Influence of Starch Molecular Weight and Sodium Alginate on Silicone Holdout for Release Papers

Peter Suchy
INFLUENCE OF STARCH MOLECULAR WEIGHT AND SODIUM ALGINATE
ON SILICONE HOLDOUT FOR RELEASE PAPERS

by

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Peter Suchy, M.S.
Western Michigan University, 2001

This research was focused on determining the influence of applying one type of potato starch of various molecular weights on silicone holdout. Also, combinations of potato starch with a rheology modifier, sodium alginate, of low, medium, and high molecular weight were studied. The base paper employed was a commercially available paper generally used to manufacture release papers.

Sizing with low molecular weight potato starch is more effective for silicone holdout than sizing with high molecular weight potato starch. This study showed that the paper sized with low molecular weight potato starch has a smoother surface, lower permeability, and a smaller average pore size compared to paper sized with the high molecular weight potato starch. Thus, this paper provides better silicone holdout than was achieved by high molecular weight potato starch.

The addition of alginates to the starch solution decreased Gurley porosity significantly. In addition, the alginates decreased the average pore size; the decrease was more evident with the lower molecular weight alginates. Due to more favorable paper properties such as lower permeability, lower water penetration rate, smaller average pore size, the silicone agent is better retained on the surface of the paper. This could lead to decreasing the amounts of silicone applied to the sized paper, resulting in lower costs for silicone treatment.
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INTRODUCTION

Release papers (Figure 1) are specialty grades of papers; they possess the important properties of fluid holdout and non-sticking surfaces. In the food industry, where some packaging is required to provide such properties, release papers are employed. Another example of usage is the covering of the surface of the product to prevent the products from sticking together. Their advantage is that after applying the product and, consequently, being removed, there is no damage either to the product or to the package. The reason is that silicone coated surfaces possess a low surface energy which results in low adhesion in comparison to other surfaces.

As already mentioned, release papers are expected to have a low adhesive and impermeable surface. These properties are developed by several treatments of the base sheet, which includes surface sizing, calendering, and silicone coating. Of these three treatments, the silicone coating is the most important and expensive process.

In general, paper is a very porous material, not uniform, and readily penetrated by fluids; thus, there is a need to increase the resistance to penetration by fluids. Surface sizing is the first step in this process. It is the addition of materials at the size
press, which is used to fill the voids and pores of the base paper, makes the surface more uniform, stiffer, smoother, and, consequently, less permeable. The sizing agents commonly applied are starches due to their natural origin and abundance; starches generally have the lowest price of all sizing agents. To further reduce the permeability of the substrate for silicone sizing, calendering is used as the finishing operation, improving the smoothness and uniformity of the sheet while further densifying it.

The silicone sizing process imparts a very thin layer of the silicone compound onto the paper. Only a very thin layer is needed to provide the desired properties. The ultimate requirement of the substrate is to have proper silicone holdout, so that the silicone is retained on the surface and provides effective release properties at a minimal coat weight, hence cost. If the holdout is poor, silicone penetrates into the substrate, losing its ability to provide the proper release at a desired coat weight. Higher coat weights must then used, increasing the cost. Therefore, to avoid this occurrence, the substrates used to manufacture release papers should provide the best possible silicone holdout.

Production of release papers must be done as cheaply as possible. The amount of silicone employed must be minimized, but must still provide sufficient efficacy. Factors contributing to this are the base sheet characteristics (formation, porosity, absorbency), surface sizing agents, and calendering.

Presently, there are not many methods for assessing silicone holdout. The key properties of the substrate that affect the liquid penetration and sizing efficiency are porosity and smoothness. The papers with less porous surface structure and smooth surface should provide better substrates for silicone sizing, thus better release papers. The stain tests are important for determining the silicone hold out. The test is based on chemical reactions between the starch molecules and the testing liquid resulting in
a dark color stain. The more stained area after the stain test, the worse is silicone holdout. This is the result of allowing the testing liquid to penetrate through the silicone film and reacting with starch, producing the stain.

The objectives of this research are to evaluate the surface properties provided by potato starches and to evaluate the influence of alginates of various molecular weights combined with potato starch on silicone hold out and release properties.
CHAPTER II

LITERATURE REVIEW

Paper

Paper is a material made from cellulose fibers; it is very porous, being readily penetrated by air or liquids. The properties of the paper can be altered to obtain paper with the desired properties; so various paper grades are marketed. When choosing the right paper grade for release papers, the properties needed to meet the requirements of the release grade manufacture must be considered. The paper must be uniform, provide low absorption, and be smooth. Paper grades employed for release papers have a high density because of better absorption of the surface treatment than less dense grades, which have a tendency to not absorb the treatment properly. The most commonly used grades in the industry are glassine, parchment, and grease proof papers.

Surface properties of the base paper need to be improved. For this purpose, surface sizing is applied.

Surface Sizing

This operation is the addition of sizing agents onto the substrate's surface resulting in high fluid resistance, level surface, higher smoothness, reduced scuffing, and many other desirable properties (1). Surface sizing is a process in which the sizing agent is applied to the surface of the paper where it cements the fibers to the body of the paper and deposits a more or less continuous film on the paper surface.
Since the surface pores of the paper are sealed, the paper has an increased resistance to fluid penetration, better smoothness, and a reduced porosity.

The most important factors that govern the final performance of any sizing agent are pickup and the location of the product within the sheet. These factors in turn depend on the properties of the sizing agent and the web, and interactions between them. Some types of sizes soak into the paper rather than stay on the surface (location), thus it is important to know the characteristics of the sizing agent. The penetration of the fluids into porous substrates can be described by the Lucas-Washburn equation as follows:

\[
L = \frac{r \sigma \cos \Theta t}{2 \eta}
\]

Where
- \( L \) thickness of penetrated layer [cm]
- \( r \) radius of the capillary [cm]
- \( \Theta \) contact angle between the liquid and the boundary wall [degree]
- \( \sigma \) surface tension [dyne/cm]
- \( \eta \) viscosity of the liquid [poise]
- \( t \) time [s]

Roughness of the sheet surface has the largest effect on the rate of wetting and depth of penetration. Excluding the nature of the paper surface, penetration is also influenced by properties of the liquid. There are many methods for measuring the penetration, such as the Cobb test, roller, and inclined plane test.

