



4-1978

Influence of Overdrying on Dimensional Stability and Certain Strength Properties of Paper

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INFLUENCE OF OVERDRYING
ON
DIMENSIONAL STABILITY AND CERTAIN STRENGTH PROPERTIES
OF PAPER

by

Shun K. Ma

A Thesis submitted to the
Department of Paper Science and Engineering
in partial fulfillment of the
Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
April, 1978

ACKNOWLEDGEMENT

The author would like to take this opportunity to thank my advisor, Mr. John Fisher, Associate Professor in the Department of Paper Science and Engineering at Western Michigan University, for his wonderful assistance during my working on this thesis. With his opinions and advice, the author could finish the work on time.

ABSTRACT

In the past, the consequences of overdrying have been examined with the drying theory. This study was designed to look at the effects of overdrying on handsheets. Comparison of the dimensional change and strength properties was made between two sets of handsheets, one conditioned in the humidity room and the other overdried at 90°C for four hours. The handsheets used in this experiment were made from five types of furnishes: Hardwood Kraft, Softwood Kraft, Hardwood Kraft and Softwood Kraft combination, and two different percentages of TiO₂ added to Softwood Kraft. The dimensional stability was measured by the Neenah Expansimeter. The Tappi Standard Testing Procedures were used to test the physical properties of the handsheets. The results of this study showed that overdrying improved the dimensional stability and tensile strength, yet reduced a certain amount of mullen, tear and fold in handsheets.

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INTRODUCTION

The drying of paper is quite simply the elimination of water from a moisture fiber mat. There are two basic methods for removing water from a wetted sheet: by mechanical means, i.e. draining and pressing, or by heating the sheet in order to drive off the water. The last method is the most expensive in water removal due to the high cost of energy.

One of the most vexing problem in manufacturing paper during the drying process is the overdrying of the paper. The effect of overdrying on dimensional instability is occasionally manifested visually on skids or piles of cut paper which are exposed to conditions of higher relative humidity. This dimensional instability causes problems such as curling, buckling, wavy edges, cockling and misregister which the printers are unhappy about when these occur during the printing process. A lot of examples show that overdrying paper has increased the embrittlement which reduces certain amount of strength properties of paper.

The cellulose and water relationship is one of the fundamental importances to an understanding of drying process in papermaking, as well as to the strength properties of paper. The structure and composition of fiber affect its absorption of water. The temperature effect during the drying process causes certain chemical changes in cellulosic material. The cellulosic material loses a certain amount of its swelling ability and flexibility if the cellulose is heated at high temperature.

This study is designed to examine the overdrying influences by comparing the effects of high temperature on the dimensional change and strength properties at two levels of conditioning handsheets: humidity room condition and overdried at 90°C for four hours.

LITERATURE SURVEY

The drying of paper is a process in which the water is eliminated from a moist fiber mat by heating the sheet with constant steam after the press section. Attwood (1) proposed the phenomena of drying curve as shown in Figure 1. The sequence from A to B is the constant rate in which the moisture is evaporated at the exposed surface at the beginning of drying. During this stage, the water evaporated from the paper surface is replaced by the water drawn from the capillaries in the wetted sheet. A dynamic balance is maintained between the heat in evaporating moisture and the heat transferred to the wetted sheet. The point B, which is called the "critical moisture content" is where moisture can no longer be supplied to the surface as rapidly as it is evaporated. As the moisture content falls along B to C, there is insufficient moisture in the sheet to keep the capillaries full. The line between B and C is called the "falling rate period" when water is drawn less and less from capillaries. At C point, there is a transition point indicating the absorbed water by the sheet was beginning to evaporate. Since this water has a lower vapor pressure, the rate of removing the moisture from the sheet will drop further. At point D, only bounded or hydrated water remain in the sheet; this water is more difficult to remove. Most paper out of the dryer should be at this point D. It is generally defined the paper as being over-dried when the sheet coming out from the dryer has less than 6% moisture. The overdrying of paper may cause better dimensional stability, but reduces other physical properties.

Paper drying depends on a combination of heat transfer and mass transfer: heat transfer is the transfer of thermal energy as the result of a temperature difference, and mass transfer is concerned with the water vapor from a moisture surface of sheet passing through a boundary layer of air.

Race (2) suggested that the transmission of heat from one surface to another is simply expressed by the formula:

$$Q = \Delta T \alpha A$$

where Q is the quantity of heat transferred
 A is the surface area of heat transfer
 α is the coefficient of heat transfer
 ΔT is the temperature gradient

And, the transmission of vapor from a wet surface during paper drying is expressed by the formula:

$$W = \frac{A \beta M_w}{RT} (P_o - P_a)$$

where W is the quantity of water evaporated
 A is the drying surface area
 M_w is the molecular weight of the vapor
 β is the mass transfer coefficient
 R is the gas constant
 T is the temperature in $^{\circ}K$
 P_o is the vapor pressure at the surface, and
 P_a is the vapor pressure at the air.

Large profile variations found on many modern paper machines forces the papermaker in practice to overdry the paper stock. Overdrying may cause considerable paper quality deficiencies. The major factors causing the variation in moisture profile of the sheet are as follows:

- (1) Non-uniform caliper during sheet formation,
- (2) Non-uniform drying process in dryer,
- (3) Non-uniform heat transfer when drying the paper,
- (4) Uneven mass transfer of water vapor from sheet to air due to the possibility of defective drying surface of drier or steam system construction.

It is also believed that drier felt tension has notable effect on the condensing rate of steam in the cylinder. Increasing the web pressure against the cylinder increases the heat transfer coefficient.

Gardner (3) in his study of moisture profile variation on paper machines demonstrated two typical profiles for a newsprint machine and another typical reel moisture profile for sized book paper as

shown in Figure 2 and Figure 3. These typical moisture profiles clearly show that the extent of drying progressively increases from a peak usually near the center to both edges of the web. He claimed that less drying of the newsprint would result in the moisture peak exceeding control limits and would cause calender breaks in the same area.

Several investigators (4,5,6) point out that fiber overdrying beyond certain points at elevated temperature will cause a change in properties such as: (a) loss in fiber strength and physical strength of the sheet, (b) loss in its ability to resorb water and ink, and (c) change in dimensional stability.

High temperature treatment of cellulosic material causes radical reaction and degradation in cellulose and hemicellulose chains. Back and his co-workers (7),(8), in their studies of thermal autocross-linking cellulosic materials, found that the crosslinking reduces the swellability of cellulosic material in water. The covalent cross-linkage can be measured by the swelling restriction in paper. Furthermore, this swelling restriction can be measured as a change in the water absorption of paper. In their further studies of the modulus of elasticity of paper when the paper is treated by heating from -80°C to 400°C , by using ultrasonic measurement technique, the modulus of elasticity decreased rapidly with increasing temperature in range between 0°C to 300°C . In Figure 4, Young's modulus for five different papers obtained from dry thermal treatment is plotted against the nip temperature. The elasticity decreases rapidly in the three temperature ranges from $0^{\circ} - 50^{\circ}\text{C}$, $170^{\circ}\text{C} - 240^{\circ}\text{C}$ and above 300°C . These reactions cause the cellulosic degradation and reduce the degree of crystallinity and the level of molecular weight of cellulose.

