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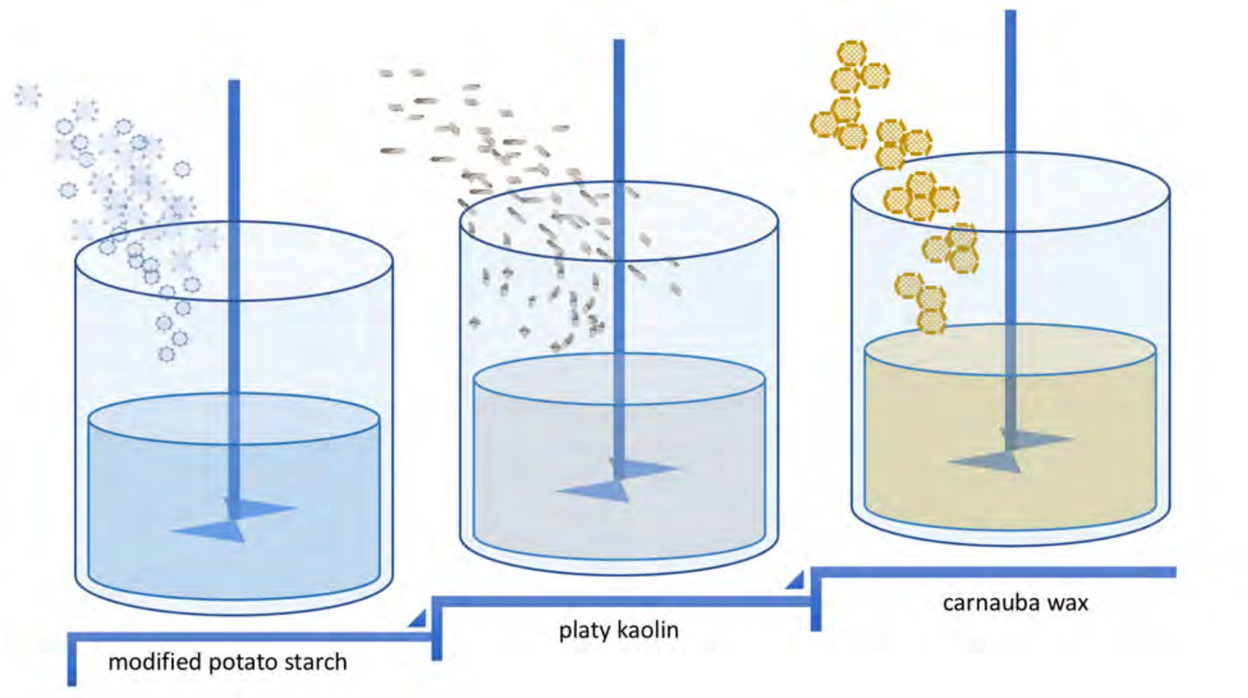

Renewable Barriers for Paper Packaging

Evaluation of barrier coatings consisting of modified potato starch, platy kaolin and carnauba wax

Bachelor's thesis in the Chemical Engineering Programme

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Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2019

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Cover: Schematic image of the components used in the barrier formulation

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Abstract

A significant part of packaging consists of petroleum-based plastics due to their advantage in barrier properties. The downside of these materials is their lack of sustainability. Paper is a good product to use for packaging since it is biodegradable and a plentiful resource. However, paper consists of fibrous networks that makes it a porous material with permeability for gas and water-vapor. To decrease permeability barriers can be used. In this project attempts have been made to develop a barrier coating made out of renewable and sustainable material.

The renewable barrier was made as a composite formulation, consisting of modified potato starch solution, natural wax dispersion and clay mineral suspension. Four different natural waxes and three different clay minerals were evaluated in terms of water-, grease and water vapor resistance. The water resistance was measured with COBB60-test, grease resistance was measured with KIT-test and water vapor was measured with water vapor transmission rate (WVTR). The additives that showed the highest water resistance and also had a good resistance for grease was selected to be used for the barrier product. Finally, the barrier formulation consisted of 45% modified potato starch solution, 15% kaolin suspension with surface factor 60 and 40% carnauba wax dispersion. It was desirable to further enhance the barrier and further attempts were made with bilayer coatings, applying different coating thickness and experimenting on a second paper substrate. Applying bilayer coating increased the barrier properties, ending up with a barrier product close to the intended results. This project has shown promising indications that it is possible to make a barrier product composed of modified potato starch, carnauba wax and kaolin pigment.

Keywords: barrier, coating, renewable, wax, filler, carnauba, kaolin, modified potato starch, COBB-test, KIT-test.

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And finally, last but by no means least, I would like to thank my husband for his never ending (almost) support and for doing most of the household chores plus taking all the "VABB".

Sofie Sjöstrand, Gothenburg, June 2019

Abbreviations

BWD	beeswax dispersion
CWD	carnauba wax dispersion
KS SF 100	kaolin suspension with surface factor 100
KS SF 60	kaolin suspension with surface factor 60
MPS	modified potato starch
MPSS	modified potato starch solution
PS	pigment suspension
SCWD	sugar cane wax dispersion
TS	talc suspension
WD	wax dispersion

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1
Introduction

BIM kemi is a leading company in manufacturing speciality chemicals for pulp and paper industry. BIM kemi has developed a coating product which also shows promising barrier properties against grease. This project is going to investigate whether it is possible to improve the barrier properties for better grease resistance and also some moisture resistance, while also making the product from renewable resources.

1.1 Background

A significant part of packaging consists of petroleum-based plastics due to their advantage in barrier properties.[1] The downside of these materials is their lack of sustainability, for instance the contribution to increasing CO_2 in the atmosphere and the build up of waste in oceans and landfills due to very low biodegradability and recycling difficulties. Alarming reports of the negative effects of global warming and approaching of the limit of the average global temperature has made the use of petroleum-based materials a very up-to-date problem, and developing substitutes has become an urgent matter.[2]

Paper is a good product to use for packaging since it is biodegradable and a plentiful resource. However, paper in itself does not have sufficient barrier properties. Paper consists of fibrous networks that makes it a porous material with permeability for gas and water-vapor. Further, paper also absorbs water from its environment due to the hydrophilic groups in the cellulose molecule. This causes the paper to loose its strength and mechanical properties.[3]

A common way to enhance papers water- and grease resistance is to use polyfluorinated surfactants (PFS) which are excellent barriers for water and grease. However, PFS is suspected to be a precursor for perfluorooctanoic acid (PFOA), which is persistent and has a strong environmental impact.[4]

There is a demand for packaging materials that are sustainable and safe for humans and the environment. Paper packaging with renewable barrier coatings is one possible solution.

1.2 Purpose

The scope of the project is to make a barrier coating for paper. The formulation for the barrier should consist of a binder, a hydrophobe and a filler. Modified potato starch solution (MPSS) will be used as a base for all formulations, and act as the binder. Natural wax will act as the hydrophobe and clay mineral as the filler.
The purpose of the product is to be used for low quality paper, for instance the wrapping for burgers in the fast food industry. For this the formulation would have to meet some specific requirements:

- COBB-value should be below 20 g/m^2

The effectiveness against moist, measured with COBB-test should have a COBB-value beneath 20 g/m^2. This is a relatively high value compared to today's market barrier products made from plastic or fluorocarbons but is considered sufficient for the products purpose.

- KIT-number should be 8 or above

The grease resistance is measured with a KIT-number, where a higher number is better. The aim was to exceed the already developed product from BIM kemi which have measured a KIT-number of 6. Therefore the aim was to attain a KIT-number of 8 or above.

- Water vapor transmission rate (WVTR) should be below 50 g/m^2

A value below 50 g/m^2 ensures a barrier product that can be used for multiple applications. For instance, if the barrier product were to be used for fast food wrapping and nothing else, a higher WVTR-value could be acceptable. The reason is that for example a hamburger paper is only used for a short time. Also, letting out the vapor keeps the bread from getting soggy.

- Stability for at least one week (no mould or separation)

A stable product is required, it cannot be used if it becomes mouldy or separated. Due to the limited extent of the project stability is only controlled for one week, although it would require 3-6 months to be considered on the market.

- Viscosity should be under 1700 mPa·s

Viscosity would have to be lower than 1700 mPa·s for the formulations to be able to work in a coating machine. Viscosity up to 500 mPa·s is the most viable and work in most coating machines. It is also important to consider the viscosity in the production of the formulation since a greater viscosity demands stronger pumps and more energy in the production.

- Total suspension solid preferably over 30 %, although 20 % is acceptable.

All the water will have to be evaporated after the coating process. Heat and energy is used when drying so a higher solids content mean less drying and is therefore a more economic and environmentally friendly process.

- Coating weight should be beneath 12 g/m^2

To work as a product in the industry the coating weight would have to be lower than 12 g/m^2.

- Limitations

In the beginning of the project some parameters will be fixed: The same paper substrate will be used throughout the experiments and it will be a Folding Box Board (FBB). Also, the same coating bar will be used. However, these parameters could be unfixed at the end of the project if there is a chance to enhance barrier properties by altering them.

Analysis of the barrier will be performed on a flat paper surface since creasing of a paper will weaken the barrier. The exposed edges of the crease will not be taken into account in this project.

2

The barrier composition

Renewable barrier coatings consists mainly of biopolymers, such as polysaccharides, lipids or proteins. They differ in barrier performance and are selected dependably on function and viability. Proteins (wheat gluten, soy protein, corn zein) are good barriers for oxygen. However, proteins are hydrophilic and are consequently poor barriers against water vapor. Polysaccharides (chitosan, plant cellulose, starch) have good adhesive properties and form strong films. They provide barrier resistance for gas, aroma and lipids. Similar to proteins, they have hydrophilic groups and are poor barriers for water vapor.[3]

Lipids (natural wax) are hydrophobic and suitable barriers against water. Coatings made from wax often becomes brittle and can form pinholes in the surface, demonstrated in Figure 2.1. Pinholes deteriorates the barrier properties considerably. A way of preventing brittleness is to prepare a composite coating that can be applied either as an emulsion/dispersion or as multilayer coatings. Applications of successive layers instead of emulsion coating results in higher water vapor permeability (WVP) resistance. The benefits of an emulsion coating is that it is easier to apply to the substrate surface than the bilayer coating.[3]

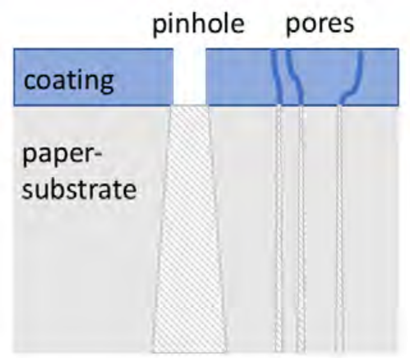

Figure 2.1: Pinhole in comparison to pores.

