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The Effects of Molecular Weight and Degree of Substitution of Cationic Starch on the Sizing Efficiency of Alkenyl Succinic Anhydride

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The Effects of
Molecular Weight and Degree of Substitution
of Cationic Starch on the Sizing Efficiency of
Alkenyl Succinic Anhydride

by:
George T. Nebel

A thesis submitted
in partial fulfillment of
the course requirements for
the Bachelor of Science Degree.

Western Michigan University
Kalamazoo, Michigan
December, 1986

Dr. Raymond Janes, Advisor

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ABSTRACT

Alkenyl Succinic Anhydride (ASA) is a cellulose reactive size used in neutral to alkaline papermaking. Since ASA exists as an oil at room temperature, it must be emulsified in cationic starch to make it compatible with the aqueous wet end environment.

The advantages of using a cationic starch in an ASA sizing system include improved retention of fines, filler, and size; improved sizing efficiency; and improved strength. Mill and laboratory experience has shown, however, that cationic potato starch is superior to corn starch. There are two main differences between potato starch and corn starch: (1) potato starch typically has a higher molecular weight and (2) contains more bound phosphate than corn starch.

The effect of molecular weight and cationic charge of quaternary ammonium waxy maize corn starches on the sizing efficiency of ASA emulsions was evaluated. The results show that increased molecular weight does not contribute to the sizing efficiency of ASA emulsions, and may actually reduce the sizing efficiency. The results also show that high charged starches are far superior to low charged starches, regardless of molecular weight.

INTRODUCTION

Alkenyl succinic anhydride (ASA) is a cellulose reactive size which has recently attracted a lot of attention. The efficiency and runnability of an ASA system, however, depends upon the use of a cationic starch. Recent literature has shown that quaternary ammonium-derivatized potato starch is superior to tertiary amino-derivatized common dent corn starch. The differences between the two starches include the type of derivatized group and the molecular weight. This thesis reviews the parameters of the ASA system and evaluates the affects of molecular weight and cationic charge of quaternary ammonium waxy maize corn starch on the sizing efficiency of ASA emulsions.

WATER AND PAPER

WETTING OF PAPER

Internal sizing is an attempt to control the water repellency of a sheet of paper. To accomplish this, however, the papermaker should understand the mechanisms involved.

When water contacts a sheet of paper several interactions are possible. These interactions result from competing liquid-liquid Van der Waal's forces (cohesion) and liquid-solid Van der Waal's forces (adhesion). The parameters controlling these cohesive and adhesive forces are described by equations 1 and 2 below. (1)

$$W_c = 2 \gamma_{lg} \quad (1)$$

$$W_a = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \quad (2)$$

The work of cohesion and adhesion are W_c and W_a , respectively, while γ_{sg} , γ_{sl} , and γ_{lg} are the interfacial excess free surface energies of the solid-gas, solid-liquid, and liquid-gas interfaces, respectively.

The first interaction, wetting, is illustrated in Figures 1a and 1b.

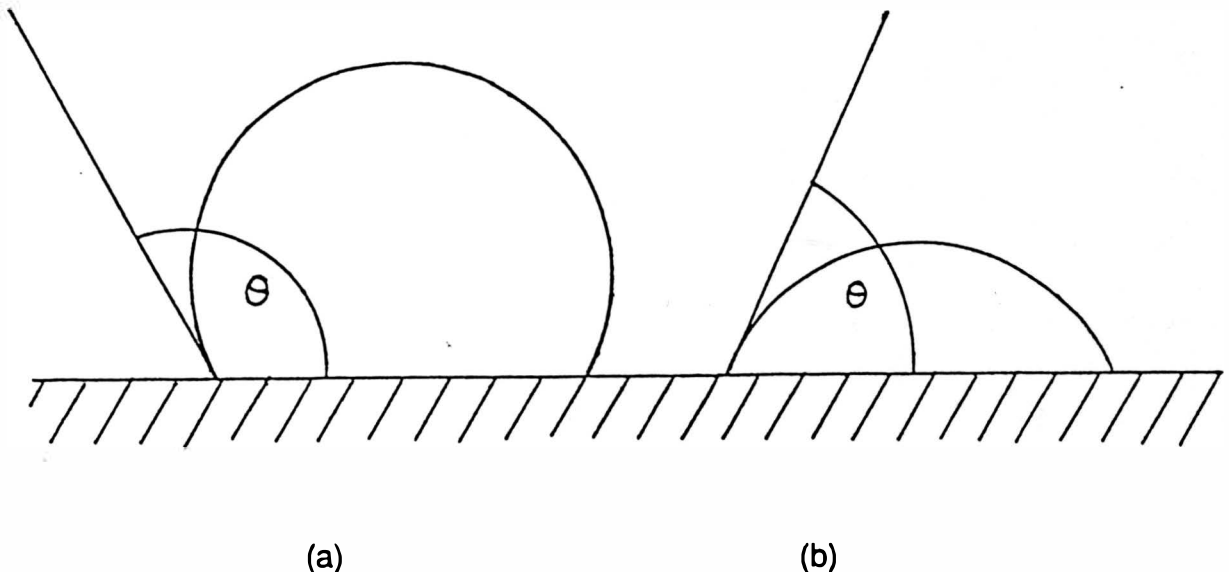


Figure 1. Wetting of a Solid where (a) Cohesional Forces Dominate, (b) Adhesional Forces Dominate.

The factors affecting this interaction are related by the Young equation. (2)

$$\gamma_{lg} \cos \theta = \gamma_{sg} - \gamma_{sl} \quad (3)$$

The contact angle, θ , is a useful measurement for quantifying the wetting process

According to equations 1-3 a liquid will wet a solid if W_a is greater than W_c , or if γ_{sg} is large and γ_{sl} is small. In the case of a pure cellulose surface (unsized) and water, γ_{sg} is very large due to the numerous hydroxyl groups on the fiber surface. Plus, γ_{sl} is very small due to the hydrogen bonding between the water and the cellulose so, θ is small and the water readily wets the fiber surface, as shown in Figure 1b.

FEATHERING

Feathering involves the spreading of the liquid over the fiber surfaces. This interaction, like wetting, also involves a competition between W_a and W_c as equations 4 and 5 explain. (1)

$$S = W_a - W_c \quad (4)$$

$$S = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg}) \quad (5)$$

The spreading coefficient, S , is used to quantify the spreading of a liquid over a solid. According to equations 4 and 5 the same mechanisms that control wetting also control feathering.

CAPILLARY PENETRATION

Up to this point the equations have only applied to ideal, smooth, flat, homogeneous, nondeformable solids, (2) but have proven helpful in understanding the interactions thus far discussed. A sheet of paper, however, is a nonideal, porous, heterogeneous, flexible structure that causes the paper to act like a sponge. (3, 4) This interaction is labeled capillary penetration.

Capillary penetration occurs through three different mechanisms: interfiber penetration (transudation), intrafiber penetration, and vapor

penetration. The parameters affecting interfiber and intrafiber penetration are related by the Washburn equation. (3-6)

$$\frac{dl}{dt} = \frac{\gamma_{lg} r \cos \theta}{4 \mu l} \quad (6)$$

where l is the distance of penetration, γ_{lg} is the surface tension of the liquid, r is the radius of the capillary, θ is the contact angle between the liquid and the capillary wall, and μ is the liquid viscosity. Since γ_{lg} , r , and μ are constant for any given system, the driving force for liquid penetration is θ . If $\theta < 90^\circ$, $\cos \theta$ is positive and penetration will occur, but if $\theta > 90^\circ$, then $\cos \theta$ is negative and the water remains on the surface. This mechanism produces a duck back effect where the liquid is partially supported by the air between the fibers. This increases the apparent contact angle.

Another useful equation is the Laplace equation shown below:

$$\Delta P = \frac{2 \gamma_{lg} \cos \theta}{r} \quad (7)$$

where ΔP is the vapor pressure differential across the meniscus. If ΔP is positive, the vapor pressure of the liquid is greater than the vapor pressure of the air over the meniscus, and vice versa. Here again, θ is the main variable. If $\theta < 90^\circ$, $\cos \theta$ is positive which makes ΔP positive. The lower vapor pressure over the meniscus creates a vacuum which pulls the liquid into the capillary. (1,2)

Vapor penetration is also related to equation 7. The lower vapor pressure over a concave meniscus causes condensation on the solid surface at the reduced pressure. (1) This decreases θ to 0 which maximizes ΔP and the rate of penetration. Crow (3) and Nissan (7) both state that this mechanism probably proceeds the bulk liquid penetration.

Other mechanisms of penetration have also been proposed. They include liquid movement through the fiber pores, surface diffusion, and

diffusion through the fiber wall. (3) The latter mechanism is instrumental in fiber swelling and affects the capillary radii of the fiber lumens. (2)

SIZING

DEFINITION

"Sizing is now defined as the process in which a chemical additive provides paper and paperboard with resistance to wetting and penetration, usually by aqueous liquids. Thus, sizing produces water repellency." (4) "A sizing agent should make fiber surfaces hydrophobic (water repelling) so that the contact angle with aqueous liquids will be very high." (4) According to these statements, sizing is an attempt to reduce γ_{sg} and increase γ_{sl} . This would reduce W_a , θ , S , and the rate of liquid penetration according to equations 2 - 7. Unfortunately, sizing does not prevent or retard water vapor penetration. (4)

REQUIREMENTS

To accomplish the above purposes, a sizing agent must meet certain requirements (5):

- (1) Hydrophobic
- (2) Retained on the fibers
- (3) Distributed on the fibers
- (4) Anchored to the fibers

Most sizing agents are organic surfactants that contain a hydrophobic carbon chain. These carbon chains must be at least 3 to 4 carbons long to impart any hydrophobic characteristics, thus, most sizing agents possess carbon chains of at least ten carbons in length

These organic surfactant sizes also contain hydrophilic polar groups. These two sided molecules tend to accumulate at interfaces. At water-cellulose interfaces these sizes orient themselves so that the polar group is attached to the fiber surface. This arrangement produces the lowest free energy for the system and is the driving force for retaining these molecules.

Distribution on the fibers generally occurs by adequately dispersing the size in the aqueous phase.

Finally, the adsorbed size must be anchored to the fibers. This generally occurs through hydrogen or covalent bonding since the forces of adsorption are not strong enough to prevent reorientation of the size molecules when they contact polar liquids, such as water. This reorientation process is suspected for the decrease in sizing of a sheet in contact with water for extended periods of time. (2,5)

TEST METHODS (4,8)

Sizing tests can be divided into two categories: (1) constant time tests and (2) variable time tests, but they all measure one or more of the following: (1) fluid penetration, (2) absorption, or (3) surface movement.

The Hercules Size Test (HST) is the most commonly used sizing test method. The HST is a variable time test that measures the rate of fluid penetration. A constant volume of test ink is applied to the top of the sheet. A photoelectric cell measures the drop in reflectance of the bottom side of the sheet due to ink penetration as a function of time. An automatic timer stops when the reflectance reaches a preset percentage of the original reflectance (usually 80%).

The standard test ink is composed of a formic acid solution of typically 1%. A green dye which has no affinity for cellulose is used as a colorant.

The test is very reproducible and sensitive since it eliminates much of the operator variability. Reflectance verses time curves are also possible, which measure changes in the penetration rate as the ink travels through the sheet.

ALKENYL SUCCINIC ANHYDRIDE

STRUCTURE AND PROPERTIES

Alkenyl succinic anhydride (ASA) is a rapid curing cellulose reactive size, which is five times more efficient than rosin size. It has been proven effective in neutral to alkaline papermaking, and is believed to form a covalent bond with cellulose. (9-12)

The structure of ASA is shown in Figure 2. ASA is a dicarboxylic acid

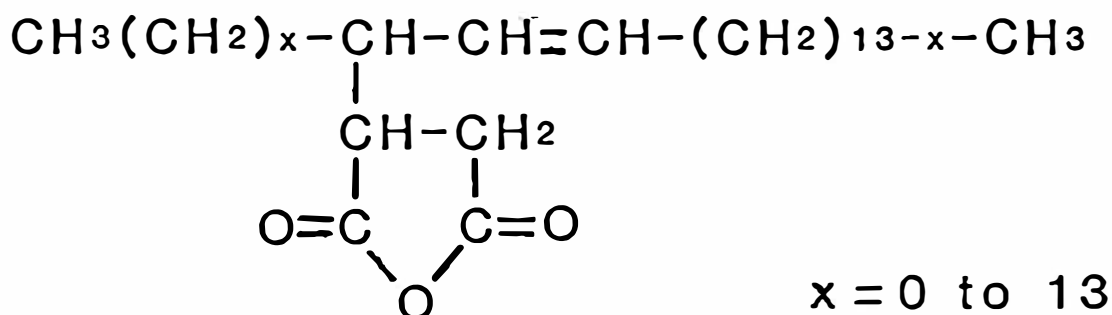


Figure 2: The Chemical Structure of ASA.

anhydride with a long hydrophobic side chain. It is prepared by isomerizing the hydrocarbon chain. The created double bond migrates along the chain until it reacts with maleic anhydride, forming the ASA molecule. (11)

The hydrocarbon chain is typically 16 to 20 carbons long and determines the melting point, solubility, reactivity, crystalline structure, ease of emulsification, and sizing efficiency. The melting point, sizing efficiency, and purchase price of the ASA increases with chain length but, the solubility, reactivity and ease of emulsification decreases. Due to the double bond in the chain, ASA is a liquid at room temperature with a viscosity of about 180 cP. The hydrophobic nature of the chain makes the ASA insoluble in water, requiring emulsification of the ASA to make it compatible with the aqueous papermaking system. (5,7, 9-11)

The anhydride group provides the reactive site through which the ASA can anchor itself to the fiber surface. (5,9-12)

REACTIVITY

ASA is believed to anchor itself to the fiber surface by forming a strong ester bond with the hydroxyls on the fiber surface as shown in Figure 3. Studies have shown that there is no appreciable loss in sizing after three years and prolonged extraction with polar and nonpolar solvents removes only a trace of the ASA. (5,9-11,13)

The reactivity of the ASA with the cellulose is strongly dependent upon temperature. Research and mill experience has shown that sizing does not develop until the dryer section. In the dryers, the retained ASA particles spread over the fibers, orienting themselves in a monomolecular layer. Once oriented, the heat in the dryers bonds the ASA molecules to the cellulose hydroxyls. Under most mill conditions, sizing development (cure) is 80 to 100 percent complete at the reel or the size press. (9-12,14)

The cure rate is also dependent upon pH. Below pH 7.0, unusually high dryer temperatures are required to cure the ASA on the machine. (11,14)

HYDROLYSIS

Unfortunately, the anhydride group is also very reactive with water (hydrolysis) as Figure 4 illustrates. This hydrolysis product (hydrozylate) is a dicarboxylic acid. It cannot form a covalent bond with the cellulose at mill conditions so it does not anchor to the fiber. Subsequently, it is an anti-sizing agent.

Wasser (11,12) found that uncured ASA at the reel reacts more readily with water vapor to form the hydrozylate, than with the cellulose to size the sheet. He found that this lowers the sizing of the sheet, even to the point where the sheet becomes unsized.

