

AN ABSTRACT OF THE THESIS OF

Daisuke Horie for the degree of Master of Science in  
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Title : THE APPLICATION OF DURABLE PRESS TREATMENT TO  
BLEACHED SOFTWOOD KRAFT HANDSHEETS.

Redacted for privacy

Abstract approved : \_\_\_\_\_

Christopher J. Biermann

There are several chemical treatments for paper to improve its strength properties. Durable press treatment is usually used as a textile chemical finishing; however, there is little information available on the application of durable press treatment for paper. The durable press treatment was applied to bleached softwood kraft handsheets using maleic acid, citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinking agents in this study. One catalyst ( $\text{NaH}_2\text{PO}_4$ ) was particularly effective toward promoting the esterification reaction between handsheets and the crosslinking agents. This reaction was confirmed by the weight gain of the handsheets, by FT-IR spectroscopy, and by the change in the paper properties. The wet strengths of handsheets were improved significantly (as high as 63% of the dry strength) when the BTCA was used as a crosslinking agent. No tensile strength losses were found from BTCA and citric

acid treatments, and the brightness of the handsheets increased with durable press treatment. However, the fold strength was severely affected by this treatment.

THE APPLICATION OF DURABLE PRESS TREATMENT TO BLEACHED  
SOFTWOOD KRAFT HANDSHEETS

by

Daisuke Horie

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Professor of Forest Products in charge of major

Redacted for privacy

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Head of Department of Forest Products

Redacted for privacy

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Dean of Graduate School

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Typed by Daisuke Horie

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## TABLE OF CONTENTS

I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	4
A. Durable Press Finishing in the Textile Industry.....	4
B. New Chemicals for the Durable Press Treatment.....	5
C. Chemistry of Durable Press Finishing.....	7
D. Chemical Modification of Papermaking Fibers.....	8
III. EXPERIMENTAL PROCEDURE.....	11
A. Wood Pulp and Preparation of Handsheets.....	11
B. Preparation of Durable Press Treating Solution.....	11
C. Chemical Treatment of Handsheets.....	13
D. Test Methods.....	14
IV. RESULTS AND DISCUSSION.....	15
A. Weight Gain and Moisture Content (EMC) of Handsheets After Durable Press Treatment.....	15
B. Physical Properties of Chemically Treated Handsheets.....	20
C. Optical Properties of Chemically Treated Handsheets.....	25
D. FT-IR Spectroscopy of Handsheet Samples.....	29
E. Chemical Reactions Between Handsheet and Carboxylic Acids.....	36
F. Curing Temperature Effects.....	37
V. CONCLUSIONS.....	43
BIBLIOGRAPHY.....	44

14. FT-IR spectra of citric acid treated handsheet samples at different catalyst addition level.....	33
15. FT-IR spectra of BTCA treated handsheet samples at different catalyst addition level.....	34
16. FT-IR spectra of each handsheet addition level.....	35
17. The weight gain of 10% BTCA treatment with elevated curing temperature.....	38
18. Wet/Dry tensile strength at different curing temperature.....	40
19. Brightness changes with elevating curing temperature for 10% BTCA treated handsheet samples.....	41
20. FT-IR spectra of BTCA treated handsheet samples at different curing temperature.....	42



## LIST OF FIGURES

<u>FIGURE</u>	<u>PAGE</u>
1. Crosslinking reaction between durable press chemical (DMDHEU) and cellulose.....	6
2. The esterification reaction of polycarboxylic acids (dicarboxylic acid in this example) with cellulose.....	9
3. Structures of polycarboxylic acids used in this study..	12
4. The weight gain (%) after durable press treatment for each handsheet.....	16
5. Moisture content changes after chemical treatment at different catalyst addition level.....	18
6. Breaking length changes at different catalyst addition level.....	19
7. Stretch changes at different catalyst addition level...	21
8. Fold endurance changes at different catalyst addition level.....	22
9. Air permeability changes at different catalyst addition level.....	24
10. Wet strength of each handsheet at the highest catalyst addition level.....	26
11. Brightness changes at different catalyst addition level.....	28
12. Opacity changes at different catalyst addition level...	30
13. FT-IR spectra of maleic acid treated handsheet samples at different catalyst addition level.....	32

# THE APPLICATION OF DURABLE PRESS TREATMENT TO BLEACHED SOFTWOOD KRAFT HANDSHEETS

## I. INTRODUCTION

" Durable Press " or " Permanent Press " is one of the important fabric finishing processes in the textile industry. This process was introduced in the early 1960s to help keep the original shape of clothing against a number of washing and drying cycles. To resist the formation of wrinkles in fabrics, resin treatments were first applied in England in 1920 and in the U.S. in 1940. With tremendous efforts dealing with fabric finishing, the durable press treatment was invented and developed <sup>1,2</sup>.

Since the 1960s, extensive research for cotton fabric finishing has been carried out by the U.S. Department of Agriculture at the Southern Regional Center in Louisiana. As a durable press treatment process, various types of chemicals have been used. Among them, formaldehyde containing chemicals were first used for fabric finishing as cross-linking agents. These chemicals are still widely used because they are inexpensive. However, it is well known that the formaldehyde containing cross-linking reagents cause serious problems in human health. The vapor of formaldehyde from the clothes have irritating effects on human eyes and skin <sup>2,13,14</sup>. To overcome this undesirable effect, new cross-linking reagents have been found with effective catalysts. Gagliardi and Shippee studied the reaction between cotton and di- or polycarboxylic acids<sup>3</sup>

in the early 1960s. At this time, no effective catalysts were found. In the late 1960s, Rowland et al. reported a rapid curing processes for cellulose cross-linking with various polycarboxylic acids as cross-linking agents <sup>4</sup>. Finally, many catalysts have been found for durable press treatments that give high durable press performance without using formaldehyde containing chemicals <sup>14</sup>. This chemical treatment can be applied not only to textiles but also to paper because both are cellulosic materials. However, there is little information on the application of these treatments to paper.

Many other chemical reactions have been reported between papermaking fibers and chemicals for strength development <sup>5</sup>. Some chemical reactions are very severe so that the chemically treated pulp or paper often gives inferior properties compared to the original pulp or paper. Ward reviewed the chemical modification of papermaking fibers <sup>6,7</sup>. He mentioned that the most effective chemical treatment for pulps might be carboxymethylation, although this is not a cross-linking agents. Several people studied this topic and reported that when the hydroxyl groups of pulp were substituted with low degree of carboxymethyl groups, some strengths properties of handsheets increased <sup>8-12</sup>.

This study is also the chemical modification of paper but this is a new approach to develop cellulose cross-linking into paper by the application of textile finishing treatment. The formation of cross-links between cellulose fibers usually

increases the wet strength of paper and also stabilizes the paper dimensions <sup>15-17</sup>. Dimensional stability of a paper is critical for some special papers and printing grade papers <sup>19</sup>. To impart the wet strength and dimensional stability of the paper, several carboxylic acids were used as crosslinking agents with a weak base catalysts ( $\text{NaH}_2\text{PO}_4$ ) in this study. The chemical reaction was verified by physical testing of the handsheets, FT-IR spectroscopy, and the weight gain of the handsheets.

## II. LITERATURE REVIEW

### A. Durable Press Finishing in the Textile Industry

The term "Durable Press" is used to describe fabrics or garments that resist shrinkage or appearance changes after a number of laundering cycles.

Before durable press finishing was invented, most clothes were pressed or ironed to remove creases after washing and drying. Only starch was used to minimize the wrinkling before the 1920s. The concept of durable press finishing has been developed since that time, and resin treatment of cotton fabrics was first applied as fabric chemical finishing. Today, the durable press treatment has become an important fabric finishing method in the textile industry.

Of commercial durable press chemicals, dimethylol-dihydroxy-ethylene urea (DMDHEU) seems to be a popular chemical in the textile industries, today. Some other chemicals have been used as a precured chemicals such as dimethylolethylene urea (DMEU) and dimethylolpropylene urea (DMPU) <sup>1,20</sup>.

There are two well known theories for improved durable press performances by the application of chemical treatment<sup>2,20</sup>. One is that the durable press chemicals develop a memory into the cellulose fiber. Due to this "molecular memory", the fibers retain their original shape. Another

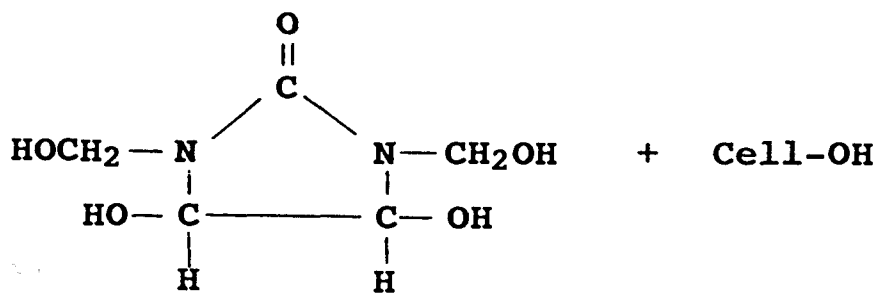
theory is that there is a chemical reaction between the fibers and the durable press chemicals. The durable press chemicals develop cross-links in the cellulose chains of the fibers (Figure-1).

A special technique, the so-called "Pad-dry-cure process" <sup>1</sup>, has been used for textile finishing since the 1960s. This process consists of three important parts. First, the fabrics are saturated with durable press finishing solution including crosslinking agent, catalyst and fabric softener. Then the fabrics are squeezed and dried at low temperature (about 85°C). Finally the fabrics are cured at high temperature (160-185°C).

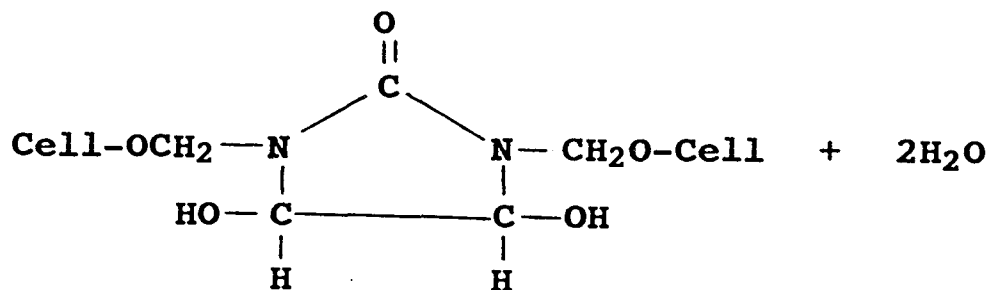
The variables such as dry-cure temperatures and times are very important for this process. The concentration of durable press crosslinking agents, catalysts is also important. These variables affect the quality of the treated fabrics, for example, the fabric strengths and brightness losses.