In past works, the thermal expansion of cellulose was measured by Ramish and Goring (9) and specific surface area was measured by Stone and Scallen (10). Herbert and his co-workers (11), by using differential thermal analysis, found some paper and carbohydrate having endothermic peaks at $135^{\circ}\text{C} - 155^{\circ}\text{C}$ and $310^{\circ}\text{C} - 360^{\circ}\text{C}$ which

indicates massive decomposition of cellulosic materials at these temperature ranges.

Methods of improvement of dimensional stability by chemical treatment of cellulose were done by Stamm (12), Fahey (13) and Morton (14). But these chemical methods promise little due to the effect on other properties and economic cost.

George (15) has examined the effect of various additives on dimensional stability. The addition of fillers, size press chemicals, and synthesis has little effect. Inert mineral fillers will reduce the equilibrium moisture content of the sheet, but will not improve dimensional stability.

EXPERIMENTAL PROCEDURE

Preparation of Furnishes and Handsheets

Five sets of handsheet were prepared from the following pulp furnishes with four different beating times:

1. Hardwood Kraft
2. Softwood Kraft
3. 60% of Hardwood Kraft and 40% Softwood Kraft
4. 5% of TiO_2 added to Softwood Kraft and 15% of TiO_2 added to furnish.

Two hundred and forty grams of dried pulp were refined in Valley Beater at 2% consistency. Take 0, 20, 40, 60 minutes refined pulps for preparation of handsheets. In the preparation of the handsheets, the Noble and Wood method was used. TiO_2 was added directly to the Noble and Wood for forming handsheet for the last two sets of handsheets.

Ten or twelve handsheets for each furnish were made on the Noble and Wood handsheet forming mold. These handsheets were of good formation and were dried through the heating cylinder drier with a constant steam pressure. Then the handsheets were conditioned in the humidity room. Half-sheet portions of handsheets were used for over-drying in the oven for four hours at 90°C.

Testing of Handsheets

Tappi Standard Methods used for the testing of physical properties were as follows:

1. Tensile strength: Tappi T-220
2. Mullen strength: Tappi T-403
3. Fold strength: Tappi T-423
4. Tear strength: Tappi T-414

Measurement of Hygroexpansivity of Handsheets

The Neenah Multiple Specimen Paper Expansimeter was used to measure the dimensional stability of specimens.

1. Each specimen was one inch wide, its length was 8 inches, and the actual of measurement length was 7.5 inches.
2. The saturated salt solutions used for control of relative humidity cycle were as follows:

Sodium Nitrite	64.8% Relative Humidity
Potassium Carbonate	43.9% Relative Humidity
Potassium Chromate	86.5% Relative Humidity

3. The change in length of each specimen for each cycle corresponding to the observed humidity was determined.
4. The change in length for the standardized change in relative humidity was calculated by using the formula:

$$X = 15C / (H_1 - H_2)$$

where X is the change in length of the specimen corresponding to a change from 86.5% to 43.9% Relative Humidity,
 C is the observed change in length of the specimen from H₁ to H₂,
 H₁ is the observed higher Relative Humidity,
 H₂ is the observed lower Relative Humidity.

5. The X value was used to calculate the percent change of length by using:

$$\frac{X}{7.5} 100\% = \% \text{ change corresponding to the specimen length}$$

PRESENTATION OF DATA

The hygroexpansivity measured by the Meenah Multiple Specimen Paper Expansimeter for the handsheets conditioned in the humidity room and overdried condition at 90°C for four hours are shown in Table I and Table II respectively. The percentage changes in 7.5 inches specimen data from Column 9 are plotted against the beating time in Figure 5.

The comparison of strength properties between the two different methods of conditioning handsheets are shown in Table III to Table VII. The physical properties such as tensile, mullen, fold and tear are plotted against the beating time in Figure 6 to Figure 9. All figures are shown in the Appendix.

Table I The Hygroexpansivity Measured by Neenah Multiple Specimen Paper Expansimeter
The Handshcets Conditioned in Humidity Room

Pulp Type (1)	Beating Time (2)	Freeness (3)	The Specimen's Length Change corresponding to Relative Humidity Change, 1/1000in.			Average in 7.5in. Specimen (7)	Change in 7.5in. Specimen (8)	% change in 7.5in. Specimen (9)
			64.8%R.H. (4)	to 43.9%R.H. (5)	86.5%R.H. (6)			
H.W.K.	0 20 40 60	662 400 200 120	0.015 0.015 0.023 0.024	0.024 0.036 0.049 0.051	0.024 0.040 0.064 0.069	0.0240 0.0380 0.0565 0.0600	0.0084 0.0134 0.0199 0.0211	0.113% 0.178% 0.265% 0.282%
S.W.K.	0 20 40 60	710 610 490 200	0.014 0.014 0.017 0.018	0.047 0.057 0.055 0.060	0.040 0.062 0.052 0.058	0.0440 0.0595 0.0535 0.0590	0.0155 0.0210 0.0188 0.0207	0.207% 0.279% 0.252% 0.277%
60% H.W.K. 40% S.W.K.	0 20 40 60	680 560 400 200	0.015 0.020 - 0.024	0.055 0.040 - 0.061	0.046 0.041 - 0.073	0.0505 0.0405 - 0.0670	0.0178 0.1420 - 0.0236	0.237% 0.195% - 0.315%
5% TiO ₂ added to S.W.K.	0 20 40 60	720 620 464 210	0.019 0.017 0.028 0.045	0.053 0.047 0.060 0.071	0.044 0.046 0.070 0.071	0.0485 0.0465 0.0650 0.0710	0.0171 0.0164 0.0229 0.0250	0.228% 0.218% 0.305% 0.333%
15% TiO ₂ added to S.W.K.	0 20 40 60	708 600 460 200	0.015 0.013 0.026 0.030	0.070 0.041 0.054 0.071	0.061 0.041 0.062 0.071	0.0665 0.0410 0.0580 0.0710	0.0230 0.0140 0.0200 0.0250	0.306% 0.192% 0.272% 0.333%

Table II The Hygroexpansivity Measured by Neenah Multiple Paper Expansimeter
The Handsheets Conditioned in Overdried Condition at 90°C for 4 Hours