The same factors affecting the ASA-cellulose reaction, temperature and pH, also affects the hydrolysis reaction. Wasser found that at 25° C, hydrolysis only occurs at a few percent per hour, with complete hydrolysis

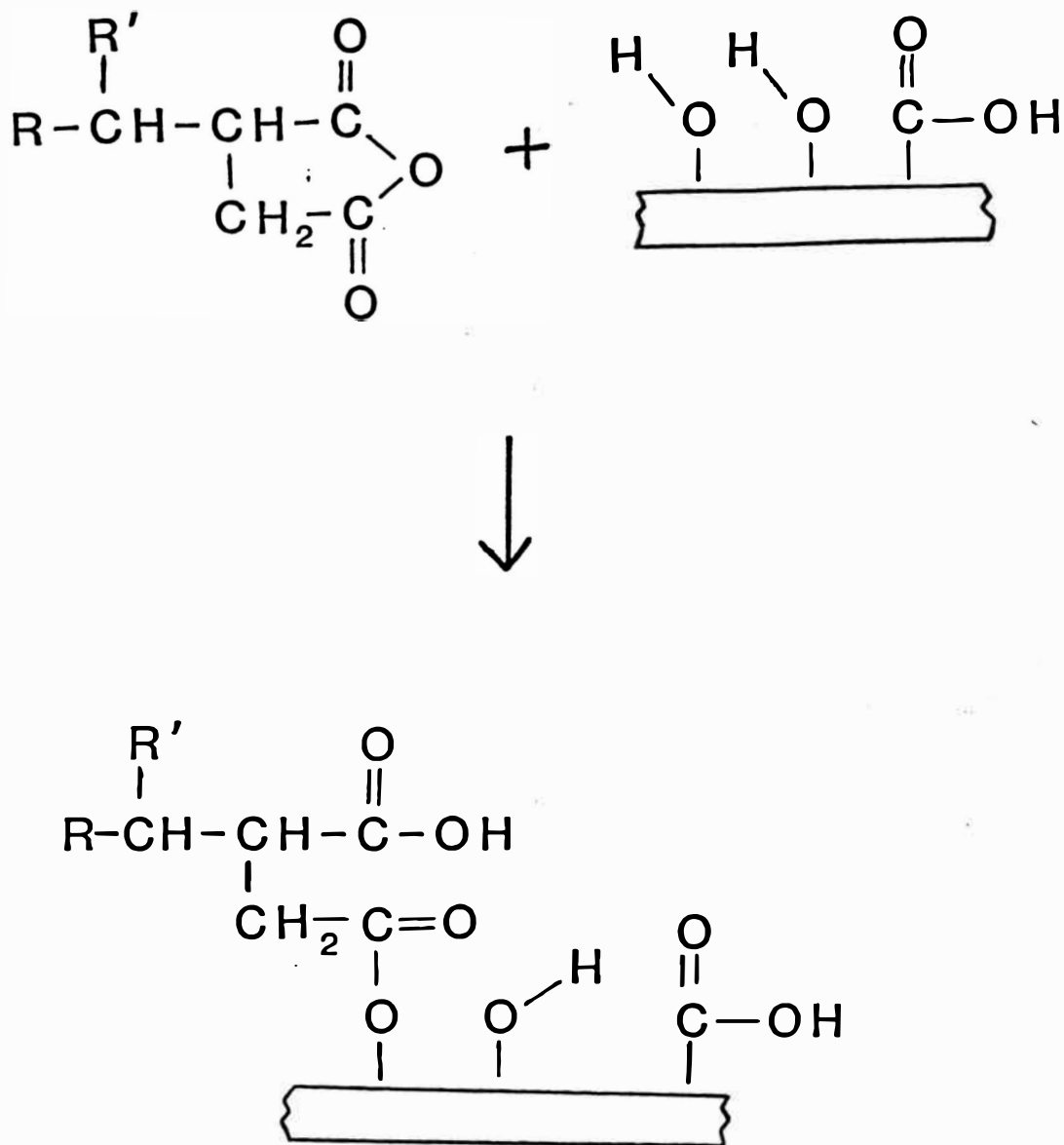


Figure 3: Reaction of ASA with Cellulose

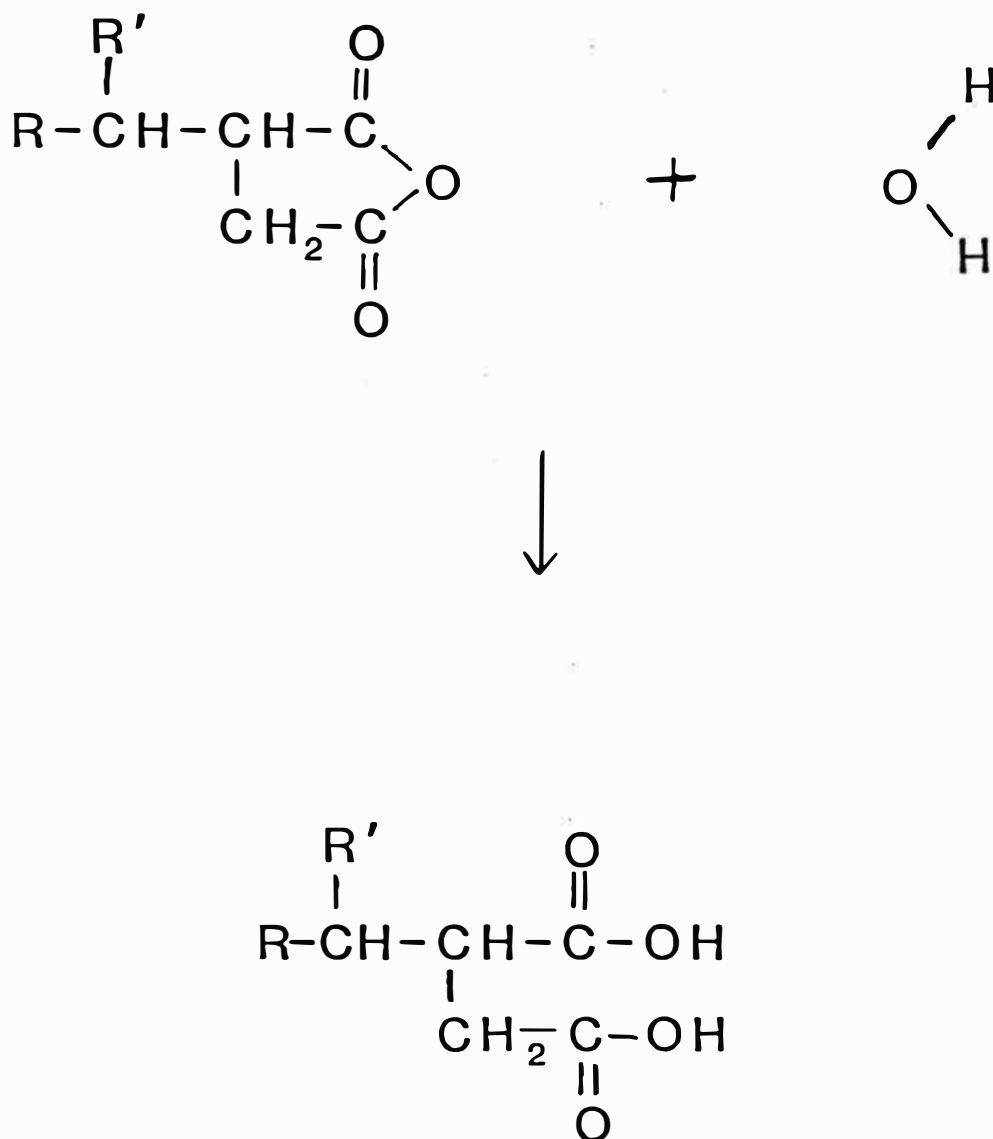


Figure 4: Hydrolysis Reaction of ASA

developing within 24 hours. However, the hydrolysis rate doubles for every 10 degree increase in temperature.

Wasser also found that hydrolysis is minimized below a pH of 4, but doubles for every 1 point rise in pH between 5 and 8.

In a typical ASA system, with the pH between 7 and 8 and the temperature around 50° C, hydrolysis becomes a major concern. At these conditions, detrimental effects due to hydrolysis occur within several minutes. Fortunately, the ASA is subjected to these conditions for only 1 to 2 minutes by the time it reaches the dryers. Wasser (11,12) found that there is a sizing loss of only a few percent during this time.

EMULSIFICATION

Since ASA is hydrophobic and is a liquid at room temperature it must be emulsified to be compatible with a papermaking system. "An emulsion may be defined as a mixture of particles of one liquid with some second liquid" (15)

A typical emulsifying system operates by injecting the ASA and activator into a turbulent flow of starch and water to form the emulsion. Obviously, there is a mechanical and a chemical contribution to the production of this stable emulsion.

A venturi is often used to provide the mechanical contribution by creating the turbulent flow. In the venturi the ASA is mixed vigorously with the water to break the ASA liquid into small particles. In this process the mechanical energy elongates the ASA drops into cylinders which break into smaller particles if the cylinder length exceeds its circumference. (15)

The chemical contribution occurs in the form of a chemical activator (surfactant) and a cationic stabilizer (cationic starch). The chemical activator (CA) is similar in structure to the ASA, containing a hydrophobic carbon chain and a polar group. (1,5,15)

The cationic starch (CS) is a high molecular weight, cationic polyelectrolyte. (16)

EMULSION STABILITY

An emulsion is considered stable if the emulsion particles remain distinct and do not agglomerate or coalesce. A stable emulsion occurs if the following factors are met. (1)

- (1) Low interfacial tension
- (2) Mechanically strong and elastic interfacial film
- (3) Electrical double layer repulsions
- (4) Narrow droplet size distribution
- (5) Relatively small volume of dispersed phase
- (6) High viscosity

Since the CA is a surfactant it accumulates at the ASA-water interface and arranges itself to lower the free energy of the system. This lowers the interfacial tension so less mechanical energy is required to make the emulsion. (1,5,15)

The CS produces a mechanically strong and elastic interfacial film. The positive groups on the CS are attracted to the negatively charged surface of the ASA emulsion. Once electrostatically attached to the emulsion surface, the CS forms a protective layer around the emulsion.

The electrical double layer repulsion is also produced by the CS. The positively charged sites on the CS produces a net positive charge to the particles. This positive charge electrostaticly repels the particles. (5)

The optimum droplet size distribution occurs from 0.5 to 3.0 microns. This size range produces a large interfacial area, which lowers the interfacial tension. Larger particles are not adequately repelled by the electrostatic repulsion and coalesce easily. Plus they are not distributed on the fibers as efficiently, requiring more ASA to size the sheet. Smaller particles require a lot more mechanical energy and are more susceptible to hydrolysis because of the larger surface area. (5,11,12,14,15)

The last two requirements are not met in an ASA emulsion, but the other factors are adequate to maintain the stability.

There are a few other factors that influence the stability of an ASA emulsion. These factors include temperature and pH, which control hydrolysis. The hydrozylate increases the interfacial tension, reduces the electrical double layer repulsion, and is mechanically sticky. These characteristics contribute to the agglomeration and coalescence of the emulsion particles. By keeping the pH between 3.5 and 4.0 and the temperature below 25° C hydrolysis will be kept to a minimum. (11,12)

RETENTION

Optimum first pass retention is required when using an ASA system since the fines will possess the majority of the ASA emulsion particles. Failure to retain these fines in the first pass allows the ASA to hydrolyze in the recycled white water, resulting in the following problems. (16,17)

- (1) Reduced Sizing
- (2) Press Picking
- (3) Deposits
- (4) Felt Filling
- (5) Holes
- (6) Decreased Production

Retention occurs by two mechanisms: coagulation and flocculation. Several mills have found that a combination of these mechanisms provides the best retention in an alkaline system. With this dual system a low molecular weight, high charge density cationic (LMHCDC) polymer is added before a high molecular weight, low charge density anionic (HMLCDA) polymer (polyacrylamides). (16)

The LMHCDC polymer is strongly attracted to the negatively charged surface of the fibers and typically adsorbs in dense patches creating localized positive areas on the fibers. These positive patches attract the negatively charged areas on neighboring fillers and fines which promotes coagulation. More importantly, however, the positive patches attract the negatively charged groups on the HMLCDA polymers. These HMLCDA polymers act as bridges between the positive patches on adjacent fibers which promotes flocculation. (16)

ALUM

BENEFITS

One of the advantages for switching to an alkaline system has been the elimination of the use of alum. The disadvantages of alum (5,18) include:

- (1) Equipment corrosion
- (2) Reduced paper strength
- (3) Machine deposits
- (4) Limited white water closure
- (5) Effluent limits

However, many mills have found that alum contributes several advantages to an alkaline system. These advantages (18-20) include;

- (1) Improved sizing
- (2) Improved drainage
- (3) Improved efficiency of anionic polyacrylamide retention aids
- (4) Improved pitch control
- (5) Reduced deposits, press picking, and press roll crumbing

ALUM CHEMISTRY

Alum chemistry has been well documented by Arnson (21,22), Strazdins (19,20), Crow (3), and others (23,24), so a detailed discussion is not necessary. However, a brief discussion will prove helpful in understanding the affects alum has on the alkaline system.

Figure 5 illustrates the distribution of the various aluminum species as a function of pH.

According to Figure 5 there are five species of aluminum possible in a water system. This diversified chemical activity is due to the high valent charge (3^+) and the small ionic radius (5.0 nm) of the aluminum ion. To reduce its charge density, the Al^{3+} acts as a Lewis acid to accept electron pairs. It often complexes with up to six ligands to form an octahedral structure. The complexing groups include H_2O , OH^- , $SO_4^{=}$, $H_2PO_4^-$, and ionized carboxyls. (21,22)

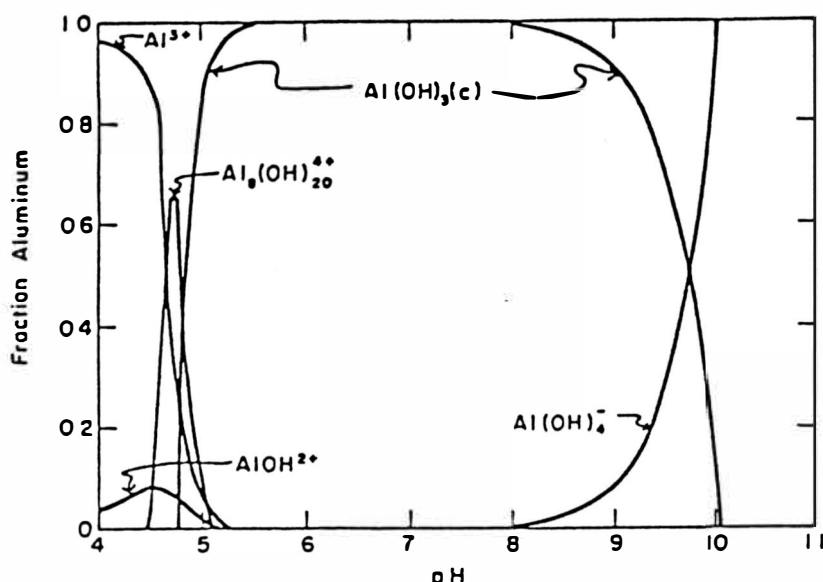


Figure 5: Distribution of 5.0×10^{-4} M hydrolyzed Aluminum (III) as a function of pH

Above pH 7, however, only the $\text{Al}(\text{OH})_3$ precipitate and the negatively charged $\text{Al}(\text{OH})_4^-$ ion are present. Since most alkaline papermaking systems operate between pH 7 and 8, only the precipitate is of interest to the alkaline papermaker.

Crow (3) states that above pH 6 essentially 100% alum adsorption occurs. He attributes this increased adsorption to the formation of the colloidal $\text{Al}(\text{OH})_3$ precipitate. Although the $\text{Al}(\text{OH})_3$ precipitate is a neutral species, Arnson and Stratton (21,22,24) claim it exists as a positively charged species up to pH 8.5-9.0 due to the adsorption of hydrolysis products onto the precipitate. Arnson has found that the small increase in the ionization of the cellulose does not account for the increase in adsorption of the precipitate.

To further complicate matters, the position of the curves in Figure 5 are affected by alum concentration and the type of alum used. The curves shift towards lower pH as the concentration of alum increases. (21,22) Plus, the curves for $\text{Al}_2(\text{SO}_4)_3$ are positioned at a lower pH than those for

AlCl_3 at the same concentrations. This shift is due to the incorporation of the $\text{SO}_4^{=}$ ion in the precipitate, which is proposed by Arnson and Stratton (21,22,24) to be $\text{Al}_8(\text{SO}_4)_5(\text{OH})_{14}$.