#### **B. New Chemicals for the Durable Press Treatment**

A problem arises when the durable press treatment with formaldehyde containing chemicals is applied to fabrics. The reason is that the formaldehyde is released and the vapor of the formaldehyde adversely affects human health. For this reason, new chemicals for the durable press treatment have been searched.



Dimethylol-dihydroxy-  
ethylene urea (DMDHEU)



Cross-linked cellulose

Water

Figure 1. Crosslinking reaction between durable press chemical (DMDHEU) and cellulose.

Welch et al <sup>13,14</sup> have studied new types of cellulose cross-linking agents for durable press textile finishing. Eventually, they found effective durable press nonformaldehyde finishing agents which were polycarboxylic acids that are used with catalysts. These chemicals gave a high levels of durable press performance compared to the conventional durable press agents. Their works were patented in the United States in 1990 <sup>13</sup>.

Early studies for using polycarboxylic acids were carried out by Gagliardi and Shippee<sup>3</sup> in 1963 and Rowland et al <sup>4</sup> in 1967. At that time, the ester type cross links between polycarboxylic acids and cotton cellulose were achieved; however, the significant strength losses of the fabrics were observed due to the application of high temperature and relatively long curing time. Finally Welch overcome the fabric's strength loss problems by the discovery of effective catalysts <sup>13,14</sup>.

### **C. Chemistry of Durable Press Finishing**

The purpose of durable press fabric finishing is to develop crosslinks into fabrics (cellulosic materials). Although there are several important crosslinking reactions for the durable press finishing, two important chemical reaction were described below.

One important reaction for cellulose crosslinks is the formation of ether bonds between durable press finishing



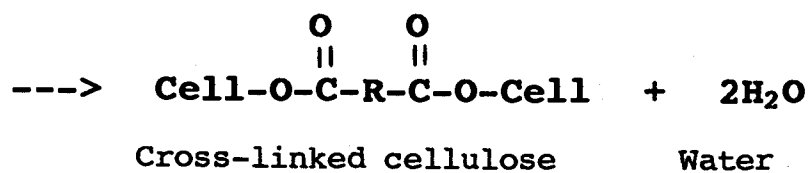
agents and cellulose molecules. The formation of ether bonds<sup>20</sup> are shown in Figure-1. Conventional durable press finishing agents such as dimethylol-dihydro-ethylene urea (DMDHU) rely on the ether type cross links.

Another important reaction is an esterification reaction between polycarboxylic acids (new durable press agents) and the hydroxyl groups of cellulose molecules. This ester type crosslinks<sup>3</sup> are shown in Figure-2. Usually this reaction does not occur at room temperature nor in the presence of water. To accelerate the reaction, both high temperature and water removal are required.

#### **D. Chemical Modification of Papermaking Fibers**

Papermaking fibers can be treated with some chemicals to modify its original characteristics and to produce desirable paper products. Goheen<sup>5</sup> reviewed the chemical reaction of fibrous cellulose in 1958 and Ward<sup>6</sup> published a book about the chemical modification of papermaking fibers in 1973. They list the major chemical reactions of fibrous cellulose are esterification, etherification, oxidation, crosslinking and grafting. However, only a few chemical reactions seem useful for the modification of papermaking fibers because many other reactions give fiber degradation.

Carboxymethylation is one of the effective chemical treatments for papermaking fibers. Paper made from low substituted carboxymethylcellulose pulp (D.S. of 0.06) gave



R: alkyl group

Figure 2. The esterification reaction of polycarboxylic acid (dicarboxylic acid in this example) with cellulose.

improvements of handsheet tensile strength, burst strength and folding endurance <sup>15-17</sup>.

In the actual papermaking process, a variety of additives are added into the wet-end to improve retention, dry-strength, wet-strength and sizing of paper <sup>21</sup>. Resins are added to improve the wet-strength of paper, and cationic starch, gums and acrylamide polymers are added to improve the dry-strength of paper. Some of the additives are able to form strong chemical bonds with cellulose fibers; however, some chemicals are only held by weak bond such as hydrogen bonds or ionic bonds.

Using formaldehyde, cross-linking of cellulose molecules in papers was studied by Stamm <sup>15,16</sup> to stabilize the paper dimensions. Crosslinking will reduce the swelling of paper because swelling agents are not able to break the ether bonds. The paper strength properties changed when the formaldehyde treatment was carried out. Dry-tensile strength and dimensional stability were increased by the treatment, but both tear and fold endurance were reduced significantly. Moreover, the formaldehyde treated paper increased the embrittlement due to the crosslinking of cellulose chains.

### III. EXPERIMENTAL PROCEDURE

#### A. Wood Pulp and Preparation of Handsheets

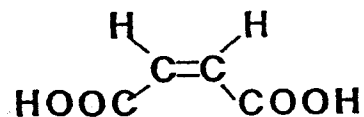
Douglas-fir breached kraft pulp was used for this study. This dried pulp was disintegrated in a standard pulp disintegrator and beaten to 400 mL CSF in a PFI mill (TAPPI test method T248cm-85). Handsheets of basis weight 100g/m<sup>2</sup> were made on the British sheet mold (TAPPI test method T205om-88). The handsheets were dried under TAPPI standard conditions (TAPPI test method T402om-88).

#### B. Preparation of Durable Press Treating Solution

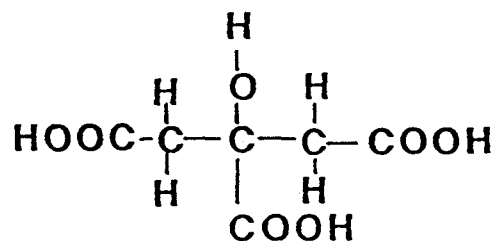
The durable press treating solution consists of polycarboxylic acid, catalyst and distilled water. Maleic acid (dicarboxylic acid), citric acid (tricarboxylic acid) and 1,2,3,4-butanetetracarboxylic acid were used as durable press treatment agents. The chemical structures of these polycarboxylic acids are shown in Figure-3. Monosodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) was used as curing catalyst. All of these chemicals were obtained from Aldrich (Milwaukee, Wisconsin).

The solution includes 10% of the polycarboxylic acid, catalyst and distilled water. The catalyst addition level was based on the molar ratio of total carboxyl groups. For example, if 200g of durable press treating solution contains 10% of BTCA, 1% of catalyst and water, the weight of the BTCA and the catalyst is 20g (0.0854 mol) and 2g (0.0145 mol)

a. Maleic Acid (dicarboxylic acid)



b. Citric Acid (tricarboxylic acid)



c. 1,2,3,4-Butanetetracarboxylic Acid

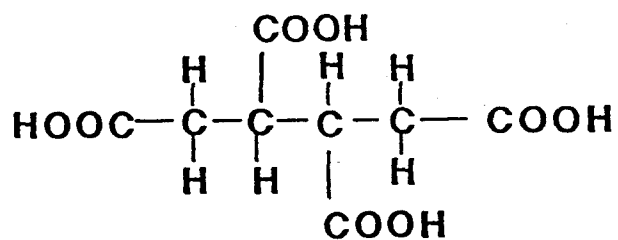


Figure 3. Structures of polycarboxylic acids used in this study.

respectively. However, BTCA contains four -COOH groups in a molecule so that 0.3416 mol ( $0.0854 \times 4$ ) of the -COOH groups must be in the solution. The molar ratio of COOH/catalyst (0.3416 mol/0.0145 mol) is 23.5 in this example. The same methods were used to adjust the catalyst addition level for maleic acid which has two -COOH groups in a molecule and citric acid which has three -COOH groups in a molecule.

### C. Chemical Treatment of Handsheets

Handsheets (100g/m<sup>2</sup>) was treated by the same method used in the durable press treatment, the so-called "Pad-dry-cure" process. The sheet-forming press was used instead of squeeze rolls. Each handsheet was immersed in the treating solution containing 10% of di- or polycarboxylic acid, curing catalyst, and water. After 1 minute immersion, each handsheet was pressed with blotting paper to remove excess solution. The immersion and press treatment was repeated. Each wet handsheet was suspended in a forced air drying oven for 5 minutes at 85°C and then cured for 90 seconds in another oven at 160°C. Each handsheet was rinsed in running water for 30 minutes to remove the catalyst and unreacted acid. Finally, the handsheets were dried under Tappi standard conditions (TAPPI test method T402om-88).

#### D. Test Methods

TAPPI standard test methods were used to measure each of the following paper properties: brightness (T452om-92), breaking length and stretch (T494om-88), wet strength (T456om-87) and fold endurance (T551om-88). For the wet strength test, the test specimen was immersed in a water bath for 16 hours. Each mechanical test was performed in triplicate on different handsheets. The weight gain (the average of four separate samples) and moisture content (single determinations) of each reaction condition were determined. The esterification reactions between the handsheets and the carboxylic acids were confirmed by FT-IR spectroscopy.

#### **IV. Results and Discussion**

The investigation of the paper properties was carried out physically, optically and chemically. The physical tests of handsheets include tensile strength, stretch, fold endurance, wet-strength and air permeability. Opacity and brightness of the handsheets characterize the optical properties. FT-IR spectroscopy was used to show the functional chemical groups present and to verify the occurrence of chemical reactions. Additionally, weight gains and moisture content of the handsheets were also determined to verify the occurrence of chemical reaction in this study.

##### **A. Weight Gain and Moisture Content (EMC) of Handsheets After Durable Press Treatment**

The weight gain of chemically treated handsheets will tell us at least whether chemical reactions occur or not. If chemical reactions occur, the handsheets will gain additional weight compared to their original weights, but if not, no weight gain should be observed. Since the handsheets were rinsed with running water for 30 minutes after the durable press treatment, unreacted chemicals should be removed completely from the handsheets.