The Specimen's Length Change corresponding to Relative Humidity Change, 1/1000in.								
Pulp Type (1)	Beating Time (2)	Freeness (3)	64.8%R.H. to 43.9%R.H. (4)	43.9%R.H. to 86.5%R.H. (5)	86.5%R.H. to 43.9%R.H. (6)	Average (7)	Change in 7.5in. Specimen (8)	% change in 7.5in. Specimen (9)
H.W.K.	0	662	0.012	0.035	0.032	0.0335	0.0120	0.157%
	20	460	0.012	0.036	0.035	0.0355	0.0125	0.169%
	40	200	0.016	0.038	0.045	0.0415	0.0146	0.197%
	60	120	0.018	0.048	0.056	0.0520	0.0180	0.244%
S.W.K.	0	710	0.017	0.032	0.023	0.0275	0.0095	0.131%
	20	610	0.011	0.046	0.032	0.0390	0.0137	0.183%
	40	490	0.012	0.044	0.038	0.0410	0.0144	0.192%
	60	200	0.016	0.047	0.044	0.0455	0.0160	0.216%
60% H.W.K. and 40% S.W.K.	0	680	0.011	0.040	0.030	0.0350	0.0123	0.164%
	20	560	0.014	0.039	0.039	0.0390	0.0137	0.183%
	40	400	0.013	0.047	0.044	0.0455	0.0160	0.213%
5% TiO ₂ added to S.W.K.	60	200	0.025	0.049	0.049	0.0490	0.0173	0.230%
	0	720	0.012	0.037	0.029	0.0330	0.0116	0.155%
	20	620	0.015	0.043	0.049	0.0460	0.0162	0.216%
15% TiO ₂ added to S.W.K.	40	464	0.019	0.058	0.050	0.0540	0.0190	0.254%
	60	210	0.022	0.054	0.061	0.0575	0.0202	0.269%
	0	708	0.009	0.038	0.028	0.0330	0.0116	0.155%
15% TiO ₂ added to S.W.K.	20	600	0.012	0.035	0.031	0.0330	0.0116	0.155%
	40	460	0.019	0.039	0.037	0.0380	0.0134	0.178%
	60	200	0.021	0.068	0.075	0.0715	0.0252	0.336%

Table III Comparison of Physical Properties of H.W.K. Handsheets Conditioned in Humidity Room and Overdried

	Humidity Room condition				Overdried condition			
	0	20	40	60	0	20	40	60
B.T.	0	20	40	60	0	20	40	60
Freeness	662	460	200	120	662	460	200	120
Tensile	1.47	9.59	12.27	15.47	1.89	11.9	17.57	15.9
Mullen	1.38	16.13	26.20	26.30	1.64	17.21	24.79	24.9
Fold	0	7.43	66.67	129.60	0	7.2	60.40	127.12
Tear	8.70	13.50	15.00	10.83	5.71	12.87	13.60	14.43

Table IV Comparison of Physical Properties of S.W.K. Handsheets Conditioned in Humidity Room and Overdried

	Humidity Room condition				Overdried condition			
	0	20	40	60	0	20	40	60
B.T.	0	20	40	60	0	20	40	60
Freeness	710	610	493	200	710	610	493	200
Tensile	5.97	18.1	19.77	24.0	1.87	14.0	22.1	18.36
Mullen	8.5	42.13	65.00	55.37	8.34	40.14	46.14	53.5
Fold	4.2	240	350	1312	3.6	243	424	490
Tear	-	-	-	-	6.37	19.8	22.91	18.36

Table V Comparison of Physical Properties of 60% H.W.K. and 40% S.W.K. Handsheets Conditioned in Humidity Room and Overdried

	Humidity Room condition				Overdried condition			
	0	20	40	60	0	20	40	60
B.T.	0	20	40	60	0	20	40	60
Freeness	680	500	390	200	680	500	390	200
Tensile	2.45	2.9	8.7	12.61	1.89	3.5	10.3	12.79
Mullen	1.13	3.17	14.8	21.0	1.63	2.47	14.44	21.74
Fold	0	0	5.5	17.2	0	0	5.0	16.33
Tear	8.0	9.67	13.5	12.5	5.44	7.0	12.29	10.13

Table VI Comparison of Physical Properties of 5% TiO₂ added to S.W.K. Handsheets Conditioned in Humidity Room and Overdried

	Humidity Room condition				Overdried condition			
	0	20	40	60	0	20	40	60
B.T.	0	20	40	60	0	20	40	60
Freeness	720	620	464	210	720	620	464	210
Tensile	2.23	5.14	8.51	11.57	2.24	5.02	7.25	10.62
Mullen	1.37	6.01	12.3	14.92	1.3	4.9	10.3	14.11
Fold	0	2.0	3.4	6.8	0	0.8	2.67	5.0
Tear	6.5	12.17	13.5	11.75	4.64	9.64	10.29	9.71

Table VII Comparison of Physical Properties of 15% TiO₂ added to S.W.K. Handsheets Conditioned in Humidity Room and Overdried

	Humidity Room condition				Overdried condition			
	0	20	40	60	0	20	40	60
B.T.	0	20	40	60	0	20	40	60
Freeness	708	600	460	200	708	600	460	200
Tensile	6.44	14.03	20.37	20.83	6.87	16.85	21.0	21.33
Mullen	9.5	30.08	41.58	45.5	8.63	29.71	37.86	41.43
Fold	2.8	155.7	256.7	384.67	2.6	108	318.3	369.83
Tear	22.67	24.5	20.0	15.86	21.0	16.29	10.29	9.71

DISCUSSION

The percentage in magnitude change in dimensional stability and physical properties are used for the analysis of data which is shown in the following table.

% Increase in Dimensional Stability and % Decrease in Strength due to Overdrying

Pulp Type (1)	B.T. (Minutes) (2)	Dimensional Change (3)	Tensile (4)	Mullen (5)	Fold (6)	Tear (7)
H.W.K.	C	-38.9	-28.6	-18.8	0	34.4
	20	5.1	-24.1	- 6.7	3.1	4.7
	40	25.7	-47.2	5.4	9.4	9.3
	60	13.5	- 2.8	5.3	1.9	-33.2
S.W.K.	C	36.7	68.7	1.9	14.3	32.0
	20	34.4	22.7	4.7	- 1.3	27.6
	40	23.8	-11.8	29.0	-21.1	4.4
	60	22.6	7.1	3.4	62.6	18.9
60% H.W.K.	0	30.8	29.6	44.3	0	-
	20	6.2	-20.7	22.4	0	-
40% S.W.K.	40	-	-18.4	2.4	9.1	-
	60	27.0	- 1.5	3.5	5.1	-
5% TiO ₂ added to S.W.K.	0	32.0	- 4.5	5.1	0	28.6
	20	1.0	2.3	18.5	0.6	20.8
	40	16.7	14.8	16.3	21.5	23.8
	60	19.2	8.2	5.4	26.5	17.4
15% TiO ₂ added to S.W.K.	0	49.4	- 6.7	9.1	7.1	7.4
	20	10.3	-20.1	1.2	30.6	33.5
	40	34.6	- 3.1	8.9	-23.9	48.6
	60	- 1.0	-2.4	8.9	3.9	38.8

This table is converted from the data in Tables I to VII. In general, it shows a significant improvement in dimensional stability when the handsheets are overdried at 90°C for four hours with exception of a couple of samples (i.e., one at zero minute of refining in H.W.K. and the other at 60 minutes of refining in the S.W.K. furnish with 15% TiO₂ added). The best improvement in dimensional stability

is in S.W.K. and 15% TiO_2 added to S.W.K.. When compared among the degrees of refining, the furnishes at 20 minutes refining showed less dimensional stability improvement and the zero minute refining furnish showed better improvement.

