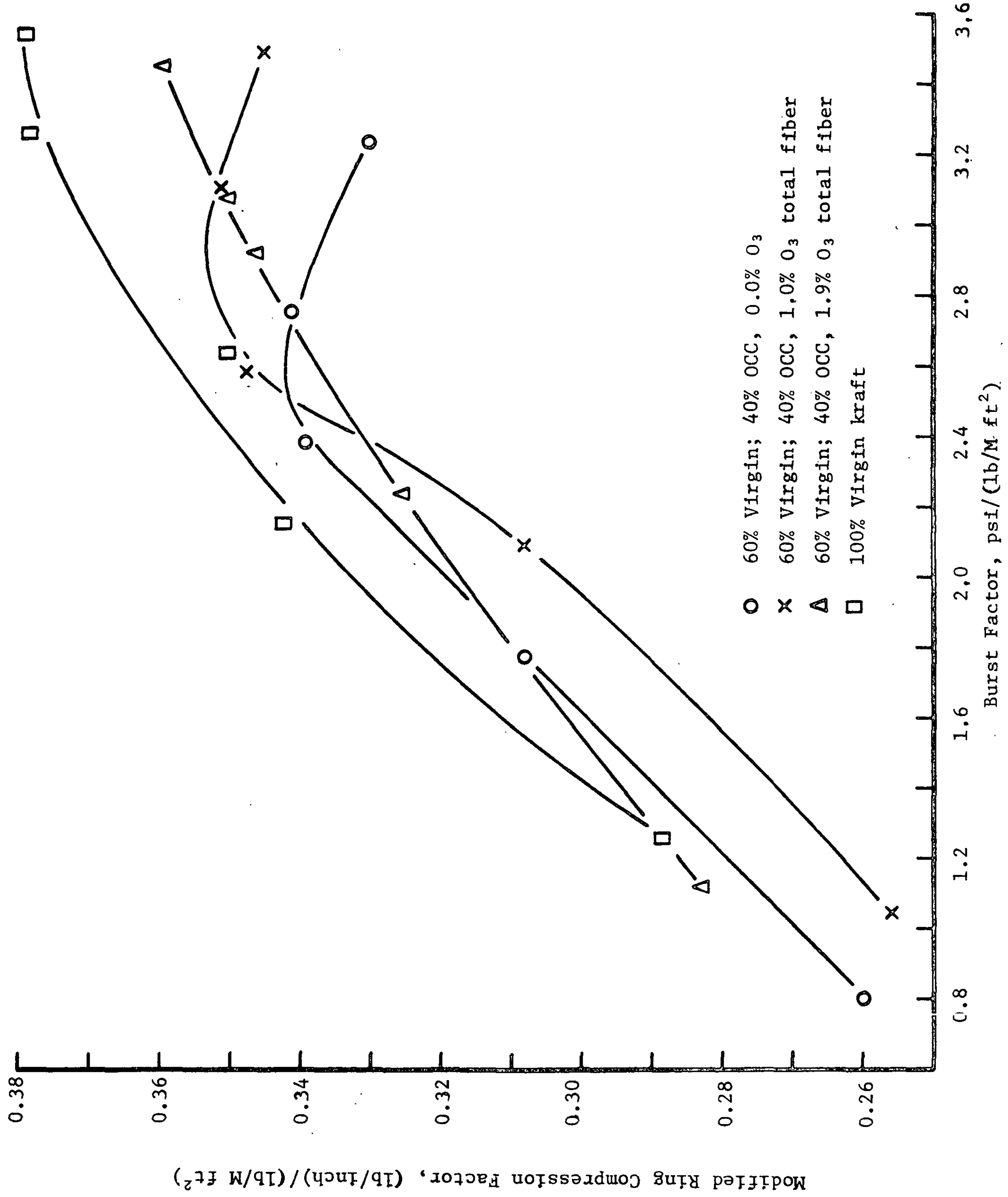


Figure 30. Burst vs. Compression for Post-Refined Stocks

BLENDING OF OZONATED OCC WITH PREREFINED VIRGIN KRAFT

As mentioned, this phase was undertaken to examine the effects of adding ozonated OCC to prerefined virgin kraft pulp. The kraft pulp was refined to two freenesses — 730 and 630 CSF. These freenesses were arbitrarily selected to maintain high drainage levels. OCC was prepared and ozonated to three levels approximating 2.5, 4.7, and 8.7% ozone consumed. The treated OCC was combined with the prerefined kraft prior to handsheet formation in a ratio of 60:40 virgin:OCC. Ozone consumed based on total fiber in the final blend becomes 1.0, 1.9, and 3.5%, respectively. Physical strength properties are shown in Table V. Graphs of burst, tensile, tear, modified ring, and TEA against freeness are shown in Fig. 31 through 33. For comparison, values for 100% OCC refined to similar freenesses are shown in the figures. The values were obtained from the OCC prerefining study (Table III).

The figures show that strength increases are roughly proportional to ozonation level independent of inital virgin kraft freeness for most properties, with the possible exception of the 1.0% ozonation level. Strength increases are more modest than shown in the 100% OCC studies because only 40% of the total furnish was ozonated. For instance, at the 1.9% level (4.7% on OCC) burst increases 19 and 11% for the 730 and 630 CSF kraft OCC combinations, respectively. At the 3.5% ozone level (8.7% O_3 on OCC) the values are 27 and 17%, respectively. When OCC is ozonated burst increases of approximately 35 and 45% at ozonation levels of 2.5 and 3.5%, respectively (from Progress Report One), are obtained. The strength increases are achieved with little or no loss of freeness as occurs in mechanical refining. These results also serve to indicate blending of ozonated OCC with virgin kraft is useful in improving sheet strength contrary to results found when ozonated OCC and kraft are combined prior to refining of the blend.

TABLE V

PROPERTIES OF HANDSHEETS FROM 60:40 BLENDS OF PREREFINED VIRGIN KRAFT AND OZONATED OCC

	100% Virgin Control	60:40 Kraft (730 CSF):OCC Blend				100% Virgin Control	60:40 Kraft (630 CSF):OCC Blend			
Ozone consumed, %										
OCC	—	—	2.51	4.69	8.68	—	—	2.51	4.69	8.68
Blend	—	—	1.00	1.88	3.47	—	—	1.00	1.88	3.47
C.S. freeness, mL	730	690	685	675	670	630	620	590	590	590
% Change[a]	—	—	-0.7	-2.2	-2.9	—	—	-4.8	-4.8	-4.8
Basis weight, lb/M ft^2	12.8	13.4	13.2	13.2	13.3	13.5	13.6	13.7	13.1	13.3
Caliper, points	4.8	5.3	4.9	4.8	4.8	4.7	5.1	5.1	4.7	4.7
Apparent density	2.67	2.50	2.70	2.73	2.78	2.86	2.64	2.71	2.78	2.83
% Change[a]	—	—	+8.0	+9.2	+11.2	—	—	+2.7	+5.3	+7.2
Burst, psig	27.1	23.4	25.8	27.7	29.5	36.4	30.6	32.7	32.9	35.1
Factor[b]	2.12	1.75	1.95	2.09	2.22	2.70	2.26	2.38	2.52	2.64
% Change[a]	—	—	+11.4	+19.4	+26.9	—	—	+5.3	+11.5	+16.8
Modified ring compression, lb/inch	3.8	3.9	4.0	4.4	4.4	4.5	4.4	4.4	4.5	4.6
Factor[b]	0.297	0.296	0.306	0.329	0.334	0.334	0.324	0.324	0.348	0.350
% Change[a]	—	—	+3.4	+11.1	+12.8	—	—	0.0	+7.4	+8.0
Tear, g	116.0	104.8	111.2	105.2	93.6	110.8	103.2	107.2	90.8	85.2
Factor[b]	9.06	7.84	8.40	7.95	7.02	8.22	7.61	7.81	6.94	6.40
% Change[a]	—	—	+7.1	+1.4	-10.5	—	—	+2.6	-8.8	-15.9
Tensile, lb/inch	15.7	15.1	16.2	16.9	17.7	18.8	17.1	18.0	18.6	19.9
Factor[b]	1.22	1.13	1.23	1.28	1.33	1.39	1.26	1.31	1.42	1.49
% Change[a]	—	—	+8.8	+13.3	+17.7	—	—	+4.0	+12.7	+18.3
Stretch, %	2.12	2.12	2.37	2.33	2.40	2.62	2.40	2.51	2.63	2.70
% Change[a]	—	—	+11.8	+9.9	+13.2	—	—	+4.6	+9.6	+12.5
Et, lb/inch	1885	1920	1954	2037	2138	2019	2021	2110	2119	2245
Factor[b]	147.2	143.7	147.6	154.0	160.4	149.8	149.0	153.6	162.1	168.7
% Change[a]	—	—	+2.7	+7.2	+11.6	—	—	+3.1	+8.8	+13.2
TEA, ft-lb/ft^2	2.9	2.7	3.2	3.3	3.5	4.4	3.4	3.8	4.1	4.5
% Change[a]	—	—	+18.5	+22.2	+29.6	—	—	+11.8	+20.6	+13.2
Concora, psi[c]	18.5	17.5	21.6	20.5	25.7	25.4	23.2	26.4	27.1	29.7
% Changed[a]	—	—	+23.4	+17.1	+46.9	—	—	+13.8	+16.8	+28.0

[a]Percent differences are based on 60:40 kraft:untreated OCC blends.
[b]Factors obtained by dividing given property value by basis weight in lb/M ft^2.
[c]Concora test made on special 26 lb handsheets.

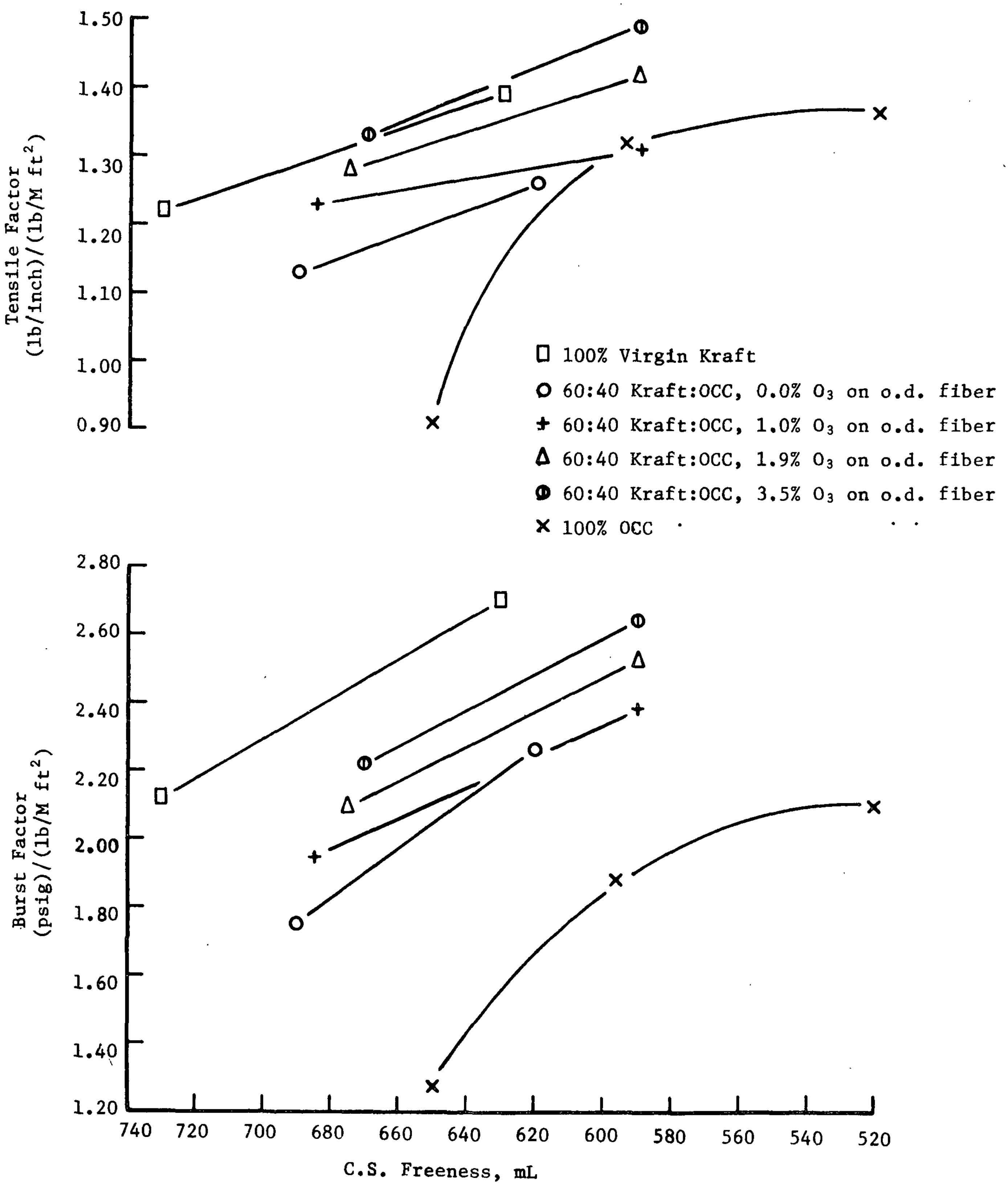


Figure 31. Effects of Blending Ozonated OCC with Prerefined Kraft on Burst and Tensile Properties

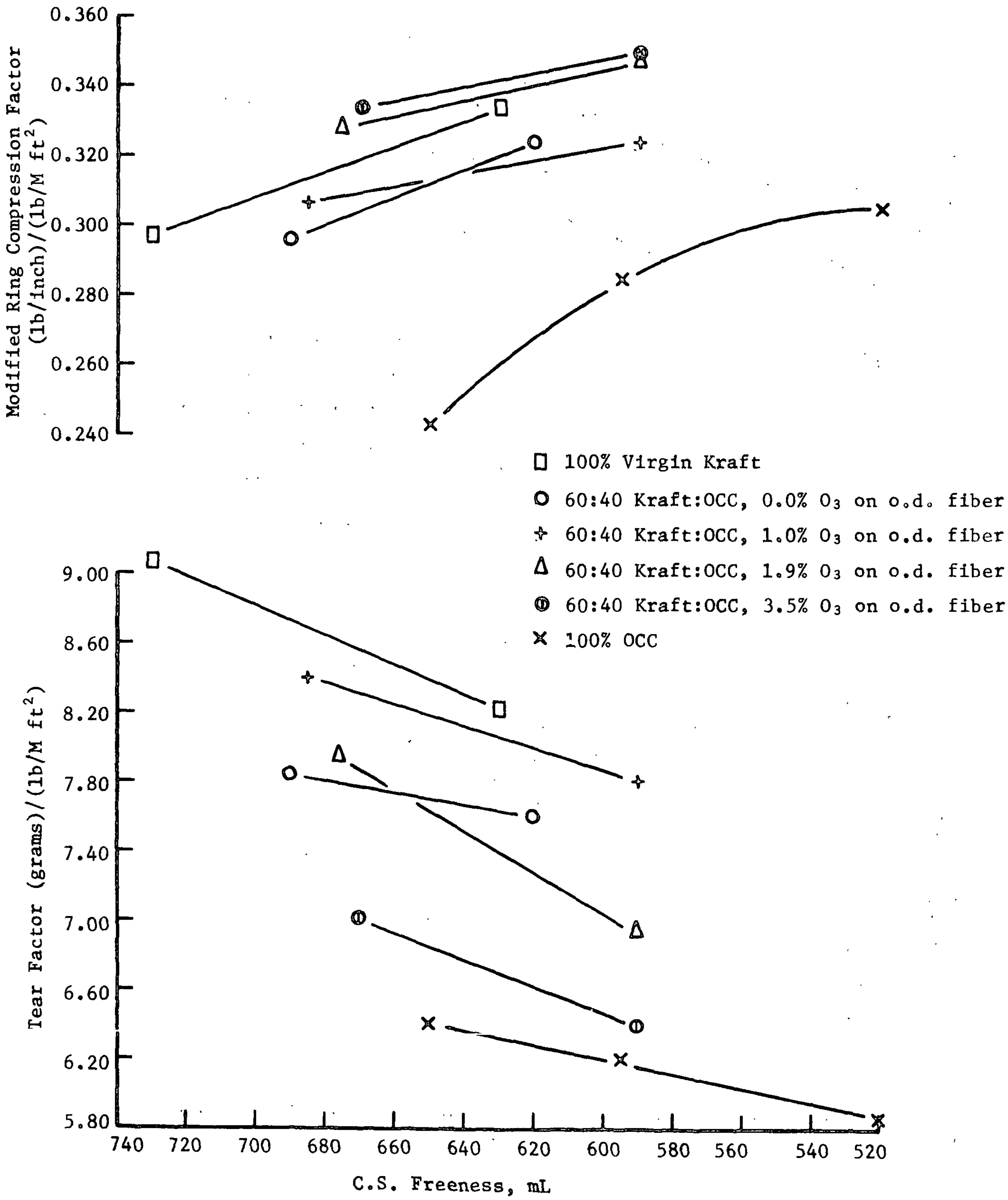


Figure 32. Effects of Blending Ozonated OCC with Prerefined Virgin Kraft on Modified Ring and Tear Properties