Figure-4 shows the weight gain of handsheets with increasing addition of catalyst. The highest weight gain



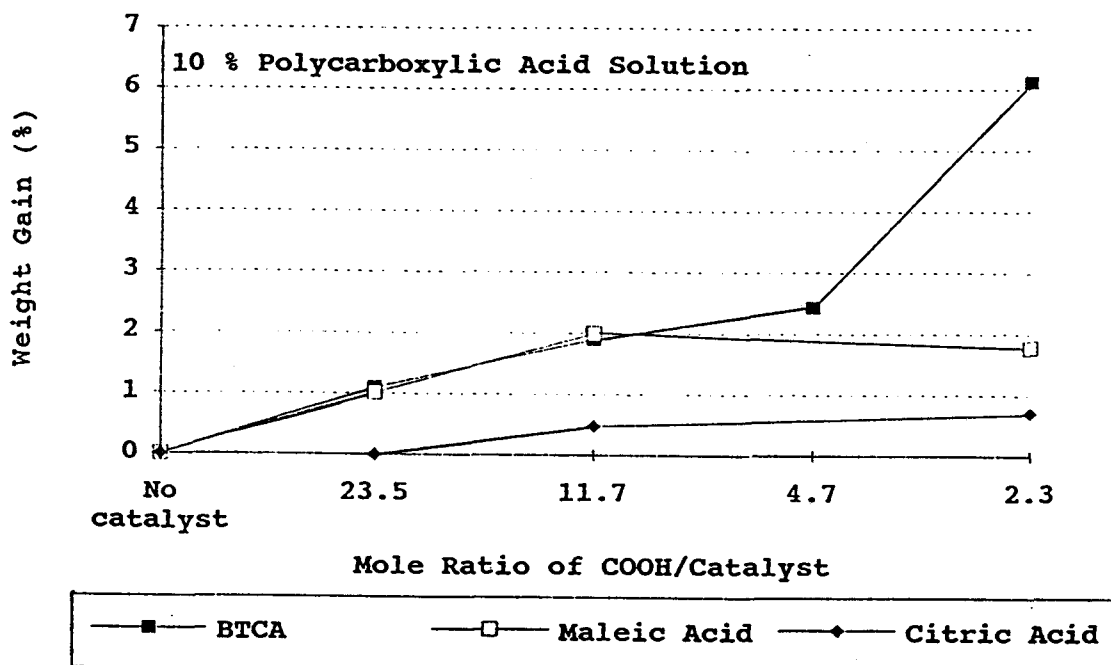


Figure 4. The weight gain (%) after durable press treatment for each handsheet

(6.12%) was obtained when the handsheets were treated with BTCA with the highest amount of catalyst (COOH/catalyst=2.3, or 10% catalyst). At the same catalyst addition level, the weight gains from maleic acid and citric acid treated handsheet were 1.78% and 0.71% respectively. These weight gain results shows that 0.52 mmol BTCA, 0.15 mmol maleic acid and 0.03 mmol citric acid were introduced per gram fiber. No weight gains were obtained without the catalyst, which demonstrates that washing is effective in removing unreacted carboxylic acid materials..

The maleic acid solution at the highest catalyst addition (COOH/catalyst=2.3) was supersaturated as observed by the presence of some crystals in the bottom of the treating bath.

It was expected that the equilibrium moisture content (EMC) of the handsheets would change after the durable press treatment. As the crosslinks of the cellulose develop, the amount of hydroxyl groups in the cellulose molecules will decrease by the crosslinking reaction. Figure-5 shows the EMC of the chemically treated handsheets. Only small differences in EMC of the handsheets were observed in this Figure. The EMC of the controls were 7.37%, the EMC of the BTCA treated handsheet was 7.15%, and the EMC of the maleic acid treated handsheet was 6.80% with the highest level of catalyst in each case.

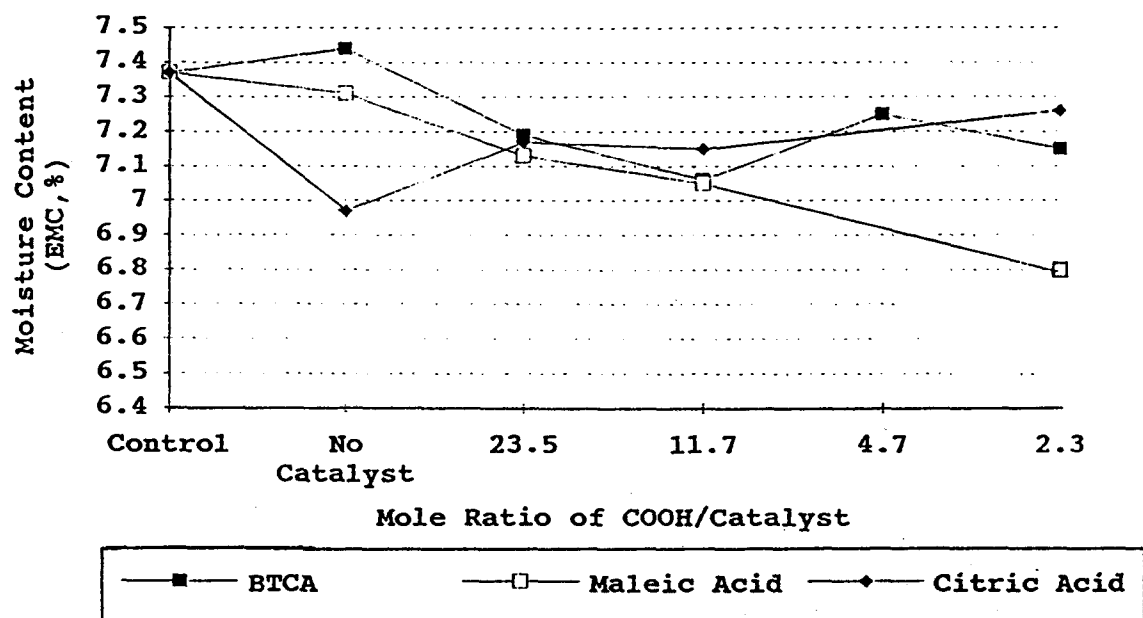


Figure 5. Moisture content changes after chemical treatment at different catalyst addition level

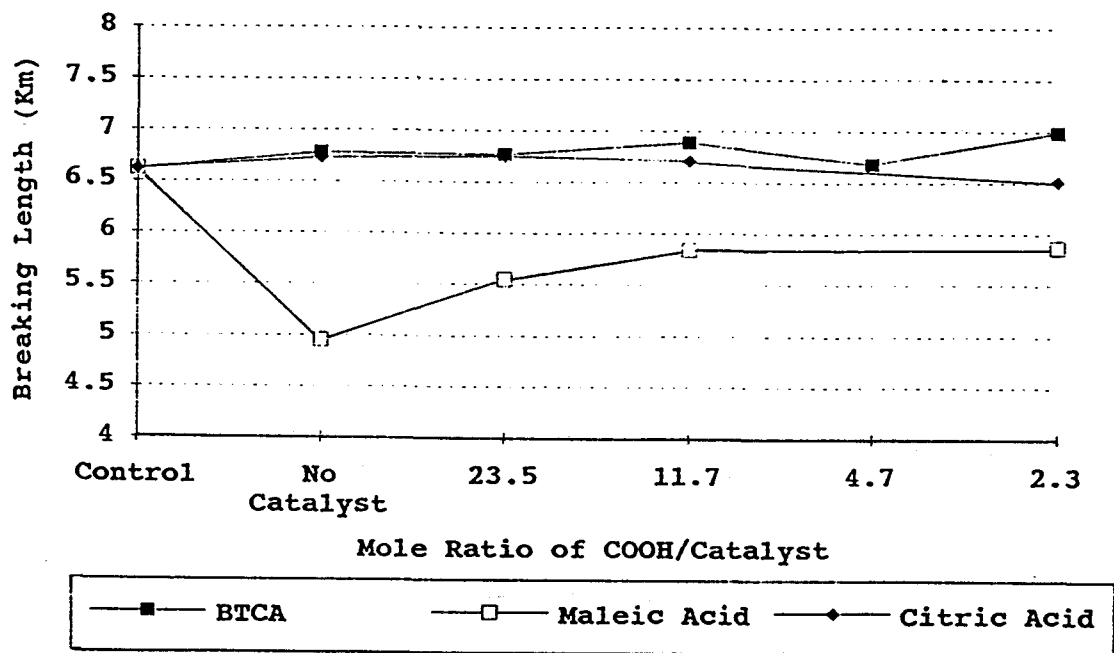


Figure 6. Breaking length changes at different catalyst addition level.

## B. Physical Properties of Chemically Treated Handsheets

The breaking length of BTCA and citric acid treated handsheets show no strength losses comparing to the control sheet (Figure-6). In the case of textile treatment, the breaking length always decrease when the fabrics were treated with durable press agents <sup>13,14</sup>. This difference may be due to the dependance of fiber-fiber bonding in paper, where as in textile the strength depends solely on the strength of the individual fibers. The breaking length decreased when maleic acid was used for the treatment. The reason may be less crosslinking reaction in handsheet compared to BTCA and citric acid treated handsheets.