The better dimensional stability improvement in S.W.K. and 15% TiO_2 added to S.W.K. can be explained by the natural structure of softwood fibers. Softwood fibers have longer fibers and greater flexibility as opposed to hardwood fibers which have large and short fibers with scalariform opening at the end of the fiber. For this reason, hardwood fiber has more contact area for moisture adsorption when it is exposed to high relative humidity. This causes the dimensional change in hardwood fiber.

The effect of overdrying on the percentage magnitude change on the strength properties of handsheet such as, tensile, mullen, fold and tear are shown from Column 4 to Column 7. Overdrying seems to improve the tensile properties in H.W.K., 60% H.W.K. plus 40% S.W.K., and 15% TiO_2 added to S.W.K. handsheets. There is more improvement in tensile strength in H.W.K., 15% TiO_2 added to S.W.K. and 60% H.W.K. plus 40% S.W.K. handsheets, whereas the S.W.K. and 5% TiO_2 added to S.W.K. furnishes display a certain amount of reduction in tensile strength. Overdrying also gives better mullen strength in H.W.K. and 60% H.W.K. plus 40% S.W.K. furnishes at a lower degree of refining. The rest of the handsheets shows a reduction in their mullen properties under overdrying conditions. The fold and tear properties of handsheets also have been damaged by the overdrying, especially in handsheets with TiO_2 added.

From the above analysis, overdrying has shown consistent improvement in dimensional stability of handsheets. But at the same time, overdrying the handsheets also sacrifices a certain amount of mullen, tear and fold properties of the sheets.

SUMMARY AND CONCLUSION

The comparison of dimensional change between the overdried handsheets and underdried handsheets show that the temperature on drying a sheet has significantly correlated with the dimensional stability and strength properties of the sheet. The high temperature treatment of the sheet will cause the change in chemistry of cellulose and physical properties of cellulosic materials. The auto-cross-linking reaction and radical reaction in depolymerization have an important role in reducing water absorption and adsorption when overdried paper is exposed to moisture. Finally, closing the pores in fiber will reduce the contact surface with moisture which will upset a certain amount of moisture adsorption to the sheet.

