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ASSESSING SILICONE HOLDOUT FOR RELEASE PAPERS

by

Rudolf Haraga

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Rudolf Haraga

ASSESSING SILICONE HOLDOUT FOR RELEASE PAPERS

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Western Michigan University, 2001

Silicone coating is widely used on papers that require low surface tension. Such papers are called release papers and are used in label, food, and packaging applications. Before silicone coating is applied, the base paper undergoes sizing procedures to smooth the surface and to cover voids present in the surface of the paper substrate. After the base paper is properly sized, it is silicone coated. This makes the surface of the base paper have a low surface energy. Therefore, when a second adhesive paper is applied to the base paper, the second adhesive paper can be easily recovered from the base paper.

There are several test methods used to assess silicone holdout. Most of them are based on the force needed to remove the adhesive paper from the release base paper. The stain test and ultrasound absorption by paper are proposed in this research. The stain test measures the area not covered by silicone and thus suggests the probable quality of the sized base paper. Ultrasound transmittance measures the change in ultrasound absorption by the base paper while the paper is being wetted, thus wetting curve is observed.

It is concluded that image analysis can provide information about silicone holdout, while ultrasound transmittance provides information about starch sizing efficiency.

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CHAPTER I

INTRODUCTION

Release papers are widely used in the food, packaging, and label industries, where demand is still growing. These papers are, however, costly; the cost is due largely to the silicone coating. On the other hand, silicone provides excellent release properties, and the reduction in silicone usage is therefore limited.

For easy release, the surface of the paper has to have a low surface energy. This is obtained by good coverage of silicone. Paper itself is and can be very porous and its surface very rough. Silicone applied on such paper migrates into the sheet, resulting in poor coverage, and high cost. To prevent the penetration of silicone into the sheet, the paper is first pre-treated with a sizing agent whose function is to fill the voids present in the paper.

Several sizing agents, mostly different types of starches and modified starches, are currently available on the market. Properties of these starches vary depending on the source of starches and their chemical modifications. Properties of most concern include flexibility, porosity, smoothness, and rheological properties. Starch is applied on the paper substrate, where it covers the substrate's surface, creating a low porosity surface. Such coated paper is then supercalendered to decrease porosity and reduce the surface roughness. The pick-up of silicone has to be such that the silicone will cover the highest peak present at the surface, hence covering the entire sheet. Figure 1 shows a schematic image of the ideal case of silicone coverage.

To evaluate the quality of the silicone coating and its surface properties, several test methods have been developed. One of them is the so-called stain test. This test consists of exposing silicone-coated paper to potassium iodide, or another stain producing dye, resulting in a yellow surface. However, if the silicone has not completely covered the surface of the paper, the starch-detecting dye will react with the starch, creating a brown stain. In the past, such stains were subjectively ranked. However, recent work by Duraiswamy (3) utilized image analysis to determine the influence of different types of starches at different coat weights on silicone holdout.

Figure 1. Schematic of Silicone-Coated Paper Substrate.

Different starches contain different distributions of components, such as amylose or amylopectin. These ingredients may react differently with potassium iodide, and, therefore, they might influence the final result of the stain test. Thus, the stain test has to be developed more thoroughly to assess properly the silicone holdout ability of different types of starches applied as sizing agents.

The next most important paper properties influencing silicone holdout are smoothness and air permeability, which is closely related to porosity. As the porosity decreases, or the smoothness increases, silicone holdout increases, resulting in better coverage and surface properties. Thus, the sizing agent influences the silicone holdout the most. Therefore, several surface properties of the sized paper substrate have to be measured to assess final silicone holdout. After the paper is sized, it is silicone coated at different pick-ups. Such coated paper is then analyzed to obtain the final results.

Starch is one of the least expensive sizing agents on the market. Thus, an understanding of its function as an agent to assist in silicone holdout might reduce the consumption of silicone and, consequently, decrease the price of the final release paper.

The objectives of this research are

(1) to develop test methods for assessing silicone holdout, and,

(2) to determine the efficiency of several starches as sizing agents.

CHAPTER II

LITERATURE REVIEW

Release papers are widely used. Their demand, therefore, is increasing, and mills are being forced to increase quality and minimize price to keep pace with their competitors. The most expensive component of the release paper is the silicone coating system. To reduce silicone usage, the paper is usually surface sized to reduce the silicone's penetration and loss into the basesheet. Currently, there are many varieties of starches on the market; however, the starch has to be chosen so that it provides a continuous film, has a high smoothness, and does not migrate too much into the sheet. Of primary importance is a film forming properties of the starch, and its cost. However, all these properties are influenced by the uniformity of paper substrate. Therefore, a good, well formed paper substrate must be used. Uniformity is the key point; otherwise, the starch penetrates non-uniformly into the sheet and does not provide good smoothness or low porosity. Further, more silicone has to be applied to cover the entire surface, resulting in an increase in the price of the sheet.

Starch Chemistry

Starch is a polymer consisting of glucopyranose units linked by 1,4-α-D-glucoside linkages; cellulose is linked by 1,4-β-D-glucoside linkages (1). The beta linkage in cellulose is responsible for rigidity, whereas the alpha linkage is responsible for flexibility. Therefore, starch is more flexible than cellulose. Figure 2 shows the glucopyranose unit and the alpha linkage. The main sources of commercial starches are corn, potatoes, wheat, tapioca, and waxy maize (2).

Natural starch consists of two ingredients. The first, amylose, is a linear polymer (Figure 2). The second, amylopectin, is derived from amylose; it is branched and contains 1,6-alpha-glucoside linkages. Figure 3 shows the chemical structure of amylopectin.

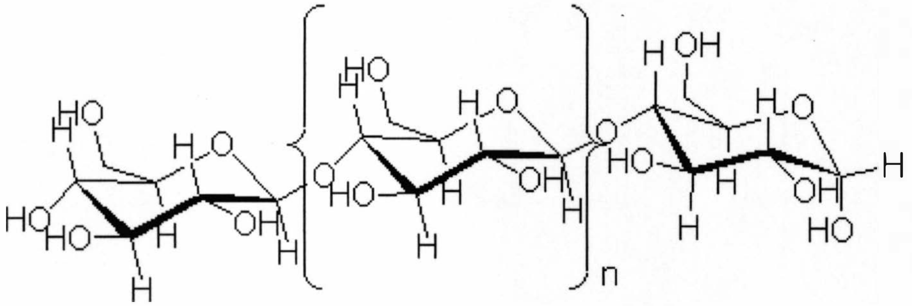


Figure 2. Chemical Structure of Amylose, The Linear Starch Component.

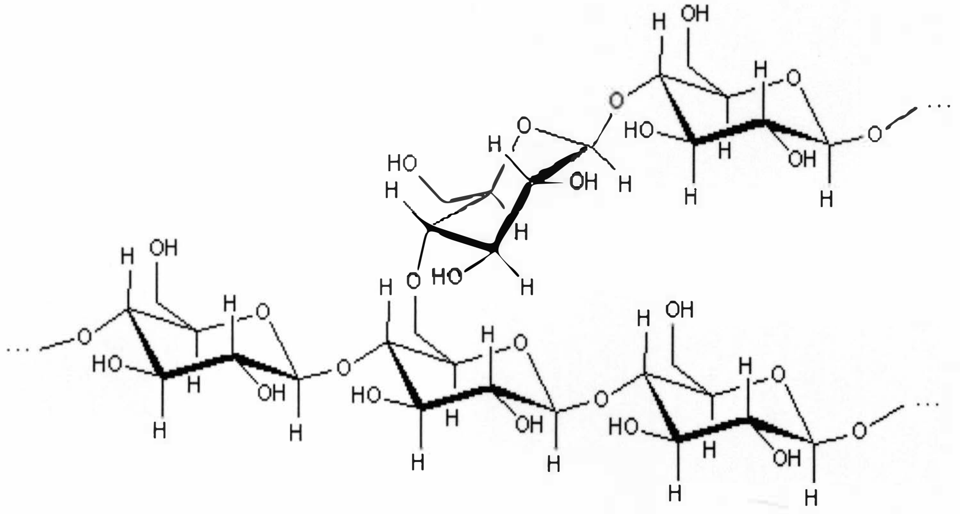


Figure 3. Chemical Structure of Amylopectin, The Branched Starch Component.

Natural starch almost always contains both amylose and amylopectin. After separating these species, both fractions become water soluble (1). Because they contain many hydroxyl groups, providing good hydrogen bonding, these fractions easily associate with like molecules and with each other. However, because amylose is linear, it aligns itself with other linear molecules. Amylopectin is a large, complex molecule that has difficulty in aligning itself to any other molecule. Amylose association is responsible for several physical effects. For example, when it cools, its viscosity increases greatly and it becomes insoluble. This is called retrogradation.

Table 1

Amylose and Amylopectin Content of Starches (2)

Starch	Amylose avg., weight %	Degree of polymerization	Amylopectin avg., weight %
Corn	28	800	72
Potato	21	3000	79
Wheat	28	800	72
Tapioca	17	3000	83
Waxy maize	0	NR	100
High-amylose corn	40-70	600	30-60
Rice	17	NR	83
Sweet potato	20	NR	80

NR = not reported

Several natural sources of starch exist. Some sources of starch, as was mentioned earlier, are rice, pearl, tapioca, potato, waxy maize, and corn. The difference between starches from these sources is the content of amylose and amylopectin units. Table 1 shows different starch sources and their amylose and amylopectin contents (2). The differences in the amylose/amylopectin ratio result in different physical and chemical properties of the starch. Another difference in the starches in Table 1 is in their degree of polymerization, which represents the average number of units present in the amylose or amylopectin molecule. This is the measurement of the molecular weight. The higher is the degree of polymerization, the higher is the molecular weight of the starch.

Chemically modified starches are often used as surface sizing agents. These types of starches are chemically improved to provide better chemical and physical properties. Modification might be based on substituting some groups for others and/or controlling the degree of polymerization. Such modified starches provide better properties, such as better viscosity, better binding to other molecules, better film forming, less migration into the sheet, flexibility after drying the sheet, and lower tendency to cracking. Several other ingredients might be added to starch to improve its properties. One of these ingredients is sodium alginate; however, it is still not known how the alginate alters the paper's surface properties to improve its barrier properties.

Starches, because of their polymeric structure, have very complex rheological properties. Viscosity is very dependent on temperature and any shear force that is applied. Amylose and amylopectin content, because of their different polymer structure, directly influence the rheological properties. Figure 4 shows how the viscosity changes while starch is being cooked. During heating, the viscosity rapidly increases. Once the temperature reaches 190 ^{o}F, starch is hydrated and the viscosity decreases with time. After the starch is completely hydrated and is being cooled, its viscosity starts to increase due to the realignment of amylose chains to each other. This is known as retrogradation.

Once the paper is sized, it is calendered to obtain better smoothness. Smoothness is a very important surface property because the silicone requirement for complete surface coverage will be influenced by the height of the starch covered peaks of the paper. Smoothness may be measured by air leakage through the space between peaks at the surface as seen in Figure 5 (2). Temperature is a very important variable as well. Calendering actually compresses the sheet to make it thinner and smoother. However, the lignin content considerably contributes to the smoothness as well. A temperature increase to about 190 °F will soften the lignin; thus, it will align more uniformly at the surface, producing a smoother sheet (2). Calendering may be done in many ways; however, it has been shown that supercalendering provides the best results (3). Such a sheet is immediately ready for silicone treatment.

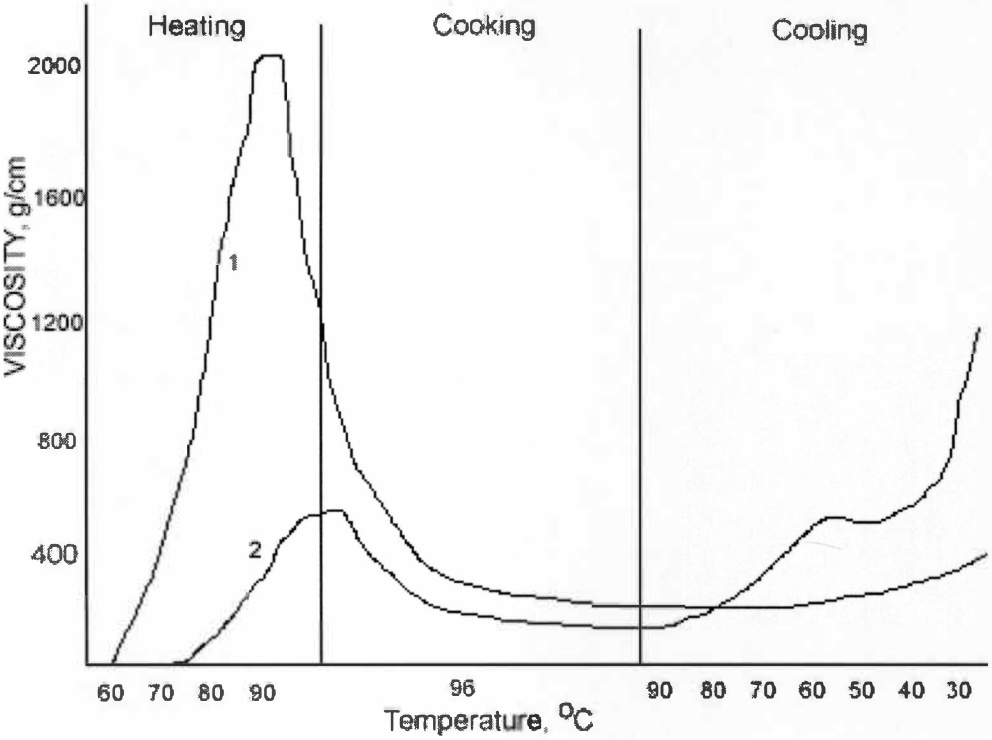


Figure 4. Viscosity vs. Temperature Curves For Commercial Starches.
(1 = potato, 2 = corn)

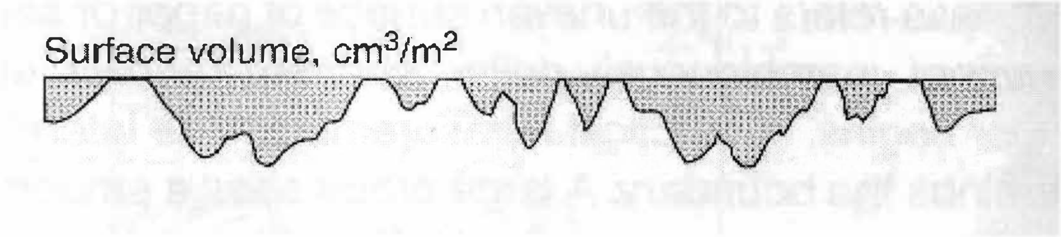
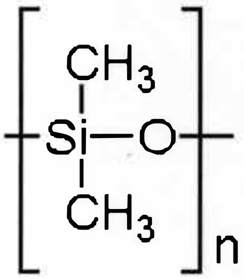


Figure 5. Parker Print-Surf Smoothness Represents an Air Leakage Volume (hatched area) Between Rough Peaks.

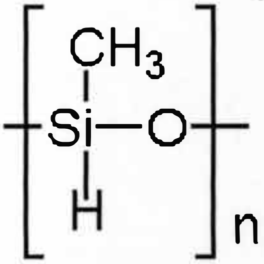
Silicone Chemistry

Silicone can reduce the forces of adhesion by 98 to 100 % (4). “Release” and “adhesiveness” are names describing the property of preventing surfaces from sticking to each other. Films of silicone resins are applied to many different kinds of surfaces to prevent other materials from sticking to these surfaces (5). These silicones are applied either as solutions or from aqueous emulsions, but, hopefully, are not drawn substantially into the paper. Expensive curing catalysts, such as zinc, tin, or lead salts of carboxylic acids, or aluminum chelating compounds, accelerate the drying, improve the adhesion, and, particularly important with release papers, prevent the migration of silicone oil into the adhesive layer (6). Dimethylpolysiloxane polymers drastically reduce adhesion. They are composed mainly of repeating units of the following structure (4):



$$\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O- \right]_n$$

Unfortunately, dimethylpolysiloxane shows very little reactivity toward cellulose. When applied to dense papers, such as vegetable parchment, it penetrates the surface. The release action can be greatly reduced if too much silicone leaves the surface of the paper (4). The first really successful silicones used for release paper treatments were methyl hydrogen polysiloxanes:



$$\left[-\overset{CH_3}{\underset{H}{Si}}-O- \right]_n$$

Solutions of these materials in toluene, xylene, or hexane were mixed with a small percentage of zinc octoate or stearate, or stannous octoate or oleate catalyst (4). Under the influence of relatively high temperatures (150 – 450 ^{o}F), these systems would cross-link and adhere to the paper surface, so that the overwhelming percentage of the treatment would remain fixed on the surface, inert and non-migratory. However, the cure would continue at room temperature for several months, and would eventually lead to a slight loss in release efficiency under certain conditions.

The next improvement came when polysiloxane fluids, end-blocked with hydroxyl units, were blended with hydrogen polysiloxanes. Figure 6 shows this reaction.

Silicone fluids of higher viscosity are more desirable for release purposes, both from the standpoint of efficiency and lack of contamination (4). Linear polymers used for release purposes vary in molecular weight from 5,000 to 250,000. Silicones may be applied in emulsified form in operations where the presence of solvent is

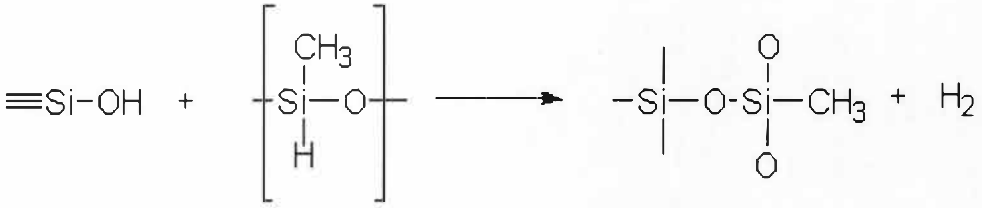


Figure 6. Condensation Reaction.

objectionable. The silicone and the catalyst are emulsified separately, generally by the chemical manufacturer. The emulsion systems are fairly stable under the influence of mechanical agitation. The cost of application is generally lower than for the solvent systems. An emulsion of a methyl hydrogen polysiloxane system is considerably less expensive. When producing release papers that will contact food, a special catalyst/emulsion system is required. Both types of silicones are also available as 100% solid materials so that they may either be emulsified or dissolved in special solvent systems (4).

After silicone is applied, it is cured. Heaters with conveyors are used to carry the silicone treated paper. Dwell time in the heater and the heater's temperature are key variables. While dwell time is adjusted by speed of the conveyor in the heater, temperature is always set to a constant value. The dwell time and temperature are determined experimentally because every modified silicone monomer and its additives influence these variables. In order to decrease the cost of the final product, a relatively constant conveyor speed in the heaters is a key issue, since it is desirable that the silicone and additives cure quickly, but completely.

Theory of Wetting

Silicone coating and starch sizing significantly influence the wetting properties of the paper. Wetting is actually the penetration of a liquid into the sheet. This process is described by the Lucas–Washburn equation. According to the equation, penetration is dependent on variables such as contact angle, time, viscosity, surface tension, and radius of the pores. The Lucas-Washburn equation is

$$\frac{dl}{dt} = \frac{\mu.r.\cos\Theta}{4.l.\eta}$$

where

l	depth of the penetration, m
μ	surface tension, Nm^{-1}
r	radius of the pores, m
Θ	contact angle, rad
t	time of the penetration, s
η	viscosity, Pa-s

After integrating in the range from $l_0 = 0$ to $l_1 = l$ and from $t_0 = 0$ to $t_1 = t$, the resulting equation is

$$l^2 = \frac{1}{2}\frac{\mu.r.\cos\Theta.t}{\eta}$$

which shows the depth of the liquid penetration into the pores.

The Dupre equation describes the driving force required to push a liquid through the paper. The Dupre equation is

$$\Delta P = \frac{2(S_{SV} - S_{SL})}{r}$$

where

ΔP difference in the pressure in and above the pore (driving force), dynes

S_{SV} free energy of the solid-vapor interface, dynes.cm^{-1}

S_{SL} free energy of the solid-liquid interface, dynes.cm^{-1}

r radius of the pore, cm

This equation describes the pressure difference in and above the pore. Eventually, this difference is the driving force that influences the penetration rate. Therefore, this equation is indirectly the equation for the rate of penetration.

