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EFFECT OF VARIOUS STARCH SOURCES ON THE SILICONE
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EFFECT OF VARIOUS STARCH SOURCES ON THE SILICONE HOLDOUT OF RELEASE PAPER

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Siliconized papers are widely being used from food and packaging industry to pressure sensitive label industry and their use has increased considerably over the last decade. Surface and structural properties of the sheet influence the silicone hold out and release properties.

Surface sizing of the sheet is done prior to silicone coating. The objective of this research is to find their film forming capabilities, fluid hold out of various starches, and the effect of the various calendering process on the release properties was also studied.

No significant difference between the starch sources were observed, except for the modified corn starch with alginate thickener. Increase in pick-up reduced the porosity of the sheet, giving better fluid hold out, and better release properties. Calendering affected the surface properties of the sheet, influencing the fluid hold out and release properties. Supercalendering produced sheets with better hold out and release properties compared to hot soft nip calendering.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

List of Figures--continued

CHAPTER I

INTRODUCTION

Many raw materials and articles of commerce are either permanently tacky or have some tendency to stick to other surfaces at some stage of their manufacture or storage. When this happens, it is usually necessary to cover the surface of the product, temporarily until the tackiness is gone or until the product is ready to be used. Release coatings are generally used to prevent things from sticking together or render surfaces anti adhesive.

Silicones in many forms offer excellent release properties. But, for them to properly work, it is necessary to form a cured film, free from migratory species to produce a surface with little or no transfer to the released surface. In the early days of silicone release coatings, specialty applications were the norm, and the cost of raw materials was not an overriding concern. But, as everyday uses became more and more common, cost concerns became more pressing. Thus, the desirability of using as little silicone as possible is certainly understandable. The minimum amount necessary will vary from substrate to substrate.

Plastic films, with their perfect holdout and smooth surface, need only about 0.1 - 0.2 grams per square meter (gsm) of silicone to provide perfect film coverage and to exhibit good release properties, whereas glassine and parchment require higher coat weight films. Due to the high cost of silicone, the base sheets are surface sized

1

with starch before being coated with silicones. As said earlier, a good release property is dependent on the starch film, which is formed on the surface of the sheet. The reasons for surface sizing the sheet with starch are to reinforce fiber to fiber bonding at the surface, provide sheet stiffness, and improve coating and fluid holdout by filling the surface voids in the base sheet. By controlling the coating holdout of a paper, surface absorbency can be controlled and made uniform.

Industries in North America have predominantly been using corn starch, whereas European industries use potato starch. The reason for this is the abundant availability of those sources in North America and Europe, respectively. No concrete information is available regarding the use of other starch sources, such as tapioca, rice, potato, or pea for surface sizing.

The main objectives of this research are to determine the sizing efficiency of various starch sources, their film forming and fluid holdout capabilities, and the effect of different calendering methods on release properties.

CHAPTER II

LITERATURE REVIEW

Starch is a high-molecular-weight polymer of alpha-D-glucose, which is a reserve carbohydrate in plants. It occurs in the form of tiny granules at various sites in plants. The main sources of commercial starches are corn, potatoes, wheat, and waxy maize (1). Nearly all starches are composed of two main fractions: amylose, a linear molecule, and amylopectin, a highly branched polymer. Amylose contains practically all 1-4, alpha-glucosidic linkages, whereas amylopectin contains mostly 1-4, alpha glucosidic linkages along with 1-6, alpha-glucosidic linkages at the branch points. The ratio of amylose to amylopectin and the average degree of polymerization are different for various starches. Size, density, and shape of starch granules vary with the source from which the starch is obtained. In general, low moisture plant tissues exhibit small, dense, polygon-shaped granules of starch, whereas high-moisture tissues exhibit large, less dense, oval shaped granules of starch.

Starch granules are insoluble in cold water because of organized, hydrogen-bonded structures. As a consequence of the "crystalline" nature and concentric layers in which starch is deposited, the granules show an interference cross when observed under a microscope with polarized light. When water suspensions of starch are heated, little change occurs until a critical temperature is reached (1). At the critical temperature, known as the pasting or gelatinization temperature, the granules lose their interference crosses and begin to swell, causing a large increase in viscosity. The large increase in viscosity is followed by rupture of the swollen granules as the temperature is increased. Cooking time enables the amylose and amylopectin chains

to extend and hydrate. Each variety of starch has a different pasting temperature range, and the properties of cooked starch paste vary considerably due to their complex colloidal nature.

Paste properties are dependent upon a number of factors, including the proportion of amylose and amylopectin, as well as conditions used for cooking the starch. Starch granules in a living plant are produced by enzymatic synthesis. Chains of glucose molecules are aligned in an orderly fashion and held together by a strong associative force, hydrogen bonding. To disperse or cook starch, it is necessary to introduce enough energy to disrupt these bonds and introduce molecules of water. The key point, though, is that realignment is not guided by any systematic process; therefore, the starch molecules cannot return to their original state. The extent of retrogradation depends on such parameters as concentration, degree and type of hyrolysis used to convert the starch to achieve a useful viscosity, extent of chemical modification or substitution on the glucose chain, temperature, and pH. The highest extent of retrogradation can be expected for a slightly hydrolysed, unmodified cereal starch after slow cooling to 170 ^{0}F and a slightly acid pH of 4.5-6.5.

Starch high in amylose content, such as that obtained from hybrid corn strains, does not cook out at atmospheric pressure; it requires cooking under pressure at 300 ^{0}F or higher to ensure thorough cook-out. When cooled, such pastes rapidly set to firm, irreversible gels, or precipitate as crystalline matter. The rate at which a gel is formed and its firmness are dependent on the amylose content. The firmness of the gel is also accentuated by mild cooking conditions, as well as by high solids and high viscosity. Formation of crystalline amylose precipitates is favored when pastes are severely cooked at low solids under conditions that give low viscosities. Complexing agents, such as lipids and alcohols, will promote the formation of amylose precipitates. Starch pastes high in amylopectin, such as waxy maize, do not gel or precipitate upon

cooling. They do, however, increase in viscosity upon cooling. Chemically derivatized starches simulate these properties. Table 1 below contains information relative to the properties of some starch pastes (1).

Table 1

Paste Viscosity, Clarity, and Rate of Retrogradation of Starches

Starch	Paste Viscosity	Clarity	Rate of Retrogradation
Corn	Medium	Opaque	High
Potato	Very high	Very clear	Medium-low
Tapioca	High	Clear	Low
Waxy maize	Medium- high	Slightly clear	Very low
Rice	High	Clear	High

Properties of starch pastes containing "normal" ratios of amylose and amylopectin are also affected by cooking conditions. Heating to the pasting temperature is not adequate to fully swell and disperse the granules. In actual practice, a minimum of 20 min at a temperature in the range of 93 ⁻ 95 ^{0}C with sufficient water and agitation are required to fully swell and disperse starches. Poorly cooked starch pastes are salve-like because of highly swollen and poorly dispersed granules. In contrast, properly cooked starch pastes, which are well dispersed, behave as hydrocolloids.

Colloidal and Polymeric Chemistry of Starches

A knowledge of the chemical and physical structure of starch is helpful in understanding the role of starch in paper coatings.

Figure 1 shows the glucopyranose ring structure, which is common to starch and cellulose. The ring is not flat, but chair-like. Each hydroxyl group or hydrogen atom is either axial or equatorial with respect to the glucose ring. In carbohydrate polymers, hydroxyl orientation and hydrogen bonding between OH groups or between OH groups and ring oxygen atoms affect solubility, precipitability from solution, and conformational stability (1). Intramolecular hydrogen bonding, between O_2 and O_3 on subsequent anhydroglucose units, for example, gives stability to helical complexes. Intermolecular hydrogen bonding between groups on adjacent molecules is a major factor governing starch dispersion and precipitation. Amylose, as indicated earlier, is characterized by alpha-1,4 linkages between the anhydrous glucose units. The alpha-1,4 linkage results in a flexible molecule with a natural extended helical twist that can reorganize into a collapsed helix under certain conditions. The beta-1,4 linked molecule, however, is rigid and flat, which partly accounts for the strength of cellulose fibers. Figure 2 shows the structure of amylose.

Amylopectin, the major, or only component, in most starches, is primarily responsible for granule structure and crystallinity. Figure 3 shows the structure of

Figure 1. Structure of Starch.

Figure 2. Structure of Amylose.

