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The Application of Chitosan to Composite Boxboard for Plybond Development

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THE APPLICATION OF CHITOSAN TO COMPOSITE

BOXBOARD FOR PLYBOND DEVELOPMENT

By:

Tracy O. Drier

A Thesis submitted
in partial fulfullment of the
course requirements for the
Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan

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ABSTRACT

The area of study during this research was the effect of the marine polymer chitosan addition rate on strength properties, and retention characteristics. Two machine trials were run on the WMU twin ply former using old corrugated container (O.C.C.).

Machine run #1 consisted of running a 1% chitosan solution at 0,6,16,18#/ton. Run #2 also used a 1% chitosan solution but lower addition rates of 0,2,5#/ton. The chitosan was added to the thick stock prior to the fan pump for both runs. No comparisons between the runs were made.

Conclusions from both runs include: 1) strength exhibits a statistically sound increase with increasing addition rate (run #1 between 16 and 18#/ton appears to be the only exception where strength generally decreases), and 2) cross machine direction properties remain relatively unchanged regardless of addition level.

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INTRODUCTION

Bonding between piles of a multi-ply board is achieved the same as within the individual plies. The formation of interply strength or lack of unintentional delamination of the board is of critical importance to the papermaker. Strength can be introduced by one or more of the following methods: type of pulp used, mechanical actions on the fiber, and chemical modification of the fibers.

This thesis is based on the addition of the marine polymer chitosan. Chitosan is a modified, natural, carbohydrate polymer derived from chitin. Chitin is extracted from shellfish waste including lobster, clam, shrimp, and crab shells. The focus of this research will be on the relationship between chitosan and the effect it has on the interfiber network of a two ply board.

THEORETICAL DISCUSSION

Delaminating Forces

Plybonding is the interfiber bonding force or energy between plies of a multiply board. This adhesion is developed by pressing newly formed plies together while still wet. Delamination of plies is one of the largest problems facing the boxboard industry today. While good plybonding is desired it must be remembered that excessive plybond can also be developed. In creasing converting operations for example, delamination is intentionally introduced and plybond strength can introduce problems such as board cracking. Plybond failure is caused by internal stresses of three forms: tensile stress, surface shear stress, and bending shear stress. In actual practice, the classification of these stresses are not this defined and delamination is usually the result of some combination of these.(1)

Tensile stresses are caused by forces normal to the plane of the board. The resistance to this stress is also known as plybond strength or z-direction tensile. One common cause is the ink tack on a printing press.

Surface shear stresses are the forces parallel to the plane of the board acting at the surface. a classical example is supercalander operation theory where shear forces are created by rolling friction in the nip area.

Bending stresses are caused by passing a board over a radius such as a roll. The smaller the radius or the larger the caliper the greater the stress.

Parameters affecting the plybond strength of board include: type of furnish, degree of refining, fines content and amount of filler, moisture of plies when couched, and pressing. Plies are held together by the same forces as the fibers within a ply (2). Therefore treatments which will

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alter bonding within a ply will also change interply bonding, although not necessarily to the same extent.

In the following paragraphs, the statements made concerning the specific properties have been generalized. The extent to which these properties are affected is determined by the pulp and pulping process used.

Furnish

Type of furnish is important for obtaining the desired properties of the board. The final product can only be as good as the initial fibers used. There are both mechanical and chemical pulps along with virgin and recycled. Mechanical pulps with their high yield contains lignin along with cellulose and hemicellulose. Since lignin has been shown not to swell to any degree and does not bond well with cellulose it is detrimental to plybond strength, however one potential advantage is the increase in bulk which can be obtained over chemical pulps. Virgin pulps possess a longer, stronger fiber as compared with once-dried recycled pulps. This is due to the loss of external fibrils on the recycled fibers. The major drawback for using virgin pulps is mainly economic. The power required to beat virgin pulp to the same level of freeness as recycled pulp is much greater. For the same amount of refining, to some minimum limit, a recycled pulp will exhibit better plybonding characteristics than will a virgin pulp due to the additional fines (3). The final specifications for the board ultimately determines the amount of virgin pulp used. Virgin pulps have better stiffness characteristics inherent in the fibers while the recycled is a bulkier pulp.

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Refining

The degree of refining has a direct relationship to plybonding. As the stock is refined (freeness decreased) the interply bonding increases. The freeness between any two plies should never be greater than 50 ml CSF for good plybonding (4). While Freeness has no correlation to fiber quality it is an indirect measure of fines content.

Fines, Fillers

There is currently no standard definition of fines in the paper industry. Some researchers(1,5,7) define it as that pulp fraction which passes through a 50 mesh Bauer-McNett classifier screen while others(6) use 100 mesh. The fines content has a direct bearing on plybond strength. It has been shown that there are different types of fines. The first is the organic fraction which consists of a mixture of primary and secondary wall fragments, ray and pyranchema cells, vessels segments and fragments, fibrils and short fiber pieces. Organic fines are characterized by large surface areas and water holding capacity (swellability). For groundwood pulps it has been suggested that different types of organic fines are created depending on the refining method(7). The second type is the inorganic fraction also known as ash. This includes ink, clay, and filler. The inorganic fraction is unable to readily bond with cellulose so its presence is unfavorable and should be kept to a minimum. The exception would be in the top liner where a smooth surface may be desirable. This is one possible reason for top liner lift. The organic fraction is that which imparts the strength to the board. The large surface area and water holding ability provided by the fines help bridge the fibers and bring them into molecular contact for bonding. The greater the fines retention the greater the plybonding. The amount of fines are only beneficial to a minimum

freeness limit. Below this limit problems such as felt loading of fines and drier limitations due to increased water load are prevalent (3). Also, too rapid dewatering in either forming or pressing tends to remove fines from the web, thus increasing freeness and decreasing plybond strength.

Moisture

It is not so critical that the moisture content of both plies be the same as much as the average moisture of the two plies be in the range of 70% to 90% (8). The fines must be mobile enough so that upon pressing they provide intramolecular contact between the plies for good bonding.

Pressing

Pressing of the plies before joining the plies will decrease plybonding due to couching of the fines to the felt. Increasing the joining pressure will increase the interply bonding because the increased pressure will provide more intimate contact as stated above (8).

