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# Method development for measuring oil and grease resistance of coated paper- and board materials

## Evaluation of ASTM- F119 test method

Bachelor's thesis in Chemical Engineering


**Sara Hassanzada**

Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY



Gothenburg, Sweden 2022

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## Abstract

Dispersion coating is an application technology that provides barrier properties for paper and board materials. The function of barriers in food packaging is to block or reduce water, gas or oil flow throughout the package. Within the pulp and paper industry, there are several methods for measuring the effectiveness of barriers against oil and grease. Often, these methods use test reagents that do not correspond to oils used in food. A common method is KIT-test which is adequate for papers treated with fluorochemicals (FC). Due to their adverse health effect, these paper products are being replaced by FC-free products. This leads to increasing demand for replacing the KIT-test with methods suitable for grease-resistant coating without fluorochemicals.

The purpose of this thesis is to implement ASTM- F119 for measuring the effectiveness of dispersion coated barriers against penetration of cooking oils. Another objective was to optimize ASTM- F119 by investigating the effect of different parameters such as temperature, amount of oil reagent and pressure. The result was compared with the reference methods, KIT-test and oleic acid test. The oil reagents were vegetable oils, such as olive oil, coconut oil, rapeseed oil, and animal fat such as butter. The penetration time was based on a subjective visual evaluation. The result shows that KIT-test can still be used to compare barriers, but there is a lack of information about how long it takes for a cooking oil reagent to go through the barriers. Therefore, ASTM F- 119 is more adequate for comparing barriers and estimating oil penetration times. The modified ASTM- F119 method shows good potential for evaluating grease resistance of different barriers using oils that correspond closely to the true food package contents and, are hence, realistic test oils.

Keywords: oil and grease resistance, dispersion coating, KIT-test

# Acknowledgments

I wish to express my gratitude to my supervisors, Sofie Sjöstrand and Petter Bragd, for all their support and generosity with their knowledge and time. You have given me a patient hearing or a helping hand in any situation. The work that has resulted in this thesis work would not have been possible without your valuable advice and inspiration ideas.

I would like to express sincere thanks to my examinator, Tiina Nypelö, for her support and sharing of knowledge.

My appreciation also to the people working at BIM that made me feel comfortable and for such a positive atmosphere. I will thank all laboratory technicians for their friendly approach and help that made a difference in my working days during the practical part of my thesis.

And finally, thanks to my family and my best friend, who always supported me.

Sara Hassanzada, Gothenburg, June 2022

# Abbreviations

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| BA | Barrier application |
| FC | Fluorochemicals |
| HG | Hand-ground |
| L&W | Lorentzen & Wettre |
| MG | Manufactured ground |
| OGR | Oil and grease resistance |
| RH | Relative humidity |
| RSD | Relative standard deviation |
| SA | Styrene Acrylic |
| SB | Styrene Butadiene |
| WVTR | Water vapor transmission rate |

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# 1. Introduction

## 1.1 Background

Packaging waste has global impacts on the environment. Petroleum-based plastic is the most used raw material in packaging applications due to its cost-effectiveness and protective properties. However, plastic's nonrecyclable and non-biodegradable nature drives concerns regarding plastic pollution both in landfills and aquatic environments. [1] Degradation of plastic can take tens to hundreds of years depending on environmental factors such as sunlight, heat, and pH conditions. [2]

Furthermore, global warming and acid rain as a consequence of climate change slow down the degradation. Consequently, plastic pollution in the ocean cause damage to organisms in the form of intestinal blockage and leads to death in the worst case. [3] Environmental protection needs to be taken seriously, and sustainable packaging plays a significant role in reducing plastic pollution and waste.

The demand for sustainable packaging makes “paper” a good alternative due to its recyclability and environment-friendly nature. The versatility of paper makes it adequate for different kinds of applications such as fast foods, frozen food and liquid products. However, barrier properties play a vital role in whether the paper meets the criteria for each application or not. For instance, the paperboard used for ready meal packaging is not grease resistant and heat-sealable itself. The paperboard needs to be treated by different technologies such as coating and lamination to form barriers against water vapor, moisture and grease. [4]

Coating means creating a layer of functional solutions on a substrate. Extrusion and dispersion coating are the most common techniques for acquiring barrier properties. Polyethylene (PE) is an example of a barrier polymer used in extrusion coating. In dispersion coating, latex – an aqueous dispersion of fine polymer particles – is used as dispersion polymer. Due to increased environmental concerns about plastic pollution an interest has grown to replace extrusion coating with recyclable, repulpable and compostable dispersion coating. [5]

Another treatment for providing grease barrier properties is adding fluorochemicals to the pulp. Their function is to create a surface with low enough surface energy to prevent oil from penetrating the paper. Fluorochemicals have been used for this purpose since 1970. Nowadays, due to its bioaccumulative and toxic properties, the production of these organic pollutants has been phased out in North America and Europe. [6,7]

Several methods are available to measure oil and grease resistance (OGR). Permeability test, Hot Mazola Oil Test and Clariant test are examples of methods that use palm kernel oil or corn oil as reagent, making them more realistic. These methods are more time-consuming than KIT-test and Turpentine test. The last-named methods are faster but less realistic. [8]

Reagents in KIT-test do not correspond closely to the true food package contents and this challenge applying the experimental findings to assessing the performance. In addition, this method is designed for papers treated with FC chemicals. Due to the prohibition of these pollutants, the KIT-test may be an irrelevant method for measuring OGR on coated papers.

## 1.2 Thesis collaboration

This bachelor thesis has been conducted in collaboration with BIM Kemi. A company that manufactures and sells process and functional chemicals for the paper industry. The company develops and produces its own dispersion barriers with the properties such as recyclability, composability and high water and grease resistance.

## 1.3 Purpose

The aim of this thesis is to implement ASTM- F119 standard method for evaluating the grease penetration time of commonly used oils in the food industry on the dispersion coated barriers to improve the equivalence of the experimental setup and achieve more realistic results than using other available OGR methods. Part of this work has aimed to develop and optimize ASTM- F119 by investigating the effect of different parameters i.e. temperature, pressure and increased amount of reagent. The desirable criteria were visual oil detection within eight hours, straightforward assessment and unambiguous results. This work further has included the characterization of oil reagents and coated paper substrates.