APPENDIX

Figure 1

DRYING RATE VS MOISTURE CONTENT

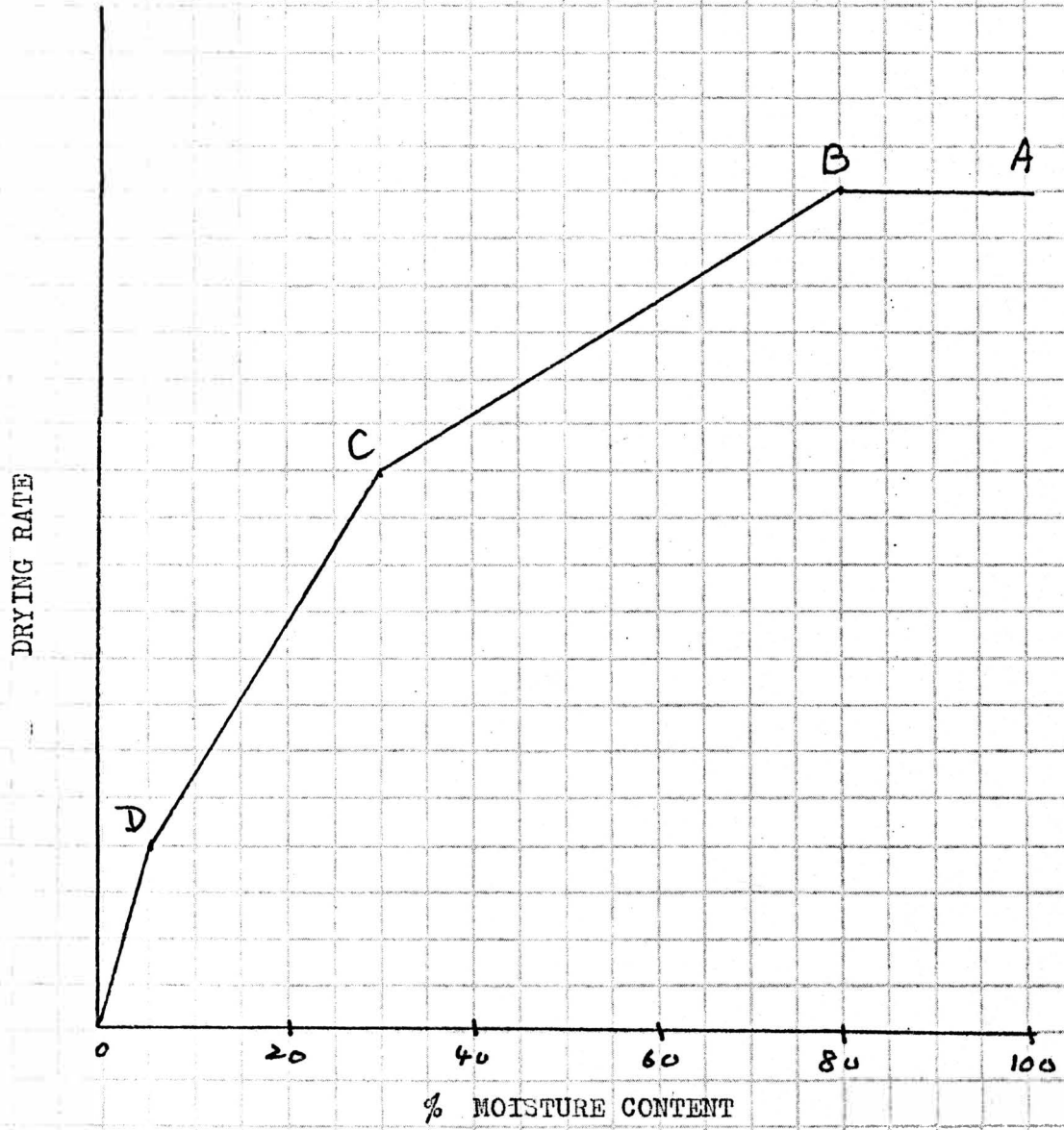


Figure 2

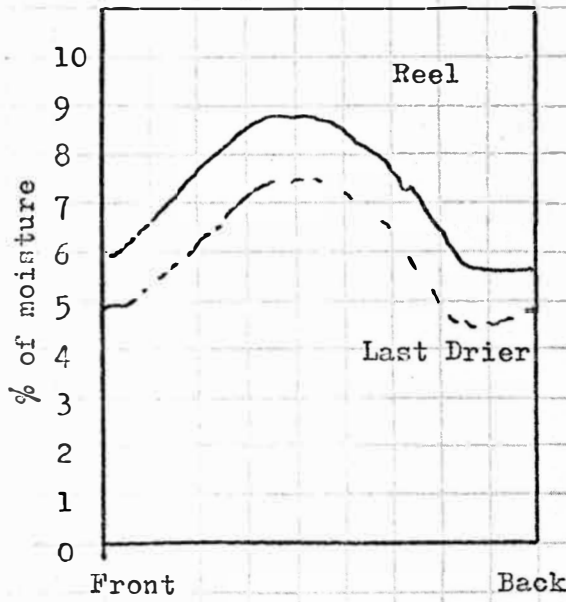


Figure 3

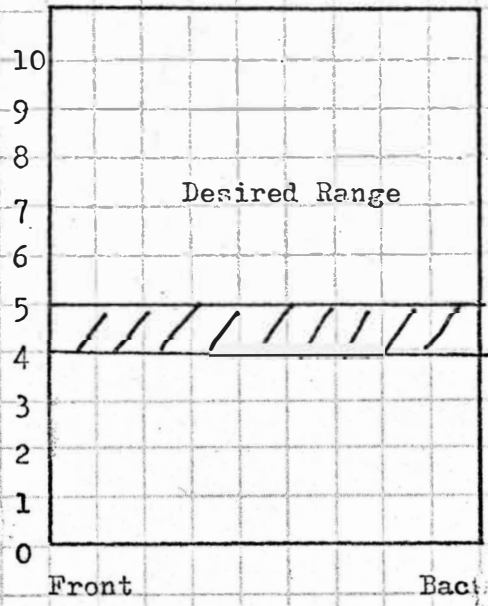
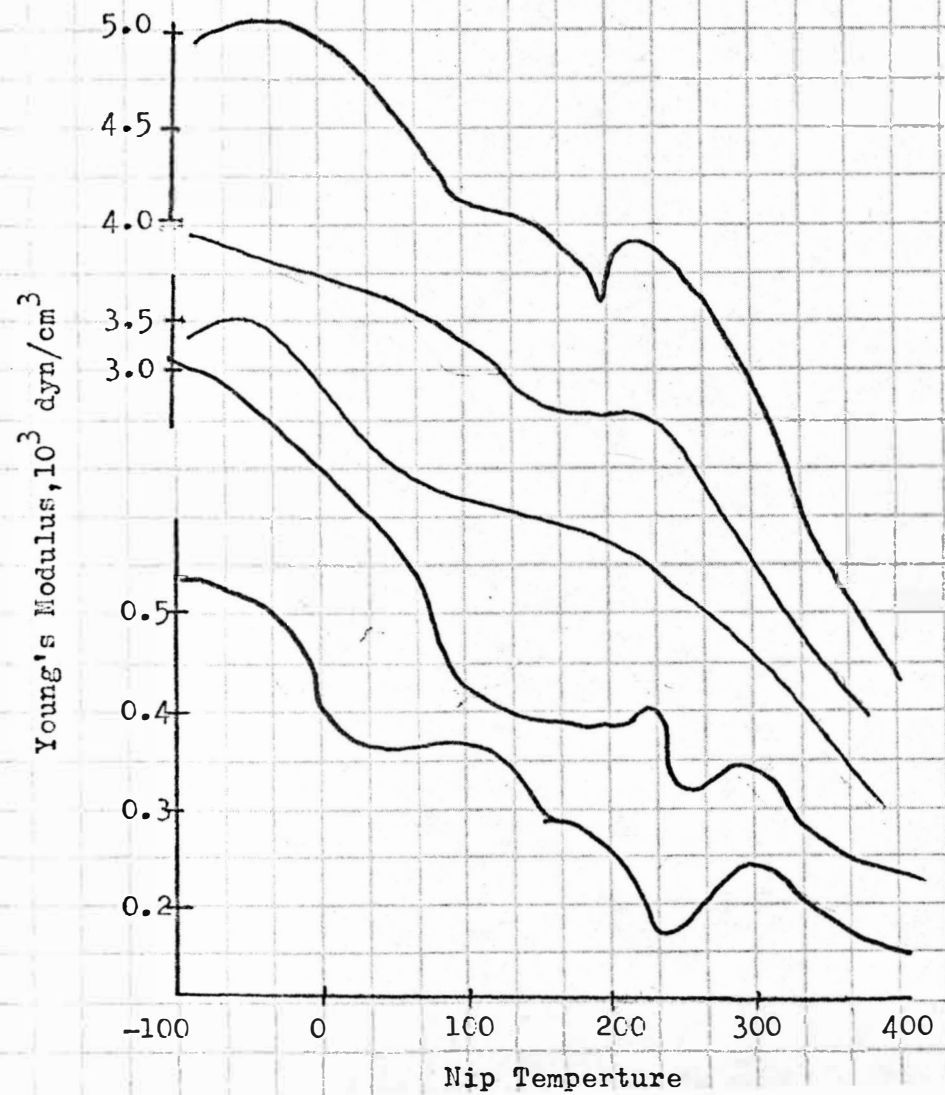


Figure 4
Young's Modulus of
Elasticity Vs Nip
Temperature



SYMBOL IDENTIFICATION FOR FIGURES 5 to 9

A is H.W.K.

B is S.W.K.

C is 60% H.W.K. and 40% S.W.K.

D is 5% TiO_2 added to S.W.K.

E is 15% TiO_2 added to S.W.K.