Other

Other conclusions from the literature on plybonding characteristics are (9):

1. The more plies in the sheet the stronger the sheet to an optimum number of plies for a given basis weight and fiber type.

2. The total strength of a multi-ply sheet is greater than the combined strength of the plies.

3. Increasing the amount of machine calandering decreases plybond strength.

4. The interweb strength approaches the intraweb strength as a limit.

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Strength Development

As previously stated, attaining good strength is only as good as the raw materials and forming process itself. These strength properties will in turn benefit the finished board. Any method which will either increase the number of bonding sites or improve the existing bonds will improve certain sheet characteristics. The two most common methods for improving strength are mechanical and/or chemical modifications of the slurry (10).

The beating or refining of pulp is a very complicated physical process. Beating consists of the mechanical abrasion of pulp fibers in water to produce a high degree of swelling of the cellulose molecules in the fibers. Other effects of beating are cutting, shortening, weakening of fibers, production of fines, solubilization of hemicellulose, internal and external fibrillation, hydration, and plasticization (11).

Chemical additives can improve the degree of bonding between fibers in paper. A good strength additive chemical should have the following characteristics(12) :

1. be soluble in water-based systems so application will be compatible with conventional papermaking systems.

2. bonds well to cellulose for good retention.

3. be similar to cellulose so that the conventional hydrogen bonds aren't disrupted.

4. have sufficient molecular weight for greater bonding possibilities between surfaces too far apart for normal hydrogen bonding.

5. be film forming.

6. contain functional groups capable of forming

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Ionic or covalent bonds.

7. be linear to allow accessibility to all

functional groups.

8. be non-toxic.

9. exhibit no serious problems with recycling or

repulping.

Chitosan

One of the natural type strength additives is the marine polymer chitosan. Chitosan is the second most abundant naturally occurring polymer with cellulose being the first. It is a high molecular weight aminopolysaccharide composed of β-1,4-linked 2-amino-2deoxy-D-glucose units. Chitin, chitosan, and cellulose molecules are shown in figure 1. As shown the only difference between the chitosan and cellulose is the replacement of the 2-hydroxyl group in cellulose with a primary amino group. The mechanism by which chitosan operates is shown in figure 2.

In addition to the hydrogen bonds present, ionic bonds are formed between the acidic functional groups of the fiber and the cationic amino groups of the chitosan (13).

Chitosan is a derivitive of chitin. Naturally occurring chitin contains from 1000 to 3000 basic units (14). Chitin can be obtained from crustacea shells, certain insects, plants, and fungi. Due to the small quantities obtainable with the latter three it is currently uneconomical to commercially extract chitin from these sources. Extraction of chitin from shellfish can either be done mechanically or chemically.
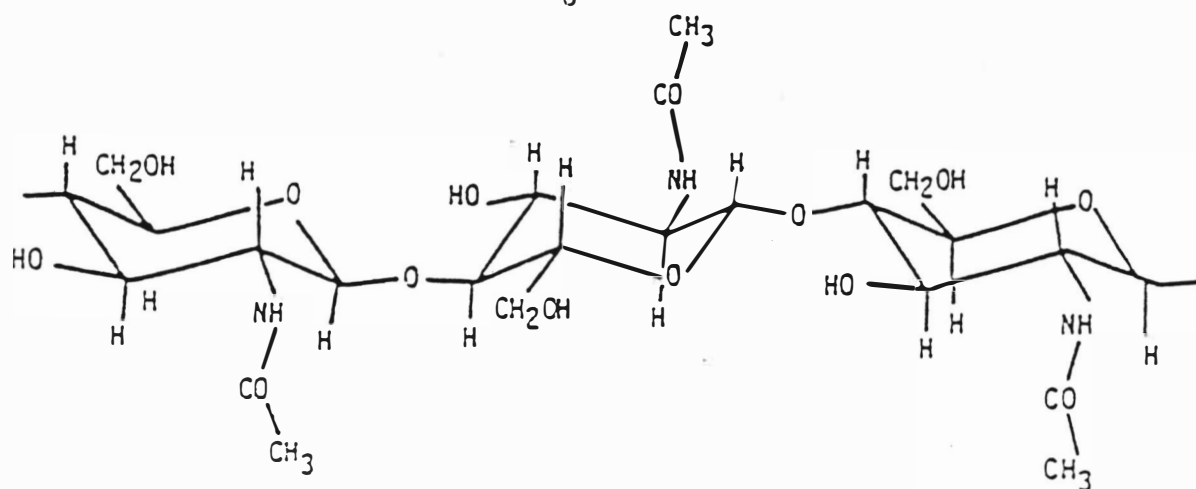
(a) CHITIN
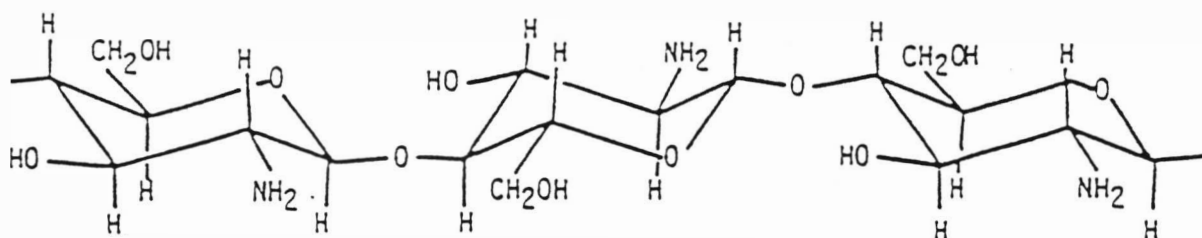
(b) CHITOSAN
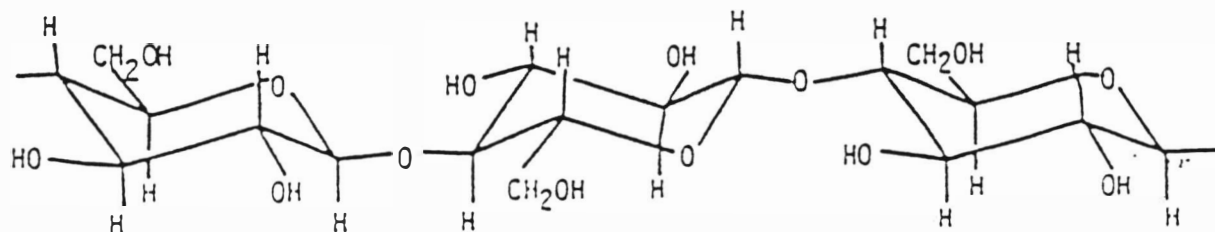
(c) CELLULOSE