Release papers usually have a very low surface tension, and the paper allows penetration of very small amounts of air and water.

Tests for Release Papers

There has always been a need to test the efficiency of the sizing agent and the silicone coating properties. However, not many test methods have been developed, and even some of the current test methods are not adequate to provide good measurement of these properties. Test methods should depend on the end use of the release papers. Papers used for bakery tray liners or interleaves for frozen hamburger patties might require different release properties.

The Keil test, the pressure test, the stripping test, and the stain test will be discussed next (4).

Keil Test

The Keil test qualitatively evaluates the silicone coating. The test consists of applying adhesive tape to the paper; the paper is then put under pressure and high temperature to simulate aging, where 20 hours might represent one year. Afterwards, these papers are put into the Keil tester, which measures the force needed to release the adhesive tape from the paper. This force depends on silicone holdout. However, additional factors may influence this property. If the silicone is not cured enough, some of the monomer could be available at the surface, which will interact with the adhesive tape. Such interaction will decrease the tackiness of the tape, thus reducing the release force.

Silicone holdout is one of the most important variables in this test. When no starch areas are present on the surface, no part of the adhesive tape will interact with them, thus silicone will provide low surface tension resulting in low release force. On the other hand, if some areas on the paper are not covered with silicone and starch is present, it will interact with the adhesive tape resulting in an increase in release force. Therefore, the Keil test is an appropriate measurement of silicone holdout, but other factors, such as incomplete cure of the monomers, that could influence the test results, should be kept in mind.

Pressure Test

The pressure test is very similar to the Keil test. Adhesive tape is applied to four or five paper samples. These are pressed in a Carver laboratory hydraulic press for 2 minutes at 400 lb / in^2 and removed. The stripping force, expressed in g/inch, is immediately measured. The test is conducted at 72 ^{o}F.

This test is a modification of the Keil test. The only difference is in the aging conditions, that are always chosen according to the end use. The exact requirements for each paper are always different, and while one paper could successfully complete the pressure test under certain conditions, the paper may not be good for all applications.

Stripping Rate

The force required to remove most adhesives from release papers usually depends on the stripping rate. Generally speaking, the slower the paper is removed, the lower the force of adhesion. High stripping rates are useful in picking out slight differences in release, particularly for aged samples. In many applications, the release paper is removed rapidly, as in printing, die cutting, and removal of “lace” in the manufacture of pressure-sensitive labels.

The difference between the stripping test and other two tests mentioned above is in the stripping rate. The Keil test and the pressure test apply a standard stripping rate; however, the stripping test reveals the influence of the stripping rate on the release force. Thus, the end use is the most important criterion in the selection of the test method to be used. For example, to simulate the printing process, where the stripping rate is very rapid, a high stripping rate should be used.

Stain Test

The stain test is used to determine the uniformity of the silicone coverage. The release paper is smeared with dye and wiped off after a set time with absorbent paper. The effectiveness of the coating can be judged by the amount of color retained by the test strip (Figure 7). With an effective coating, the paper shows very little staining.

Figure 7 shows a photograph captured from image analysis. The yellow areas represent silicone coverage. The staining dye neither interacts nor reacts with the silicone. However, in places where good silicone coverage is not present, the starch reacts with the dye producing a brown spot. As seen in the picture, these spots do not follow any order and are irregular. It is possible to determine the number of spots and evaluate them in light of other silicone holdout properties.

Application Variables

Besides paper, silicone, and starch properties, there are other application variables that substantially influence final silicone holdout. Such variables include the size press conditions, such as the roll diameter and loading, and nip pressure. Size press conditions affect mostly surface sizing, which would indirectly influence silicone holdout.

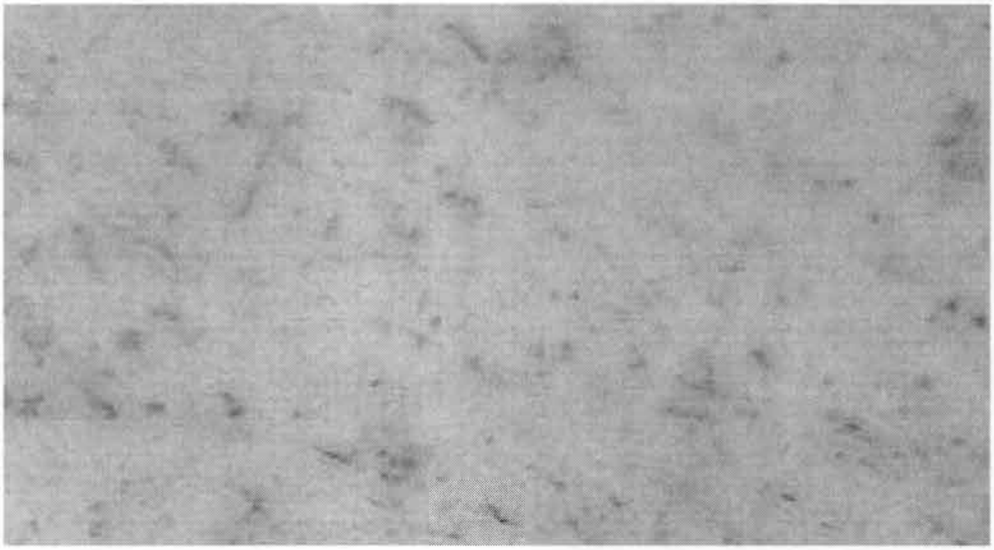


Figure 7. Stain Test on a Release Paper.

Application variables include such factors as drying temperature, sheet tension, paper machine speed, and dryer rolls. Increased nip pressure will enhance starch penetration through the sheet, thus sealing the paper more uniformly. Sheet tension affects elongation and fiber – starch alignment. Paper machine speed is important because of the dwell time that influences the starch penetration (7).

CHAPTER III

STATEMENT OF THE PROBLEM AND OBJECTIVES

Because of the high demand for release papers,. this market has become very competitive, and price and quality have become the key issues. Both quality and price are influenced by silicone usage. Silicone is used to lower the surface energy of the paper, thus making a non-sticky surface.

However, the silicone's influence can be enhanced by pre-treatment of the paper. Starch is applied to the paper to smooth it and to close the voids in the sheet. Thus, silicone will not migrate into the sheet and will not be wasted in filling the voids. Several hundred different types and different modifications of starch are available at present. Starch-coated paper is then supercalendered to decrease the roughness by leveling the CD profile of the sheet.

Regardless of the starch coat weight, silicone contributes the most to the final cost. Therefore, the less silicone used, the lower is the cost; but also, the lower is the quality. Quality is, however, a nonspecific term. Quality measurements consist of several test methods, where one of them is based on visual perception by the observer.

The objectives of this research are

(1) to develop test methods for assessing silicone holdout, and,

(2) to determine the efficiency of several starches as sizing agents.

CHAPTER IV

EXPERIMENTAL DESIGN AND METHODOLOGY

The experimental strategy used during this research was first to investigate surface properties obtained by application of different starch sources and modifications and their effect on final silicone holdout, and, second, to develop test methods for assessing silicone holdout. This strategy was further split into two stages. These are schematically represented in Figures 8 and 9.

First, it was necessary to select appropriate starches and to investigate their rheological properties. Different tests were conducted, such as viscosity versus temperature and viscosity versus shear curves. These rheological data are extremely important to determine the appropriate trial conditions, such as percent solids and temperature of starch being applied at the size press. If the solids are too low, this may lead to not being able to achieve certain pick-ups due to low starch content. On the other hand, if the solids are too high, this may dramatically increase the starch viscosity, and, thus, the starch would not be able to be applied onto the paper uniformly. Temperature is the only variable that can move the viscosity to the correct range. However, temperature is a variable that can be always controlled at the size press. Therefore, rheological curves had to be very carefully studied before any decision could be made relative to starch solids that can be applied on any size press.

The second stage consisted of selection of an appropriate paper and surface sizing with different pick-ups and starches. Important surface properties such as porosity and roughness had to be measured. These properties are closely related to silicone coverage because surface roughness controls the coverage uniformity and porosity controls silicone penetration. In all, the paper sheets were silicone coated with three different silicone coat weights. Coat weight is the key variable because it is important for quality and the final cost. Roughness and Gurley porosity were measure five times to reduce the error of measurements. Additional tests such as the stripping or curing test, stain test, and ultrasound absorption by paper were also performed. Stain test results were analyzed using the image analyzer and further improvements were made. To use the Washburn equation, pore distribution, silicone penetration, and contact angle tests were also performed.

To obtain comparable results that could be used to evaluate relationships between two dependent variables during this experiment, all the procedures had to be kept uniform and no important variable was ignored. Outliers, identified as such, were carefully studied and were omitted from the final regression analyses when appropriate.

Experimental Procedure

Phase I

Due to different contents of amylose and amylopectin in the various starches, and due to different chemical modification influences several starches were chosen for study. The starches were chosen so that the effect of amylose and amylopectin on the stain test could be obtained as well as the chemical modification. The starches chosen were (OSA = octenylsuccinateanhydrate treatment):

1. tapioca (3% OSA treated)
2. waxy maize (6% OSA treated)
3. waxy maize (degraded)
4. waxy maize (acetylated)

Tapioca starch, as can be seen in Table 1, contains about 17% amylose and 83% amylopectin. Waxy maize, on the other hand, is pure amylopectin. Amylose is responsible for retrogradation; therefore, waxy maize starch should be used where retrogradation must be avoided. Amylose is responsible for starch flexibility and fluidity. Tapioca is more flexible than waxy maize starches. Octenylsuccinateanhydrate (OSA) treatment makes the starch hydrophobic; thus, starch stays more on the surface, rather than penetrating into the negatively charged paper. Table 2 summarizes the physical properties of chosen starches.

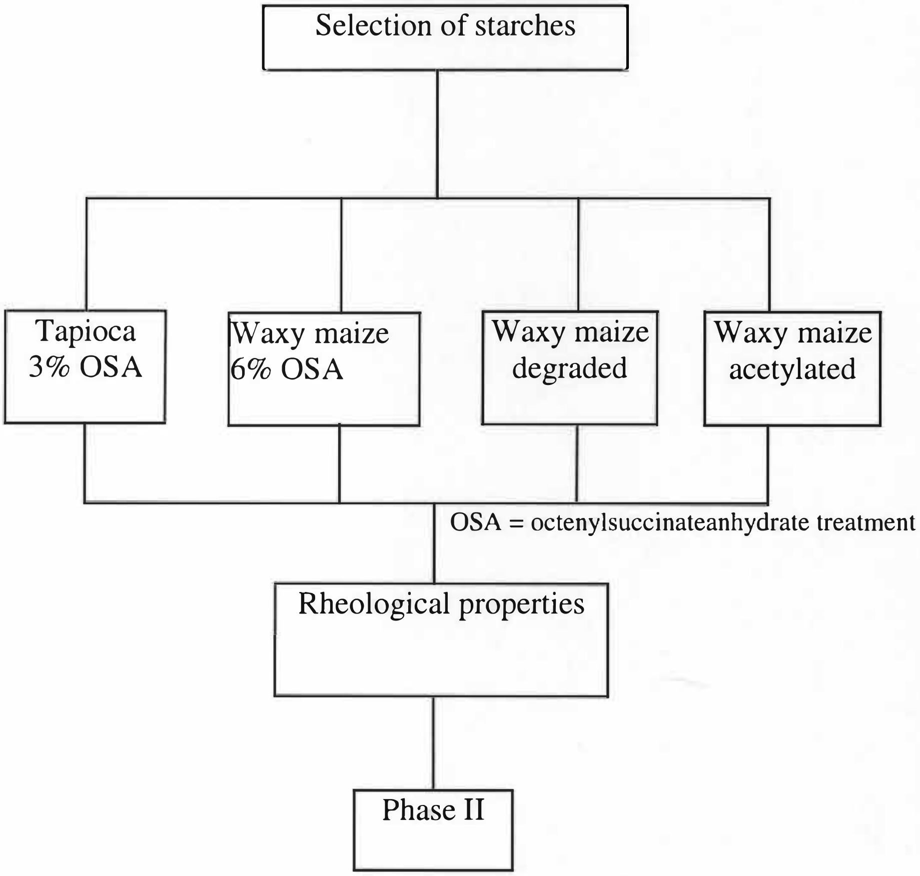


Figure 8. Phase I of the Experimental Design.

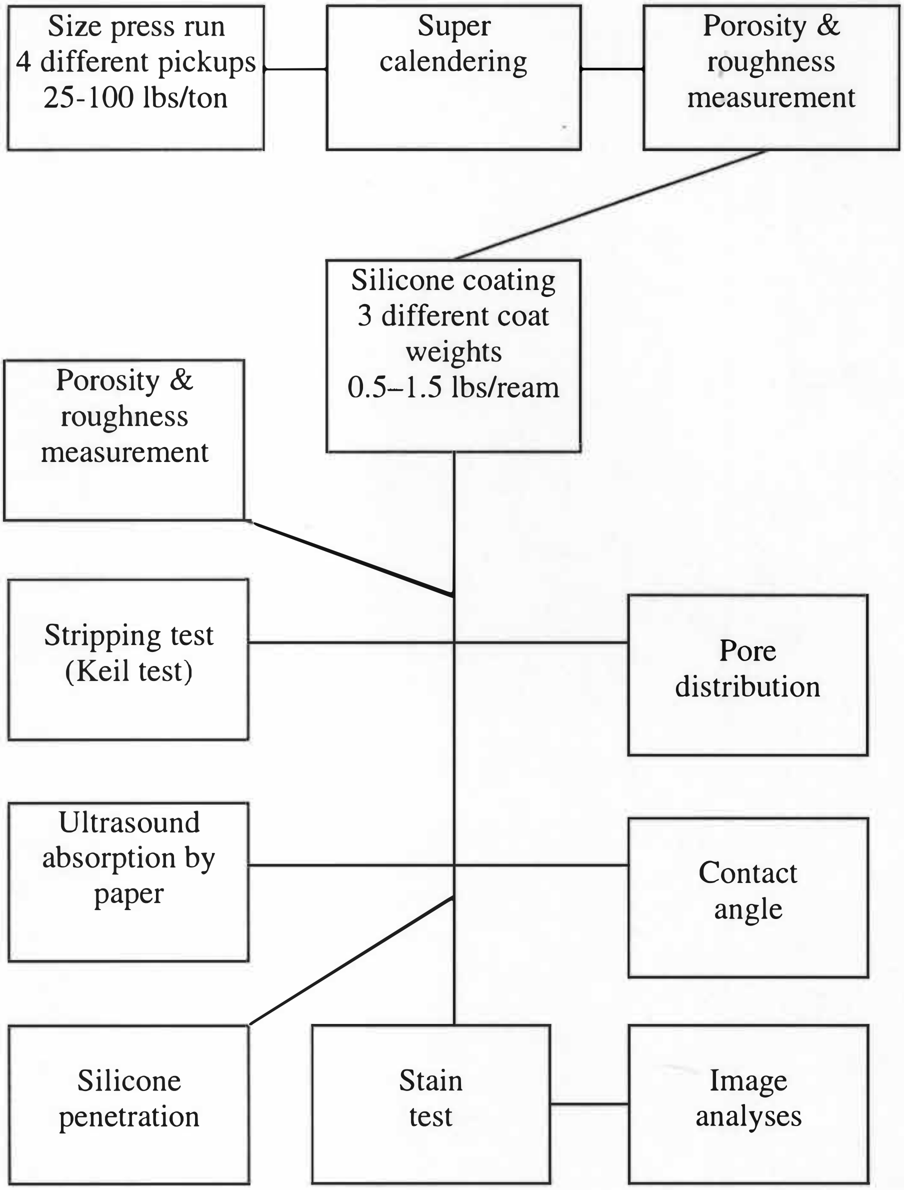


Figure 9. Phase II of the Experimental Design.

Table 2

Physical Properties of Chosen Starches

Starch source	Starch name	Type	pH	Moisture
Tapioca (3%OSA*)	FilmKote370	Hydrophobic starch	5.5-5.7	15%
Waxy maize (6% OSA*)	FilmKote550	Hydrophobic, hybrid corn starch	6.0-8.0	15%
Waxy maize (degraded)	StacKote4	Hybrid corn starch	6.5-8.5	15%
Waxy maize (acetylated)	KoFilm250	Acetylated hybrid corn starch	5.0-6.5	15%

OSA = octenylsuccinateanhydrate treatment (hydrophobic)

A sample of each starch was analyzed. Starches were cooked for 30 min at about 90 °C in a steam cooker. Starches were cooked at the highest possible solids, mostly in the range of 15-20%. Then, they were kept at 60 °C and the rheological properties were measured. Part of the starch was diluted down several times, and again the rheological tests were performed. They were cooled by 10 °C and again the rheological properties were measured. This was repeated until the temperature was 30 °C. Rheological testing consisted of generating a viscosity vs. temperature curve. Viscosities were taken with a Brookfield viscometer at 10 rpm; spindle number 4 was used. Next, a viscosity versus shear curve was generated on the stress rheometer, which has a temperature bath that keeps the sample at a predetermined constant temperature. During a size press process, shear is applied; therefore, this curve reveals how the viscosity changes while starch is in the size press.

After all these data have been collected, the temperature and percent solids are chosen for the size press process. The parameters chosen for each starch are summarized in Table 3.

Table 3

Cooking Solids and Size Press Temperature for Selected Starches

Starch	Solids, %	Temp, °F
FilmKote370	20	166
FilmKote550	20	148
Stackot4	20	130
KoFilm250	20	130

Phase II

Commercially available paper, containing no internal sizing, was used. Starches were cooked at the pre-selected solids, and a size press was used to surface size the paper. After reaching the desired pick-up, the starch was diluted and a lower pick-up was achieved. Four different pick-ups were applied, and a sample of each pick-up was taken. Targeted pick-ups were 100, 75, 50, and 25 pounds per oven dry ton of paper.

These samples were cut to 12 by 12 inches. Supercalendering at 2000 psi and

200 °F was performed. Four passes were made, alternating the sides and directions. Supercalendering was performed on a lab supercalender at the Plainwell Paper Corporation, Plainwell, MI.

Roughness measurements of all samples were taken with a Parker Print-Surf roughness tester, Model No. ME-90. Pressure was set to 490 psi and a soft backing was used. Gurley porosity was measured as well, using the same device at 980 psi.

These paper sheets were cut again to 6 x 12 inches and were taken to Dow Corning Corporation, Midland, MI, for silicone coating. Silicone, Syl-Off(R) 7676 Coating and 7678 Crosslinker, were used. A 20 ml mixture of 20 parts of the 7676 Coating and 0.94 parts of the 7678 Crosslinker was prepared. This silicone mixture was applied to the paper using a Euclid Tool blade coater at various blade pressures. Blade pressure was directly related to the silicone coat weight. However, the same blade pressure for different starch pick-ups and different starch sources resulted in different silicone coat weights. The samples were then cured on Bluemax Driers for 30 sec at 220 °F. The Bluemax drier has a dual zone for a total length of 6 ft. Final silicone coat weight was measured on an Oxford Instruments Lab-X 3000 EDRF (X-ray) unit.

After the silicone was applied and completely cured, all samples underwent stain testing. The dye, Shirlastain A, was used with the Cobb Ring set for two minutes and then blotted dry. The area covered by the silicone became yellow, and the starch covered or non-silicone covered area became brown. This could have been due to the roughness of the paper and insufficient silicone coverage of the paper or the migration of the silicone was too high. Silicone migrates into the sheet due to surface cracking or insufficient starch weight. Such samples were submitted for image analysis to the Paper and Printing Science and Engineering Department at Western Michigan

University. The image analyzer evaluated a stained area of the sample. The results were reported in percent area of brown spots. Therefore, the lower the percentage, the better is the coverage. The use of image analysis to evaluate the area of stain was first used by Duraiswamy (3). However, in his study, Duraiswamy measured the number of brown spots rather than the area of them. In the above mentioned study, two brown spots with different areas were evaluated as two spots. One of them could have been several times bigger than the other one. Thus, small ten brown spots can have a lower area than one big brown spot. Hence, this big brown spot would affect the increase in release force much more then the ten small spots. Therefore, evaluating stained area as a number of spots is incorrect and, in this study, their area was measured instead. This has never been done and published before and is a new method to assess brown spot coverage. Figure 10 shows an exaggerated view of the stain sample.