1 is humidity room condition

2 is overdried condition

FIGURE 5 COMPARISON OF DIMENSIONAL CHANGE FOR SPECIMEN CONDITIONED IN HUMIDITY ROOM AND OVERDRIED CONDITIONS

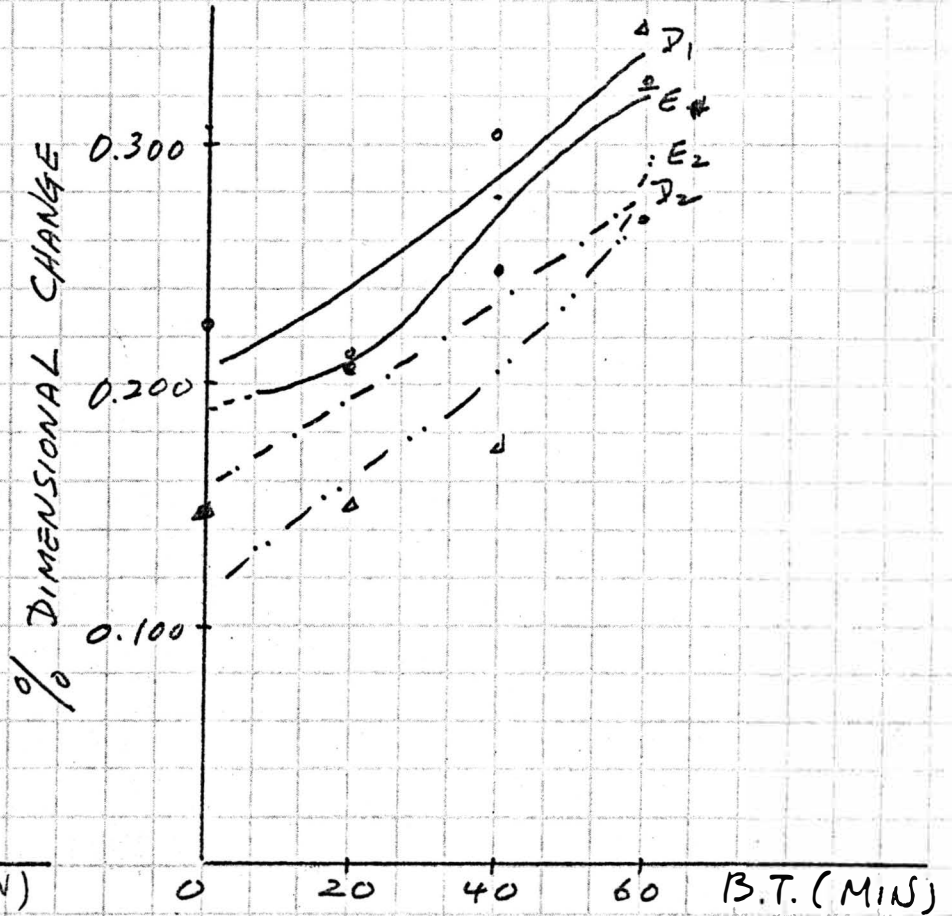
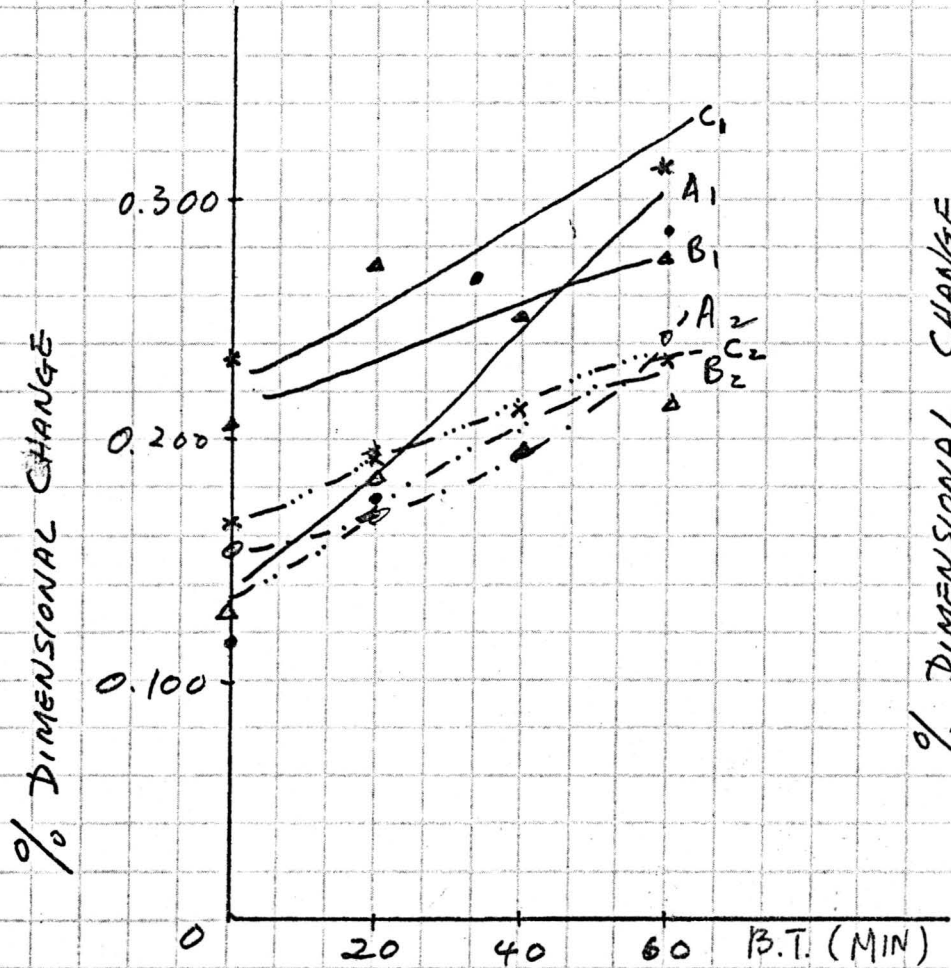


Figure 6

COMPARISON OF MULLEN PROPERTIES BETWEEN SPECIMEN
CONDITIONED IN
HUMIDITY ROOM AND OVERDRIED AT 90°C FOR 4 HOURS

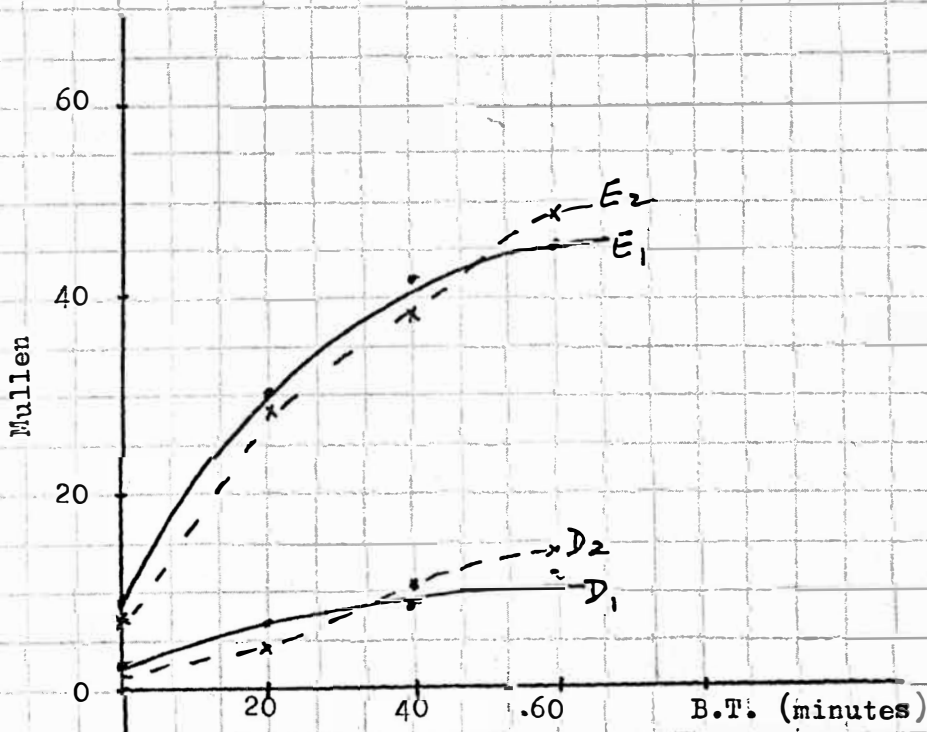
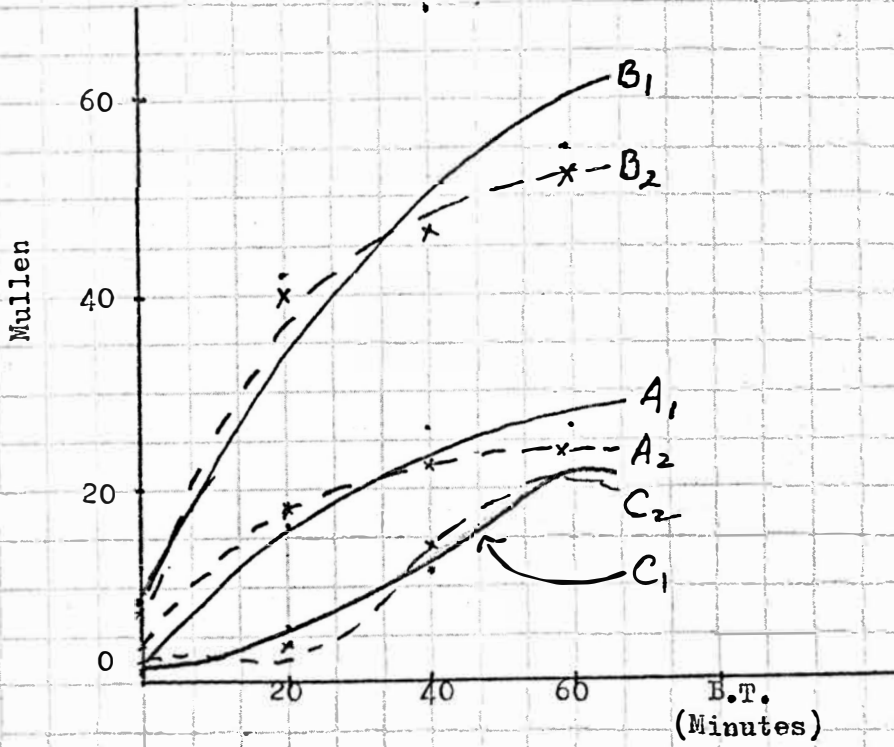