Inert fillers can be used to enhance the barrier properties. Pigments such as kaolin or talc can be used as fillers. Kaolin and talc are natural clay minerals with platy structures, meaning a structure of thin flat sheets. The structures increase the molecular orientation and make the path through the barrier more tortuous, and the barrier more difficult to permeate.[5] The filler also occupy volume in the coating and reduces the fiber content, making the paper material more viable.

Other additives are dispersing agents that are used to evenly distribute the pigments in the coating. Bactericides and fungicides are often added to stabilize the coating formulation and to prevent formation of mildew.[6]
In this project a composite barrier coating consisting of modified potato starch, natural- wax and minerals will be evaluated. The modified potato starch is selected

as the main component of the barrier and it is used primarily for its binding qualities. It adheres to the surface of the substrate but also ties in the composites. The natural wax act as a hydrophobe and the minerals act as a filler.[7]

2.1 Starch

Starch is a semi-crystalline polymer built up from amylose and amylopectin. The ratios vary depending on what plant species the starch is derived from.[5] It can be derived from a wide range of crops, for example potato, rice, corn and wheat. The utilization of starch is sustainable and economically viable since starch is abundant and accessible at relatively low cost. Potato and corn are the two most used sources for starches in the European paper industry.[1] A high content in amylose is wanted because it gives film-forming properties to the coating. The problem is that too high amylose content is difficult to disperse. Chemical modifications like gelatinization, is used to improve the properties for coating applications.[8] Corn starch has higher crystallinity and amylose values than potato starch which makes corn starch more difficult to gelatinize than potato starch. Also, corn starch contains fatty acids which might complicate the gelatinization by forming complexes with the amylose.[1] The modification by gelatinization causes the organized structure of the starch granules to lose their interference crosses and begin to swell. As the swollen granules increase their contact the viscosity increases as well. Further modifications are made to lower the viscosity and increasing the viscosity stability.

The modified potato starch used in this project is a pregelatinized potato starch ether. The three hydroxyl groups present on each glucose molecule are active sites for substitution reaction. The hydrogen in the hydroxyl group is removed and an ether group is formed instead. The primary function is colloidal stabilization by stericly hinder the association of starch molecules in solution. This gives the solution greater stability.[8]

2.2 Natural waxes

Waxes can be used as additives in order to get a better moisture resistant barrier coating. Common for most waxes is that they are solid, kneadable and polishable at room temperature. Waxes can be made *synthetically* or *naturally*. Natural waxes come from animals and plants and exhibit their wax properties without chemical treatment, whilst synthetic waxes attain their waxy properties by chemical treatment.

Three common natural waxes are *beeswax*, *carnauba wax* and *sugarcane wax*. *Beeswax* is a natural and non-toxic animal wax, is the by-product from honey production, produced by the honeybee. The beeswax have high hydrophobicity due to high content in esters of long-chain fatty alcohols and acids as well as long chains of alkanes. The *carnauba wax* is a vegetable wax from the carnauba palm tree, most found in Brazil. It is one of the hardest and of the highest-melting of the natural waxes and it has a fine smooth crystalline structure. It consists mainly of aliphatic esters, diesters and free alcohols. *Sugarcane wax* is formed as a powdery deposit on sugarcane stalks. It can be found in Brazil, China and South Africa. The wax consists mainly of aliphatic and sterol esters and free fatty- and waxy acids.[9]

2.3 Natural minerals

Pigment additives in barriers are added to occupy volume. It is economical but also enhances the barrier properties by creating obstacles. Pigments that can be used are for example clay minerals such as Kaolin, talcs, calcium carbonate, silicas and micas. Kaolin is a clay mineral which is made out of aluminium silicate.[7] Kaolin is important because it has a special stratified structure *platy*, which means it has a structure of thin sheets. The platy structure improves gas barrier performance.[10] The platy kaolin used in this project is a thin crystal kaolin with a higher surface factor than regular kaolin, as demonstrated in Figure 2.2. Increased surface factor means that the mineral pigments, crystals, have large plate diameters and thin plate thicknesses.

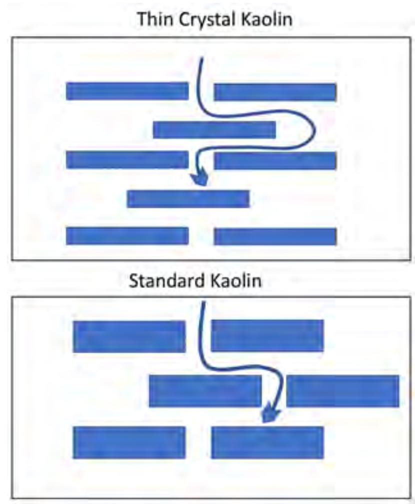

Figure 2.2: Comparison of regular kaolin and thin crystal kaolin

3

Methods

This section explains the methods that have been used to evaluate the quality of the formulation and the barrier performance of the coated paper substrate.

3.1 COBB-test

The COBB-test is used to determine the quantity of water that can be absorbed by the surface of paper or board in a given time. The apparatus allows the sample surface to be wetted uniformly as soon as the test begins, and also rapid removal of water from the sample at the end of the test. It is a good method to use for a first screening of the barrier water resistance. The simplest test COBB60, was used for this project, meaning the water exposure time was 45 s and time for weighing was 15 s. The COBB-value is received by calculating the weight of the absorbed water, divided with the exposed surface as seen in Equation 3.1,

$$\frac{a-b}{A} = COBB(g/m^2) \tag{3.1}$$

where, a=weight after (g), b=weight before (g) and A=cylindrical surface (m^2).

3.2 KIT-test

Grease resistance is measured with the KIT-test, where the results are reported in a value between 0 to 12. The higher the value of KIT the better grease barrier properties. The KIT-test consists of 12 solutions with different parts of castor-oil, toluene and N-heptane. Solution number one consists of only castor-oil and solution number twelve consists of the highest amount of N-heptane thus being the strongest solvent. The substrate is exposed to the different KIT-solutions for a set time and is observed visually. The KIT-test solution with highest number that does not penetrate the surface is the noted grease resistance (KIT-number) for the substrate.

3.3 WVTR

The WVTR of the barrier and paper is measured by exposing the coated paper to a moist (75% relative humidity, 23 °C) environment for two days. The sample is placed as a lid on top of a cylindrical container holding a highly hygroscopic salt. By weighing the container before and after, the amount of absorbed water vapor into the salt can be calculated. The WVTR-value is reported as grams of water that has penetrated a given area of material in a specified time. The stronger the barrier the lower permeability and thus lower WVTR value.[5]

3.4 SEM

The scanning electron microscope (SEM) is a qualitative method used for studying surface conditions. It is used for obtaining images of nano- and micro structures of a material.

A beam of primary electrons is focused with an array of magnetic lenses onto the sample. The kinetic energy from the electron beam cause secondary electrons to leave the surface of the sample. The number of secondary electrons depend on the surface composition. The electron beam scans the sample and the number of detected secondary electrons at each point produces the image. Many detected electrons generate a bright image point. No detected electrons generate a black image point, and in between there is a grey scale. [11]

4

Experimental

All formulations were made with MPSS (*modified potato starch solution*) as a base. PS (*pigment suspension*) and/or WD (*wax dispersion*) was added into the MPSS giving a two- or three component formulation, as demonstrated below in Figure 4.1.

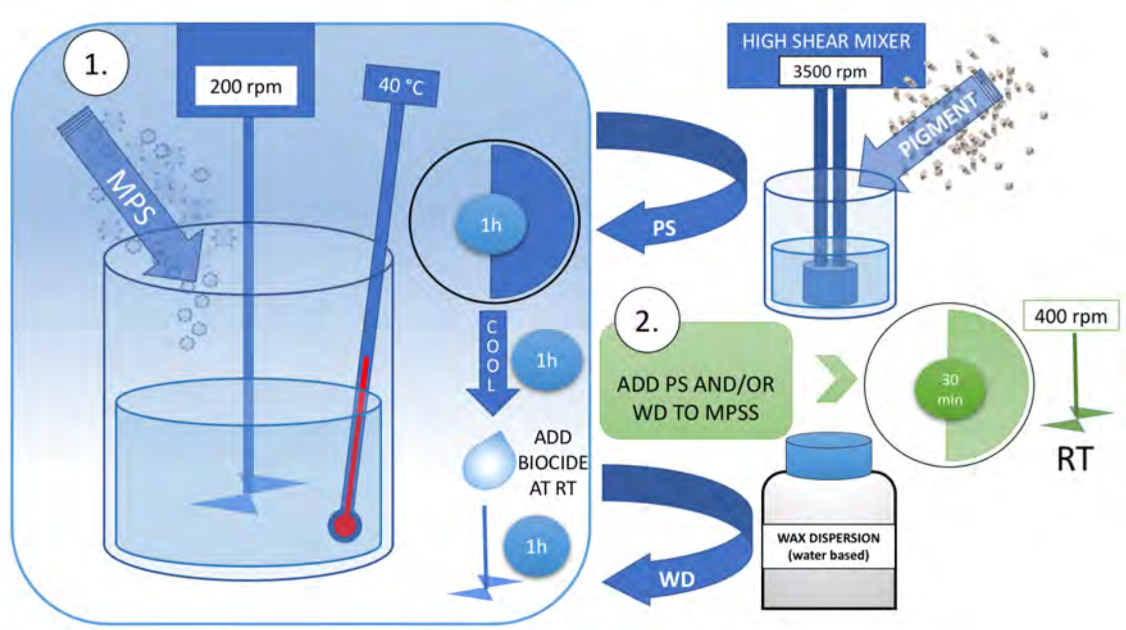

Figure 4.1: Schematic figure of formulation method. In step 1. the MPSS was prepared by adding MPS-powder into a beaker with tap water during continuous stirring. The temperature was set to 40 °C and stirring kept at around 200 rpm for 1 hour. The solution was then set to cool in a water bath for 1 hour before adding a preservative biocide. In step 2. PS and/or WD was distributed into the MPSS with continuous stirring at approx 400 rpm for 30 minutes at room temperature (RT).