## 2. Dispersion coated barrier

The barrier dispersion coating is about the application and drying of latex to create a physical barrier on the paper substrate against liquid or water vapor penetration. Latices contain a considerable amount of water and polymers. An ideal dispersion coating has low absorption into the paper substrate. [5,9]

The most widely used paper coating latex throughout the world is styrene-butadiene (SB). Styrene-*n*-butyl acrylate (SA) is another type of paper coating that is used more in Europe. SB-latexes produces by an emulsion polymerization reaction between modified copolymers of styrene and butadiene. SA-latexes are latexes of modified styrene and n-butyl. Another group of barrier latexes is biopolymers from natural sources or bacteria. The advantage of a dispersion barrier based on biopolymer is biodegradability. The disadvantage is lower barrier level than petroleum-based barriers. [5,10]

A latex dispersion also contains additives and fillers. Additives can be stabilizers, biocides, thickeners and waxes, etc. Paraffin, microcrystalline, or Carnauba wax are the most frequently used waxes. The functionality of additives and fillers is to obtain and improve desired barrier properties. Fillers also improve runnability, optical properties and cost-effectiveness. Talc, titanium dioxide and calcium carbonate are common fillers. [5]

Application of latex on paper and boards can be performed by air knife as well as Mayer bar, blade or rotogravure, flexographic and spraying. Film press and roll coaters using a rod or blade are the most common coaters. As shown in Figure 1, the coating process begins with unwinding the uncoated roll. A coater applies latex dispersion onto the base paper. The next step is metering the coating, which means removing the excess coating. Drying of the coating performs in several units. The first drying unit is commonly an infrared radiator. After that, the coated substrate goes through two units of air dryer. The final step is cooling the substrate before rewinding. [5,10]

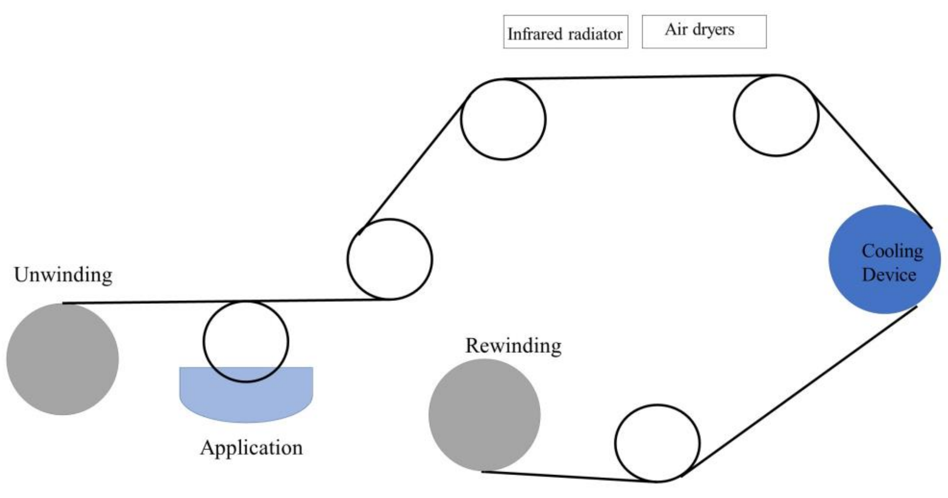


*Figure 1. Dispersion coating process.*

# 3. Oil and grease resistance methods

Grease resistance tests measure the effectiveness of barriers against oil penetration. The basic idea of ASTM- F119 is to measure the time necessary for the oil to go through the paper substrate under specified conditions while grease resistance evaluation of the KIT-test and oleic acid test is based on visual changes during a predetermined standardized time.

## 3.1 ASTM- F119

The grease penetration time of barriers is determined based on a subjective visual evaluation. The standard reagents in this method are animal oil, mineral oil and vegetable oil. The paper substrates creased or uncreased are exposed indirectly to grease on the coated side and are covered by cotton patches and a weight. The time required for the wetting to be visible on a frosted glass plate is recorded.

## 3.2 KIT-test

The standard KIT-test for measuring the oil and grease resistance is used as the reference method. The reagents used in this method are twelve solutions of castor oil in different amounts of castor oil, toluene and *N*-heptane. The test method is based on visually detecting the darkening of the test specimen. The test is continued until the highest numbered KIT solution does not darken the surface of the paper substrate. The result is reported as the substrate's KIT-number in a value between 0 to 12 where the higher the number, the more effective the substrate is against oil and grease.

## 3.3 Oleic acid test

This method is used as the second reference method to measure the grease resistance of paper substrates. A series of mixtures of castor oil, oleic acid and octanoic acid are used as reagents. The evaluation of the test can be divided into three parts “failure”, “stain” and “pinholes”. A “failure” is any visual changes observed after wiping off excess reagent. A “stain” is a dark oil stain caused by wetting the paper substrate while oil penetration has occurred. “Pinholes” are small dark oil traces that indicate nonoptimal coverage of the barrier. The highest numbered solution that does not cause a “fail” or “stain” is reported as the test value. “Pinholes” is reported qualitatively and are not taken into consideration when determining the test value.

# 4. Experimental part

The experimental plan of this work consisted of three parts. In the first part, the ASTM-F119 method was set up and preliminary tests were made with standard configuration. The second part aimed to develop and optimize the method by investigating how different parameters affect visual penetration and time. The focus of the last part was to use the modified ASTM- F119 to examine the effectiveness of various barriers against different oils.

## 4.1 Coating procedure and materials

Three different barriers were used for coating the base substrate. The main functionality of the barriers is to provide oil and grease resistance at different levels. Depending on the product's end-use, the barrier can be applied inside or outside the packaging. A summary of the barrier’s chemical formulation, function and end-use used in this work can be seen in Table 1. Henceforth, the barriers are named after their main characteristic, BA-1 is named bio-barrier, BA-2 fat barrier and BA-3 water barrier.