The tensile stretch (Figure-7) decreased with increasing addition of catalyst. The crosslinked structures that form between the cellulose molecules and this structures increases the paper's rigidity. The fold endurance (Figure-8) also decreased with increasing addition of catalyst. The fold endurance of maleic acid treated handsheets decreased significantly at any catalyst addition level. The fold endurance of BTCA treated handsheets decreased with increasing levels of catalyst and reached zero at the highest catalyst addition level. Citric acid treated handsheets had relatively high fold endurance compared to the other two chemical treatments. It is hypothesized that citric acid holds three carboxyl groups (-COOH) and one hydroxyl group (-

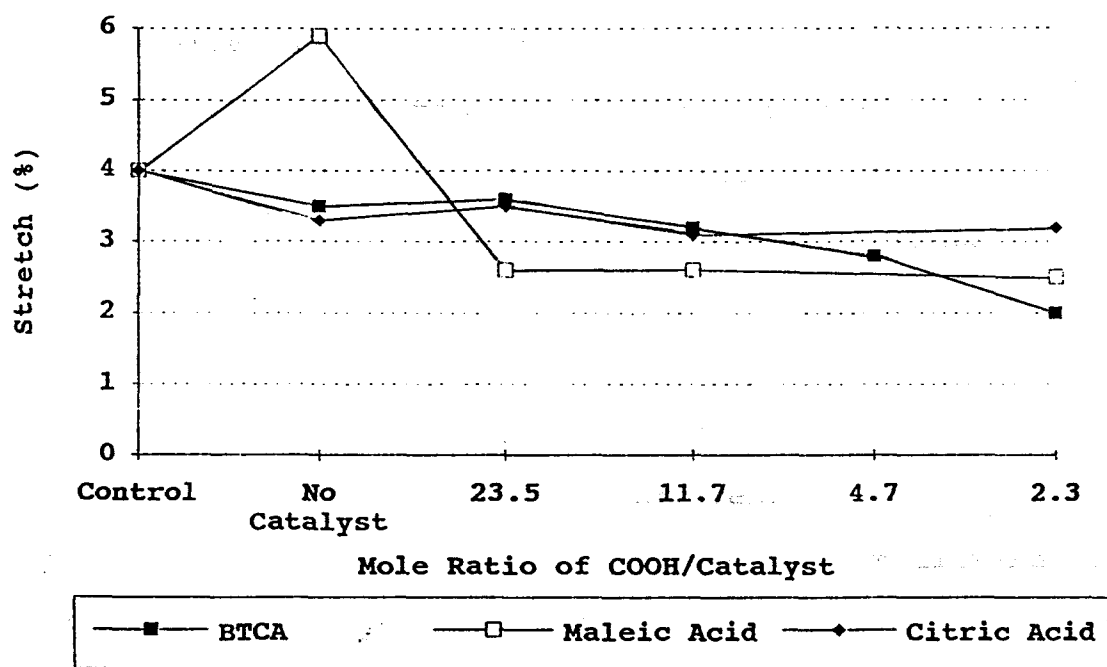


Figure 7. Stretch changes at different catalyst addition level.

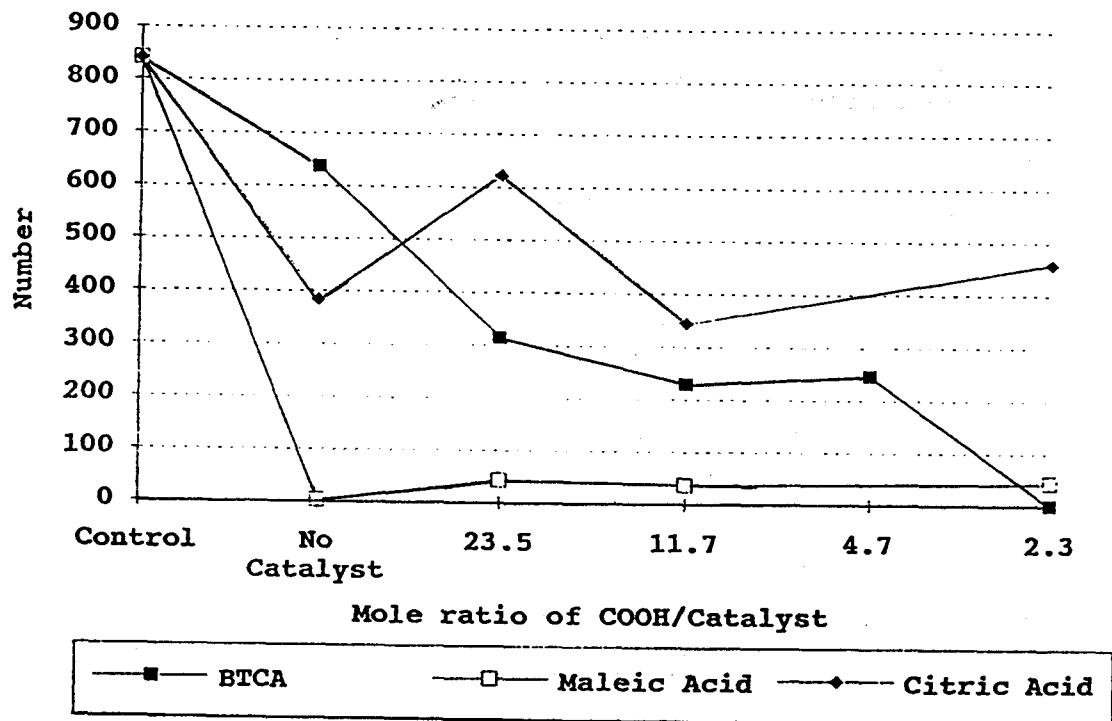


Figure 8. Fold endurance changes at different catalyst addition level.

OH) so that this hydroxyl groups will soften the handsheets. Both breaking length results and folding endurance results indicate that the treated handsheets lost flexibility. The embrittlement of paper has been shown to increase with cellulose crosslinking <sup>6,15,16</sup>.

For the paper porosity, air permeability (air resistance) of the treated handsheets was measured and the results were shown in Figure-9. The air resistance of paper is usually used to indicate the beating degree of pulp and the absorbancy of paper. This measurement also gives some clue of the internal structure and the surface characteristics. This method was used to estimate the change of both the internal structure and the surface characteristics by the durable press treatment.

The porosity of the maleic acid and citric acid treated handsheets show the decrement tendency with increasing addition of catalyst; however, only a slight difference were observed for BTCA treated handsheets comparing to the control sheets. It is difficult to say that whether the development of crosslinks will make the paper porous or not from these results because the highly crosslinked BTCA treated handsheets gave no change of air permeability compared to control sheet.

One very important result was obtained from the wet-strength test. The wet strength of the paper, the ability to retain some strength when paper products are exposed to humid



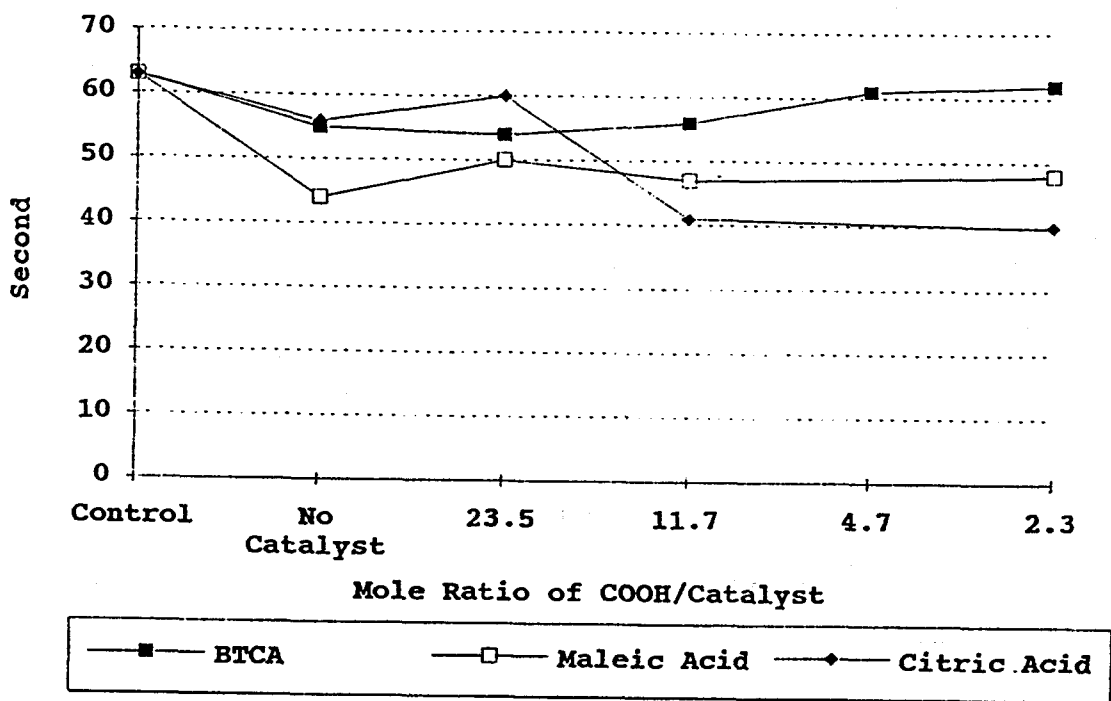


Figure 9. Air permeability changes at different catalyst addition level.

environments, is extremely important in some paper grades such as multicolored printing papers, map papers, drawing papers and tissue papers. The wet strength is usually represented by a percentage of the dry strength.

The wet tensile strength was determined for the chemically treated handsheets with the highest catalyst addition level for each of the crosslinking agents (Figure-10). Compared to the control wet strength of the handsheet, all of the carboxylic acid treatments increased the wet strength. Notably, the wet strength of BTCA treated handsheets shows 63% of the dry tensile strength. Since 20-40% is typical in the wet-strength of commercial papers, the wet strength improvement of the BTCA treated handsheets must be one of the highest value reported for the wet strength of paper with no affect on dry strength.

This improvement of the wet strength must be due to the high degree of cellulose crosslinking in the handsheet. Since BTCA holds four carboxyl groups in one molecule, it has the highest possibility to form ester type crosslinking between cellulose molecules compared to the other two chemicals. The BTCA also gives the best durable press performance in treated textiles <sup>13,14</sup>.