The formulations were evaluated with quality parameters: pH, solids and viscosity. Thereon the formulations were coated onto a paper substrate and put to acclimatize in a climate room with temperature 23° C and relative humidity (RH) 50 ± 1%. The amount of coating was evaluated by subtracting the weight of a reference paper substrate from the weight of the coated sample. Water resistance was evaluated with COBB-test and grease resistance with KIT-test. Some samples were also evaluated for their water vapor permeability with WVTR-test. Surface characterizing was complemented with SEM.

4.1 Quality Parameters

The finished formulations were tested for their quality parameters: pH, solids and viscosity. The pH value was collected using Jenway 3040 Ion Analyser. For viscosity Model DV-II digital viscometer from Brookfield was used. The MPSS is a shear thickening fluid, meaning the value for the viscosity will increase while running the test. Therefore the instant value was noted down as the correct viscosity. Solid wt% was measured with Sartorius Infrared moisture analyzer. The analyzer evaporates all the volatile material, weighing just the solid material left. The weight is divided by its starting weight, giving the solid wt%. Product stability was supervised by adding approximately 50 ml sample into a transparent container, which was visually monitored during the time of the project.

4.2 Preparing formulations and coating procedure

For the coating characterization the formulations were coated onto the revered side of a folding box board (FBB) substrate, as shown in Figure 4.2. The coating machine used was K Control Coater from RK Printcoat Instruments, and Meyer bar coating was used for the application. Speed was set to 9 out of 10, 15 m/min being the highest speed.

The Meyer bar was a stainless steel rod winded with stainless steel wire of different diameters thus creating different film thickness. If nothing else is stated the bar with red color code was used. Data for the different bars can be seen in Table 4.1. The coated paper were thereon dried at 180 °C for 2x45 seconds in an Enz Technik CH-6075 oven. Lastly, the samples were put in a climate room (23 °C, RH 50 ± 1%) to acclimatize for at least 1 hour before further testing.

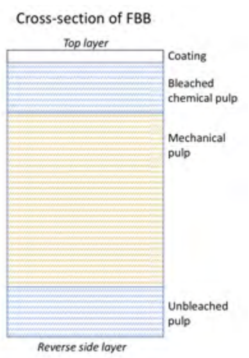

Figure 4.2: Coating was applied to reverse side layer

Bar No.	Color code	Wire diameter mm	Wet film deposit μm
0	White	0.05	4
1	Yellow	0.08	6
2	Red	0.15	12
3	Green	0.30	24
4	Black	0.51	40

Table 4.1: Data for standard K101 Meyer bar with color coded handles. Data adapted from the manual for "K Control Coater, K Paint applicator", by RK Print-Coat Instruments Ltd., Accessed: 2019-05-20, from `https://www.rkprint.com/`

4.2.1 Preparation of MPSS

MPSS was prepared by mixing the MPS powder with tap water using an overhead stirrer with a mixing paddle, see Figure 4.3.

749.5 g of tap water was measured into a beaker and put on a heater. The temperature was kept at 40 °C. 150 g of MPS powder was evenly dispersed into the water while mixing. In the beginning the mixing speed was kept at around 50 rpm to not splash water outside of the beaker. As the solution thickened the rpm was raised until a small vortex emerged from the impeller, around 200 rpm. The solution was left stirring for an hour and then taken off the heater. The solution was cooled to room temperature in a water bath with continued stirring, around 100 rpm for approx 1 hour. The solution was then removed from the water bath. Lastly, 0.5 g preservative biocide was added and left to stir for 1 hour.

Figure 4.3: Mixing paddle used when preparing MPSS

4.2.2 Preparation of additives

The waxes were received as water based dispersions from supplier and needed no preparation.

The kaolin suspensions (KS SF100/KS SF60) were made by mixing dry powder with tap water. The maximum wt% solids were used. First the water was weighed into a beaker, 222.2 g for KS SF100 respectively 187.5 g for KS SF60. Then 277.8/312.5 g (KS SF100/KS SF60) of powder was slowly and evenly dispersed into the water while mixing. First an overhead mixer was used and found to not be strong enough (this was insinuated by the formulations separating). The equipment was changed into a Silverson L4RT high shear mixer. When all the powder had slowly been dispersed into the water the shear mixing was continued for another 10-15 minutes. Lastly, the suspension was passed trough a 250 nm filter bag.

The talc suspension was received as a water based slurry from supplier.

4.3 Coating characterization

The coating characterization consisted of measuring the coating weight, evaluating the water and grease resistance and also water vapor permeability. Lastly, SEM-images were taken for a visual characterization.

4.3.1 Coating weight

The coated paper substrate sample was cut into a 50 cm^2 circle using a Lorentzen Wettre circle cutter. The sample was weighed on a Sartorius LA620S Precision balances ($>=$ 0.001 g). The amount of coating was determined by subtracting the weight from a reference substrate from the sample substrate's weight.

4.3.2 COBB-test

IGT Cobb Sizing Tester was used for measuring the water absorbency of the paper substrate. The paper substrate were cut into two smaller samples for double testing. The samples were cut to fit on top of the cylindrical liquid container of diameter 5.6 cm, in the COBB-tester. The liquid container was filled with 25 ml of distilled water and the first sample was weighed on a Sartorius LA620S Precision balances ($>=$ 0.001 g). The sample was then put on top of the liquid container and cinched with the lid of the COBB-tester. The sample holder was turned up side down and simultaneously a timer was started. The COBB 60 second test was conducted and the sample was in contact with the water for 45 s. The remaining 15 s of the test the sample was taken out of the holder and put between blotting paper. A pressing roller was run over the sample enclosed by the blotted paper, making the excessive water transfer into the blotted paper instead of the sample. The weight was noted. Same procedure was made with the second sample and an average was taken.

4.4 KIT-test

Three drops of KIT-solution was transferred to the paper sample with glass Pasteur pipettes. The sample was exposed for 15 seconds and afterwards the KIT-solution was wiped of. This procedure was adjusted until the KIT-test solution with highest number, that did not penetrate the barrier, was found. The parts for the different KIT-test solutions is accounted for in table 4.2.

The paper sample was visually observed for grease stains and smudge. The grease stains occurred when the barrier had been penetrated. Smudges occurred when the barrier was affected but not entirely penetrated. The smudges were sometimes very hard to determine and were not used for deciding the KIT-value. Only the grease stains were taken into account when evaluating the grease resistance.

KIT-value	Castor oil *parts*	Toluene *parts*	N-heptane *parts*
1	100	0	0
2	90	5	5
4	70	15	15
6	50	25	25
9	20	40	40
10	10	45	45
11	0	50	50
12	0	45	55

Table 4.2: Parts of castor oil, toluene and N-heptane in KIT-test solutions.

4.5 WVTR

Water Vapor Permeation Analyzer from Büchel B.V. was used for measuring the water vapor transmission rate (WVTR). The bottom of the chamber was filled with a salt solution of 200 g ammonium sulfate in 250 g of water, to receive RH 75 %. The sample containers were prepared by adding 3/4 of their volume with a highly hygroscopic salt (98 % calcium chloride) that had been dried and stored in a desiccator. The samples were cut into roundels using a template and was put in place on top of the container holding the salt. A frame with rubber and steel gaskets was screwed onto the sample container, securing the sample. The sample container was weighed and then put in the chamber of the WVP analyzer. The sample was then removed and weighed again after 24 hours and 48 hours. After the measurements the cleaned sample containers and the calcium chloride salt were dried for 1-2 hours, and then kept in a desiccator.

4.6 SEM

The samples were mounted on a stub covered with conductive tape. A small amount of silver conductive paint was added to connect the conductive tape and the paper substrate. The paint was dried with nitrogen gas. The sample was coated with gold plasma in a Quorum Q150R S Sputter Coater.

The surface of the paper samples were examined by SEM using a JEOL JSM-7800F Prime Field emission scanning microscope. The samples had been stored in room temperature under no controlled conditions, for 18 days before use.

5

Results and Discussion

The most promising formulation produced in this project consisted of 45 % MPSS, 15 % kaolin suspension surface factor 60 (KS SF60) and 40 % CWD. The performance of the barrier did not meet the desired results for KIT-, COBB- or WVTR-value. Attempts were made to enhance the barrier properties further by making bilayer coatings, applying different coating thickness and experimenting on a second paper substrate. Adding the coating as two layers enhanced the barrier qualities significantly and some intended results were reached. All gathered data is included in Appendix 1.

5.1 Selecting components

In the beginning of the project four different waxes and three different pigments were used. The first step was to narrow the study into fewer candidates. To find the best performing additives of wax and pigment they were first tested separately with MPSS in different parts of additive and MPSS. The best performing additives and ratios where then combined into a three-component formulation, with MPSS, pigment suspension (PS) and wax dispersion (WD), as illustrated in figure 5.1.