AFFECTS ON ASA SIZING AND RUNNABILITY

Meyer (25,26) found that without alum, acceptable sizing levels could not be developed with ASA. His results show that at low alum levels, adding alum to the size emulsion was most effective, while at higher levels, it was more advantageous to add the alum to the virgin stock. On the other hand, some mills are currently applying ASA successfully without any alum at all. (27,30) Obviously, the conditions from mill to mill vary considerably, and no generalizing statements can be made.

Scalfarotto (31) showed that alum competes with magnesium and calcium for the hydrolyzed ASA to form a nonsticky precipitate, unlike the calcium and magnesium salts. Thus, alum reduces headbox and suction box deposits, and press picking. It may also improve sizing by removing the hydrozylate which acts as an anti-size.

CATIONIC STARCH

BENEFITS

Cationic starch (CS) or amphoteric starch (AS) is often added to the stock as well as being used in the emulsification of ASA. The advantages attributed to CS include:

- (1) Improved retention
- (2) Improved sizing efficiency
- (3) Improved formation
- (4) Improved bonding
- (5) Improved strength
- (6) Improved drainage
- (7) Improved porosity
- (8) Reduced steam consumption
- (9) Faster machine speeds
- (10) Lower BOD loads

These benefits result from the CS acting as an emulsion stabilizer and as a retention aid for the emulsion, fiber fines and filler. In the emulsion the CS is commonly added at a 2:1 to 3:1 ratio of starch to ASA, while stock additions of ten pounds per ton of fiber is common. (11,12,32-36)

STRUCTURE AND PROPERTIES

"Starch is a polysaccharide in which the basic repeating unit is an anhydro-glucose unit (AGU)." (32) It comes from a variety of sources including corn, potato, tapioca, and rice. In its unmodified state, starch is nonionic and therefore ineffective for the alkaline system.

To be effective then, the starch must be modified. This modification occurs by chemically adding charged groups to the AGU's. This is called derivatization, and determines whether the starch will be cationic, anionic, or amphoteric.

DERIVATIZATION

"Derivatization is measured in terms of the number of moles of reagent substituted or bonded per AGU which is expressed as degree of

substitution (DS)." (32) The maximum DS possible is three since each AGU contains 3 hydroxyl groups.

The reagent used in the derivatization determines the type of modified starch. Aminoethylation in an alkaline environment produces CS, like those in Figure 6. Phosphorilation, carboxylation, and sulphonation reactions produce anionic starches, with phosphorilation being most common. Amphoteric starch is produced from a combination of the above reactions. (17,32,36,37)

MECHANISMS

Addition of these charged groups changes the properties of the starch. These changes include:

- (1) Improved hydrophilic nature of the starch
- (2) Lower gelatinization temperature
- (3) Increased solubility
- (4) Increased solution viscosity

These effects are attributed to the charged groups repelling each other which increases the chain extension in solution. (33)

These cationic charges also have a big effect on the adsorption of the starch onto the fiber surface. Marton (36) and Maher (33) have done considerable work in this area. Marton states that adsorption of CS onto the cellulose occurs by two processes: (1) physical adsorption due to electrostatic attraction, and (2) chemophysical adsorption due to hydrogen bonding. This combination produces irreversible and 100% complete adsorption. The factors affecting CS adsorption are the available surface area, fiber structure, fiber composition, and fiber surface charge. He states that the fiber surface area and the fiber structure depends upon the amount of fines and filler present, since they have 6 to 7 times the hydrodynamic surface area of the fibers and adsorb about 5 times more of the CS. He postulates that the fines, which amount to less than 1/3 of the furnish,

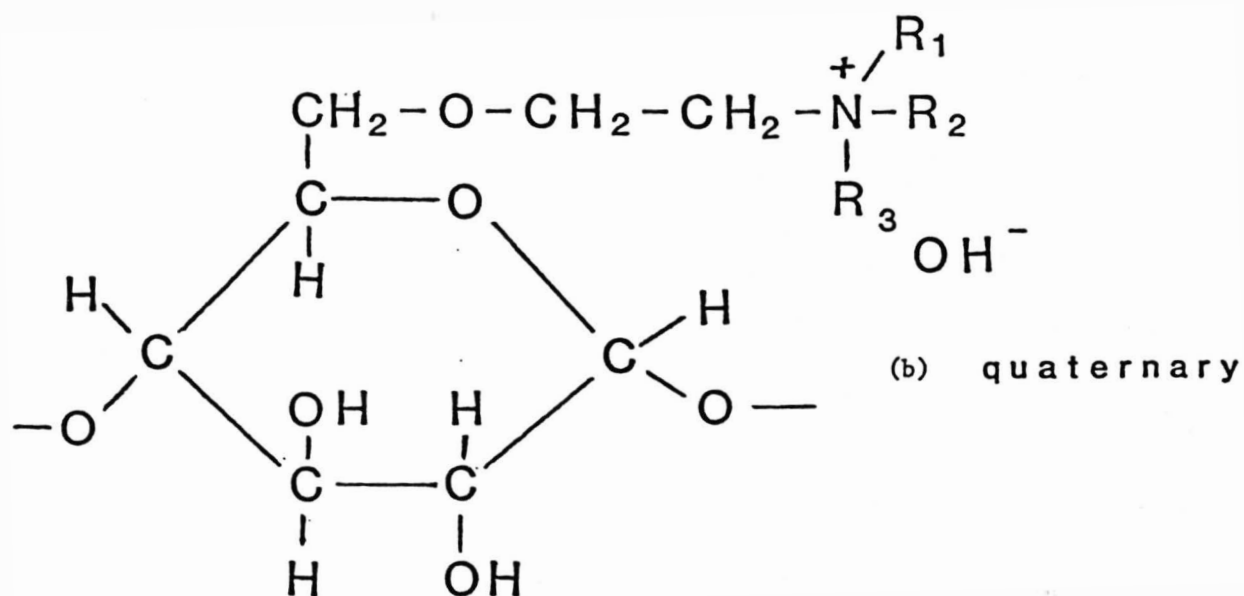
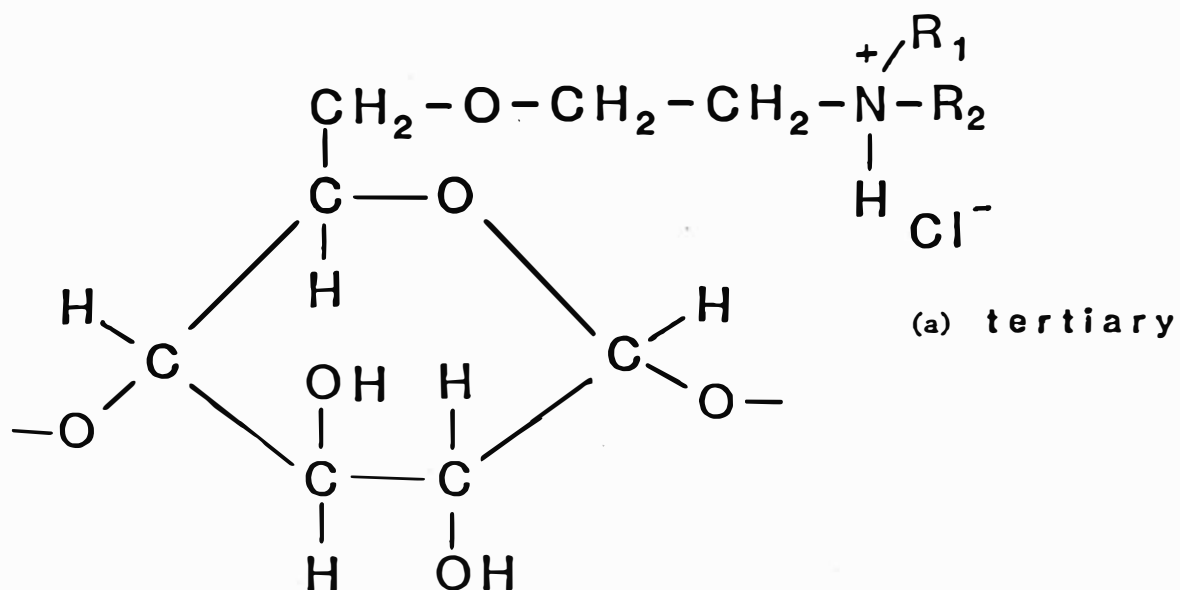


Figure 6: Cationic Starches where, (a) Tertiary Derivatized and (b) Quaternary Derivatized

adsorb 2/3 of the CS.

The fiber composition is affected by the concentration of the carboxyl groups on the fiber surface. Lignin concentration also plays a big role by contributing anionic sulphonate groups to the fiber surface.

The fiber surface charge is dependent upon the degree of ionization of the carboxylates and the amount of adsorbed ions on the fiber surface, particularly alum. Besides reducing the electronegativity of the furnish, alum also occupies hydrogen bonding sites, thereby reducing the physical and chemophysical adsorption processes. Halabisky (38) has found that alum levels greater than 60 pounds per ton will give the furnish a net positive charge. Linscott and Biervliet (17) and Harvey (35) state that AS is not as sensitive to alum adsorption as CS because of the presence of the negative groups. Fortunately, at alkaline conditions the alum exists as the uncharged precipitate, which drastically reduces its effect on the adsorption of CS or AS. Crow and Stratton (23) found that there was a big rise in the alum and CS adsorption curve at the pH where the alum precipitate forms (pHp). The pHp occurs between pH 4 and 5 depending upon the alum concentration. They attributed this adsorption rise to the formation of the neutral precipitate. They also found that $\text{Al}_2(\text{SO}_4)_3$ does not change the charge on the fibers as much as AlCl_3 since Al^{3+} does not complex with Cl^- and retains more of its positive charge. The $\text{SO}_4^{=}$ ion is more efficient at neutralizing the cationic charge on the aluminum cation than the hydroxyl groups. They have also found that with $\text{Al}_2(\text{SO}_4)_3$ above the pHp, adsorption of cationic polyelectrolytes (CS) occurs onto the precipitate, insinuating that the precipitate does not reduce the number of bonding sites for the CS. This is of questionable validity.

The CS affinity for cellulose causes it to act like a retention aid in the wet end, while its hydrogen bonding contribution increases the sheet

strength. (36) Marton (36) has found that the new hydrogen bonding sites produced by the CS are actually stronger than the original fiber-fiber bonds.

Even though amphoteric starches contain both positive and negative charges, they are predominantly positive. This combination of charges, however, gives the amphoteric starch some interesting characteristics. Of primary significance is the reduced pH and zeta potential sensitivity, which increases the useful range of these starches. Of particular importance is the ability of the negatively charged groups to tie up soluble cations like Ca^{2+} and Mg^{2+} . Both of these ions are detrimental to the alkaline system since they form sticky buildups on the machine. (32,37)

The effects of CS on the ASA emulsion have previously been discussed under the emulsion stability section.

STARCH COMPARISONS

Several factors affect the performance of cationic and amphoteric starches. The factors primarily depend upon the type of derivatized groups and the type of base starch.

Derivatized amino groups are generally tertiary or quaternary (Figure 6), depending upon the number of carbon groups attached to the nitrogen. Tertiary groups, which have only three carbon groups, have been found to be less effective than quaternary groups, which possess four carbon groups. This inferiority occurs since the hydrogen on the tertiary group can be removed by a hydroxyl in alkaline conditions. This renders the group neutral, and like an unmodified starch, very ineffective. The quaternary groups on the other hand are not sensitive to pH because the carbon groups can not be removed by hydroxyls. (32,35)

The differences between corn and potato base starches are numerous.

To begin with there is a big difference in the starch granules. Potato granules are larger and bulkier which allows a more uniform and complete

derivatization process. The dense corn granules create steric hinderances to the derivatization chemicals, reducing the chemical mobility within the granule.

The composition of the granules also differs. Maher (33) states that potato starch contains 21% amylose where corn starch contains 29%. More importantly however, he states that the degree of polymerization (DP) of the amylose fraction of the potato starch is 3000 where it is only 800 for the corn starch. He claims the binding power of a starch is due to the DP of the amylose fraction, suggesting that the derivatization occurs there. This would explain the superiority of the potato starch over the corn starch.

Winters and Best (34) compared an ammonium-derivatized potato starch (A) with an amino-derivatized common dent corn starch (B). They compared the starches at different starch pH levels and at different addition levels to the stock in the wet end. Their pH results show that starch A improved the sizing efficiency at all pH levels but was most effective at pH 5. However, starch B was effective only at pH 5. Above pH 5 the emulsion particles were large and irregular. This proves the starch did not adequately stabilize the ASA emulsion at the higher pH.

In the wet end, starch A was beneficial at all pH and loading levels. Starch B, on the other hand, was effective only at pH 5 and at 5 pounds per ton. They found that starch B lost its positive charge at the higher pH and thus lost its effectiveness.

LITERATURE SUMMARY

The purpose of internal sizing is to control the water repellency of a sheet of paper. To do this, the surface energy of the solid must be reduced. This is most easily accomplished by attaching a hydrophobic material to the fiber surface, otherwise known as sizing.

One of the most efficient sizing agents known is alkenyl succinic anhydride (ASA). It is composed of a 16-20 carbon chain and an anhydride group. The anhydride group readily reacts with the hydroxyls of cellulose or water. The reaction with water produces an hydrozylate which cannot bond to the fibers and reduces sizing. The hydrozylate is also responsible for runnability problems like machine deposits, press roll crumbing, and press picking.

Because of the unacceptable properties of the hydrozylate, the ASA must be emulsified at the mill. This emulsification process involves mixing the ASA and an activator with a cationic starch (CS) solution. The activator lowers the free energy of the ASA-water interface, promoting emulsification, while the CS adsorbs onto the ASA particle surface forming a strong interfacial film and creating an electrical double layer around the particles. These affects contribute to a stable emulsion with particle sizes ranging from 0.5 to 3.0 microns. Once made, however, the emulsion must be used within 30 minutes and stored below 25° C and between pH 3.5 to 4.0 to minimize hydrolysis.

One of the big advantages for switching to an ASA system has been the elimination of alum. However, many mills are finding that they cannot develop adequate sizing levels without the use of alum. At alkaline conditions the alum exists as a neutral precipitate but is essentially 100% adsorbed onto the fibers. It is claimed that the precipitate holds a positive charge up to pH 8.5-9.0 due to adsorption of hydrolyzed aluminum. This small positive charge promotes adsorption without reversing the charge on

the cellulose.

Alum has also been found to compete with Ca and Mg to form hydrozylate soaps. The sticky Ca and Mg soaps have been linked to the formation of machine deposits, press roll crumbing, and press picking. The aluminum soap, on the other hand, forms a nonsticky precipitate that tends to flush out of the system rather than form deposits.

On the machine, the biggest factor affecting sizing efficiency is retention of the fines and filler. The positively charged emulsion particles are essentially 100% retained on the fibers, but since the fines and filler possess about 6 to 7 times the surface area of the cellulose, the fines may adsorb 2/3 of the size. If the fines are not retained, the ASA that they hold will hydrolyze during recycling of the white water, which reduces sizing efficiency and causes runnability problems. Therefore, a good retention system is a must.

Many mills have found that a dual retention system works best. A low molecular weight, high charge density, cationic polymer is added to create localized positive areas on the fibers, fines, and filler. A high molecular weight, low charge density, anionic polymer is also added to bridge between the positive areas on neighboring fibers, holding them together.

Many mills also add cationic starch to the stock to improve retention, sizing efficiency, and strength. The positively charged starch readily adsorbs to the negatively charge fiber surfaces. The long starch molecules act like retention aids by bridging between fibers and by reducing the fibers negative surface charge. Besides retaining fines and filler, the starch also retains the size particles. It has also recently been discovered that the hydrogen bonds formed between the fibers and the starch are actually stronger than the fiber-fiber bonds, thereby, strengthening the sheet.