Figure 7

COMPARISON OF TENSILE PROPERTIES
BETWEEN SPECIMEN CONDITIONED IN
HUMIDITY ROOM AND OVERDRIED AT 90°C FOR 4 HOURS

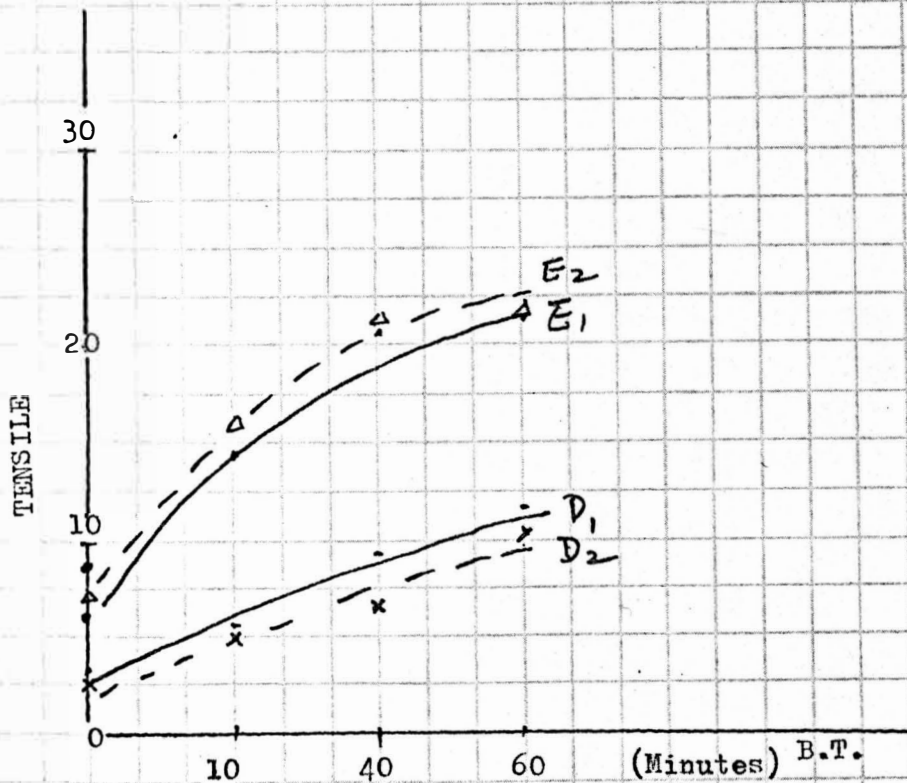
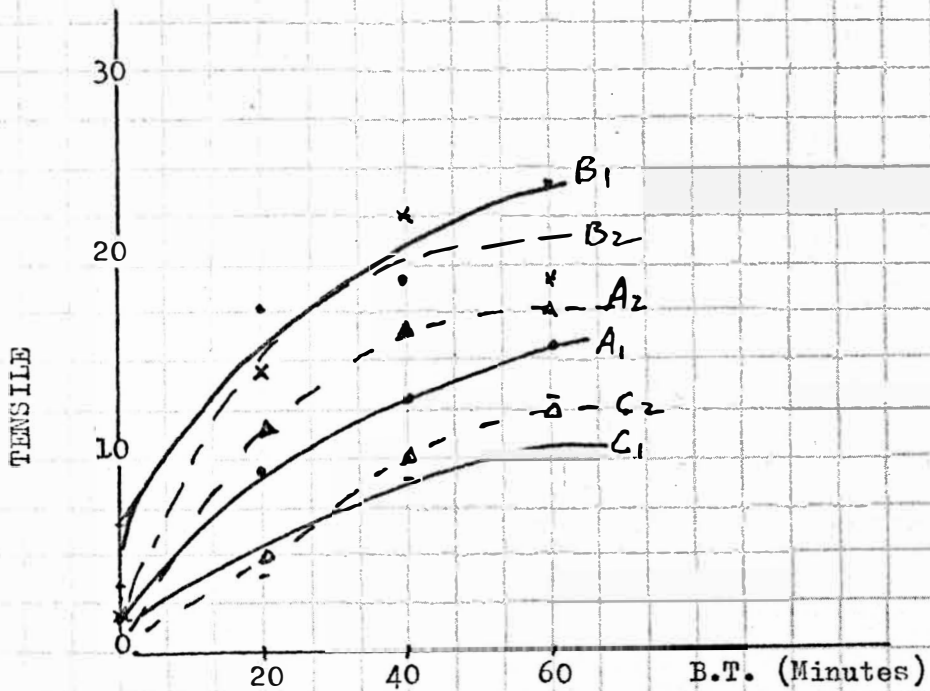