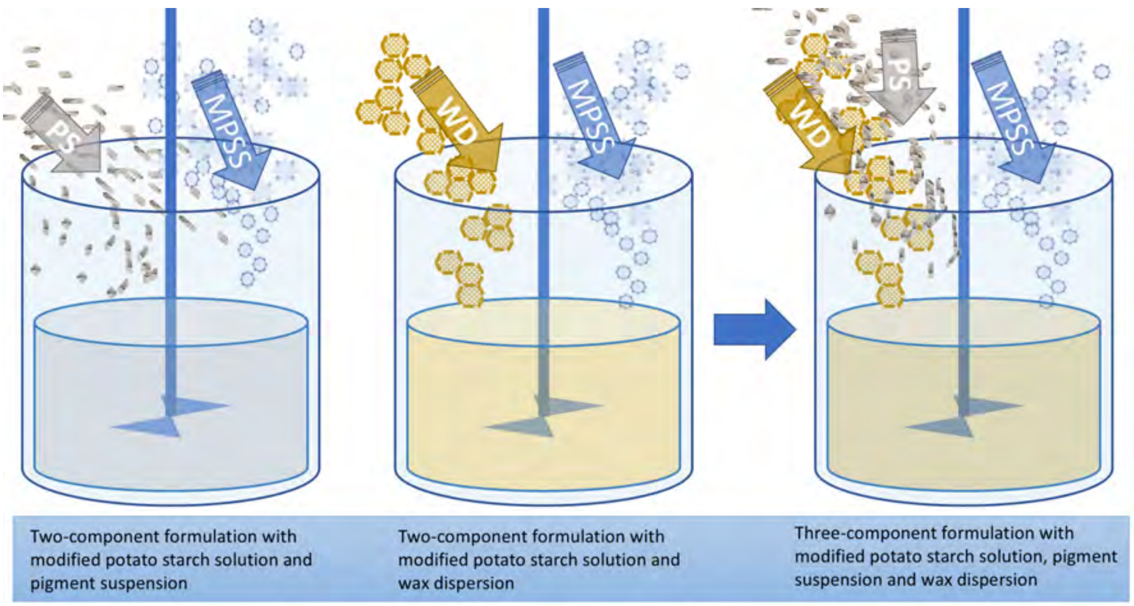

Figure 5.1: Illustration of method for selecting pigment- and wax components and amounts, for a three-component formulation.

5.1.1 Selecting the wax component

The four natural wax components consisted of two different sugarcane wax dispersions (SCWD) denoted A and B, and also beeswax dispersion (BWD) and carnauba wax dispersion (CWD). After a first evaluation, the SCWD A was suspected to be a poor candidate due to high viscosity, see figure 5.2. By increasing the amount of wax the viscosity decreased for all MPSS:WD formulations except the one containing SCWD A, which was then excluded from further experiments.

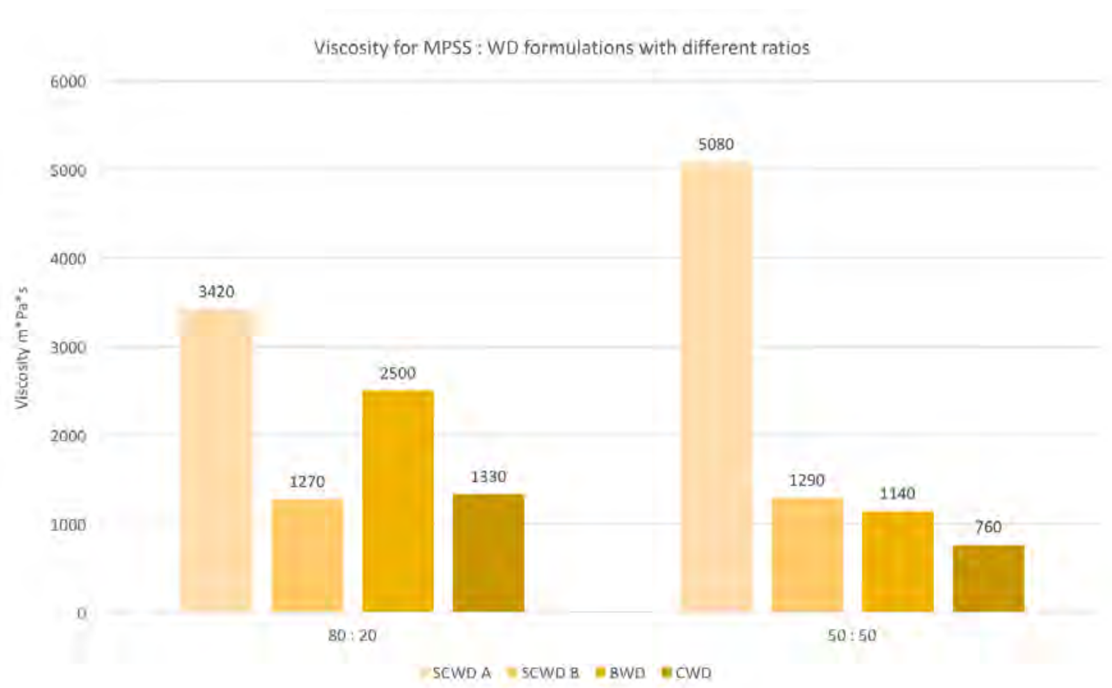

Figure 5.2: MPSS:WD was mixed into formulations with two different ratios and was tested for viscosity. First section shows ratio MPSS:WD 80:20 and second section shows ratio MPSS:WD 50:50.

The remaining three wax candidates were evaluated based on their performance in COBB- and KIT-test, seen in 5.3. A paperboard substrate with only MPSS coating was used as a reference. The lowest value possible is desired for the COBB-test. The reference had a COBB-value of 32 g/m^2. This was an average taken from tests with five different batches of MPSS. For a MPSS:WD formulation to be of interest, it had to have a lower value than the reference. As can be seen in figure 5.3 only 60:40 MPSS:CWD formulation reached a COBB-value that lied beneath the reference value at 32 g/m^2.

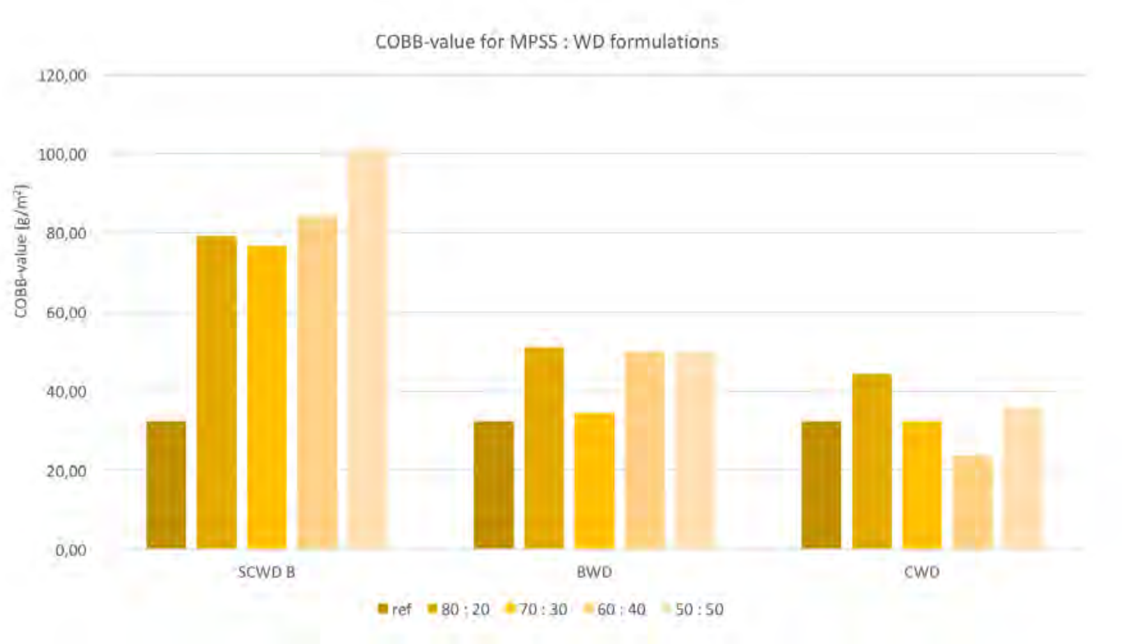

Figure 5.3: COBB-value for MPSS:WD formulations with different ratios, coated onto paperboard. Values are compared to a reference which is MPSS formulation coated onto paperboard.

The MPSS:WD formulations were also tested with KIT which measures grease resistance. All the formulations had values between 0-4. Since wax itself is a hydrophobic substance it is not expected to give barrier properties against grease. The KIT-value for uncoated paperboard was 0 and the value for MPSS-coated paperboard was 0-2, depending on which MPSS-batch was used. The 60:40 MPSS:CWD formulation performed KIT-value 4 and thus enhanced the grease barrier qualities to some extent. CWD was selected as the wax component to continue the experiments with.

5.1.2 Selecting the pigment component

The three pigments used in the project consisted of two platy kaolin-components with different surface factor and one talc-component. The pigment component is used as a filler which takes up volume in the coating, and also creating a more tortuous path for the permeants. It is a cheap material to use and also lowers the material cost. It is desirable to add as much pigment as possible without loosing barrier qualities. Too much pigment causes the formulation to separate. Pigments also increase the number of pores giving weaker barrier qualities.

A first evaluation showed that all MPSS:TS formulations separated, even at low concentrations down to 5 %. The TS-component was excluded from further experiments.

KS SF100 and KS SF60 were further evaluated. The first few formulations were mixed with an overhead stirrer. This method caused the MPSS:KS SF60 formulations to separate at even low amounts of KS (5 % was lowest amount tested). MPSS:KS SF100 formulations was a bit more stable: formulations with 8-10 % KS were stable for about one week while formulations with 5 % respectively 12-15 % separated after one day.

New formulations were made with a high shear mixer and the stability of both KS SF100 and KS SF60 was improved. Before changing the equipment, 10 % KS was evaluated to be the most stable amount of additive, and due to time limit 10 % was used in three-component formulations that was further analyzed with WVTR.