Recent literature has shown that potato starch is superior to corn starch. A study by Winters and Best (34), in particular, compared quaternary ammonium-derivatized potato starch with tertiary amino-derivatized common dent corn starch at different pH levels and wet end addition levels. They showed that the potato starch improved the sizing efficiency at all pH levels where the corn starch was effective only at pH 5. The wet end data showed that the potato starch was effective at all loading levels and pH levels where the corn starch was effective only at 5 pounds per ton and at pH 5.

They attribute the superiority of the potato starch to its higher molecular weight and the ability of the quaternary group to retain its charge in alkaline conditions. The tertiary group lost its charge to hydroxides at alkaline conditions.

STATEMENT OF PROBLEM

The preceding literature analysis demonstrates the complexity of the ASA sizing system. The use of cationic starch is but a small part of the system, yet complexity exists even there.

Laboratory studies and mill trials have shown that potato starch is superior to corn starch. The various reasons for explaining the differences include differences in molecular weight, degree of substitution, type of derivatized group, and amylose content. Winters and Best (34) attempted a study to examine these differences. In their study they chose a quaternary ammonium-derivatized potato starch and an tertiary amino- derivatized common dent corn starch. They compared the two starches at different pH levels and at different loading levels in the wet end. Their results showed that potato starch was superior to corn starch. But, was the superiority due to the potato starch or the type of derivatized group, or was some other factor, like degree of substitution, responsible? The inability to answer these questions proves the need for more work in the area.

This thesis proposes to study individually the affect of molecular weight and degree of substitution on the efficiency of the ASA size to better understand the importance of these factors. If time permits, a comparison between potato starch and corn starch will also be undertaken.

EXPERIMENTAL

EXPERIMENTAL APPROACH

A water soluble quaternary ammonium potato starch, supplied by American Cyanamid, was used to establish a reproducible emulsion and handsheet procedure. Once statistically reproducible results were obtained, the effect of molecular weight and degree of substitution was studied. A set of 15 quaternary-ammonium derivatized waxy maize corn starches varying in molecular and cationic charge were available. Four of the 15 starches were chosen for testing. These four starches possessed the extremes in molecular weight and cationic charge and were labeled 1-4. Their properties are listed below in Table 1.

Table 1
Characteristics of Tested Corn Starches

Starch Number	:	1	2	3	4
% Ammonium Persulfate	:	0.100	0.100	0.000	0.000
Molecular Weight Range	:	Low	Low	High	High
Degree of Substitution	:	0.0136	0.0852	0.0140	0.0833

The water soluble potato starch was used as a control and labeled C.

The effect of these starches on the sizing efficiency of the ASA emulsion was measured using the Hercules Size Test.

Experimental Procedure

Furnish

The stock consisted of 75% bleached kraft hardwood and 25% bleached kraft softwood. The stock was refined to 310 CSF in deionized water with the Valley Beater. The beaten stock was treated with 150 ppm biocide (Betz RX-41) and dewatered to 27% consistency with a centrifuge. The dewatered stock was stored in a refrigerator at 8°C to further preserve the furnish during the course of the semester.

Starch Preparation

The cold water soluble potato starch, Accosize 72, supplied by American Cyanamid, was in the flake form. It was prepared at 5.0% solids in cold deionized water by mixing with a variable speed mixer for 25 minutes.

The corn starches were prepared at 5.0% solids in distilled water. Steam was used to heat the starch and water mixture between 180 and 190°F for 20-30 minutes. Once dissolved the starches were cooled below room temperature and the water lost to evaporation was replaced, maintaining a 5.0% solution.

ASA Emulsification

The ASA used in this thesis was Accosize 17, supplied by American Cyanamid. The ASA was emulsified in a 5.0% cationic starch solution using a waring blender equipped with an 8 ounce glass jar. The following emulsification procedure and recommendations were obtained from Richard B. Wasser of the American Cyanamid Company. The amounts, however, were scaled down to accomodate the small size of the glass jar. Wasser claims that the particle size of the emulsion produced by this procedure is in the optimum range of 1-3 microns.

The emulsion procedure is as follows:

1. Add 54.31 grams of 5.0% starch to the waring blender and mix for 10 seconds at high speed.
2. Weigh 0.69 grams of ASA by difference in a syringe.
3. Add the 0.69 grams of ASA to the blender and mix at high speed for 2.5 minutes to produce 55 grams of 1.25% ASA emulsion.
4. To prevent hydrolysis of the ASA, adjust the pH of the emulsion between 3 and 4 and cool below 50°F.

Wasser states the emulsion should be stable for about eight hours.

This emulsion was then diluted to 0.25% ASA by diluting 50 grams of the 1.25% ASA emulsion with deionized water to a total of 250 grams. Diluting the emulsion increased the accuracy of the addition rate.

This emulsion was prepared at a starch to ASA ratio of 4:1 instead of the typical 2:1 ratio found in industry. The higher starch content was used to improve emulsion retention since no internal starch or retention aid was used in the handsheet procedure.

Emulsion Addition

The addition level of ASA was 3.6 lbs./ton (0.18%) based on a 2.50 gram o.d. Noble and Wood handsheet.

$$2.50 \times 0.0018 = 0.0045 \text{ grams ASA per sheet}$$

$$0.0045 \text{ grams ASA} / 0.25\% \text{ ASA emulsion} = 1.8 \text{ grams } 0.25\% \text{ ASA per sheet}$$

Handsheet Procedure

Figure 7 shows a schematic diagram of the handsheet procedure.

The stock was redispersed in deionized water at about 1.0% consistency under high agitation for at least 30 minutes. This ensured the elimination of any undispersed flocks. The 1% consistency stock was then diluted with deionized water to 0.25% consistency in the Noble and Wood proportionator.

One liter samples of stock were pH adjusted between 7 and 7.8 with NaOH and then placed under agitation. The variable speed mixer was set at 500 rpm to maintain a constant rate of agitation.

Note: The pH of the stock in the proportionator was not adjusted. It was found that the pH dropped about one pH unit every 10 minutes. This created steadily decreasing sizing results due to incomplete cure.

The Noble and Wood sheet mold was filled to the first dot with deionized water.

Note: To ensure a constant source of dilution water, a 55 gallon drum was filled with deionized water. This water was then pH adjusted to between 7 and 8 with NaOH.

3.6 lbs./ton of ASA was added to the stock under agitation and mixed for one minute. The stock was immediately added to the sheet mold, mixed three times, drained, pressed, and dried.

Note: The variable speed dryer can was set at 3.0 which corresponds to a 3 minute pass through the dryer can at 248°F. These drying conditions oven dried the sheets.

Once dried, the handsheets were placed between two sheets of blotter paper in an oven at 105°C for 30 minutes to ensure complete cure of the ASA.

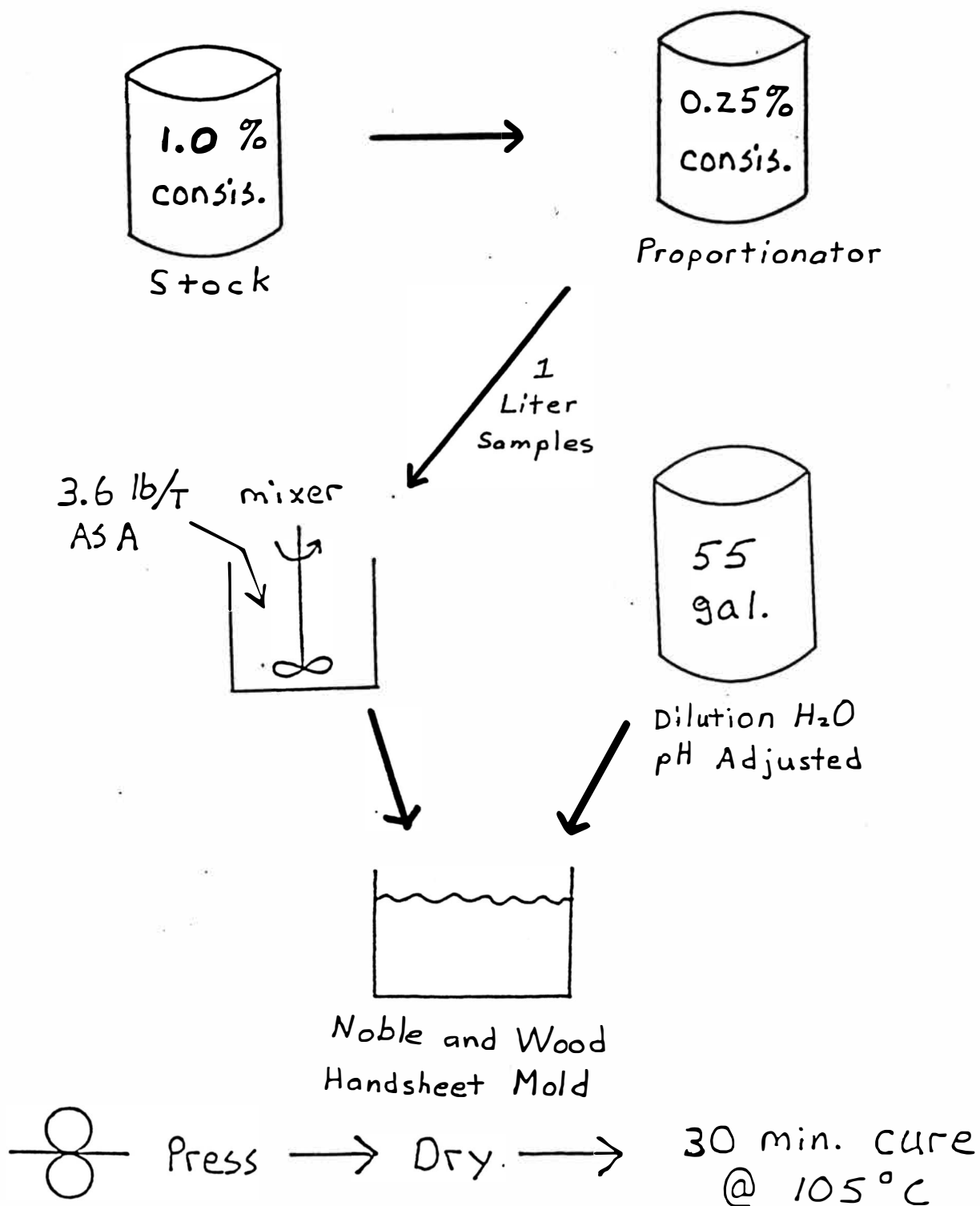
Handsheet Testing Procedure

The handsheets were conditioned for 24 hours at 50% relative humidity and 72°F in the paper testing laboratory prior to testing. Each sheet was then cut into quarters. Each quarter was tested for sizing development using the Hercules Size Test at 80% reflectance loss according to TAPPI Method T 530 pm-75. (39) Hercules test ink #2 with 1% acidity was used.

Starch Comparison Procedure

Starches 1-4 and starch C were simultaneously prepared as 5% solutions. Five emulsions were prepared from each starch within a 50 minute period and labeled according to the starch from which they were prepared. Three sets of handsheets were made with these emulsions. The first two sets were composed of two handsheets from each emulsion. The third set was similar to the first two except three handsheets were made using emulsion 3. The order of addition between the five emulsions was randomized for each set to eliminate systematic errors. (see Table 3, Appendix III)

FIGURE 7
HANDSHEET PROCEDURE



RESULTS

The results are presented graphically, showing the sizing level (seconds) plotted against some variable (typically handsheet order). The average sizing value is represented by a dot through which a line has been drawn representing the standard deviation of the average value.

The t-test (see Appendix I) was used to statistically evaluate any differences between handsheets, sets of handsheets, and starches. A two-way analysis of variance (ANOVA) was also used to evaluate the effect of molecular weight and cationic charge on the sizing efficiency of the starches.

Experimental Reproducibility

Figures 8-12 represent the sizing results of five different sets of handsheets and illustrate the reproducibility between handsheets obtained with the handsheet procedure described earlier. Except for the first sheet in Figure 8, the sizing level from sheet to sheet within a set is statistically not different, with standard deviations averaging between 20 and 35. The first sheet in Figure 8, however, is significantly lower than all but the fifth sheet in Figure 8.

Figure 13 illustrates the reproducibility between sets of handsheets. The points on Figure 13 represent the average sizing results of the five handsheet sets illustrated in Figures 8-12. The t-test reveals statistically significant differences between the sets with the highest sizing levels and those with the lowest sizing levels. The average and standard deviations for the sets ranged from 256 to 305 and 25 to 31, respectively, while the overall average and standard deviation was 281 and 35.

Starch Comparison

Figures 14-18 illustrate the sizing results from starches C-4. The t-test shows no significant differences between sheets for Figures 14, 16, and 18, representing starches C, 2, and 4, respectively.

For starch 1, the t-test shows a significant difference between the last sheet and the rest of the sheets. For starch 3, the t-test shows a significant difference between the fifth sheet and the rest of the sheets, plus a statistically significant difference between sheets 1 and 6.

Figure19 compares the average sizing level for each starch. The t-test and the two-way ANOVA both show no significant difference between starches 1 and 3 and starches 2 and 4. However, both tests show large differences between the two groups. The t-test also shows significant differences between the potato starch and the corn starches.

Figure 8: Sizing Reproducibility Within a Set of Handsheets.

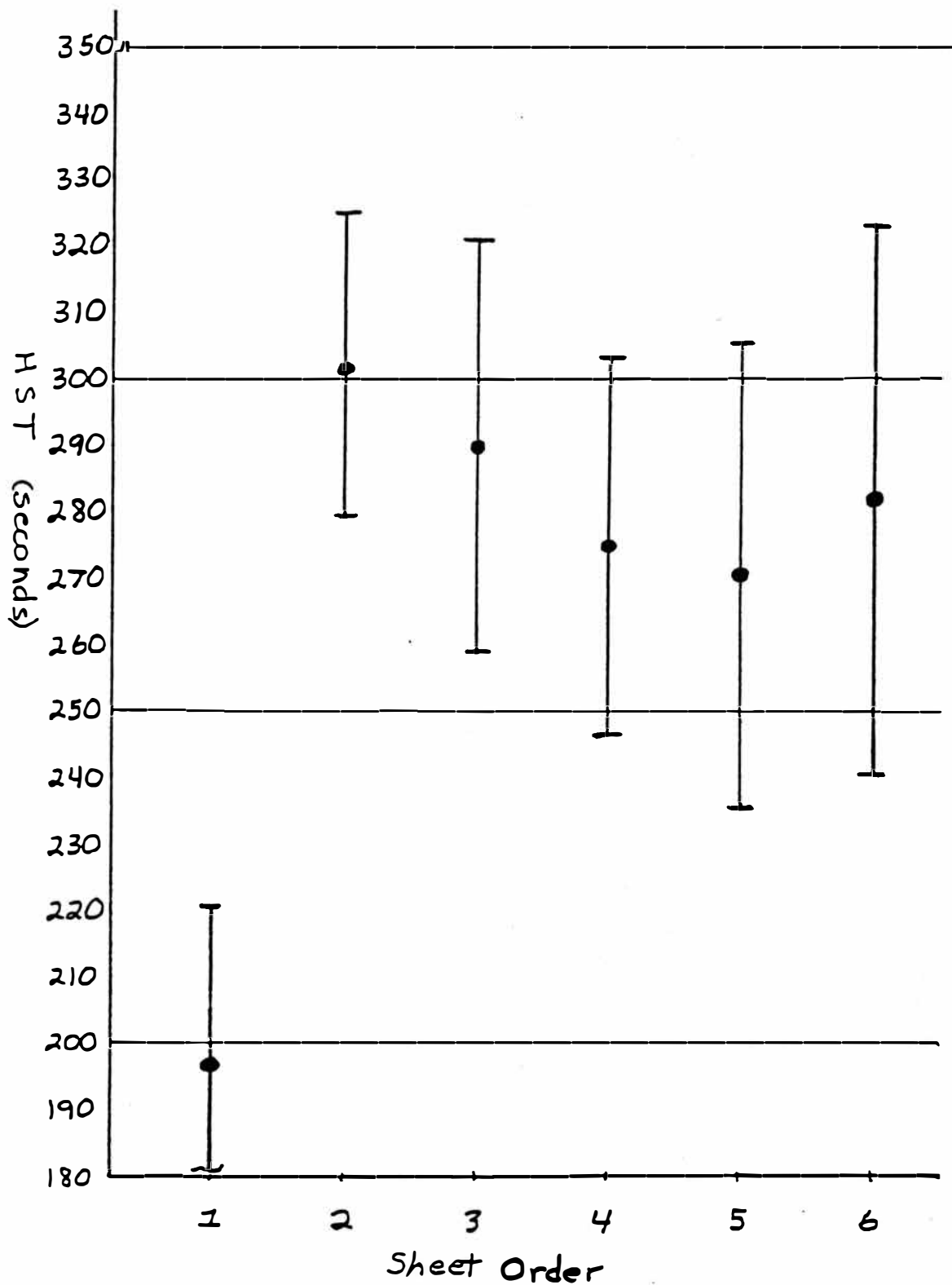


Figure 9: Sizing Reproducibility
Within a set of Handsheets.