*Table 1. The barrier’s specification.*

| | BA-1<br>Bio-based barrier | BA-2<br>Fat barrier | BA-3<br>Water barrier |
|---|---|---|---|
| **Chemical formulation** | Bio latex<br>Bio wax | SA-latex/SB-latex<br>Paraffin wax | SB-latex<br>Paraffin wax |
| **Functionality** | - Moderate hydrophobicity<br>- Oil and grease resistance | - Excellent oil and grease resistance<br>- Hydrophobicity | - Excellent barrier against water and moisture<br>- Oil and grease resistance |
| **End-use examples** | Liner wrappings for paper reels | Hot food trays | Liner wrappings for paper reels |

Mayer bar coating is a method for applying adhesive on paper substrates. The coating was performed using an applicator machine, K control Coater from RK Printcoat Instruments. As shown in Figure 2, the barrier solution was applied onto the rougher side of KRAFT paper with a grammage of 48 g/m$^2$ unilaterally. A Mayer bar manufactured of wire-wound stainless steel rod was used to maintain a consistent coating weight. Different coating weights can be obtained using Mayer bars with varying wire diameters.

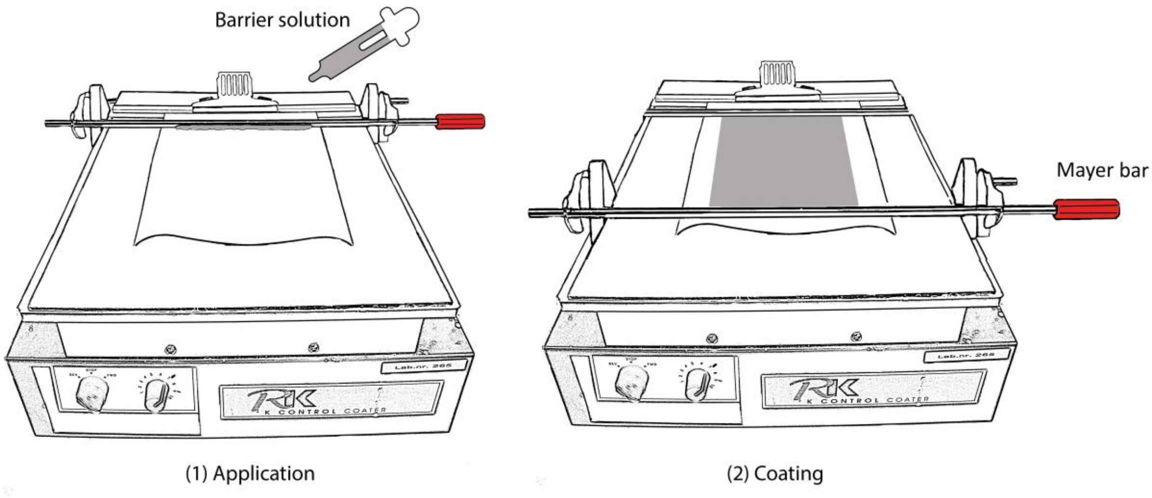


*Figure 2. The coating procedure of experimental paper substrates.*

The applied wet barrier film smoothed out with the red bar, except in one case where the target was to study the effect of thickness. In this case, a black bar was used to obtain a higher coating weight. The coating speed was set to 7 out of 10 m/min, where 10 is the maximum speed of 15 m/min. The data for different bars are presented in Table 2. The coated papers were dried in a drying conveyor from Enz Technik at 120 °C. The last step in the coating process was to acclimatize the test samples in the climate room (23 °C, RH 50%) for at least two hours before continued testing.

*Table 2. Mayer bars specification. Adapted from https://www.rkprint.com*

| 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 |

## 4.2 ASTM- F119 standard method procedure

The procedure for preliminary tests was according to ASTM- F119 recommendations, as shown in Figure 3. Three flat specimens, 36 $cm^2$ of each substrate, were provided. The test specimens with coating side up were placed on a glass plate followed by two cotton patches 20 mm in diameter and a 50-g weight. The entire assembly was preheated in the oven (40 and 60 ±1 °C) for 30 min. The test at 40 °C was performed in the BINDER forced circulation oven as recommended. At 60 °C, a hotbox oven was used, which meant slower heat recovery after opening the oven. After preheating, the assembly was taken out of the oven. Then, six drops of reagent were added dropwise to cotton patches with a glass Pasteur pipette. Lastly, the weight was replaced, and the assembly was put back in the oven. Oil penetration was observed from the surface of the glass plate against a dark background.

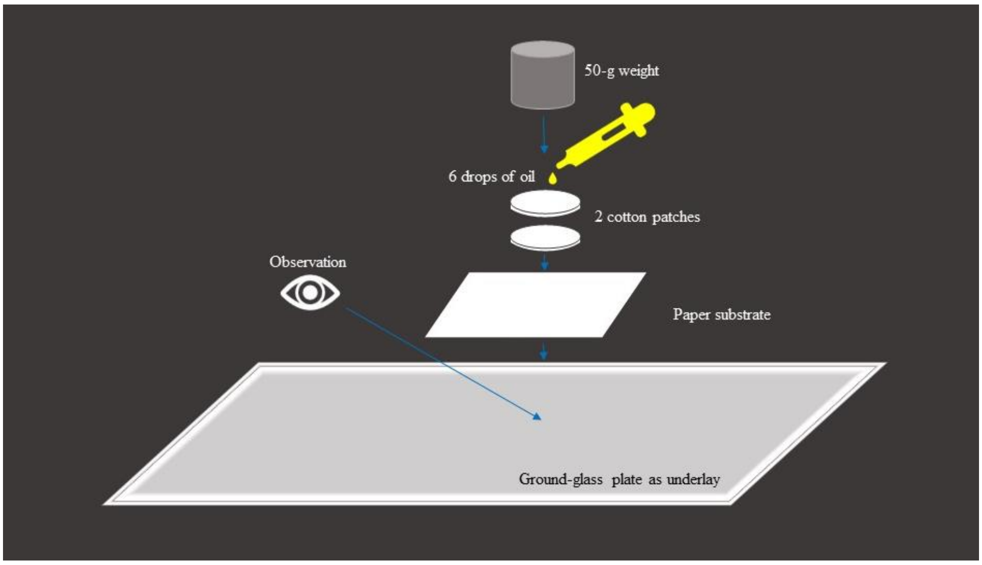


*Figure 3. Schematic drawing of ASTM- F119 procedure.*

## 4.3 Altered test conditions

The preliminary tests that were performed according to the standard method recommendation showed any visible wetting on the manufactured ground (MG) glass plate. It can depend on the special surface treatment of the MG glass plate. Hence, the test conditions were changed to achieve a working method. The altered test conditions were underlays such as glass plates and paper. Also, test parameters such as the amount of the oil and pressure.