Evaluation of MPSS : KS : CWD with parts 50 : 10 : 40

Formulation	COBB-value g/m^2	KIT-value	WVTR-value g/m^2
Ref	48.8	0	602.05
MPSS	32.0	2	252.69
KS SF60	29.6	4	352.35
KS SF100	29.2	4	441.00

Table 5.1: COBB-, KIT- and WVTR-test on paperboard coated with MPSS:KS:CWD 50:10:40 formulations. The reference is a plain paperboard and MPSS is a paperboard with only MPSS coating.

Table 5.1 show that there is not much difference in KIT- and COBB-value for the MPSS:KS:CWD formulations. However, the WVTR-value shows big difference to advantage of the KS SF60-component. Both MPSS:KS:CWD formulations perform inferior to plain MPSS coating when evaluating water vapor barrier qualities. This could be an indication that the fillers caused an increase in pores.
Due to KS SF60 performing better than KS SF100 in the WVTR-test it was chosen as the pigment candidate to continue with.

5.1.3 Ratios for three-component formulation

The barrier formulation was decided to consist of MPSS, KS SF60 and CWD. Formulations with different ratios of additives were analysed to find the most favourable conditions. As can be seen in table 5.2 the ratio with best barrier performance was the one with 40 % WD and 15 % KS. It is close to the desired solids at 30 wt%. It has a beneficial coating weight and the viscosity is not too high (maximum 1700 mPa·s). However, the COBB-value sholud be below 20 g/m^2, thus is the value 27.60 g/m^2 too high. Also, the KIT-value should be at least 8 which means 4 is not a satisfying result.

Evaluation of MPSS : KS SF60 : CWD

Parts	Viscosity *mPa·s*	Solids *wt%*	Coating weight *g/m²*	COBB-value *g/m²*	KIT-value
70:10:20	1350	19.33	5.8	29.4	2
65:15:20	1670	25.20	3.9	28.6	0
50:10:40	1200	27.27	5.0	29.6	4
45:15:40	1290	29.52	5.5	27.6	4

Table 5.2: Evaluation of formulation MPSS:KS SF60:CWD with different parts additive.

5.2 Enhancing barrier qualities by changing coating parameters

When analysing the paperboard with the KIT-test it was noted that grease resistance decreased closer to the edges of the coating, this implied that the coating was unevenly distributed. This can happen when applying a coating to a rough and uneven surface, which applies to the surface of the paperboard. By adding a first coating layer that smoothen the surface, the coverage could be enhanced. For that reason experiments were continued with bilayer coatings. Also, another paper substrate with smoother surface was tested.

5.2.1 Coating coverage

A second paper substrate was brought into the project as a way of comparing the coverage of the coating. A better coverage would give the same grease resistance for the entire coating area. Also, a higher coating weight could be an indication to a more even coating layer.

The substrate brought in was a parchment with smoother surface than the paperboard. The formulations that were coated onto booth substrates is accounted for in table 5.3 and the analysed results for them can be seen in table 5.4.

Formulation and parts used in table 5.4

No.	Formulation	Parts
1	MPSS:KS SF100:CWD	60:10:30
2	MPSS:KS SF60:CWD	50:10:40
3	MPSS:KS SF100:CWD	50:10:40
4	MPSS:KS SF60:BWD	40:10:50
5	MPSS:KS SF100:BWD	40:10:50
6	MPSS:KS SF100:CWD	70:10:20
7	MPSS:KS SF100:CWD	65:15:20
8	MPSS:KS SF60:CWD	65:15:20
9	MPSS:KS SF60:CWD	70:10:20
10	MPSS: KS SF60	85:15
11	MPSS:KS SF60:CWD	45:15:40

Table 5.3: Index for formulations used in table 5.4

Comparison of coating coverage onto different paper substrates

	Paperboard			**Parchment**		
No.	Coating weight g/m^2	COBB-value g/m^2	KIT-value	Coating weight g/m^2	COBB-value g/m^2	KIT-value
1	5.2	32.4	4	7.4	32.8	6
2	5.0	29.6	4	6.1	28.0	6
3	4.2	29.2	4	6.3	27.2	6
4	4.8	27.6	2	6.1	33.6	4
5	2.4	35.6	2	6.2	31.6	2
6	2.4	35.6	4	9.1	28.2	8
7	2.8	40.4	2	9.6	29.0	6
8	3.9	28.6	0	9.1	30.8	6
9	5.8	29.4	2	9.6	32.2	8
10	5.2	25.2	6	9.2	33.6	6
11	5.5	27.6	4	7.8	32.0	4

Table 5.4: Comparison of coating coverage onto different paper substrates using paperboard and parchment substrates.

When comparing the results from the two different paper substrates the most obvious difference was the KIT-value, which was higher or equal for all coatings on the parchment substrate. This indicates a better coating coverage. For instance, number 2 (MPSS:KS SF60:CWD 50:10:40) on paperboard was sidenoted to withstand KIT-solution number 8 in the middle area, but closer to the edges it could not sustain more than KIT-value 4. When coated onto a parchment both edges and middle area sustained KIT-number 6. This is a clear indication that a better coverage has been achieved onto the parchment than the paperboard. It can also be seen from the results that the coating weight is higher for the coating onto the parchment, this indicates a thicker and more dense coverage. The coating for number 6 (MPSS:KS

SF100:CWD 70:10:20) and 7 (MPSS:KS SF100:CWD 65:15:20) increased the most when changing paper substrate. The coating weight on the parchment increased more than 200 % from its coating weight on the paperboard. This might be an indication that the starch binder perform different in order to the substrate, like a paper glue performing optimal on paper but not so well on glass.

It was also attempted to apply different coating thickness to the paperboard substrate by using the green Meyer bar which applies a thicker coating. In figure 5.4 it can be seen that the coating weight increases. However, it does not have to mean the coating layer is more even. The KIT-values seen in figure 5.5, also increase with the green bar and could be an indication for a more even coating layer, or at least a better coverage near the edges. The COBB-values are ambiguously improved as can be seen in figure 5.6. The data gathered is not sufficient for making any assumptions regarding benefits or disadvantages with different Meyer coating bars as to enhancing or diminishing the COBB-value.

Changing paper substrate or applying thicker coating increased the grease resistance but seemingly did not do much for the water resistance.

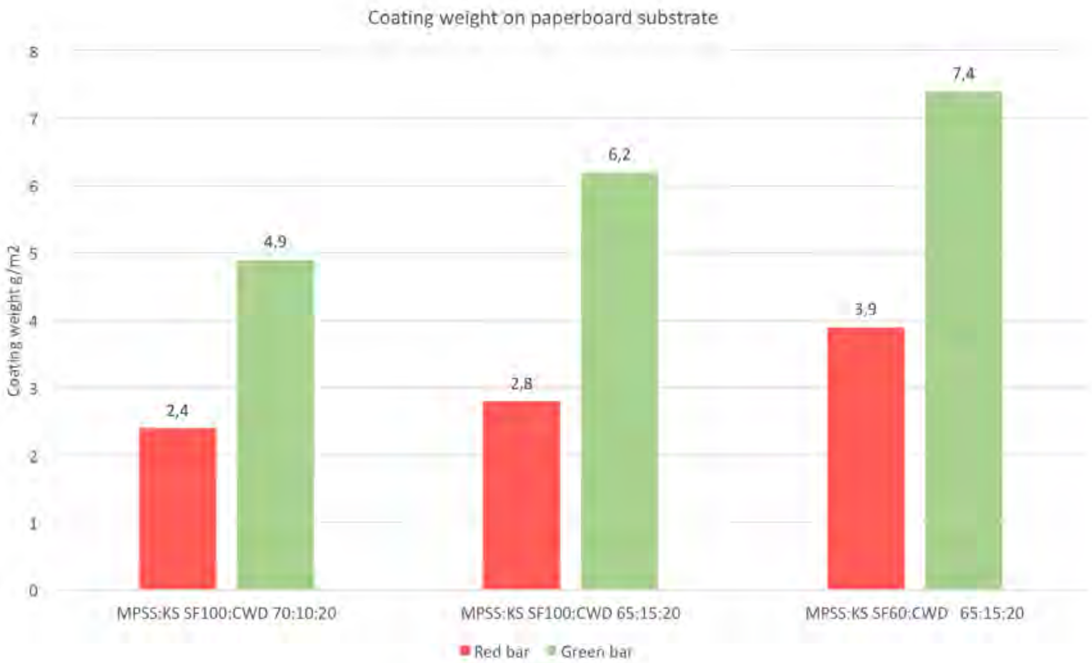

Figure 5.4: Coating values for coating with red and green Meyer bar on paperboard substrate

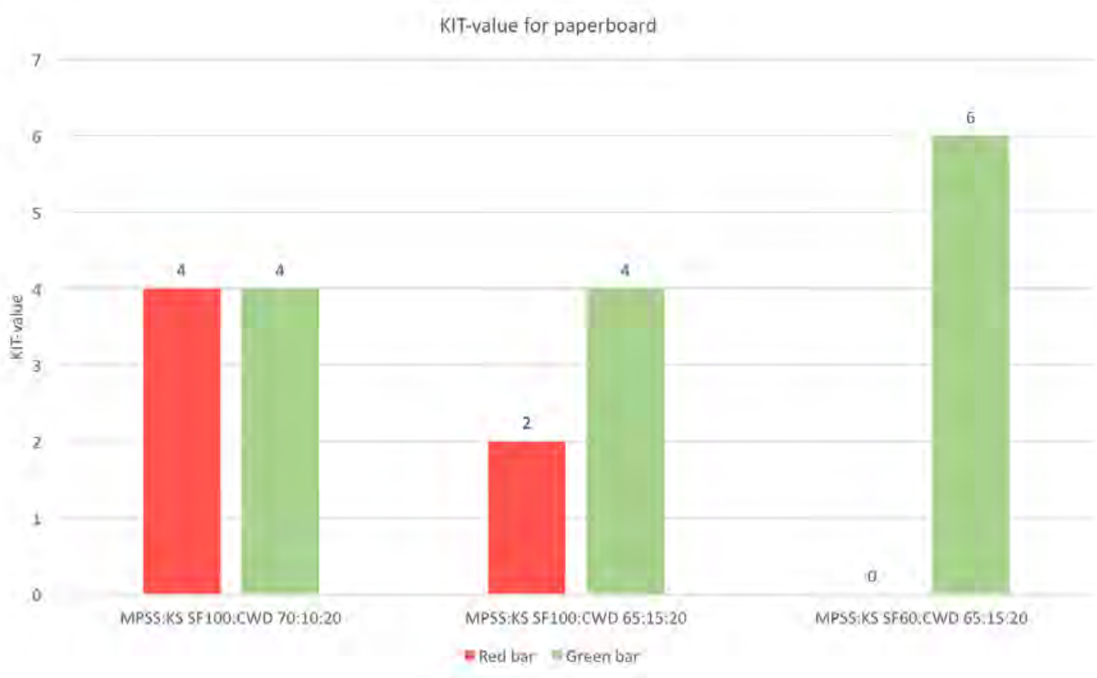

Figure 5.5: KIT-values for coating with red and green Meyer bar on paperboard substrate