Image analysis was used for evaluating the color of the stained area as well. Red, green, and blue channels to create separation were used, and histograms of R, G, and B grey scale values were made. The relationship between the stained area, release force, and the histograms of the R, G, and B values was then determined.

A standard tape was applied to each sample. Samples were aged for one day. The stripping or cure test was performed using an Instrumentors ZPE 1000 Peel tester, where the release rate was 400 inches per minute. The lower the stripping force, the better is the coverage. However, if the coat weight was in the higher range, it is hypothesized that not all SiH groups were cured, and they could be interacting with adhesive tape, resulting in the higher release force.

The next step was to measure the surface properties of the silicone coated samples. Again, roughness at 500 psi and Gurley porosity at 1000 psi were measured using a Parker-Print Surf Porosity tester.

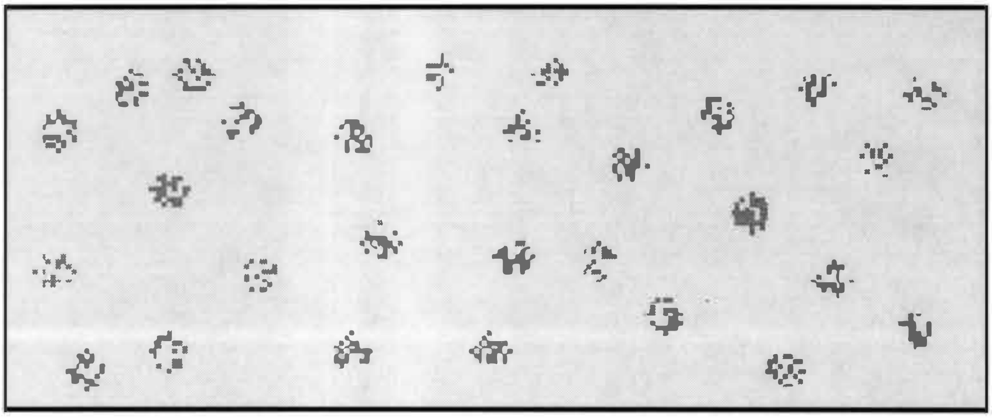


Figure 10. Exaggerated View of the Sheet Showing Silicone Coverage and Brown Starch Specks.

To evaluate the Lucas-Washburn equation, several tests were performed. Pore distribution was measured using an Autopore II 9220. Both low and high pressure analyses were performed. Next, silicone penetration was measured by EDS (Energy dispersive X-ray system). Lastly, the contact angle was measured using a FTA2000 instrument.

To evaluate sizing efficiency of different starches, an ultrasound absorption test method was used. The principle of this test method is based on the fact that ultrasound conductivity by fibers is dependent on their moisture content. Therefore, ultrasound absorption versus time is being observed, while the paper is being wetted. The final wetting curve reveals the absorption properties of the paper.

Samples were immersed in water, and silicone monomer to measure the wetting curve for both liquids. An instrument DPM Emco from Elektronische Mess- und Steuerungstechnik, GmbH, was used.

After all the experiments were conducted, the data were analyzed using the Minitab software package to find the best regression model. This strategy assessed the silicone holdout using the most important dependent variables. The General Linear

Model (GLM) method was used for building the mathematical model. From the observations of the tests used, recommendations for improvements were made.

CHAPTER V

RESULTS AND DISCUSSION

The main objective is to study the influence of release properties and process variables on silicone holdout. There is no evidence of any other published results except (3); however, different test methods have been chosen. Hence, all of these results cannot be compared with any other findings.

Experimental Data Analyses

All data were analyzed using Minitab statistical software package. The general linear model (GLM) was used to perform the analyses.

The data collected in this study produced an unbalanced design. No silicone coat weight replicates were performed. It was decided to use entire data set to obtain a good estimate of experimental error. This, however, will cause a loss of precision of the significance of the effect. Each test was performed several times, and a mean value was used in the analyses. Statistical analyses consisted of the two phases described below.

Phase I

Collection of all data was performed. Data were split into 4 sets, where each set represents different starch sources or chemical modifications. These sets cannot be mixed, because, e.g., two variables with a linear relationship will not be linear if a third variable is added. In this case, a different starch source is the third variable and thus linearity of the former two variables could lose its significance.

Correlation coefficients were calculated for every variable in each set. Thus, the linear influence of variables on each other was obtained. Results are in Appendix A.

Phase II

In this phase multivariable influence analyses were performed. The study focused on how two or more variables effect the response variable. Two methods were chosen for this analysis.

A stepwise regression analysis performs a regression with a dependent and a response variable. If the result is significant, another variable is added and regression is repeated. If the result is not significant, this variable is omitted and another variable is chosen for the regression. All omitted variables are added again, once any other variable is added to test the significance of these omitted variables while other variables are already included. The final result is the list of all significant variables.

The second method, the best-subsets option in the Minitab statistical software package, calculates the list of all significant possible combinations of variables predicting the response variable.

Response Variable

The response variable is the variable being predicted. In this case, the response variable is silicone holdout, or, in other words, the quality of release paper. However, silicone holdout is indirectly measured by stain tests or release force. Selection of the response variable is very important, because it will affect the entire analysis. Silicone coat weight increases the quality of the release paper; however, it is not a measurement of silicone holdout. One paper might have the same release properties with lower silicone coat weight than another.

The stain test measures the area not covered by silicone. Less silicone results in a higher release force. In other words, higher silicone coat weight lowers the release force. However, in reality, a too high silicone coat weight contains uncured monomers. The uncured monomers interact with the adhesive tape, producing a higher release force. End use of the release paper almost always includes application of any adhesive force to the surface of the release paper. Sooner or later, this tacky material will be removed from release paper. Thus, the release force is the most important variable in such an application. However, a low release force does not reflect high quality release paper if part of the surface coating migrates into the tacky material.

Both stained area and release force were used as response variables. If correlation shows significant linear relationship between these two variables, one variable would be used instead. However, as Table 4 shows, the correlation coefficients varied from 0.259 to 0.984, where most coefficients are in the range from 0.7 to 0.95. All samples show a tendency to increase the release force with increasing silicone-uncovered area. However, it can be concluded that stained area and release force are not significantly correlated, and, thus, both variables will be used as response variable.

Gurley Porosity

Once the paper is supercalendered, its Gurley porosity and roughness is minimized. At this point, the sheet will be sealed and no silicone migration into the sheet should occur. However, if the sheet is not significantly sealed, migration of silicone will take place and silicone will not cover the entire sheet. Surface "peaks" will cause the roughness and Gurley porosity to increase.

Figure 11 shows the relationship between Gurley porosity and starch pickup for uncalendered sheets with different starch sizing. Figure 12 shows Gurley porosity after supercalendering was performed. Approximately 70 % reduction in porosity is observed after supercalendering. For example, the Gurley porosity of Stackote4 is reduced by

(104 – 30) * 100 / 104 = 71.2 % for the lowest starch pickup.

Table 4

Correlation Coefficients Between Stained Area and Release Force for All Starch Sources and Chosen Percent Solids. Data are in Appendix A.

Starch	Solids, %	Correlation Coefficient
FilmKote370	17.0	0.729
FilmKote370	3.9	0.941
FilmKote550	16.6	0.259
FilmKote550	4.5	0.862
Stackot4	15.8	0.940
Stackot4	4.5	0.984
KoFilm250	15.8	0.790
KoFilm250	4.3	0.655

After silicone is applied, starch sizing is the only variable that influences its

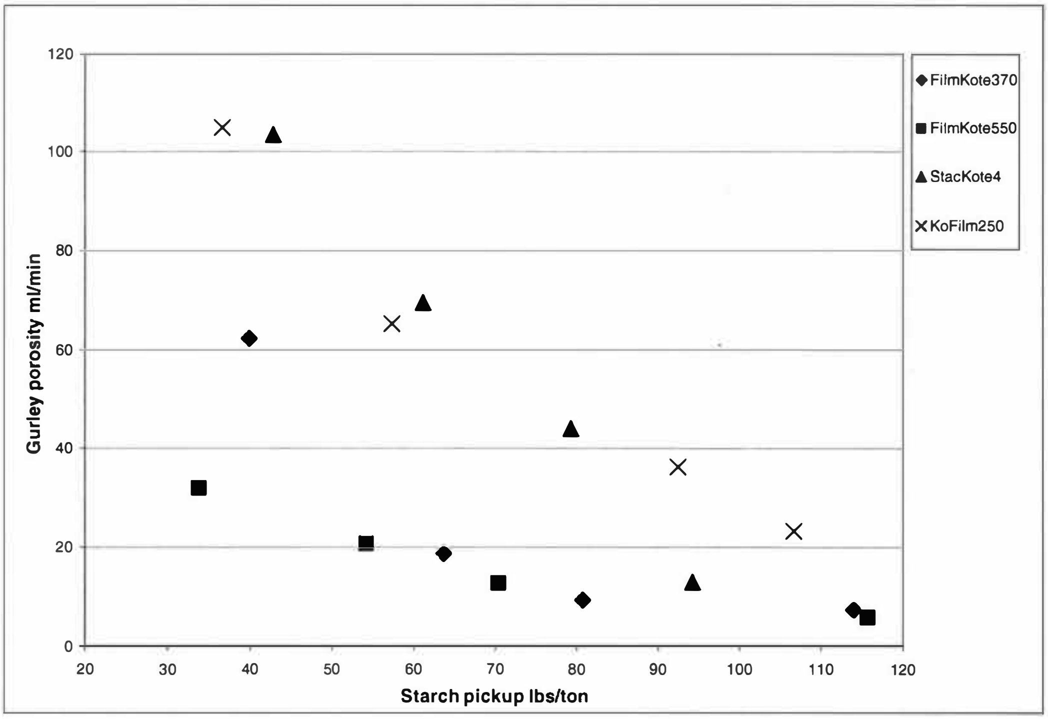


Figure 11. Gurley Porosity and Starch Pickup Influence for Uncalendered Sheets.

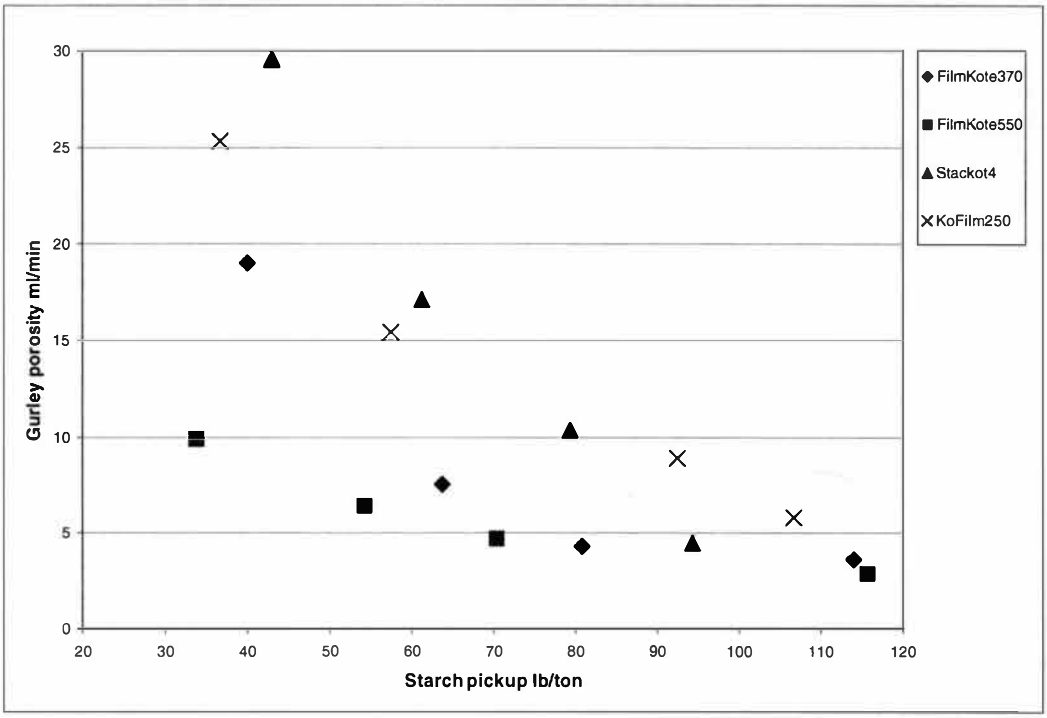


Figure 12. Gurley Porosity and Starch Pickup Influence for Calendered Sheets.

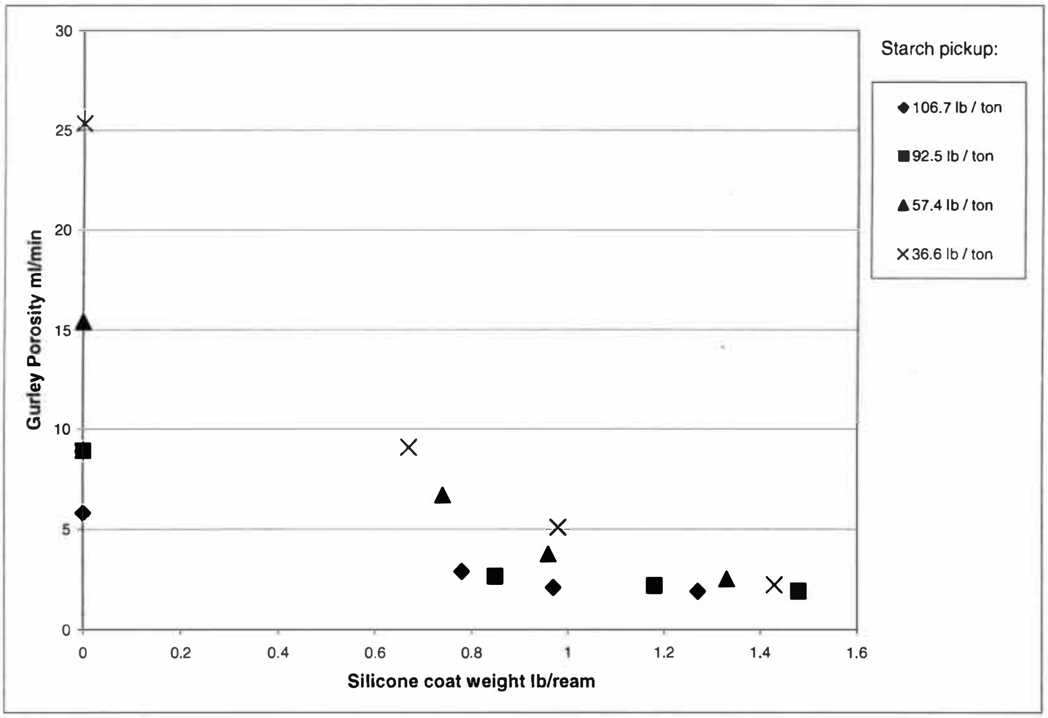


Figure 13. Gurley Porosity and Silicone Coat Weight Influence for KoFilm250.

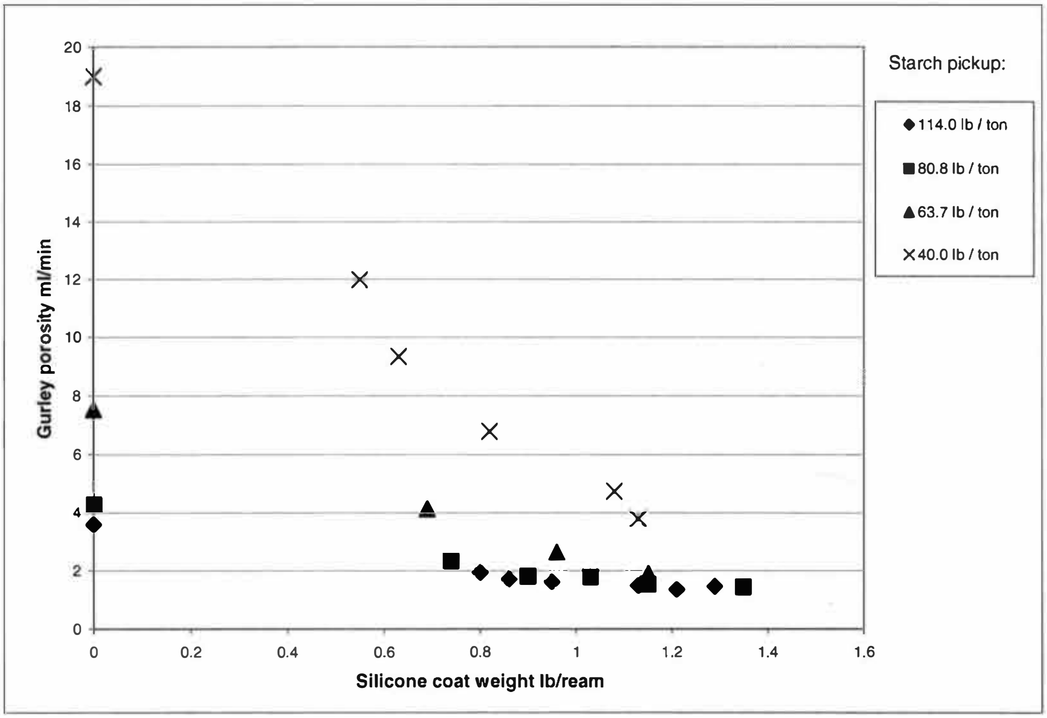


Figure 14. Gurley Porosity and Silicone Coat Weight Influence for FilmKote370.

migration. The higher the migration, the higher is the porosity in the sheet. Figures 13 and 14 show the relationship between Gurley porosity and silicone coat weight for two selected starches. From these figures, it can be observed that porosity is significantly decreasing with increasing silicone coat weight. Silicone is sealing the top pores and is closing up the sheet. Air thus has a higher resistance to flow through the sheet resulting in lower Gurley porosity.

It can be concluded that supercalendering and silicone coating significantly reduce porosity.

Roughness

Roughness is the key variable in assessing how much silicone is needed to cover the surface. As has been discussed earlier, higher roughness means bigger peaks on the paper surface, and, hence, more silicone is needed.

After supercalendering roughness was measured it can be concluded that supercalendering considerably decreases roughness.

Figure 15 shows relationship between roughness and silicone coat weight for KoFilm250. It can be observed that roughness considerably decreases with starch pickup. Silicone coat weight decreases roughness as well, but only to a certain level. Once this value is reached, an increase in coat weight will not result in significant decrease in roughness. However, Figure 16 shows the same relationship for FilmKote250, but these curves have different tendencies. Curves for the two highest starch pickups show the same tendencies as described above. However, curves for lower starch coat weights show first a slight increase in roughness and then a significant drop. This is even more significant for Stackot4 as can be seen in Figure 17. But, again this tendency occurred for the two lowest starch pickups only.

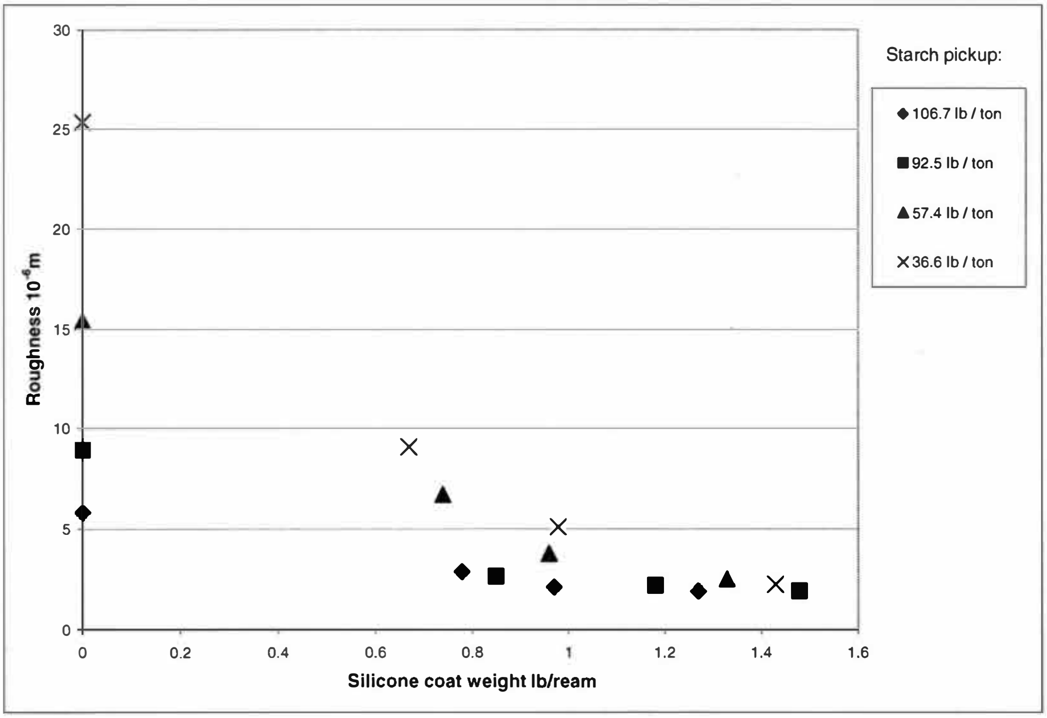


Figure 15. Roughness and Silicone Coat Weight Influence for KoFilm250.