The principal surface sizing agent used commercially is starch. Surface sizing agents can be applied in a size press, in a size tub, by spraying, as foam, or at the calender. Surface sizing is primarily concerned with surface films, and hence it is usually desirable to keep the size on the surface of the paper as much as possible. This
is particularly true when using expensive sizing agent such as PVOH, or functional coatings such as silicone. On the other hand, it is desirable on some grades of paper, when starch is the sizing agent, to obtain considerable penetration of starch into the paper to fill the internal voids of the paper. Commercial papers surface sized with starch vary from papers showing very little penetration to papers where the starch has penetrated completely through the sheet (2). Most commercial papers surface sized with starch have a somewhat uneven, discontinuous film of starch on their surface. A small amount of foam in size press starch solutions, or air displaced from voids in the sheet, tends to leave pinholes in the films that form.

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

Depending on the desired properties after sizing, different types of sizes with additives are used, each showing various rheological features. In respect to material variables, the characteristics of the size such as viscosity, solids content, and temperature are important. Also, the stability of the starch or retrogradation tendency is important.

The roll diameter controls the pick up, the roll loading and its ability to squeeze the size out of the web, and the crown roll are the machine variables. The hardness of the rolls also influences the pick up. The nip pressure and machine speeds affect the penetration of the size into the web. Also, drying is very crucial, because too rapid drying results in cracking, picking, or flaking problems.

The web variables include the surface properties and the web structure. The most important surface property is smoothness. The paper with the smoothest surface can better absorb the surface sizing and provide a more even film due to better solution transfer. The density, formation, pore size, basis weight, internal sizing, and
moisture content are the web structure characteristics. These variables are influenced by the amount of refining and fillers present. Highly refined pulp produces paper denser due to fibrillation and shortening of the fibers resulting in less porous material, which is less penetrated by liquids. The higher the amount of internal sizing, the less penetrable paper, and the wettability is decreased. With higher moisture content in the web, the free energy of the web is changed, and the rate of penetration is decreased. Optimal moisture content is 5-12%.

**Starch**

Starch is of the most widely distributed substances in nature and is the chief reserve carbohydrate of plants (4). Starch consists of tiny spherules or granules, and the size and shape are specific for each variety of starches (Table 1).

<table>
<thead>
<tr>
<th>Grain Characteristics of Some Starches</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starch</strong></td>
</tr>
<tr>
<td>Potato Tuber</td>
</tr>
<tr>
<td>Maize Grain</td>
</tr>
<tr>
<td>Wheat Grain</td>
</tr>
<tr>
<td>Tapioca Root</td>
</tr>
<tr>
<td>Waxy maize Grain</td>
</tr>
</tbody>
</table>
Starch is a polymer of periodically repeating alpha-D-glucose units (Figure 2). If the polymer is linear, connected only by 1-4 linkages, it is called amylose. If the polymer is branched also by 1-6 linkages, the polymer name is amylopectin. Almost every type of starch is composed of both of amylose and amylopectin.

![Figure 2. Unit of Glucose.](image)

Greenwood has concluded that the granule shape and size vary with the apparent amylose content (5). The amylose content is also a determinant factor in starch dispersion. The main sources of commercial starches are corn, potato, wheat, and waxy maize (6).

In the natural state, starch is insoluble in cold water. The starch granules and viscosity do not change in appearance until a critical temperature, the gelatinization temperature, is reached. At this point, which varies according to the starch type, granules start to swell due to water penetration and subsequent hydration of the starch molecule. Concomitantly, molecularly dispersed amylose is leached from the swollen granule. As a result, viscosity increases rapidly as the swollen granules come into contact and form a continuum throughout the medium. After achieving this temperature and continuous heating, the viscosity decreases due to bursting of the swollen granules. A point is reached in the dispersion process at which the swollen granules begin to disintegrate and the viscosity then decreases.

The crucial factors affecting the paste properties are the ratio of amylose and
amylopectin (Table 2), molecular weight, and cooking conditions. When cooking the starch, it is important to introduce enough energy to break down strong hydrogen bonds of the polymers of the starch. Generally, a minimum time of 20 minutes, temperature in the range of 93-95°C, a sufficient amount of water, and agitation are conditions required to cook the starch properly. Some types of starches, commonly with a high content of amylose need to be cooked under pressure in order to disrupt the bonds.

Table 2

<table>
<thead>
<tr>
<th>Starch</th>
<th>Amylose %</th>
<th>Amylopectin %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td>Maize</td>
<td>28</td>
<td>72</td>
</tr>
<tr>
<td>Wheat</td>
<td>26</td>
<td>74</td>
</tr>
<tr>
<td>Tapioca</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

Subsequent cooling of the pastes results in rapid viscosity increases and ultimately leads to gelling. When starch undergoes cooling, retrogradation takes place. Retrogradation is the reverse of dispersion, a process in which starch molecules tend to regroup into a form, which is less soluble and less adhesive than the gelatinized starch (4). The firmness of the gel and the rate of gelling are dependent
upon the amylose content. There are two types of retrogradation. Crystallizing occurs when the linear molecules of starch are allowed to re-associate. The second one, congealing, is caused by association of all the starch chains resulting in a three-dimensional entanglement.

Once the hydrogen bonds are disrupted and separated, the starch has gained the adhesive nature due to the large number of free hydroxyl groups capable of bonding with other polymers. If the groups are allowed to reassociate, the starch loses its ability to bond.

Starches are polymers with repeating units of glucose joined through hemiacetal or glycosidic bonds. The formula is identical to that of cellulose, but the starch repeating units are connected by alpha rather than beta bonds (Figure 3).

Figure 3. Shows Glucose both in the Linear Structure and in the Two (more stable) Ring Structures (mesomer structures).

Chemically (7), the starch consists of amylopectin (70-80 %) and amylose (20-25 %). The presence in starch of both linear amylose (Figure 4) and branched amylopectin (Figure 5) molecules with molecular weights of the order of several hundred thousand to several million, respectively, is another and important structural
difference from cellulose. The amylopectin is branched chiefly through the primary hydroxyl with one branched point for every 18 to 27 glucose. The hydroxyl groups of starch confer solubility in polar solvents including hot water. 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 (5).