Figure 5.6: COBB-values for coating with red and green Meyer bar on paperboard substrate

5.2.2 Bilayer coatings

Lastly, experiments with bilayer coatings were made. The two-component coating with MPSS:KS that had shown most promise was used as a primer coating layer. After drying the first coating layer a second layer was applied, using the best performing two-component MPSS:WD formulation. Different Meyer coating bars were used to decrease the coating weight. The most interesting bilayer coating was MPSS:KS SF60 85:15 coated with yellow Meyer bar as primer and MPSS:CWD 60:40 coated with red Meyer bar as top layer. The data for all bilayer tests can be seen in appendix A.5.

The intended results was to have a coating weight beneath 12 g/m^2 and desirably even lower. The water resistance measured with COBB, was supposed to be below 20 g/m^2. Grease resistance measured with KIT, was supposed to be higher than 8 and water vapor permeability measured with WVTR, below 50 g/m^2.

Final results

	coating weight g/m^2	COBB-value g/m^2	KIT-value	WVTR g/m^2
Ref: uncoated	0	48.80	0	602.1
Ref: MPSS-coated	2.9	32.32	2	252.6
Monolayer coating	5.4	29.75	5.5	268.8
Bilayer coating	9.2	22.35	11.3	290.6
Intended results	≤ 12.0	≤ 20.00	≥ 8	≤ 50

Table 5.5: Results showing the best performing bilayer coating MPSS:KS SF60 85:15 [yellow] + MPSS:CWD 60:40 [red] and the best three-component formulation with monolayer coating, MPSS:KS SF60:CWD 45:15:40 [red]. Values are mean values from several testings. The references consist of uncoated paperboard and MPSS-coated paperboard.

The bilayer coating outperformed the single layered coating and succeeded in reaching some of the intended results, as can be seen in Table 5.5. The desired COBB-value was almost reached, the KIT-value and coating weight was satisfying. However, the WVTR-value was far from reached.

The SEM-images of x500 magnifications, Figure 5.7, show that coverage of the fibres is fully attained with the bilayer coating (bottom right image). Coatings with MPSS and MPSS:KS SF60:CWD (top right and bottom left) exhibit voids or potentially pinholes.

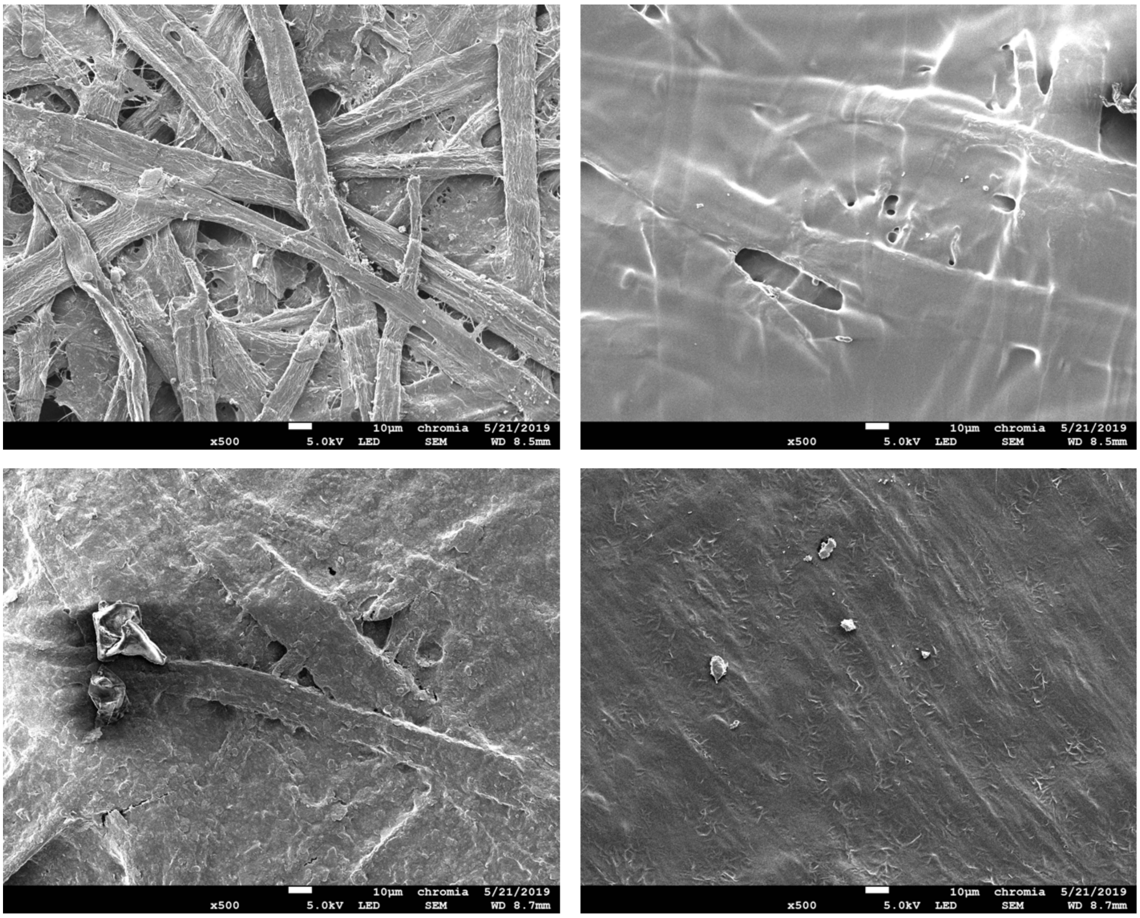

Figure 5.7: SEM-images x500 magnification. Top left: Reference uncoated paperboard. Top right: MPSS-coated paperboard. Bottom left: Monolayer coating, MPSS:KS SF60:CWD 45:15:40 [red]. Bottom right: Bilayer coating MPSS:KS SF60 85:15 [yellow] + MPSS:CWD 60:40 [red].

With magnification x5000, Figure 5.8, it is possible to see some flaky structure from the kaolin (bottom left image) and also some pores. The samples of MPSS-coating and the bilayer-coating (top layer) are absent in inorganic molecules which makes it hard to get sharp SEM images.

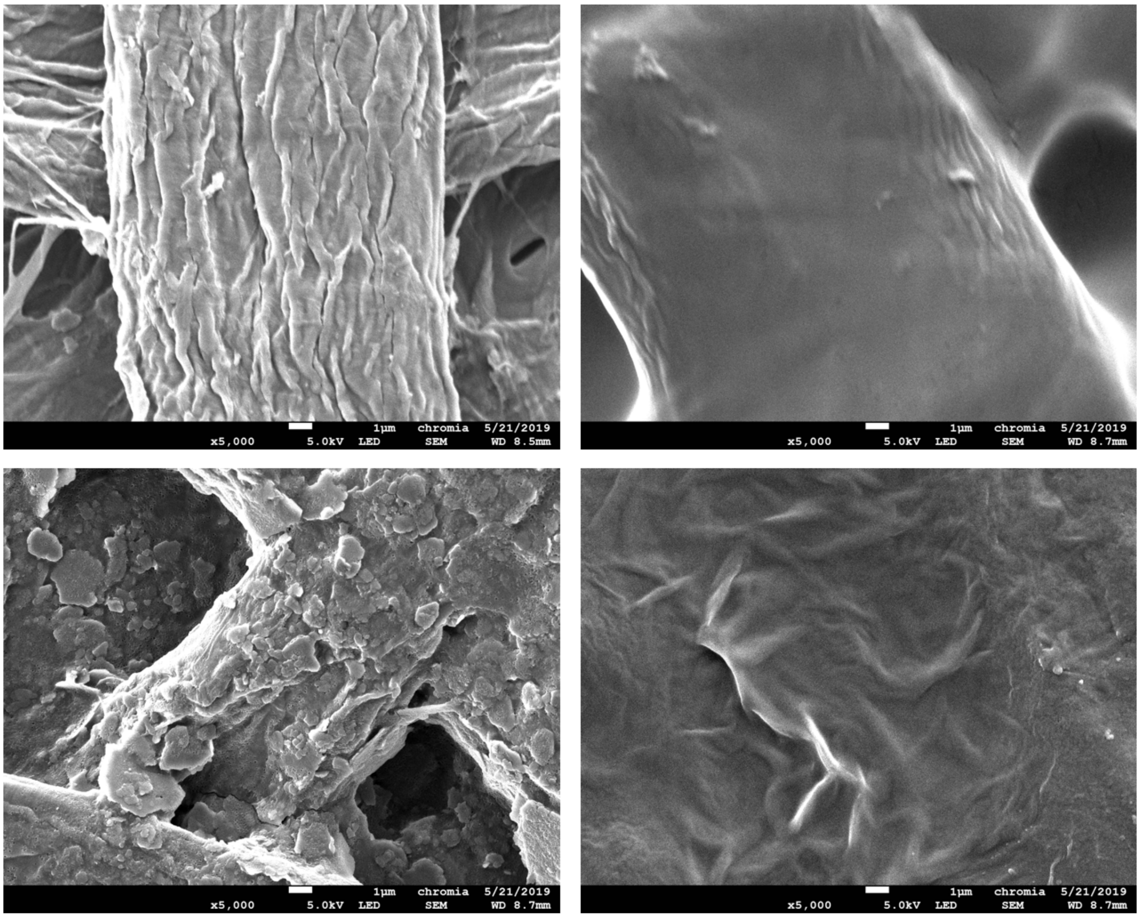

Figure 5.8: SEM-images x5000 magnification. Top left: Reference uncoated paperboard. Top right: MPSS-coated paperboard. Bottom left: Monolayer coating, MPSS:KS SF60:CWD 45:15:40 [red]. Bottom right: Bilayer coating MPSS:KS SF60 85:15 [yellow] + MPSS:CWD 60:40 [red].