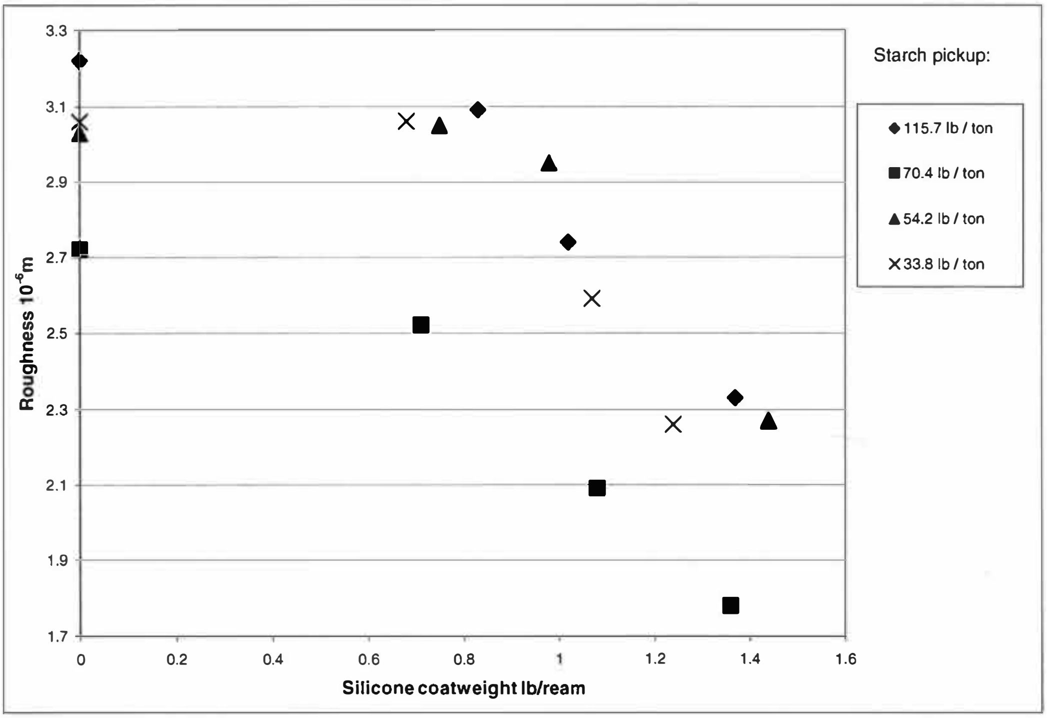


Figure 16. Roughness and Silicone Coat Weight Influence for FilmKote550.

Why is the roughness increasing at low starch pickups with increasing silicone coat weight in low ranges? One of the explanations is that the sheets with low starch pickups have higher roughness and porosity. When a little silicone is applied with the blade, this silicone is forced to go down into the sheet. Thus, the sheet is being sealed internally rather then on the surface; hence, porosity is always decreasing as was described earlier. On the other hand, pores that are at the surface are being forced from the blade pressure and silicone migration resulting in opening these pores at the surface, thus increasing the roughness. When more silicone is applied, it attempts to migrate down into the sheet, but the sheet is already sealed up with the silicone previously applied, and, therefore, pores are being filled and roughness and porosity drastically decrease.

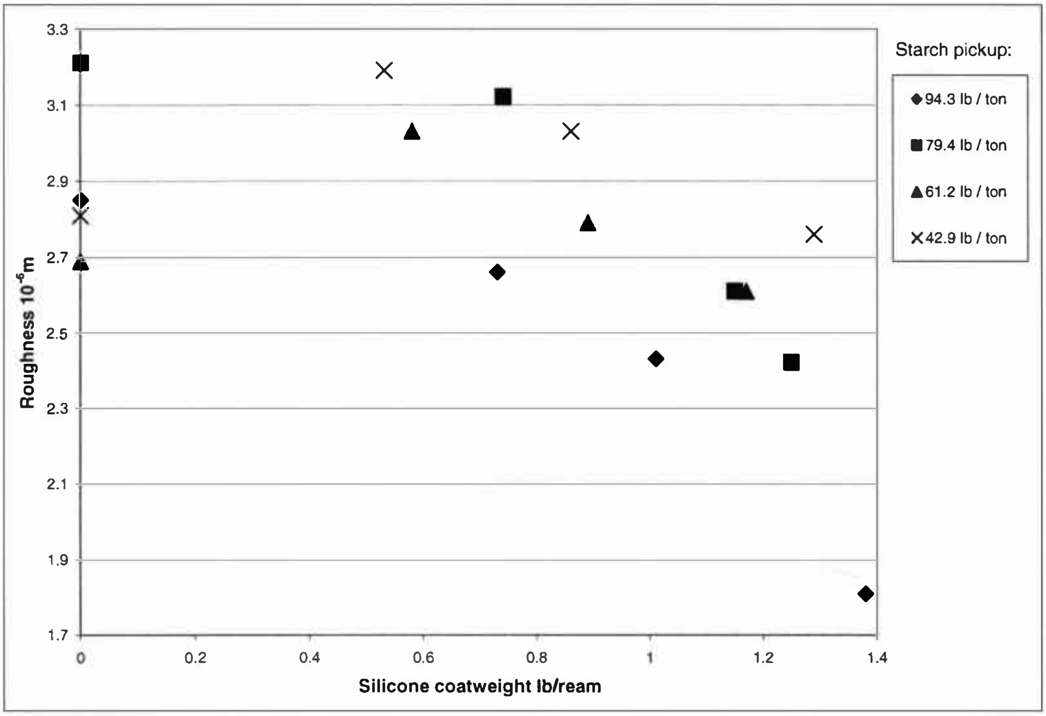


Figure 17. Roughness and Silicone Coat Weight Influence for Stackot4.

This roughness increase tendency varies for different starch sources; for some starch types, this tendency does not even occur, or it does occur, but at much lower silicone coat weights than was examined in this study. The answer why this tendency is so different is that different starches seal the paper differently. High molecular weight starch or starch with more complex amylopectin will seal the pores much efficiently than low molecular weight starch or a starch with a high amylose content. Natural starch sources contain different amount of these macromolecules with different molecular weights, resulting in different sizing efficiencies. Therefore, high sizing efficiency will not reflect any roughness decrease after even a small amount of silicone is applied. However, low sizing efficiency will make the roughness decrease after too little silicone is applied (Figures 15, 16, and 17).

Image Analysis

The surface of the paper becomes stained, as has been described above, when dye interacts with starch. Such starch is not benefiting from the silicone coverage. The more silicone that is applied, the less starch that is uncovered, and the less stained area that is produced. The color spectra from these stains were analyzed. First, red, green, and blue filters were used to obtain these color values. Figure 18 shows the stained sample color separation to RGB gray scale values.

By visual examination, good, medium, and bad silicone covered samples were chosen. Histograms of R, G, and B gray scale values of these samples were taken and they can be seen in the Figures 19, 20, and 21, respectively. Average gray scale values and their standard deviations are included in Table 5.

The most significant change in color distribution, as seen in Table 5 and Figures 19, 20, and 21, is for the green and blue channel. Red channel gray scale values do not significantly change. Blue channel gray scale values, however, are in

Image using red filter

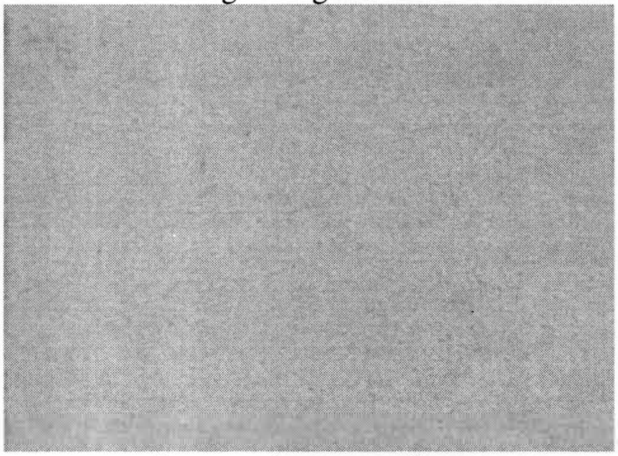


Image using green filter

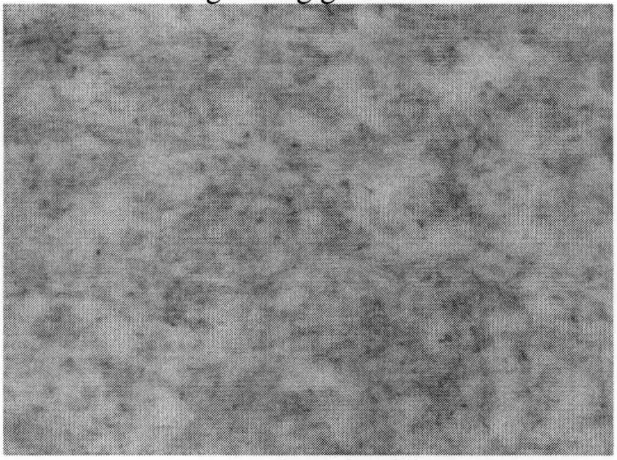


Image using blue filter

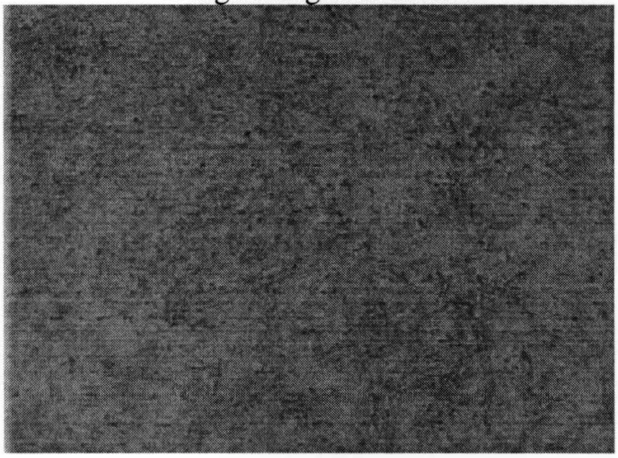


Figure 18. Color Separation of Stain Using Red, Green, and Blue Channels.

the range between 32 and 75. This is closer to zero, or the black region, than to 255, or white region. Therefore, this entire area is within the dark region (Figure 21). Standard deviations reveal that the blue channel gray scale values are more distributed when the average is closer to the white region, represented as the gray scale value, 255. Green channel gray scale values, however, vary between 210 and 252. Thus, it is closer to value 255, or to the white region. Standard deviations reveal that the closer the average is to 255, the less distributed green color is, hence the distributions have less standard deviation. Under a blue filter, areas that are good silicone-covered are dark and areas without good coverage are darker (Figure 21). Under a green filter, good silicone-covered areas are light and uncovered areas are dark (Figure 20).

Table 5

RGB Average Gray Scale Values and their Standard Deviations for Three Different Samples

Color	Sample	Average	Stand. Dev.
Red	Good	99	2.0
	Medium	104	2.7
	Bad	105	2.2
Green	Good	251	2.1
	Medium	231	7.5
	Bad	211	9.5
Blue	Good	33	2.9
	Medium	45	3.5
	Bad	75	5.5

Several reasons arise why a green channel should be used for assessing silicone holdout:

1. the better the silicone coverage, the lower the standard deviation of the green channel gray scale values
2. the entire range of green channel gray scale values is within the light region, and thus more visible and distinguishable to the human eye
3. silicone covered and uncovered areas are clearly distinguishable by dark and white areas, whereas under a blue channel, these areas are dark.

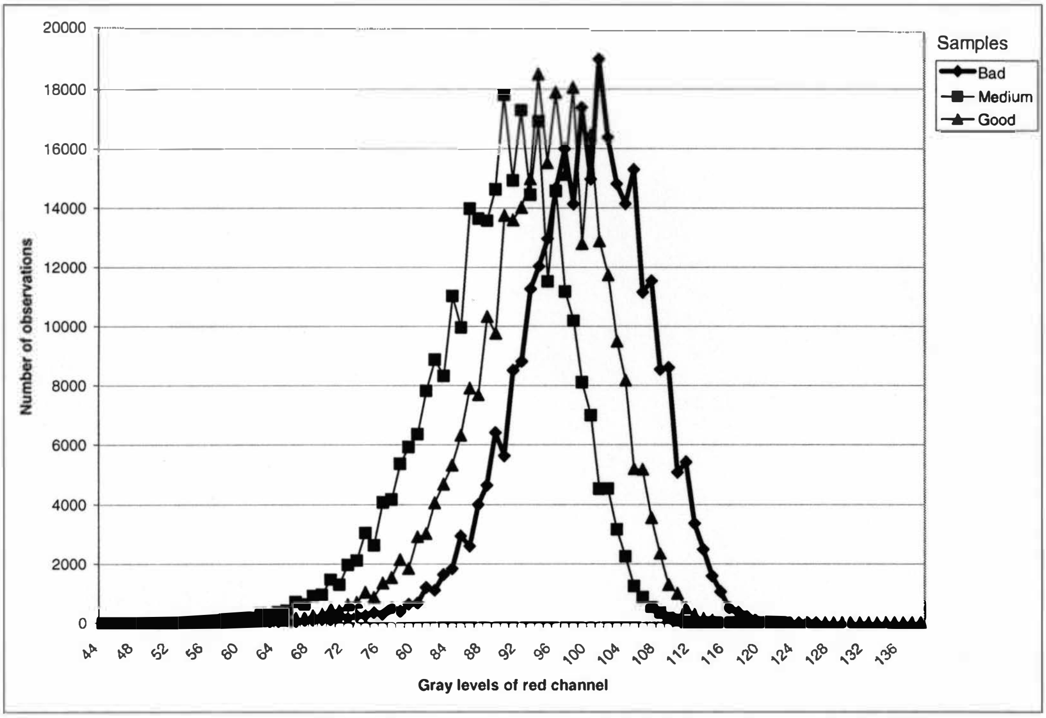


Figure 19. Histograms of Gray Values Using Red Channel for Three Different Samples.

Figure 22 shows green channel gray value changes with different starch pickups and different silicone coat weights. Figure 23 shows green channel gray values for different starch sources and different silicone coat weights, but for the same starch pickup. It can be observed that waxy maize (6% OSA) starch does not

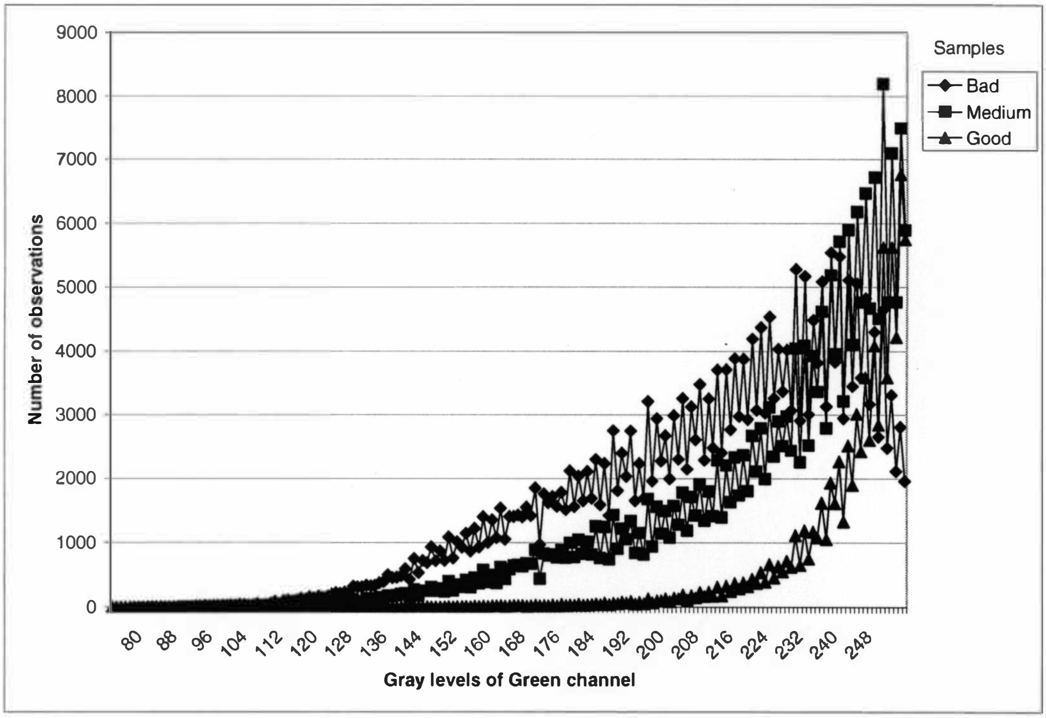


Figure 20. Histograms of Gray Values Using Green Channel for Different Samples.

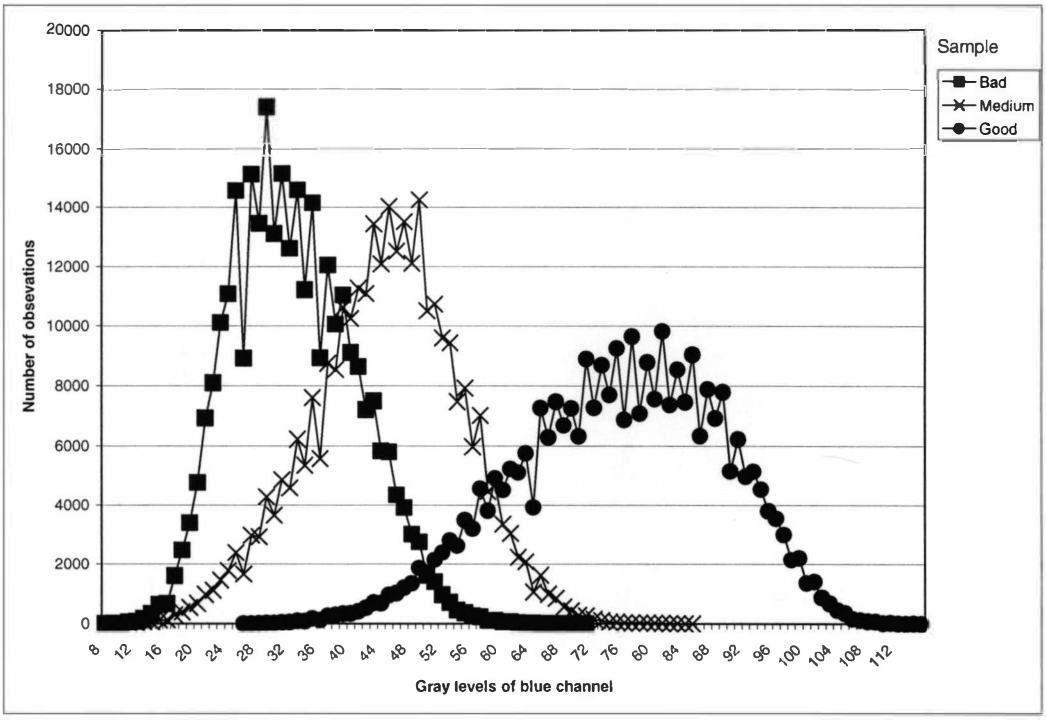


Figure 21. Histograms of Gray Values Using Blue Channel for Different Samples.