The altered test parameters can be seen in Table 3 compared with the standard set. The amount of oil was increased to 9 drops in set A and the number of weights was doubled in set B. Tests were performed at two different temperatures for each substrate and only rapeseed oil was used as reagent. The test specimens were placed on a glossy glass plate. The surface of the glass plate was observed under a table lamp.  Thoroughly cleaning of the glass plate was taken into consideration.

*Table 3. Different sets of the modified ASTM- F119.*

| | Standard set | Set A | Set B |
|---|---|---|---|
| **Target** | —— | To observe the effect of the increased amount of oil | To observe the effect of doubled pressure |
| **Number of cotton patches** | 2 | 2 | 2 |
| **Number of oil drops** | 6 | 9 | 9 |
| **Number of weight** | 1 | 1 | 2 |

To clarify which underlay could be adequate further testing was performed using set A. In this phase, testing was performed using rapeseed oil due to its homogeneity in the results at two temperatures for each substrate. The criteria were easier visual detection of oil traces on the underlay without using light. Also, the maximum penetration time was set to 8 hours. Due to the invisibility of oil traces on the glossy glass plate with naked eyes, the experimental part was continued by testing other underlay alternatives.

Further, KRAFT paper was used as underlay. Testing was performed with dyed and undyed rapeseed oil for all paper substrates. Sudan Blue II (0.001 wt%) from Sigma-Aldrich was used as a dye. Note that the addition of the dye changed the viscosity of rapeseed oil slightly.

As yet, the glossy glass, MG glass and the KRAFT paper did not meet the criteria. Another alternative was grinding a glossy glass to remove outermost layer. Hence the glossy glass plate was ground manually using aluminum oxide-coated sandpaper with 80, 60 and 36 corn grits from Biltema. Grinding was continued until the glass surface was rough and white in color. Note that the surface of the glass plate became matt during its residence in the oven and needed grinding again. Finally, an additional test was performed parallelly on the KRAFT paper and hand-ground (HG) glass to confirm the conclusions with assuredness.

## 4.4 Modified ASTM- F119 procedure

As mentioned in the previous part, another attempt in this project was modifying the test conditions of the standard method to achieve a rapid evaluation of the barrier's grease resistance. Set A and hand-ground glass were used in the modified version of ASTM- F119. The procedure was generally the same as shown in Figure 2.

The reagents were olive oil, rapeseed oil, clarified butter and coconut oil. Test samples were bio-based, fat and water barriers. Unlike the standard method, testing was continued despite observing first oil traces on the surface of the frosted glass plate. The paper substrates were turned over, and uncoated sides were photographed. Also, the surface of the glass plate was photographed at each observation. The evaluation of these tests has been based on two principles: the time was recorded for a first visible wetting on the glass if a darkened area on the backside of the paper substrate has appeared.

The time interval for the observation is shown in Table 4, where a cross represents an observation. The observation was periodic for the first six hours every 30 minutes or hour. After that, test samples were allowed stand overnight in the oven, which means within 6-23 hours, the test samples were not observed. Also, this differs from the standard method recommendation, where the observation is interrupted after detecting the smallest little sign of oil traces. The tests were performed on different days, which led to inhomogeneity in time intervals.

*Table 4. Inspection time.*

| Time interval (h) | 0 | ½ | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 | 4.5 | 5 | 5.5 | 6 | | 23 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **BA 1- 40** | | × | × | × | × | × | | × | | × | | × | × | | × |
| **BA 1- 60** | | × | × | × | × | × | | × | | × | | × | × | | × |
| **BA 2- 40** | | × | × | × | × | × | | × | | × | | × | × | | × |
| **BA 2- 60** | | × | × | | × | | × | | × | × | × | × | × | | × |
| **BA 3- 40** | | × | × | × | × | × | × | | × | × | × | × | × | | × |
| **BA 3- 60** | | × | × | × | × | | × | | × | | × | | × | | × |

## 4.5 KIT-test

Paper samples with the coating side up were placed on a clean, flat surface. Three drops of test solvent were dropped on three areas of the testing surface. After 15 seconds, the excess test solvent was wiped off. Then, the tested area was examined against a light table. The darkening of the tested area indicated penetration of the test solution. Therefore, the KIT-value was set equal to the highest numbered KIT solution that did not indicate darkening on the paper sample.

The composition of KIT solvents is collected in Table 5. Note that the amount of castor oil decrease in KIT solvents 2-10, whereas the ratio of toluene and *N*-heptane is the same.

*Table 5. Composition of KIT-test solvents.*

| KIT-value | Castor oil (wt % ) | Toluene (wt % ) | *N*-Heptane (wt % ) |
|---|---|---|---|
| 1 | 100 | 0 | 0 |
| 2 | 90 | 5 | 5 |
| 3 | 80 | 10 | 10 |
| 4 | 70 | 15 | 15 |
| 5 | 60 | 20 | 20 |
| 6 | 50 | 25 | 25 |
| 7 | 40 | 30 | 30 |
| 8 | 30 | 35 | 35 |
| 9 | 20 | 40 | 40 |
| 10 | 10 | 45 | 45 |
| 11 | 0 | 50 | 50 |
| 12 | 0 | 45 | 55 |

## 4.6 Oleic acid test

One drop of all test solutions 1-11 was dropped on the coated side of the paper substrates. The whole equipment consisting of test specimens on a clean glass plate, was placed in the oven at 40 °C. After 6 minutes, the entire equipment was taken out of the oven and the drops were wiped off. The highest number of test solution that did not cause penetration on the paper substrate was reported.

Oleic acid test solutions and their composition is collected in Table 6. It can be noticed that test solutions 1-3 consist of the different ratios of castor oil and oleic acid except number two. The amount of oleic acid decreases in solutions, 4-11 whereas the amount of octanoic acid increases.