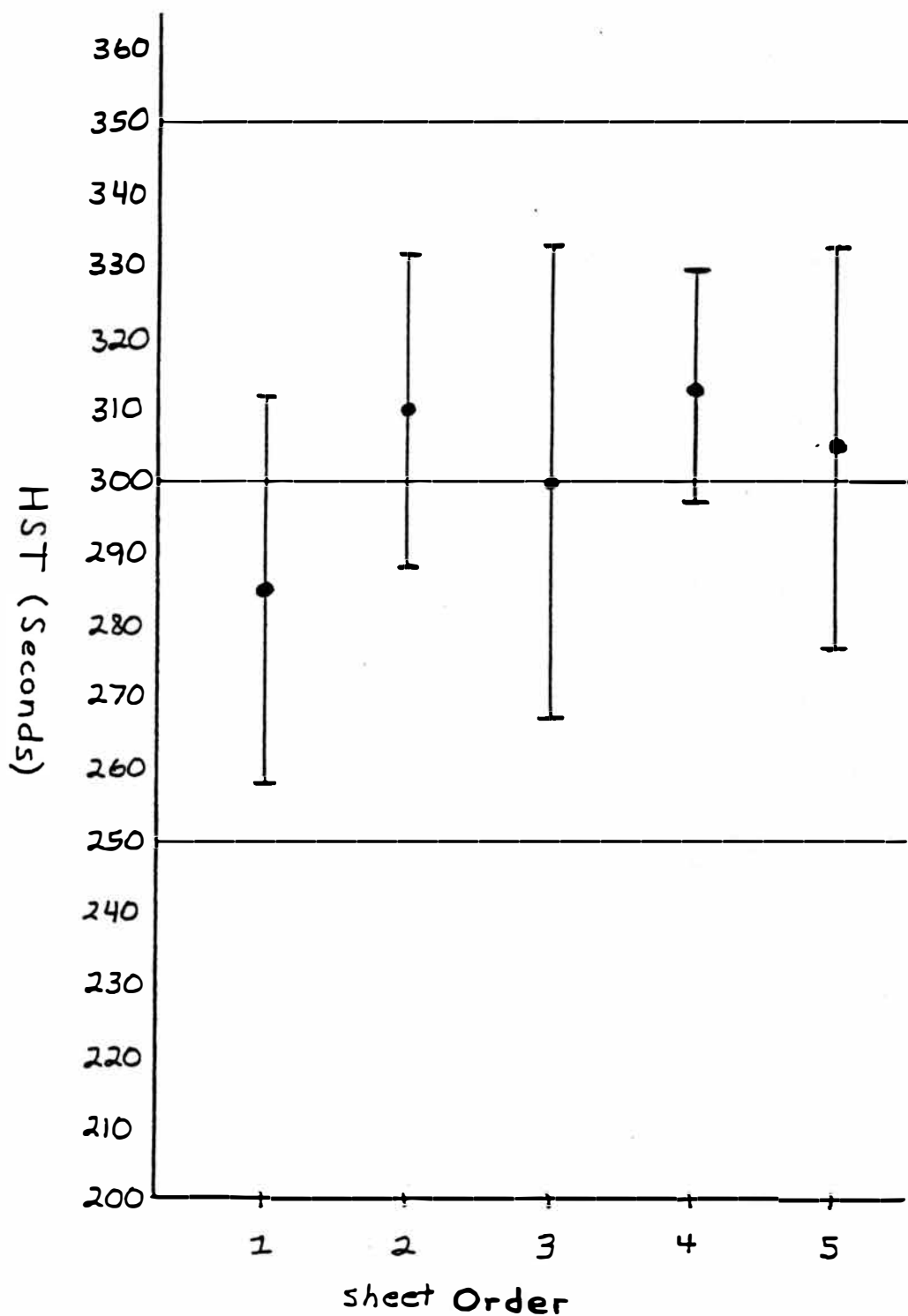


Figure 10: Sizing Reproducibility Within a Set of Handsheets.

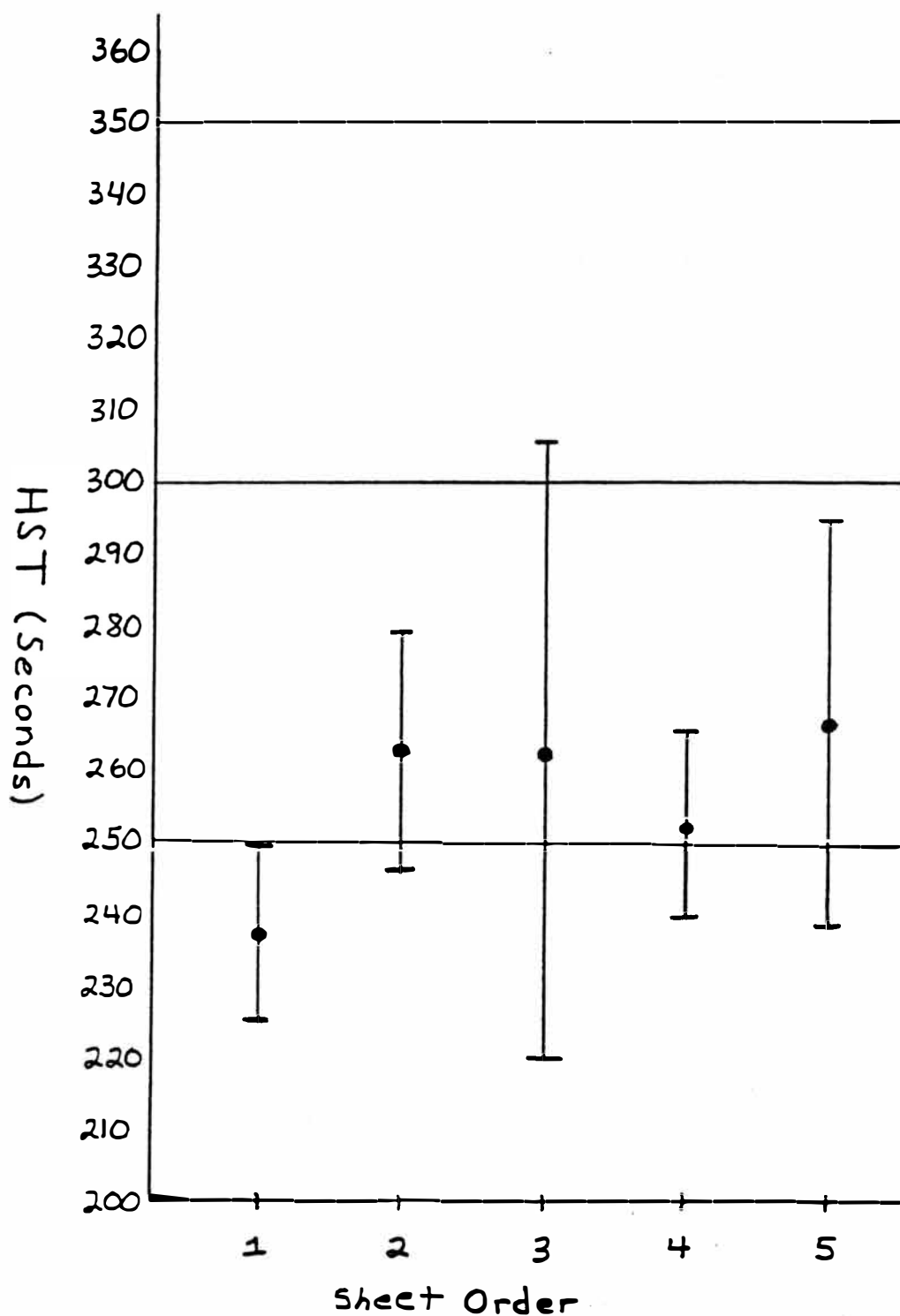


Figure 11: Sizing Reproducibility Within a Set of Handsheets.

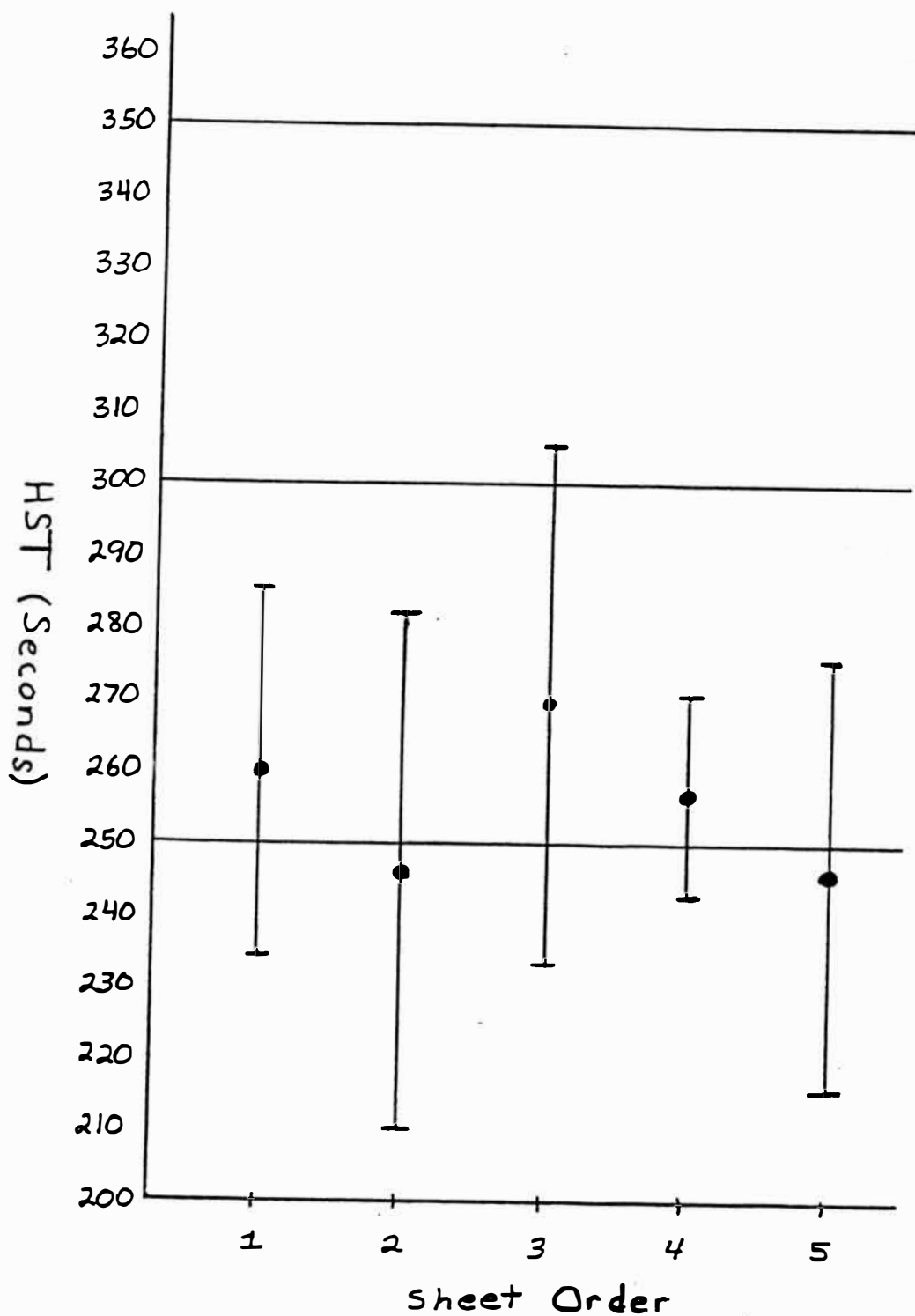


Figure 12: Sizing Reproducibility Within a Set of Hand sheets.

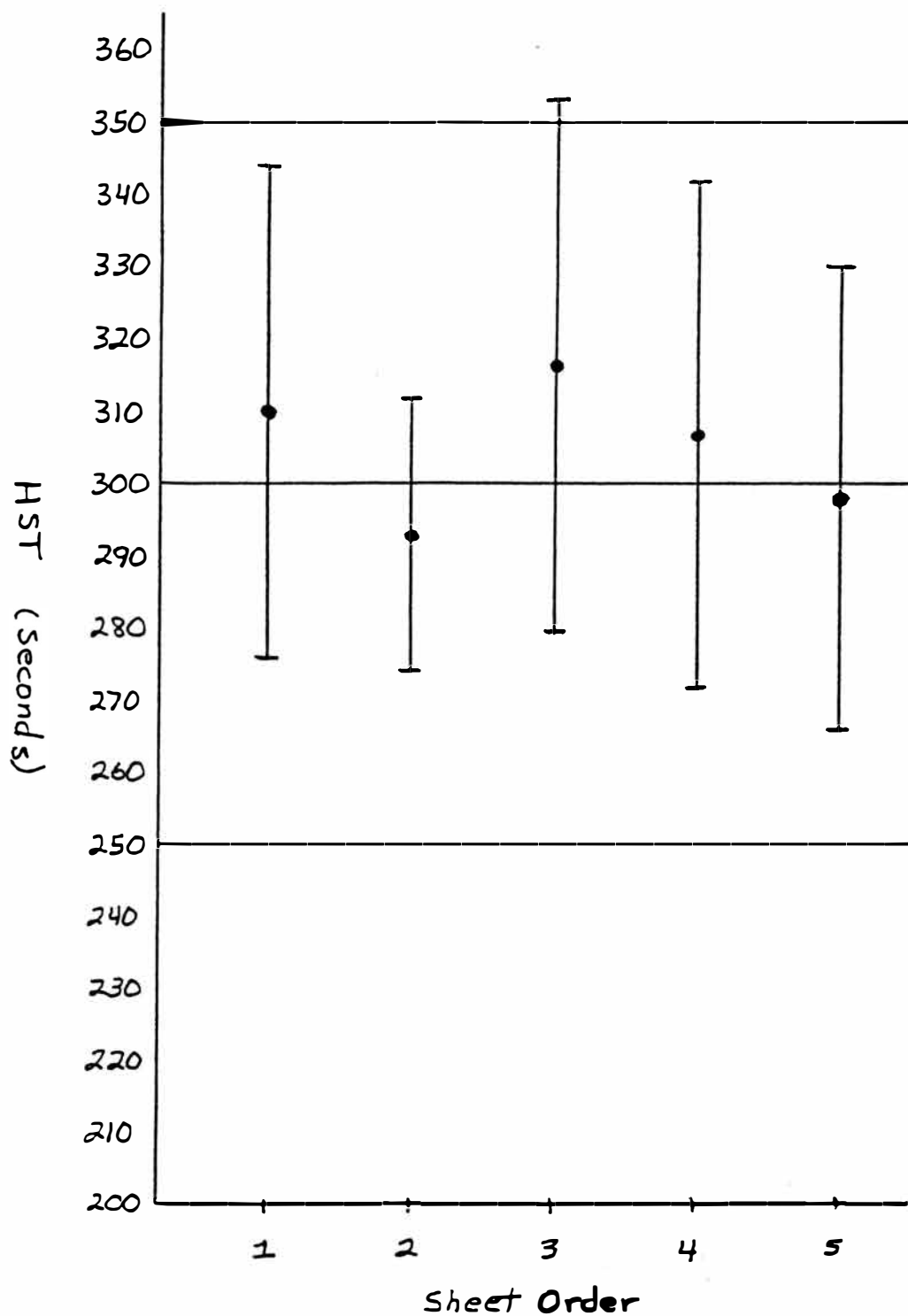


Figure 13: Sizing Reproducibility Between Sets of Handsheets.