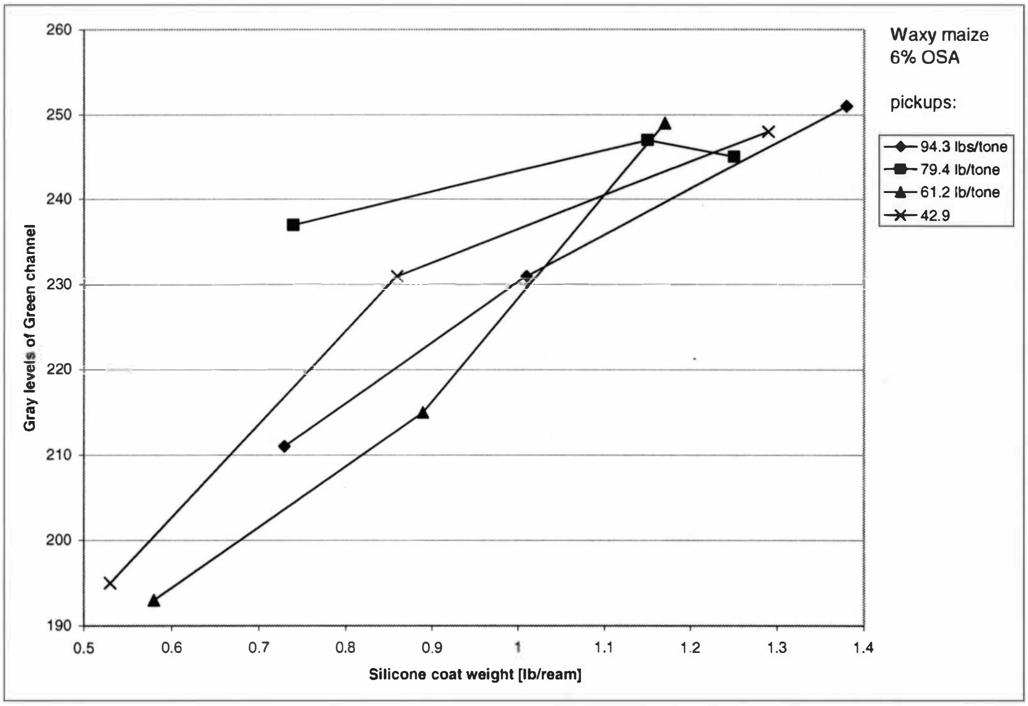


Figure 22. Relationship Between Gray Values Using Green Channel and Silicone Coat Weight for Different Pickups of Waxy Maize. (6%OSA treated)

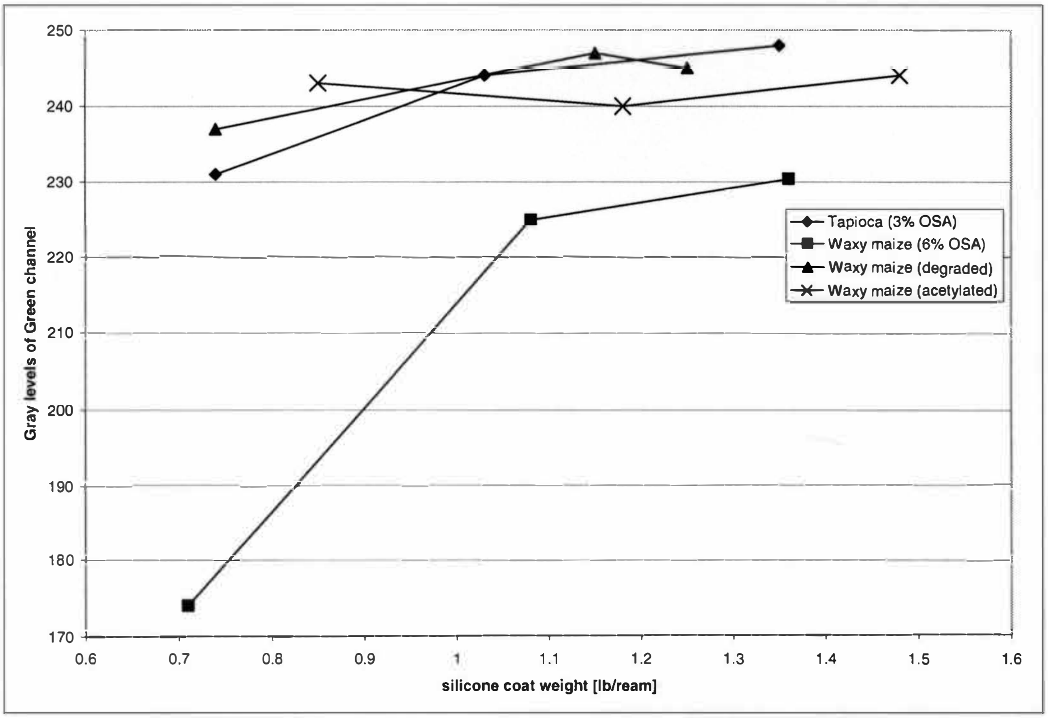


Figure 23. Relationship Between Gray Values Using Green Channel and Silicone Coat Weights for Different Starches at Similar Pickups. (70 – 90 lbs/ton)

significantly provide as good of coverage as the remaining starches.

Stained Area

In order to evaluate the stained area, the boundary between silicone covered and uncovered areas has to be identified. From the image obtained with green channel (Figure 20), it cannot be clearly seen where this boundary is. Therefore a statistical average of "good" and "bad" samples' green values has to be made. This average will represent a boundary between the stained area and non-stained area. According to Table 5 this average will be:

$$211 + 9.5\ x = 251 - 2.1\ x$$

$$x = 3.4$$

$$211 + 9.5 * 3.4 = 243.3$$

All samples were submitted to the image analyzer and photographs with a green color channel were made. Then, all areas with gray levels below 243 were selected, and this area was measured as a percentage of total area. In this case, a gray level of 243 represents the boundary between the stained and non-stained area. Areas with gray values above 243 are non-stained ones, and those with gray values below 243 are stained. Such percent stained area measurements were collected for all samples.

Figure 24 very nicely shows how the stained area rapidly increases with increasing porosity. Porosity effects silicone migration; thus high porosity means silicone is not kept at the surface and more starch is exposed, hence a higher stained area will be produced.

Why does the same porosity, but produced by different starch sources, result in different stained areas? Similar porosity values mean similar air permeability

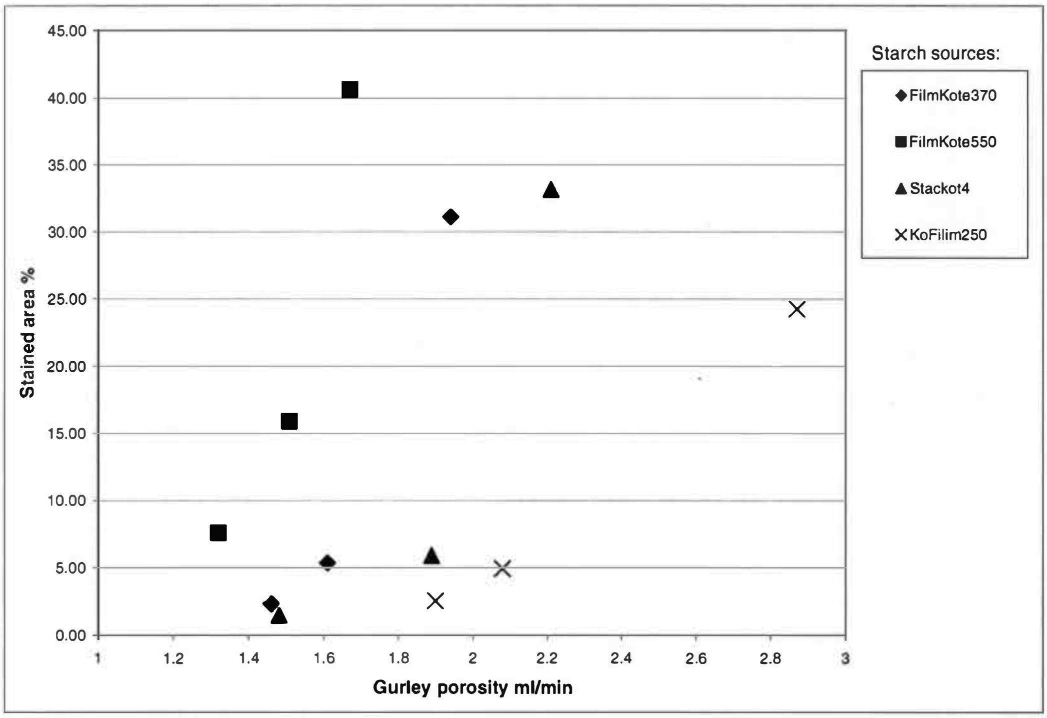


Figure 24. Stained Area and Gurley Porosity Influence for Similar Starch Pickups. (90-115 lbs/ton)

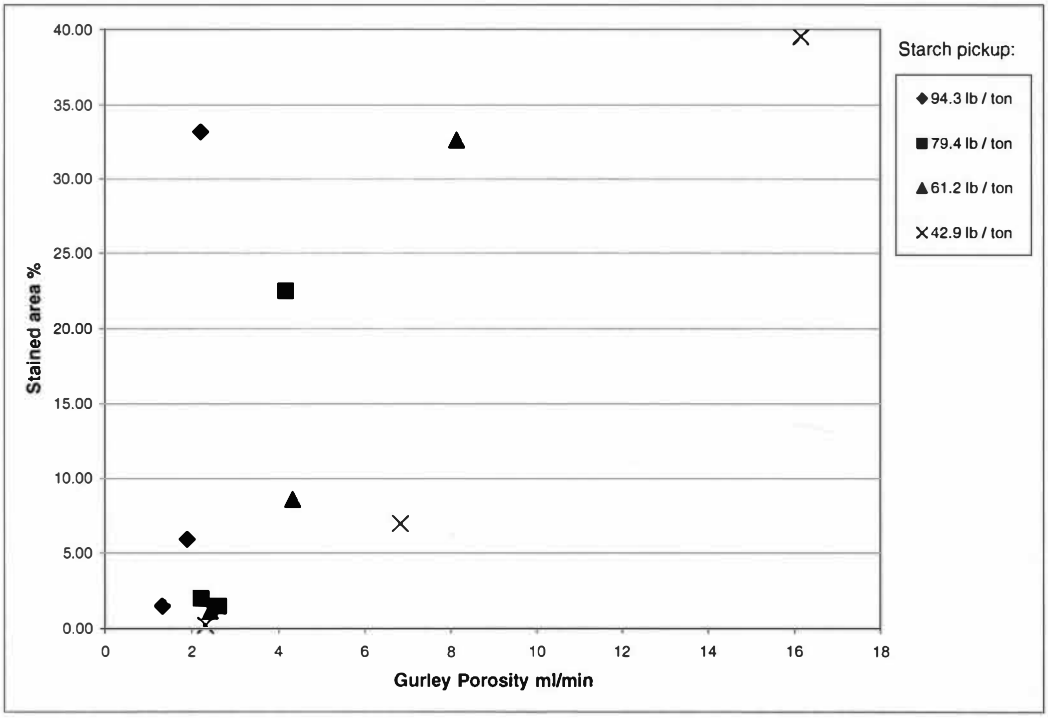


Figure 25. Stained Area and Gurley Porosity Influence for Stackot4.

characteristics. Equal air flow in two different sheets can be reached when one sheet has a lot of small pores and almost no big ones to allow the air to penetrate, and the second sheet has almost no small pores and fewer larger pores. A few big pores can result in the same airflow through the sheet as a large number of small pores. Therefore, there is a trade-off is between the pore distribution and its frequency.

Next, Figure 25 reveals how the starch pickup reflects stained area. The higher the starch pickup, the lower is the Gurley porosity and the steeper is the slope of the curve. Slope, or the derivative of the stained area versus porosity, reveals how much the stained area will change with one unit change of porosity. In Figure 25, porosity indirectly reflects silicone coat weight. It can be observed that slopes for the higher starch pickups are steeper, thus much less silicone has to be applied to obtain a significant decrease in stained area. Figure 26 shows the same phenomenon, but for a different starch type.

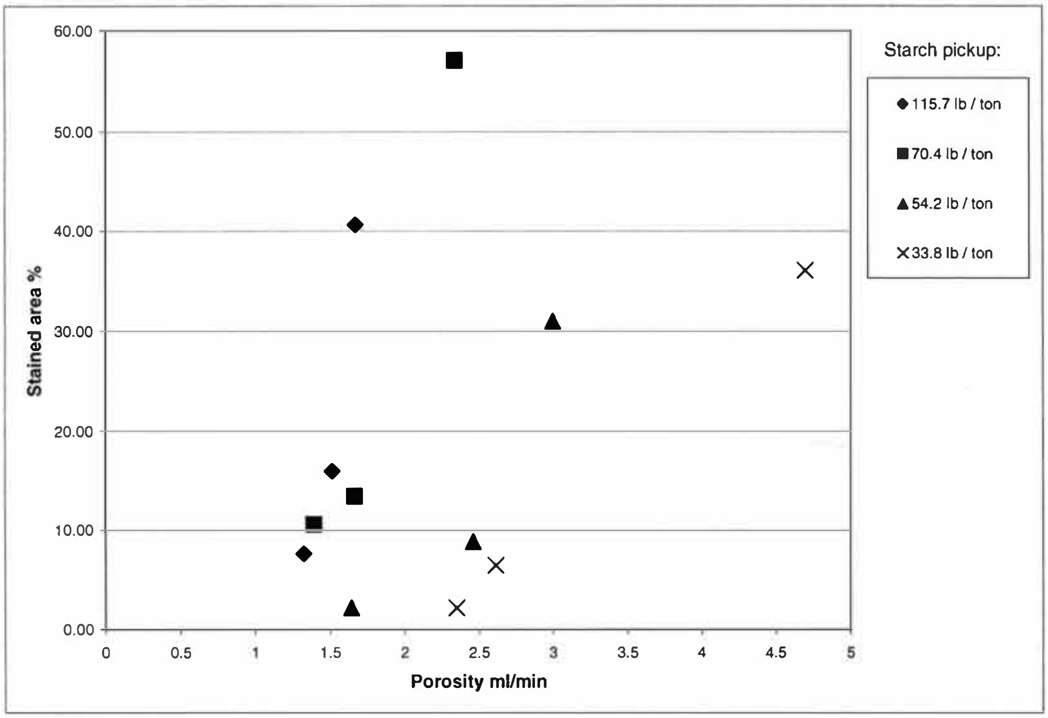


Figure 26. Stained Area and Porosity Influence for FilmKote550.

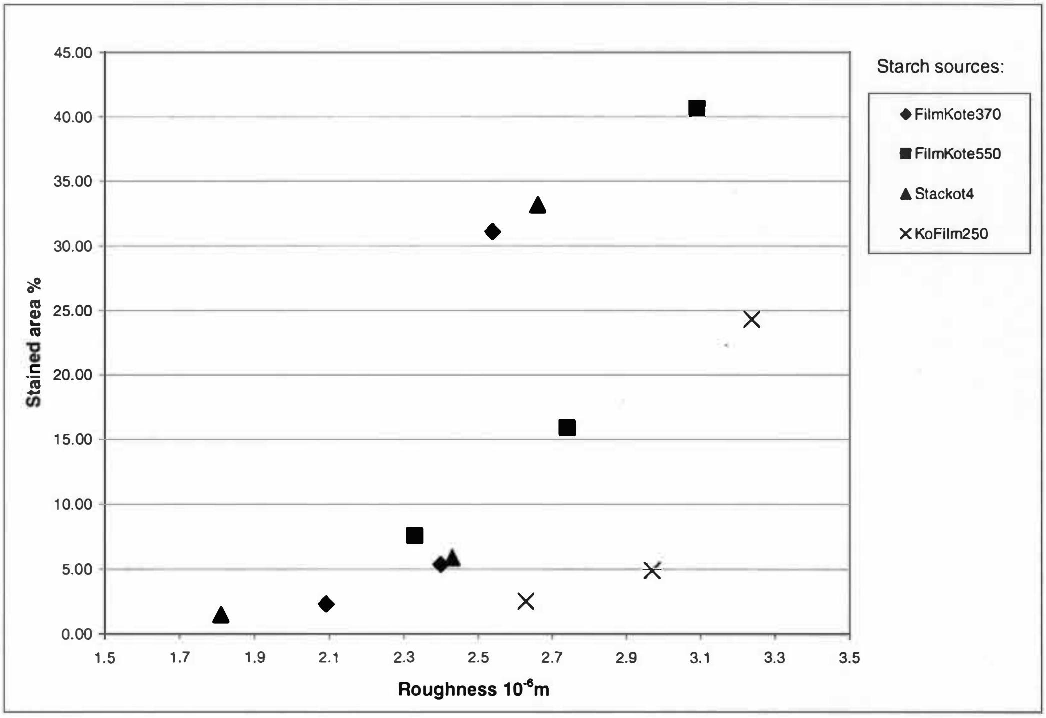


Figure 27. Stained Area and Roughness Influence for Similar Starch Pickups. (95 – 115 lbs/ton)

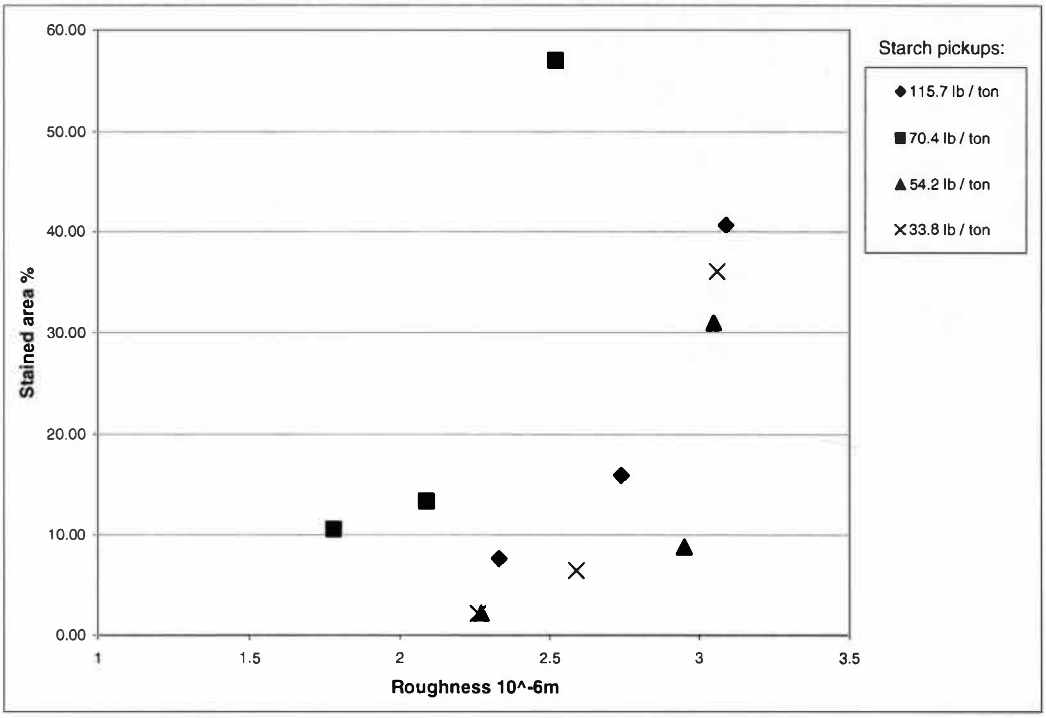


Figure 28. Stained Area and Roughness Influence for FilmKote550.