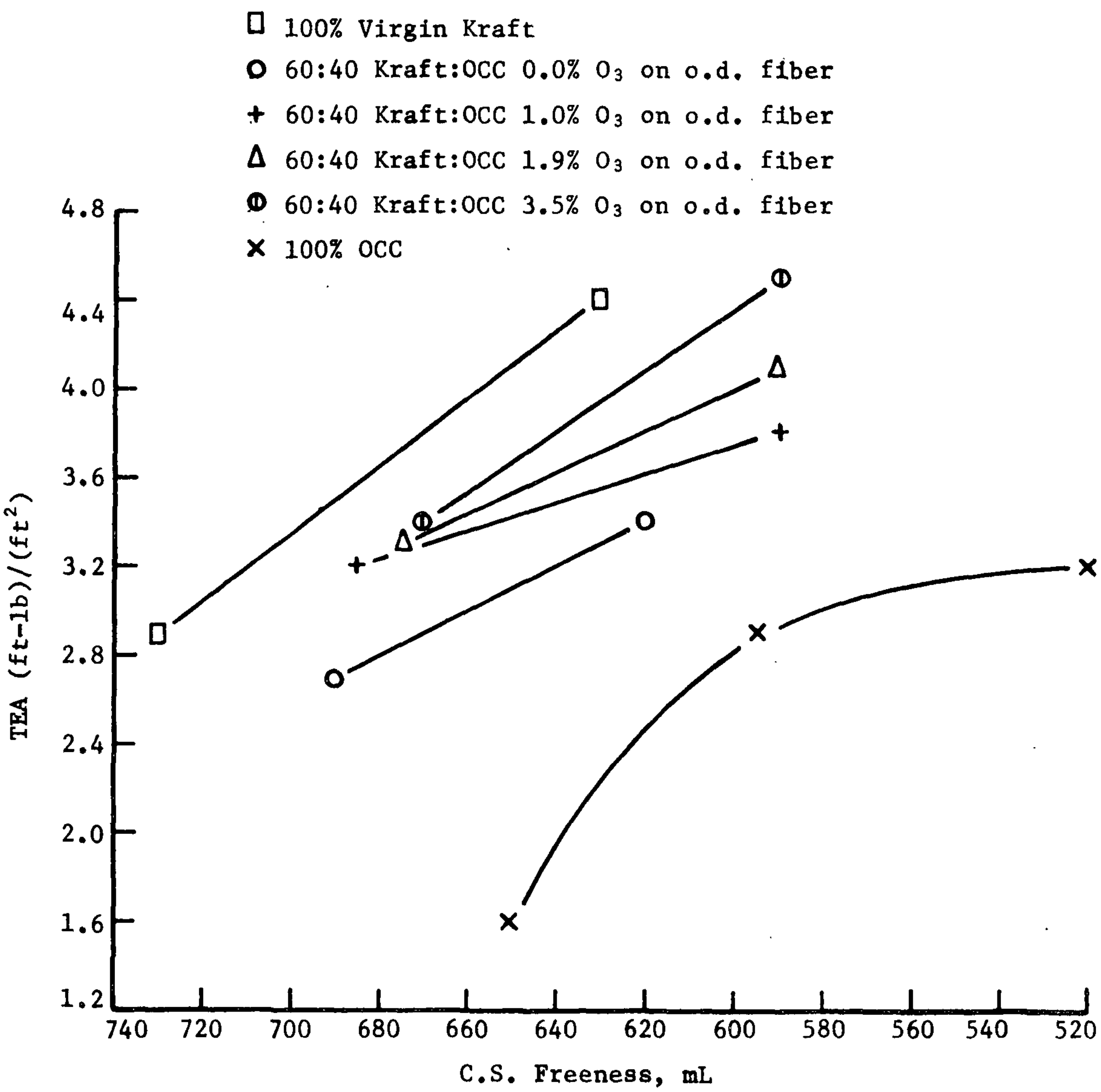


Figure 33. Effects of Blending Ozonated OCC with Prerefined Kraft on Tensile Energy Absorption

The burst and edgewise compression factors are plotted vs. density in Fig. 34 and 35. Ozonation of the OCC fraction of the blend increased the density and bursting strength at each of the two virgin kraft prerefining levels. For example, using virgin kraft refined to 730 mL, the percentage improvements in burst were 11.4 and 19.4% at O_3 levels of 1.0 and 1.9% of total fiber (2.5 and 4.7 O_3 on OCC), respectively. At the prerefining level of 630 mL, the O_3 treatment increased burst but the percentage improvements were lower. It should be kept in mind that the OCC received no refining in these trials. Some refining of the OCC prior to O_3 treatment should produce larger burst changes but with some loss of freeness. The edgewise compression results in Fig. 35 show similar effects.

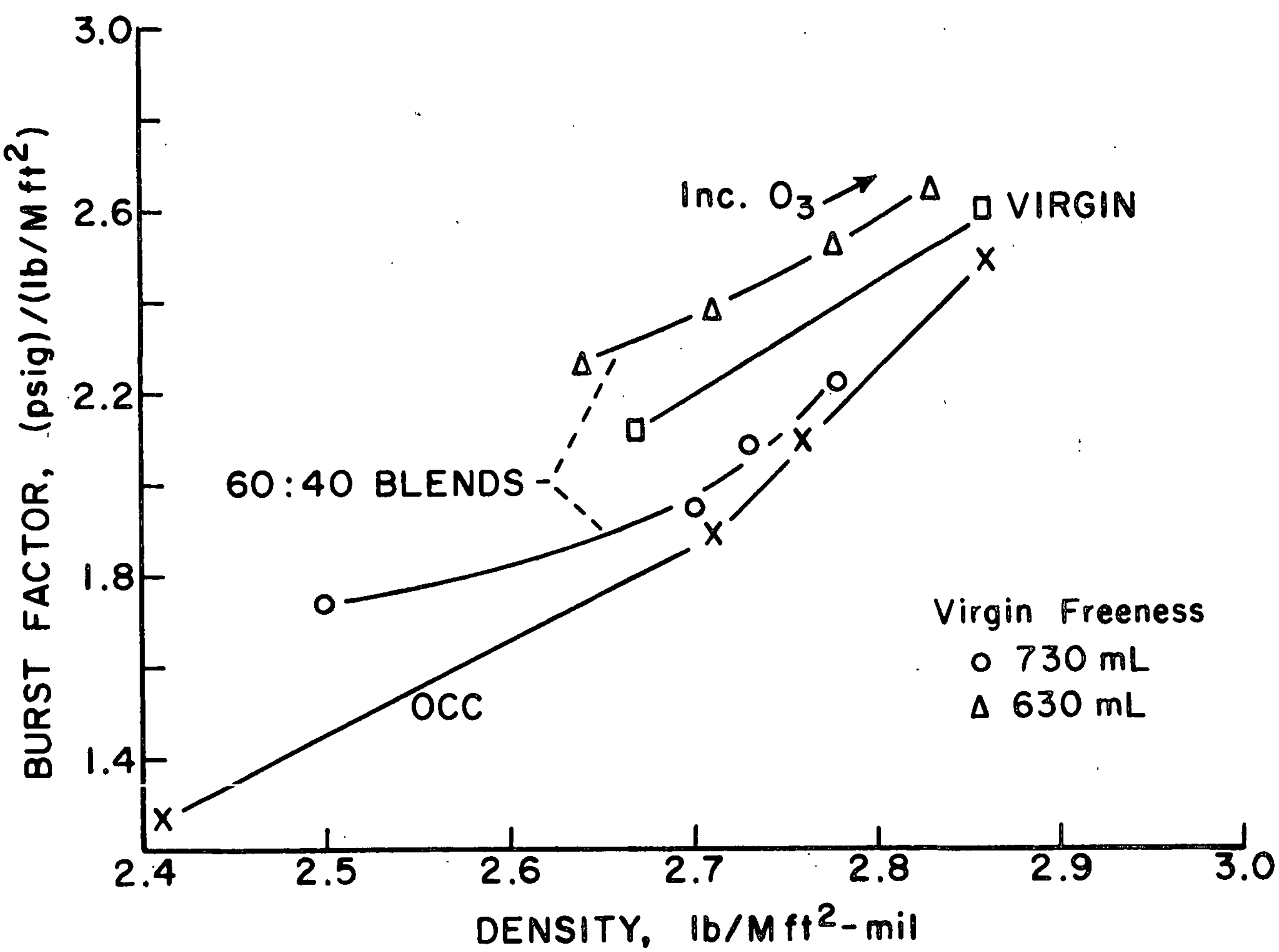


Figure 34. Burst vs. Density on Blends of Ozonated OCC with Prerefined Virgin Kraft

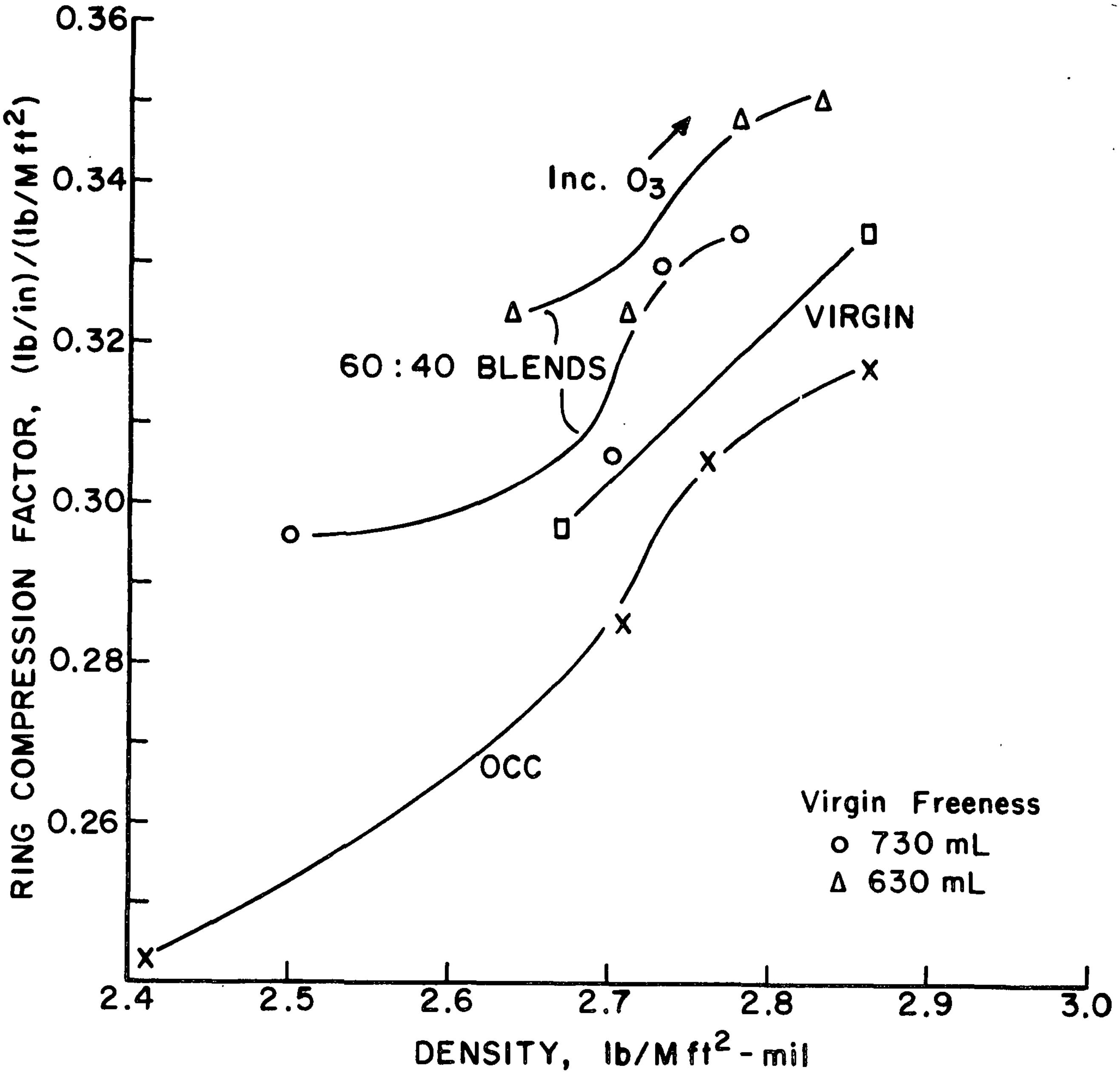


Figure 35. Edgewise Compression Strengths vs. Density on Blends of Ozonated OCC with Prerefined Virgin Kraft

Figure 36 shows that ozonation simultaneously increases the burst and compression strengths of the blends. In general, the blends show slightly higher edgewise compression strengths at a given burst level. Relatively large amounts of O_3 would be required to approximately equal the burst strengths of the virgin kraft pulp at this blend ratio without doing some refining work on the OCC.

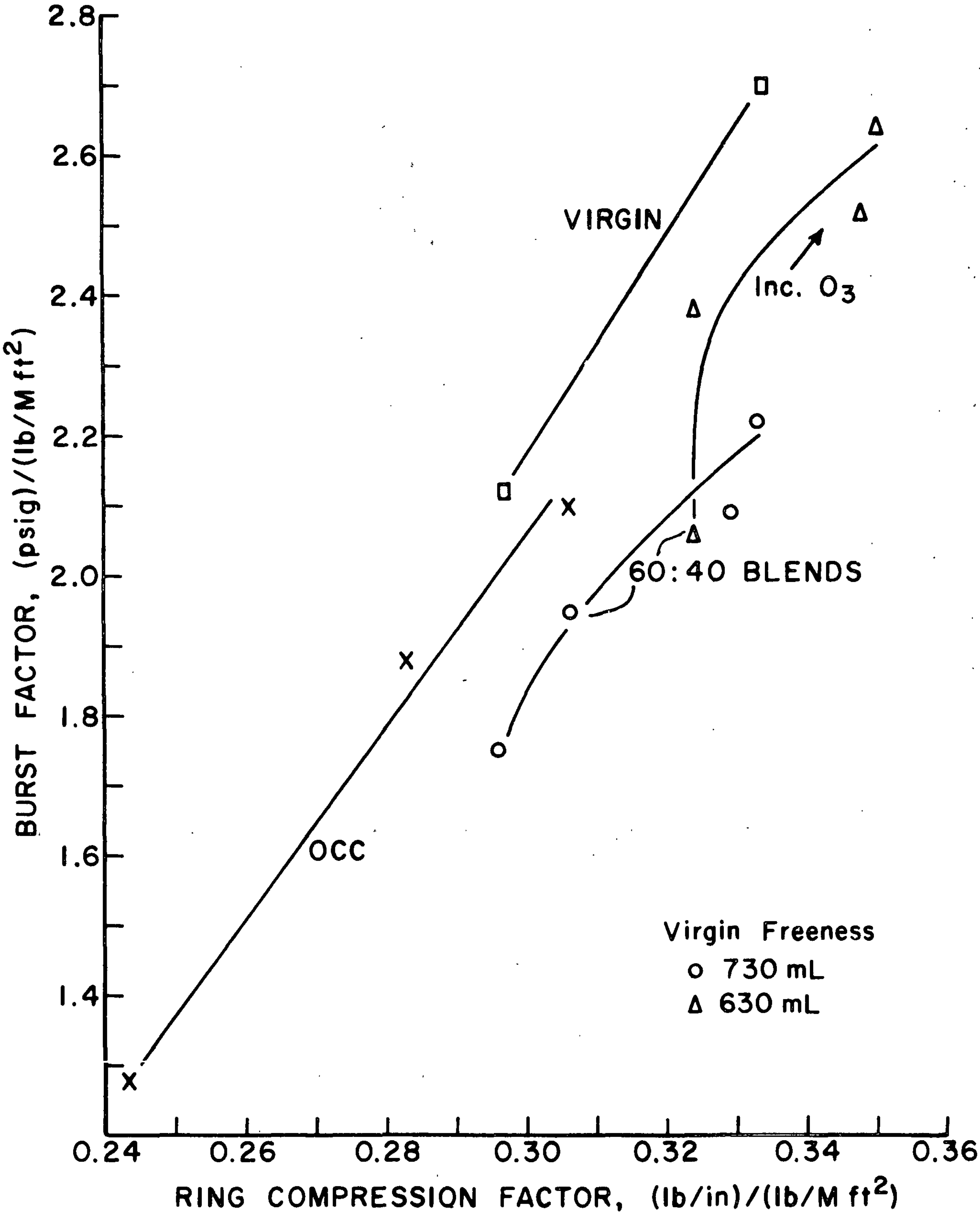


Figure 36. Burst vs. Edgewise Compression Strength on Blends of Ozonated OCC with Prerefined Virgin Kraft

The tensile vs. tear results in Fig. 37 show that at low O_3 treatment levels of the OCC the tensile and tearing strengths of the blends are increased. Higher ozonation levels continue to increase tensile strength but the tearing strength decreases.

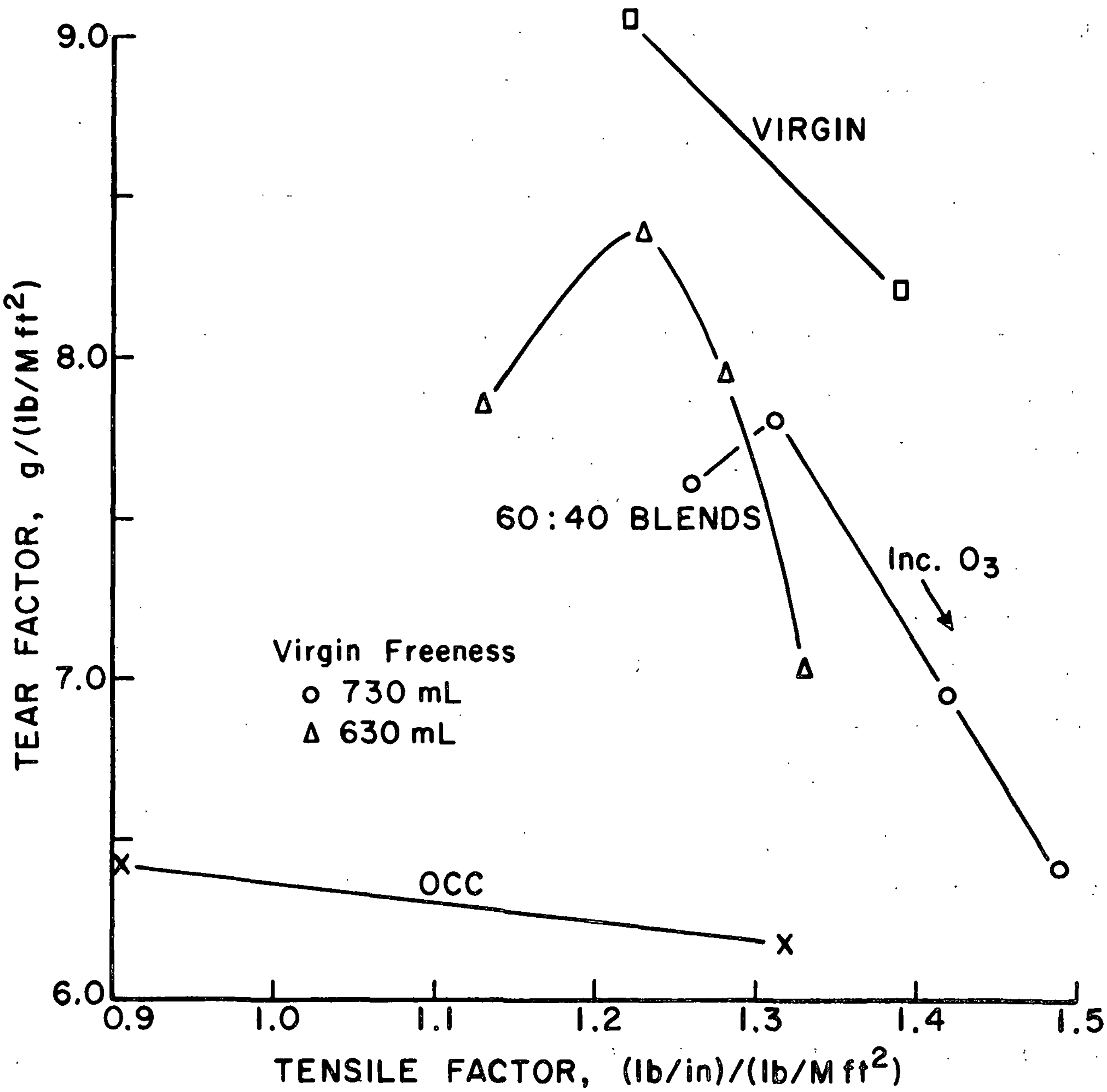


Figure 37. Tensile vs. Tear on Blends of Ozonated OCC with Prerefined Virgin Kraft

WET PRESSING OF OZONATED PULPS

All the studies of ozonated OCC have shown little or no reduction in freeness due to ozonation. Therefore it was presumed the normal level of productivity on the wet end of the paper machine could be maintained. However, water removal at the presses and on the dry end of the machine might be modified. SEM studies of the fiber surface show microfibrillation and microcavitation of the fiber surface. Both of these conditions could increase the water holding capacity of the fiber in a manner which would not seriously affect freeness but affect pressing behavior.