Fig. 1. Molecular structures of chitin (a), chitosan (b), and cellulose (c).
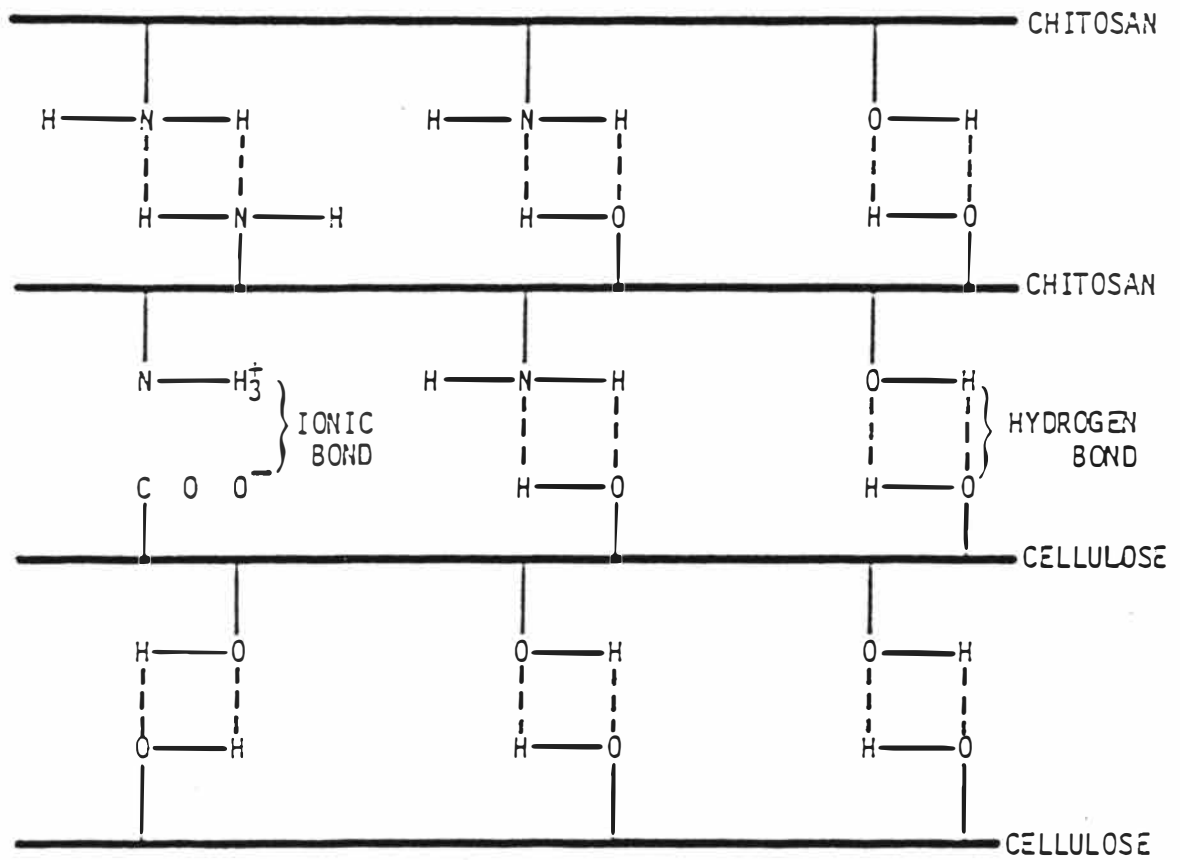
Fig. 2.   Cellulosic fiber-chitosan binder system (20)

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Chitosan Extraction Methods

A schematic for mechanical classification of chitin is shown in figure 3. The shellfish is dried, ground up, and subjected to air classification where the lighter portion (chitin and calcium salts) is separated from the heavier portion (protein and calcium carbonate). Screening of the lighter portion further separates the calcium salts from the active chitin (15).
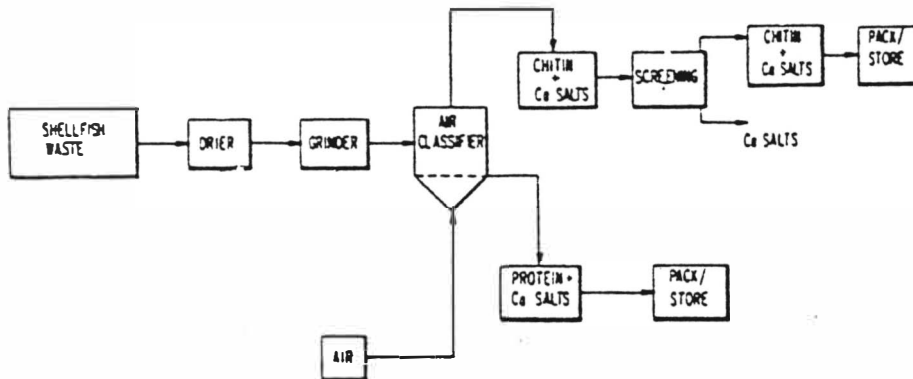
FIGURE 3: Mechanical Classification of Chitin