Figure 3. Structure of Amylopectin.

amylopectin.

In starches, where both amylose and amylopectin are present, mixed crystal formation is possible since both crystallize into joint structures. Amylose and amylopectin are chemically similar in that they both consist of anhydroglucose units connected at the first and fourth carbons, but differ in that amylopectin also has

branches that connect the first and the sixth carbon units. Physically they are similar; both are packed in the same granule, when both are present, and must be gelatinized to be effective. They differ, however, in that amylose takes the form of a linear chain and amylopectin takes the form of a branched chain (1).

These two polymers have significant differences. The first is the average molecular weight. Amylose is much lower in molecular weight than amylopectin, having a degree of polymerization of about 1000 anhydroglucose units, compared to approximately 100,000 units for amylopectin. Amylose, being essentially unbranched, is prone to retrogradation. The gel and film forming properties of starch polymers are a function of molecular weight and molecular weight distribution. Table 2 shows the amylose content of various starches (1).

Table 2

Amylose Content of Various Starch Sources

Starch	Amylose content
Rice	17%
Tapioca	18%
Potato	22%
Modified corn	2%
Unmodified corn	28%

Dispersion of Starches

The extent of granule gelatinization during heating in a static system is shown as a function of temperature in Figure 4.

Figure 4. Viscosity vs. Temperature Profile.

Starch must always be dispersed in well-agitated cold water. An adequate quantity of water must be used to uniformly disperse the starch granules. Starch can be only useful if the granules are dispersed well. After the dispersion of the starch in well-agitated cold water, the temperature of the mixture is increased steadily. With the increase in temperature, there is an increase in viscosity. This increase in viscosity is due to the swelling of the starch granule. Penetration of water into the granular structure causes the molecules to swell. Thus, a starch molecule, with a further increase in temperature, swells and reaches a point where it has maximum viscosity. The temperature corresponding to this point is called the gelatinization temperature (1). After the gelatinization temperature, there is a decrease in the viscosity. Bursting of the swollen starch granules causes this decrease in viscosity. Starches are not

heated after this gelatinization point. The cooling curve indicates the increase in viscosity, which is due to the reorganization of the cooked and dispersed starch molecule. This reorganization is called retrogradation and can occur via two different methods: congealing and crystallizing. Congealing takes place when amylose and amylopectin chains associate, or entangle, and even entrap water in a three dimensional network. The crystallizing process occurs when the linear molecules of amylose are allowed to re-associate and align. Steric hindrance prevents branched amylopectin from crystallizing.

As starch is gelatinized, the adhesive character is developed. The objective of starch pasting is to separate the double helices and dissociate the hydrogen bonding between the hydroxyl groups to maximize the amount of free hydroxyls. Once freed, it is equally important to keep the groups separated so that they are available to form bonds with other molecules such as pigments in the coatings and the fibers of the base sheet (1). The adhesive character of starch is irreversibly lost if the hydroxyl groups are allowed to re-associate and retrograde.

Starch Modification

Upon cooking, unmodified varieties of starch gelatinize into a relatively high-viscosity molecular dispersions (pastes). As a result, use of unmodified starches as paper coating binders is definitely limited. Today, the starches used in the coating area of the paper industry are modified starches. The two types of modification carried out on the starch molecule are conversion, or molecular chain scission, and chemical derivatization. Conversion allows the formulation of coatings at higher solids. Chemical derivatization is done to improve the stability of the cooked starch paste.

Conversion, or scission, is the process of reducing the length of the starch molecule chain. Most commonly, conversion is accomplished by the use of enzymes, acids, or oxidizing agents, but mechanical shear can also be used. The end result is similar in all cases in that the molecular weight of the starch molecule and the viscosity of the starch paste are reduced. Chemical derivatization of starch molecules takes place when a chemical group is substituted onto the starch molecule. Most derivatized starches are manufactured by starch suppliers. Several derivatization methods have been developed, and each produces a product that is characteristic of the type of chemical linkage or chemical group. In each case, derivatives are attached to both amylose and amylopectin chains. With enough substitution, the straight amylose chains take the appearance of branched chains. The end result is a stable molecule with enough steric hindrance to inhibit retrogradation (1). Many of the derivatives will also contribute strength through the addition of hydroxyl groups for hydrogen bonding and charged groups for ionic bonding.

Surface Sizing

There are probably as many definitions for surface sizing as there are papermakers in the world. Size can be defined as any chemical, other than bleach, fillers, pigments, and dyes, which are added to the paper making furnish, or subsequently applied after the web is formed, which alter those characteristics of the sheet that relates to its resistance to the transudation or absorption of liquids which come into contact with the web. Surface sizing of paper improves the furnish, produces a better surface for printing, minimizes scuffing, controls air permeability, prevents excessive or undesirable penetration of other finishing agents, improves appearance, and improves strength characteristics.

Theory of Surface Sizing

Wetting and penetration of all solids is dependent on a number of basic principles, which are best expressed by the classic Dupre and Lucas-Washburn equations (2).

In the phenomenon of wetting, the contact angle between the liquid and solid determines whether the sheet is wettable or non-wettable (2). If the sheet is to resist wetting, the free energy of the solid-vapor interface must be less than or equal to the free energy of the liquid plus that of the solid-liquid interface. The angle, θ, when this situation is obtained, is above 90^0, and the sheet is referred to as non-wettable.

Dupre further developed a mechanism for penetration of the liquid into the sheet which is related to the driving force.

$$\Delta P = 2(S_{sv} - S_{SL}) / r$$

ΔP = pressure differential driving force, dyne

S_{sv} = free energy of the solid-vapor interface, dyne . cm

S_{SL} = free energy of the solid-liquid interface, dyne . cm

r = pore radius, cm

Resistance to wetting therefore would require a small driving force. This would be obtained by making the value of the free energy of the solid-liquid interface close to that of the solid-vapor interface. In addition to the driving force, the rate of penetration of liquid into the sheet is important.

Lucas-Washburn present the following equation for the rate of penetration.

$$V = l/t = (r \, S_l /4 \, l \, u) \cos \theta$$

V= rate of penetration, cm/sec

l = depth of penetration, cm

t = time, sec

r = pore radius, cm

S_l = surface tension of the liquid, dynes/sq cm

u = viscosity, poise

θ = contact angle of the liquid on the surface, degrees

This equation gives a measure of the penetrative power of the liquid in a given situation. The Lucas-Washburn equation was further modified by Cobb; his equation measures the depth of penetration at any given time. The free energy of the solid interfaces can be reduced by the addition of internal size and other compounds, the pore radius can be plugged by fillers, surface compounds and other additives, or by the use of small fibers and fiber fines.

Variables in Surface Sizing

There are three sets of variables in the surface sizing process: material variables, machine variables, and web variables (3).

Material Variables

Due to its uniformity of quality, its plentiful supply, its wide range viscosities, and, in particular, its low price, starch has been the most commonly used raw material for producing starch. Corn, potato, and tapioca are the predominant types of starches in the market. In the U.S., corn is the most widely used of the three. In addition to starch, other agents are presently being used for surface sizing. Some of these agents include animal glue, polyvinyl alcohol, alginates, and carboxymethylcellulose.

A second variable in the materials category is a group of interrelated factors. Temperature, solids concentration, and viscosity are the components of this group variable. One other important variable of the size press solutions is their stability characteristics. Some products have a retrogradation problem, sometimes setting up like a jell, other times crystallization caused by incomplete cooking.

Machine Variables

In the size press, sizing operations are affected by some uncontrolled variable factors. The major variables include the roll loading, because of its ability to squeeze the size out of the sheet; roll diameter influence on the amount of pick up and the crown required for the roll. Today, controlled crown rolls are used to minimize the roll diameter and smaller crowns are desirable because high nip pressures can then be applied. The hardness of the roll will change the pick up. A softer roll gives a better pick up. The speed at which the paper machine is running is important because of the dwell time that influences the penetration (3). Other factors include dryer temperatures, sheet tension going through the press, teflon dryer rolls, and bowed rolls. Increasing the nip pressure, which is influenced by the above machine variables, will increase the penetration. The nip pressure causes a large pressure difference or driving force causing the fluid to penetrate the sheet.

Web Variables

This set of variables can be broken down into two sub classes: surface and sheet structure. One surface property of interest is smoothness, which aids in regulating the size pick up. Another key property is wettability of the surface. Another factor is the amount of internal size that has been added to the sheet. The

larger the amount in the sheet, the less will be picked up at the size press. The distribution of the internal size will also affect the size pick up.