Recently the Institute constructed a wet press simulator based upon a design by Zotterman and Wahren (1). Thus it was deemed desirable to develop some preliminary data concerning the "pressability" of the ozonated fiber pads. Fibers ozonated to the 2.5 and 4.7% level as well as an untreated control were formed on the 8 x 8-inch Noble and Wood mold at a basis weight of 150 g/m^2. The handsheets sandwiched between blotters were couched to the desired initial wetness utilizing repeated passes of a copper couch roll. The handsheets were placed between polyethylene sheeting and five 1-1/2 inch disks were cut from each handsheet. Initial solids were determined and pressing followed. A brief description of the wet press simulator may be found in the article by Zotterman and Wahren. Similar conditions were maintained for all pressings. Results are shown in Table VI and Fig. 38. In general the results indicate that ozonation does increase the water holding capacity of the fiber to a degree proportional to the degree of ozonation. It appears that slight increases in pressing pressures would be required to maintain consistencies into the dryer section.

TABLE VI

WET PRESSING OF OZONATED PULPS

0% Ozone Level			2.51% Ozone Level			4.69% Ozone Level[a]		
Unpressed Solids, %	Pressed Solids, %	Solids Increase, %	Unpressed Solids, %	Pressed Solids, %	Solids Increase, %	Unpressed Solids, %	Pressed Solids, %	Solids Increase, %
25.42	39.75	14.33	24.93	37.68	12.75	--	--	--
25.07	39.59	14.52	24.71	37.55	12.84	--	--	--
25.18	39.51	14.33	24.99	37.73	12.74	--	--	--
25.28	39.48	14.20	25.40	37.78	12.38	--	--	--
25.41	39.44	14.03	26.42	37.99	11.57	--	--	--
30.56	40.68	10.12	31.12	39.24	8.12	33.03	38.93	5.90
31.37	40.82	9.45	31.03	39.44	8.41	32.10	38.70	6.60
30.57	40.86	10.29	31.36	39.59	8.23	32.24	38.74	6.50
32.23	41.06	8.83	31.96	39.52	7.56	32.50	38.89	6.39
30.59	40.62	10.03	32.34	39.61	7.27	32.24	37.95	5.71
34.96	41.07	6.11	36.25	41.03	4.78	36.39	40.17	3.78
35.02	41.23	6.21	35.70	40.94	5.24	36.51	40.30	3.79
34.91	41.22	6.31	35.31	40.66	5.35	36.40	40.18	3.78
35.27	41.28	6.01	35.33	40.82	5.49	37.04	40.65	3.61
34.75	41.34	6.59	35.75	41.08	5.33	37.36	40.84	3.48

[a]For this screening examination pulps left over from other ozonation studies were utilized. Hence insufficient pulp at the 4.69% ozone level was available to study 3 consistency levels at this time.

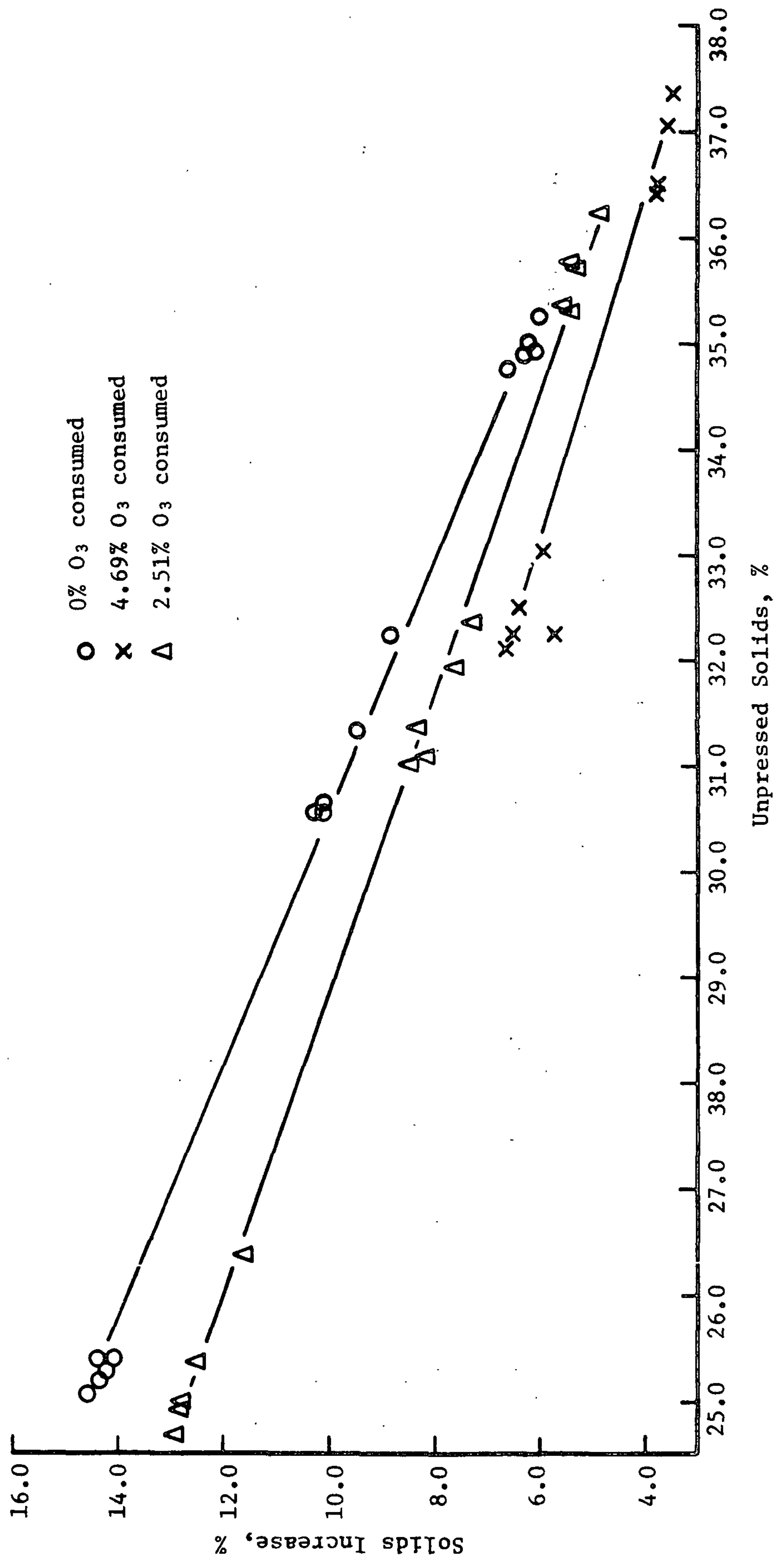


Figure 38. Effect of Ozonation on Wet Pressing

OZONE TREATMENT OF COMMERCIAL OCC

Research utilizing the IPC model OCC indicated ozone treatments significantly improved the physical properties. However, the IPC model OCC is substantially equivalent to kraft corrugated clippings or "preconsumer waste" without the usual contaminants or treatments potentially associated with commercial OCC pulps. Therefore a number of commercial OCC pulps were procured from four companies for comparison evaluations. The pulps obtained were as follows:

1. Company A: one pulp — reported to contain 75% OCC; 25% kraft corrugated cuttings
2. Company B: one pulp — OCC not otherwise identified
3. Company C: two pulps — obtained before and after the asphalt dispersion (A/D) process
4. Company D: two pulps — obtained before and after the A/D process

Upon receipt, each pulp was centrifuged to remove excess water, fluffed, ozonated, formed into handsheets, and tested for physical strength properties. Procedures followed were those established for the Institute model OCC as described in Progress Report One, Project 2697-53. Single trials at ozonation levels of approximately 2.4 and 4.6% ozone consumed, based upon the o.d. fiber weight, were performed. These O_3 consumptions correspond to treatment times of 15 and 30 minutes. In previous trials on the Institute model OCC, treatment times ranging up to 90 minutes were employed. For these comparisons, it was expected the shorter treatments and lower O_3 consumptions would be of more practical interest.

Tables VII-VIII tabulate the physical test data for the commercial pulps examined. Comparable data for the Institute model OCC is also included in Table VII for direct comparison with the commercial stocks.

TABLE VII

PROPERTIES OF HANDSHEETS PREPARED FROM COMMERCIAL OCC OBTAINED FROM COMPANIES A AND B

	Company A			Company B			IPC Model OCC[a]		
Ozonation time, min	0	15	30	0	15	30	0	15	60
Ozone applied, % o.d. fiber	--	2.54	5.04	--	2.58	5.16	--	2.35	9.41
Ozone consumed, % o.d. fiber	--	2.46	4.68	--	2.48	4.77	--	2.31	8.53
Reaction efficiency, %	--	96.5	92.8	--	96.0	92.4	--	98.3	90.6
C.S. freeness, mL	595	560	575	610	560	550	633	617	567
% Change	--	-5.9	-3.4	--	-8.2	-9.8	--	-2.5	-10.4
Basis weight, lb/M ft^2	13.5	13.7	13.4	13.5	13.9	13.5	13.2	13.2	13.5
Caliper, points	5.3	5.2	5.0	5.5	5.3	5.3	6.1	5.6	5.3
Apparent density	2.57	2.64	2.69	2.46	2.63	2.56	2.16	2.34	2.54
% Change	--	+2.7	+4.7	--	+6.9	+4.1	--	+8.3	+17.6
Bursting strength, psig	19.0	27.4	27.4	16.0	25.0	27.3	17.2	23.2	33.1
Factor[b]	1.40	2.00	2.05	1.19	1.81	2.02	1.30	1.76	2.45
% Change	--	+42.9	+46.2	--	+52.1	+69.7	--	+35.4	+38.5
Mod. ring compression, lb/inch	3.8	4.3	4.3	3.6	4.1	3.9	3.8	4.0	4.8
Factor[b]	0.277	0.317	0.320	0.267	0.299	0.292	0.284	0.307	0.353
% Change	--	+14.4	+15.5	--	+12.0	+9.4	--	+8.1	+24.3
Tear, grams	91.6	88.4	75.0	98.0	88.4	82.8	87.6	85.1	71.9
Factor[b]	6.76	6.45	5.66	7.26	6.38	6.13	6.64	6.45	5.31
% Change	--	-4.6	-16.3	--	-12.1	-15.6	--	-2.9	-20.0
Tensile, lb/inch	13.3	16.3	16.1	12.3	15.2	16.6	12.4	15.6	20.0
Factor[b]	0.98	1.19	1.20	0.91	1.10	1.23	0.94	1.19	1.48
% Change	--	+21.4	+22.4	--	+20.9	+35.2	--	+26.6	+57.4
Stretch, %	2.09	2.63	2.46	1.95	2.32	2.50	1.86	2.18	2.43
% Change	--	+25.8	+17.7	--	+19.0	+28.2	--	+17.2	+30.6
Et, lb/inch	1763	2023	2039	1690	1958	2058	1640	1946	2326
Factor[b]	130.2	147.6	151.9	125.2	141.3	152.4	124.2	147.8	172.0
% Change	--	+13.4	+16.7	--	+12.9	+21.7	--	+19.0	+38.5
TEA, ft-lb/ft^2	2.4	3.7	3.4	2.1	3.1	3.6	2.0	2.9	4.1
% Change	--	+54.2	+41.7	--	+47.6	+71.4	--	+45.0	+105.0

[a] Data obtained from Progress Report One, Project 2697-53 entitled "Effect of Ozonation on Recycled Fiber," dated September 24, 1978.

[b] Factors are determined by dividing the given test property data by the basis weight in lb/M ft^2.

TABLE VIII

PROPERTIES OF HANDSHEETS PREPARED FROM OZONATED COMMERCIAL OCC
OBTAINED FROM COMPANIES C AND D

	Company C						Company D					
		Before ADP			After ADP			Before ADP			After ADP	
Ozonation time, min	0	15	30	0	15	30	0	15	30	0	15	30
Ozone applied, % of o.d. fiber	--	2.42	4.87	--	2.43	4.87	--	2.52	4.96	--	2.47	5.02
Ozone consumed, % of o.d. fiber	--	2.30	4.56	--	2.28	4.37	--	2.44	4.66	--	2.29	4.75
Reaction efficiency, %	--	94.9	93.7	--	93.9	89.8	--	96.8	93.9	--	92.7	94.6
C.S. freeness, mL	570	525	485	545	510	470	550	535	520	590	570	550
% Change	--	-7.9	-14.9	--	-6.4	-13.8	--	-2.7	-5.5	--	-3.4	-6.8
Basis weight, lb/M ft^2	13.3	13.3	13.5	13.7	13.6	13.4	13.8	13.3	13.5	13.2	13.4	13.4
Caliper, points	5.1	4.9	4.8	5.2	5.1	4.8	5.7	5.2	5.2	5.4	5.2	5.1
Apparent density	2.60	2.69	2.80	2.64	2.68	2.78	2.42	2.55	2.57	2.45	2.56	2.63
% Change	--	+3.5	+7.7	--	+1.5	+5.3	--	+5.4	+6.2	--	+4.9	+7.3
Bursting strength, psig	17.3	21.5	26.3	16.4	20.6	22.6	20.5	24.2	29.2	18.2	22.3	24.8
Factor[a]	1.30	1.63	1.95	1.20	1.52	1.69	1.49	1.82	2.17	1.38	1.66	1.86
% Change	--	+25.4	+50.0	--	+26.7	+40.8	--	+22.2	+45.6	--	+20.3	+34.8
Mod. ring compression, lb/inch	3.2	3.6	3.9	3.3	3.3	3.4	4.0	4.1	4.1	3.8	4.0	3.9
Factor[a]	0.240	0.275	0.290	0.240	0.247	0.254	0.290	0.312	0.305	0.285	0.302	0.292
% Change	--	+14.6	+20.8	--	+2.9	+5.8	--	+7.6	+5.2	--	+6.0	+2.5
Tear, grams	82.4	86.0	77.6	90.0	92.8	84.4	93.1	85.2	79.2	109.2	99.2	90.0
Factor[a]	6.19	6.49	5.77	6.55	6.83	6.31	6.75	6.41	5.89	8.30	7.39	6.73
% Change	--	+4.8	-6.8	--	+4.3	-3.7	--	-5.0	-12.7	--	-11.0	-18.9
Tensile, lb/inch	11.4	12.8	15.4	10.5	12.0	13.3	13.1	15.6	16.6	11.3	13.5	15.1
Factor[a]	0.85	1.04	1.15	0.77	0.89	1.00	0.95	1.17	1.24	0.86	1.01	1.13
% Change	--	+22.4	+35.3	--	+15.6	+29.9	--	+23.2	+30.5	--	+17.4	+31.4
Stretch, %	2.18	2.53	2.49	2.57	2.79	3.01	2.34	2.60	2.50	2.55	2.90	2.99
% Change	--	+16.1	+14.2	--	+8.6	+17.1	--	+11.1	+6.8	--	+13.7	+17.3
Et, lb/inch	1529	1749	1974	1396	1577	1685	1754	1926	2083	1512	1740	1918
Factor[a]	114.9	131.9	146.7	101.6	116.1	125.9	127.4	144.8	154.9	114.9	129.7	143.4
% Change	--	+14.8	+27.7	--	+14.3	+23.9	--	+13.7	+21.6	--	+12.9	+24.8
TEA, ft-lb/ft^2	2.2	3.1	3.4	2.5	3.1	3.7	2.7	3.6	3.6	2.6	3.5	4.1
% Change	--	+40.9	+54.5	--	+24.0	+48.0	--	+33.3	+33.3	--	+34.6	+57.7

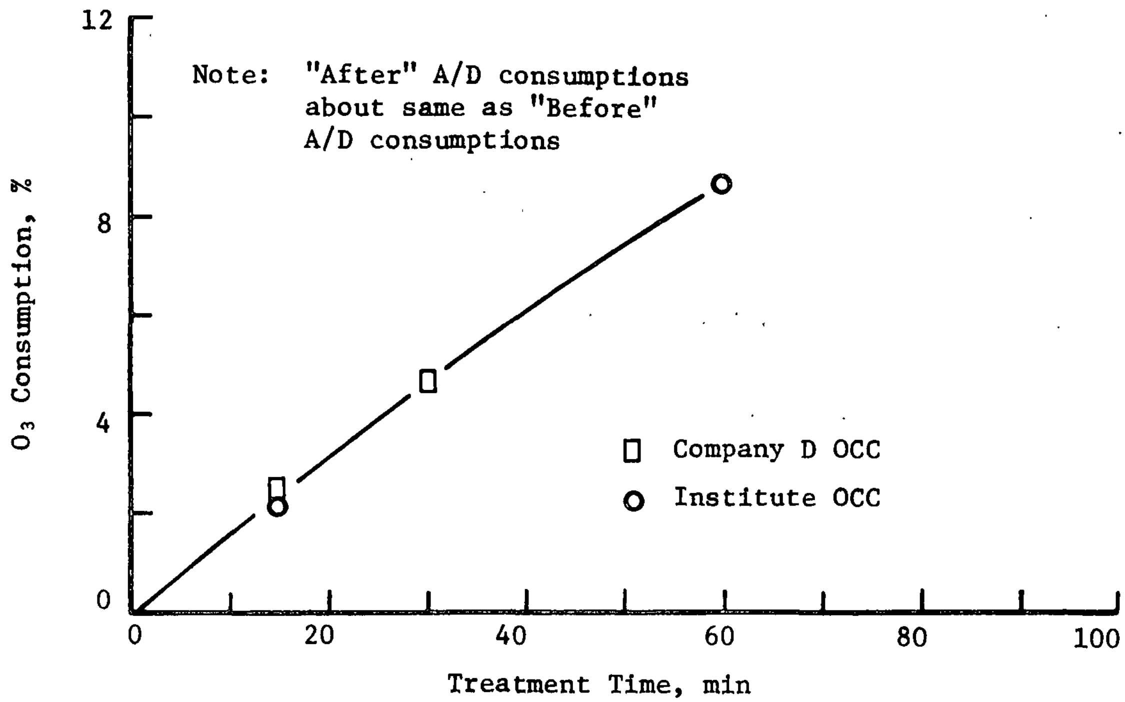
[a]Factors are determined by dividing the given test property data by the basis weight in lb/M ft^2.