Figure 4 shows the schematic for chemical extraction of chitin. Protein is extracted from the shellfish waste with NaOH. The remaining calcium carbonate is then dissolved with dilute acid and filtered off. The residue is nearly pure chitin (16).

```
┌──────────┐     ┌──────────┐     ┌──────────┐              ┌──────────────┐
│ WASHED   │     │  SIZE    │     │TREAT WITH│              │SHELL RESIDUE │
│ CRUSTACEA│────▶│REDUCTION │────▶│  NaOH    │──────┬──────▶│ [ CHITIN ]   │
│ WASTE    │     │          │     │          │      │       └──────────────┘
└──────────┘     └──────────┘     └──────────┘      │       ┌──────────────┐
                                                    └──────▶│ PROTEINATE   │
                                                            │ SOLUTION     │
                                                            └──────────────┘
```
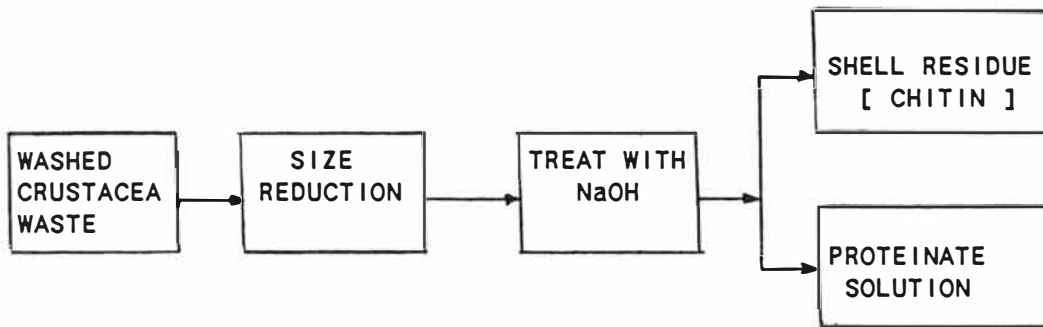
FIGURE 4: Chemical Extraction of Chitin

Just as fibers do not bond well unless beaten or refined, chitin will not bond well unless it is modified.   Deacetylation with caustic has the effect of exposing the free amino groups creating chitosan.

Ten pounds of high molecular weight chitosan was donated by Protan Laboratories in Redmond, Washington.   It was obtained in a dry flaked form. The make-down procedure is as follows: The chitosan is disolved in an acid with a pH range between 2.0-5.5.   Dilute acetic acid is usually used due to the ease of handling and availability. While other acids can be used, care should be taken to assure there are no adverse affects to the pulp. A trial to test this is recommended. Agitation can be used to aid in dissolving the chitosan. Filtering will remove any insolubles present. The "grade" of the chitosan will determine the amount of insolubles present.

From the literature (13) chitosan addition to pulps range from .1% to 5% by weight based on dry pulp weight.   Less than .1% there are no observable effects, while greater than 5% is excessive. The perferred range from previous studies is between   .2% to 1%.   For this study a 1% solution will be used.

Chitosan viscosity also plays a roll in determination of strength development. The viscosity is dependent on the amount of deacetylation of

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```

the chitin.  The amount of deacetylation determines the amount of amino groups available for ionic bond formation.  In general, the higher the viscosity, the greater the tendency for it to be effective (17).

## Methods of Addition

According to Muzzarelli (18) the effectiveness of any polymer in increasing paper sterngth depends on the method of incorporation into the cellulose.  One method is equilibrium absorption whereby a solution of chitosan is dispersed into a pulp slurry, adjusted to a 5 pH, and formed into a sheet.  This method has been proven to be rather inefficient, especially at higher addition levels (19).  The charge differences between the chitosan and fibers are quickly neutralized and hence the rate of equilibrium attainment decreases. The higher addition rates cause fiber flocculation which in turn produces a poorly formed sheet with losses in physical properties.  Low retention efficiencies along with fiber flocculation would seem to eliminate this method as a viable addition medthod.

Precipitation of chitosan onto the fibers is done exactly as the previously described method except the pH of the solution is adjusted to 6.7-7.0 or above.  This will cause the chitosan to precipitate from solution onto the fibers.  This gives good results for chitosan as a retention aid (20).

The most direct method of chitosan application is by direct application (spraying) to the sheet.  Virtually 100% retention is obtained with this method.

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## EXPERIMENTAL PROCEDURE OVERVIEW

Two pilot scale trials were run on the WMU twin ply former. The first trial was run on January 26, 27, 1987 and trial #2 on February 23, 24, 1987. The first days of each trial were for stock preparation, chitosan makedown, and machine set up. Day 2 was for the actual trial. The machine was operated by pilot plant staff, while student employees and I assisted

The stock used for both trials was unbleached old corrugated container (O.C.C.). It was pulped 20 minutes in the hydropulper with no additional refining. It was then screened and cleaned and pH adjusted to 7.0. Consistency and freeness were determined. The method of chitosan application was precipitation of the chitosan onto the fibers. The actual machine itself has no drier section so samples were removed at each condition, cut into sheets MD long, and dried on the Noble & Wood drier cans located in the pilot plant. Headbox and whitewater samples were taken for consistency, retention, and fiber length determination. Wet paper was also removed and tested for moisture. All paper was conditioned for one week prior to testing and tested according to Tappi Standards or other. Appendix 1 contains a listing of tests performed. Once the data was gathered, results were compared against each other for statistical significance. This was to determine if the changes occuring at differing addition rates were actually significant.

No comparisons between trials will be attempted in this report. This is because pulp from run #1 is different than that of run #2. To preserve continuity of the two trials, each run will be written up with separate sections on procedure, results, and discussion.

## EXPERIMENTAL PROCEDURE – Run #1

The initial target conditions for trial 1 were:

| Base liner | Top liner |
|------------|-----------|
| 300#/hour stock | 300#/hour stock |
| 3,5,10#/ton addition rate | 3,5,10#/ton addition |

* 1% chitosan solution

* also run a blank (0#/ton) for comparison at the beginning of the trial.


After determining the feed rated for the chitosan it was discovered that there were no pumps large enough for our needs. It was then decided to increase the chitosan concentration to 2% and readjust the addition rates to 0,3, and 8#/ton.

The procedure for the 2% chitosan makedown was as follows:

- disperse 3# chitosan in 17.6 gallons of water

- add 1272 ml glacial acetic acid

- agitate for 45 minutes

- pass through a 60 mesh screen to remove insolubles


The viscosity was too great for any of our agitators at 2% so the amount of water was doubled to dilute it to 1%. Our feed rates were doubled to compensate for this.

Once the machine was running and stabilized, the controls remained constant throughout the run. To prevent any runnability problems the machine operator ran the machine at half the speed initially planned. This was an unanticipated change causing twice the chitosan to be added as was origionally planned. This

change was unknown at the beginning of the run so all effects were unknown. This change resulted in extra stock after completion of the planned rates. It was then decided to open the metering pump wide-open for an additional condition. After completion of the trial the wide open pump capacity was determined to be 9#/ton. Multiplying by two times the chitosan yields 18#/ton.