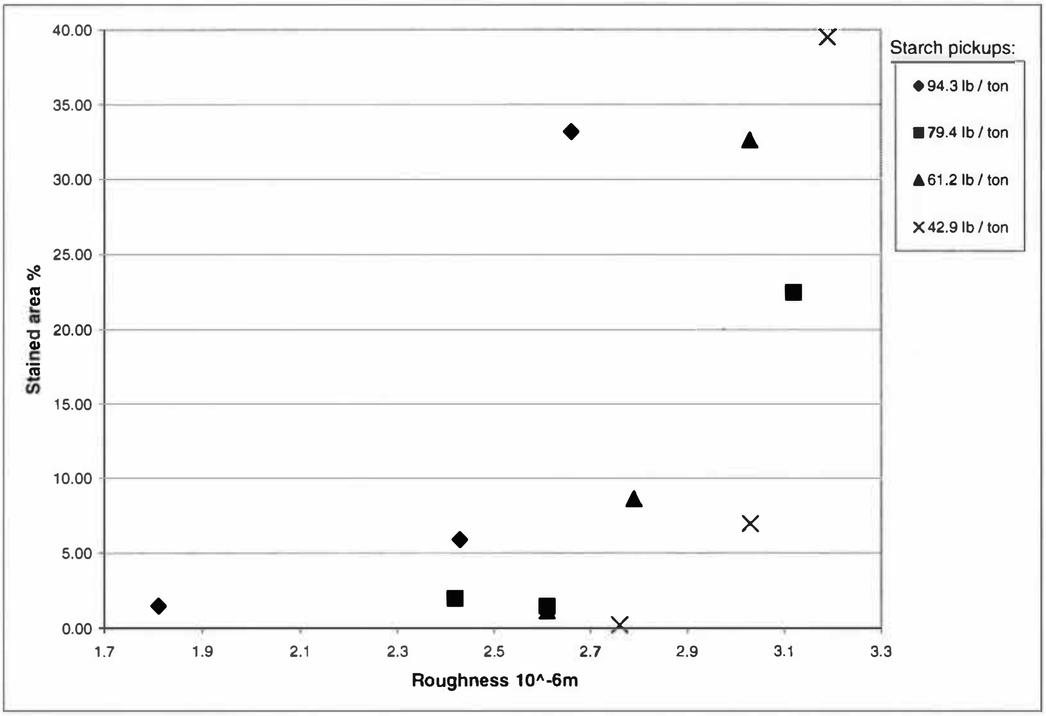


Figure 29. Stained Area and Roughness Influence for Stackot4.

Stained area versus roughness is a little bit more complicated. However, it can be concluded that stained area increases as roughness increases. The trend, though, is not as clear as it was for the porosity data. Figure 27 shows the relationship between the stained area and the roughness for all available starch sources at their highest pickup. Stained area rapidly decreases with smoothing action down to a certain point where very little change of stained area is observed with a decrease in roughness.

The effect of different starch pickups on this relationship is shown in Figures 28 and 29. Starch pickup moves the point, where the line curves, to the right or left according to the corresponding roughness.

Release Force

Release force and stained area are not highly correlated. Therefore, other

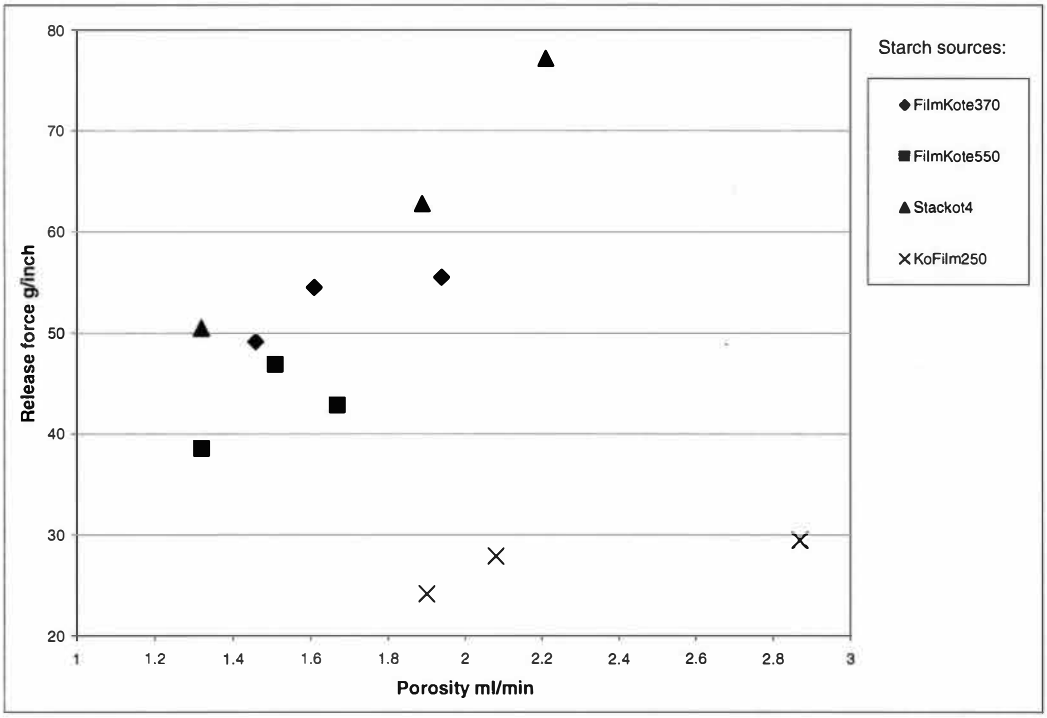


Figure 30. Release Force and Porosity Influence for Similar Starch Pickups. (90 – 115 lbs/ton)

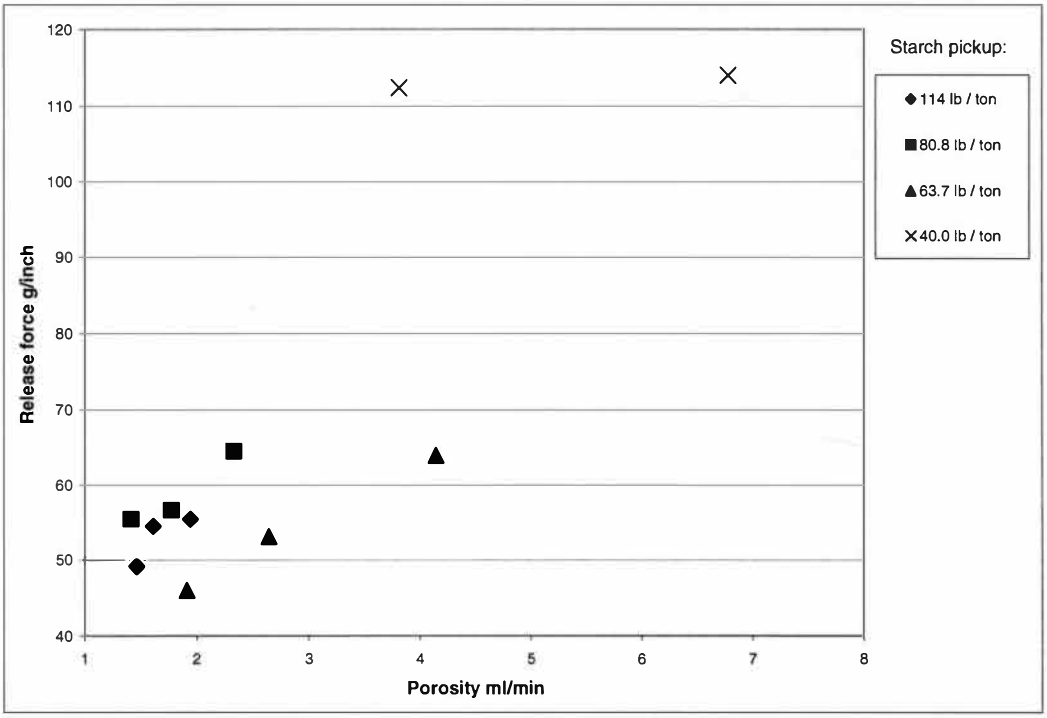


Figure 31. Release Force and Porosity Influence for FilmKote370.

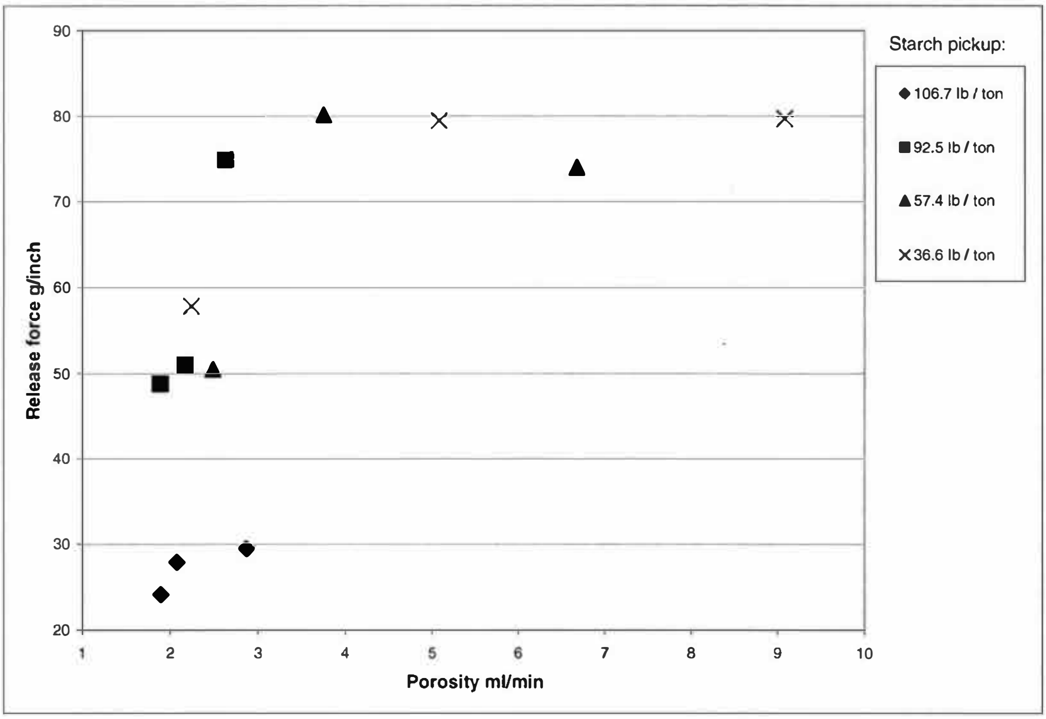


Figure 32. Release Force and Porosity Influence for KoFilm250.

parameters that could be correlated with stained area were sought. Figure 30 shows this trend. No steep slopes are present. Release force is decreasing, as expected, with decreasing porosity. However, the starch source is effecting this force in a significant way. FilmKote550 does not effect the release force too much, but Stackot4 does. On the other hand, KoFilm250 provides much less release force than the remaining starch sources.

When Figures 31 and 32 are examined, it can be seen that a reduction in release force is reached with decreasing porosity. However, for FilmKote370, the lowest starch pickup significantly increases the porosity, and, hence, the release force as well. On the other hand, KoFilm250 has the three lowest starch pickups in the same range, but the highest pickup significantly reduces the release force. Therefore, starch structure again effects the final silicone holdout and indirectly the release force.

Release force versus roughness follows almost the same tendency as Gurley porosity. Release force as a function of porosity showed almost no significant difference between three starch sources (Figure 30). For roughness, this difference is more significant. Figures 33 shows again that KoFilm250 has the lowest release force with the highest roughness. The remaining starches are more distinguished than in Figure 30. This is due to the fact that the same stained area does not necessarily mean the same release force. Silicone coat weight influence on release force is shown in Figures 34 and 35. These trends are very similar to those with porosity. However, it can be observed that some starches tend to increase release force at high silicone coat weights. This is due to uncured monomer being retained at the surface of the paper.

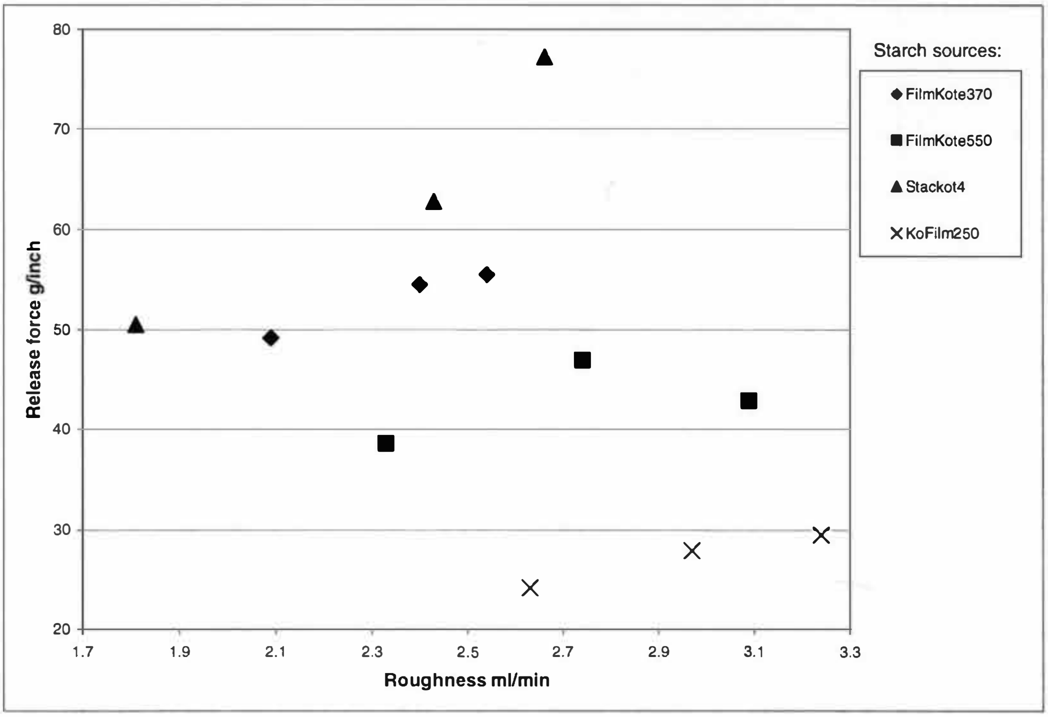


Figure 33. Release Force and Roughness Influence for Similar Starch Pickups. (90 – 115 lbs/ton)

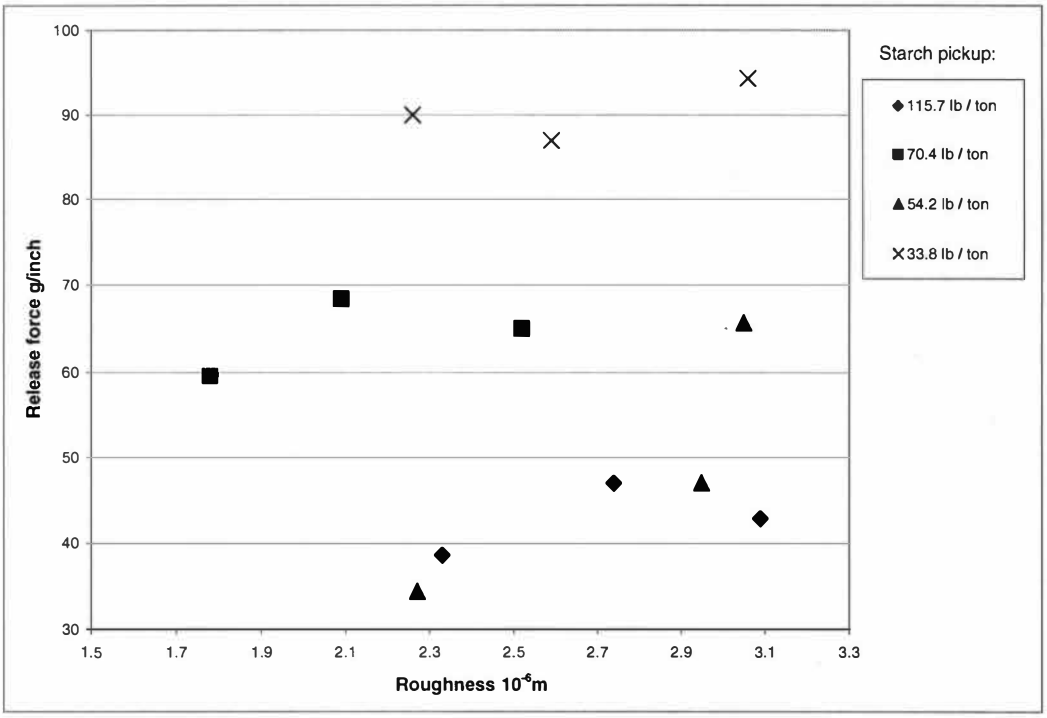


Figure 34. Release Force and Roughness Influence for FilmKote550.

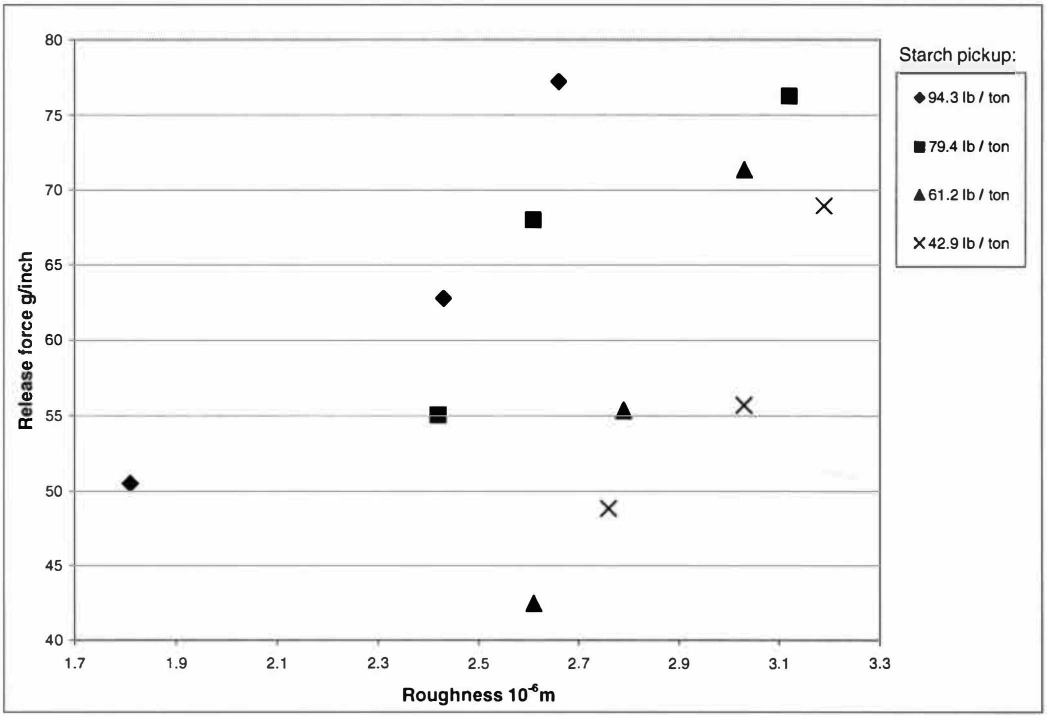


Figure 35. Release Force and Roughness Influence for Stackot4.

Such unreacted monomer strongly reacts with adhesive tape, resulting in less tackiness, and, consequently, in lower release force. Better or longer curing is necessary in such cases; however, then it will not be cost effective because of the additional energy used or slower productivity.

As was described above, both porosity and roughness significantly affect final silicone holdout. Porosity and roughness are results of prior variables such as calendering, sizing, starch pickup, and silicone coat weight. All these variables effect final roughness and porosity. For a silicone holdout, or, in other words, release paper quality, neither release force nor stained area is correct as a single variable. However, both in combination can assess final silicone holdout and release properties.

Ultrasound Absorption

Samples were tested for ultrasound absorption while being wetted by water and silicone monomer. From the output graph, two kinds of information are available: first, the time that it takes liquid to penetrate into the pores, and, second, the wetting curve. As can be seen in the Figure 36, transmittance increases with time to a certain level. After this level, transmittance significantly decreases to the point where it does not change anymore with time. The first transmittance increase is due to penetration of the water into the fibers. Air that is present in the voids has low ultrasound conductivity, and thus while being replaced by water, which has higher ultrasound conductivity, transmittance increases. The time, t_{MAX}, (Figure 36) is the time of the maximum transmittance; it represents the time needed for the water to replace all air voids, and thus is the maximum penetration point. After this point is reached, water starts to interact with fibers and wetting occurs. Fibers are being released and loosed which results in lower transmittance. The curve reveals how fast fibers absorb the water.