Figure 4. Molecule of Amylose is a Linear Chain, Consisting of α-1-4 Linkage Glucose Units (1000 units).

Figure 5. Amylopectin linkage, D- Glucose Units Linked in the 1-4 Position Then Joined to Other Chains by 1-6 Linkages (100,000 units).
However, the familiar set back or gelling of concentrated starch solutions involves intermolecular hydrogen bonding of starch hydroxyls. The molecular size and the amount of the amylose component determine the severity of the starch paste gelling (Table 3). The properties of the gel also depend on the molecular weight and distribution. Table 3 provides information about the giration radius, Rg, for amylose and amylopectin. The giration radius is a measure of the size of the molecule. In fact, it is the average distance from the 'edge' of the polymer to the middle of the mass.

Table 3

Molecular Index Numbers of Some Starches

<table>
<thead>
<tr>
<th>Starch</th>
<th>Rg [nm]</th>
<th>Branches / molecule.</th>
<th>Units / branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize</td>
<td>19 213</td>
<td>2800</td>
<td>248</td>
</tr>
<tr>
<td>Amylomaize</td>
<td>60 238</td>
<td>560</td>
<td>759</td>
</tr>
<tr>
<td>Potato</td>
<td>32 224</td>
<td>565</td>
<td>665</td>
</tr>
</tbody>
</table>

Potato starch has a relatively strong anionic character due to the presence of the naturally occurring phosphate groups (Table 4). With potato starch, phosphorus occurs as a phosphate group esterified to an alcohol group on the starch. The phosphate group is responsible for the high viscosity of the potato starch and also makes the starch solutions more stable. These charges prevent ready reassociation in solution, thereby retarding retrogradation and related gelling. The presence of the
charged groups also prevents close molecular associations that otherwise would resist hydration during cooking. This property is evident in the remarkable swelling power of the potato granule.

After the native starch has been prepared, it is frequently modified or altered in some ways to make the starch more suitable for some particular use. Physical, chemical, and genetic modifications and combinations of these have been invoked to enhance the useful properties of starches.

Table 4

<table>
<thead>
<tr>
<th>Starch</th>
<th>Moisture, %</th>
<th>Fat, %</th>
<th>Protein, %</th>
<th>Phosphorus, %</th>
<th>Smell / Taste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>19</td>
<td>0.1</td>
<td>0.10</td>
<td>0.08</td>
<td>neutral</td>
</tr>
<tr>
<td>Maize</td>
<td>13</td>
<td>0.8</td>
<td>0.35</td>
<td>0.02</td>
<td>strong</td>
</tr>
<tr>
<td>Wheat</td>
<td>13</td>
<td>0.9</td>
<td>0.40</td>
<td>0.06</td>
<td>strong</td>
</tr>
<tr>
<td>Tapioca</td>
<td>13</td>
<td>0.1</td>
<td>0.10</td>
<td>0.01</td>
<td>neutral</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>13</td>
<td>0.2</td>
<td>0.25</td>
<td>0.01</td>
<td>medium</td>
</tr>
</tbody>
</table>

These modifications vary in degree from those in which practically no chemical change results in the molecules, which make up the starch granule to those in which a significant change can be detected. Subsequently, two types of modifications of starch are found: conversion and chemical derivatization.

1. Conversion is the process, by means of enzymes, oxidizing agents, or
mechanical action, whereby the starch chains are degraded, resulting in shorter chains. The natural starches commonly have high viscosity, which during sizing is a big concern. By degrading long starch chains into shorter ones, the viscosity is decreased proportionally, and a starch with lower viscosity, molecular weight, and better rheological properties is obtained.

2. Chemical derivatization treats the starch with chemical agents resulting in substituting some functional groups of the starch for other ones. The intent is to improve the starch features. In many cases, there is an effort to impart more hydroxyl or carboxyl groups, so that the starch provides better adhesive properties, is more stable, and has a lower tendency to retrograde.

The viscosity can be altered by addition of a rheology modifier (thickener). Generally, thickeners increase the viscosity, and impart some other surface properties, such as flexibility, pick up, and smoothness. Sodium alginate is a typical thickener employed in the industry.

**Alginate**

Algin or alginic acid is a high molecular weight carbohydrate polymer, glycuronan, comprised solely of D-mannuronic acid and L-guluronic acid, obtained from a certain type of seaweed growing off the West Coast of the United States. Alginic acid is insoluble in water, but it contains a high percentage of carboxyl groups that can be reacted with alkali to produce water-soluble salts known as alginates. Industrially, the most important water-soluble derivatives are sodium and ammonium alginates.

Because of its high molecular weight and molecular rigidity, sodium alginate forms solutions of unusually high apparent viscosity, even at low concentrations (8).
Algin polymers react with most polyvalent cations to form crosslinkages. As the amount of the cation increases, the algin solution thickens, gels, and precipitates due to the interactions between the alginate molecules, which produce a three-dimensional structure.

Alginates are employed for surface sizing alone or in combination with starch and other sizing agents. Also, alginates tend to remain on the surface when applied, provide very viscous size, and thus can be employed at lower concentrations.

Alginates are also used in the food and general industry because of their unique colloidal behavior and their ability to thicken, stabilize, emulsify, form films, and gels (8).

Calendering

The goal of this mechanical treatment is to develop smoothness, gloss, uniform layer, and densification. The basic principle of this operation is that the surface of the web mirrors the surface of the rolls in which it comes in contact. Compression and temperature of the nip are responsible for the reorganization of the structure of the substrate altering some properties. There are several factors influencing the overall characteristics:

1. Nip pressure is the one with the largest impact; the higher the nip pressures, the greater the tendency to develop higher smoothness and gloss.

2. Temperature softens the fibers, and coats and allows them to more easily achieve the desired features.

3. Moisture helps the substrate to be more compressible; thus, a higher moisture content provides better results.

4. Time; the faster the process runs, the less time the substrate can be
calendered; therefore, inferior results are obtained.

5. The roll smoothness and number of nips have a crucial affect as well.

In calendering, various types of nips are employed, with different types of rolls and conditions. Roll selection is based on the substrate type and desired characteristics. The calenders most commonly used for release grades are supercalenders, which densify and smooth the sheet.