### **C. Optical Properties of Chemically Treated Handsheets**

The optical properties were determined in terms of the sheet brightness and opacity. Brightness of paper is a

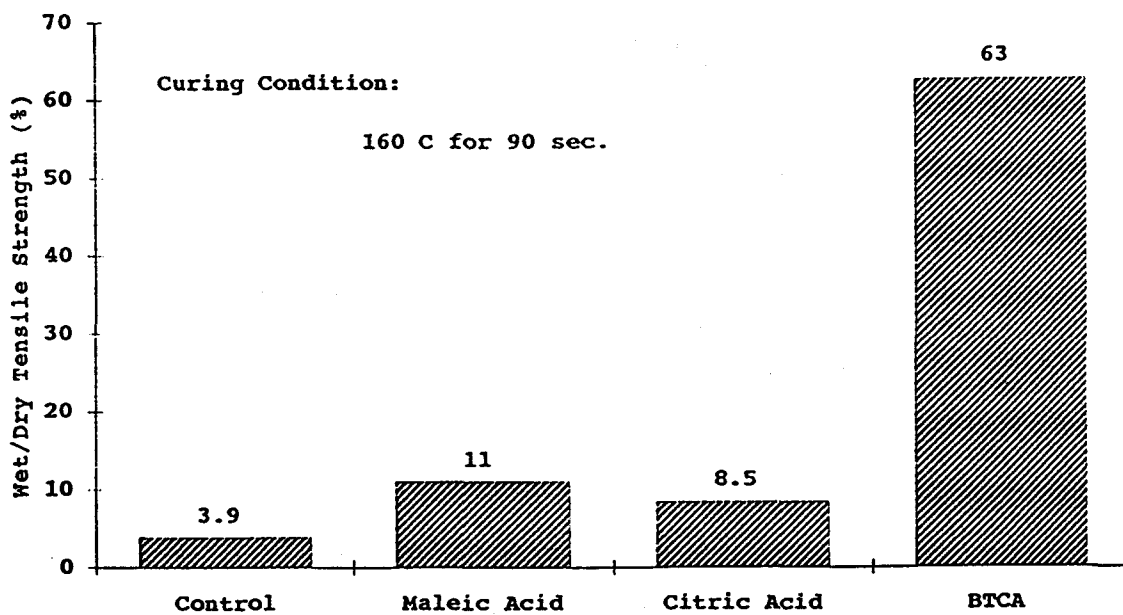


Figure 10. Wet strength of each handsheet at the highest catalyst addition level.

important factor to evaluate the paper qualities. Generally, most people prefer white paper so that papermakers use several bleaching chemicals to whiten the paper. Opacity is also a very important factor for printing grade paper. Since both side of the paper will be printed, show-through of the printed letter causes difficulty during reading. For these reasons, optical properties are controlled by papermaker depending on the end use of the paper.

Often, the chemical modification of paper or papermaking fibers induces degradation of papermaking fibers so that the chemically treated paper is inferior in some regard.. Of course, this is an undesirable feature for paper products. Although the chemical modification of paper is an interesting area for papermakers, those undesirable factors make commercial applications difficult. The depression of optical properties in this study was, therefore, of concern.

Figure-11 shows the sheet brightness with increasing addition of catalyst. Surprisingly, the brightness of the handsheets increased 2-4 points by the chemical treatment in spite of the application of the high curing temperature (160°C). The maleic acid treated paper with the highest catalyst addition level gave the highest brightness 79.7%. This phenomena may be due to the color of the treating chemical itself or the occurrence of some chemical reactions between the handsheets and the acid, but it is not clear. The lowest brightness was obtained from BTCA treated paper 74.0%

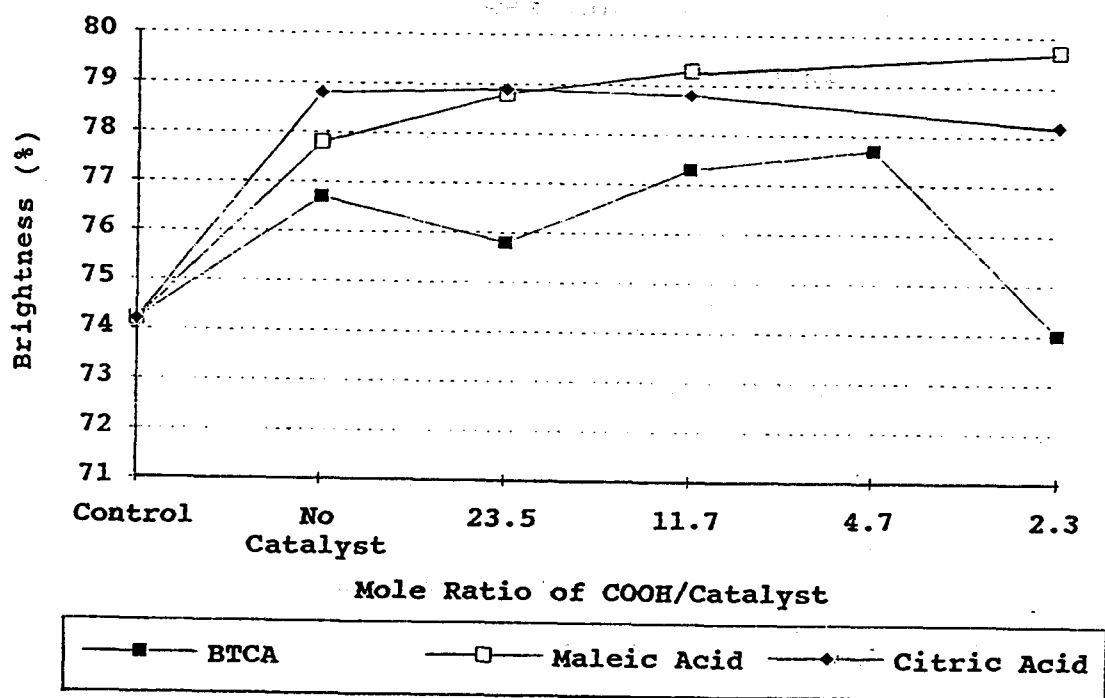


Figure 11. Brightness changes at different catalyst addition level.

with the highest catalyst addition level. Compared to the control sheet brightness, no loss of brightness was observed from the durable press treatment.

The opacities of the handsheets showed a tendency to decrease with chemical treatment except for the BTCA treated paper with the highest catalyst addition (Figure-12). This means that the chemically treated paper became more translucent than before the chemical treatment.

#### **D. FT-IR Spectroscopy of Handsheet Samples**

FT-IR (Fourier Transform Infrared) spectroscopy is a powerful tool to characterize and to identify the functional groups in organic chemicals. The advantages of FT-IR are its speed and its high sensitivity so that it provides more sharp and clear adsorption spectrums more quickly than that of simple IR spectrometer <sup>22</sup>.

Using FT-IR spectroscopy, the identification of the functional groups were carried out. The IR absorption of the functional groups in carboxylic acids and esters are strong and were especially useful in this study.

The O-H bond of the carboxyl group has a very broad absorption between 2400  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  and is not separated from the O-H of cellulose. The stretch of C=O and C-O bond of carboxyl group are observed at 1700-1730  $\text{cm}^{-1}$  and 1210-1320  $\text{cm}^{-1}$  respectively. The normal esters have the C=O

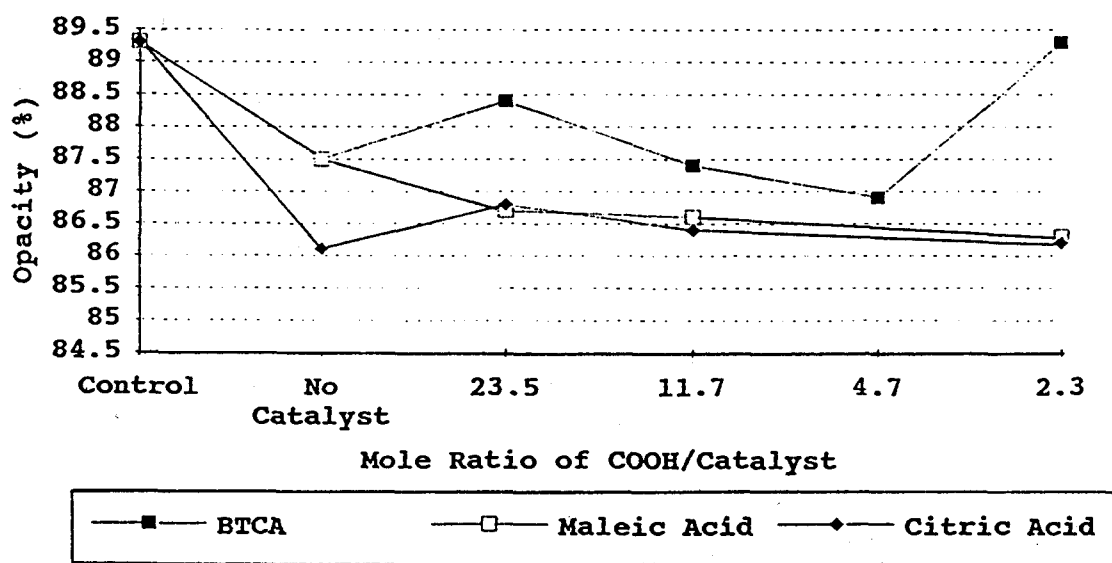


Figure 12. Opacity changes at different catalyst addition level.

absorption at  $1735\text{ cm}^{-1}$  and the C-O absorption at  $1000\text{--}1300\text{ cm}^{-1}$ .

Figure-13 shows the FT-IR spectra for maleic acid treated handsheet samples with different levels of catalyst addition. Compared to the control handsheet which was untreated, strong absorptions were observed at  $1721\text{ cm}^{-1}$  from each handsheet samples even with no catalyst addition. Some absorption at  $1721\text{ cm}^{-1}$  was obtained from citric and BTCA treated handsheets (Figure-14,15). Especially, a very strong absorption at  $1720\text{ cm}^{-1}$  was observed from BTCA treated sample at the highest catalyst addition level. This strong absorption was directly related to the high weight gain of these handsheets. Figure-16 shows the FT-IR spectra of chemically treated handsheet samples at the highest catalyst addition level. It is easy to observe that the absorption of the BTCA treated handsheet is larger than that of the other samples. It is difficult to identify whether the functional group is a carboxyl group or an ester because the wave numbers of both absorptions are very close to each other. However, the ester must be formed from the wet strength result of BTCA because the wet strength would be weak if free carboxyl groups existed in paper.