*Table 6. Oleic acid test solution composition.*

| Solution number | Castor Oil (wt %) | Oleic Acid (wt %) | Octanoic Acid (wt %) |
|---|---|---|---|
| 1 | 100 | 0 | 0 |
| 2 | 50 | 50 | 0 |
| 3 | 30 | 70 | 0 |
| 4 | 0 | 100 | 0 |
| 5 | 0 | 80 | 20 |
| 6 | 0 | 70 | 30 |
| 7 | 0 | 55 | 45 |
| 8 | 0 | 35 | 65 |
| 9 | 0 | 20 | 80 |
| 10 | 0 | 10 | 90 |
| 11 | 0 | 0 | 100 |

## 4.7 Characterization of barriers and oils

The main function of dispersion coated barriers is to provide barrier properties. The quality of paper substrates was evaluated by WVTR, Cobb-test and contact angle.

### *4.7.1 Coating weight and thickness*

The dimension of paper substrates was taken with a template. From one A-4 paper substrate, 6 test pieces were made. The thickness of each test piece was measured in five positions by Lorentzen & Wettre (L&W) micrometer. The coating weight gave a physical value to the amount of coating. The weight of a single coated sample was measured and subtracted from the weight of a reference sample. The average and standard deviation of the measurements were reported.

### *4.7.2 WVTR*

Water vapor transmission rate describes the amount of water vapor transmitted through the paper substrate. Here, WVTR was determined by the cup method. As shown in Figure 4, the equipment consisted of aluminum cups (EZ-Cup Vapometer) in the same quantity of test specimens filled with 1/3-1/2 parts anhydrous calcium chloride. In order to eliminate inaccurate WVTR results, the granule size of salt was taken into consideration visually by separating too large grains of salts. For each cup, two gaskets followed by a seal were used to hold the specimen in place. Lastly, the specimens were sealed using aluminum rings. The aluminum cups were weighed and placed in a climate chamber. The weighing of aluminum cups was repeated after 24 hours and one more time after 48 hours.

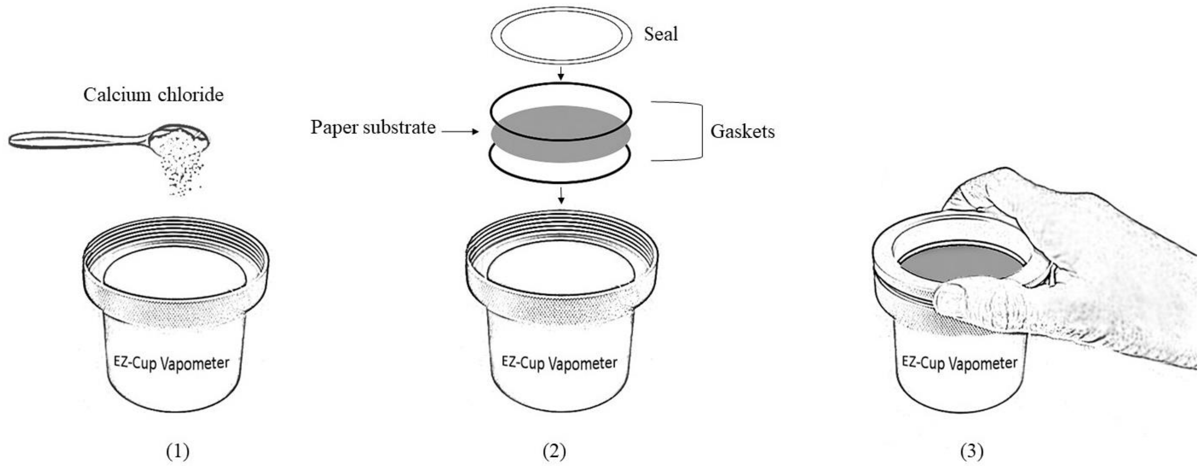


*Figure 4. The procedure of the cup method.*

The humidity of the climate chamber was set to 75% RH at 23 °C. The measurement was carried out on two test samples for each substrate. The WVTR over 48 hours was calculated according to the formula below.

$$WVTR = \frac{\text{mass (after 48 h)} - \text{mass (start)}}{\text{Area } \times 48}$$

### *4.7.3 Cobb-test*

The water absorptiveness of the paper substrate was measured by two types of L&W cobb sizing tester. Two round double samples were prepared using L&W template and weighted with four decimal precisions. As shown in Figure 5, the first sample was positioned on a base plate with the coating side up. A hollow cylinder was strapped to the surface and filled with 25 ml of distilled water. After 885 seconds, the water was poured off. During the remaining 15 s, the sample was placed between two blotting papers. A couch roller was used to remove the excess water. The sample was weighed again.

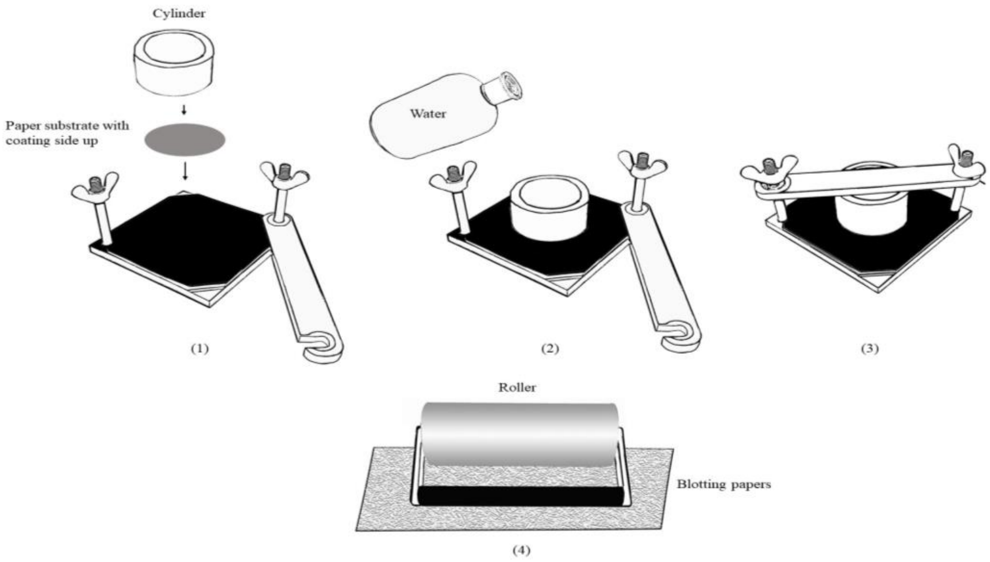


*Figure 5. Cobb sizing tester.*

The IGT Cobb tester, which can be seen in Figure 6, was used for the parallel measurement. The cylindrical liquid container built in a ring was filled with 25 ml of distilled water.