**Silicone Sizing**

The goal of any surface sizing process is to achieve a desired final property at minimum cost of materials. Barrier coatings serve to minimize the penetration of the expensive functional coating (9). The barrier coating in release papers is mostly starch with other additives, and usually is applied by a conventional flooded nip size press, which actually saturates the paper with the barrier coating. By doing this, the penetration of the expensive coating is minimized.

Sizing agents used for producing release papers are silicone polymers, which are expensive. Silicones have the important property of making paper highly water resistant when applied in thin films. Silicone agents employed in sizing are commonly organosilicone polymeric compounds (polysiloxane). The structure of these agents can be described as a periodically repeated Si-O-Si unit, where each atom of Si possess two functional groups, e.g., methyl or ethyl (10). As a coated layer, the oxygen atoms tend to hydrogen bond to the paper substrate, and the methyl groups become oriented to the surface and present very low surface energy. Silicones used for release coatings are supplied in solvent solution or aqueous emulsion form. The former one generally provides better release properties. Curing is needed in the
drying stage to make the coating adhere to the substrate and to prevent it from being labile.

There is great variety of silicone products with different properties, depending upon the functional groups on the Si atoms. In general, silicones can withstand high temperatures, resist chemical degradation, have low flammability, have high surface activity, and exhibit a hydrophobic character. Silicone coating, which forms a plastic film on the surface, is in reality a chemical reaction, a condensation (Figure 6), of the silicone polymer and a cross-linker. It requires the action of catalyst and high temperature (11). Tin, zinc, zirconium, and titanium are common catalysts employed. Enough heat and time has to be provided to the reaction to assure a complete reaction between monomer and crosslinker. Depending on silicone coat weight, the longer time is needed with the higher coat weight. This is the last stage of manufacturing release papers.

![Figure 6. Example of a Condensation Reaction.](image-url)
Theory of the Penetration of the Liquids

This theory deals with interactions between liquid and the paper. There are two stages of interaction: wetting of the surface and penetration of the liquid into the paper resulting in swelling (12). The drop of liquid on the surface alters its shape to reach an equilibrium of forces on the surface as described by Young's Equation:

\[ \delta_{sg} - \delta_{sl} = \delta_{lg} \cos \theta \]

Where \( \delta_{sg} \) is free energy of the solid-vapor interface [dyne cm]
\( \delta_{sl} \) is free energy of the solid-liquid interface [dyne cm]
\( \delta_{lg} \) is free energy of the liquid-vapor interface [dyne cm]
\( \theta \) is the angle of the contact of the liquid [degrees]

Figure 7. Exaggerated Drop of Liquid on the Surface in Equilibrium.

When the angle \( \theta \) is less than 90°, the sheet is said to be wettable. When the angle is greater than 90°, the sheet is non-wettable due to the low surface tension (provided by silicones).
Penetration is the flow of the liquid through the pores, the driving force is pressure as described by Kelvin’s Equation:

\[ p = 2 \delta_g \cos \theta / r \]

- \( p \) is the driving pressure [dyne]
- \( \delta_g \) is free energy of the liquid-vapor interface [dyne cm]
- \( \theta \) is the angle of the contact of the liquid [degrees]
- \( r \) is the radius of the pore [cm]
CHAPTER III

STATEMENT OF PROBLEM AND OBJECTIVE

Release papers are specialty papers that play a niche role in the paper industry due to their low adhesive surface resulting in the property of not sticking to other surfaces. This ability of the paper is imparted by the specialty treatment; silicone agents are employed to remove tackiness. There are two aspects influencing this treatment that must be taken into account. The first is the surface characteristics of the substrate, and the second is the effort to employ silicone agents in the most effective manner due to the cost of the silicone. Generally, paper is a very porous material, not uniform, and readily penetrated by fluids; thus, there is a need to increase the resistance to penetration by fluids. The remedy is to pre-treat the base paper with surface sizing, and, subsequently, to calender the sized paper. As surface agents, many starches are applied due to their low price and abundance.

There are many types of starches, unmodified or modified, with different characteristics such as the amylose:amylopectin ratio, granule dimensions, gelatinization temperature, and molecular weight. Consequently, each type exhibits unique properties as a sizing agent. Also, with the addition of a rheology modifier into the starch dispersion, the final substrate features are influenced and changed.

The objective of this research is to determine the influence of applying one type of starch, potato starch, having various molecular weights (Emcoat K85, Emcoat K55, Kalamazoo Paper Chemicals, Kalamazoo, MI), in combination with a rheology modifier, sodium alginate, having low, medium and high viscosity (S700, S300, S100, SNP, Durham, NC), on silicone holdout.
CHAPTER IV

EXPERIMENTAL DESIGN AND METHODOLOGY

The purpose of this experiment is to determine the effect of the molecular weight of potato starch and the influence of the addition of the sodium alginate of different molecular weights on the release properties of the paper, especially on silicone holdout. The schematic representation of this experiment is shown on Figure 8.

Firstly, the starches were checked for viscosity. It was conducted on a Rheometrics Dynamic Stress rheometer under controlled conditions of temperature and shear. The relationship of viscosity to temperature was determined. This step was important to obtain the temperature range in which the viscosity values fell for an application on a pilot flooded nip size press between 140 -170 cP. The temperature range of 120-140 °F was found to be suitable for starch application at the size press.

Initially, solutions of potato starches of various molecular weights with and without combinations of sodium alginate at low, medium and high viscosity were prepared. Potato starch and alginates were added and dispersed in cold water under agitation. The amount of starches and alginates used were based on four desired pick ups in the range of 25-100 lb/ream. The amount of alginates was kept constant at 5 % of the dry weight of the starch. The percentage of solids was between 4-17 %. Jet-cooking was employed for cooking the solutions due to its ability to disrupt the granules of starches thoroughly, thus assuring proper cooking, and due to the fact that it is a less time consuming process. The starch solutions were applied immediately after cooking.
The base sheet was first surface sized with high molecular weight starch at four different pick ups, then the process repeated with the starch in combination with high molecular weight alginate, followed by combination with medium molecular weight alginate, and eventually with low molecular weight alginate. For each combination, four pick ups were obtained in the desired range of 25-100 lb/ream. The same procedure was repeated for the low molecular weight starch.