The sheet structure consists of density, pore size, moisture content, and formation. In respect to density, the amount of beating time which aids the fiber packing and the type of wood which influences individual fiber density must be considered. Increasing sheet density will decrease pore size which, from the previous discussion of the Lucas-Washburn equation, should reduce the penetration. The density could also affect the free energy of the sheet, which would change the contact angle and, therefore, the wettability of the sheet. An increase in the sheet density due to the above reasons will decrease the pickup.

Pore size and pore size distribution in the basesheet influence wetting. Pore size is partially due to refining, but the fiber furnish is also an influential factor. The pores perform the disservice of letting water into the sheet, so surface size is added to reduce the number and/or size of the pores to reduce wettability. Increasing the radius in the Dupre equation decreases the driving force which should lower penetration. It should, however, from the Lucas-Washburn equation, increase the rate of penetration. Since the pressure difference (driving force) in the Dupre equation is altered by nip pressure, larger pore sizes should increase the penetration.

The moisture content would possibly affect the free energy of the solid, thus increasing the contact angle. It may reduce the driving force and inhibit the rate of penetration, thus increasing the contact angle. Pickup is increased with increasing moisture content within the range of 5-12 %.

In respect to strength properties, the burst, tensile, and fold strength will increase with increases in the surface size. Smoothness, pick resistance, and scuff resistance is improved by increasing the surface size. Optical tests reduced by increasing the surface size are opacity and brightness, but gloss is found to increase

with increase in surface size (3).

Influence of Alginates on Surface Sizing

Alginates are used as thickeners; they help to thicken the modified starches and increase the viscosity. They have a better pick up in the size press. They also help starch in forming a flexible, uniform film. They improve the surface properties, ink acceptance, and smoothness. In paper coatings, they control the rheology of the coating and prevent dilatancy at high shear (4).

Size Press

The size press is a useful, and, for some products, indispensable part of the paper machine. As a means of impregnation or surface treatment for paper, it has many advantages over the addition of beater additives or off-machine coating. A simple and inexpensive method of applying additives to the paper is to surface size them with the size press. One of the major objectives of surface sizing papers is to improve coating and fluid holdout (5). By controlling the coating holdout of a paper, surface absorbency can be controlled and made uniform. Papers are typically surface sized by applying a film of starch using a size press to fill the surface voids of the basesheet. This reduces the pore radii, and, therefore, the rate of penetration by fluids. Modifications to the conventional size press have increased its acceptance as a coater for applying pigmented coatings. However, one niche market in which the conventional size press continues to be preferred, is the application of barrier coatings. Barrier coatings are normally applied as a pre-coat for specialty grades to which an expensive functional top coating is applied. Examples of functional coatings are fluorocarbons for grease proof papers, chromium complexes (quillon) for water

resistant papers, and silicones for release papers. The expensive top coat makes the barrier coatings play an important role in optimizing the use of functional coatings.

In the production of basepapers for silicones, one of the most important variables is the holdout capability of the base sheet. The holdout is primarily affected by the characteristics of the sheet relating to the smoothness and surface structure. Barrier coatings serve to minimize the penetration of the expensive functional coating (6). For release papers, the barrier coating usually consists of a binder (starch) and a thickener (alginate), which are applied using a conventional flooded nip size press. The advantage of using a flooded nip size press rather than a metered size press or other coating applicators is that the sheet is saturated with the barrier coating as it passes through the nip of the coater. The metered size press and other coating applicators (blade, roll, and rod) do not saturate the sheet. By saturating the sheet, the porosity is minimized, providing a barrier, which will prevent or minimize the penetration of the top-coating layer.

Silicone Chemistry

The silicones are polymeric organosilicone compounds containing Si-C bonds. They are polymers in which the silicone atoms are bound to each other through oxygen atoms. The tendency to form single bonds, Si-O-Si, causes silicone to combine with oxygen to give polymeric compounds, while carbon is capable of forming single molecules with oxygen. By changing the various functional groups attached to the Si atom, a variety of products from fluids, greases, lubricants, resins, and rubbers can be produced (7).

Silicone is used to produce release grades of paper due to several of its important characteristics. First, it has a very low surface tension. Secondly, the

silicone molecule has a low molecule polarity, which is very important to the binding or cross linking of the silicone to the cellulose to the paper. The general appearance of the of the silicone molecule is shown in Figure 5.

Figure 5. General Appearance of the Silicone Molecule.

The methyl groups can be replaced by ethyl or phenyl groups. Silicones used in paper finishing usually have side chains of methyl groups that are exposed on the surface. The oxygen atoms in the Si-O-Si bonds form a hydrogen bridge with the substrate, and the methyl groups orient themselves outward from the surface. The amount of silicone that is applied varies considerably, but the typical coating ranges used are 0.1-0.3 gsm (8).

Some general properties of silicones are that they are an intermediate between polymeric and organic substances. They resist extreme temperatures, have good insulating properties, chemical stability, low inflammability, high surface activity, hydrophobic nature, and anti-adhesive behavior with various types of adhesives and glues. The following properties of the organosilicone compounds are utilized in the finishing of paper: the adhesive (anti-adhesive) property, the hydrophobic and surface properties that counteract the foaming of the saturation baths and coating mixes. The methyl-hydrogen-polysiloxanes, the methyl group silicones, form networks under the action of a catalyst and high temperature, forming a "plastic film" on the surface paper with the adhesion and hydrophobic properties desired (9). The catalysts usually used

are tin, zinc, zirconium, and titanium. The silicone molecules at the surface become oriented to the surface, while the methyl groups stick out on the outside. The methyl groups create a very high tension at the inter-phase surface, which disappears in the presence of low surface tension compounds like liquid glues, lacquers, and tacky glues.

<center>Release Papers</center>

Many raw materials and articles of commerce are either permanently tacky or have some tendency to stick to other surfaces at some stage of their manufacture or storage. When this happens, it is usually necessary to cover the surface of the product at least temporarily until the tackiness is gone or until the product is ready to be used. For this purpose, the so called "release papers" are almost always employed. A release paper may, therefore, be defined as a web, composed partially of cellulose fibers that show low enough adhesion to some other material so that it may be removed easily without damage to either the paper or the product. By far the most effective release treatment is the silicones. If applied in the prescribed manner, these materials will reduce the forces of adhesion by 98 to 100%, depending upon conditions (10). Silicones are by far the most widely used release agent. Although the effectiveness of the release treatment has much to do with the success or failure of a release paper in a particular application, the exact characteristics of the paper itself are equally important.

Paper, as normally made, is a porous material of cellulose fibers that can be readily penetrated by the release treatment or the tacky material itself under the conditions of actual use. The so-called "dense papers", such as glassine, parchment, and grease proof, are good for release treatment (11). Less dense papers have a

tendency to absorb the treatment in an irregular manner that can lead to irregularity in release. There are a number of good testing procedures available to determine the relative effectiveness of release treatment once applied to the paper and the ability of the treatment to resist the adhesion build up under accelerated aging conditions. The same tests can check the uniformity of release and the amount of contamination the release paper may cause. The stain test, Kiel test, pressure test, and stripping time test can be performed on these release papers to check uniformity and contamination. The final silicone coated basesheet is normally used as the base for the application of an adhesive coated label. Further descriptions of the base sheet and composite sample can be found in Figure 6.

Figure 6. Exaggerated View of Silicone Coated Base Sheet.

Usually the release coating consists of the polymer, a crosslinker, and a catalyst. A condensation reaction occurs as shown in Figure 7 with the liberation of hyrdogen and formation of a cross-linked silicone network.

When looking at Figure 8, which is exaggerated, the importance of the caliper of the basesheet can be seen (12).

In most commercial applications, this composite sample is passed through a high speed, die-cut machine and the label is attached to a product while the base sheet is collected and disposed of. Without proper caliper control, the knives may cut too

Figure 7. Condensation Reaction Between the Polymer and the Cross Linker.

Figure 8. Composite Label Example.

little or too much of the base sheet, causing the entire production line to come to a stop. Thus, caliper control is one of the most important quality control variables in the production of release backing paper.