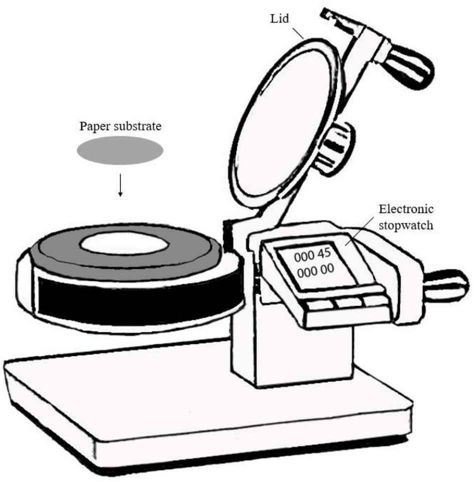


*Figure 6. IGT Cobb tester.*

The second sample with coating side down was positioned on top of the liquid container. The lid was moved down to lock the ring. The start signal was sent to the electronic stopwatch by rotating the handle mounted beside the ring. The exposure time was the same as for the first sample. The test ended by moving the ring backward and following the same steps as previously mentioned to pour off the excess water. Afterward, the weight of the second sample was noted.

An average Cobb value of both parallel measurements was reported. The Cobb value was calculated according to the formula below.

$$Cobb\ value = \frac{\text{mass (final)} - mass\ (start)}{\text{Area}}$$

### 4.7.4 Contact angle

Contact angle measures the wettability of a solid by a liquid. The measurement was carried out by FTA200 contact angle analyzer (First Ten Ångströms) using the sessile drop technique. The contact angle of pure water with a volume of 1 µl was measured at 23 °C. The CCD camera system in the instrument captured images of pure water behavior continuously. The image capturing began when the drop detached from the dispense tip until the interaction between the drop test and substrate occurred.

The instrument recorded a total of 43 frames in 51.6 s. These captured images were analyzed automatically by FTA200 image software. The average of three measurements for each substrate was calculated.

### 4.7.5 Viscosity of oils

Viscosity was measured with DV1 digital viscometer from AMETEK Brookfield. A volume of 200 ml oil was heated to the desired temperature using a heat block. A digital thermometer was put in the oil to ensure the correct temperature. A lower viscosity requires a thicker spindle. Spindle number 61 was attached to the device and then immersed in the oil. The measurement was started when the spindle was rotated.

# 5. Result and discussion

The result of the characterization of barriers and oils has carried out in this part. Also, the result of the modified ASTM F-119 method has been presented.

## 5.1 Technical measurement

### *5.1.1 Coating Weight and thickness*

The results of coating weight and thickness are collected in Table 7. Note that the data belongs to six test pieces from one coated A-4. The coating weight and thickness vary between each substrate which is expected because of barrier solutions' different viscosity, solids content and particle size.  These properties make differences in coating quality. It has also been observed that the coating weight can vary depending on the person who performs the coating.

*Table 7. Variation in coating coverage in six positions of one coated A-4.*

| | | Bio-based barrier | Fat barrier | Water barrier |
|---|---|---|---|---|
| | Average | 7.8 | 6.8 | 6.9 |
| Coating weight ($g/m^2$) | %RSD | 7.2 | 8.1 | 7.9 |
| Thickness | Average | 4.2 | 3.8 | 3.1 |
| (μm) | %RSD | 4.3 | 26.1 | 9.9 |

The relative standard deviation (RSD) in coating weight and thickness of fat barrier for four sheets is shown in Table 8. The common condition for coating was the same. It is shown that the coated substrates are not consistent in uniformity in and between each attempt. Using the same barrier solution during the experiment is essential to avoid differences in viscosity and coating weight.

*Table 8. Measured coating weight and thickness of four pieces fat barrier.*

| | | Sheet 1 | Sheet 2 | Sheet 3 | Sheet 4 |
|---|---|---|---|---|---|
| | Average | 7.6 | 6.5 | 6.1 | 8.4 |
| Coating weight ($g/m^2$) | %RSD | 8.8 | 1.8 | 3.4 | 3.0 |
| Thickness | Average | 4.4 | 3.9 | 3.3 | 4.3 |

| (µm) | %RSD | 15.5 | 15.4 | 10.0 | 5.6 |
|---|---|---|---|---|---|

### *5.1.2 WVTR and Cobb-test result*

The results from WVTR and Cobb-test can be seen in Table 9. The water barrier showed the lowest water vapor transmission rate, a desirable property in the food packaging industry. Also, the Cobb value is low, meaning the paper substrate can resist moisture penetration. The rate of moisture permeation through the fat barrier is higher than the bio-based barrier. However, the difference between these two paper substrates is slight. A higher Cobb value of fat barrier indicates inefficiency in resisting moisture.

*Table 9. WVTR and Cobb-test results.*

| | Bio-based barrier | Fat barrier | Water barrier |
|---|---|---|---|
| | | WVTR (g/m$^2$ /48 h) | |
| Average | 0.61 | 0.64 | 0.48 |
| %RSD | 11.48 | 1.56 | 22.92 |
| | | Cobb value (g/m$^2$) | |
| Average | 4.65 | 4.90 | 1.85 |
| %RSD | 59.31 | 17.32 | 49.69 |

### *5.1.3 Contact angle*

The contact angle of water on paper substrates at 0.1s, 11.0 s, 19.3 s, 39.0 s and 51.6 s can be seen in Figure 7. The bio-based barrier shows the lowest contact angle which means the surface has high wetting and the water droplet spreads out on the surface more. A contact angle greater than 90º indicates high surface wetting and a lower ability of water to wet the surface of paper substrates. The result shows that fat and water barrier are hydrophobic. The water barrier has the lowest surface energy and, consequently, the most hydrophobic test barrier as its characterization.