**Figure 8. Experimental Design Diagram.**
The samples were calendered on the pilot supercalender located at the Plainwell Paper Corporation, Plainwell, MI. The calendering was performed on samples 12 by 12 inch square at 200°F and 200 psi. Four passes were made through the calender nip while changing the sides and directions. The roughness and porosity measurements of the samples were performed on a Parker Print tester, Model No. ME-90. For the roughness readings, a soft-backing plate was used at 500 and 1000 psi. The Gurley porosity measurements were performed at 2000 psi.

The mercury porosity measurements were performed on a Micromeritics Autopore II 9220. The pore size distribution and the average pore diameter were obtained. The contact angles were determined with a First Ten Ångstroms DCA instrument with water as a testing liquid.

As a new method of evaluating the paper and its interactions with the liquids, the ultrasound transmission measurements performed on a Emco DPM 30 were employed. The principle of this measurement is based on detecting the dynamic interaction between liquids and paper. When the paper is immersed into the liquid, the absorption takes place. The absorption process basically involves the physical and chemical interactions between the liquid and substrate. During the absorption, structural and material changes may occur to the substrate. Because the ultrasound is transmitted through the dry paper via the fibers, any physical change to the fiber and ingredients of the paper through reflection, absorption, or dispersion has an effect on the transmission (13). The ultrasonic transmission is very susceptible to changes in the modulus of elasticity of the paper while absorbing the water.

The sheets were silicone sized at Dow Corning Corporation, Midland, MI. Each sample was silicone coated at three pick ups in the range between 0.5-1.5 lb/ream. The silicone used was Syl-Off(R) 7676 Coating in combination with 7678
Crosslinker. The silicone and crosslinker were mixed in a ratio of 20 parts of the 7676 Coating and 0.94 parts of the 7678 Crosslinker. The silicone was then applied to the paper using a Euclid Tool & Die Co. blade coater at various blade pressures to obtain the desired coating weights. The samples were then cured in a Bluemax Oven for 30 seconds at 220° F. The Bluemax Oven has a dual drying zone for a total length of 6 feet. The silicone cure test was performed by measuring the tape adhesion properties to determine the cure of the film. The silicone cure test also enables a determination, if there is any silicone migration. The measurement is based on measuring the resistance of tape to being pulled apart from it. It is measured by applying the tape onto the surface, pulled off and both ends put together and pulled apart. This resistance provides information about migration of silicone.

The release was pulled at 400 inches per minute on the Instrumentors ZPE 1000 Peel tester. Results are in grams per inch width. There are several factors that affect release, one is the coating coverage and the other is cure. Some of the samples with higher coat weight also have higher release. This could indicate that the cure on these samples may have been part of the cause for the higher release as the adhesive interacts with uncured SiH in the coating; thus, the higher the coat weight, the more SiH and the higher is the release. That makes it more difficult to just compare release to coating coverage/holdout.

The coat weights were determined with an Oxford Instruments Lab-X 3000 EDRF (X-Ray) unit calibrated for silicone coat weights. Results are in pounds per 3000 square feet. Samples were tested for dye penetration with Shirlastain "A" dye using a Cobb Ring set for two minutes and then blotted dry. If the sheet was not uniform in silicone coverage, the solution would penetrate and react with starch, resulting in a dark brown color. Sheets with many brown spots indicate poor silicone
coverage.

The image analyzer at the Paper, Printing Science, and Engineering Department, Western Michigan University, was used to evaluate the samples from the stain test. The stained areas representing the samples were magnified and the percentage of the stain areas compared to the whole investigated area was obtained. The lower percentage of stain represented better silicone hold out.

The last step was to record roughness and porosity of the silicone coated samples. The conditions for these tests were kept the same.
CHAPTER V

RESULTS AND DISCUSSION

The objectives of these experiments were to determine the influence of starch molecular weights and the effects of alginates of various molecular weights on the sizing efficiency and silicone holdout of potato starches.

The base paper employed had properties as follows: CSF 520 (T 227), caliper 0.0004 inch (T 551), brightness 84 (T 452), smoothness 6.43 microns at 1000 psi (Parker smoothness), 89.5 % dry weight, Hercules test 1s (T 530), basis weight 68 g/m² (T 220), average fiber length 0.54 mm (T 271), ash content 1% (T 211).

Influence of Molecular Weight of Starch on Roughness

The level of solids of the starch solution, which was in the range of 4-17 %, controlled the pick up on the size press. The paper was sized with potato starches. The starch with the highest average molecular weight employed was Emcoat K85 and the starch with the lowest molecular weight was Emcoat K55. After calendering, the roughness was recorded for both of the starches at 500 and 1000 psi. This was conducted to determine the compressibility of the substrates by dividing the roughness readings at 1000 psi with readings at 500 psi. The closer the value is to 1, the stiffer, or less compressible, is the surface of paper. The base paper had roughness readings of 6.70 and 6.30, respectively, and a compressibility factor of 0.94. When comparing the compressibility of the papers sized with both the potato starches at the same pick up, the potato starch with higher the molecular weight seems to provide a
slightly less compressible film (Figure 9). This may be an effect of the molecular weight of the starch, indicating that the lower molecular weight starch provided more flexible and compressible films.

Figure 9. The Compressibility of Paper Sized with Both Potato Starches After Calendering at 70 lb/ton and 50 lb/ton Pickups.

Influence of Addition of Alginates on Roughness

The combinations of alginates, rheology modifiers, and potato starch changed the roughness and compressibility factor. The solutions with alginates S700 and S300 provided higher roughness, but lower roughness than with alginate S100 (Figure 10). The comparison is based on 70 lb/ton pick up. The high and medium molecular weight alginates have the tendency to provide more solid and rougher films. On the other hand, the low molecular weight alginate seems to improve the roughness, while maintaining or improving the flexibility of the film. This can be concluded when comparing the compressibility of the papers sized at 70 lb/ton (Figure 11).
Figure 10. Effect of Alginates in Combination With LMW Starch on Roughness of the Paper Sized With 70 lb/ton After Calendering.

Figure 11. Comparison of Compressibility of LMW in Combination With Alginates S700, S300, and S100 at 70 lb/ton Pick up.
The tendency of the roughness is to decrease with the molecular weight of alginates. The effect of the molecular weight of alginates on roughness and porosity tends to be the same as observed for the potato starches. That is, with higher molecular weight alginate, the films are rougher and stiffer.