Figure 39 shows that ozone consumptions obtained on commercial OCC from Company D were about the same as obtained on the Institute OCC at equal treatment times. In Fig. 39, the O_3 consumptions on the "before" A/D stock are plotted; however, similar results have been observed for all the commercial pulps treated. Reaction efficiencies, viz., the ratio of O_3 applied to O_3 consumed by the pulp on an o.d. basis, also were similar for the commercial pulps and the Institute OCC. Reaction efficiencies of approximately 95% are shown at the 2.4% level and about 93% at the 4.6% O_3 consumed level.

The commercial OCC stocks also exhibited small decreases in freeness with increasing ozonation in the same manner as the Institute furnish. Figure 39 shows the trends for Company D stocks.

Figures 40-42 show that tensile and bursting strengths obtained on ozonated commercial OCC stocks exhibit strength increases similar to those obtained on the Institute OCC. The pulp obtained after the A/D process from both Companies C and D exhibits lower burst and tensile strengths than the stock obtained before A/D process as expected from the literature. Nonetheless, the A/D process does not appear to affect rate of improvement in burst and tensile with increasing ozonation.

Figures 43-45 show the changes in tearing strength of the commercial pulps as ozonation proceeds. Again, the rate of change in tearing strength after ozonation shows trends similar to the Institute OCC. The tearing strengths of the pulps "before" A/D tend to be lower than the strengths "after" A/D for the comparable pulps obtained from both Companies C and D. However, the differences in initial tearing strengths did not appear to alter the trends due to ozonation; and losses in tear tended to be nominal.



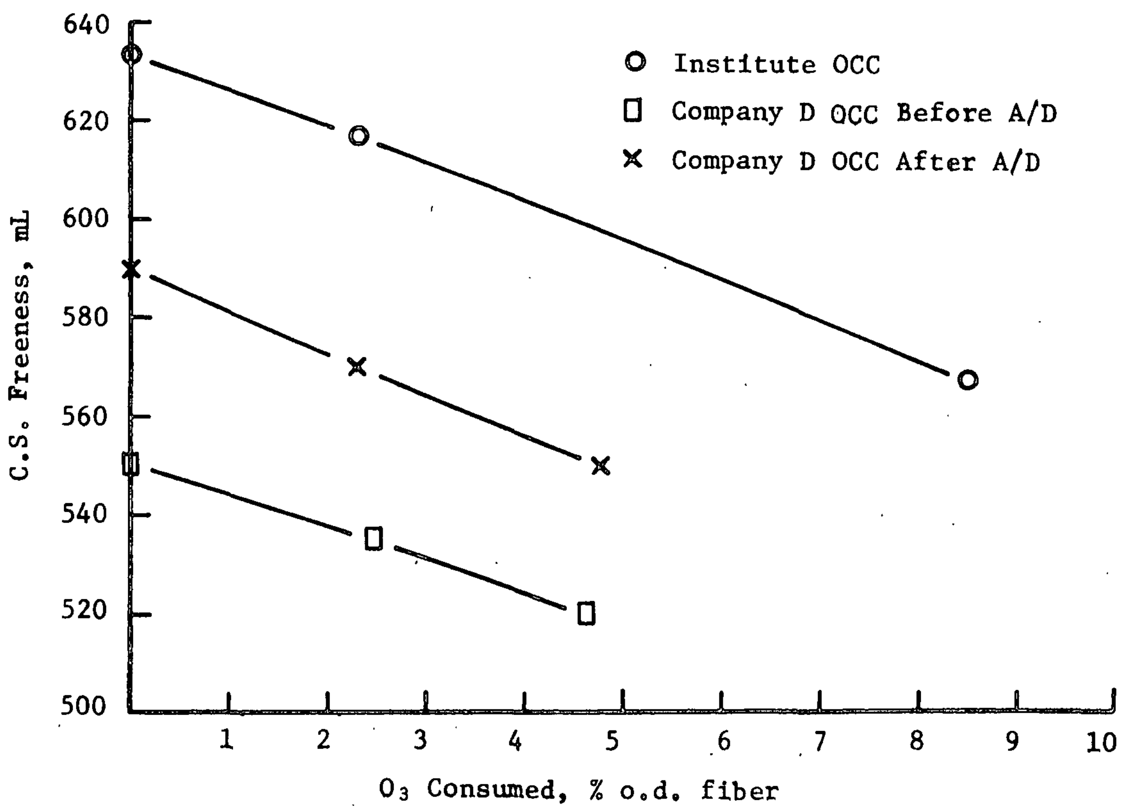


Figure 39. Ozone Consumption and Freeness Trends of Commercial OCC Pulps Compared with Institute Model OCC

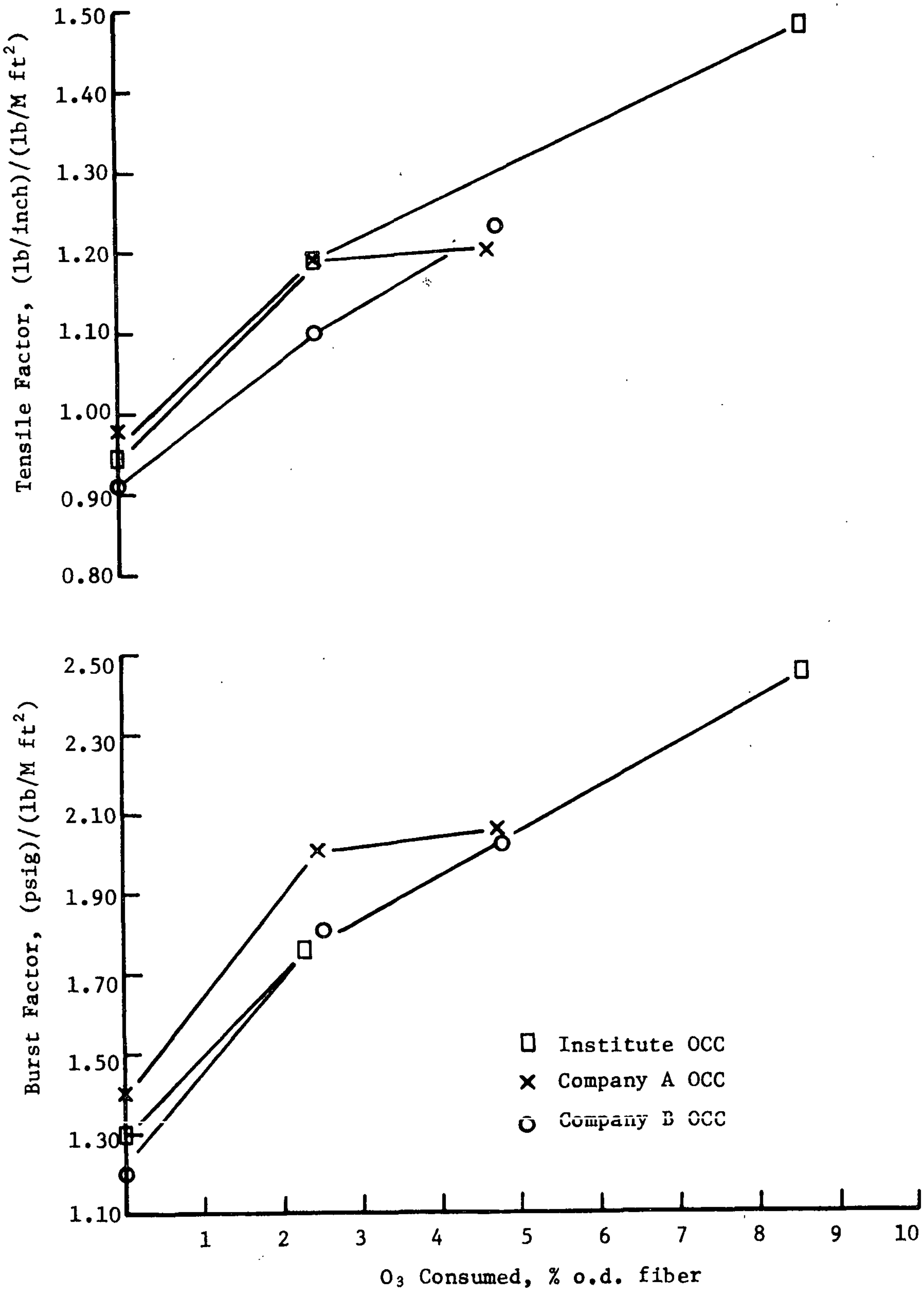


Figure 40. Tensile and Burst Trends for Commercial OCC Pulp from Companies A and B