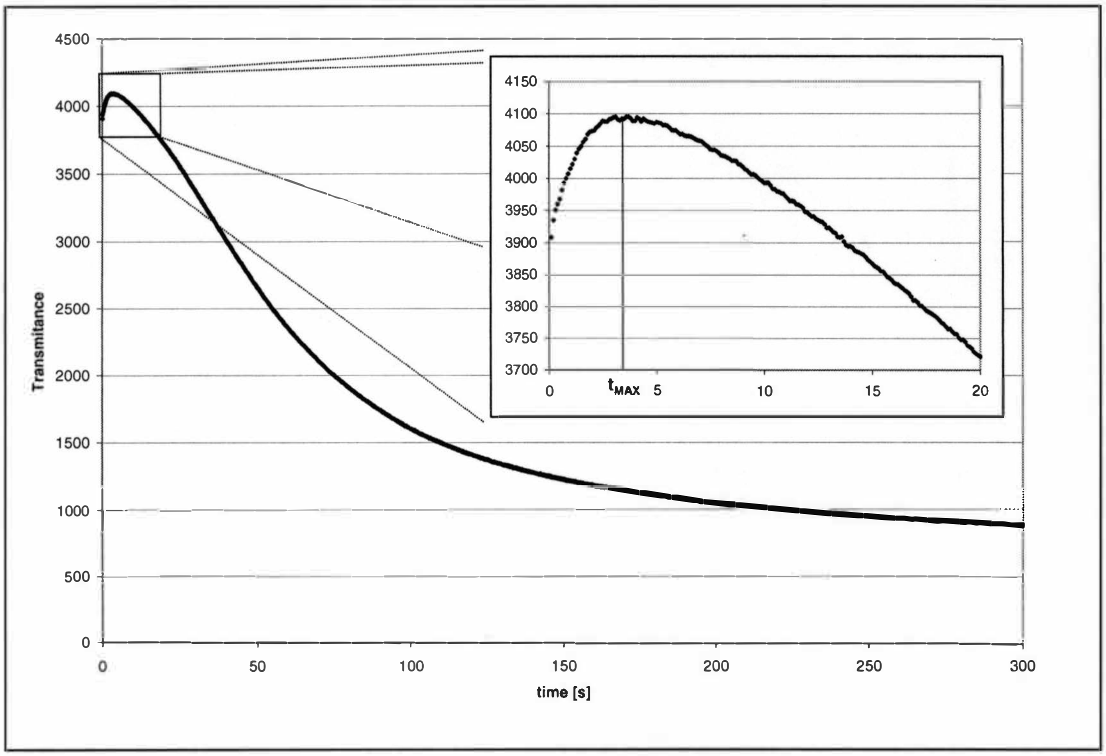


Figure 36. Transmittance and Time Relationship for Stackot4 and Water.

The time that can be observed from these curves is a very important variable in the Lucas-Washburn equation. Application of this equation will be discussed later in this chapter. To understand the wetting curve, several samples were compared. The basesheet, which is very porous and was expected to have a very high penetration, the surface sized basesheet, which is more closed up, and has lower penetration, and two different silicone coat weight sheets, which are very sealed and were expected to have very low penetration, were chosen to study this wetting curve. Figure 37 shows the wetting curves for these sheets. As can be observed from this figure, the basesheet has a very steep slope and the curve reaches a "constant" value within 20 seconds. The next curve, the starch coated sheet, does not have so steep a slope and within 300 seconds the curve is still not at its "constant" value. Next, two curves belong to silicone coatings, and it is clearly seen that within 700 seconds these sheets are still absorbing water. Therefore, the general rule is that open structure sheets have very steep slopes, and the curves reach their steady state value within a short period of time. On the other hand, closed structure papers have a gradual slope, and their curves do not reach their steady state values within short periods of time.

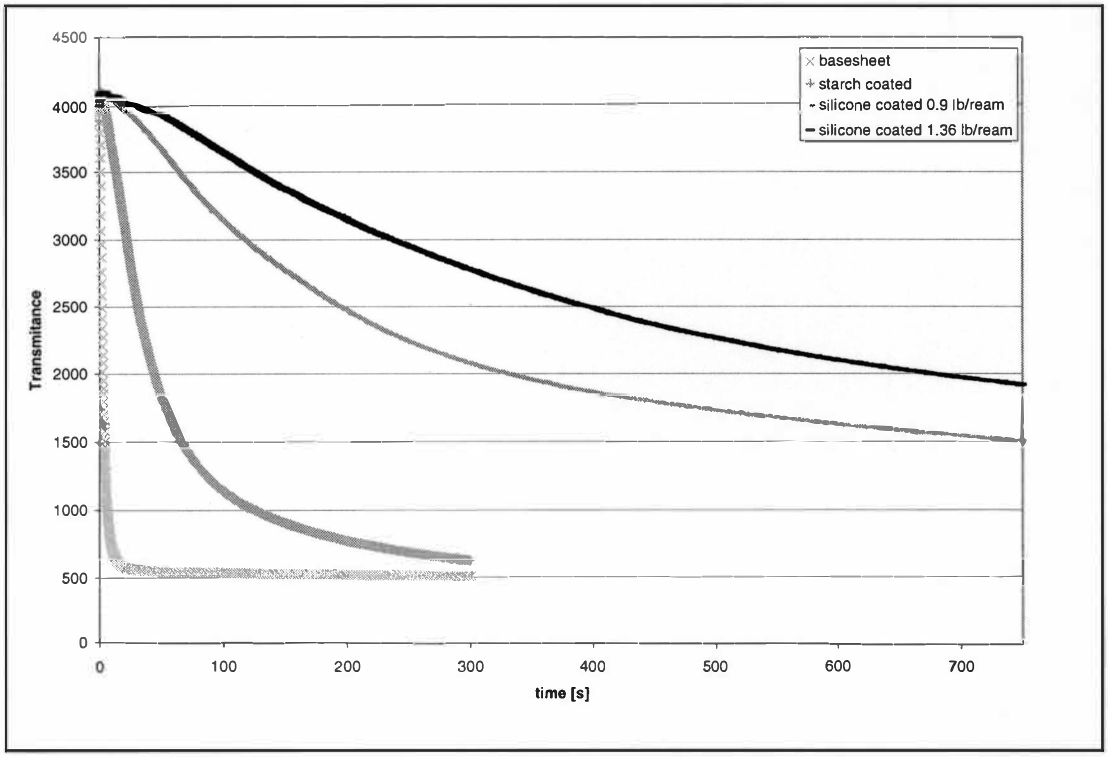


Figure 37. Comparison of Ultrasound Transmittance for Different Structured Papers.

To understand how the ultrasound transmittance changes for different starch pickups, Stackot4 was chosen and three sheets with different pickups were tested. As is seen in Figure 38, the highest pickup of starch results in a very closed structure sheet. Its penetration is low in comparison to the remaining curves. Next, two lower pickups result in sheets with a very similar wetting curve, and hence, the penetration rate is almost the same. For comparison, a basesheet wetting curve is included.

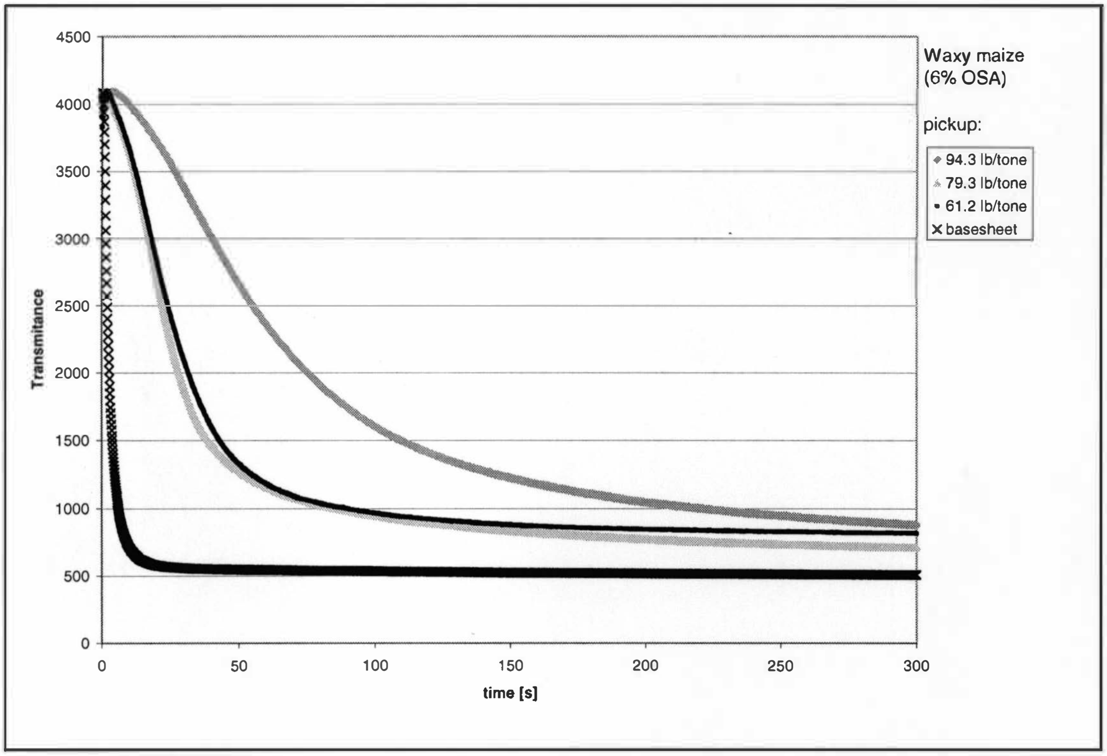


Figure 38. Wetting Curve for Stackot4 and its Three Different Pickups.

Different starches used as sizing agents result in different sheet properties. In order to study wetting curve for different starches, samples for each starch with one pickup were selected and tested. Pickups are in the range of 70 – 90 lb/ton. From Figure 39 it can be observed that tapioca (3% OSA) has the best sealing properties. The sheet is most closed and penetration is very low. It is very good for silicone holdout, because the silicone is less likely to migrate into the sheet than for the other starches. The worst starch, waxy maize (acetylated), has a steep slope, and within about 180 seconds it reaches the same level of transmittance as the basesheet. This means that within 180 seconds the amount of penetration is equal to the basesheet. Waxy maize (degraded) is a starch that lies between those two described above. It provides some sealing, but not as good as tapioca does. Waxy maize (6% OSA) when compared to waxy maize (degraded), provides slower penetration, but, in the final result, it absorbs more water. To conclude, tapioca provides the best sealing properties, and waxy maize (acetylated) is the worst starch as a sizing agent.

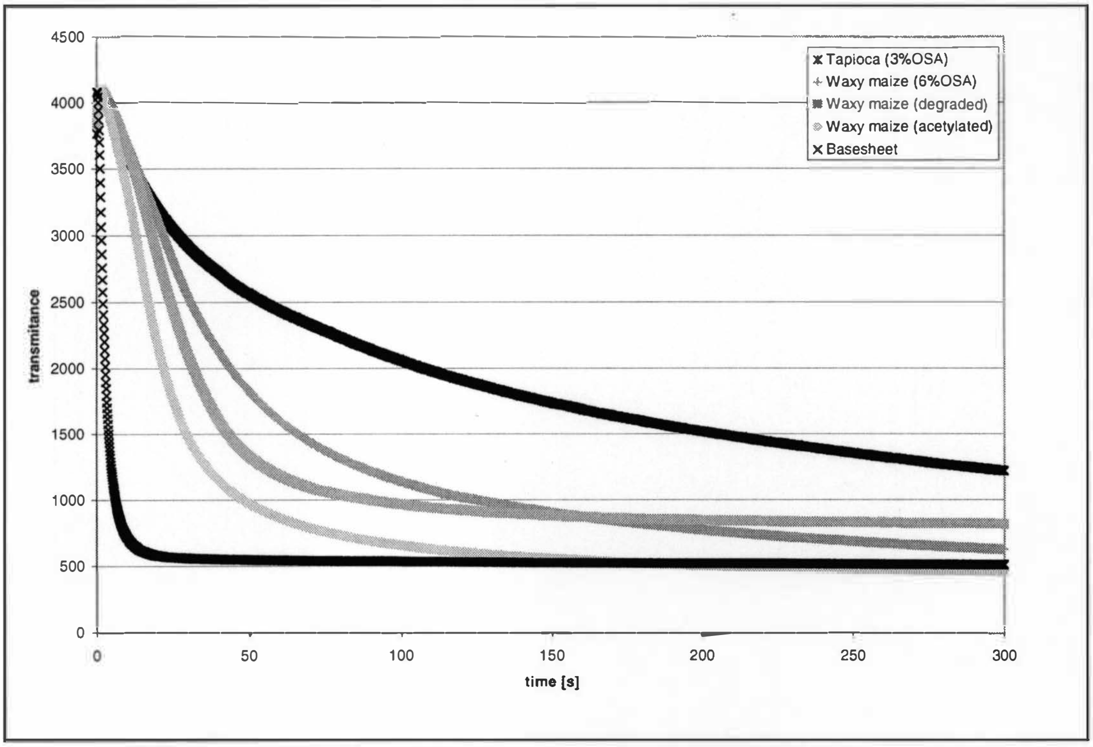


Figure 39. Ultrasound Transmittance Comparison for Different Starches.

When silicone monomer, instead of water, was used for testing ultrasound transmittance, different types of curves were observed (Figure 40). Again, as for water, initial transmittance increase can be observed; however, the curve does not decrease anymore as for water, but, in some cases, it even increases. The first peak again comes from replacing air voids by silicone. Therefore, again the time of penetration can be observed. However, it is not clearly understood why transmittance continues to increase with time. It is expected that different types of fiber-liquid interaction exist for silicone than for water. Water is able to hydrogen bond; silicone

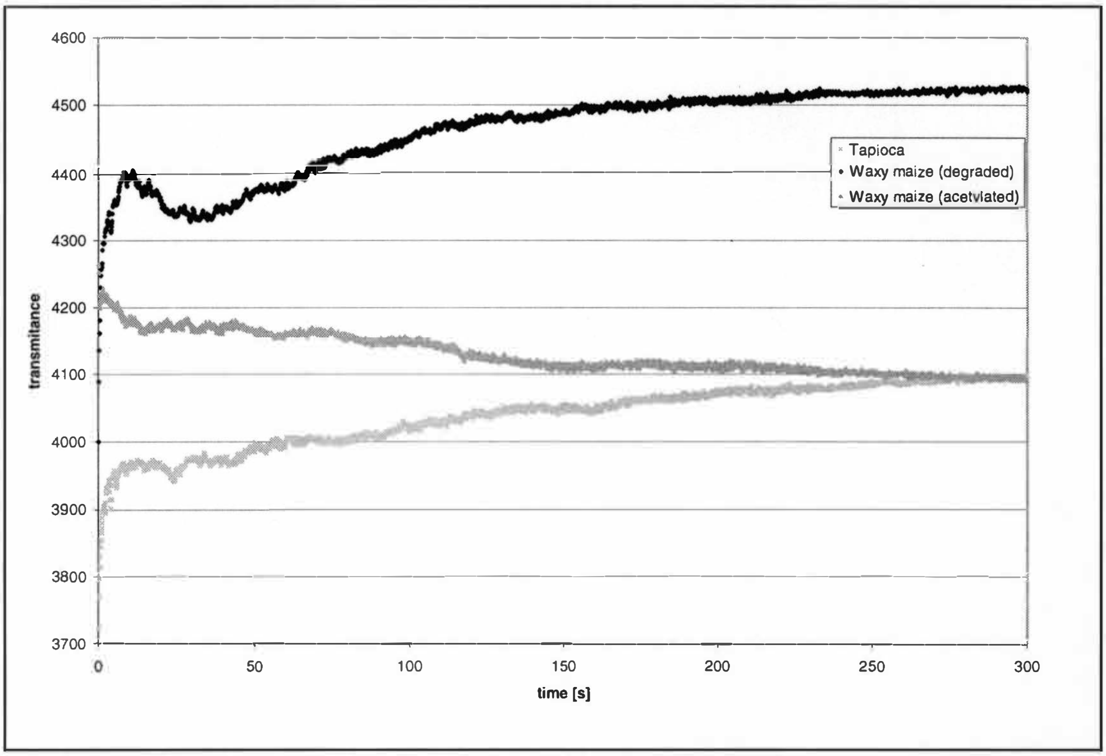


Figure 40. Wetting Curve for Different Starches and Silicone Monomer.

contains oxygen as well, but it is not available for hydrogen bonding because of its position. Additionally, silicone contains large methyl ($-CH_3$) groups that might interact with fibers. After the samples were tested and were taken from the instrument, it was observed that these samples became very stiff and brittle. This suggests that different types of interaction were present. However, further research should be done to understand this interaction.

Lucas-Washburn Equation

As was described earlier, the Lucas-Washburn equation is used to calculate the depth of penetration of liquid into the pores. Therefore, several parameters were collected in order to calculate this equation. Table 6 summarizes these variables, and it already includes the result calculated from Lucas-Washburn equation. The radius of the pores was measured by mercury intrusion. The time needed for penetration was obtained from the ultrasound transmittance curves. However, these curves were not so clear for all samples. Therefore, only two curves were studied and their time variables were collected. Viscosity and surface tension values of silicone were collected from the Dow Corning Co., who provided these materials. The contact angle for the water-fiber interface was easily collected; however, the silicone-fiber interface was very difficult to measure. After a drop of silicone monomer was released onto the sheet surface, this drop immediately spread over the surface and no interface was observable. It is not clear whether this silicone was absorbed or simply spread. Further research is needed to elucidate this phenomenon. From this observation, it can be concluded that the contact angle of the silicone-fiber interface was very close to 0^{o}.

$$\lim_{t\to 0} \Theta = 0$$

Table 6

Lucas-Washburn Equation Variables and Results

Starch pickup [lb/ton]	Radius of pores [m]	Time [s]	Contact angle [rad]	Penetration [m]
61.2	$2.75\ 10^{-9}$	11	0	$9.8\ 10^{-9}$
79.3	$2.1\ 10^{-9}$	5.2	0	$3.5\ 10^{-9}$

Finally, the depth of penetration was calculated. As can be seen from Table 6, the sheet with the higher starch pickup has the lower penetration. Therefore, higher starch pickup is closing the sheet more up, and thus the penetration is less as shown by ultrasound transmittance testing. Results of this equation were expected to be compared with EDS measurements. However, the edge of the sheet was not measurable by EDS because the signal of silicone was very low and it was not within a detectable region of the EDS instrument. However, a photograph of the cross section of the edge from the image analyzer was taken. A cross section of the edge of "good" and "bad" silicone covered sheets are shown in Figures 41 and 42, respectively. It is seen that "good" silicone coverage has a very low staining dye penetration, whereas "bad" silicone coverage has a high dye penetration, resulting in a darker stain in the green region, as was described earlier.

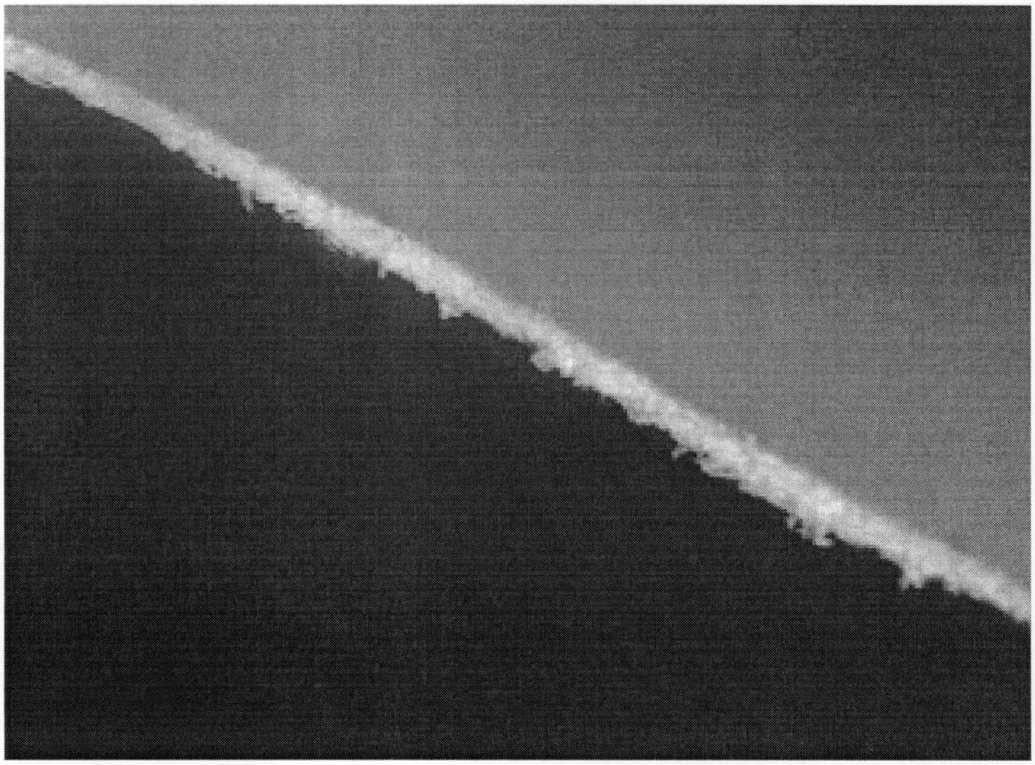


Figure 41. Edge Photograph of "Good" Covered Stained Sample.