The final conditions for run #1 were:

| Base Liner | Top Liner |
|---|---|
| 150#/hr stock flow rate | 150#/hr stock flow rate |
| 6,16,18#/ton addition rate | 6,16,18#/ton add. rate |

* 1% chitosan solution.
* a blank (0#/ton) was run a beginning of the trial for
  comparison.

The overall 'feel' of run #1 was good. While it seemed rushed and disorganized as should be expected for the first run, the paper and equipment ran smoothly. The paper produced had a uniform formation and CD profile. For the first three conditions the two whitewater streams were sampled as one stream. So in determining percent first pass retention for condition #4 - the average consistency between the two streams were taken.

# STOCK AND MACHINE CONDITIONS FOR RUN #1

## Stock

Consistency:    1.72%

Freeness:       515 CSF

Initial pH:     9.3

Final pH:       7.2

* Chitosan was added to the thick stock prior to the fan pump.

| Machine | Blank | 3#/t | 8#/t | 9#/t |
|---|---|---|---|---|
| Flow: (gal/min) | | | | |
| cylinder #1 | | | | |
| stock | 20 | 20 | 20 | 20 |
| water | 110 | 110 | 110 | 110 |
| cylinder #2 | | | | |
| stock | 20 | 20 | 20 | 20 |
| water | 100 | 100 | 100 | 100 |
| Presses: (pounds) | | | | |
| 1st | 20 | 20 | 20 | 20 |
| 2nd | 30 | 30 | 30 | 30 |
| 3rd | 40 | 40 | 40 | 40 |
| Vacuum: (In. Hg) | | | | |
| 1st | 5.5 | 5.3 | 5.4 | 5.3 |
| 2nd | 6.5 | 6.4 | 6.4 | 6.3 |
| 3rd | 5.0 | 5.1 | 5.0 | 4.9 |
| 4th | 5.0 | 5.0 | 4.9 | 5.0 |

## PRESENTATION OF RESULTS — Run #1

Chitosan addition to secondary stock showed a stastical increase in all strength properties analyzed comparing the blank against 6#/ton, 16#/ton, and 18#/ton. Exceptions include CD tensile factor and stiffness. There were insignificant increases between successive addition rates in certain cases.

Percent moisture increases with rate of addition until 16#/ton at which point starts to decrease. The range from 0 to 6#/ton shows the greatest increase with a more gradual increase from 6 to 16#/ton. The moisture content then drops between 16 and 18#/ton. First pass retention decreases from 0 to 3#/ton remains constant until 16#/ton and it rises between 16 and 18#/ton.

An attempt was made to determine if chitosan was actually being absorbed onto the fibers at the given addition rates. This was done by measuring the elemental nitrogen content of the sheet. The amino groups of the chitosan should increase the nitorgen content if it is being absorbed. Kjeldahl nitrogen analysis was the test performed. Kar Laboratories in Kalamazoo, Michigan performed all kjeldahl testing for this thesis.

## Kjeldahl Nitrogen Analysis For Run #1
(results expressed as mg/kg)

| Sample | Total | Kjeldahl | Nitrogen |
| --- | --- | --- | --- |
| | Test 1 | Test 2 | Average |
| Chitosan (solid) | 74,800 | 82,600 | 78,700 |
| Chitosan (liquid) | 687 | 791 | 739 |
| Paper (blank) | 334 | 376 | 355 |
| Paper (6#/ton) | 365 | 385 | 375 |
| Paper (16#/ton) | 585 | 516 | 551 |
| Paper (18#/ton) | 807 | 618 | 713 |

# Z—Direction Tensile VS Addition Rate

For Run #1



Y-axis: ZDT ( x10 pounds)

X-axis: Chitosan Addition Rate (#/ton)

X-axis categories: blank, 6, 16, 18

# Scott Bond vs Addition Rate

For Run #1



*Axis labels:* Scott Bond (1/1000 ft−lb) — vertical axis; Addition Rate (#/ton) — horizontal axis with categories blank, 6, 16, 18.

# Stiffness vs Addition Rate

For Run #1



Stiffness (gm-cm)

Addition Rate (#/ton)
MD    CD

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# Tensile Factor vs Addition Rate

## For Run #1

Figure 9:

# Burst Factor VS Addition Rate

For Run #1

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# Percent Moisture VS Addition Rate

## For Run #1

# First Pass Retention VS Addition Rate

## For Run #1

# Statistical Significance Between Conditions of Run #1

| Avg. Teat Values: | | blank | 6#/ton | 16#/ton | 18#/ton |
|---|---|---|---|---|---|
| ZDT (x 10lb) | | 4.7 | 5.9 | 6.6 | 6.5 |

statistical
significance?
```
|-- yes --|--- yes ---|- yes -|
|---------- yes ----------|
|---------- yes ------------------|
```

| Scott Bond (1/1000 ft-lb) | | 40 | 60 | 80 | 75 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- yes --|--- yes ---|- yes -|
|---------- yes ----------|
|---------- yes ------------------|
```

| Stiffness (gm-cm) | MD | 50 | 44 | 45 | 45 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- yes --|--- no ---|- no --|
|---------- yes ----------|
|---------- yes ------------------|
```

| | CD | 42 | 39 | 38 | 43 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- yes --|--- no ---|- no --|
|---------- yes ----------|
|---------- no ------------------|
```

| Tensile Factor (N-.m/g) | MD | 40.7 | 42.3 | 43.4 | 45.1 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- yes --|--- no --|--- no -|
|---------- yes --------|
|---------- yes ---------------|
```