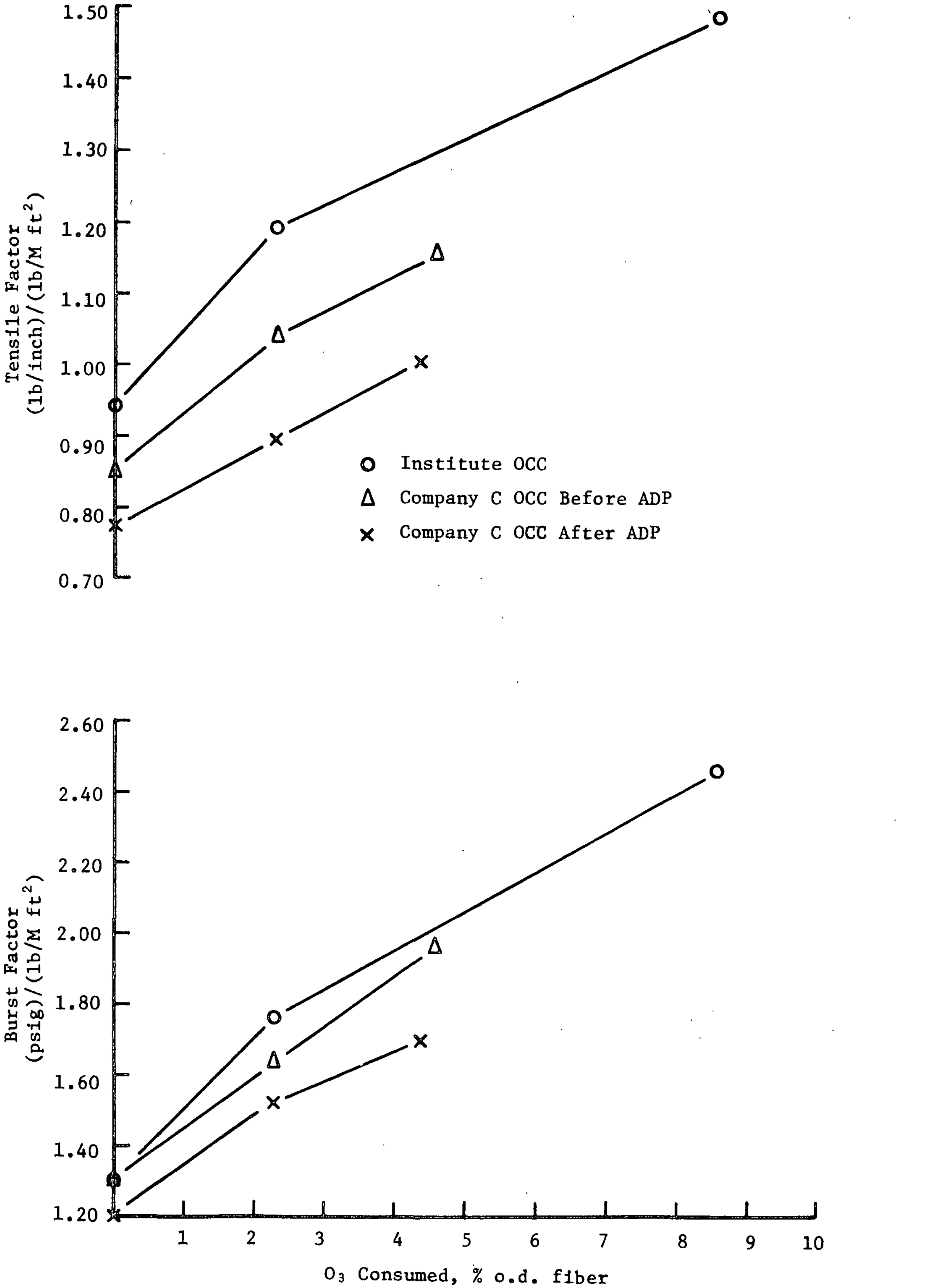


Figure 41. Tensile and Burst Trends for Commercial OCC Pulp from Company C

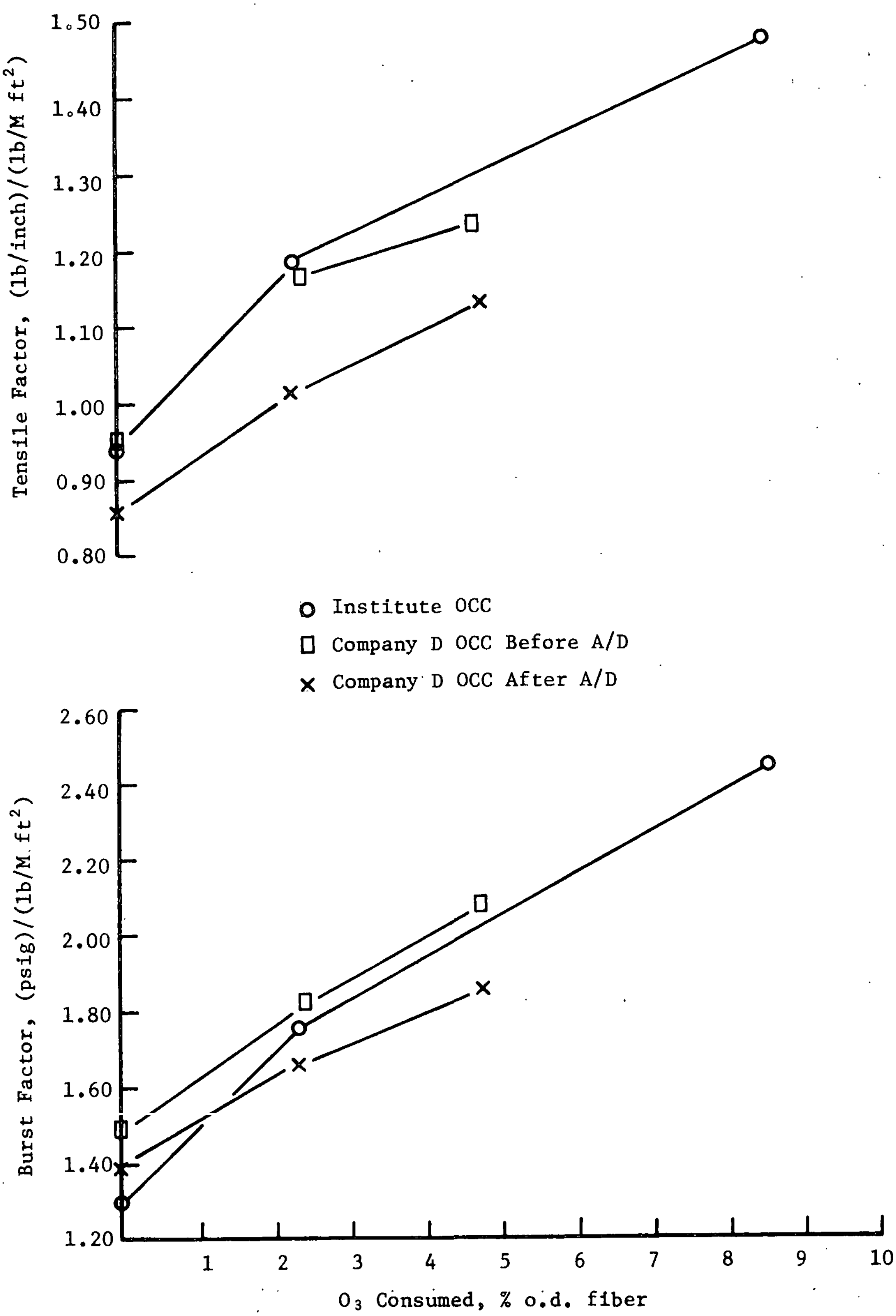


Figure 42. Tensile and Burst Trends for Commercial OCC Pulp from Company D

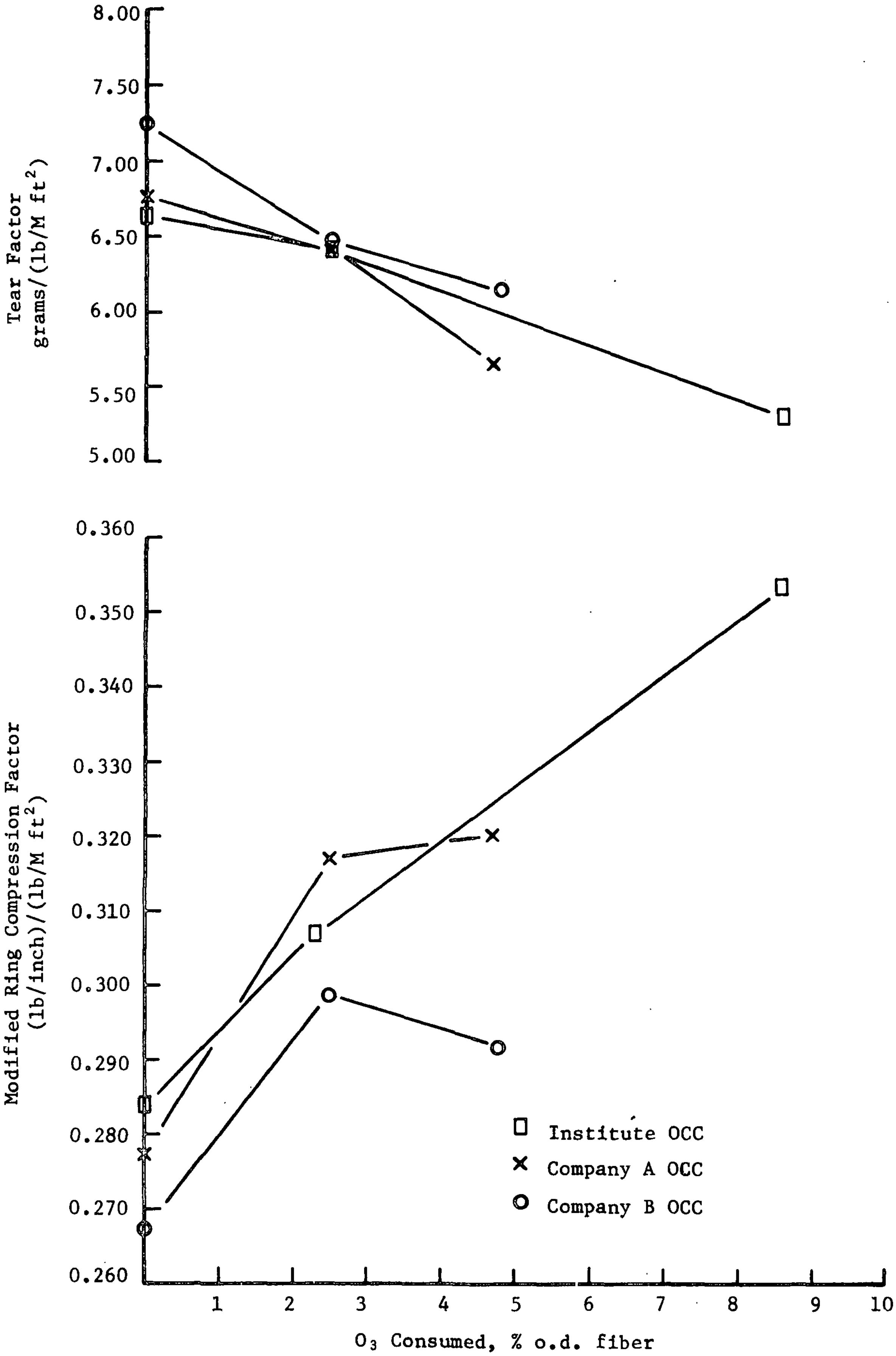


Figure 43. Tear and Ring Compression Trends for Commercial OCC Pulp from Companies A and B

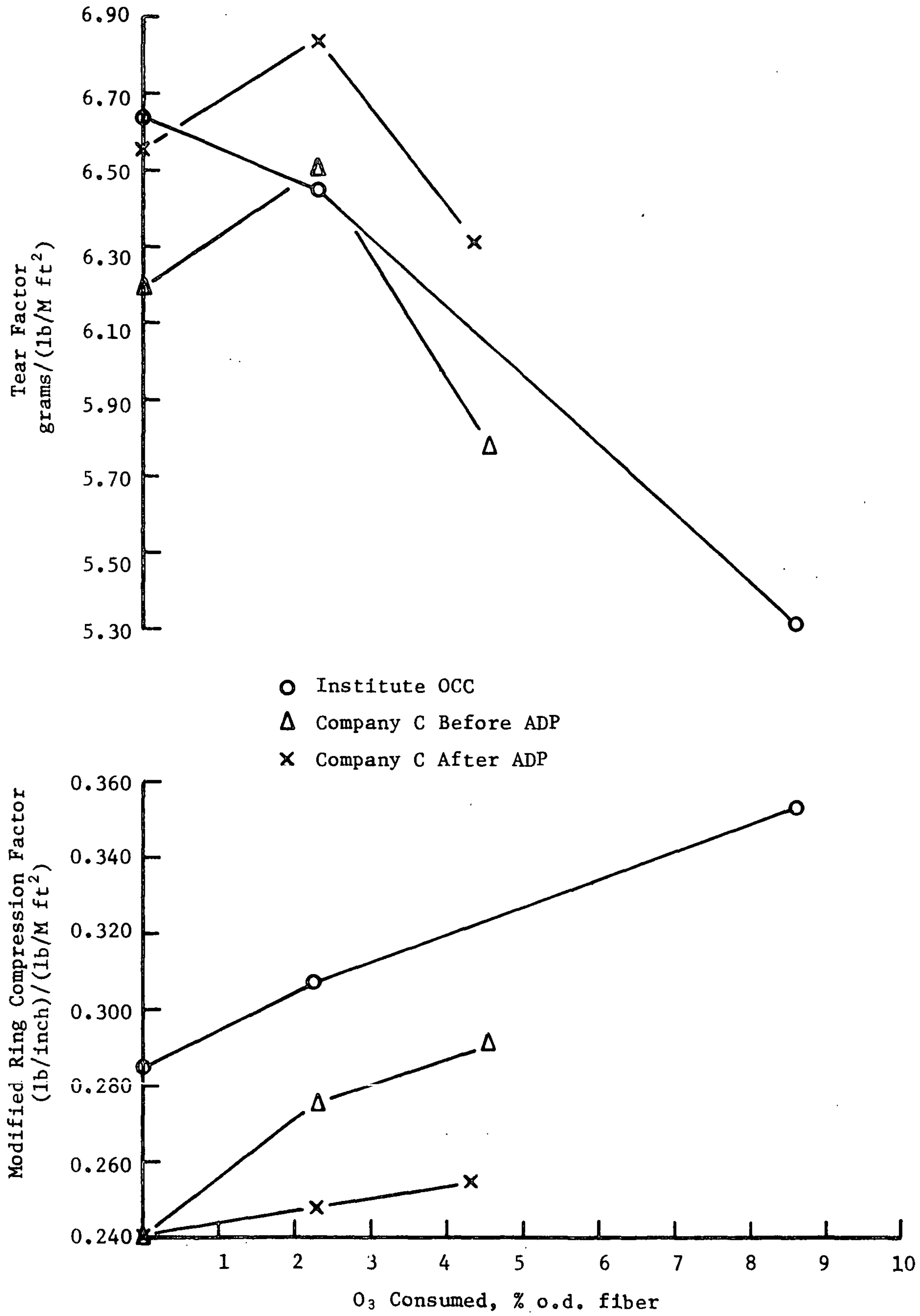


Figure 44. Tear and Ring Compression Trends for Commercial OCC Pulp from Company C

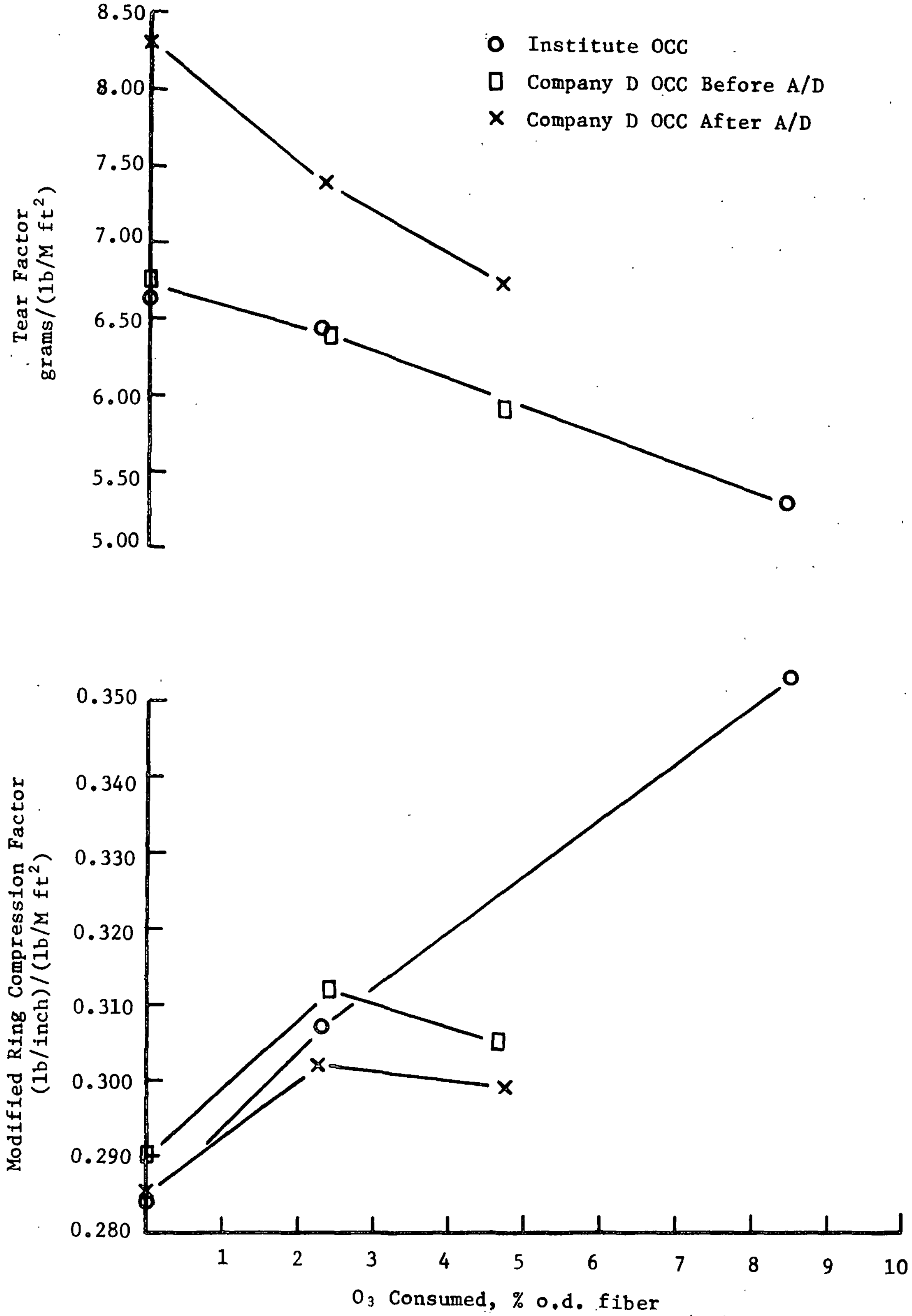


Figure 45. Tear and Ring Compression Trends for Commercial OCC Pulp from Company D

Modified ring compression results are shown in Fig. 43-45. Increased strength trends for all the commercial stocks are similar to that exhibited by the Institute OCC at the 2.4% O_3 consumed level. At the 4.6% consumption level, no further increases in ring strength were obtained on pulps from Companies A, B, and D. Compression tests on "thin" sheets are, however, difficult to determine and tend to be erratic.

Briefly summarizing, these results indicate that commercially cleaned OCC pulps respond to ozonation in a similar manner to the corrugated furnish used in current and past research in the project. There is no evidence that residual contaminants or the utilization of the A/D process in the cleaning operation will affect the ozonation of commercial OCC pulps.

Bauer-McNett classifications on the OCC pulps from Companies A, B, and D were determined and compared with the Institute OCC. Figure 46 indicates that all pulps exhibited quite similar fiber length distributions.

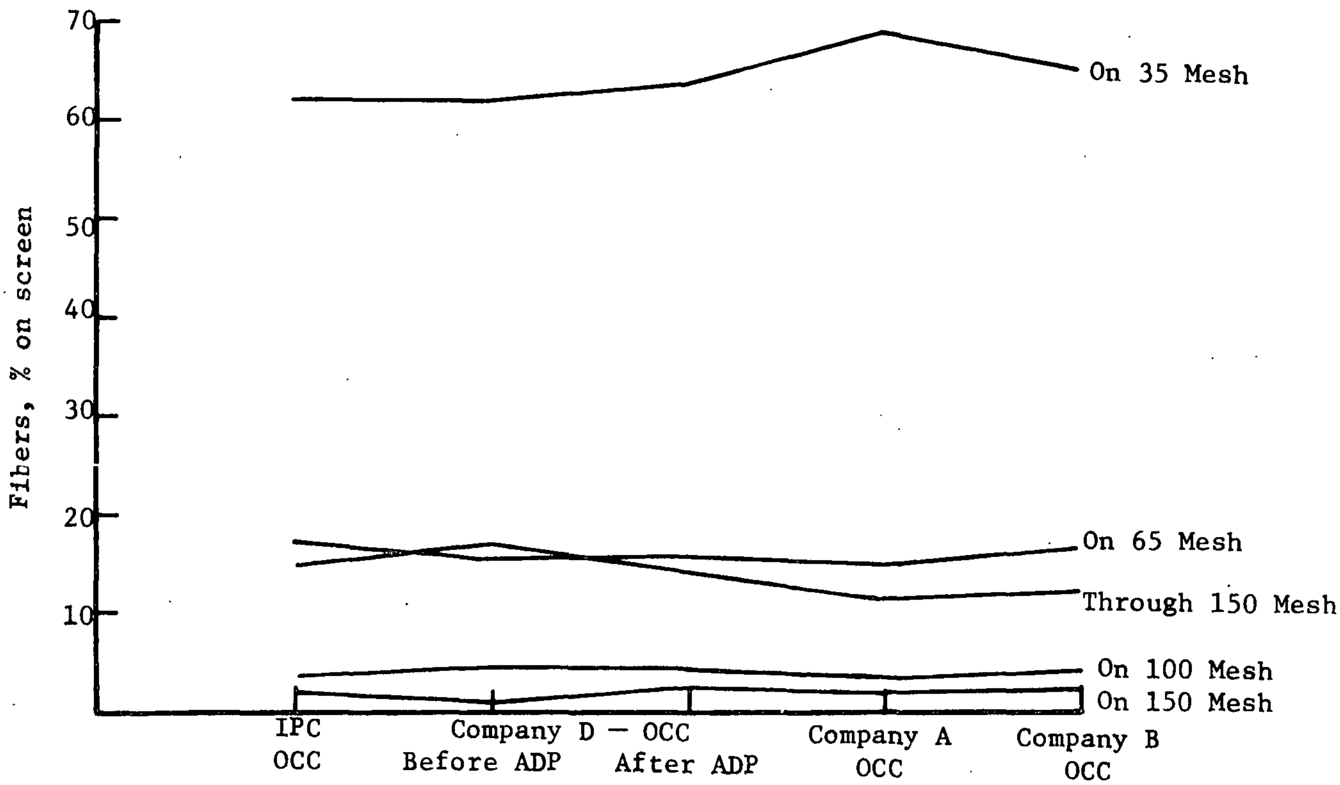


Figure 46. Bauer McNett Results on Institute and Commercial OCC Pulps

C stain fiber analysis studies of the untreated and ozonated commercial pulps were undertaken. The fiber analysis of the untreated pulps indicated that the major components of the commercial furnishes were softwood kraft and hardwood NSSC similar to the Institute OCC although a broader array of trace pulps and species were present. C stain color responses shifted from the typical shades of yellow for unbleached pulps to blue upon increasing ozonation in a manner similar to the Institute OCC as reported in Progress Report One, Project 2697-53.

Observation of fibers and handsheets from Company D stocks were also made utilizing the SEM (scanning electron microscope). Several limited differences were noted. The Company D pulp appeared to present a more "coated" surface upon SEM viewing and pigment particles were observed. Limited evidence suggests the particles were clay and titanium pigments. As a result, total ash was determined and found to be about 2.5% as compared with 1.3% for the Institute OCC. Similar tests were not performed upon the other commercial pulps since potential nonfibrous residuals did not appear to affect ozonation trends. It is expected, however, that significant solubles will also be found in the commercial pulps, based upon observations of the water removed during centrifuging.

STUDY OF OZONATION VARIABLES

The research reported in Progress Report One, 2697-53, indicated ozonation of recycled fiber is effective in improving its strength properties under the treatment conditions evaluated. The conditions chosen were based principally upon literature information. None of this information dealt directly with OCC fiber. It was therefore deemed desirable to evaluate a number of ozonation variables specifically with respect to OCC fiber. These variables included fiber preparation, fiber consistency, and ozone application rate.

EFFECT OF FLUFFING

In previous and current work the effects of ozonation on physical properties have been evaluated relative to the untreated "control" OCC pulp. The untreated "control" pulp is processed and fluffed in the same manner as the ozonated pulps. The laboratory fluffing (described in Progress Report One) serves two purposes: (1) to increase pulp consistency to the desired value and (2) to uniformly distribute the moisture throughout a bulky very open fiber mass to allow thorough penetration of the O_3/O_2 gaseous mixture to individual fiber surfaces. There has been a question whether the laboratory fluffing alters the physical properties of the "control" stock from that expected for OCC "as received." If the "control" stock properties are altered, the effects of ozonation on physical properties would also be biased when compared with OCC "as received." Therefore a preliminary comparison of physical properties of fluffed and unfluffed untreated OCC was undertaken. Results are shown in Table IX. The data indicate that there is essentially no difference in physical properties due to the processing and fluffing of the OCC. The fluffed OCC exhibits slightly higher burst, tensile, tear, and stretch values, although none of the differences appear to be statistically significant. There is a small difference in Canadian Standard freeness (30-35 mL) between the fluffed and unfluffed pulps. However, the freeness on these unrefined controls is sensitive to small variations in handling and dispersion and the difference obtained here may not be a significant factor.