In Figure 5.9 it is no longer possible to attain a distinct image of the MPSS-coated paperboard and no image is taken (organic material is more difficult to analyse with SEM). The two bottom images of the monolayer and bilayer coated substrates, show some pores. Pores can arise when adding fillers and also from the waxy component. Pores and pinholes also arise from air pockets during the coating process. The reference sample demonstrates that no pores existed before the coating process.

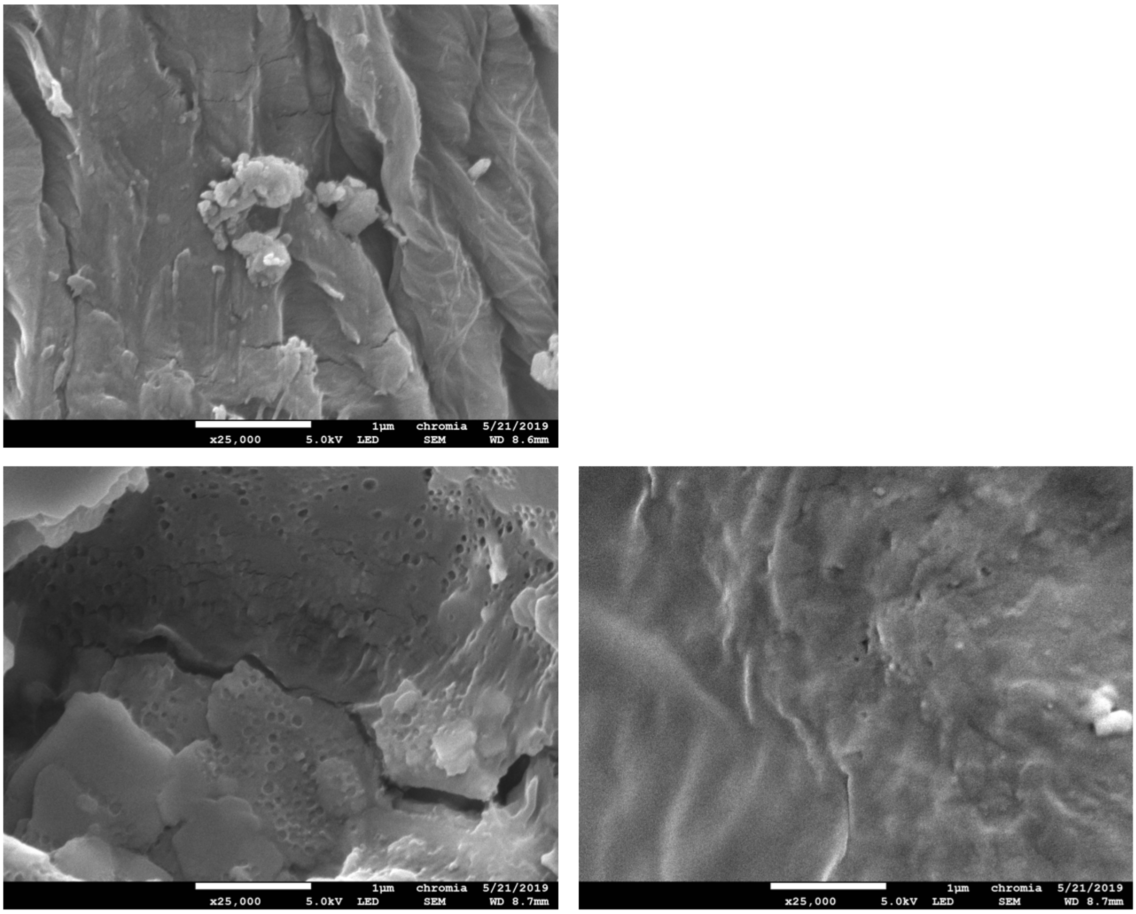

Figure 5.9: SEM-images x25000 magnification. Top left: Reference uncoated paperboard. Bottom left: Monolayer coating, MPSS:KS SF60:CWD 45:15:40 [red]. Bottom right: Bilayer coating MPSS:KS SF60 85:15 [yellow] + MPSS:CWD 60:40 [red].

5.3 Deviations

When making the formulations and measuring the components some amount of component has in general been lost during transfer between vessels. When mixing powders some amounts may have been lost due to dusting. The solid wt% is controlled afterwards but when making duplicates of formulations as for the MPSS, deviations may occur.

The MPSS formulations performed somewhat differently when measuring quality parameters, see Table 5.6. Some deviations might occur due to differences in measurements but also due to the size of the batch. Generally a larger batch (still in laboratory scale) gets higher quality than a smaller batch. Also, during the project, the formulations also improved because of the experience gained. However, the last batch, no 5 was used for all the formulations that were relevant to the final results. Hence, the final results will not have deviations due to differences in MPSS-batches.

MPSS with theoretical solid 15 wt%

No.	pH	Viscosity $mPa{\cdot}s$	Solids $wt\%$	Coating weight g/m^2	COBB-value g/m^2	KIT-value g/m^2
1	8.59	1480	16.25	2.6	35.0	2
2	8.60	2690	17.25	2.4	32.2	2
3	8.57	1550	16.85	4.2	32.0	2
4	8.60	1400	16.80	2.4	31.0	2
5	8.65	1950	16.42	5.0	31.4	0

Table 5.6: Deviations for different batches of MPSS

Somewhere in the middle of the project the RH in the climate room became unstable. The normal RH is supposed to be 50 ± 1 % . For the later middle of the project the RH varied between 31-43 %. This can create deviations in the measurements of coating weight, COBB, KIT and WVTR.

The WVTR-tests were made at approximately 70 % relative humidity (RH) instead of 75, probably it was too low amount of salt solution in the bottom of the chamber resulting in the lower value. Since the RH value might have varied between testings, comparison between the tested samples could be deceptive.

The coatings were applied with a Meyer bar, and the formulation sample was applied close to the bar with a pipette. When applying the formulation it is important to apply an even layer and not have any air pockets, i.e. bubbles to avoid formation of pinholes. This technique improved over time as experience was gained. Differences in the coating application affects the properties for the coating weight, COBB-, KIT- and WVTR-values.

The coatings were applied to only one paper substrate and samples were cut out for one coating weight-test and one double COBB-test. Then KIT-solutions were applied to remaining unharmed surfaces, such as the sample for coating weight and also the edges of the coated paper. For the coating weight-test a circle cutter was used to derive samples of equal sizes. This method was quite sensitive, and the tiniest of irregularity to the paper caused during cutting, would cause a deviation for the coating weight.

Multiple tests were made for the two final coatings, the monolayer coating: MPSS:KS SF60:CWD 45:15:40 [red bar], and the bilayer coating: MPSS:KS SF60 85:15 [yellow bar] + MPSS:CWD 60:40 [red bar], as can be seen in Tables 5.7 and 5.8. The formulations were coated onto four papers each and then prepared likewise as to the other test-samples.

Deviation for MPSS:KS SF60:CWD monolayer coating

Test no:	Coating-weight g/m^2	COBB-value g/m^2	KIT-value
1	5.5	27.6	4
2	3.0	31.0	6
3	7.0	31.8	6
4	6.2	28.6	6
Mean value	5.425	29.75	5.5
Variance	1.49	1.71	0.87

Table 5.7: Standard deviation in coating weight, COBB- and KIT-value for monolayer coating: MPSS:KS SF60:CWD 45:15:40 [red bar]

Deviation for MPSS:KS SF60 + MPSS:CWD bilayer coating

Test no:	Coating-weight g/m^2	COBB-value g/m^2	KIT-value
1	8.8	22.4	12
2	5.3	23.8	9
3	11.1	23.0	12
4	11.4	20.2	12
Mean value	9.15	22.35	11.25
Variance	0.97	1.34	1.30

Table 5.8: Standard deviation in coating weight, COBB- and KIT-value for bilayer coating: MPSS:KS SF60 85:15 [yellow bar] + MPSS:CWD 60:40 [red bar]

The tests for deviation show that the values can vary quite a bit. For trustworthy values it would be recommended to always coat three papers and taking the mean value. However, as in the beginning of this project when fast evaluation and selection were made, this might be overly ambitious and wasteful of time and resources.

6
Conclusion and Outlook

This project has shown promising indications that it is possible to make a barrier product for low quality paper, composed of modified potato starch, carnauba wax and kaolin pigment. The key for reaching better results is probably to test other modified potato starches. The starch used in this project were found to possess barrier properties in another product produced by BIM Kemi but it is not marketed as a product for barriers and it is not marketed as to be film forming. Film forming properties, meaning formation of a continuous film that is pliable and cohesive, is of high importance for the component acting as the binder in the barrier coating.

The WVTR test showed that the emergence of pores was a present problem. The pores most likely arose from addition of pigment. In order to have fewer pores other formulation methods could be evaluated, for example addition of pigment during the formulation of the modified potato starch solution.

The methods used for evaluating grease- (KIT) and water resistance (COBB) are fast and easy and very relevant methods. In future outlook, if reaching better results, surface contact angle analysis could be of interest for a more precise water resistance measurement. Also, using a different application method could help increasing the barrier performance. Application of the barrier in pilot scale production would give a smother and denser coating layer and could help reducing potential pinholes.