| | CD | 22.5 | 26.4 | 27.5 | 26.4 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- no --|--- no --|--- no -|
|---------- yes ----------|
|---------- no ------------------|
```

| Burst Factor (kPa-m/g) | | 2.5 | 2.8 | 3.1 | 3.3 |
|---|---|---|---|---|---|

statistical
significance?
```
|-- yes --|--- yes --|- yes -|
|---------- yes ---------|
|---------- yes ------------------|
```

* All statistical analysis run with IBM Statgraphics Software.

# Kajaani Fiber Length Analysis - Run #1

* Number of fibers counted:  3523 to 3528

* Optics #3 was used.

| Condition | Add. Rate | pH | Arithmatic | Weighted | Cubed |
|-----------|-----------|-----|-----------|----------|-------|
| 1. | Blank | | | | |
| | #1 Hdbx. | 7.7 | .73 | 1.69 | 2.8 |
| | WW | 7.7 | .32 | 1.11 | 2.57 |
| 2. | 6#/ton | | | | |
| | #1 Hdbx. | 7.5 | .75 | 1.78 | 2.9 |
| | WW | 7.5 | .26 | .81 | 1.91 |
| 3. | 16#/ton | | | | |
| | #1 Hdbx. | 7.6 | .78 | 1.79 | 2.92 |
| | #2 Hdbx. | 7.4 | .77 | 1.79 | 2.90 |
| | WW | 7.6 | .26 | .72 | 1.52 |
| 4. | 18#/ton | | | | |
| | #1 Hdbx. | 7.7 | .66 | 1.38 | 2.27 |
| | #2 Hdbx. | 7.3 | .84 | 1.84 | 2.91 |
| | #1 WW | 7.7 | .26 | .87 | 2.16 |
| | #2 WW | 7.5 | .41 | 1.01 | 1.99 |

WW = combined white water from both cylinders (unless specified)

## Averages Generated By Kajaani FS-100

1. Arithmetic Average:  $\dfrac{Ni(Li)}{N}$

2. Weighted Average:  $\dfrac{Ni(Li)2}{N(Li)}$

3. Cubed Average:  $\dfrac{Ni(Li)3}{N(Li)2}$

* Weighted and cubed averages lend strengths to the longer distributions

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## DISCUSSION OF RESULTS - Run #1

Looking at average kjeldahl nitrogen values, it is shown that chitosan is being absorbed at every addition level. The least amount absorbed at 3#/ton had the greatest overall impact on strength property increases when compared with the blank. They ranged from a high of 33% in ZDT to a low of .9% in moisture. Burst and CD tensile are the only exceptions of this trend. As shown by these strength increases it is obvious that chitosan is interacting between the two plies and more than likely within the plies themselves also. There were no statistics performed on the kjeldahl values , and no samples of a known nitrogen composition were tested for a reference; it is impossible to say how accurate these kjeldahl numbers are. Since there is overlap between the 0#/ton and 6#/ton it cannot be known if in fact chitosan was absorbed at 6#/ton.

The addition of chitosan has the most statistically sound results on the Z-direction properties of ZDT and Scott Bond. Burst factor is also included in this category. Based on statistical anaylsis of the test results chitosan was shown to have the least effect on CD properties. One explanation for this lack of cross machine strength is that just as fibers exhibit MD tendencies so does chitosan.

The moisture of the sheet reflects the overall trends of the strength properties as is expected. Water is retained from the formation of a more coherent web and after some point the added charge to the system causes a 'breakdown' of formation resulting in the decrease in moisture.

First pass retention is critical for a mill whose main concerns are purely economic. Based on previous works and the nature of logic itself concerning strength additives it would seem that retention would increase. As shown however, this is not the case. A possible explanation of this is

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that the charges on the chitosan and fibers initially attract each other and at some addition level start to repel the fibers and each other causing retention to decrease. This theory could have been checked had our Zeta potential meter not been in for repairs. Since cellulose and chitosan are so fundimentaly simular it is possible that they behave according to the receptor theory. That is, the molecules align themselves and are attracted to each other. Eventually the chitosan is so saturated onto the fiber that they start to repel. This receptor theory is another possible explanation for the lack of CD strength; chitosan aligning with the machine oriented fibers do not link in the cross machine direction well.

## EXPERIMENTAL PROCEDURE-run#2

For run #2 it was decided to lower the addition rates since the rates for run #1 would be economically unfeasible in any comercial mill environment.  It was also decided to use the adsorption method of chitosan addition along with the precipitation method.

The initial target conditions for run #2 were:

|  | Base Liner | Top Liner |
|---|---|---|
| pH 7 | 150#/hr stock | 150#/hr stock |
|  | 2,5#/ton add. rate | 2,5#/ton add. rate |
| pH 5 | 150#/hr stock | 150#/hr stock |
|  | 2,5#/ton add. rate | 2,5#/ton add. rate |

* use a 1% chitosan solution

* a blank (0#/ton) was run at the beginning of  each run for comparison purposes

The procedure for the 1% chitosan makedown was as follows:

- disperse 2# chitosan in 23.3 gallons of water

- add 85.7 ml glacial acetic acid

- agitate 45 minutes

- pass through a 60 mesh screen to remove insolubles

My overall impression of run #2 was better than that of run #1 after the first day spent in preparation and day 2 during  the first  part of the trial.  After run #1 in January the little details that make for a smoother run were noted and they indeed made for  a  less  hectic  atmosphere (even

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though some was inevitable). This was up until the pH 7, 2#/ton condition. At this point it became obvious that there was insufficient stock to complete our projected conditions. This is when the atmosphere got alittle tense. A decrease in basis weight was becoming apparent during the 5 pH, 2 #/t condition when we did run out of stock. Two reasons warranted the omission of the 5 pH conditions obtained from discussion in this report. These were: 1) no adequate testing samples from the 5 pH, 2 #/t condition, and 2) the pH was not allowed enough time to stabilize from 7 to 5 pH. Another bad point during run #2 was the fact we had no idea of the flow rate status of the #2 cylinder headbox since it had gotten stuck in some open position. It formed a good sheet that plied well with the top sheet and that is all that was known.