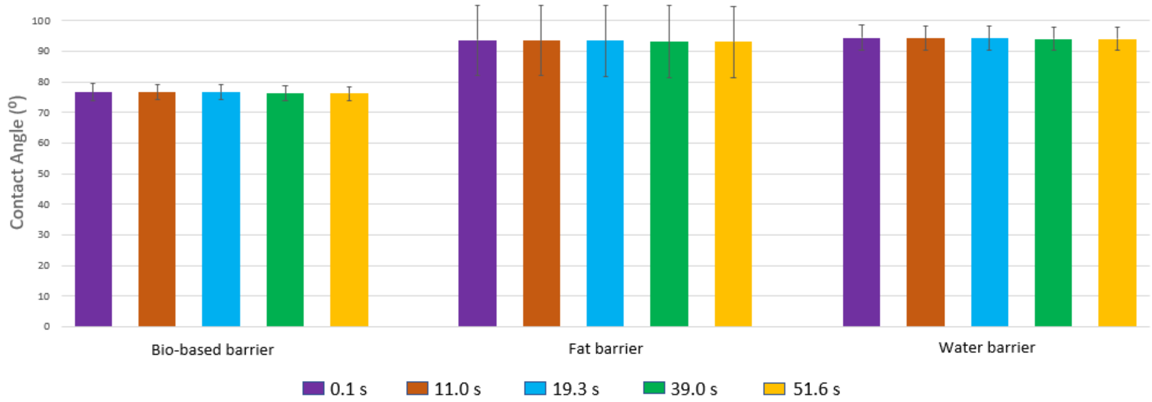


*Figure 7. Water contact angle of the test barriers.*

### 5.1.4 Fatty acid composition of oils and viscosity

Cooking fats and oils commonly come from animal or vegetable sources. Different categories of fats are saturated, monounsaturated and polyunsaturated, to name only a few. Saturated fats mean that all the carbon atoms are connected by a single bond. There is a double bond between two carbon atoms in monounsaturated fats, whereas polyunsaturated fats have two or more double bonds. As presented in Table 10, butter and coconut fat mostly contain saturated fatty acids with an abundance of shorter-chain carbons. Rapeseed oil and olive oil are high in amounts of monounsaturated fatty acids. [11] The first number on fatty acid presents number of carbons in fatty acid chain and the second number after the colon presents number of double bonds in the fatty acid chain.

*Table 10. Fatty acid composition of some common cooking oils. [11]*

| | Saturated | | | | Monosaturated | | Polyunsaturated | |
|---|---|---|---|---|---|---|---|---|
| | C4:0-C12:0 | C14:0 | C16:0 | C18:0 | C16:1 | C18:1 | C18:2 | C18:3 |
| **Butter** | 13 | 11 | 27 | 12 | 2 | 29 | 2 | 1 |
| **Coconut oil** | 62 | 18 | 9 | 3 | | 6 | 2 | 1 |
| **Rapeseed oil** | | | 4 | 2 | | 62 | 22 | 10 |
| **Olive oil** | | | 13 | 3 | 1 | 71 | 10 | |

An earlier study states that the OGR time of saturated oils is longer than unsaturated oils on polyethylene-coated papers. Longer OGR time indicates higher resistance to penetration of the grease. Other factors that affect oil sorption into the paper substrates are carbon chain length, amount of double bonds and molecule size. [12]

Figure 8 shows that the higher the temperature, the lower the viscosity of test oil reagents. Coconut oil has the lowest viscosity value, whereas butter has the highest viscosity value at 40 and 60 °C. Butter and coconut oil are solid at room temperature.

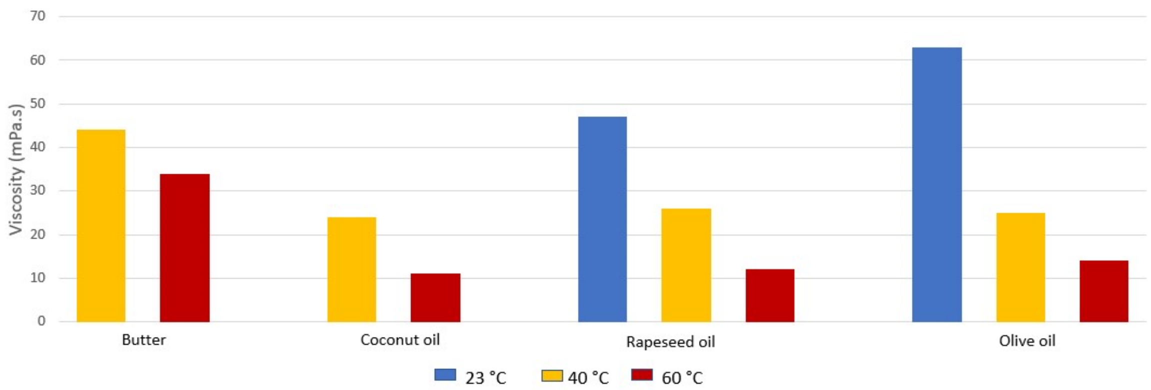


*Figure 8. The viscosity of test oil reagents.*

## 5.2 Comparison of different parameters

Many preliminary tests showed that a modified test condition that was presented in Table 3 could lead to optimized results. Therefore, the conditions for a BIM-customized ASTM-F119 test were established to nine drops of oil, two cotton patches, and one weight. The standard set is compared to modifies sets A and B at two temperatures, as shown in Figure 9. A fourth set was also tested with one cotton patch, one weight and 6 drops of oil. One cotton patch caused the oil to spread out of the place of weight. Further testing with this set was not continued.