**Influence of Molecular Weight of Starch on Porosity**

With a surface sizing process, the pores and voids become filled by the size, thus making the paper more fluid resistant and less permeable. As expected, the Gurley porosity decreases with the pickup (Figure 12). The lower molecular weight starch decreased the Gurley porosity more efficiently as evidenced by the slope of the two lines. This may be because the lower molecular weight starches are able to penetrate deeper and fill more small voids compared to the higher molecular weight starches that are mostly retained on the surface.

![Figure 12. Influence of Molecular Weight of Starches on Gurley Porosity at Different Pick ups](image-url)
The HMW starch seems to provide less permeable papers at low pick-ups than LMW starch. The reason could be in the ability of the HMW starch to better fill up the large voids in the paper than LMW starch does. At higher pick up, the permeability comes down to small pores, which are better covered by the LMW starch. Thus, the Gurely porosity is lower for the paper sized by LMW starch.

**Influence of Addition of Alginates on Porosity**

When the starches were mixed with alginates, the Gurley porosity decreased significantly with pickup (Figure 13, and 14). The alginates seem to close up the structure of paper more effectively compared to the starch films, thus making the paper less permeable.

![Figure 13. Effect of Alginates Combined With LMW Starch on Gurley Porosity.](image)

For both types of potato starch combined with alginates, the tendency of the decrease in porosity of the paper was similar, without significant differences between the alginate types (Figure 15).
Figure 14. Effect of Alginates Combined With HMW Starch on Gurley Porosity.

Figure 15. Gurley Porosity Comparison of Potato Starches, HMW and LMW in Combination With Alginates.
Pore Size Distribution of the Sized Paper

The pore size distributions of the sized samples were determined with a mercury porosimeter. This experiment was performed to indicate the extent of the decrease of the pore size with the sizing process. As expected, the sizing process decreased the amount and size of the pores of the base paper. The most significant decrease of the pore size of the paper was observed for the pores with the largest diameter (Figure 16). Also, the number of the pores with a diameter in the range of 1-3 micrometers decreased.

Figure 16. Pore Size Distribution of the Base Paper Compared to the Paper Sized With Both HMW and LMW Potato Starch at 70 lb/ton Pick up.

The difference between the LMW and HMW potato starch is not significant, although the use of LMW seems to provide films with a lower number of pores in the range of 1-3 micrometers. The reason could be in the ability of the LMW potato starch to better penetrate and fill small voids.
The effect of the alginates combined with the potato starch on the pore size is evident. The alginates tend to decrease the pore size of the paper. The alginates with lower molecular weight provide films with the smallest pore sizes (Figure 17).

Figure 17. Effect of Alginates on Pore Size Distribution at 70 lb/ton Pick up.

**Ultrasonic Transmission Measurement**

When paper is immersed into water, the interactions include the liquid absorption by the fiber and destruction of the hydrogen bonds between fibers (13). Sound is transported by the fibrous composite. During these interactions, a change in modulus and compression of fibers occurs. This leads to a decrease of the ultrasound amplitude at the penetration. The initial rise of the signal is caused by air, which absorbs the sound and is eventually displaced by water (13). As expected, the base paper was the most absorbent, and was almost immediately soaked. There was not a significant difference between LMW and HMW starch (Figure 18). The alginates decreased the penetration of water significantly (Figure 19).
Figure 18. Comparison of the Penetration Rate of Base Paper and Paper Sized With Both Potato Starches at 70 lb/ton Pick up.

Figure 19. Effect of the Alginate on the Penetration Rate; Comparison Based on Papers Sized at 70 lb/ton.
EDX Analyses

EDX analyses are usually performed on a Scanning Electron Microscope and can be used to determine chemical composition for regions as small as 0.1µm at low voltage, even smaller for elements of high atomic number. The depth of analysis also can be as little as 0.1µm or, again, much less for elements of high atomic number. These two parameters are functions of the beam voltage and the sample composition. In this process, the sample is bombarded with a beam of electrons. The energy of the beam is typically in the range 10-20 keV. Occasionally, one of the incoming electrons will knock a core shell electron loose and a second electron will fall into its place, losing some energy in the process, which is given off as a photon of energy in the X-ray range. The energy with which it leaves the atom is a function of only the energy levels of the 2 electrons of the atom and so is characteristic of the particular set of interactions and the element. The energy of the X-rays emitted depends on the material under examination. Thus, by knowing the energy of the X-ray photon, one can determine from what element it was emitted.

The EDX analyses were employed to investigate the surfaces of the starch sized paper and paper sized with starch in combination with alginate. The analyses of the surfaces of the papers showed the presence of the calcium on the surface of the paper sized with starch in combination with alginates. The spectrum of the paper sized only with starch showed no presence of the calcium, (Figure 20, 21). The alginates generally contain high amounts of the calcium. The presence of the calcium in the spectrum of the sample may be the result of the alginate that is retained on the surface of the paper. Thus, the alginates seem to not penetrate into the structure of the paper, but tend to retain on the surface.
Figure 20. EDX Analyses for the Paper Sized With HMW Potato Starch.

Figure 21. EDX Spectrum for the Paper Sized With HMW Potato Starch in Combination With HMW Alginate.
Influence of Sizing Efficiency of Starches on Fluid Holdout

To determine the efficiency of silicone sizing, the Gurley porosity, strip test and fluid holdout of the silicone-sized paper were measured. Paper was sized with silicone in a range of 0.5 - 1.5 lb/ream. The lower is the porosity of the sized paper, the lower is the migration of the silicone agent into the structure, resulting in proper release properties. With the higher starch pickup, the porosity of the silicone sized paper decreases rapidly (Figure 22). This figure shows the relationship between the silicone coat weight and porosity of the paper sized with LMW starch. The starch pick ups were 78, 64, and 50 lb/ton. In other words, it shows that paper sized with higher pickups of potato starch provide lower Gurley porosity after silicone sizing.

![Figure 22. Influence of Starch Pick up of LMW Potato Starch (Emcoat K55) on the Gurley Porosity After Silicone Sizing.](image)

When comparing the Gurley porosity values of the silicone treated papers sized with both potato starches at the same starch pickup, 70 lb/ton, differences were
observed. The low molecular weight potato starch provides less permeable films when silicone coated with the same amounts (Figure 23).