The final conditions for run #2 were:

|  | Base Liner | Top Liner |
|---|---|---|
| pH 7 | 150#/hr stock | 150#/hr stock |
|  | 2,5#/ton add. rate | 2,5#/ton add. rate |

* 1% chitosan solution

* A blank (0#/t) was run at the beginning of the run for comparison.


All procedures for machine conditions, sample gathering, and sample testing were the same as that for run #1. The only exception was a more thorough collection of headbox and white-water samples from their respective points.

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## STOCK AND MACHINE CONDITIONS FOR RUN #2

### Stock

| | | |
|---|---|---|
| Consistency: | 1.80% | |
| Freeness: | 580 CSF | |
| Initial pH: | 8.8 | |
| Final pH: | 7.0 | |

\* Chitosan was added to the thick stock prior to the fan pump.

| Machine | Blank | 2#/ton | 5#/ton |
|---|---|---|---|
| **Flow: (gal/min)** | | | |
| Cylinder #1 | | | |
| stock | 20 | 20 | 20 |
| water | 110 | 110 | 110 |
| Cylinder #2 | | | |
| stock | --- | --- | --- |
| water | 100 | 100 | 100 |
| **Presses: (pounds)** | | | |
| 1st | 40 | 40 | 40 |
| 2nd | 30 | 30 | 30 |
| 3rd | 20 | 20 | 20 |
| **Vacuum: (In. Hg.)** | | | |
| 1st | 4.5 | 4.7 | 4.6 |
| 2nd | 5.5 | 5.3 | 5.5 |
| 3rd | 3.5 | 3.5 | 3.4 |
| 4th | 3.0 | 3.0 | 3.2 |

## PRESENTATION OF RESULTS - RUN #2

As with run #1, the addition of chitosan showed an increase in strength properties. ZDT, Scott Bond, CD tensile factor, and burst factor all had statistically significant increases at all addition levels. MD stiffness was unaffected at any addition level while CD stiffness was affected only between the blank and 5#/ton. MD tensile showed no effect at the 2#/ton addition but was good for the remainder of the levels.

Percent moisture increases from 0#/ton to 2#/ton and remains constant over the 2 to 5 #/ton range. First pass retention in the 1st cylinder increases 3% between the blank and 2#/ton and .01% between the 2 and 5#/ton. For cylinder #2 the effect was not as pronounced; blank and 2#/ton remained constant and a .01% increase is shown between 2 and 5#/ton.

Kjeldahl Nitrogen Analysis For Run #2
(results expressed as mg/kg)

|                        | Total Kjeldahl Nitrogen | | |
|------------------------|--------|--------|---------|
| Sample                 | Test 1 | Test 2 | Average |
| Chitosan (liquid)      | 418    | 435    | 428     |
| Paper (blank, 0#/t)    | 205    | 226    | 215     |
| Paper (2#/ton)         | 399    | 417    | 408     |
| Paper (5#/ton)         | 319    | 386    | 353     |

Figure 12:
Z-Direction Tensile vs Addition Rate
For Run #2

ZDT ( x10 pounds)

Addition Rate (#/ton)

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# Scott Bond vs Addition Rate

## For Run #2



Scott Bond vs Addition Rate for Run #2. X-axis: Addition Rate (#/ton) with categories blank, 2, 5. Y-axis: Scott Bond (1/1000 ft-lb) ranging 0 to 60. Bars: blank ≈ 40, 2 ≈ 45, 5 ≈ 60.

Figure 14:
# Stiffness vs Addition Rate
For Run #2

Stiffness (gm-cm)

Addition Rate (#/ton)
MD    CD

# Tensile Factor vs Addition Rate

For Run #2

# Burst Factor vs Addition Rate

## For Run #2

# Percent Moisture VS Addition Rate

For Run #2

Figure 18:

# First Pass Retention VS Addition Rate

For Run #2

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St a istcal Significance Bet weenCondit ons of Run #2

| Avg. Test Value: | | blank | 2#/ton | 5#/ton |
|---|---|---|---|---|

ZDT (x 10lb)                    3.7            4.0              4.0

st a istcal
significance?        |◄---- yes ----►|◄----- yes ----►|
                     |◄------------ yes -----------►|


Scott Bond                      40             45               65
(1/1000 ft-lb)
                     |◄---- yes ----►|◄----- yes ----►|
                     |◄------------ yes -----------►|


St ffness          MD   52             54               55
(gm-cm)
                     |◄---- no -----►|◄----- no -----►|
                     |◄------------ no -----------►|


                   CD   40             4 1              45

                     |◄---- no -----►|◄----- no -----►|
                     |◄------------ yes -----------►|


Tensile Fact or    MD   37.5           37.0             4 0.2
(N-.m/g)
                     |◄---- no -----►|◄----- yes ----►|
                     |◄------------ yes -----------►|


                   CD   17.1           18.2             20.4

                     |◄----- yes ----►|◄----- yes ----►|
                     |◄------------ yes -----------►|


Bur stFact or           29             37               4 1
(kP a-m/g)
                     |◄---- yes ----►|◄----- yes ----►|
                     |◄------------ yes -----------►|

* All st a ist icaanalysis r unwit hIBM St a g aph¢s soft wa e.

# Kajaani Fiber Length Analysis — Run #2

* Number of fibers counted:  3299 to 3306

* Optics #3 was used.

| Condition | Add. Rate | pH | Arithmatic | Weighted | Cubed |
|-----------|-----------|------|------------|----------|-------|
| 1. | Blank | | | | |
| | #1 Hdbx. | 7.5 | .80 | 1.89 | 3.02 |
| | #2 Hdbx. | 7.4 | .80 | 1.89 | 3.00 |
| | #1 WW | 7.7 | .26 | .80 | 2.16 |
| | #2 WW | 7.7 | .51 | 1.55 | 2.81 |
| 2. | 2#/ton | | | | |
| | #1 Hdbx. | 7.7 | .77 | 1.73 | 2.76 |
| | #2 Hdbx. | 7.6 | .81 | 1.89 | 3.02 |
| | #1 WW | 7.8 | .24 | .69 | 1.71 |
| | #2 WW | 7.6 | .54 | 1.63 | 2.91 |
| 3. | 5#/ton | | | | |
| | #1 Hdbx. | 7.6 | .78 | 1.78 | 2.89 |
| | #2 Hdbx. | 7.7 | .81 | 1.80 | 2.98 |
| | #1 WW | 7.6 | .25 | .78 | 2.25 |
| | #2 WW | 7.6 | .42 | 1.48 | 3.24 |

## DISCUSSION OF RESULTS - RUN #2

Kjeldahl nitrogen shows more chitosan is being absorbed at the 2#/ton level than at the 5#/ton. The receptor theory could again be used to explain this. The samples taken to Kar Labs were clearly and correctly marked. Human error is always possible and further research needs to be done before any conclusions can be drawn.

Based on successive addition rates, Scott Bond, MD and CD tensile factor show a greater percent difference between the 2 and 5#/ton while ZDT and burst factor show the greater percentage between the blank and 2#/ton. MD and CD stiffness both show insignificant statistical differences between successive addition levels however, there is a difference between the blank and 5#/ton in CD stiffness.