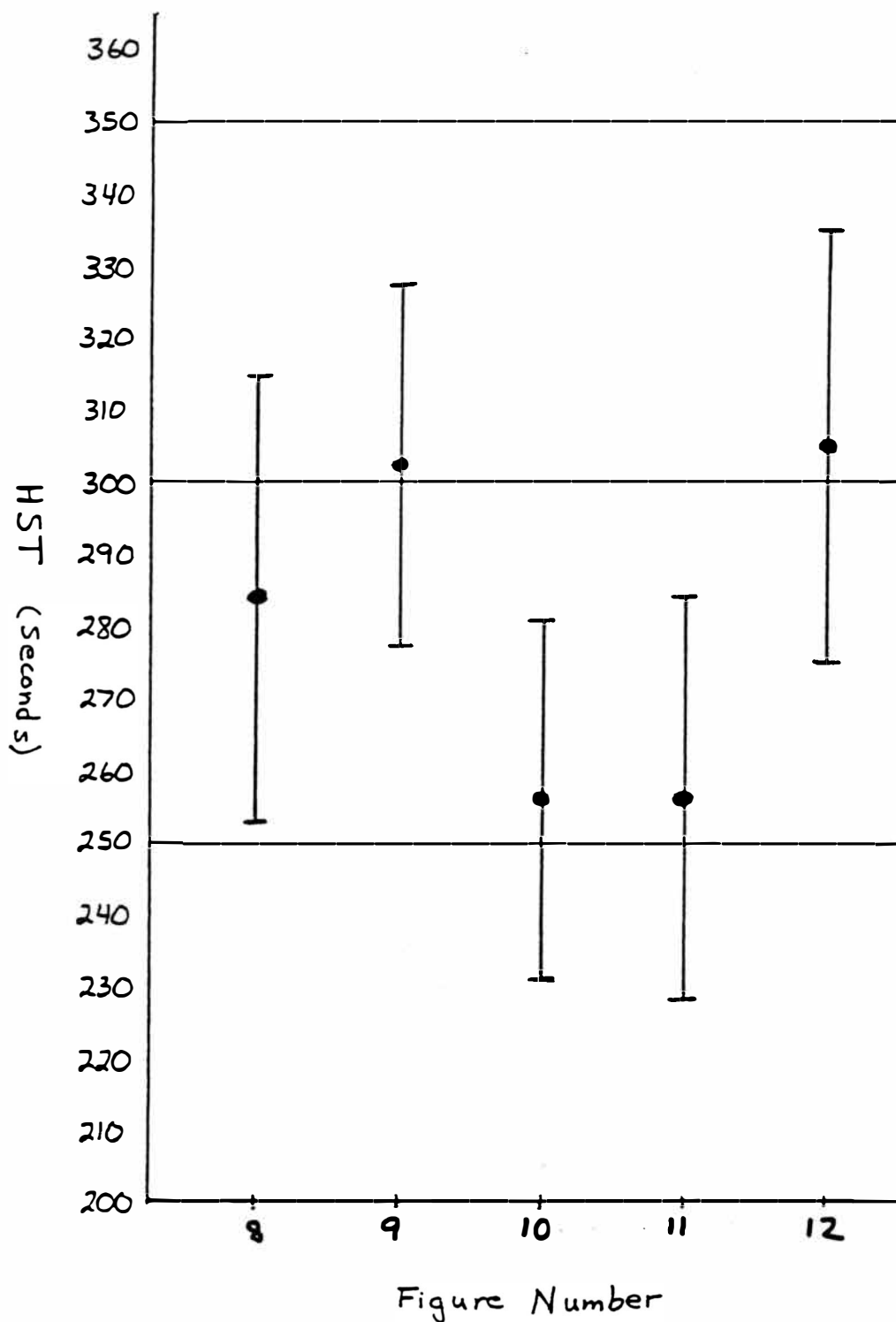


Figure 14: Control Starch Reproducibility

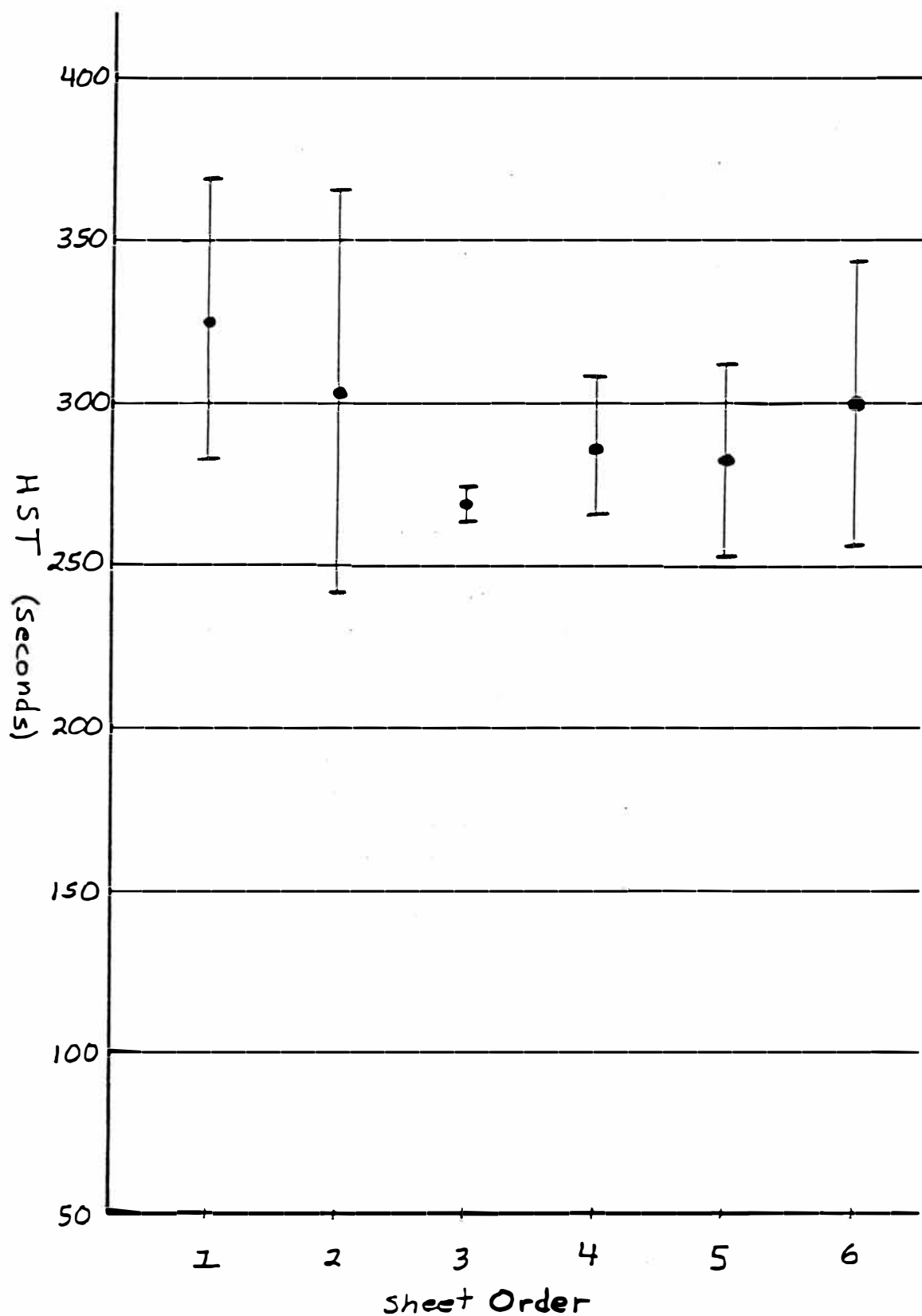


Figure 15: Starch 1 Reproducibility

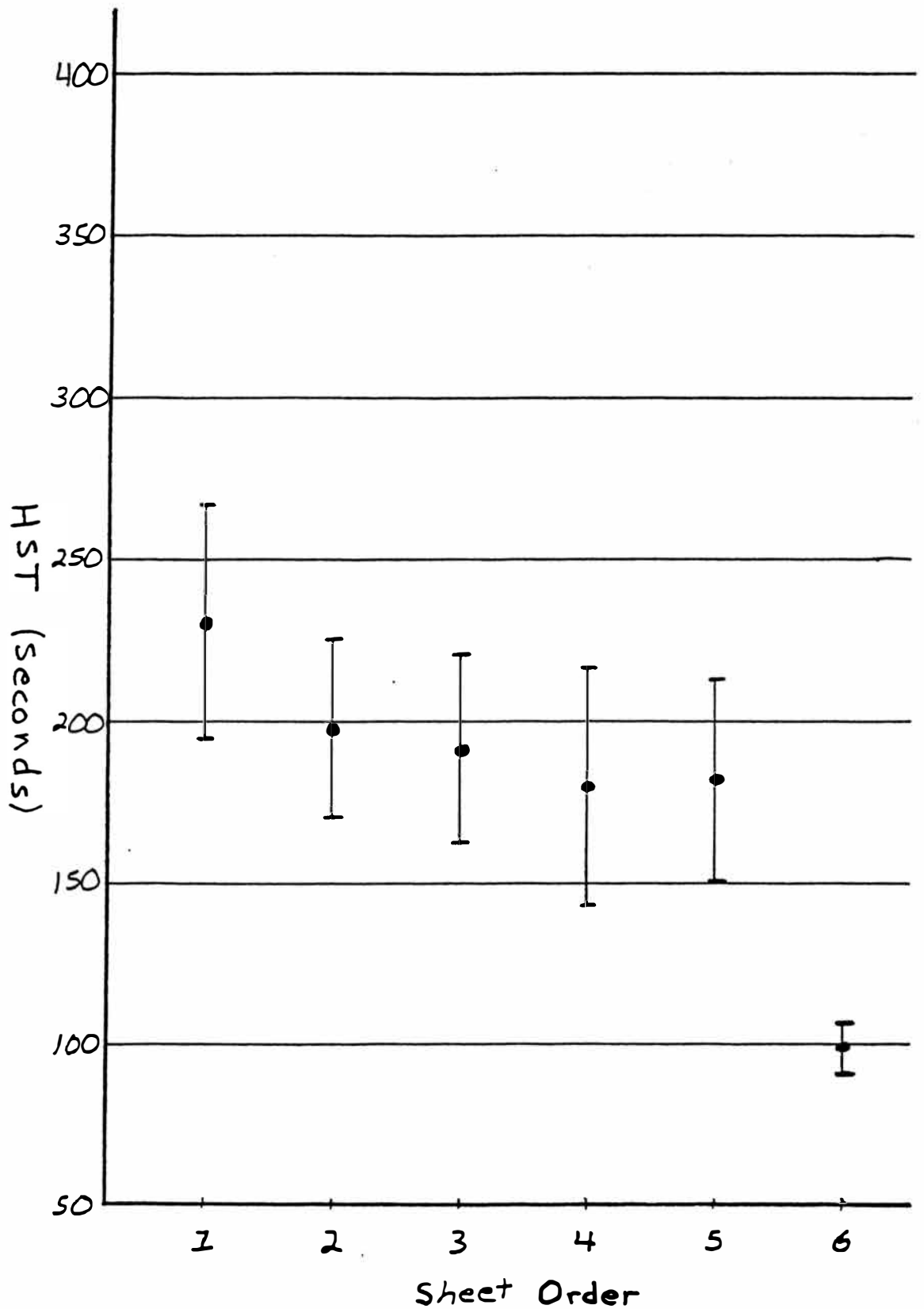


Figure 16: Starch 2 Reproducibility

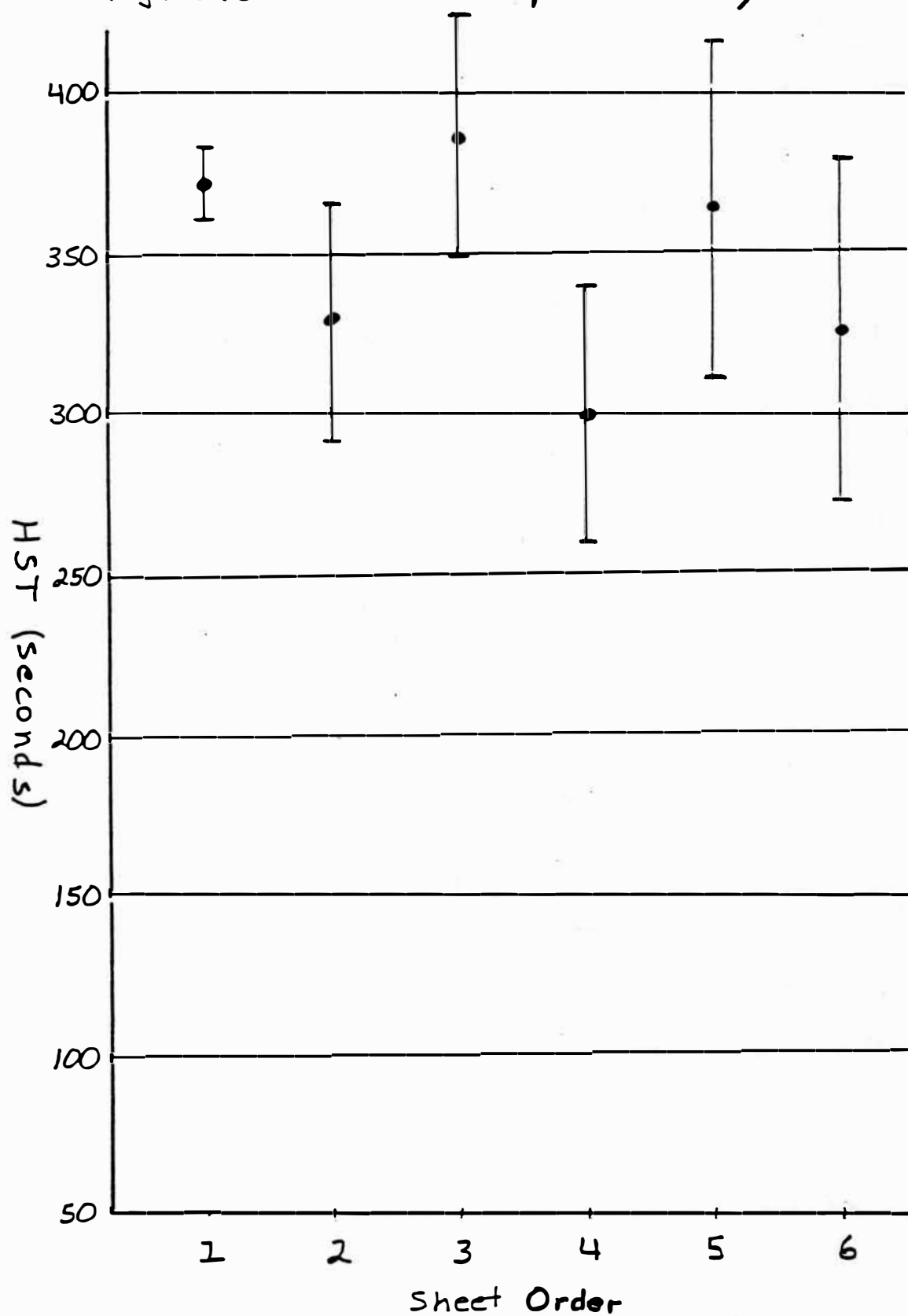


Figure 17: Starch 3 Reproducibility

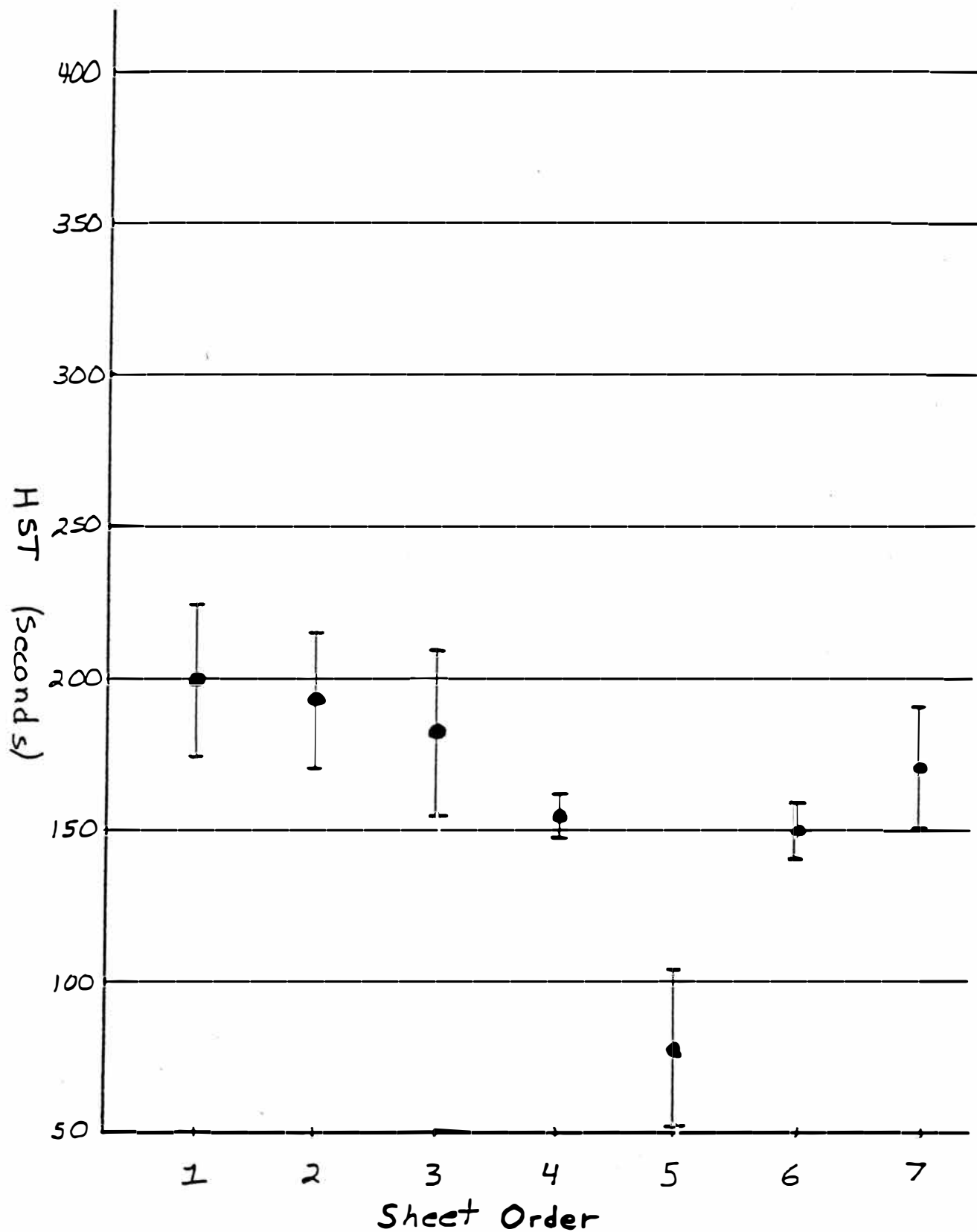


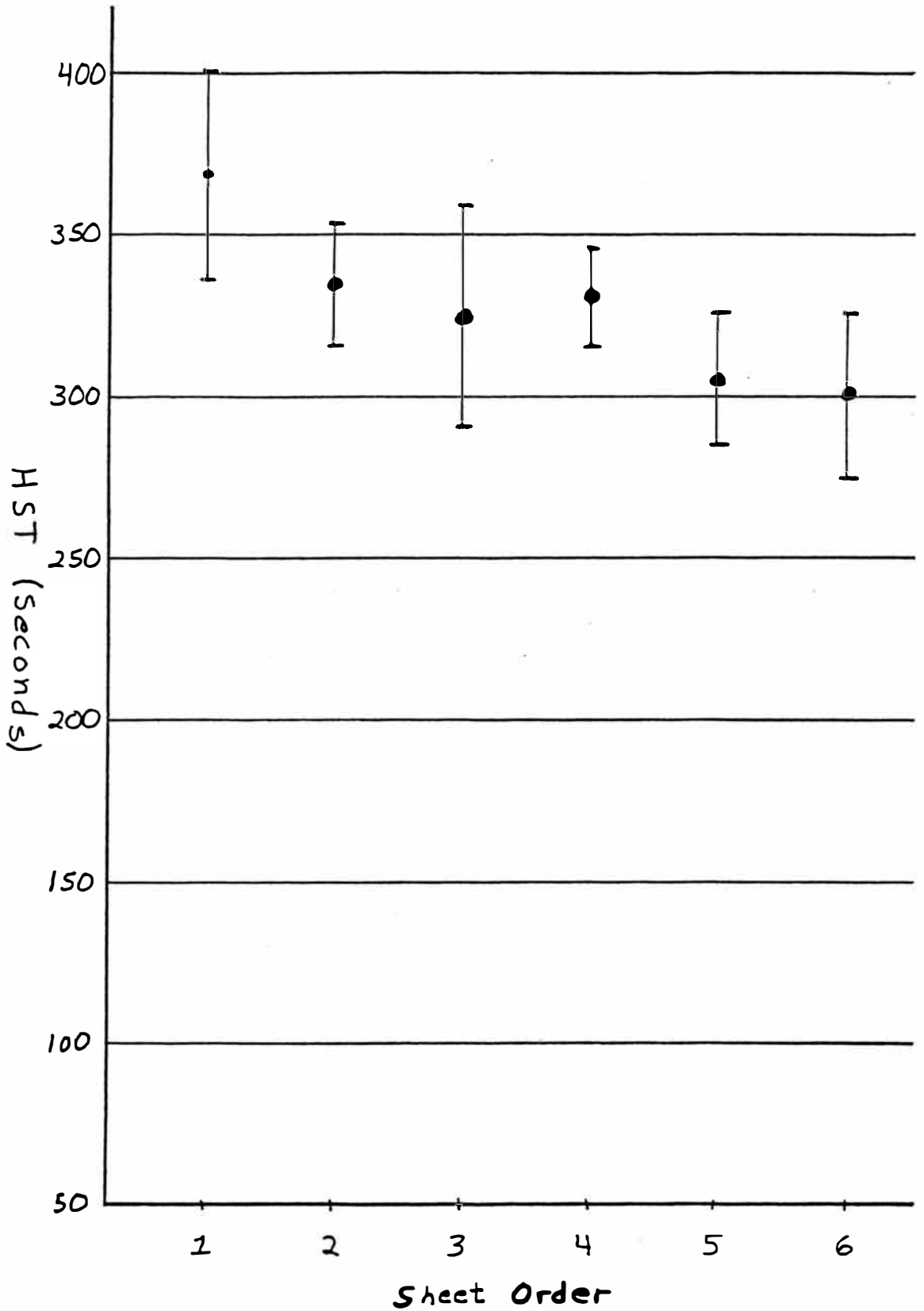
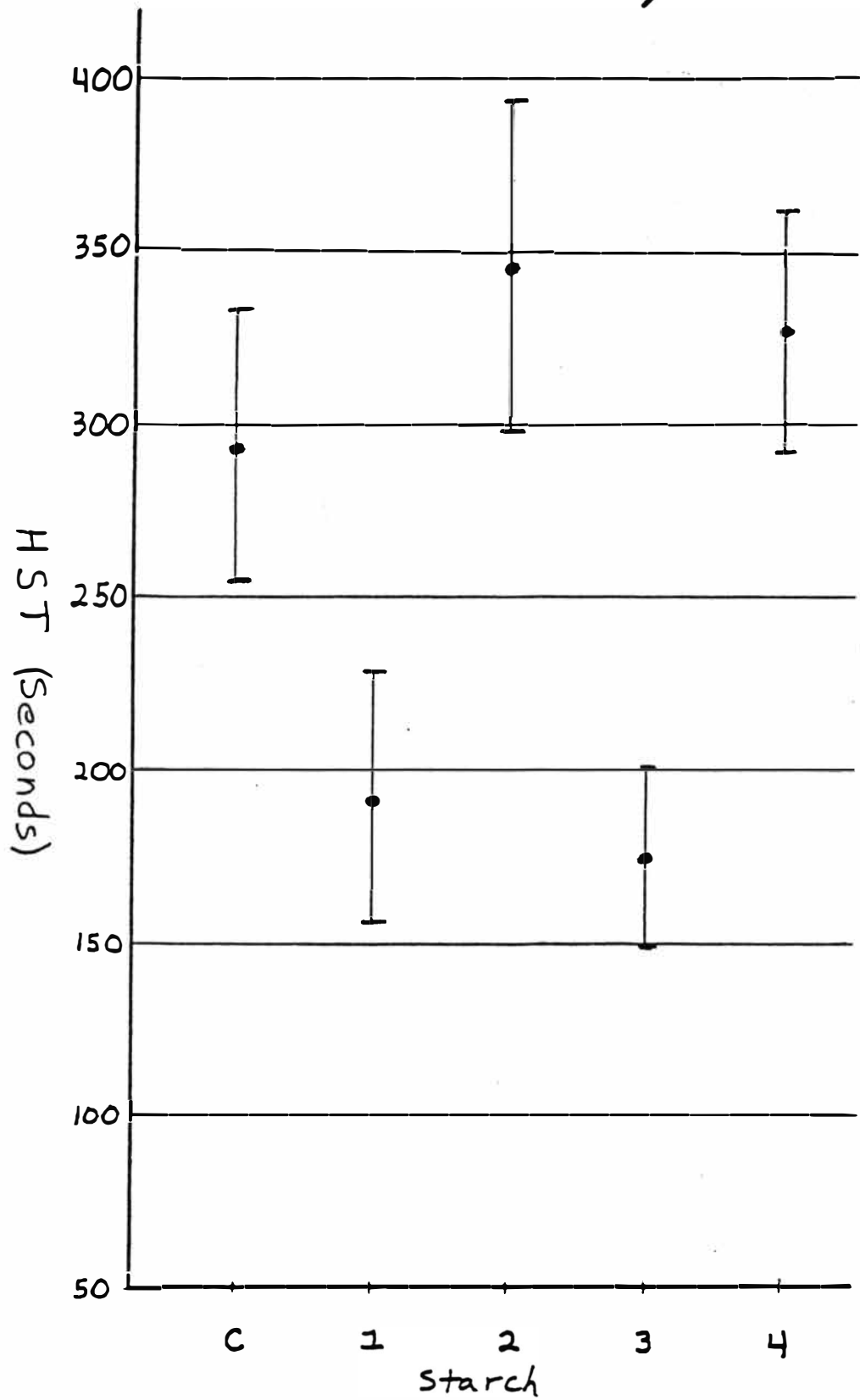
Figure 18: *starch 4 Reproducibility*

Figure 19: Starch Efficiency Comparison



DISCUSSION OF RESULTS

Experimental Reproducibility

Historically, major problems with ASA sizing reproducibility have occurred in the lab. These problems arise from the high sizing efficiency of ASA, which is drastically affected by the particle size, pH, and temperature of the emulsion and the retention, formation, and drying of the handsheets. The starch and emulsion preparation procedure and the handsheet making procedure employed in this thesis demonstrate the attention given to detail.

This attention to detail has resulted in very reproducible results within a set of handsheets as Figures 8-12 illustrate. The significantly lower sizing of the first sheet in Figure 8 resulted from adjusting the pH of the stock to 8.4, well above the desired 7-7.8 pH range. Increased hydrolysis at this pH is suspected for reducing the sizing by about 100 seconds. The data from this handsheet was not included in Figure 13.

Even though reproducibility within a set of handsheets was very good, reproducibility between sets was not, as Figure 13 shows. The t-test reveals significant differences between the two highest and the two lowest sets. However, Figures 9 and 10 and Figures 11 and 12 represent consecutive sets of handsheets made from the same emulsion.

Concerning Figures 9 and 10, the first set of handsheets were made between 3:20 and 4:00 pm and the second set between 4:20 and 5:00 pm, using the same emulsion. The average sizing level decreased from 302.5 to 256 seconds. This decrease cannot be attributed to hydrolysis for two reasons. First, there was only a 20 minute time gap between the handsheet sets, while there was a 40 minute gap between the first and last handsheets in each set, and Figures 9 and 10 show no consecutive loss in sizing from sheet to sheet within the sets. Secondly, Figures 11 and 12 represent a similar situation, but the average sizing level increased from 256 to 305 seconds, the exact opposite of Figures 9 and 10.

In each case, the only thing that changed between sets was a new batch of stock in the proportionator and new dilution water. Since the stock supply was the same and each liter sample was individually pH adjusted, identifiable stock changes can be eliminated. In a similar manner, the dilution water was taken from the same deionized water source and pH adjusted to 7.4, 8.0, 7.2, and 7.3 for Figures 9-12, respectively.