Calendering and Supercalendering

Calendering is a mechanical surface treatment for paper or board carried out

by passing the sheet between rollers at high speed. The temperature of the roll can be increased or kept at room temperature. The purpose of calendering is to increase the smoothness, increase gloss, reduce the sheet thickness or caliper and reduce the wire and felt markings (13). Different types of rolls can be employed like king, queen, plain calender roll, soft, and heated calender roll to achieve the goal. The theory behind calendering is that the compression and the time of compression administered between the nips is responsible for the surface improvements. Thus, the current trend is to use fewer nips with high pressure.

There are various factors which affect the calendering process. They are the nip pressure, dwell time, roll smoothness, moisture content of the sheet, and temperature. Nip pressure increases sheet compaction and evens the caliper. However, care must be taken not to crush the sheet. Sheets with higher moisture content are more compressible. As a result, devices are sometime installed prior to the calender stack to add moisture back to the sheet. Higher temperatures on the roll favor compression of the sheet. Therefore, by heating the sheet or one of the rolls, the smoothness of the sheet can be improved with less nip pressure, and, consequently, less compaction (13). There are different types of calenders available in the market. Supercalender, hard nip calander, soft nip calender, hot/soft nip calender, and brush calender are some of the various types (see Table 3).

Supercalendering is a well-established technology. The heart of the supercalender is the configuration of alternating metal and resilient rolls. Resilient supercalender rolls are composed of discs of compressed natural fibers. After compression, the discs are locked together by end plates and then turned and ground. Different fiber mixtures can be used to produce rolls of varying hardness. Supercalendering is only used for surface finishing (smoothness, gloss). It is not used for improving the caliper profile of the base sheet or correcting the surface

Table 3

Load Ranges of Various Calenders

Calender types	Load ranges (psi)
Machine Calender	400-1000
Supercalender	2000-4000
Soft calender	400-1800
Hot soft nip calender	2000-4000

irregularities. Hard nip calenders are used for machine finished papers to impart smoothness and low gloss levels. They are also used with water boxes to improve the smoothness of boards. Soft nip calendering on the other hand uses resilient and chilled iron rolls. Hot soft nip calenders are same the as soft nip calenders with the exception that the hot metal roll is heated (13).

Variables Used to Monitor the Quality of the Basesheet

Air Permeability

The air permeability of the sheet is one of the most commonly used indicators for monitoring the production of the basesheet. The longer it takes the air to penetrate, the better the base sheet is for silicone coating. When this variable is not met, the size solution is usually changed to help improve this variable. Thus, supercalendering is the last step carried out before the basesheet is silicone coated, so this step allows the producer a last opportunity to refine the sheet characteristics to the needs of the silicone coating (14). Adhesion of the siliconized paper is reduced as

the air permeability increases dramatically. This is one reason why this variable is used to closely monitor the quality of the base paper.

Surface Absorption

The surface absorption of the sheet has an important role in the absorption of the silicone into the sheet, but this role is not as great as that of air permeability and the smoothness of the sheet, although each of these is connected in some way. On papers that are treated with silicone without size added, this parameter is very important. But, the addition of even a low concentration of size will improve this parameter immensely (14). Surface absorption is particularly important in base papers that are treated with an aqueous silicone solution. From the literature, the air permeability is still considered to have a greater effect on the release properties of siliconized papers than the surface absorption of that paper.

Smoothness

The smoothness of the basesheet is primarily controlled by the supercalendering of the sheet. The smoothness is directly related to the surface characteristics of the sheet, which is where the layer of silicone will be applied (14). The rougher the surface, the greater chance there is for non-uniformity in the coating, causing problems. The surface sizing will help the smoothness by helping to fill in some voids and surface pockets before supercalendering and silicone coating.

CHAPTER III

STATEMENT OF THE PROBLEM AND OBJECTIVES

The use of pressure-sensitive labels in manufacturing has increased considerably over the last decade. Their use has required that the release paper used in their manufacture be of the highest quality and be competitively priced. Siliconized papers are not only used in the pressure-sensitive label industry, but also in the packaging of many products, both industrial and food.

The properties that are considered the most important in the sheet before siliconizing are high smoothness, dense structure, low absorptivity, and low permeability. To hold the silicone to the sheet, the base sheet ought to be surface sized. Surface sizing is carried out by the application of starch to the sheet on the size press.

The objectives of this research are to study the sizing efficiency of various starche sources, their silicone holdout, film forming properties, and to study the effect of various calendering processes on release properties.

CHAPTER IV

EXPERIMENTAL DESIGN AND METHODOLOGY

The experimental design used during this study was to investigate the sizing efficiency of various starch sources, their fluid holdout properties, film forming properties, and the effect of various calendering processes on release properties. The experimentation was split into two phases. The film forming properties, clarity, and viscosity temperature curves were studied for various starches in the first phase. Sizing efficiency, fluid holdout, and effect of calenderring processes were studied in the second phase.

The schematic representation for both phases are shown in Figure 9 and Figure 10, respectively. Initially, the starches are selected according to their molecular weight. Lower molecular weight starches form discontinuous, brittle films compared to high molecular weight starches. By conducting the viscosity vs temperature study, the behavior of starches at different temperatures can be studied, and also the gelatinization temperature ranges for the various starches can be obtained. The study of the viscosity vs. % solids confirms the maximum solids range which can be run on the size press. The clarity of the starch films are analysed to find if there is an influence of the starch type and their amylose content on the clarity. Phase II involves the size press treatment of the various starches at specified conditions obtained from Phase I studies. Porosity measurements were made on the surface sized sheets and, from the pick up and the porosity values, the sizing efficiency of the starches were analysed. The surface sized sheets were calendered using the hot soft nip and

Experimental Design Diagram

Phase I

```
              ┌──────────────────────────┐
              │   Selection of starches  │
              │   based on molecular     │
              │        weight            │
              └──────────────────────────┘
```

| Modified Corn | Potato | Rice | Tapioca | Pearl | Mod.Corn/ Alginate |

```
              ┌──────────────────────────┐
              │   Clarity of starches    │
              │ Viscosity vs. temperature│
              │  Viscosity vs. % solids  │
              └──────────────────────────┘
                          │
                      Phase II
```

Figure 9. Schematic Representation of Phase I Experimentation.

supercalender. The porosity values were noted for the sheets before and after calendering to study the influence of the type of calendering on the release properties. The calendered sheets were coated with silicone, with a coat weight of 1 lb/ream and 1.5 lb/ream. The coated sheets were tested for the film cure, by performing the tape adhesion test. The coated sheets were tested for silicone coverage by performing the stain test. The results obtained from the stain test were quantitatively interpreted to study the fluid holdout of various starches. The results thus obtained are analysed and

Experimental Design Diagram

Phase II


```
┌─────────────────────────┐
│      Size press run of   │
│        starches at       │
│       5 - 10% solids     │
│    Pickup 25-75 lb/ton   │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Gurley Porosity,    │
│       Contact angle      │
│       Measurements       │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Supercalendering    │
│                          │
│   Hot soft nip calendering │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Gurley Porosity     │
│       Measurements       │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Silicone cure test  │
│    (tape adhesion test)  │
│                          │
│   Silicone coverage test │
│ (quantitative interpretation) │
└─────────────────────────┘
```

Figure 10. Schematic Representation of Phase II Experimentation.

discussed further in Chapter V.

Experimental Procedure

Phase I Procedure

Selection of the starches was made depending on their molecular weight. High molecular weight starches form continuous flexible films compared to low molecular weight starches. Rice, tapioca, pearl, modified corn, and modified corn with alginate thickener were the starches selected. The clarity of the starch films was looked into to find any difference between the starches. Drawdowns of the starches were performed using Mylar rods at 40 ^{0}C and at 60 ^{0}C to determine the variation in starch clarity with temperature. The clarity was measured by measuring the opacity of the films.

The variation of viscosity with temperature was studied by using the stress rheometer. The stress rheometer has a temperature bath that maintains the temperature of the starch sample at the set point, with viscosity being measured at that point. Thus, the temperatures were varied and the viscosity data was collected for all the starches. The gelatinization temperature for each of the starches can be found using this method. The stress rheometer is operated under the same conditions for all the starches.

The effect of solids on the viscosity was studied by using the Brookfield viscometer. Starches were prepared at 5, 8, and 10% solids, and the viscosity was measured with the Brookfield viscometer. Spindle No. 4 was used for all starches and the rpms were kept constant at 10 for all the starches. These data show the solid ranges for each starch which is applied on the size press.