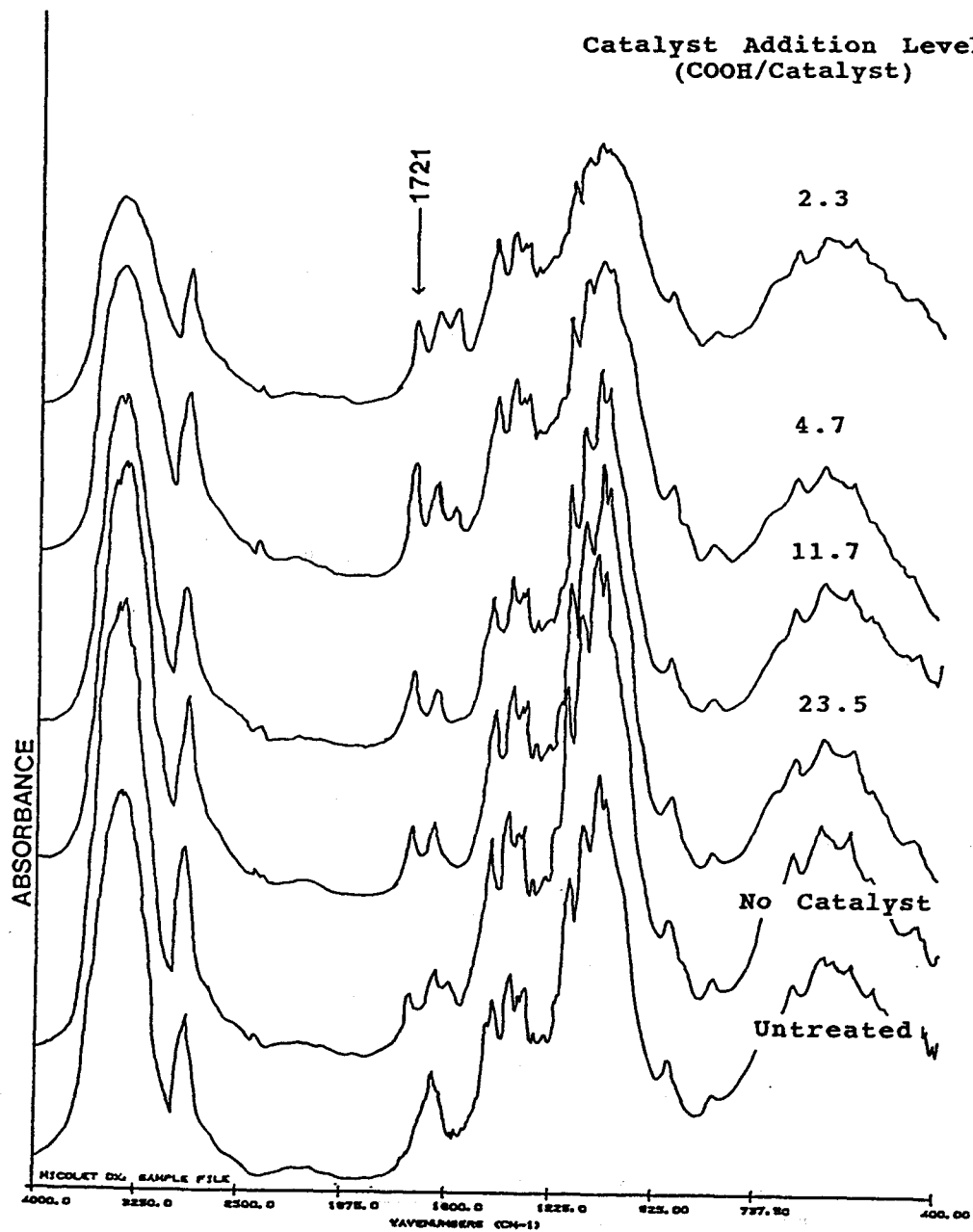


Figure 13. FT-IR spectra of maleic acid treated hand-sheet samples at different catalyst addition level.

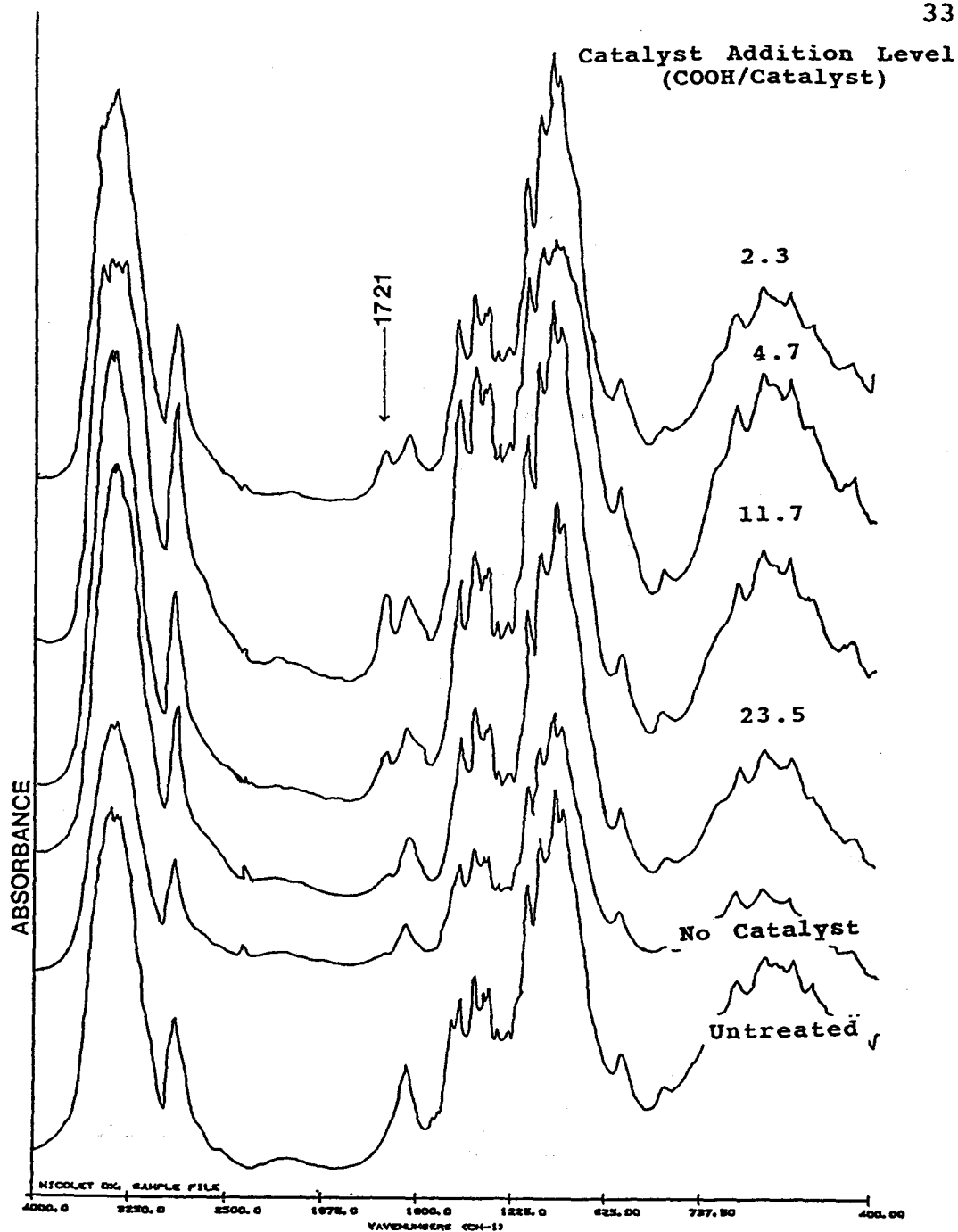


Figure 14. FT-IR spectra of citric acid treated hand-sheet samples at different catalyst addition level.

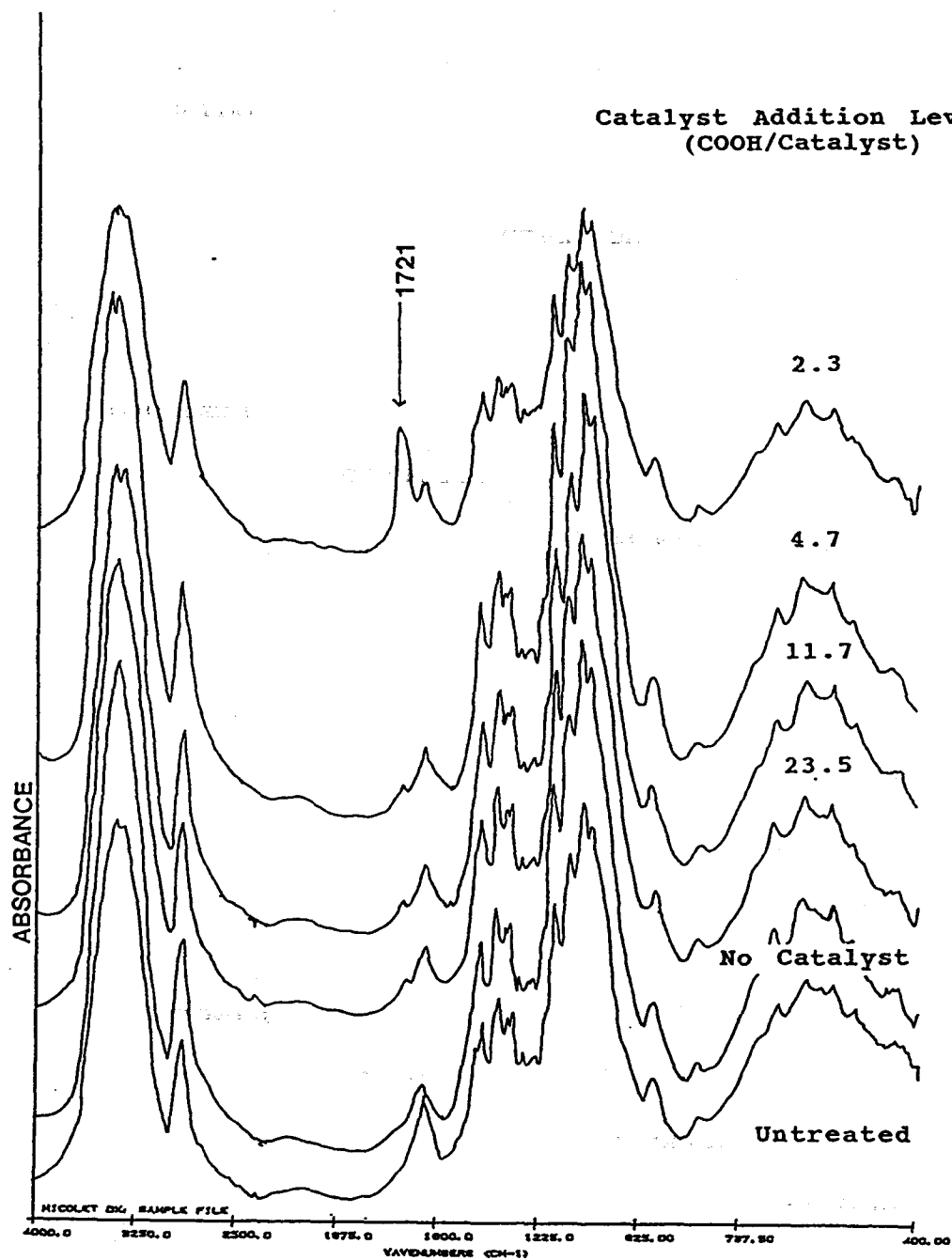


Figure 15. FT-IR spectra of BTCA treated handsheet samples at different catalyst addition level.