TABLE IX

EFFECT OF FLUFFING

	Unfluffed, untreated OCC	Fluffed, untreated OCC[a]	Difference, %[b]
C.S. freeness, mL	665	633	-4.8
Basis weight, lb/M ft^2	13.8	13.2	--
Caliper, points	6.1	6.1	--
Apparent density, (lb M ft^2)/pt	2.25	2.16	-4.0
Bursting strength, psi	17.6	17.2	--
Factor[c]	1.28	1.30	+1.6
Tensile, lb/inch	12.3	12.4	--
Factor[c]	0.89	0.94	+5.6
Tear, grams	85.6	87.6	--
Factor[c]	6.21	6.64	+6.9
Modified ring compression, lb/inch	4.2	3.8	--
Factor[c]	0.304	0.284	-6.6
Stretch, %	1.73	1.86	+7.5
Et, lb/inch	1741	1640	--
Factor[c]	126.3	124.2	-1.7

[a]Project 2697-53, Progress Report One, page 15.
[b]Based on unfluffed as reference.
[c]Factors are determined by dividing the given property value by basis weight in lb/M ft^2.

Proper fluffing does appear to have a significant effect upon ozone treatment uniformity and reaction efficiency independent of consistency. It is speculated the degree of fluffing relates to the bulk density of the pulp which in turn determines the ability of the O_3/O_2 gaseous mixture to penetrate the fiber mass and "find" suitable fiber/moisture/gas interfaces for maximum reaction. Comparison of very early screening trials with current results also points to the fact that reaction efficiency, viz., the relationship of O_3 applied to O_3 consumed in reaction with the pulp is highly dependent upon fluffing. The literature has reported fiber/moisture/gas balance is very important to reaction.

HIGH CONSISTENCY STUDIES

The literature reports consistency of the pulp is critical to effective ozonation. Consistencies above 30% are reported to be necessary to provide reasonable reaction efficiencies. Therefore a study was undertaken to determine the desirable consistency range for OCC pulp.

For this purpose the OCC was centrifugally dewatered to about 30% consistency and then given a sufficient number of passes through the fluffer to obtain consistencies of about 30, 40, 53, and 67% prior to ozonation. The bulk densities of the so-treated pulps tended to vary inversely with the consistency, viz., the higher the consistency, the lower the bulk density. Each pulp was ozonated using treatment intervals of 15 and 30 minutes corresponding to ozone consumptions of about 2.5% and 4.5%, respectively. Handsheets were prepared and the usual physical properties were determined. Results are shown in Table X. Graphs in Fig. 47-49 compare burst, tensile, modified ring tear, freeness, and reaction efficiency as a function of consistency and ozonation. In general, a broad range of consistencies above 30% provide equivalent results depending on the property involved. Consistencies of 40 to 50% appear to be optimum. At 67% a down turn in ozonation effectiveness

Table X

EFFECT OF PULP CONSISTENCY UPON OZONATION

	Control	Ozonation to the 2.5% Level Pulp Consistency, %				Ozonation to the 4.5% Level Pulp Consistency, %			
		30.8	39.0	52.9	66.8	30.8	40.9	52.9	66.8
Ozone applied, % o.d. fiber	--	2.52	2.54	2.77	2.61	5.16	5.24	5.18	5.22
Ozone consumed, % o.d. fiber	--	2.22	2.45	2.66	2.49	4.06	4.74	4.89	4.73
Reaction efficiency, %	--	88.1	96.2	96.0	95.4	78.8	90.5	94.5	90.6
C.S. freeness, mL	681	630	615	650	660	610	580	600	640
% Change	--	-7.5	-9.7	-4.6	-3.1	-10.4	-14.8	-11.9	-6.0
Basis weight, lb/M ft^2	13.6	13.3	13.4	13.2	13.3	13.4	13.4	13.6	13.8
Caliper, mils	5.4	5.1	5.1	4.7	5.0	5.0	4.8	4.7	4.9
Apparent density	2.54	2.63	2.65	2.77	2.66	2.67	2.80	2.88	2.79
% Change	--	+3.5	+4.3	+9.1	+4.7	+5.1	+10.2	+13.4	+9.8
Bursting strength, psig	17.0	21.8	23.8	22.8	19.8	22.9	27.5	28.8	24.9
Factor[a]	1.25	1.64	1.77	1.73	1.49	1.71	2.06	2.11	1.81
% Change	--	+31.2	+41.6	+38.4	+19.2	+36.8	+64.8	+68.8	+44.8
Mod. ring compression, lb/inch	3.4	3.4	3.7	3.6	3.4	3.8	3.9	3.9	4.0
Factor[a]	0.247	0.259	0.275	0.273	0.255	0.285	0.295	0.290	0.294
% Change	--	+4.9	+11.3	+10.5	+3.2	+15.4	+19.4	+17.4	+19.0
Tear, grams	89.6	82.8	84.4	84.0	90.4	76.4	79.2	84.8	86.0
Factor[a]	6.58	6.21	6.28	6.38	6.79	5.72	5.91	6.22	6.24
% Change	--	-5.6	-4.6	-3.0	+3.2	-13.1	-10.2	-5.5	-5.2
Tensile, lb/inch	11.8	14.3	14.3	14.7	13.0	15.0	17.0	17.3	15.9
Factor[a]	0.87	1.07	1.07	1.11	0.97	1.12	1.27	1.27	1.16
% Change	--	+23.0	+23.0	+27.6	+11.5	+28.7	+46.0	+46.0	+33.3
Stretch, %	2.01	2.28	2.32	2.37	2.11	2.23	2.50	2.41	2.42
% Change	--	+13.4	+15.4	+17.9	+5.0	+10.9	+24.4	+19.9	+20.4
ET stiffness, lb/inch	1617	1899	1846	1910	1774	1955	2058	2213	2098
Factor[a]	118.8	142.5	137.4	145.0	133.2	146.4	153.7	162.2	152.3
% Change	--	+19.9	+15.7	+22.1	+12.1	+23.2	+29.4	+36.5	+28.2
TEA, ft-lb/ft^2	2.0	2.8	2.9	3.0	2.4	2.9	3.6	3.6	3.3
% Change	--	+40	+45	+50	+20	+45	+80	+80	+65

[a]Factor is found by dividing the value of a given property by the basis weight in lb/M ft^2.

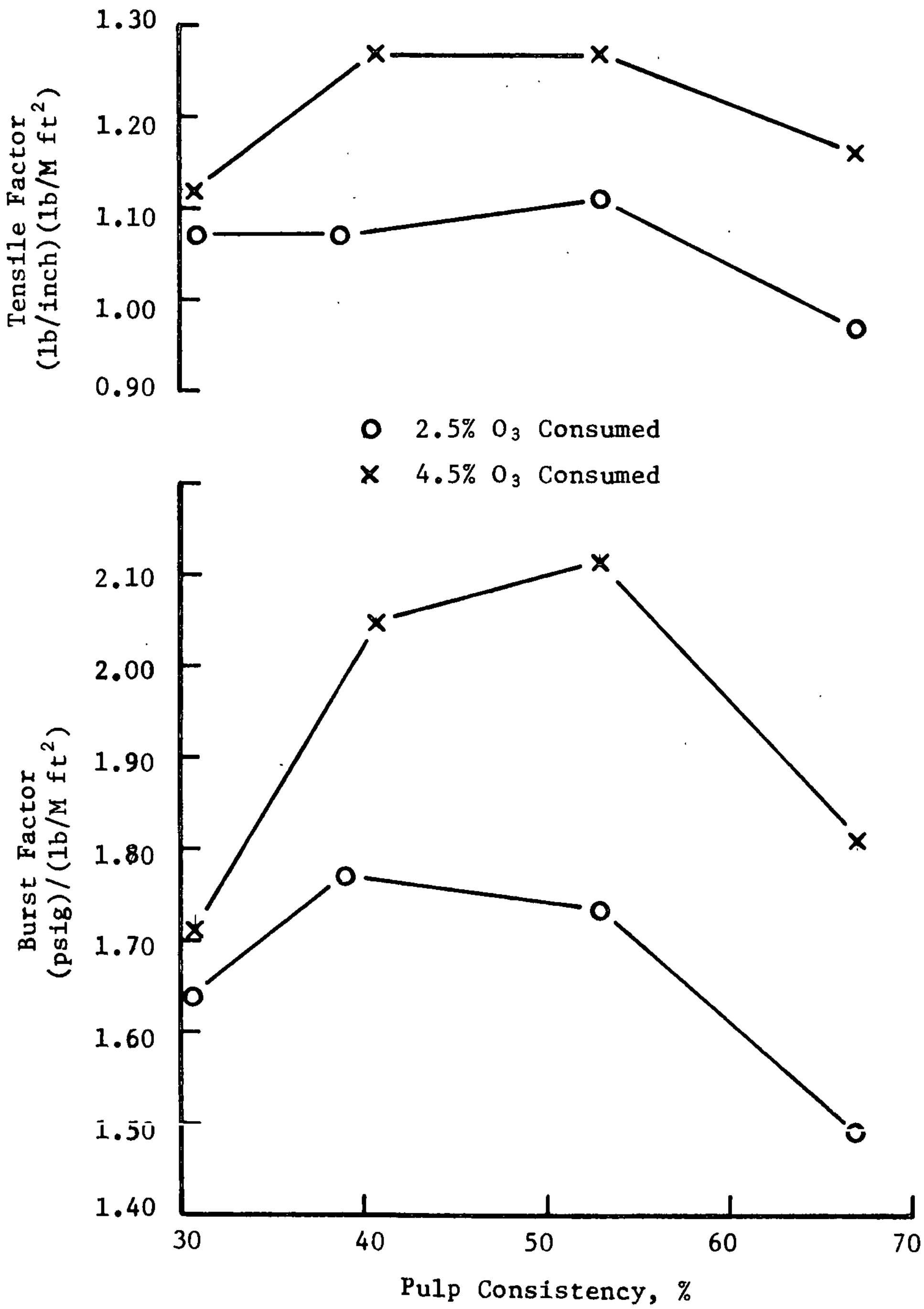


Figure 47. Burst and Tensile Trends at Various Pulp Consistencies During Ozonation

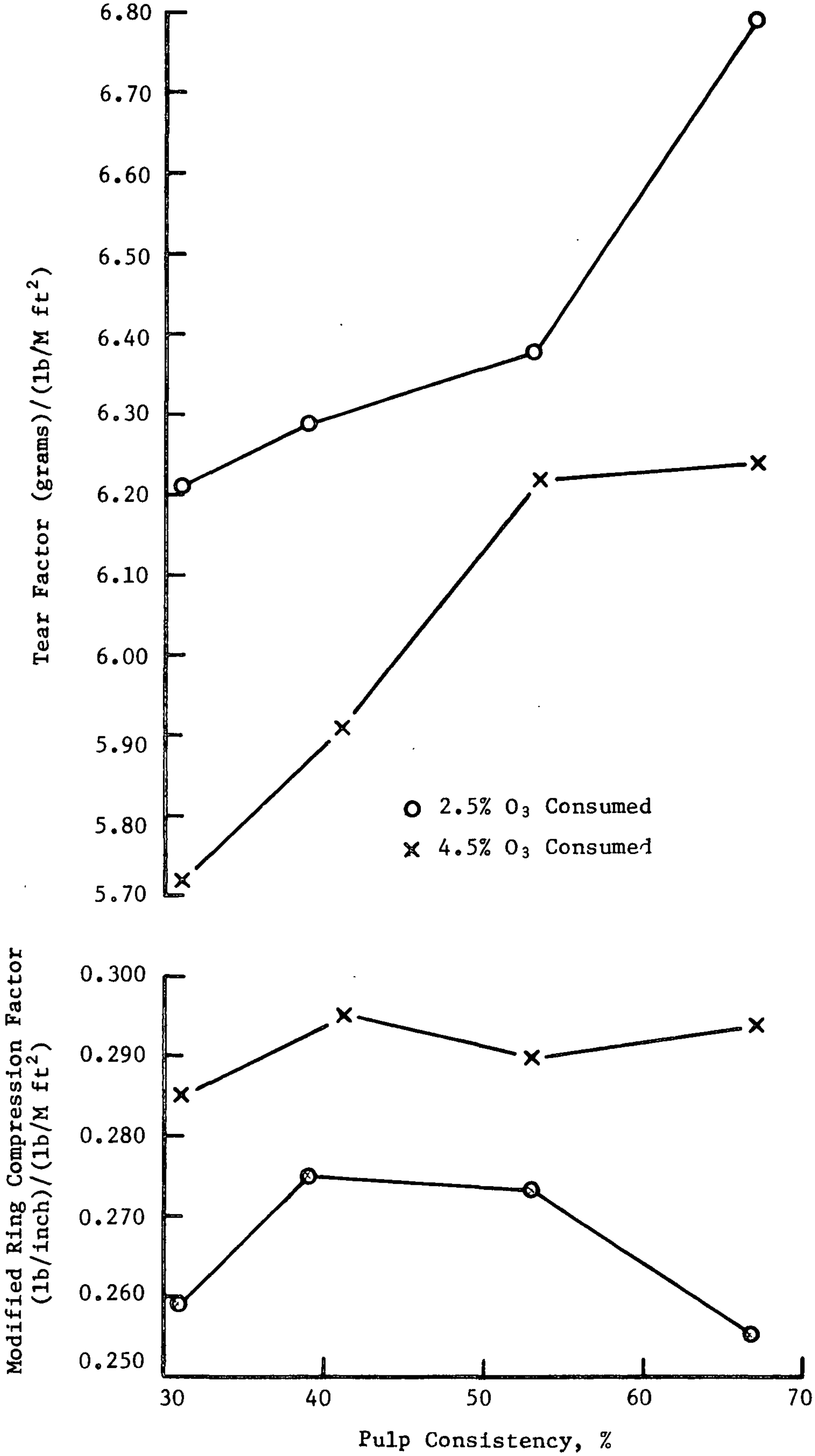


Figure 48. Tear and Ring Compression Trends at Various Pulp Consistencies During Ozonation

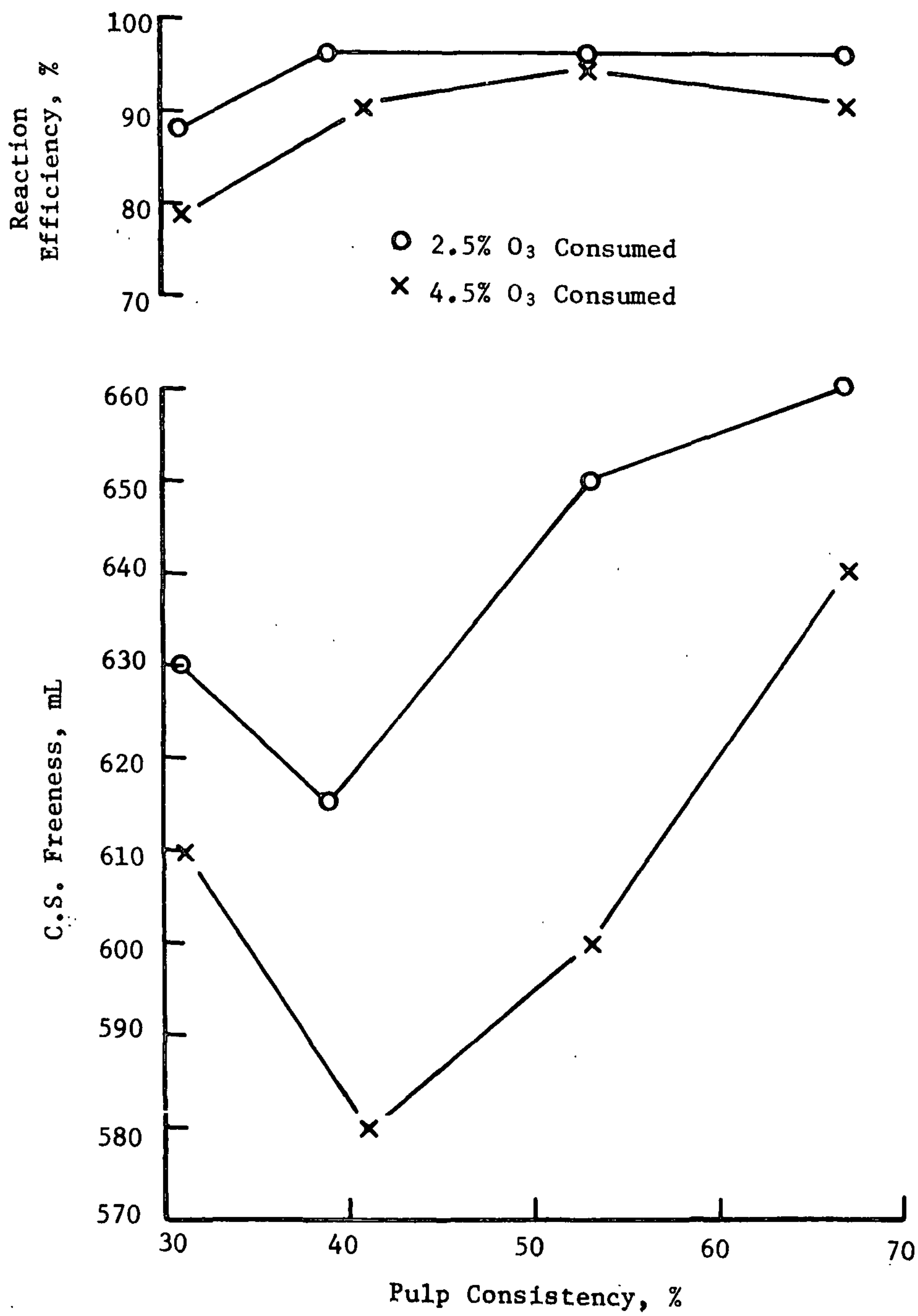


Figure 49. Freeness and Reaction Efficiency Trends at Various Pulp Consistencies During Ozonation

is definitely observed. This is in accord with the literature which suggests ozone reaction is related to the fiber surface moisture balance. At 30% consistency the results are also somewhat less than optimum. Visual assessments during the process of ozonation, however, would suggest possible reasons for the lower values. It was observed that considerable "balling" into fiber clumps occurred at the 30% consistency. It is expected this "balling" significantly affected the bulk density resulting in reduced ozone gas transfer and reaction throughout the pulp mass. The reaction efficiency was significantly reduced as is shown in Fig. 49 and Table X. Reaction uniformity may also be affected. The observations suggest that consistency is not the sole factor which controls ozonation efficiency and resulting pulp quality. The ability of the ozone to penetrate the fiber mass and reach favorable fiber surface sites for reaction may be equally important to effective treatment. Bulk density of the fiber mass in combination with thickness of the surface water film on a given fiber may well control the reaction process. The potential interdependence of these factors cannot be thoroughly assessed with current laboratory ozonation equipment.