It was expected that stiffness of the sheet would increase since wet and/or dry strength additives improve the degree of bonding between fibers (12). This improved bonding can increase the stiffness of the paper since the fiber is being held more securely in the network of the sheet.

# CONCLUSIONS

## Run #1

Strength improves upon addition of chitosan up to a point. Cross machine direction appears unaffected by addition levels. The range between 16 and 18#/ton appears to show a saturation point being reached. This is characterized by an overall decrease in strength between these two points. This decrease is mirrored in the percent moisture. First pass retention showed a decrease with addition which was unexpected. This was more than likely due to the high addition rates causing a repulsion instead of attraction between the chitosan and cellulose.

When dealing with secondary fibers, cost must be kept to minimum in achieving acceptable strength values. Otherwise it would be just as easy to use virgin fiber. For this reason alone the addition rates for run #1 were too excessive for any type of comercial application.

## Run #2

Run #2 shows inproved bonding strength upon addition of chitosan. The overall greatest effect was shown at the 5#/ton level. MD and CD stiffness showed little/no statistical difference between addition levels. Scott Bond showed the greatest overall increase with 38.5% between the blank and 5#/ton. Moisture behaves as would be expected as does first pass retention. Both of these show an increase.

While some of the initial objectives of this thesis had to be abandoned either due to unavoidable circumstances or error on my part; this will all be part of the paper mill work environment once I am out in the work force.

While this is by no mean comparable to machine trials in an actual mill, it does give one an idea of the many factors involved in a machine run that can not be experienced in a laboratory setting.

## RECOMMENDATIONS

A couple areas of additional investigation have come to mind after completion of this project. These are to look at: 1) effects of differing points of addition on strength/retention. or 2) the different methods of chitosan application. A third area of interest would be to do some type of power study to determine the effectiveness of chitosan addition as a refiner substitution. It would be of great interest if it could be shown that it is cheaper to chemically 'refine' fiber as compared with traditional mechanical refining.

When first discussing the idea of working with chitosan last fall, my advisor and I talked about looking at different points of addition. This in addition to the other aspects of the project would have been too time consuming. In addition, due to the layout of our facilities here at WMU, we can not easily change addition points in the given time constraints of a run on the two ply former. With some work this problem could be easily overcome.

Concerning other methods of addition; the adsorption method of addition was initially attempted but due to circumstances byond our control had to be discarded for this report. One critical area of importamce that was overlooked by myself was the addition of raw acid to the whitewater stream to adjust the pH to a level below 6.0. This must be done in addition to the adjustment of the stock. The other method of addition is the direct application of the chitosan between the two plies by an atomized spray bar. Granted, given current market prices for chitosan this would not seem to be economically viable. It would however be an interesting area of research. Engineering details concerning the atomizing spray bar and catch pan would have to be worked out before this could be done on our two ply machine here at Western.

# APPENDIX 1

| Physical Testing | Procedure |
|---|---|
| Tensile Strength | TAPPI T 494 |
| Scott Bond  (model B) | according to instruction manual |
| ZDT | Custom Scientific Instruments, according to instruction manual |
| Stiffness | TAPPI T 489 |
| Bursting Strength | TAPPI T 403 |

## CHITOSAN

## CERTIFICATE OF ANALYSIS

Lot Number    C46-572-01

% Moisture    8.7    ±    .1

% Ash    .21    ±    .07

% Deacetylation    78.2    ±    .2


## Solution Parameters

1% Viscosity    4100 cps    ±    700

(2.5 gram/247.5 ml 1% acetic acid, 20°C, Brookfield LVT, 30 rpm, appropriate spindel)


Intrinsic Viscosity    10.4    ±    —
    dl/g (0.1M acetic acid & 0.2M NaCl)

Viscosity Average Molecular Weight    1.55    X $10^6$ Daltons

% Insolubles    .47    ±    .22


Analysis By    G. P. Hutchings
Date    4/11/86

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ANALYTICAL REPORT

To:  Mr. Tracy Drier
     339 Hoekje Hall
     WMU
     Kalamazoo, MI  49007

Date:  2-18-87

Laboratory Code:  87190

P.O. Number:  78323P

Re:  Total Kjeldahl Nitrogen analysis of six samples submitted
     2-9-87.

     Results are expressed as mg/kg.

|    | Sample Identification | Total Kjeldahl Nitrogen | | |
|----|----------------------|----------|----------|----------|
|    |                      | Trial #1 | Trial #2 | Average |
| 1) | Chitosan (liquid)    | 687      | 791      | 739     |
| 2) | Chitosan (solid)     | 74,800   | 82,600   | 78,700  |
| 3) | Paper (WO)           | 807      | 618      | 713     |
| 4) | Paper (3)            | 365      | 385      | 375     |
| 5) | Paper (8)            | 585      | 516      | 551     |
| 6) | Paper (Blank)        | 334      | 376      | 355     |

Respectfully submitted,

KAR Laboratories, Inc.

William H. Bouma, Ph.D.
Director

WHB/mcm

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## ANALYTICAL REPORT

To: Mr. Tracy Drier
339 Hoekje Hall
WMU
Kalamazoo, MI 49007

Date: 4-15-87

Lab Code: 87424

P.O. # 74722P

Re: Total Kjeldahl analysis of four samples submitted
3-23-87.

Results expressed as mg/kg.

|  | Sample Identification | Total Kjeldahl Nitrogen | | |
|---|---|---|---|---|
|  |  | Trial #1 | Trial #2 | Average |
| 1) | 2#/T Paper Sample | 399 | 417 | 408 |
| 2) | 5#/T Paper Sample | 319 | 386 | 353 |
| 3) | Blank Paper Sample | 205 | 226 | 215 |
| 4) | Chitosan Liquid | 418 | 435 | 428 |

Respectfully submitted,
KAR Laboratories, Inc.

*William H. Bouma*

William H. Bouma, Ph.D.
Director

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