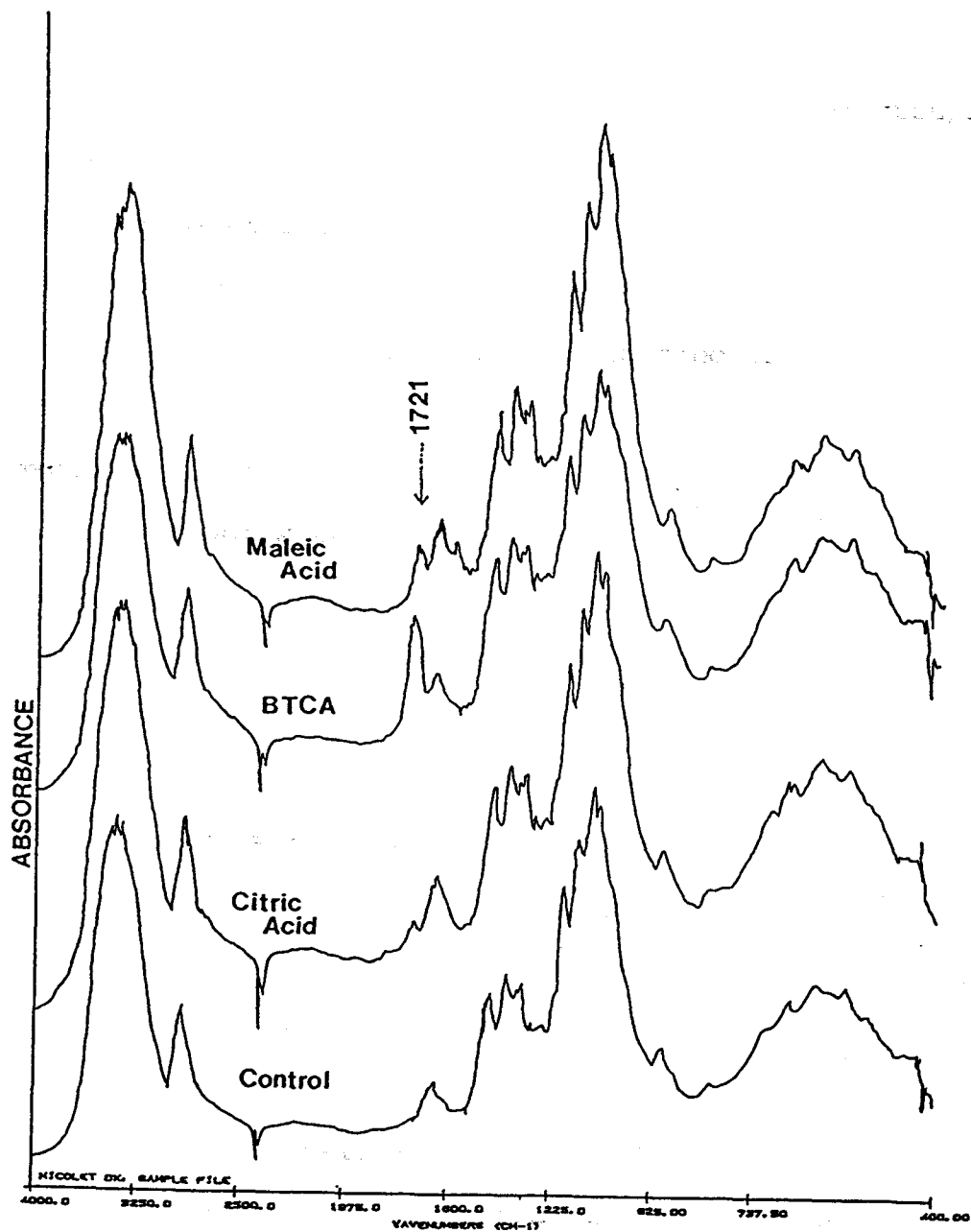
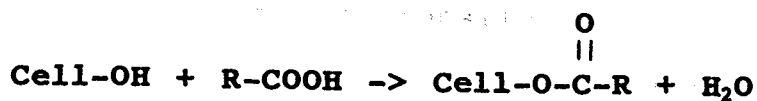


Figure 16. FT-IR spectra of each handsheet sample at the highest catalyst addition level.

### E. Chemical Reactions Between Handsheet and Carboxylic Acids

Since the main components in handsheet are cellulosic materials, the reaction between handsheets and carboxylic acids is the esterification of the hydroxyl groups in cellulose with the carboxyl groups in acids.

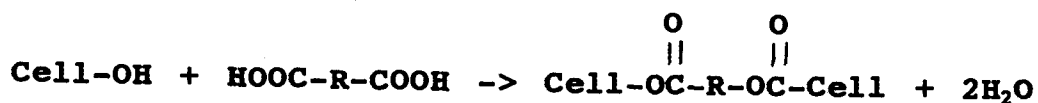


To accelerate this reaction, high temperatures and catalysts are necessary. In addition, the removal of water is an important factor. For this experiment, both high temperature (160°C) and catalyst were applied. Although acid catalysts are usually used in esterification reaction, the weak base catalyst (NaH<sub>2</sub>PO<sub>4</sub>) which is reported in two publications <sup>13,14</sup> was used as a rapid cure catalyst in this study. The reaction mechanism of the catalyst is not clear but the hypothetical reaction is described in the U.S. patent of Welch et al <sup>13</sup>.

If the cellulosic materials are treated with polycarboxylic acids, several possible reactions may occur. For example, if the cellulosic materials are treated with tricarboxylic acid, there will be four possibilities between them.

- (1) No reaction
- (2) One carboxyl group reacted: two free carboxyl groups remained
- (3) Two carboxyl groups reacted: one free carboxyl group remained
- (4) Three carboxyl groups reacted: no free carboxyl group remained

Crosslinking of cellulose occurs when two or more carboxyl groups react with cellulosic materials.



These results are also relevant in introducing C=C groups to fibers for possible graft copolymer formation.

#### F. Curing Temperature Effects

It is necessary to apply relatively high temperature to accelerate the esterification reaction described above. The temperature effects of the durable press treatment were determined with setting two different curing temperatures, 140°C and 180°C to compare to the standard temperature (160°C).

The weight gain result of each sheet was shown in Figure-17. The highest weight gain was obtained when the temperature of 180°C was applied to the handsheets, while a

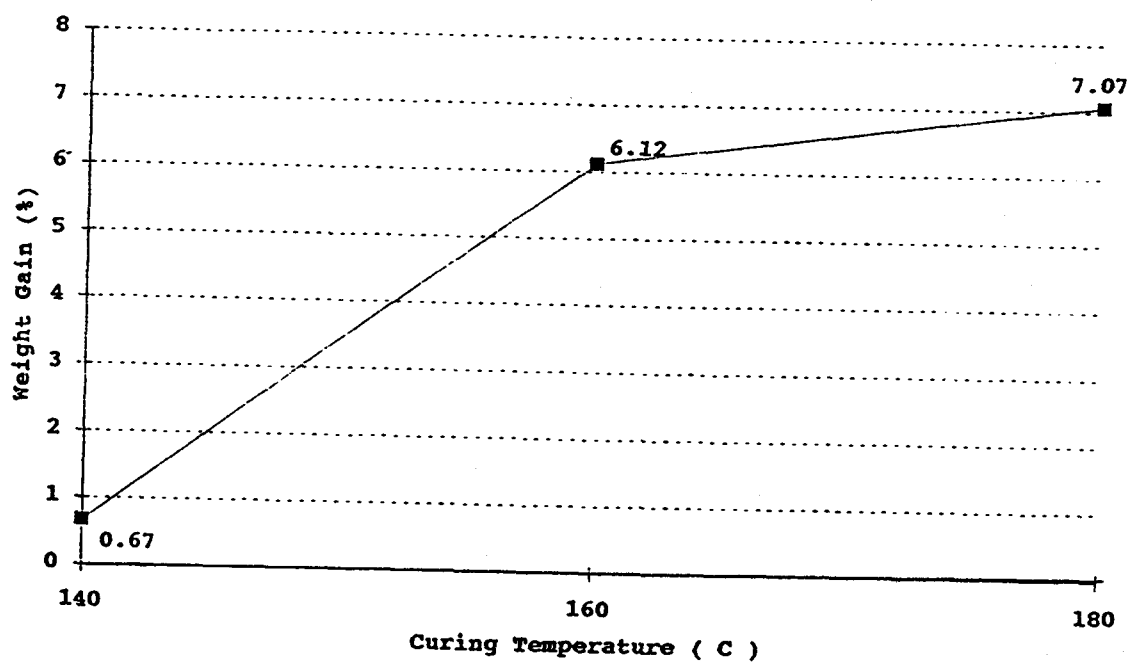


Figure 17. The weight gain of 10% BTCA treatment with elevated curing temperature. ( Catalyst level at COOH/catalyst=2.3)

very small weight gain was observed at 140°C. This result indicates that the applied temperature is critical for the esterification reaction. The wet strength result (Figure-18) also indicates how the applied temperature is important for the reaction. At low curing temperature (140°C), only 7.9% of dry tensile strength was obtained. This value is very low comparing to the wet/dry tensile strength of at 160°C and 180°C. The reason is that it was not enough heat to develop cellulose crosslinks in the handsheet at low curing temperature. However, the applied high temperature caused the sheet discoloration. The brightness decreased with elevating curing temperature. An appreciable loss of brightness was found when the curing temperature was 180°C (Figure-19).