LOW CONSISTENCY STUDIES

Much of the research on ozonation of pulp has involved the treatment of pulps in the 30-50% consistency range with gaseous ozone. However, Dr. C. A. Lindholm (2) has reported that low (1-3%) consistency treatments can be used to improve the strength and optical properties of groundwood using a special ozone reactor system. Low consistency treatments could reduce the capital costs of ozonation and may provide processing advantages.

Preliminary screening trials have been carried out at IPC by merely bubbling ozone through 0.1 and 1% slurries. These trials were encouraging inasmuch as marked increase in brightness of the ozonated pulps resulted suggesting significant reactions were occurring. C stain studies of these pulps also indicated reactions were following trends exhibited by the high consistency ozonated pulps. SEM studies, however, suggested some variation in reaction may occur. These studies suggest that fiber surface microcavitation, viz., erosion/pitting is emphasized at the possible expense of surface microfibrillation. More studies would be needed to confirm these preliminary observations. Unfortunately it was not possible to treat sufficient stock to carry out strength tests; and the simplified means of treatment served to point the real need for properly designed equipment if uniform and high reaction efficiencies are to be maintained.

From previously published work by Lindholm and others there is strong evidence to indicate that ozonation of fiber at low consistency results in preferential reaction of the ozone with the fines fraction. This could be undesirable in the ozonation of OCC unless the fines fraction has been removed. This has been the approach that others, including Lindholm, have undertaken.

The key to ozonation at low consistency is the fiber/water/ozone reaction process or mechanism. There has been general agreement that a high degree of turbulence is required at the time of the introduction of the ozone to the fiber slurry. If this is achieved by rather violent dynamic agitation the results are masked by the refining action of the mixing process. Lindholm utilizes an ejector type reaction process chamber to achieve appropriate turbulence levels without the usual prolonged agitation. In personal contacts, Dr. Lindholm suggested that the use of a properly designed static inline mixer may be an attractive reaction unit. This process has been successfully used for treatment of fiber slurries with gases such as chlorine. Data gathered from several manufacturers of static mixers tends to support this theory providing a sufficiently high Reynolds number can be achieved within the static mixer and immediately following the introduction of the vapor or gas phase component.

Construction of a suitable reaction chamber would involve considerable design time and expense. For this reason further work in this area has been deferred until the process engineering work on high consistency ozonation in progress is completed.

REDUCTION OF OZONE APPLICATION RATE

Early ozonation studies were carried out utilizing approximately 2% ozone in oxygen at a flow rate of 4 liters per minute. Physical test results on handsheets prepared from the ozonated fibers receiving less than 2.5% ozone consumed tended to be erratic. It was speculated that the erratic results were due to the laboratory process used in ozonation of the fibers which failed to allow sufficient time for diffusion of the O_3/O_2 gas through the fiber mass. Reaction times of 5 to 10 minutes corresponding to approximately 0.8 and 1.5% O_3 consumed were potentially insufficient to achieve necessary equilibrium. To check this hypothesis, the process was modified to provide a flow rate of 1 liter per minute of oxygen containing 2% ozone. Effective reaction time intervals were thus increased by a factor of four for a given ozone consumption level.

Physical test results are shown in Table XI. The changes in strength at the low O_3 levels were about the same at the two O_3 addition rates. However, most of the strength properties increased with increasing O_3 as expected.

The C stain examination of these treated fibers suggested there may be a more uniform treatment of the fibers at the lower oxygen flow rate, but the results were not completely clear-cut. SEM studies proved to be more interesting.

TABLE XI

COMPARISON OF PROPERTIES OF HANDSHEETS PREPARED FROM OCC OZONATED AT DIFFERENT O_3 RATES

O_2 Feed Rate (∿2% O_3 in O_2)	1 Standard Liter/Min				4 Standard Liters/Min[a]			
Ozonation time, min	0	20	40	60	0	5	10	15
Ozone applied, % of o.d. fiber	--	0.732	1.539	2.261	--	0.820	1.61	2.35
Ozone consumed, % of o.d. fiber	--	0.731	1.535	2.252	--	0.814	1.59	2.31
Reaction efficiency, %	--	99.9	99.7	99.6	--	99.2	98.5	98.3
C.S. freeness, mL	660	615	630	610	633	647	627	617
% Change	--	-6.8	-4.6	-7.6	--	+2.2	-0.9	-2.5
Basis weight, lb/M ft^2	13.5	13.5	13.6	13.6	13.2	13.9	13.6	13.2
Caliper, points	6.0	5.7	5.7	5.7	6.1	6.4	6.1	5.6
Apparent density	2.26	2.37	2.39	2.41	2.16	2.18	2.21	2.34
% Change	--	+4.9	+5.8	+6.6	--	+0.9	+2.3	+8.3
Bursting strength, psig	16.6	2.37	2.39	2.41	2.16	2.18	2.21	2.34
Factor[b]	1.23	1.41	1.50	1.64	1.30	1.36	1.49	1.76
% Change	--	+14.6	+22.0	+33.3	--	+4.6	+14.6	+35.4
Modified ring compression, lb/inch	4.0	3.6	4.3	4.3	3.8	4.3	4.2	4.0
Factor	0.300	0.267	0.312	0.319	0.284	0.311	0.312	0.307
% Change	--	-11.0	+4.0	+6.3	--	+9.5	+9.9	+8.1
Tear, grams	86.4	92.4	94.0	89.6	87.6	56.7	98.5	85.1
Factor[b]	6.39	6.85	6.90	6.57	6.64	6.93	6.87	6.45
% Change	--	+7.2	+8.0	+2.8	--	+4.4	+3.5	-2.9
Tensile, lb/inch	12.0	12.9	13.7	14.7	12.4	13.3	13.8	15.6
Factor[b]	0.89	0.96	1.00	1.08	0.94	0.95	1.01	1.19
% Change	--	+7.9	+12.9	+21.4	--	+1.1	+7.4	+26.6
Stretch, %	2.04	2.07	2.04	2.20	1.86	1.96	2.11	2.18
% Change	--	+1.5	0.0	+7.8	--	+5.4	+13.4	+17.2
Et, lb/inch	1640	1735	1866	1922	1640	1767	1802	1946
Factor[b]	121.3	128.6	137.0	141.0	124.2	127.0	132.5	147.8
% Change	--	+6.0	+12.9	+16.2	--	+2.3	+6.7	+19.0
TEA, ft-lb/ft^2	2.2	2.4	2.4	2.8	2.0	2.2	2.5	2.9
% Change	--	+9.1	+9.1	+27.3	--	+10.0	+25.0	+45.0
ZDT, psi	45.2	52.4	53.4	57.6	52.7	45.4	51.1	61.7
% Change	--	+15.9	+18.1	+27.4	--	-13.9	-3.0	+17.1
Brightness, %	16.4	17.1	19.0	20.2	16.6	18.2	19.1	20.2
% Change	--	+4.3	+15.9	+23.2	--	+9.6	+15.1	+21.7
Zero span factor, km	13.25	12.86	13.98	13.42	12.98	12.94	12.81	12.95
% Change	--	-2.9	+5.5	+1.3	--	-0.3	-1.3	-0.2

[a] Data obtained from Progress Report One, Project 2697-53, entitled "Effect of Ozonation on Recycled Fiber," dated September 24, 1978.

[b] Factors are determined by dividing the given property value by basis weight in lb/M ft^2.

It was noted that trends in fiber modification could be observed between the successive increments of ozone consumption. Visual changes on the fiber surface at the 0.7% level were very limited and could not be readily characterized. At the 1.5% level, a trend toward microcavitation, viz., pitting or erosion of the surface was definite, but little or no surface fibrillation could be observed. At the 2.3% level, "pitting and erosion" increased and the first evidences of limited fibrillation were observed. It is speculated that fibers undergo a series of modifications during ozonation:

1. An initial molecular surface reaction occurs which cannot be physically observed.
2. Secondly, a pitting or erosion of the apparently smooth fiber surface occurs which causes the surface to become "spongy" and reduces rigid surface stresses;
3. Finally, the surface becomes sufficiently modified to reveal surface microfibrils with reduced bonding to the parent fiber.

Since a general trend toward strength increase is shown even at the 0.7% ozone level, it may be suggested that all of the above changes affect one or more of the strength properties; but the rate at which a given property is increased may be related to a certain critical level of modification of the fiber surface. Early changes might be expected to modify fiber stiffness or conformability, but real increases in fiber surface may not be achieved until microfibrillation occurs. It appears that more fundamental studies are required to better understand ozone/fiber reactions.

RAPID OZONATION OF FIBER PADS

Several screening trials were carried out to determine if ozonation would proceed rapidly in an excess of ozone. To achieve these goals, it was necessary to ozonate only small quantities of fiber in an appropriate reaction unit. Thin fiber pads of approximately 1-1/4 inches in diameter were formed in a Gilman filter unit at a consistency of 30-50%. Consistency was difficult to maintain but appeared to approximate consistencies normally achieved by fluffing. Pads contained about 35 mg of o.d. pulp. The pad was placed into an aluminum Gilman in-line filter which became the reaction vessel. Oxygen containing 2% ozone was applied to the pad at a flow rate of 4 liters per minute. Pads were treated for 1, 2, 4, and 8 minutes.

Visual examination of the pads showed increases in brightness occurred. This indicated that O_3 reacts with the fiber under these conditions. It was also noted that the pads became dryer during the treatment due to the flow of the extremely dry gas through the pads. The pad after 8 minutes of treatment was essentially air dry to the touch. Thus, the idealized fiber consistency, viz., fiber moisture balance, may have existed for only a short period of time during the reaction interval.

The treated fibers were stained with C stain. Color changes on fibers from the 1 minute ozonation interval suggested the fibers consumed in excess of 2.5% ozone. At the 8 minute ozonation interval, color changes were roughly equivalent to 12% ozone consumed. Comparable time intervals under previous ozonation procedures were 15 to 90 minutes, respectively.

These preliminary trials suggest that ozonation proceeds rapidly when sufficient ozone is present and processing conditions are optimized. Results indicate the reaction rate was increased by a factor of ten. With better control of process variables, such as pulp consistency, further improvements might be expected. On that basis a continuous ozonation process based upon moving fibers or fiber webs through an ozonation zone may be feasible and more cost effective than a batch process.

SOLUBLE PRODUCTS OF OZONATION

Samples of original OCC board, the fluffed but unozonated OCC pulp, and handsheets containing OCC ozonated to approximately 12% O_3 consumed were analyzed for hot and cold water solubles and total organic carbon in the solubles. Results are shown in Table XII.

TABLE XII

ANALYSIS OF SOLUBLES

	OCC Board	Fluffed Untreated Pulp	Handsheet 12% O_3 Consumed Based on o.d. Fiber
Cold water solubles, %	1.5	1.0	2.1
Hot water solubles, %	1.7	1.1	1.0
Total solubles, %	3.2	2.1	3.1
Total organic carbon, mg/L in cold water solubles	65.5	37.5	76.5
Total organic carbon, mg/L in hot water solubles	188.5	146.5	156.0
Total organic carbon, mg/L	245.0	184.0	232.5

These results suggest that yield and effluent problems should be nominal due to ozonation as anticipated. There is a washing step after ozonation in addition to handsheet preparation which may have removed some cold water solubles.

However, the residual in the handsheet when compared with the fluffed but untreated pulp should be indicative of the solubles produced in ozonation. Because the increase in solubles upon ozonation is only about 1% of the fiber weight, the affect on yield and effluent may be expected to be minimal. Analysis of the ozonated OCC before further treatment would be ideal, but the current laboratory ozonation process does not lend itself well to recovery of the pulp at that point.

MICROSCOPY STUDIES OF OZONATED FIBERS

Microscopy studies of the ozonated fiber have been an integral part of this program. Early observations are reported in Progress Report One. Initial trials revealed C stain could be used to monitor treatment level and uniformity by reason of a color shift from yellow for the untreated fibers to blue with increasing ozonation levels. Various fiber cell groups appear to respond to ozonation at different rates. The response seems to be related to cell wall thickness and/or density. Thin walled hardwood vessels and softwood earlywood fibers shift from yellow to the blue more rapidly than the thicker walled hardwood fibers and softwood latewood fibers. C stain can therefore be utilized to monitor treatment level and uniformity under the changing experimental conditions of ozonation. In some cases it forms the primary basis of assessment as in the instances of low consistency ozonation and rapid ozonation of fiber pads discussed in other sections of this report. In those experiments only small quantities of treated fiber could be generated and handsheets for physical property tests could not be prepared.

Limited C stain observations of treated fibers at high magnifications have also offered an insight concerning the depth of penetration of the reaction into high density fibers such as the softwood latewood. These preliminary observations have led to the consideration of a combination of bright field and fluorescence microscopy for further examination. Lignin is known to fluoresce at a characteristic wavelength. It is possible that the depth of lignin modification can be followed by comparison of bright field and fluorescence photomicrographs.

Initial scanning electron microscope (SEM) studies (see Progress Report One) suggested definite fiber surface modifications were taking place. Two potentially significant trends were observed: lightly attached microfibrils seemed to appear on the fiber surface and a tendency toward erosion or pitting of the surface in a regular fashion occurred. Further work has been carried out to relate the physical changes to known and accepted fiber wall structure. In addition, based upon findings with C stain relative to different reaction rates for the four major cell types, (hardwood fibers and vessels and softwood early- and latewood), it was decided to examine them under the SEM.

Figures 50 and 51 show a softwood earlywood fiber ozonated to the 11.7% level. The first electron micrograph shows a segment of the softwood earlywood in perspective at low magnification. Succeeding micrographs at increasing magnifications show features of the area framed in the first in greater detail. Micron scales are included for size assessments. For comparison, a diagram of the cell wall structure of a typical softwood fiber is included in Fig. 50 (3). Fiber microscopists typically recognize a middle lamella of essentially lignin covering the fiber outer wall of adjacent fibers. A thin primary wall is then observed which is rich in lignin but contains a limited number of fibrils in fairly random orientation. A secondary wall composed of several layers is next encountered. Each layer contains a number of sublayers. Fibril spiral windings within these layers vary from essentially perpendicular to the fiber axis in the outer secondary or S1 layer to increasingly parallel to the axis in deeper layers. Fibrils within an intertracheid pit area are shown to form concentric rings about the pit.

The electron micrograph of the pit area of the treated fiber at the highest magnification (Fig. 51a) shows the "erosion or pitting" associated with the ozone treatment does form concentric rings about the pit opening. It is speculated that the erosion due to ozonation follows the cleavage areas between microfibril windings. The electron micrograph at intermediate magnification (Fig. 51b) shows erosion in