Figure 8

COMPARISON OF FOLD PROPERTIES
 BETWEEN SPECIMEN CONDITIONED IN
 HUMIDITY ROOM AND OVERDRIED AT 90°C FOR 6 HOURS

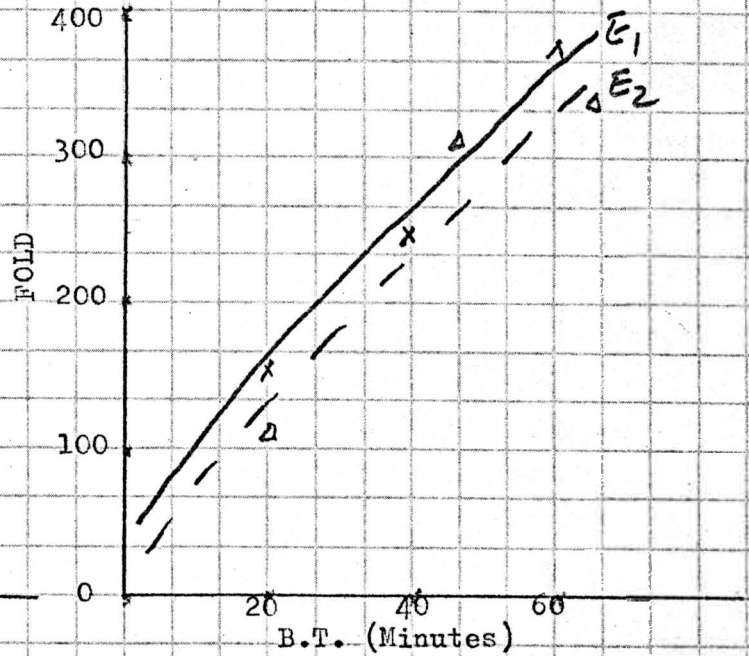
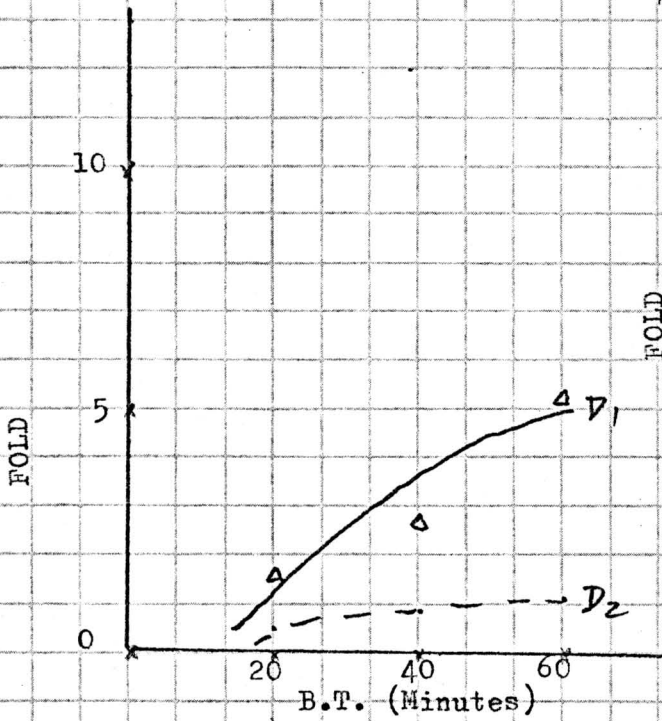
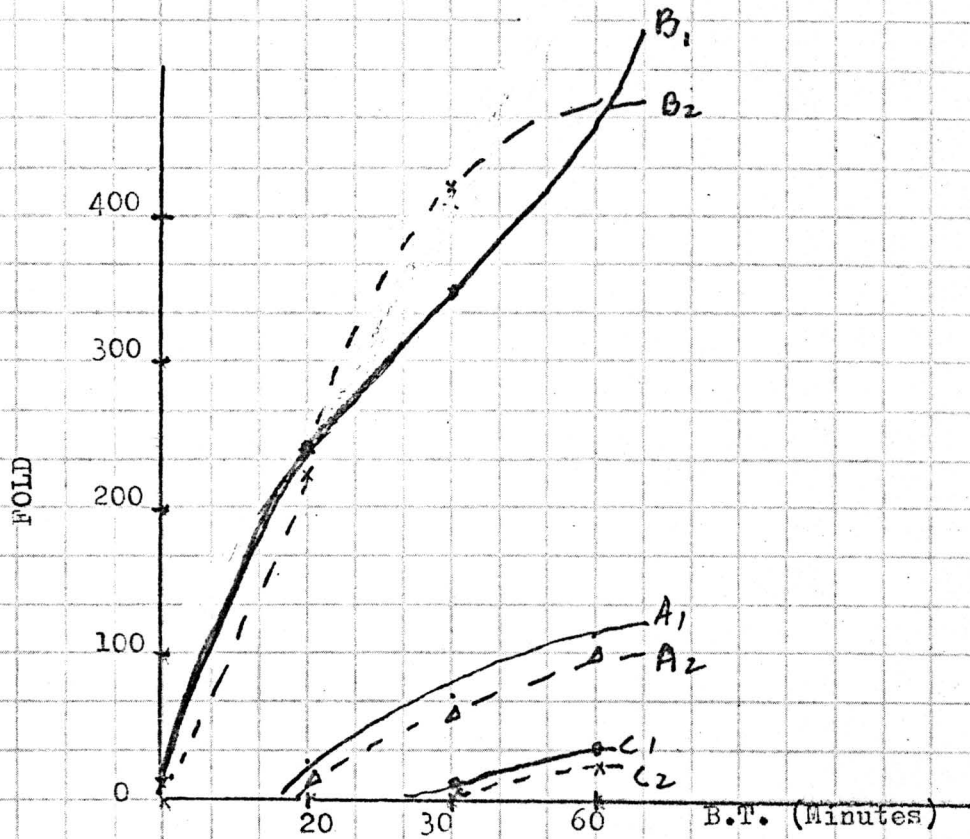
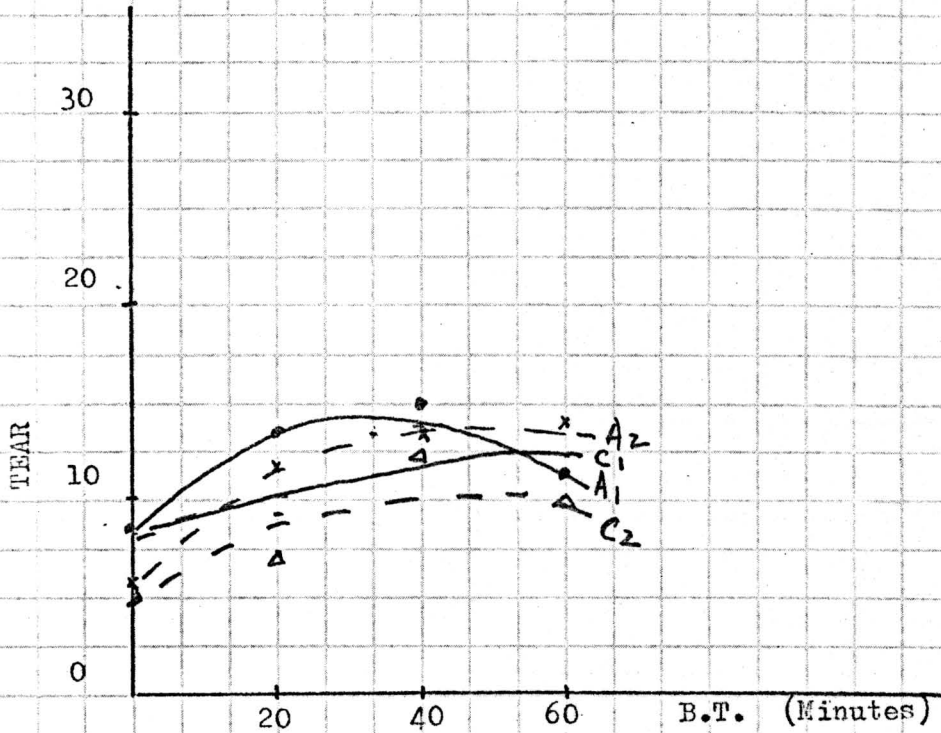


Figure 9

COMPARISON OF TEAR PROPERTIES
BETWEEN SPECIMEN CONDITIONED IN
HUMIDITY ROOM AND OVERDRIED AT 90°C FOR 4 HOURS



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