![Figure 23. Comparison of Gurley Porosity Provided by Both Potato Starches at 70-lb/ton of Starch Pickup and 1.15; 1.0 lb/ream of Silicone.](image)

As already mentioned, starches combined with alginates provide more flexible films, which impart better overall surface properties to the substrate. As a result, the papers possess lower Gurley porosity compared to papers sized with pure starch solutions before and after treatments with silicone. The influence of alginates on porosity of the paper after silicone treatment is shown in Figure 24. The base paper was sized with a LMW potato starch in combination with a high, medium, and low molecular weight alginate at 50 lb/ton pickup. The Gurley porosity of the silicone treated samples decreased significantly. The same effect was observed for HMW potato starch in combinations with alginates at 70 lb/ton pickup (Figure 25).
Figure 24. Influence of Alginates Combined With LMW Potato Starch at 50 lb/ton Pick up on Gurley Porosity After Silicone Sizing.

Figure 25. Influence of Alginates Combined With HMW Potato Starch at 70 lb/ton Pick up on Gurley Porosity After Silicone Sizing.
An influence of alginates on porosity after silicone sizing is evident while the difference between the particular types of alginates is not significant.

Strip tests were performed to determine the coating coverage. The values of the release are expected to decrease with higher silicone pickup. There are several factors that affect release, one is the coating coverage and the other is cure. Some of the samples with higher coating weight also have higher release. This could indicate that the cure on these samples may have been part of the cause for the higher release as the adhesive interacts with uncured SiH in the coating; thus, at high coating weight, more SiH means higher release. That makes more difficult to just compare release to coating coverage/holdout. Figure 26 shows the release values of the paper sized with the high molecular weight potato starch at four pickups: 109, 68, 50, and 33 lb/ton, which was silicone coated with 1 lb/ream of the silicone agent. As expected, the release shows an increasing trend with lower pickups of starch.

![Graph](image)

Figure 26. Comparison of Average Release Values of the Paper Sized at Different HMW Starch Pick ups and Silicone Sized by 1 lb/ream of Silicone.
The addition of alginates changed the release properties; the alginates provide more uniform coverage, which resulted in an increase in silicone holdout. In other words, the release properties decreased with the addition of alginates. Figure 27 shows a comparison of the release values of the high molecular weight potato starch at pick up of 70 lb/ream and 1.1 lb/ream of silicone coat weight. The differences between the particular alginates employed are not significant. Due to the reasons mentioned before, it is hard to elucidate the exact relationship between the molecular weight of alginates, starches and the release properties.

![Figure 27. Effect of Alginates on Release at 70 lb/ton Starch Pick up and 1.1 lb/ream of Silicone Coat Weight.](image)

After performing the stain test, the samples were analyzed with an image analyzer. The stained area was compared to the overall area, and the percentage of stain was determined. The lower the values of the percentage of stained area, the better are the release properties of the substrate. The coat weight of silicone played a very important role in this test. If the amount of silicone applied was not sufficient to
evenly cover the surface structure of the substrate, the stain area increased. The reason is that the low coat weights of silicone provide only a very thin and not uniform film. Thus, the iodine based testing liquid readily penetrates and reacts with the starch, resulting in dark spots. Consequently, the surface properties of the substrate before silicone treatment are very important. The fact is that with higher pick ups the substrate possesses a rougher surface and lower porosity. With high molecular weight starches at high pick ups, the point may be reached when roughness of the paper will increase such that the low silicone coat weights are not able to provide sufficient coverage. Figure 28 shows the relationship between the starch picks up and the stained area. The comparison is based on paper sized with LMW potato starch at pick ups of 78, 62, and 51 lb/ton silicone treatment with 0.6 lb/ream of silicone.

![Bar Chart](image)

Figure 28. Influence of Potato Starch Pick up on Stain %.

Comparing the effect of molecular weights of potato starches on stain area, as expected, the LMW starch resulted in less stained area. This was the result of a
smoother and less porous substrate obtained by using the LMW starch as a sizing agent. Subsequently, the paper absorbed the silicone treatment more effectively. The stained areas of paper sized with both potato starches at 70 lb/ton and silicone treated with 1.0 and 1.15 lb/ream of silicone were compared (Figure 29).

The starch solutions combined with alginates provided better performance compared to the pure starch solutions. There were less stain areas on samples sized with starch in combinations with the alginates, indicating that the addition of alginates improves silicone coverage. Figure 30 shows the % stain area of the paper sized with the HMW potato starch in combination with the alginates at a pick up of 70lb/ton, after silicone treatment with 1.1 lb/ream of silicone agent. Figure 31 represents the paper sized with LMW potato starch and alginates with a pick up of 50 lb/ton and silicone treated with 0.8 lb/ream of silicone agent. Both figures show a tendency of the stain area to decrease with the molecular weight of the alginate.

Figure 29. Effect of Molecular Weight of Potato Starches on Stain %.
Figure 30. Influence of Alginates on Stain % of Paper Sized With 70 lb/ton of HMW Potato Starch and 1.1 lb/ream of Silicone Agent.

Figure 31. Influence of Alginates on Stain % of Paper Sized With 50 lb/ton of LMW Potato Starch and 0.8 lb/ream of Silicone Agent.
The samples from the stain tests were scanned and the quality of the stain areas was determined by comparing the samples to the jpg files provided by Dow Corning Corporation. The evaluation of the quality of the samples was based on a range between 1-10, where 10 was the best and 1 the worst quality (Appendix A). The commercially used sample had a value between 9-10. The evaluation and the jpg files are presented in the Appendix.
CHAPTER VI

CONCLUSIONS

The following conclusions have been drawn from the experimental results obtained in this study:

1. The low molecular weigh potato starch provided films that were smoother, more compressible, less permeable, and with a smaller average pore size compared to the high molecular weight potato starch. Thus, the molecular weight of the starch plays an important role in surface sizing; lower molecular weight starch seems to be more effective.

2. Due to the better surface properties of the paper sized by low molecular weight potato starch, the paper has higher silicone holdout compared to paper sized by high molecular weight potato starch.

3. The addition of alginates to the starch solution decreased Gurley porosity significantly. In addition, the alginates decreased the average pore size, and the effect of the decrease was more evident with lower molecular weight alginates. The alginates also tended to increase the roughness and stiffness of the films, but this trend decreased as the molecular weight of the alginates is decreased.