700 X Magnification

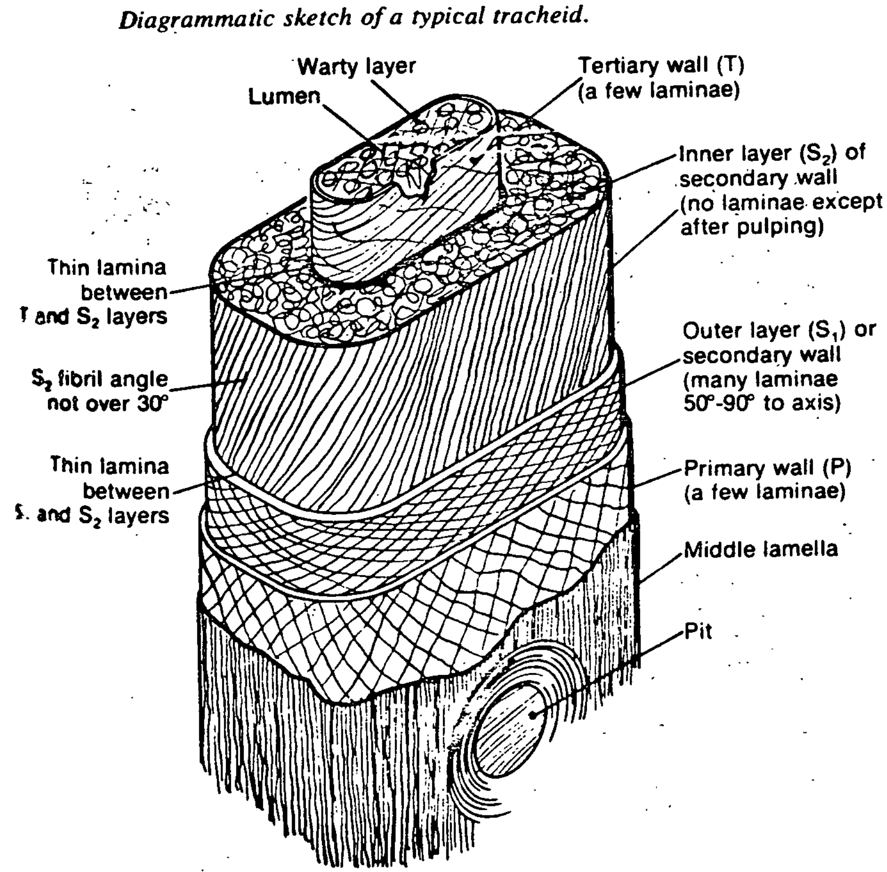
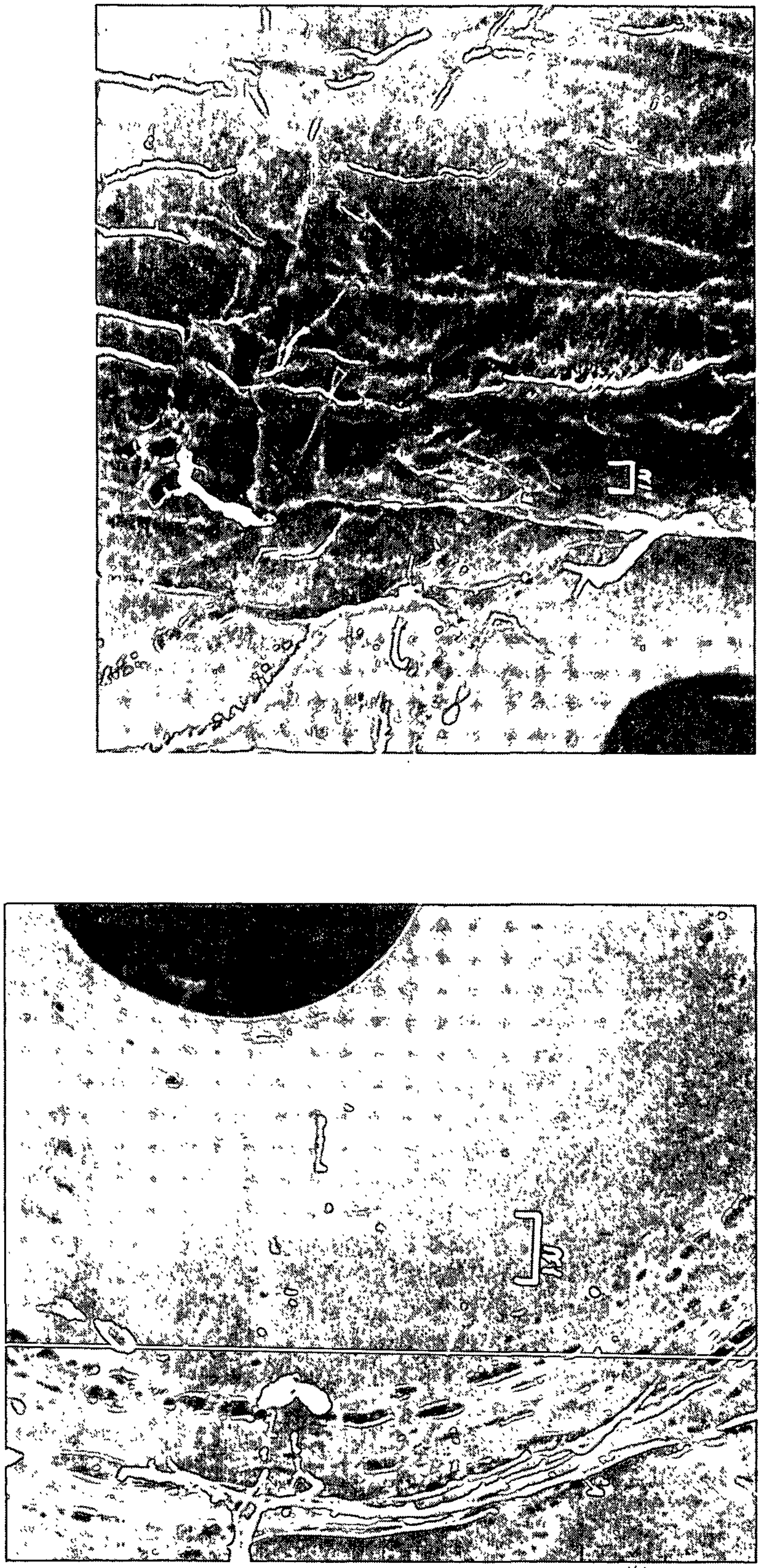


Figure 50

Critical Point Dried Softwood Early Wood Fiber Ozonation Level 11.7%

Diagram Wall Structure of a Softwood Fiber



a
10,000 X Magnification

b
5,000 X Magnification

Figure 51. Critical Point Dried Softwood Early Wood Fiber Ozonation Level 11.7%

the body of the parent fiber as well as the pit area. This "erosion" appears to form a pattern essentially perpendicular to the fiber axis suggesting the surface exhibited is an outer layer of the S1 wall. The lightly bonded fibrils may be from the primary wall or the S1 wall.

Clark (3) suggests a size definition for fibril strands. Strands less than 200 A in diameter are termed nanofibrils. Those 20 nm to 200 nm or 0.2 micron in diameter are termed microfibrils. 0.2 Micron is about the lower limit of visibility of a very good light microscope. Above 0.2 micron the fibril bundles may be called macrofibrils or simply fibrils. The fibrils exhibited in the SEM examinations are generally less than 0.2 micron in diameter. Thus they fall into the microfibril range rather than the macrofibril range normally associated with mechanical refining and readily observed with the compound light microscope.

Concurrently untreated softwood earlywood fibers were examined at comparable SEM viewing magnifications. Fibrillation and pitting or erosion were not observed. Instead, the fiber surface appeared to be coated with a nonfibrous material and fibrous surface detail could not be readily observed. No micrographs of untreated softwood are included in the report. However a micrograph of an untreated hardwood vessel surface is shown in Fig. 53 which exhibited the general character and texture of all untreated cells.

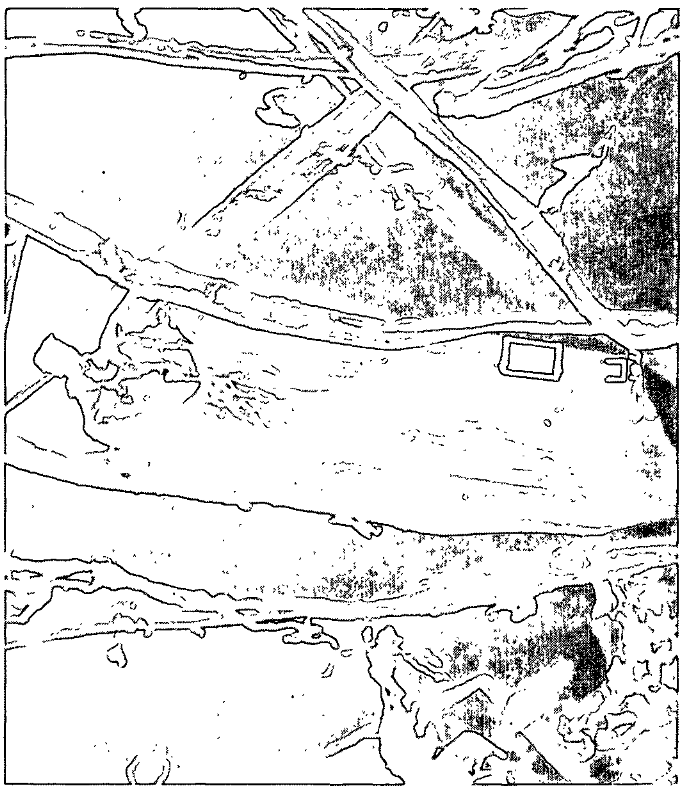
Treated summerwood latewood fibers were also examined. Fibrillation and erosion were not observed even at the 11.7% ozone consumed level. The result was not wholly unexpected because C stain studies indicated reactions of the softwood latewood were incomplete even at the 11.7% level. SEM photographs, in effect, confirm the C stain observations which suggested the more dense or thick-walled latewood fibers responded much more slowly than the thin-walled earlywood fibers.

Untreated and ozonated hardwood vessels are shown in Fig. 52 and 53 at increasing viewing magnifications. As magnification increases (Fig. 53) significant overall pitting of the vessel surface becomes readily apparent. None is observed on the untreated vessel. In fact, the fibrous surface detail is minimal. The surface of the untreated vessel exhibits a similar "texture" at the highest SEM magnifications utilized. This "coated texture" is typical of all untreated fibers, both softwood and hardwood.

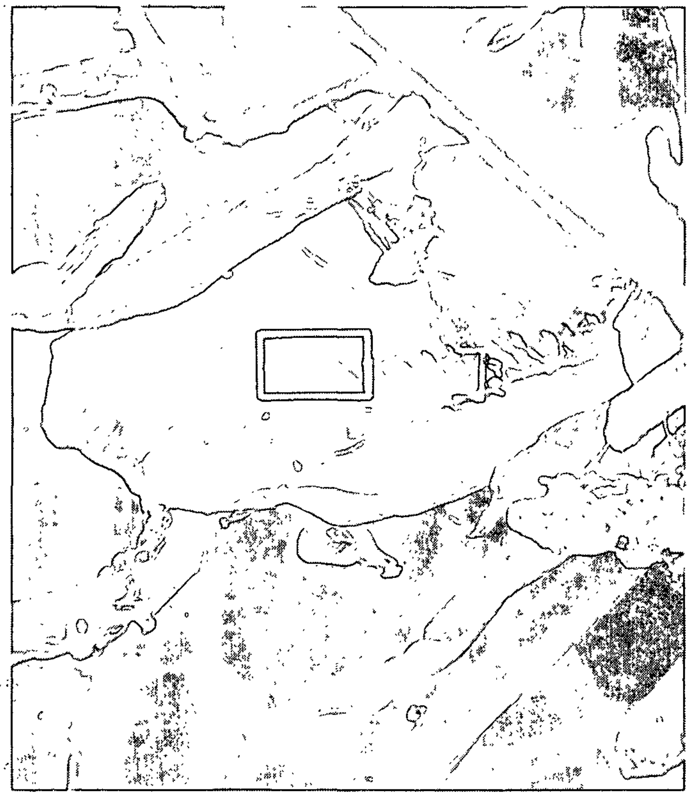
Figure 54a shows the pitting of the ozonated vessel at still higher magnifications. The extensive pitting is large and appears to be of significant depth. In the central area, pits have appeared to cohere resulting in fibril strands bridging and connecting the crevasses formed.

A hardwood fiber ozonated to the 11.7% level is shown in Fig. 54b and 55. At the intermediate magnification a limited amount of microfibrillation is observed. A ridge pattern essentially perpendicular to the fiber axis also seems to be forming but it is indistinct. However, at still higher magnifications (Fig. 55b) very small pits have formed. The size and frequency are far less than shown by the hardwood vessel (Fig. 54a) at a comparable magnification or by the softwood earlywood (Fig. 51).

Briefly summarizing, these studies indicate that ozone modifies the fiber surface by causing pitting and fibrillation. SEM studies confirm previous C stain observations which suggest that the low density fiber cells respond much more rapidly than the high density thick-walled cells.



Untreated Vessel Element; 300 X Magnification



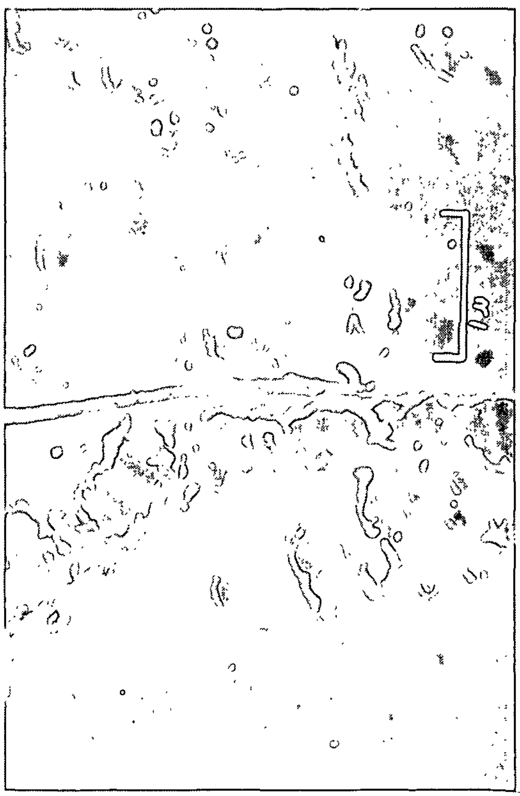
11.7% Ozonated Vessel Element; 700 X Magnification

Figure 52. Critical Point Dried Hardwood Vessel Elements Before and After Ozonation — Low Magnification

11.7% Ozonated Vessel Element; 5,000 X Magnification

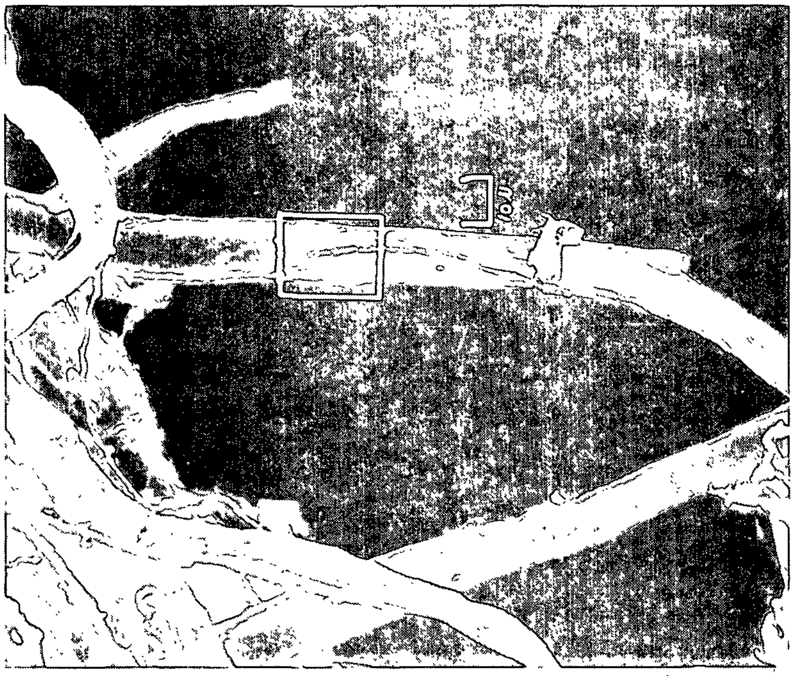
Untreated Vessel Element; 5,000 X Magnification

Figure 53. Critical Point Dried Hardwood Vessel Elements Before and After Ozonation



a

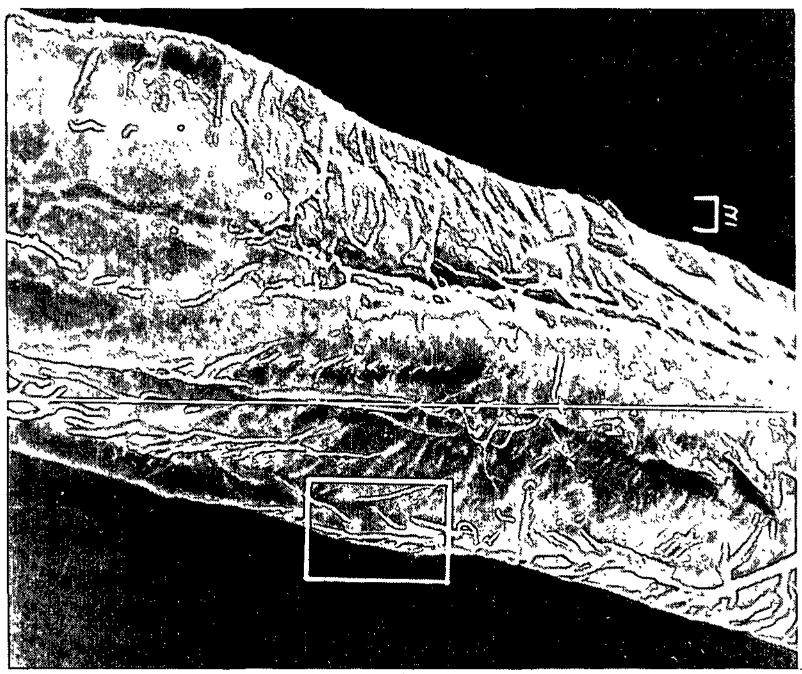
Critical Point Dried Hardwood Vessel Element; Ozonation Level 11.7%; 20,000 X Magnification



b

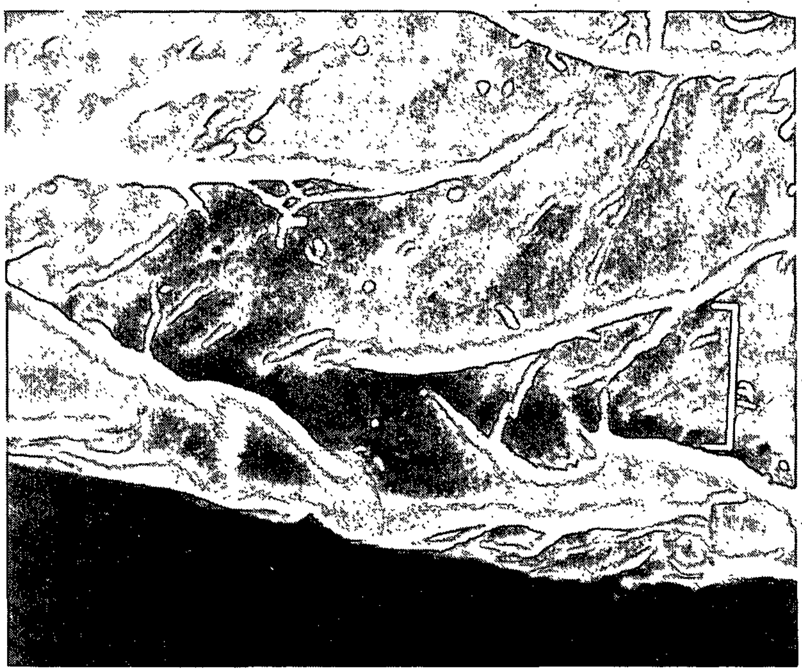
Critical Point Dried Hardwood Fiber; Ozonation Level 11.7%; 700 X Magnification

Figure 54



a

500 X Magnification



b

20,000 X Magnification

Figure 55. Critical Point Dried Hardwood Fiber 11.7% Ozone Consumed

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LITERATURE CITED

1. Zotterman, C. and Wahren, D. A technique for simulating production quality of high-speed wet press runs. Paper Trade J. 162(16):37-8, 64(Aug. 15-31, 1978).

2. Lindholm, C. A. Papper Och Tra (1):17-20(1977).

3. Clark, J. d'A. Pulp technology and treatment for paper. Miller Freeman Publications, Inc., San Francisco, 1978.

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