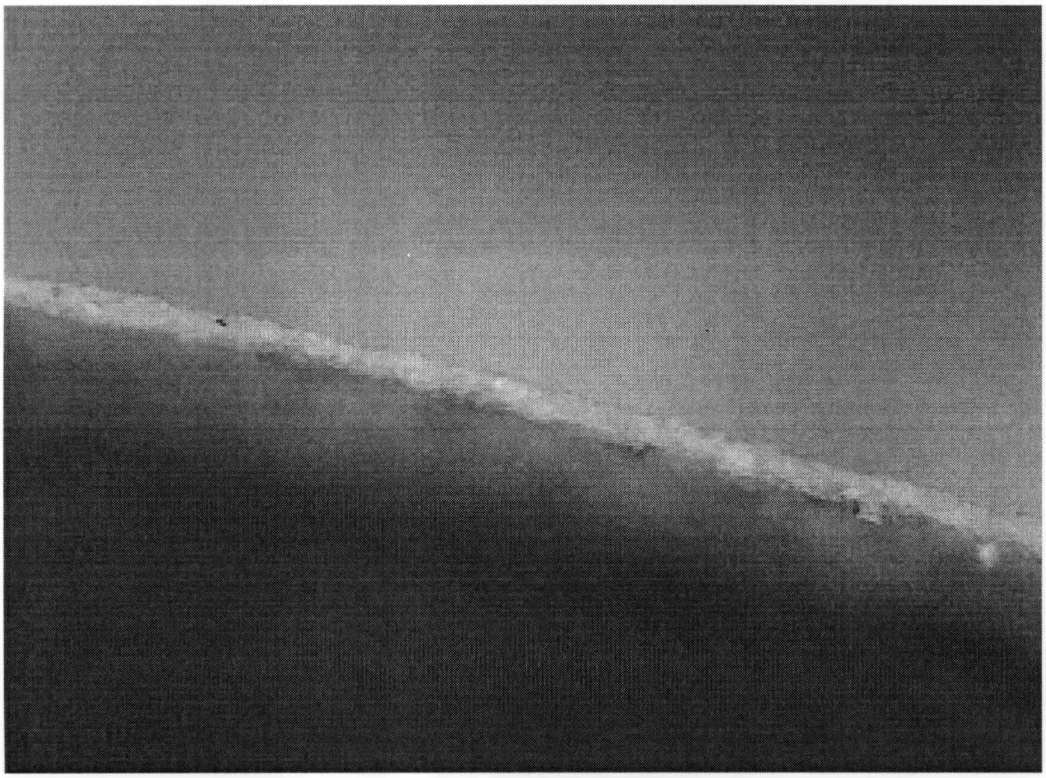


Figure 42. Edge Photograph of “Bad” Covered Stained Sample.

Multivariable Statistic Data Results

It can be observed from the correlation coefficients in Appendix A that starch pickup and starch solids are quite linear. For no starch, this coefficient is less than 0.97. Appendix B shows multivariable statistical analyses with the response variable being release force. It can be observed that in all starches the most significant variables are starch pickup or starch solids and silicone coat weight. All constants are significantly negative which means that the higher variable will predict a lower response variable. R^2 values ranging from 72% to 95% indicates the accuracy of the regression analyses. Roughness and porosity have been chosen once only to predict release force along with silicone coat weight and starch pickup or solids. Therefore, it can be concluded that starch pickup and silicone coat weight are the most important variables in predicting release force.

The stained area is a more difficult response variable. According to the datain Appendix C, no matter which starch is used, high silicone coat weight will hide all starch defects and will provide good coverage. The only significant variable in predicting response variable stained area was silicone coat weight.

KoFilm250 did not show any variable that significantly predicted the stained area.

CHAPTER VI

CONCLUSIONS

Several hundred starches are available as sizing agents, but not all of them are suitable for all application. Selection of starches for release papers is not easy. Test methods for assessing silicone holdout are not developed in detail, and they do not provide a lot of information about the starch itself. From this research it can be concluded that:

1. image analysis using green channel separation of the stained sample provides and significant information about the silicone coverage.
2. ultrasound transmittance very clearly shows the wetting curve of the sheet. Time for liquid to penetrate into the sheet can be measured. Several sheets can be tested and a very clear informative chart can be drawn. This test provides information concerning what efficiency the sizing agent provides, hence how good the silicone holdout will be.
3. from the selected starches, tapioca provides the best sizing efficiency. Ultrasound transmittance shows that tapioca closes the sheet pores the most. On the other hand, waxy maize (acetylated) provides the worst sizing efficiency. From image analysis, waxy maize (6% OSA) provides the worst histogram of gray values using green channel. The remaining starches have better coverage and do not provide significantly different histograms of gray values using green channel.

CHAPTER VII

RECOMMENDATIONS

This research was focused on developing the test methods. However, new test methods were proposed and several factors may influence the results of these test methods. Therefore, further research is recommended on the following issues:

1. silicone-fiber interactions for ultrasound transmittance tests. Silicone interacts with fibers in a different way and thus produces a different wetting curve. The time needed for silicone to penetrate into the sheet should be studied further
2. when the silicone coat weight is too high (>1.0 lb/ream), uncured monomer is probably present on the surface of the release paper. This monomer interacts with adhesive tape, thus causing error in the release force measured. The next research should focus on how much of the silicone is not cured and thus wasted, and how large is the ratio between silicone coat weight and its uncured part and its influence on final release properties.
3. non-internal sized paper was used. It is recommended that internal sized paper be used that provides good liquid holdout. Ultrasound transmittance can provide useful information about fiber-liquid behavior for different sheets.
4. a better EDS instrument for silicone detection in the cross section of the edge of the paper should be used.

Appendix A

Phase I – Correlation Coefficients

Table 7

Correlation Coefficient for All Variables for FilmKote370

Variables						
Variables	Starch solids	Starch pickup	Stained area	Rough-ness	Gurley porosity	Release force
Pickup	0.997					
Stained Area	0.251	0.265				
Roughness	-0.375	-0.371	0.248			
Gurley Porosity	-0.668	-0.646	0.228	0.337		
Release Force	-0.808	-0.781	-0.098	0.366	0.746	
Silicone Coat weight	0.194	0.191	-0.652	-0.442	-0.619	-0.290

Table 8

Correlation Coefficient for All Variables for FilmKote550

	Variables					
Variables	Starch solids	Starch pickup	Stained area	Rough-ness	Gurley porosity	Release force
Pickup	0.973					
Stained Area	0.214	0.168				
Roughness	-0.173	-0.071	0.497			
Gurley Porosity	-0.510	-0.473	0.364	0.527		
Release Force	-0.718	-0.718	-0.107	0.040	0.698	
Silicone Coat weight	0.110	0.112	-0.834	-0.700	-0.769	-0.355

Table 9

Correlation Coefficient for All Variables for Stackot4

	Variables					
Variables	Starch solids	Starch pickup	Stained area	Rough- ness	Gurley porosity	Release force
Pickup	0.996					
Stained Area	-0.114	-0.099				
Roughness	-0.491	-0.518	0.596			
Gurley Porosity	-0.592	-0.593	0.695	0.404		
Release Force	0.303	0.284	0.768	0.454	0.327	
Silicone Coat weight	0.114	0.115	-0.908	-0.528	-0.718	-0.734

Table 10

Correlation Coefficient for All Variables for KoFilm250

	Variables					
Variables	Starch solids	Starch pickup	Stained area	Roughness	Gurley porosity	Release force
Pickup	0.999					
Stained Area	-0.334	0.319				
Roughness	-0.057	-0.066	0.501			
Gurley Porosity	-0.517	-0.517	0.076	0.280		
Release Force	-0.770	-0.757	-0.347	0.196	0.650	
Silicone Coat weight	0.147	0.148	-0.455	-0.674	-0.754	-0.375

Appendix B

Phase II –Multivariable Statistic: Response Variable Release Force

Table 11

Regression Analysis for FilmKote370 and Response Variable Release Force

Predictor	Coef	SE Coef	T	P
Constant	94.79	23.57	4.02	0.002
Starch pickup	-0.5042	0.2348	-2.15	0.057
Gurley porosity	4.353	2.254	1.93	0.082

S = 17.31 R-Sq = 71.5%

Source	DF	SS	MS	F	P
Regression	2	7533.8	3766.9	12.57	0.002
Residual Error	10	2997.0	299.7		
Total	12	10530.9			

Table 12

Regression Analysis for FilmKote550 and Response Variable Release Force

Predictor	Coef	SE Coef	T	P
Constant	432.55	44.35	9.75	0.000
Starch solids	-19.720	3.017	-6.54	0.000
Starch pickup	2.5112	0.4524	5.55	0.001
Roughness	-82.12	11.36	-7.23	0.000
Silicone coat weight	-122.65	15.26	-8.04	0.000

S = 5.577 R-Sq = 95.3%

Source	DF	SS	MS	F	P
Regression	4	4439.7	1109.9	35.69	0.000
Residual Error	7	217.7	31.1		
Total	11	4657.4			

Table 13

Regression Analysis for Stackot4 and Response Variable Release Force

Predictor	Coef	SE Coef	T	P
Constant	115.71	18.96	6.10	0.000
Silicone coat weight	-35.430	5.399	-6.56	0.000
Starch solids	7.885	3.401	2.32	0.049
Starch pickup	-1.4949	0.7695	-1.94	0.088

S = 4.923 R-Sq = 86.3%

Source	DF	SS	MS	F	P
Regression	3	1221.89	407.30	16.80	0.001
Residual Error	8	193.91	24.24		
Total	11	1415.80			

Table 14

Regression Analysis for KoFilm250 and Response Variable Release Force

Predictor	Coef	SE Coef	T	P
Constant	285.19	81.40	3.50	0.010
Starch solids	-33.45	12.57	-2.66	0.032
Silicone coat weight	-93.25	21.76	-4.28	0.004
Roughness	-52.04	17.45	-2.98	0.020
Starch pickup	4.849	2.029	2.39	0.048

S = 6.801 R-Sq = 93.5%

Source	DF	SS	MS	F	P
Regression	4	4672.0	1168.0	25.26	0.000
Residual Error	7	323.7	46.2		
Total	11	4995.7			

Appendix C

Phase II – Multivariable Statistic: Response Variable Stained Area

Table 15

Regression Analysis for FilmKote370 and Response Variable Stained Area

Predictor	Coef	SE Coef	T	P
Constant	25.100	7.839	3.20	0.009
Silicone coat weight	-27.364	7.521	-3.64	0.005
Starch pickup	0.13050	0.06251	2.09	0.063

S = 6.051 R-Sq = 60.0%

Source	DF	SS	MS	F	P
Regression	2	549.24	274.62	7.50	0.010
Residual Error	10	366.18	36.62		
Total	12	915.42			

Table 16

Regression Analysis for FilmKote550 and Response Variable Stained Area

Predictor	Coef	SE Coef	T	P
Constant	67.21	12.12	5.55	0.000
Silicone coat weight	-57.02	10.29	-5.54	0.000
Starch solids	1.1212	0.5879	1.91	0.089

S = 9.069 R-Sq = 78.4%

Source	DF	SS	MS	F	P
Regression	2	2682.4	1341.2	16.31	0.001
Residual Error	9	740.2	82.2		
Total	11	3422.6			

Table 17

Regression Analysis for Stackot4 and Response Variable Stained Area

Predictor	Coef	SE Coef	T	P
Constant	58.070	6.861	8.46	0.000
Silicone coat weight	-46.748	6.841	-6.83	0.000

S = 6.480 R-Sq = 82.4%

Source	DF	SS	MS	F	P
Regression	1	1960.9	1960.9	46.70	0.000
Residual Error	10	419.9	42.0		
Total	11	2380.8			

For KoFilm250 no significant variables were found to predict response variable stained area.

Appendix D

Raw Data

Legend for Raw Data Tables

A	Silicone coat weight [lb/ream] (ream = 3000 sheets),
B	Starch solids being applied on the size press [%],
C	Starch pickup [lb/ton],
D	Stained area [%],
E	Roughness [10^{-6} m],
F	Standard deviation for E,
G	Gurley porosity [ml/min],
H	Standard deviation for G,
I	Release force [g/inch]
*	Samples with no silicone coverage and before supercalendering

Table 18

Raw Data: FilmKote370

A	B	C	D	E	F	G	H	I
0*	17	114				7.29	0.54	
0	17	114		2.83	0.15	3.59	0.24	
0.8	17	114	31.11	2.54	0.09	1.94	0.04	55.5
0.86	17	114		2.99	0.08	1.7	0.1	
0.95	17	114	5.35	2.4	0.1	1.61	0.05	54.5
1.13	17	114				1.47	0.05	
1.21	17	114		2.69	0.14	1.34	0.05	
1.29	17	114	2.23	2.4	0.11	1.46	0.05	49.2
0*	12	80.8				9.27	0.44	
0	12	80.8		2.82	0.05	4.26	0.21	
0.74	12	80.8	9.0	2.75	0.08	2.33	0.06	64.5
0.9	12	80.8		2.85	0.08	1.8	0.12	
1.03	12	80.8	4.14	2.88	0.09	1.77	0.08	56.7
1.15	12	80.8		2.68	0.06	1.52	0.05	
1.35	12	80.8	4.14	1.96	0.06	1.41	0.05	55.5
0*	8.5	63.7				18.70	0.33	
0	8.5	63.7		2.74	0.06	7.55	0.43	
0.69	8.5	63.7	15.35	3.00	0.11	4.14	0.22	64
0.96	8.5	63.7	8.09	3.05	0.06	2.64	0.12	53.2
1.15	8.5	63.7	1.12	2.52	0.15	1.91	0.06	46
0*	3.9	40				62	5.3	
0	3.9	40		2.76	0.03	19	1.11	
0.55	3.9	40	18.19	2.98	0.07	12.0	0.12	116
0.63	3.9	40		3.16	0.06	9.33	0.55	
0.82	3.9	40	3.39	2.82	0.06	6.78	0.52	114
1.08	3.9	40	1.86	2.66	0.07	4.73	0.41	122
1.13	3.9	40	1.12	2.71	0.07	3.81	0.45	112.4

Table 19

Raw Data: FilmKote550

A	B	C	D	E	F	G	H	I
0*	16.5	115.7				5.82	0.33	
0	16.5	115.7		3.22	0.06	2.85	0.12	
0.83	16.5	115.7	40.7	3.09	0.06	1.67	0.05	42.9
1.02	16.5	115.7	16.0	2.74	0.07	1.51	0.02	46.9
1.37	16.5	115.7	7.6	2.33	0.04	1.32	0.07	38.6
1.5	16.5	115.7		2.32	0.05	1.23	0.09	
0*	12.3	70.4				12.77	0.76	
0	12.3	70.4		2.72	0.06	4.71	0.16	
0.71	12.3	70.4	57.1	2.52	0.06	2.34	0.16	65.0
0.86	12.3	70.4		2.77	0.03	1.87	0.12	
1.08	12.3	70.4	13.4	2.09	0.05	1.66	0.06	68.4
1.16	12.3	70.4		2.34	0.1	1.49	0.06	
1.36	12.3	70.4	10.6	1.78	0.07	1.39	0.07	59.5
0*	8.3	54.2				20.73	0.44	
0	8.3	54.2		3.03	0.09	6.43	0.20	
0.75	8.3	54.2	30.98	3.05	0.05	3.00	0.08	65.7
0.98	8.3	54.2	8.78	2.95	0.07	2.46	0.12	47.0
1.21	8.3	54.2		2.64	0.08	1.90	0.11	
1.44	8.3	54.2	2.18	2.27	0.12	1.64	0.09	34.4
0*	4.5	33.8				31.99	1.16	
0	4.5	33.8		3.06	0.04	9.92	0.55	
0.68	4.5	33.8	36.1	3.06	0.03	4.7	0.28	94.4
0.90	4.5	33.8		3.00	0.04	3.5	0.26	
1.07	4.5	33.8	6.4	2.59	0.12	2.61	0.13	87.0
1.24	4.5	33.8	2.1	2.26	0.15	2.35	0.14	90.0
1.36	4.5	33.8		2.77	0.41	2.44	0.27	

Table 20

Raw Data: Stackot4

A	B	C	D	E	F	G	H	I
0*	15.8	94.3				12.84	0.88	
0	15.8	94.3		2.85	0.07	4.47	0.29	
0.73	15.8	94.3	33.2	2.66	0.05	2.21	0.18	77.2
1.01	15.8	94.3	5.9	2.43	0.11	1.89	0.11	62.8
1.20	15.8	94.3		2.55	0.04	1.48	0.13	
1.38	15.8	94.3	1.5	1.81	0.11	1.32	0.04	50.5
0*	13.5	79.4				44.06	3.07	
0	13.5	79.4		3.21	0.06	10.34	0.06	
0.74	13.5	79.4	22.5	3.12	0.08	4.18	0.34	76.3
0.85	13.5	79.4		2.96	0.04	3.92	0.22	
1.15	13.5	79.4	1.5	2.61	0.15	2.61	0.08	68.0
1.25	13.5	79.4	2.0	2.42	0.1	2.21	0.18	55.1
0*	8.5	61.2				69.45	1.93	
0	8.5	61.2		2.69	0.05	17.09	0.56	
0.58	8.5	61.2	32.6	3.03	0.03	8.15	0.64	71.4
0.66	8.5	61.2		3.14	0.07	7.51	0.58	
0.89	8.5	61.2	8.6	2.79	0.02	4.33	0.33	55.4
1.17	8.5	61.2	1.2	2.61	0.09	2.42	0.30	42.5
0*	4.5	42.9				103.5	3.9	
0	4.5	42.9		2.82	0.11	29.56	1.84	
0.53	4.5	42.9	39.5	3.19	0.05	16.60	0.68	69.0
0.64	4.5	42.9		3.21	0.04	13.46	1.02	
0.78	4.5	42.9		3.12	0.07	8.95	0.84	
0.86	4.5	42.9	7.0	3.03	0.07	6.83	0.25	55.7
1.13	4.5	42.9		2.75	0.06			
1.29	4.5	42.9	0.2	2.76	0.07	2.31	0.19	48.9

Table 21

Raw Data: KoFilm250

A	B	C	D	E	F	G	H	I
0*	15.8	106.7				23.22	2.08	
0	15.8	106.7		3.18	0.06	5.79	0.30	
0.78	15.8	106.7	24.3	3.24	0.05	2.87	0.20	29.5
0.97	15.8	106.7	4.9	2.97	0.08	2.08	0.08	27.9
1.27	15.8	106.7	2.6	2.63	0.12	1.90	0.13	24.2
1.48	15.8	106.7		2.52	0.12	1.59	0.07	
0*	13.0	92.5				36.26	3.52	
0	13.0	92.5		3.12	0.10	8.92	0.50	
0.85	13.0	92.5	1.6	2.97	0.10	2.63	0.13	74.9
0.95	13.0	92.5		2.98	0.07	2.77	0.21	
1.18	13.0	92.5	4.5	2.45	0.08	2.17	0.12	51.0
1.48	13.0	92.5	1.5	2.19	0.08	1.89	0.06	48.8
0*	7.8	57.4				65.29	3.45	
0	7.8	57.4		3.20	0.09	15.40	0.79	
0.74	7.8	57.4	3.1	3.21	0.06	6.68	0.23	74.0
0.77	7.8	57.4		3.05	0.07	5.56	0.64	
0.96	7.8	57.4	5.1	2.63	0.06	3.76	0.27	80.2
1.33	7.8	57.4	4.7	2.48	0.08	2.49	0.06	50.5
0*	4.3	36.6				105.00	3.70	
0	4.3	36.6		2.66	0.07	25.34	1.43	
0.62	4.3	36.6		3.07	0.08	10.82	0.70	
0.67	4.3	36.6	7.9	3.33	0.07	9.08	0.70	79.7
0.98	4.3	36.6	1.6	2.85	0.08	5.09	0.19	79.5
1.43	4.3	36.6	0.1	2.50	0.06	2.24	0.10	57.9

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