Phase II Procedure

The basesheet was manufactured at the Western Michigan University paper pilot facility. The release grades require a tougher sheet with a high tensile value. The hardwood to softwood ratio was 1:2, and the hardwood and softwood were refined separately to a Canadian standard freeness (CSF) between 200-275 mls and then refined together to a final freeness value of 250 mls. The base sheet was surface sized with various starches with a pick up in the range of 25-100 lb/ream. The solid ranges were between 5 and 10 %. The Gurley porosity of the surface sized sheets was measured. The sheets were then calendered using the supercalender and the hot soft nip calender. The supercalender was operated at 2000 psi, temperature of 200^0F, and 4 passes were made, alternating the sides and the direction. The hot soft nip calender was operated at 40 psi, 150^0F temperature, with the same 4 passes alternating the sides and direction.

Porosity measurements were made again on the calendered sheets. The calendered sheets were taken to Dow Corning Corporation, Midland, MI, for silicone coating. The ideal silicone coat weight for the release grades are between 1 and 1.5 lb/ream. The calendered sheets were silicone coated using a Dow bench coater; a coat weight of 1 and 1.5 lb/ream was kept constant on all the surface sized sheets calendered by both processes. A silicone cure test was done on the coated sheets. This test uses an adhesive tape which is taped on the surface of the silicone coated sheet. Once applied, the tape is pulled off and both ends of the tape put back together and once again pulled apart. The resistance of the tape was then noted. Less resistance is interpreted as meaning that there is no silicone migration from the surface, and no change in resistance implies absence of migration.

The samples are then checked for silicone coverage. This test involves

staining the sample with dye for a period of time and quantifying based on the brown spots on the dyed area. Potassium iodide solution is put on the sample placed in a Cobb tester and the sample is kept for 2 minutes. Uniform silicone coverage, if present, prevents the dye from wetting the surface size and produces a yellow color dyed area. Non-uniform silicone coverage allows the dye to penetrate and reach the starch and turning it brown. Sheets with uniform coverage with very few brown spots are required. The dyed samples were scanned and stored as jpeg files and opened in Photoshop and taken to the image analyzer, which helps to quantify the number of brown spots in the sheets. This enabled data to be obtained on the fluid holdout and sizing efficiency of the various starches. The use of the image analyzer to quantify the severity of iodine staining has not been previously reported. Thus, it was also the goal of this study to determine the usefulness of this test method as a tool for measuring sizing efficiency and silicone holdout. All tests carried out are described and are listed in Table 4.

Table 4

Experimental Test Methods

Name of the Test	Test Equipment	TAPPI Test
Porosity	Gurley Porosimeter	T-460 om-88
Canadian Standard Freeness	Freeness Tester	T-227 om-89
Clarity	Opacimeter	T-425 om-86

CHAPTER V

RESULTS AND DISCUSSION

The main objectives were to study the sizing efficiency of various starches, their film forming and fluid holdout capabilities, and the effect of calendering on release properties. There is no evidence of any other published results and, hence, this study is the first of its nature and these results cannot be compared with the findings of any earlier research.

Experimental Data Analysis

Data analysis was performed using SAS, a statistical software package to analyze the collected data. In performing the analysis, the GLM (General Linear Model) procedure was used instead of ANOVA. GLM produces ANOVA tables, but handles missing data points more rigorously than ANOVA. Duncan's multiple range test was used to observe the differences between means for effects determined to be significant. The test compares the mean of the highest value to the second highest value and on to the lowest value. In this way, all treatment means for an effect are compared to determine if any statistical significance exists between one treatment and another in a given effect.

The data collected in this experiment produced an unbalanced design. No replicates were performed in this experiment. A choice then had to be made about the data. Either the 36 means or duplicate of the test measurements for the data set had to be used. It was decided to use the data set with all measurements to obtain a good

estimate of the experimental error. This, however, will cause some loss in the precision of the significance of the effect. The analysis was performed on both data sets, the means, and the complete data set. The fact of whether effects were significant or not did not change with the two data sets; however the data set using means produced results of less significance than use of complete data sets. This was the expected result because of the difference in number of data points used to calculate the error term and its accompanying degrees of freedom. The statistical analysis consist of three phases, each of them described below.

Phase I

Classify the dependent and independent variables. Run a model for the main effects to identify which variables are significant by their P-values. Finally, the most significant variable is identified as the one having the highest F- value. This analysis is performed using one response variable at a time.

Phase II

Run the model of main effects and interactions for each response variable. This phase identifies if any interaction between the main effect variables contributed significantly to the results. If a significant interaction was found, then the effect variable was paired with one significant main effect variable. To answer the question, "Are effects significant when one main effect is dominating?", the dominating main effect variable was removed and a model was run with the other two main effect variables to evaluate their effects.

Phase III

Removing the most significant main effect variable, a model was run with the other main effect variables, looking at their significance and comparing their means. If a main effect variable was significant, Duncan's comparison of means test was used to evaluate the significance of the main effect variable within the treatments performed for that effect. This test shows if any real significance exists between the means of the main effect evaluated.

Contact Angle

All the main effect variables were significant, but calendering was most significant as its F-value is an order of magnitude greater than pick-up or starch. The difference in calendering could be seen by looking at the Duncan's comparison of means where supercalendering had a 10^0 greater contact angle than hot soft nip calendering. Removing the impact of calendering, the effects of starch and pick-up on contact angle were identified. Pick-up was most significant and contact angle was found to increase with increase in pick-up. No significant difference between the starch types was found. Refer to Tables 9, 10, and 12 for details.

Gurley Porosity

All the main effect variables were significant, but calendering once again was the most significant effect as its F-value is an order of magnitude greater than pick-up or starch. The difference in calendering is seen by looking at the Duncan's comparison of means where supercalendering had greater Gurley porosity value than hot soft nip calendering. Removing the impact of calendering, the effect of starch and

pick-up on porosity was identified. Pick-up was most significant and porosity values were found to increase with increase in pick-up. Modified corn with alginate thickener was found to be the best among the starch types. Refer to Tables 9, 10, 12, 13, 14, and 15 for details.

Speck Counts

All the main effect variables were significant, but calendering was most significant effect and is an order of magnitude greater than pick-up, starch, and coat weight. The difference in calendering was be seen by looking at Duncan's comparison of means where supercalendering had less speck counts than hot soft nip calendering. Removing the impact of calendering, the effects of starch, silicone coat weight, and pick-up on speck counts were identified. Starch, coat weight, and pick-up were significant and speck count values were found to decrease with increase in pick-up. Modified corn with alginate thickener was found to be the best among the starch types. The counts were found to decrease as coat weight increased from 1 lb/ream to 1.5 lb/ream. Refer to Tables 9, 10, 16, 17, 18, and 19 for details.

Film Forming Capabilities and Clarity of Starches

The film forming capabilities of the starches were analysed by examining the films and looking at their flexibility and strength. Table 5 describes the flexibility and strength of various starch films. The starches, as discussed earlier, function as a surface size, closing the pores and voids present in the sheet. A starch film which is soft and most flexible is required. If the film is hard and brittle, it tends to erode easily, thereby rendering the surface sizing useless. The above results show that modified corn, tapioca, and modified corn with alginate form flexible, strong films

Table 5

Flexibility and Strength

Starch	Flexibility and strength
Rice	Soft and brittle
Pearl	Soft and brittle
Tapioca	Soft and most flexible
Potato	Hard and flexible
Modified corn	Soft and flexible
Modified corn/alginate	Soft and flexible

capable of providing a good surface sizing compared to rice, pearl, and potato.

The clarity of the starches was also studied apart from the film strength and flexibility. Table 6 shows the clarity of the starches measured by the opacity of the starch films.

Table 6

Clarity of Starches

Starches	Opacity Values (%)	
	40^0C	60^0C
Rice	7.9	7.8
Pearl	8.5	8.3
Tapioca	8.1	8.0
Potato	10.1	9.8
Modified corn	9.6	9.4

The clarity of the starches does not change with an increase in temperature. The opacity values at the two temperatures have no large variation, showing temperature has no large influence on clarity of starch.

Viscosity vs. Temperature and Viscosity vs. % Solids Study

The viscosity vs temperature data were determined for all the starches. The gelatinization temperature for the various starches was determined from the curve. The starches for this study were cooked at 8% solids. Figure 11 shows curves for the effect of temperature on viscosity for various starches.

The viscosity vs temperature curve below corresponds to the theoretical curve.

Figure 11. Effect of Temperature on Viscosity.