The chemical reaction was verified from FT-IR (Figure-20) spectra as well as the weight gain of the handsheets. When the curing temperatures of both 160°C and 180°C were applied, a very strong absorption was observed at 1721  $\text{cm}^{-1}$ . As described before, this peak would be the absorption of the ester C=O bond from the crosslinking reaction. Although a weak absorption at 1721  $\text{cm}^{-1}$  was observed when the temperature of 140°C was applied, this result indicates that at least 160°C of the heat will be required to develop cellulose crosslinking in the paper.



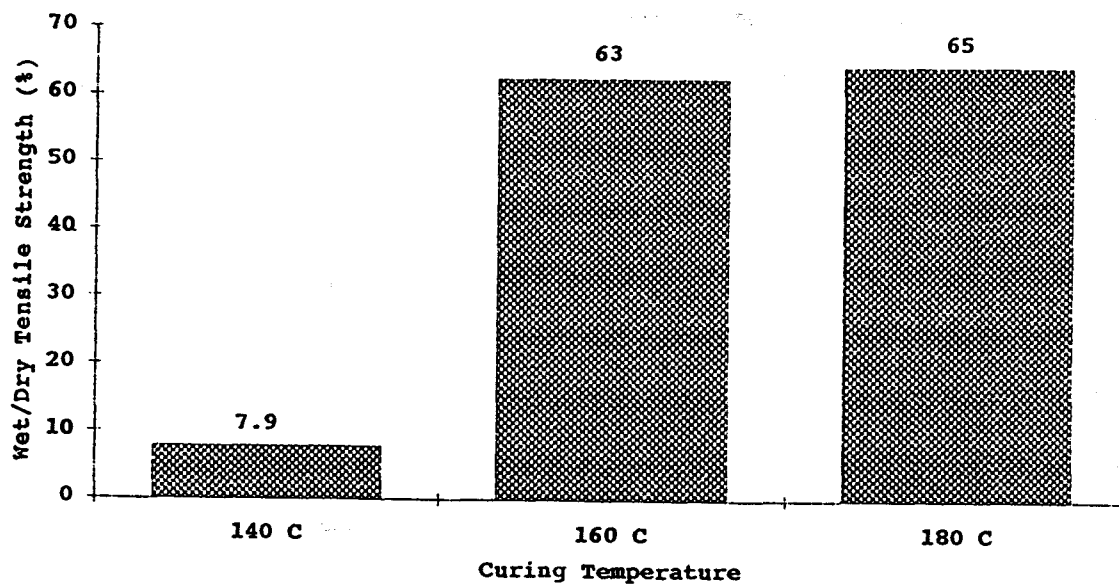


Figure 18. Wet/Dry tensile strength at different curing temperature. (Catalyst level at COOH/catalyst=2.3)

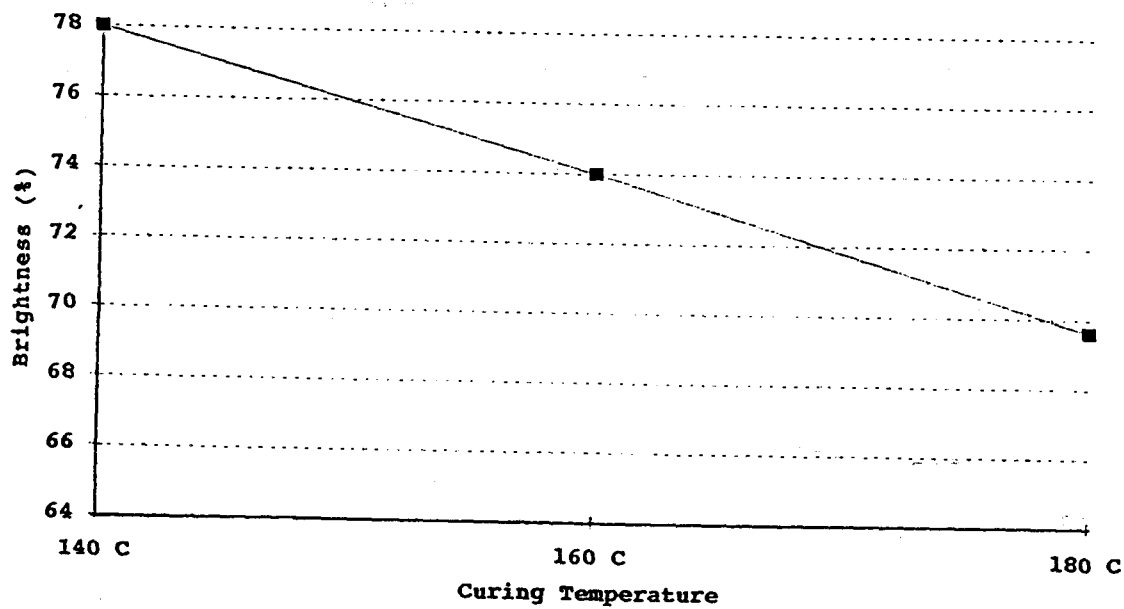


Figure 19. Brightness changes with elevating curing temperature for 10% BTCA treated handsheet samples. (Catalyst level at COOH/catalyst=2.3)

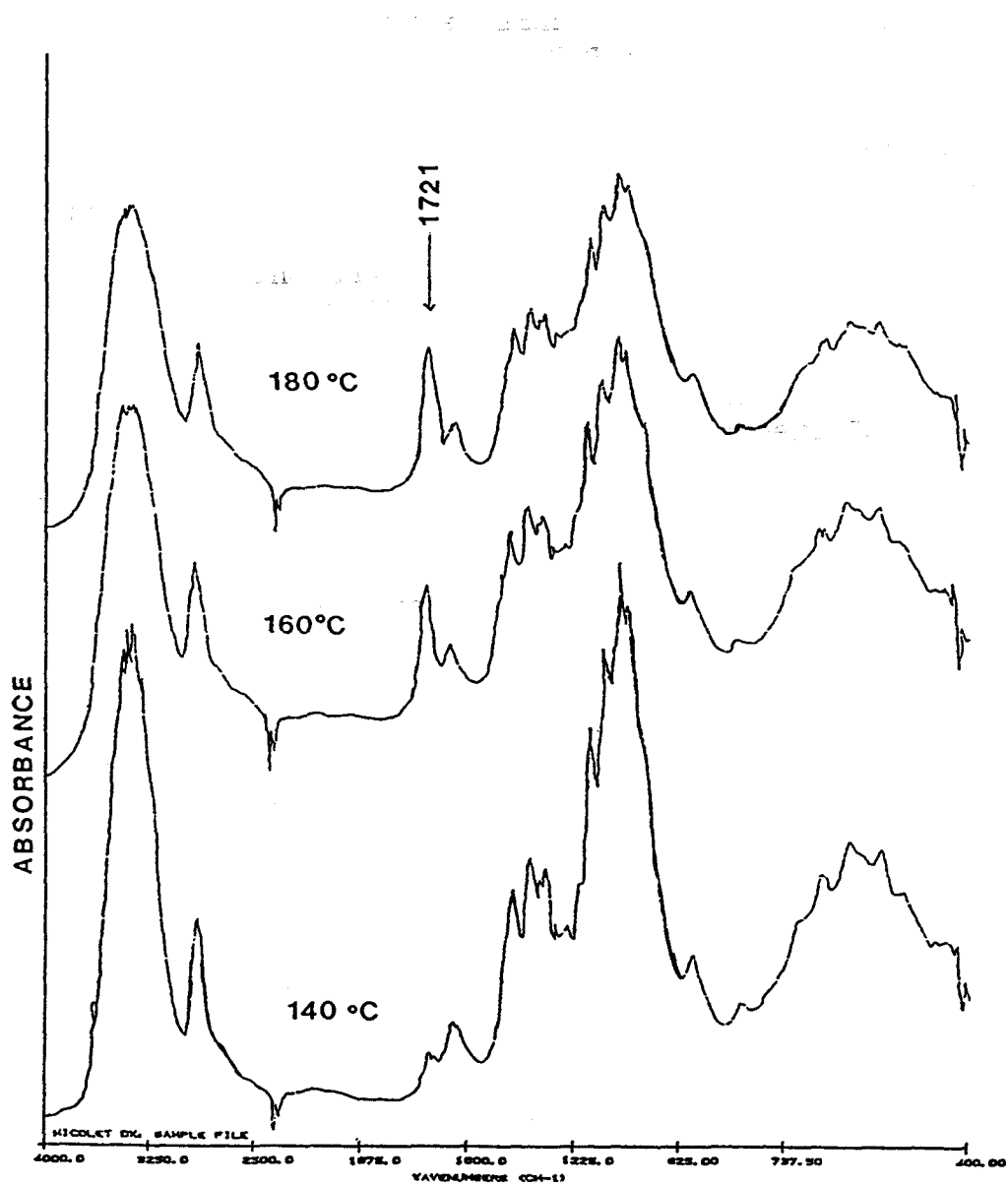


Figure 20. FT-IR spectra of BTCA treated handsheet samples at different curing temperature. (Catalyst level at COOH/catalyst=2.3)

## V. CONCLUSIONS

The introduction of several crosslinking agents into paper was accomplished by applying the "Durable Press" textile finishing treatment. BTCA was the most effective chemical as measured by FT-IR spectroscopy and weight gain. No breaking strength losses were found from BTCA and citric acid treatments but the embrittleness of paper was found. The wet strength of BTCA treated paper improved significantly due to the high degree of crosslinking (63% of the dry strength). For this crosslinking reaction, it is necessary to apply relatively high temperature (at least 160°C); however, higher curing temperatures (180°C) induce the discoloration of paper. To avoid this paper darkening, the curing condition should be controlled carefully.

Several resins are usually used in the paper industry to increase the wet strength of paper. However, it is obvious that polycarboxylic acids are effective wet strength chemicals when used with suitable catalysts. In addition, although the dimension stability of paper was not determined in this study, the crosslinking of cellulose in paper should contribute to the dimensional stability of paper.

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