4. The solutions of potato starch in combination with alginates provided better silicone hold out than pure potato starch solutions. Due to better paper properties such as lower permeability, penetration rate, and smaller average pore size, the silicone is more effectively retained on the surface of the paper. This could lead to decreasing the amount of silicone required.
CHAPTER VII

RECOMMENDATIONS FOR FUTURE STUDY

To determine the effect of molecular weight of starch on silicone hold out, more than three starches of various molecular weights, but of the same type, should be employed in the experiment. Then, the trend of the molecular weight effect can be determined with more accuracy.

The range of the starch pick ups should be kept low, but appropriate, so that the tests performed of each type of starch can be compared to one another.

The rheology of the starches should be studied, relationships between viscosity, $G'$, $G''$, stress, relaxation can help to better understand the principles of starch behavior when sizing.

When performing silicone sizing, the samples should be carefully checked by the silicone cure test to assure that the silicone monomer has completely reacted. Only samples like that can be taken for subsequent tests such as the release test.
Appendix A

Samples of Stain Test From Dow Corning Corp. Used for Evaluation
Appendix B

Samples From Stain Tests and Evaluation [Silicone coat weight/Rating]

Emcoat K85 (HMW)
Emcoat K85

Starch pick up 109.12 lb/ton

0.69 lb/ream / 4
1.0 lb/ream / 7-8
1.55 lb/ream / 8-9

Starch pick up 68.72 lb/ton

0.73 lb/ream / 7-8
0.96 lb/ream / 8
1.11 lb/ream / 8

Starch pick up 50.64 lb/ton

0.71 lb/ream / 7-8
1.01 lb/ream / 8
1.38 lb/ream / 9

Starch pick up 33.35 lb/ton

0.62 lb/ream / 7
1.05 lb/ream / 7-8
Emcoat K85 + Alginate S700

Starch pick up 116.16 lb/ton

0.79 lb/ream / 7-8
1.10 lb/ream / 8
1.57 lb/ream / 9-10

Starch pick up 72.26 lb/ton

0.84 lb/ream / 7-8
1.11 lb/ream / 8
1.54 lb/ream / 9-10

Starch pick up 58.28 lb/ton

0.64 lb/ream / 7
1.12 lb/ream / 8
1.78 lb/ream / 9

Starch pick up 33.36 lb/ton

0.68 lb/ream / 7
0.99 lb/ream / 7-8
1.49 lb/ream / 8-9
Emcoat K85 + Alginate S300

Starch pick up 92.67 lb/ton

- 0.83 lb/ream / 7-8
- 1.12 lb/ream / 8
- 1.59 lb/ream / 9-10

Starch pick up 71.76 lb/ton

- 0.74 lb/ream / 7-8
- 1.03 lb/ream / 8
- 1.54 lb/ream / 9

Starch pick up 55.18 lb/ton

- 0.67 lb/ream / 7
- 0.97 lb/ream / 8
- 1.47 lb/ream / 9-10

Starch pick up 34.86 lb/ton

- 0.56 lb/ream / 7
- 0.94 lb/ream / 8
Emcoat K85 + Alginate 100

Starch pick up 54.74 lb/ton

- 0.61 lb/ream / 7
- 0.82 lb/ream / 7
- 1.29 lb/ream / 8-9

Starch pick up 36.90 lb/ton

- 0.55 lb/ream / 7
- 0.94 lb/ream / 8
Appendix C

Samples From Stain Tests and Evaluation [Silicone coat weight/Rating]

Emcoat K55 (LMW)
Emcoat K55

Starch pick up 78.95 lb/ton

0.69 lb/ream / 7-8  1.07 lb/ream / 8-9  1.22 lb/ream / 9

Starch pick up 70.65 lb/ton

1.14/ream / 8-9  1.05 lb/ream /8-9

Starch pick up 64.97 lb/ton

0.61lb/ream / 7  0.88 lb/ream / 8  1.10lb/ream / 8-9

Starch pick up 51.66 lb/ton

0.61 lb/ream / 7  0.78 lb/ream / 7-8
Emcoat K55 + S700

**Starch pick up 74.84 lb/ton**

- 0.76 lb/ream / 7-8
- 1.06 lb/ream / 8
- 1.37 lb/ream / 9

**Starch pick up 69.61 lb/ton**

- 0.82 lb/ream / 7-8
- 1.14 lb/ream / 8
- 1.54 lb/ream / 9-10

**Starch pick up 52.81 lb/ton**

- 0.71 lb/ream / 7-8
- 0.91 lb/ream / 8
- 1.20 lb/ream / 8-9

**Starch pick up 46.64 lb/ton**

- 0.72 lb/ream / 7-8
- 0.92 lb/ream / 8
- 1.28 lb/ream / 8-9
Emcoat K55 + S300

Starch pick up 91.83 lb/ton

0.82 lb/ream / 7-8
1.14 lb/ream / 8
1.65 lb/ream / 9-10

Starch pick up 71.72 lb/ton

0.77 lb/ream / 7-8
1.06 lb/ream / 8-9
1.58 lb/ream / 9-10

Starch pick up 44.57 lb/ton

0.67 lb/ream / 7-8
0.82 lb/ream / 7-8
1.17 lb/ream / 8-9

Starch pick up 41.53 lb/ton

0.52 lb/ream / 7
0.69 lb/ream / 7-8
0.92 lb/ream / 8
Emcoat K55 + S100

Starch pick up 91.52 lb/ton

0.82 lb/ream / 8  1.19 lb/ream / 8  1.54 lb/ream / 9-10

Starch pick up 71.70 lb/ton

0.71 lb/ream / 7-8  0.97 lb/ream / 8  1.408 lb/ream / 9

Starch pick up 51.26 lb/ton

0.65 lb/ream / 7-8  0.82 lb/ream / 8

Starch pick up 30.55 lb/ton

0.50 lb/ream / 6  1.04 lb/ream / 8
1. West, C.J., Some applications of starch in the coating and sizing of paper, Appleton, Wis.: Institute of Paper Chemistry, 1941


3. Ramp, J., The effects of starch on pickup, as influenced by the solids, temperature, viscosity, and depth of penetration on sheet properties, Tappi Journal, 1990