The gelatinization temperature ranges for the various starches were determined. These curves were obtained by measuring the viscosity in the cooling region. Due to the reorganization of the starch molecules, there is increase in viscosity with decrease in temperature. Table 7 shows the gelatinization temperature ranges for the starches.

Table 7

Retrogradation Temperature Range

Starch	Temperature Range (^{0}C)
Rice	61-78
Pearl	62-72
Tapioca	52-64
Potato	56-66
Modified corn	63-72

The effect of % solids on the viscosity was also studied with the use of Brookfield viscometer. With the increase in solids there is an increase in viscosity for all the starches. Water is required to disperse all the granules; with an increase in solids, not adequate water is available, which is the reason for the increase in viscosity. Figure 12 shows the variation in viscosity with % solids. The first phase involved the study of the film forming capability of starches and behavior of viscosity with temperature and % solids.

Influence of Starch Pick-up and Starch Type on Porosity

Starch pickup at the size press is dependent on basesheet absorbency, solution

Figure 12. Effect of Solids on Viscosity.

viscosity, and dwell time and pressure in the nip. To control the pickup of the sizing solution, the level of starch solids was increased from 5-10%. A 5, 8, and 10% level of starch addition provided pick ups of 25, 50, and 75 lb/ton, respectively. Figures 13- 15 show the influence of pickup and the starch type on basesheet porosity before calendering.

The modified corn starch with alginate thickener provided the maximum porosity for the uncalendered basesheet. For all starches, porosity decreased with pickup and calendering. Supercalendering decreased the porosity more than hot soft nip calendering, even though the samples were calendered to the same smoothness and gloss values.

As expected, Figures 14 and 15 show an increase in Gurley porosity values, or

Figure 13.   Influence of Pickup and Starch Type on Basesheet Porosity Before Calendering.

decrease in porosity, with starch pick up, regardless of the calendering method applied. It is known that starch pick up reduces the number of air voids present in the basesheet by filling the pores and voids present in the base sheet with starch. Since the Gurley porosity value is a measure of the rate of air flow through the sheet, a reduction in air voids present in the sheet reduces the air flow, hence increasing the Gurley porosity. The Gurley porosity was highest for the ethylated corn starch with alginate thickener. A comparison of the porosity values before and after the addition of alginate shows the addition of alginate to significantly decrease the air permeability through the basesheet.   It is believed that the addition of alginate improves the flexibility of the starch films, enabling the starch sizing solution to better fill the pores

Figure 14.   Influence of Starch Pickup and Starch Type on Porosity After Supercalendering.

in the basesheet. This was confirmed by comparing the flexibility of free films formed from the starch solutions on aluminum foil using a Mayer coating rod. Coat weights of 20 g/m^2 were produced to enable a free film of each sample to be formed without cracking or breaking. Although the films containing the alginate were observed to be more flexible, additional measurements using a dynamic mechanical analyzer are needed to quantify the difference in stiffness between the two starch films.

A comparison of Figures 14 and 15 shows the supercalendered sheets to be less porous. The porosities of the supercalendered sheets are lower because of the densification sheet.

Figure 15. Influence of Starch Pickup and Starch Type on Porosity After Hot Soft Nip Calendering.

Influence of Sizing Efficiency of Starches on Fluid Holdout

To determine the sizing efficiency of the starches, the porosity and fluid holdout of the sheets were measured. Generally, sizing efficiency is measured by determining the amount of starch required (pick up) to provide the desired porosity or silicone holdout value. The less starch required to reduce the porosity of the paper and improve holdout of the sheet, the better the sizing efficiency of the starch. Fluid holdout was determined by coating the samples with silicone, then staining the samples with a solution of iodine. Samples with poor holdout containing dark spots were counted using an image analyzer. Figures 16-19 show the influence of sizing

Figure 16. Influence of Sizing Efficiency of Starches on the Fluid Holdout for Supercalendered Sheets at 1 lb/Ream Silicone Coat Weight.

efficiency on the silicone holdout for the super and hot soft nip calendered sheets at three different levels of starch pick up (25, 50, and 75 lb/ton) and two different silicone coat weights, 1 and 1.5 lb/ream. The amount of starch applied is indicated next to each point on the graph to enable the influence of porosity on silicone holdout to also be examined.

Figure 16 shows a decrease in speck counts with a decrease in porosity. The fluid holdout increases with increase in pickup and sizing efficiency. The same trends are observed for the supercalendered (Figures 16 and 17) and hot soft nip calendered (Figures 18 and 19) samples at the two silicone coat weights of 1 and 1.5 lb/ream. A sheet giving fewer speck counts at a reduced level of silicone is considered to have better holdout. The silicone prevents the iodine solution from penetrating into the
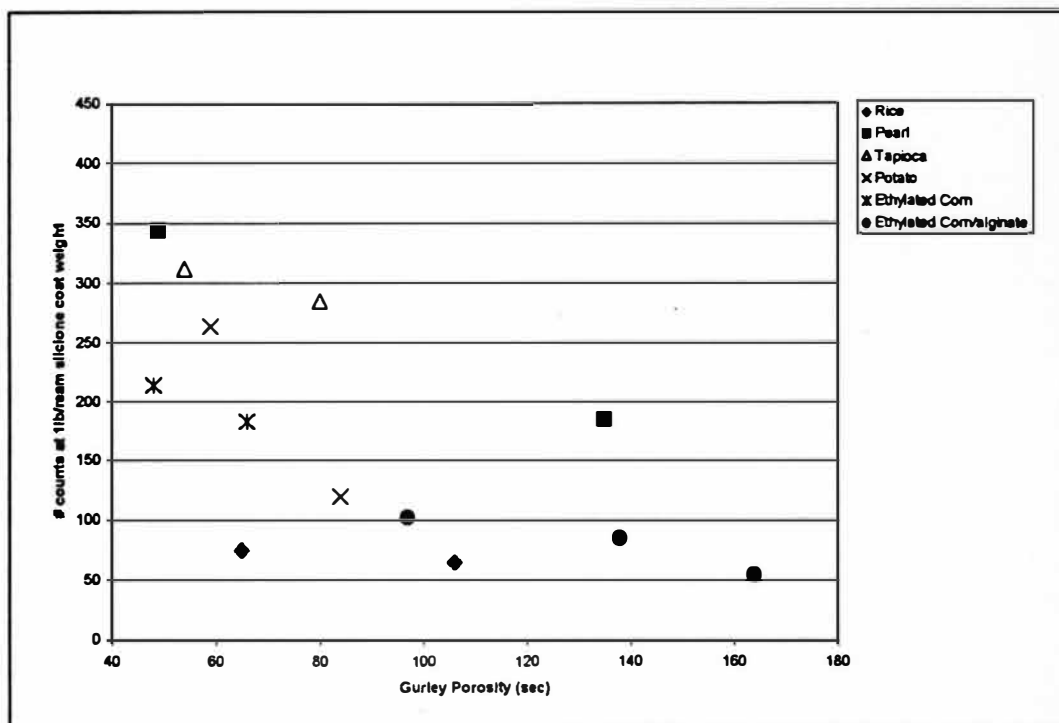
Figure 17. Influence of Sizing Efficiency of Starches on the Fluid Holdout for Supercalendered Sheets at 1.5 lb/Ream Silicone Coat Weight.

Figure 18. Influence of Sizing Efficiency of Starches on the Fluid Holdout After Hot Soft Nip Calendering (1 lb/Ream Silicone Coat Weight).

Figure 19. Influence of Sizing Efficiency of Starches on Fluid Holdout After Hot Soft Nip Calendering (1.5 lb/Ream Silicone Coat Weight).

starch layer, thus reducing the number of dark spots present after staining. The better the starch coverage, the less silicone required to cover the surface of the paper, thus, the better the appearance of the sheet after staining. Silicone holdout is desired to reduce the cost for obtaining the desired release properties.

It is observed that as the level of starch sizing increased, less silicone was required to produce a stained sheet with less dark spots (fewer counts). The higher the Gurley porosity values, the fewer the dark spots. Although the trend was the same for both the supercalendered and hot soft nip calendered sheets, with the modified corn with alginate providing the best holdout, the appearance of the supercalendered sheets were better, for all the starches tested.