The amount of ASA addition, agitation rate, agitation time, and drying conditions were all identical. Plus, the sheets were conditioned in the paper testing lab for the same period of time and each group of sets were tested on the same day.

TAPPI Method T 530 pm-75 and T 1206 os-69 (39,40) state the repeatability for the Hercules Size Test between sets of 10 sizing values on the same material is 7%. At 280 seconds this allows for a range of ± 20 seconds, which may account for the sizing variation between the sets. This is unlikely, however, since the sets were tested consecutively.

From the sizing reproducibility data, it was concluded that the average sizing between sets using the quaternary potato starch is 280 ± 30 seconds.

Starch Comparison

In general, Figures 14-18 show that the average sizing values between sheets for each starch were statistically not different, even though the sheets were made from three consecutive sets. The statistically significant difference in the last sheet in Figure 15 and the fifth sheet in Figure 17 result from the high stock pH of 7.9 and 8.4, respectively. In each case, the high pH resulted in a sizing reduction of about 100 seconds. This agrees with the results found with the first sheet in Figure 8. The sizing values for these sheets were not used in Figure 19.

The t-test also shows a significant difference between the first and

the sixth sheet in Figure 17. This difference results from the unusually low standard deviation of the sixth sheet. A standard deviation of 20 (which is normally low), instead of 9, would have showed no significant difference between the two sheets. Therefore, the difference, if any, is minimal.

Since no significant differences between sheets from different sets were detected with the t-test, the conditions in each set, except for the order of emulsion addition, are believed to be the same. This assumption is supported by the potato starch's average sizing level of 294 seconds, which is well within the range set by the reproducibility data for Figure 13.

Figure 19 compares the average sizing levels for the different starches. The t-test and the two-way ANOVA (see Appendix IV) point out three significant results from the data. First, starches 1 and 3 produced sheets with significantly lower sizing than starches 2 and 4. Table 2 shows that starches 1 and 3 are the low charged starches, while starches 2 and 4 are the high charged starches. This difference in charge affected the sizing efficiency to such an extent that the two-way ANOVA produced an F-probability of 0.00...0, which means there is a 100% probability that cationic charge will affect the sizing efficiency of the ASA emulsion.

The effect of charge on sizing efficiency may occur for several reasons. To begin with, high charged starches would produce high charged emulsion particles which would form stable emulsion due to the high electrostatic repulsion forces (see Emulsion Stability, page 14). On the other hand, low charged starches would produce low charged emulsion particles which would tend to aggregate and reduce the sizing efficiency.