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A
Appendix 1

Quality parameters data

No:	Formulation:	Parts	pH	Viscosity $m{\cdot}Pa{\cdot}s$	Solids %	Theoretical Solids %	Sep** 1 W
1	MPSS1:SCWD A	80:20	7.77	3420	20.77	19.15	N
2	MPSS1:SCWD B	80:20	7.83	1270	20.61	18.90	N
3	MPSS1:BWD	80:20	6.71	2500	18.51	17.00	N
4	MPSS1:CWD	80:20	6.63	1330	19.68	18.00	N
5	MPSS2:SCWD B	50:50	6.24	1820	22.14	24.75	N
6	MPSS2:BWD	50:50	5.38	1150	24.53	20.00	N
7	MPSS2:CWD	50:50	7.24	1580	27.69	22.50	N
8	MPSS3:KS SF100*	90:10	7.95	1670	21.18	19.00	N
9	MPSS3:KS SF60	90:10	7.77	1600	21.58	19.80	N
10	MPSS3:TS	90:10	8.74	1940	21.71	19.60	Y
11	MPSS2:CWD	70:30	6.15	1390	21.73	19.5	N
12	MPSS4:TS	95:05	8.61	1110	18.63	17.30	Y
13	MPSS3:KS SF100*	85:15	7.83	1990	23.37	21.00	Y
14	MPSS3:KS SF60	95:05	8.06	1360	19.57	17.40	N
15	MPSS4:CWD:KS SF100*	60:30:10	6.03	1550	25.88	23.50	N
16	MPSS4: KS SF100*	88:12	8.09	2890	22.07	19.80	Y
17	MPSS4:SCWD B	70:30	7.37	1450	23.06	21.00	N
18	MPSS4:BWD	70:30	6.62	2140	20.09	18.00	N
19	MPSS4:KS SF100*	92:08	7.87	1480	20.49	18.20	N
20	MPSS4:KS SF100*	95:05	8.02	1340	18.56	17.00	Y
21	MPSS4:SCWD B	60:40	7.22	1390	19.94	23.00	N
22	MPSS4:CWD	60:40	5.69	1030	22.78	21.00	N
23	MPSS4:BWD	60:40	6.40	1460	20.35	19.00	N
24	MPSS4:CWD:KS SF100*	50:40:10	5.57	1020	25.99	25.00	N
25	MPSS4:CWD:KS SF60	50:40:10	5.58	1200	27.27	25.80	N
26	MPSS4:CWD :KS SF100	50:40:10	5.68	1150	26.88	25.00	N
27	MPSS5:KS SF100	90:10	7.93	1340	21.07	19.00	N
28	MPSS5:KS SF100	85:15	7.92	1320	22.32	21.00	N
29	MPSS5:SCWD A	50:50	7.77	5080	22.38	25.38	N
30	MPSS5:SCWD B	50:50	7.09	1290	22.19	24.75	N
31	MPSS5:CWD	50:50	5.31	760	23.84	20.00	N
32	MPSS5:BWD	50:50	6.29	1140	21.27	22.50	N
33	MPSS5:BWD:KS SF60	40:50:10	6.36	1630	25.02	25.56	N
34	MPSS5:BWD:KS SF100	40:50:10	6.41	1400	20.34	24.60	N
35	MPSS5:CWD:KS SF100	70:20:10	6.42	1100	23.34	22.00	N
36	MPSS5:CWD:KS SF100	65:20:15	6.39	1110	26.21	29.70	N
37	MPSS5:CWD:KS SF60	65:20:15	6.22	1670	26.78	25.20	N
38	MPSS5:CWD:KS SF60	70:20:10	6.39	1350	19.33	22.80	N
39	MPSS5:KS SF60	85:15	6.22	1670	26.78	22.20	N
40	MPSS5:CWD:KS SF60	45:40:15	5.56	1290	29.52	28.20	N

Table A.1: Index of all the formulations and their quality parameters. **Overhead stirrer used instead of High shear mixer. **Visually observed separation of formulation for one week. Yes/No.*

Analysis data for coating onto paperboard

No:	Formulation:	Parts	Coating weight g/m^2	COBB-value g/m^2	KIT-value
1	MPSS1:SCWD A	80:20	2.60	46.60	4
2	MPSS1:SCWD B	80:20	3.60	79.20	2
3	MPSS1:BWD	80:20	3.10	51.00	0
4	MPSS1:CWD	80:20	4.90	44.20	4
5	MPSS2:SCWD A	50:50	1.90	44.40	4
6	MPSS2:BWD	50:50	3.40	34.40	4
7	MPSS2:CWD	50:50	5.50	92.40	4
8	MPSS3:KS SF100	90:10	4.40	29.00	4
9	MPSS3:KS SF60	90:10	8.40	32.00	4
10	MPSS3:TS	90:10	-	-	-
11	MPSS2:CWD	30:70	3.10	32.40	4
12	MPSS4:TS	95:05	-	-	-
13	MPSS3:KS SF100	85:15	-	-	-
14	MPSS3:KS SF60	95:05	7.40	34.08	4
15	MPSS4:CWD:KS SF100	60:30:10	5.20	32.40	4
16	MPSS4: KS SF100	88:12	-	-	-
17	MPSS4:SCWD B	70:30	4.20	76.60	2
18	MPSS4:BWD	70:30	1.90	34.40	2
19	MPSS4:KS SF100	92:08	8.90	28.00	4
20	MPSS4:KS SF100	95:05	6.00	29.60	0
21	MPSS4:SCWD B	60:40	4.80	84.20	0
22	MPSS4:CWD	60:40	4.00	23.60	4
23	MPSS4:BWD	60:40	2.70	50.00	2
24	MPSS4:CWD:KS SF100	50:40:10	4.60	38.80	4
25	MPSS4:CWD:KS SF60	50:40:10	5.00	29.60	4
26	MPSS4:CWD:KS SF100	50:40:10	4.20	29.20	4
27	MPSS5:KS SF100	90:10	3.90	32.00	0
28	MPSS5:KS SF100	85:15	5.00	35.20	2
29	MPSS5:SCWD A	50:50	5.30	77.20	2
30	MPSS5: SCWD B	50:50	7.30	101.00	0
31	MPSS5:CWD	50:50	2.60	35.80	4
32	MPSS5:BWD	50:50	2.20	49.80	2
33	MPSS5:BWD:KS SF60	40:50:10	4.80	27.60	2
34	MPSS5:BWD:KS SF100	40:50:10	2.40	35.60	2
35	MPSS5:CWD:KS SF100	70:20:10	2.40	35.60	4
36	MPSS5:CWD:KS SF100	65:20:15	2.80	40.40	2
37	MPSS5:CWD:KS SF60	65:20:15	3.90	28.60	0
38	MPSS5:CWD:KS SF60	70:20:10	5.80	29.40	2
39	MPSS5:KS SF60	85:15	5.20	25.20	6
40	MPSS5:CWD:KS SF60	45:40:15	5.50	27.60	4

Table A.2: Analysis of formulations coated onto paperboard substrate.

Parchment coating data

No:	Formulation:	Parts	Coating weight g/m^2	COBB-value g/m^2	KIT-value
15	MPSS4:CWD:KS SF100	60:30:10	7.40	32.80	6
25	MPSS4:CWD:KS SF60	50:40:10	6.10	28.00	6
26	MPSS4:CWD:KS SF100	50:40:10	6.30	27.20	6
33	MPSS5:BWD:KS SF60	40:50:10	6.10	33.60	4
34	MPSS5:BWD:KS SF100	40:50:10	6.20	31.60	2
35	MPSS5:CWD:KS SF100	70:20:10	9.10	28.20	8
36	MPSS5:CWD:KS SF100	65:20:15	9.60	29.00	6
37	MPSS5:CWD:KS SF60	65:20:15	9.10	30.80	6
38	MPSS5:CWD:KS SF60	70:20:10	9.60	32.20	8
39	MPSS5:KS SF60	85:15	9.20	33.60	6
40	MPSS5:CWD:KS SF60	45:40:15	7.80	32.00	4

Table A.3: Analysis of formulations coated onto parchment substrate.

Data for bilayer coatings onto paperboard substrate

1st coating formulation	Bar color	2nd coating formulation	Bar color	Coating weight g/m^2	COBB-value g/m^2	KIT-value
MPSS5:KS SF60	red	MPSS5:CWD	green	13.00	21.20	12
MPSS5:KS SF60	red	MPSS5:CWD	red	8.90	21.80	8
MPSS5:KS SF60	yellow	MPSS5:CWD	red	8.80	22.40	12
MPSS5:KS SF60	green	MPSS5:CWD	green	13.30	22.80	12
MPSS5:KS SF60	yellow	MPSS5:CWD	red	5.30	23.80	9
MPSS	green	MPSS5:KS SF60	red	10.70	25.20	6
MPSS5:KS SF60	red	MPSS5:CWD	yellow	9.00	25.60	12
MPSS	red	MPSS5:KS SF60	red	5.60	26.40	6
MPSS5:KS SF60	red	CWD	red	9.70	30.00	9
MPSS5:KS SF60	green	CWD	yellow	12.70	31.00	12
MPSS5:KS SF60	red	CWD	yellow	9.30	31.60	12

Table A.4: Data for bilayer coatings onto paperboard substrate. Formulation MPSS5:KS SF60 with parts 85:15 and formulation MPSS5:CWD with parts 60:40 was used.

Data for bilayer coatings onto parchment substrate

1st coating formulation	Bar color	2nd coating formulation	Bar color	Coating weight g/m^2	COBB-value g/m^2	KIT-value
MPSS5:KS SF60	white	CWD	white	14.50	23.60	12
MPSS5:KS SF60	yellow	CWD	yellow	15.30	23.80	12
MPSS5:KS SF60	red	CWD	yellow	13.00	25.40	11
MPSS5:KS SF60	white	MPSS5:CWD	white	14.80	32.20	12
MPSS5:KS SF60	red	MPSS5:CWD	red	16.30	36.20	12

Table A.5: Data for bilayer coatings onto parchment substrate. Formulation MPSS5:KS SF60 with parts 85:15 and formulation MPSS5:CWD with parts 60:40 was used.