Influence of Calendering on Fluid Holdout

Calendering changes the surface and interior properties of the sheet. During calendering, the sheets are passed through one or more nips formed between two rolls. The nip of a supercalender consists of a hard roll and a soft roll. Supercalendering produces a glossy, smooth sheet with a uniform density rather than a uniform caliper. The hot soft nip calender produces a sheet with a non-uniform density because the small scale fiber concentrations (flocs) are forced to occupy the same thickness as light-weight spots because the hard rolls concentrate pressure on the high points. Figures 20-23 show the influence of calendering on the fluid holdout for the supercalendered and hot soft nip calendered sheets coated with silicone at 1 lb/ream coat weight, at 25, 50, and 75 lb starch/ream. The differences between supercalendered and hot soft nip calendered sheets are due to the density differences resulting from the calendering process. The densification of the sheets during supercalendering resulted in the sheets being less porous. As a result, the silicone holdout improved. The influence of starch type was found to have less of an effect on silicone holdout than calendering. However, under the same calendering conditions, the type of starch used was found to also influence holdout.

A comparison of Figures 21-24, the speck counts for the various starches at the same coat weights, shows the ethylated corn/ alginate has a better fluid holdout, with minimum speck counts as compared with other starches. This indicates that the films formed on those sheets are uniform and continuous as compared to the other films.

Relationship Between Dynamic Contact Angle and Silicone Holdout

There is a considerable influence of calendering on the film properties.

Modified corn / Alginate

Modified corn

Pearl

Rice

Potato

Tapioca

Figure 20. Scanned Images – Supercalendered at 1.5 lb /Ream Silicone Coat Weight.

Figure 21. Influence of Calendering on Fluid Holdout for Supercalendered Sheets at Silicone Coat Weight of 1 lb/Ream.

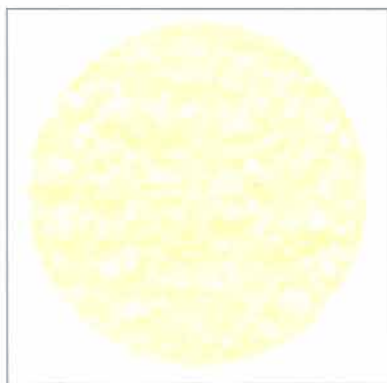Figure 22. Influence of Calendering on Fluid Holdout for Supercalendered Sheets at a Silicone Coat Weight of 1.5 lb/Ream.

Figure 23. Influence of Calendering on Fluid Holdout for Hot Soft Nip Calendered Sheets at Silicone Coat Weight of 1 lb/Ream.

Figure 24. Influence of Calendering on Fluid Holdout for Hot Soft Nip Calendered Sheets at Silicone Coat Weight of 1.5 lb/Ream.

Differences in the contact angle made by the silicone drop with the supercalendered sheets and hotsoft nip calendered sheets were found. An increase in the contact angle with an increase in starch pickup, and an increase in the pickup producing a uniform sizing on the base sheet with low surface tension was observed, thereby, preventing penetration by fluids. A significant difference in contact angle for the sheets calendered using the supercalender and hot soft nip calender was also found.

From Figures 25 and 26, the contact angle increase with the increase in the starch pick up and contact angle is found to be greater for the supercalendered samples compared to the hot soft nip calendered samples. The contact angle for the ethylated corn starch with the alginate (thickener) was the highest. This is because the alginate plasticizes the starch films, preventing them from breaking and making them more flexible. This reduces the speck counts and increases the fluid holdout.

Figure 25. Influence of Calendering on the Film Properties for Supercalendered Paper.

Figure 26. Influence of Calendering on Film Properties for Hot Soft Nip Calendered Paper.

The dynamic contact angle was measured with the silicone drop on the supercalendered and hot soft nip calendered sheets at various pick-ups. Figures 27 and 28 shows the variation of dynamic contact angle with increase in pick-up for various starches calendered by supercalender and hot soft nip calender.

As the starch pick-up increases more starch is laid on the surface, producing a surface with low surface tension, which causes an increase in the dynamic contact angle. The contact angle was higher for the sheets calendered using supercalender than hot soft nip calendered sheets. Supercalendering causes densification of the sheet and causes better ink holdout and produces surface with lower surface tension compared to the hot soft nip calender.

Modified corn starch with alginate (thickener) was found to have the surface

Figure 27. Influence of Pick-up on Dynamic Contact Angle (Supercalendered).

with lowest surface tension for both supercalendered and hot soft nip calendered sheet. There was a difference of 100 in the dynamic contact angle between the sheets calendered by hot soft nip calender and supercalender.

Figure 28. Influence of Pick-up on Dynamic Contact Angle (Hot Soft Nip Calendered).

CHAPTER V

CONCLUSIONS

From the experimental results obtained in this study, the following conclusions have been drawn:

1. Soft and flexible starch films provide better fluid holdout, thereby influencing release properties. Modified corn starch, modified corn starch with alginate thickener, and tapioca starch were found to form the most flexible and soft films compared to other starches.

2. Influence of starch type and pick-up on porosity studies show that there is an increase in porosity with increasing pick-up. The increase in porosity with increase in pick-up is due to more uniform and efficient surface sizing provided by the starch. Modified corn starch with alginate thickener was found to have maximum Gurley porosity values at each pick-up. This explains the uniform, efficient surface sizing provided by the starch, thereby covering the voids present in the sheets.

3. The study of the influence of sizing efficiency of the starches on the fluid holdout shows the modified corn starch with alginate thickener has the minimum speck count and maximum fluid holdout at 1 and 1.5 lb/ ream silicone coat weight. This can be explained from the soft, continuous, flexible nature of the starch of the starch film.

4. Studies on the influence of calendering show that supercalendering produces sheets with lower speck count values, better fluid holdout, and better release properties compared to sheets that were hot soft nip calendered.

5. The influence of calendering on the film properties were studied and the

results show that supercalendering produces sheets with better film properties and higher contact angles compared to sheets that were hot soft nip calendered. Supercalendering was found to produce better release properties compared to hot soft nip calendering.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDY

The results have shown the usefulness of image analysis to quantify silicone holdout and that the density of the basesheet is the overriding parameter influencing silicone holdout. Due to the expense of silicone, its holdout is one of the most desired properties by the manufactures of release grade papers. However, holdout cannot be obtained with materials that negatively impact the rate of silicone cure. Based on these findings, it is recommended that additional studies be performed to determine the parameters which most significantly effect the base sheet density. Future studies could be directed towards studying the use of non-wood fibers and wood fibers of varying coarseness. The contribution of formation and parameters influencing basesheet formation should also be studied.

In addition to basesheet density, the results also showed the addition of sodium alginate reduced the porosity of the basesheet, hence improving the silicone holdout. Additional studies are needed to understand the mechanism of his finding. Studies are needed to determine if the alginate alerts the distribution of the starch within basesheet, improves the flexibility of the starch film, and/or both. Fundamental studies are needed to determine the distribution of starch and alginate in the base sheet and to understand the influence of the distribution of the starch and alginate in the basesheet and to understand the influence of the distribution of starch on silicone holdout.

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APPENDICES

Appendix A

Phase I Data

Table 8

Classification of Dependent and Independent Variables

Main Effect Variables (Independent variables)	Response Variable (Dependent Variables)
Starch type (6)	Contact angle
Pick-up (3)	Gurley porosity
Calendering (2)	Counts
Coat weight (2)	

Table 9

Evaluation of Significant and Most Significant Variable

Response variable	Main effect variable	F- value	Pr < F $\alpha = 10$
Contact angle	Starch	7.54	0.0001
	Pick-up	47.38	0.0001
	Calendering	477.21	0.0001
Gurley porosity	Starch	34.77	0.0001
	Pick-up	49.60	0.0001
	Calendering	133.26	0.0001
Counts	Starch	7.95	0.0001
	Pick-up	17.96	0.0001
	Calendering	122.09	0.0001
	Coat weight	15.10	0.0001

Appendix B

Significant Effects and Interactions – Phase II

Table 10

Evaluation of Significant Interactions

Response variable	Main effect variable	F- value	Pr < F α = 0.10
Contact angle	Starch	7.70	0.0001
	Pick-up	48.38	0.0001
	Calendering	487.33	0.0001
	Starch*pick-up	1.44	0.1993
	Starch*calender	1.53	0.2006
	Pick-up*calender	1.89	0.1629
	Starch*pick-up*calender	0.24	0.9869
Gurley porosity	Starch	44.33	0.0001
	Pick-up	63.24	0.0001
	Calendering	169.91	0.0001
	Starch*pick-up	2.46	0.0111
	Starch*calender	2.73	0.0036
	Pick-up*calender	10.88	0.0001
	Starch*pick-up*calender	0.86	0.6304
Counts	Starch	9.54	0.0001
	Pick-up	21.57	0.0001
	Calendering	146.64	0.0001
	Coat weight	18.13	0.0001
	Starch*pick-up	0.34	0.9610
	Starch*calender	9.39	0.0001
	Starch*coat weight	2.54	0.0366
	Pick-up*coat weight	0.37	0.6890
	Pick-up*calender	2.40	0.0949
	Starch*pick-up*calender	0.76	0.6549
	Pick-up*weight*calender	0.54	0.6538
	Starch*pickup*weight	1.86	0.0638
	Starch*calender*weight	0.29	0.9193
	Starch*calender*pick-up*weight	0.29	0.9574