Plus, highly cationic emulsion particles would also be retained more efficiently on the negatively charged fibers. The opposite would also be true for low charged particles.

Finally, the high charged starches may also hinder hydrolysis by more

effectively covering the negative anhydride groups, reducing their availability for hydrolysis. This is not supported by the data, however, since the low charged starches did not show a consecutive decrease in sizing with time.

Secondly, the t-test and the two-way ANOVA show there is no significant difference between starches 1 and 3 as a group and starches 2 and 4 as a group. However, this does not mean that the starches within the two groups are statistically the same.

Table 2 shows that starches 1 and 2 are the low molecular weight starches while starches 3 and 4 are the high molecular weight starches. Since there was no statistical difference between starches 1 and 3 and starches 2 and 4, molecular weight does not significantly affect the sizing efficiency of ASA emulsions. In fact, the interaction probability from the two-way ANOVA shows that within the limitations of this thesis, molecular weight tends to decrease the sizing efficiency of ASA emulsions.

The t-test reveals the third significant result which shows that the potato starch produced a more efficient size than starches 1 and 3, which is expected, but a less efficient size than starches 2 and 4. This is unexpected since the literature results claim that potato starches are superior to corn starches for the sizing efficiency of ASA emulsions. (34) Unfortunately, no molecular weight or charge information is attainable on the potato starch, but it is likely that the molecular weight of the potato starch is higher than even the high molecular weight corn starches. If this is the case, the less efficient size from the potato starch may result from its higher molecular weight, which agrees with the two-way ANOVA results on the effect of molecular weight. However, the significantly lower sizing may also result from a lower cationic charge on the potato starch or some other unidentified factor.

CONCLUSIONS

The following conclusions have been drawn from the data resulting from this study. These conclusions, however, may not apply with different starches or under different conditions.

- (1) Within the limitations of this thesis, the sizing efficiency of ASA emulsions is not affected by the molecular weight of the cationic starch.
- (2) The sizing efficiency is, however, vitally dependant on the cationic charge of the starch. High charged starches produce more efficient ASA emulsions than low charged starches.
- (3) The development of handsheet sizing with ASA emulsions is very dependant on stock pH. Above pH 7.9, a loss of about 100 seconds in sizing over a period of one minute can be expected.
- (4) Quaternary potato starches are not superior to high charged quaternary waxy maize corn starches for developing the sizing efficiency of ASA emulsions.

RECOMMENDATIONS

The purpose of this thesis was to study the effect of molecular weight and cationic charge of waxy maize corn starches on the sizing efficiency of ASA emulsions. Even though several significant conclusions were found, a lot of work still remains to be done. The following work is recommended.

- (1) Inconsistent laboratory results still plague attempts to achieve reproducible sizing results, particularly between handsheet sets. For this reason more work needs to be performed to determine the still unknown variables that affect sizing efficiency.
- (2) The actual molecular weights of the 15 starches are not known. Careful capillary viscometer measurements in conjunction with the K and a factors of the Mark-Howink equation could quantify the actual molecular weights of the starches. This information would contribute greatly to the significance of the apparent negligible affect of molecular weight on the sizing efficiency of ASA.
- (3) Only four of the fifteen starches were evaluated in this thesis. It would be beneficial to determine whether the results of this thesis apply to the starches possessing intermediate molecular weights and cationic charge. Plus, it is not known whether charge affects the sizing efficiency in a linear manner. There may exist a threshold charge where additional charge is not beneficial or there may be a threshold charge that is required to obtain any benefit from an increase in charge.
- (4) The results of this thesis are based on the use of quaternary ammonium waxy maize corn starches. However, it is not known whether these results apply for all types of corn and potato starches. Similar work evaluating other starches would be beneficial.

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APPENDIX I

Statistical Analysis (41)

Two types of statistical analysis were used to evaluate the experimental data. The t-test was used to evaluate the sizing reproducibility results and evaluate differences between the quaternary corn starches. In addition, the corn starches were also analyzed using a two-way analysis of variance (ANOVA).

The t-test is a significance test to evaluate the difference between means of two samples. It is performed by letting \bar{X}_1 and \bar{X}_2 be the means of two independent samples of sizes n_1 and n_2 from normal populations, with corresponding sample variances $(s_1)^2$ and $(s_2)^2$. The quantity

$$t = (\bar{X}_1 - \bar{X}_2) [(n_1 + n_2 - 2) n_1 n_2]^{1/2} / \{(n_1 + n_2) [(n_1 - 1)(s_1)^2 + (n_2 - 1)(s_2)^2]\}$$

is distributed according to the t-distribution with $m = n_1 + n_2 - 2$ degrees of freedom. A level of significance, ϵ , is selected to evaluate whether the samples come from the same normal population. If the value of t calculated from the sample exceeds t_ϵ , the hypothesis that the two samples come from the same normal population would be rejected at that level. Though the t-test can determine significant differences it cannot state whether two means are equal.

An ϵ -level of 0.01, which corresponds to a 99% confidence limit, was chosen. Some $t_{.01}$ values at different degrees of freedom, m , are listed below in Table 2.

Table 2

$t_{.01}$ Values at Different Degrees of Freedom

m	6	35	40	45
$t_{.01}$	3.707	2.724	2.704	2.690

APPENDIX I Cont.

The two-way ANOVA compares the isolated and synergistic effects of two variables, molecular weight and cationic charge, on the tested property. A two factorial ANOVA program on a Heath Zenith Z-100 personal computer equipped with Monostat software by Ecosoft was employed.

The two-way ANOVA produces three F-probabilities, one for each variable, and the third for the interaction of the two variables. If the F-probability is less than the selected α -level, the variable listed under "source" significantly affects the tested property.

APPENDIX II

Sizing Reproducibility

Data for Figure 8: Sizing Reproducibility Within a Set of Handsheets.

Date Made: 11-26-86

Emulsion Prepared: 2:00 pm, pH = 3.1

Handsheets Made: 2:20 - 3:30 pm

Dilution Water: pH = 7.7, Conductivity = 1.93 micromhos

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Stnd Dev
*1	2.64	8.45	188, 179, 188, 233	197	24
2	2.64	7.4	323, 320, 280, 285	302	23
3	2.63	7.3	297, 251, 286, 327	290	31
4	2.60	7.5	278, 269, 243, 310	275	28
5	2.61	7.0	297, 294, 222, 269	270.5	35
6	2.61	7.3	319, 225, 301, 282	<u>282</u>	<u>41</u>
				284	31

* high pH, data not used in average

$t_{1,5} = 3.463$; $t_{1,4} = 4.230$; $t_{2,5} = 1.504$

Data for Figure 9: Sizing Reproducibility Within a Set of Handsheets.

Date Made: 11-28-86

Emulsion Prepared: 2:40 pm, pH = 2.85

Handsheets Made: 3:20 - 4:00 pm

Dilution Water: pH = 7.4, Conductivity = 0.437 micromhos

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Stnd Dev
1	2.64	7.4	282, 315, 250, 293	285	27
2	2.64	7.7	321, 332, 280, 308	310	22
3	2.58	7.25	273, 337, 271, 319	300	33
4	2.64	7.45	334, 294, 313, 310	313	16
5	2.64	7.3	314, 338, 272, 294	<u>304.5</u>	<u>28</u>
				302.5	25

$t_{1,4} = 1.784$

APPENDIX II Cont.

Data for Figure 10: Sizing Reproducibility Within a Set of Handsheets.

Date Made: 11-28-86

Emulsion Prepared: 2:40 pm, pH = 2.85

Handsheets Made: 4:20 - 5:00 pm

Dilution Water: pH = 8.0, Conductivity = 0.429 micromhos

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Std Dev
1	2.56	8.1	241, 240, 249, 220	237.5	12
2	2.49	7.95	282, 246, 269, 254	263	16
3	2.54	7.4	286, 211, 245, 309	263	43
4	2.52	7.45	257, 268, 246, 239	252.5	13
5	2.52	7.4	302, 276, 240, 248	<u>266.5</u>	<u>28</u>
				256	25

$$t_{1,5} = 1.904, t_{1,2} = 2.550$$

Data for Figure 11: Sizing Reproducibility Within a Set of Handsheets.

Date Made: 11-30-86

Emulsion Prepared: 1:30 pm, pH = 3.0

Handsheets Made: 1:45 - 2:15 pm

Dilution Water: pH = 7.2, Conductivity = 0.606 micromhos

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Std Dev
1	2.48	7.55	271, 289, 250, 230	260	26
2	2.41	7.75	206, 240, 293, 247	246.5	36
3	2.40	7.4	290, 241, 310, 237	269.5	36
4	2.44	7.55	276, 244, 255, 252	257	14
5	2.44	7.4	250, 204, 258, 273	<u>246</u>	<u>30</u>
				256	28

$$t_{3,5} = 1.003$$

Data for Figure 12: Sizing Reproducibility Within a Set of Handsheets.

Date Made: 11-30-86

Emulsion Prepared: 1:30 pm, pH = 3.0

Handsheets Made: 2:55 - 3:30 pm

Dilution Water: pH = 7.3, Conductivity = 0.545 micromhos

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Std Dev
1	2.62	7.8	348, 302, 323, 267	310	34
2	2.51	7.8	286, 321, 276, 290	293	19
3	2.64	7.55	286, 337, 285, 358	316.5	37
4	2.54	7.6	326, 324, 255, 324	307	35
5	2.56	7.6	270, 280, 342, 300	<u>298</u>	<u>32</u>
				305	30

$$t_{2,3} = 1.130$$

APPENDIX II Cont.

Data for Figure 13: Sizing Reproducibility Between Sets of Handsheets.

<u>Figure Number</u>	<u>Avg Sizing</u>	<u>Std Dev</u>	<u>Number of Samples</u>	<u>t Values</u>
8	284	31	20	$t_{8,9} = 2.077$
9	302.5	25	20	$t_{9,10} = 5.882$
10	256	25	20	$t_{11,12} = 5.340$
11	256	28	20	$t_{8,10} = 3.144$
12	<u>305</u>	<u>30</u>	20	$t_{8,12} = 2.177$
	281	35		$t_{10,12} = 5.611$

APPENDIX III

Starch Efficiency

Table 3

Handsheet Order and Experimental Conditions of the Three Sets of Handsheets

	<u>First Set</u>	<u>Second Set</u>	<u>Third Set</u>
Handsheet Order	1-2	3-4	5-6,7
Time Made	3:40-4:05	5:05-5:40	6:10-6:40
Dilution Water pH	7.3	7.4	8.1
Dilution Water Cond.	0.970	1.213	1.267
Starch Emulsion Order			
First Set	C, 1, 2, 3, 4, 2, 3, C, 4, 1		
Second Set	4, 3, 2, 1, C, 3, C, 1, 4, 2		
Third Set	1, 2, C, 3, 4, 4, C, 3, 1, 2, 3		

Data for Figure 14: Control Starch Reproducibility

Date: 12-4-86

Starch: pH = 8.2

Emulsion Prepared: 1:35 pm, pH = 3.2

<u>Order Made</u>	<u>Sheet Wt (g)</u>	<u>Stock pH</u>	<u>HST (Seconds)</u>	<u>Avg</u>	<u>Std Dev</u>
1	3.00	7.3	377, 302, 343, 281	326	43
2	2.65	7.4	259, 376, 335, 246	304	62
3	2.46	7.45	283, 263, 254, 275	269	5
4	2.54	7.1	277, 319, 273, 279	287	21
5	2.79	7.4	312, 277, 245, 296	282.5	29
6	2.72	7.6	265, 362, 293, 280	<u>300</u>	<u>43</u>
				<u>294</u>	<u>39</u>

$$t_{1,3} = 2.633$$

Data for Figure 15: Starch 1 Reproducibility

Date: 12-4-86

Starch: pH unknown, Color: Brown

Emulsion Prepared: 1:50 pm, pH = 3.1

<u>Order Made</u>	<u>Sheet Wt (g)</u>	<u>Stock pH</u>	<u>HST (Seconds)</u>	<u>Avg</u>	<u>Std Dev</u>
1	2.55	7.3	234, 274, 186, 230	231	36
2	2.60	7.1	202, 232, 164, 193	198	28
3	2.41	7.5	177, 148, 202, 146	191.5	29
4	2.46	7.4	130, 215, 178, 198	180	37
5	2.65	7.2	190, 222, 164, 153	182	31
*6	2.47	7.9	102, 108, 91, 94	<u>99</u>	<u>8</u>
				192	36

* high pH, data not used in average

$$t_{1,4} = 1.976, t_{1,5} = 2.063, t_{4,6} = 4.279$$

APPENDIX III Cont.

Data for Figure 16: Starch 2 Reproducibility

Date: 12-4-86

Starch: pH = 9.6, Color: Brown

Emulsion Prepared: 2:09 pm, pH = 2.9

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Stnd Dev
1	2.62	7.3	359, 367, 384, 379	372	11
2	2.51	7.3	372, 330, 282, 333	329	37
3	2.63	7.45	404, 331, 296, 416	387	38
4	2.43	7.4	354, 259, 296, 289	299.5	40
5	2.62	7.3	344, 442, 326, 342	363.5	53
6	2.67	7.55	272, 296, 392, 340	325	53
				346	48

$$t_{3,4} = 3.172, t_{1,4} = 3.495$$

Data for Figure 17: Starch 3 Reproducibility

Date: 12-4-86

Starch: pH = 10.4, Color: Clear White

Emulsion Prepared: 2:20 pm, pH = 2.9

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Stnd Dev
1	2.55	7.4	225, 216, 190, 170	200	25
2	2.62	7.4	194, 204, 214, 162	193.5	23
3	2.45	7.25	146, 209, 195, 177	182	27
4	2.46	7.4	154, 160, 146, 160	155	7
*5	2.46	8.4	54, 60, 86, 111	78	26
6	2.51	7.3	142, 159, 142, 155	149.5	9
7	2.55	7.45	180, 195, 158, 152	171	20
				175	26

* high pH, data not used in average

$$t_{1,4} = 3.467, t_{1,6} = 3.801, t_{5,6} = 5.197$$

Data for Figure 18: Starch 4 Reproducibility

Date: 12-4-86

Starch: pH = 9.7, Color: Clear White

Emulsion Prepared: 2:27 pm, pH = 2.9

Order Made	Sheet Wt (g)	Stock pH	HST (Seconds)	Avg	Stnd Dev
1	2.63	7.5	337, 383, 406, 349	369	32
2	2.66	7.7	315, 356, 342, 326	335	18
3	2.87	7.0	276, 398, 301, 315	325	34
4	2.64	7.5	328, 354, 325, 319	331.5	15
5	2.51	7.45	305, 332, 302, 284	306	20
6	2.56	7.2	303, 329, 269, 301	300.5	25
				327	35

$$t_{1,6} = 3.374$$

APPENDIX III Cont.

Data for Figure 19: Starch Comparison

<u>Starch Number</u>	<u>Avg Sizing</u>	<u>Std Dev</u>	<u>Number of Samples</u>	<u>t Values</u>
C	294	39	24	$t_{C,1} = 8.943$
1	192	36	20	$t_{C,2} = 4.119$
2	346	48	24	$t_{C,3} = 12.438$
3	175	26	24	$t_{C,4} = 3.085$
4	327	35	24	$t_{1,3} = 1.816$
				$t_{2,4} = 1.567$
				$t_{1,4} = 12.576$

APPENDIX IV

Statistical Results from the Two-Way ANOVA

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Ratio</u>	<u>F Probability</u>
Cols *	14036.2	1	14036.2	3.582	0.0617
Rows	543525.1	1	543525.1	138.703	0.00...0
Interaction	45907.1	1	45907.1	11.715	0.0009
Error	344838.1	88	3918.6		
Total	948306.5	91			

* Cols = Molecular Weight, Rows = Cationic Charge