Appendix C

Evaluations of Other Significant Main Effect Variables and Interactions

Table 11

Evaluation of Significant Main Effects – By Calendering

Response Variable	Main Effect variable	F-value	Pr<F	α =0.10
	Supercalender			
Contact angle	Starch	5.36	0.0011	
	Pick-up	26.10	0.0001	
	Starch* pick-up	0.89	0.5480	
	Hot soft nip calender			
Contact angle	Starch	3.45	0.0180	
	Pick-up	24.81	0.0001	
	Starch* pick-up	0.73	0.6738	

Table 12

Evaluation of Gurley Porosity by Calendering

Response Variable	Main Effect variables	F-value	Pr<F	α =0.10
	Uncalendered base sheet			
Gurley Porosity	Starch	47.74	0.0001	
	Pick-up	51.56	0.0001	
	Starch* pick-up	5.56	0.5480	

Table 12 - Continued

Response Variable	Main Effect variables	F-value	Pr<F	α =0.10
	Supercalendered			
Gurley Porosity	Starch	13.31	0.0001	
	Pick-up	31.42	0.0001	
	Starch* pick-up	1.18	0.3233	
	Hot soft nip calendered			
Gurley Porosity	Starch	22.62	0.0001	
	Pick-up	13.90	0.0001	
	Starch* pick-up	1.43	0.1938	

Table 13

Evaluation by Calender/Pick-up

Response variable	Main Effect Variable	Pick-up	F-value	Pr<F	α =0.10
	Uncalendered base sheet				
Gurley porosity	Starch	25	9.32	0.0001	
		50	14.40	0.0001	
		75	27.64	0.0001	
	Supercalendered				
Gurley porosity	Starch	25	22.47	0.0001	
		50	5.14	0.0024	
		75	4.06	0.0144	
	Hot soft nip calendered				
Gurley porosity	Starch	25	12.90	0.0001	
		50	8.35	0.0001	
		75	8.37	0.0004	

Table 14

Evaluation by Calender/Starch

Response variable	Starch	Main effect variable	F-value	Pr<F α =0.10
		Uncalendered base sheet		
Gurley porosity	Rice	Pick-up	9.93	0.0029
	Pearl		23.15	0.0001
	Tapioca		14.49	0.0052
	Potato		7.54	0.0076
	Modified corn		3.78	0.0535
	Modified corn/alginate		14.32	0.0007
		Supercalendered		
Gurley porosity	Rice	Pick-up	13.16	0.0009
	Pearl		14.21	0.0007
	Tapioca		4.58	0.0647
	Potato		9.22	0.0037
	Modified corn		3.52	0.0627
	Modified corn/alginate		2.19	0.1550
		Hot soft nip calendered		
Gurley porosity	Rice	Pick-up	1.82	0.2046
	Pearl		3.54	0.0654
	Tapioca		3.20	0.1114
	Potato		1.09	0.3662
	Modified corn		2.86	0.0962
	Modified corn/alginate		5.01	0.0263

Table 15

Evaluation by Calendering/Starch/Coat Weight

Response variable = Gurley Porosity

Starch	Coat weight	Main effect variable	F-value	Pr < F α =0.10
		Supercalendered		
Rice	1	Pick-up	0.75	0.5136
Pearl	1		4.36	0.0677
Tapioca	1		0.09	0.7824
Potato	1		7.97	0.0205
Modified corn	1		1.74	0.2530
Modified corn/alginate	1		2.17	0.1959
Rice	1.5	Pick-up	3.5	0.0983
Pearl	1.5		0.79	0.4955
Tapioca	1.5		2.55	0.1859
Potato	1.5		15.29	0.0044
Modified corn	1.5		0.23	0.8021
Modified corn/alginate	1.5		5.09	0.0510
		Hot soft nip calendered		
Rice	1	Pick-up	0.67	0.8343
Pearl	1		3.16	0.1683
Tapioca	1		1.09	0.9645
Potato	1		0.97	0.1508
Modified corn	1		4.04	0.8740
Modified corn/alginate	1		0.13	0.3986
Rice	1.5	Pick-up	1.6	0.1435
Pearl	1.5		1.05	0.3452
Tapioca	1.5		0.75	0.1645
Potato	1.5		11.12	0.0578
Modified corn	1.5		3.52	0.9676
Modified corn/alginate	1.5		4.09	0.0923

Table 16

Evaluation by Calendering - All Interactions

Response Variable	Main Effect variables	F-value	Pr<F	α =0.10
	Supercalendered			
Count	Starch	29.95	0.0001	
	Pick-up	15.30	0.0001	
	Coat weight	27.88	0.0001	
	Starch* pick-up	1.52	0.1603	
	Starch*coat weight	3.33	0.0095	
	Pick-up* coat weight	3.16	0.0485	
	Starch*pick-up*coat weight	2.31	0.0251	
	Hot soft nip calendered			
Count	Starch	2.05	0.0831	
	Pick-up	9.41	0.0002	
	Coat weight	3.21	0.0777	
	Starch* pick-up	0.20	0.9937	
	Starch*coat weight	0.67	0.6494	
	Pick-up* coat weight	0.54	0.5835	
	Starch*pick-up*coat weight	0.63	0.7687	

Table 17

Evaluation by Calendering/Starch

Response variable	Starch	Main effect variable	F- value	Pr<F	α =0.10
		Supercalendered			
		Pick-up			
Counts	Rice		3.44	0.0610	
	Pearl		2.97	0.0843	
	Tapioca		0.63	0.4463	
	Potato		6.15	0.0121	
	Modified corn		1.94	0.1799	
	Modified corn/alginate		5.48	0.0175	

Table 17 – Continued

Response variable	Starch	Main effect variable	F- value	Pr<F α =0.10	
		Supercalendered			
		Coat weight			
Counts	Rice		13.20	0.0027	
	Pearl		9.42	0.0083	
	Tapioca		10.43	0.0103	
	Potato		0.85	0.3728	
	Modified corn		0.04	0.8485	
	Modified corn/alginate		40.06	0.0001	
		Hot soft nip calendered			
		Pick-up			
Counts	Rice		6.84	0.1276	
	Pearl		1.28	0.4387	
	Tapioca		15.07	0.1605	
	Potato		0.83	0.5479	
	Modified corn		22.24	0.0430	
	Modified corn/alginate		14.39	0.0650	
		Coat weight			
Counts	Rice		1.20	0.3870	
	Pearl		0.96	0.4305	
	Tapioca		31.23	0.1127	
	Potato		0.08	0.8050	
	Modified corn		0.06	0.8334	
	Modified corn/alginate		9.91	0.0878	

Table 18

Evaluation by Calendering/Pick-up

Response Variable	Main effect variable	Pick-up	F- value	Pr<F α =0.10
		Super calendered		
Counts	Starch	25	10.10	0.0001
		50	6.11	0.0006
		75	16.11	0.0001
	Coat weight	25	18.35	0.0002
		50	4.18	0.0502
		75	2.55	0.1231
		Hot soft nip calendered		
Counts	Starch			
		25	0.68	0.6436
		50	0.80	0.5602
		75	1.44	0.2519
	Coat weight			
		25	4.72	0.0381
		50	0.55	0.4653
		75	0.08	0.7783

Table 19

Evaluation by Calendering/Coat Weight

Response variable	Main effect variable	Coat Weight	F- value	Pr<F α =0.10
	Supercalendered			
Count	Pick-up	1	11.05	0.0038
		1.5	1.59	0.3110
	Starch	1	10.61	0.0014
		1.5	6.44	0.0082
	Hot soft nip calendered			
Count	Pick-up	1	14.01	0.0017
		1.5	9.21	0.0049
	Starch	1	2.50	0.1096
		1.5	4.35	0.0272

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