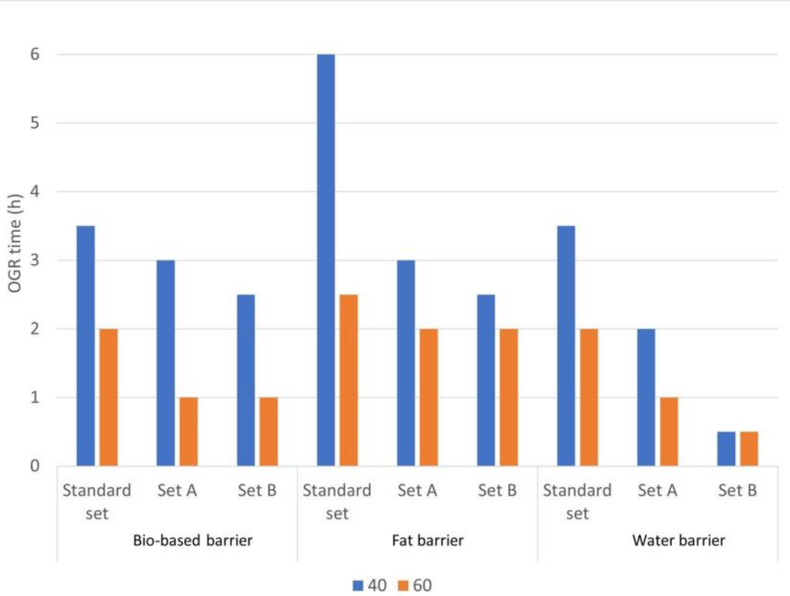


*Figure 9. The average OGR time of a triplicate test for each set at two temperatures.*

Set B showed shorter OGR time which was desirable but time-consuming in performance. Set A showed a shorter OGR time in comparison with the standard method. At 40 °C, set B shows an OGR time shorter than other sets. At 60 °C, doubled pressure makes the visual inspection easier but does not necessarily lead to a shorter penetration time. For highly viscous oils, higher pressure is required. However, an increase in the amount of oil leads to a shorter penetration time at both temperatures.

## 5.3 Comparison of different underlays

The criteria sheet for tested underlays is shown in Table 11. The manufactured ground-glass does generally not meet the criteria. The penetration could not be observed during the inspection time, which was 19 hours. The glossy glass does not either fulfill the requirement. On the contrary, the frosted glass and KRAFT paper was adequate according to the preliminary criteria.

*Table 11. The preliminary criteria sheet for the underlays.*

| Criteria | Manufactured ground (MG) glass | Glossy glass | Hand-ground glass (HG) | KRAFT paper |
|---|---|---|---|---|
| OGR time within 8 hours | — | × | × | × |
| Observation without using a table lamp | — | — | × | × |

The oil penetration time of undyed rapeseed oil is almost the same on the glossy and HG glass. However, in some cases, the OGR time of dyed oil on paper has also been the same. Moreover, the lack of visibility of undyed rapeseed oil on the paper makes estimating of the OGR time uncertain. Hand-ground glass facilitated the observation without the need to use extra light. Pictures were taken on the upside of the underlay and backside of paper substrates, as seen in Appendix A.

It is important to use a glass plate without special surface treatment. Grinding glass with sandpaper removes a layer of the surface. The frosted glass ground with the roughest sandpaper (number 36) causes scratches. Hence a combination of sandpaper (number 80 and 60) with a lower roughness level contributed to a smoother surface.

## 5.4 The oil and grease resistance of barriers

Figure 10 shows the normalized penetration time of three oil reagents at two temperatures. Normalization is done by dividing the OGR time by coating weight for each sample. The unnormalized OGR time measurements are added in Appendix B.

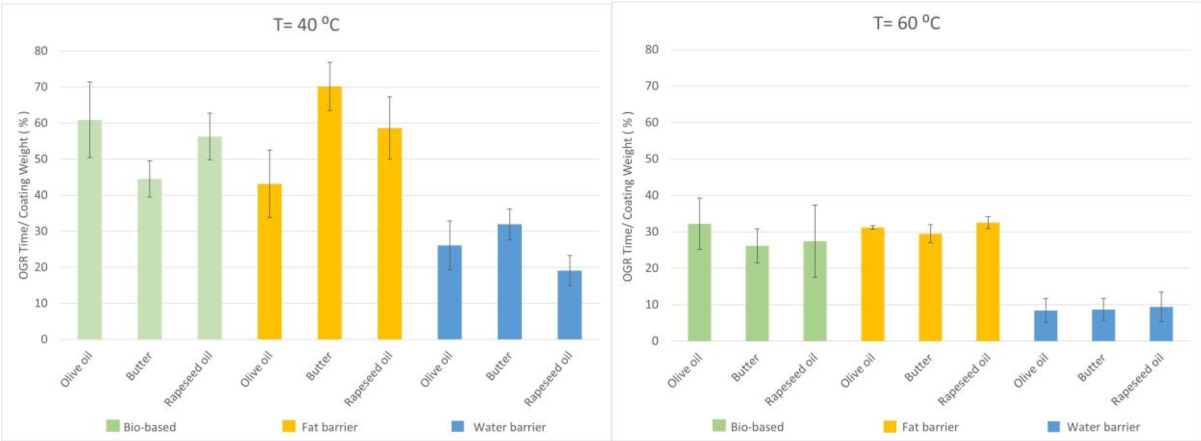


*Figure 10. The average OGR time by coating weight of oil reagents on three different barriers at 40 °C on the left and 60 °C on the right.*

At higher temperatures, the oil penetration time was shorter in all cases. Also, the visual detection of oil traces was easier. The results indicate that this method can be applied to barriers with different formulations. At both temperatures, the water barrier shows the shortest OGR time, which corresponds to its barrier properties. The inspection time needs to be adapted to the type of barrier. For instance, at 60 °C, the water barrier needs to be observed more frequently within 30 minutes after the start.

A higher standard deviation in barrier coating weight has led to a higher standard deviation in OGR time for most cases. For instance, at 60 °C, olive oil traces for a test sample of bio-based barrier with a lower coating weight appeared earlier than a higher coated test sample. Pictures taken of these tests are presented in Appendix C.

## 5.5 Comparison of reagents

In pre-tests, clarified coconut fat was also tested and the OGR time could not be determined within the desired time frame. Therefore, a triplicate test of the bio-based barrier was allowed to stay in the oven overnight. The OGR time was between 24-25 hours at 40 °C. At 60 °C, coconut oil showed a breakthrough time within a workday corresponding to 6.5 hours. A blend of 50 wt % coconut oil and 50 wt % rapeseed oil shortened the OGR time.

Further testing was performed using olive oil, butter and rapeseed oil at two different temperatures, as shown in Figure 11. At 40 °C, butter has a longer penetration time than rapeseed oil on the fat and water barrier. This can be explained by the higher level of saturation of butter that makes the penetration time longer. The bio-based barrier has low affinity to vegetable oils at both temperatures, which might lead to longer OGR time.

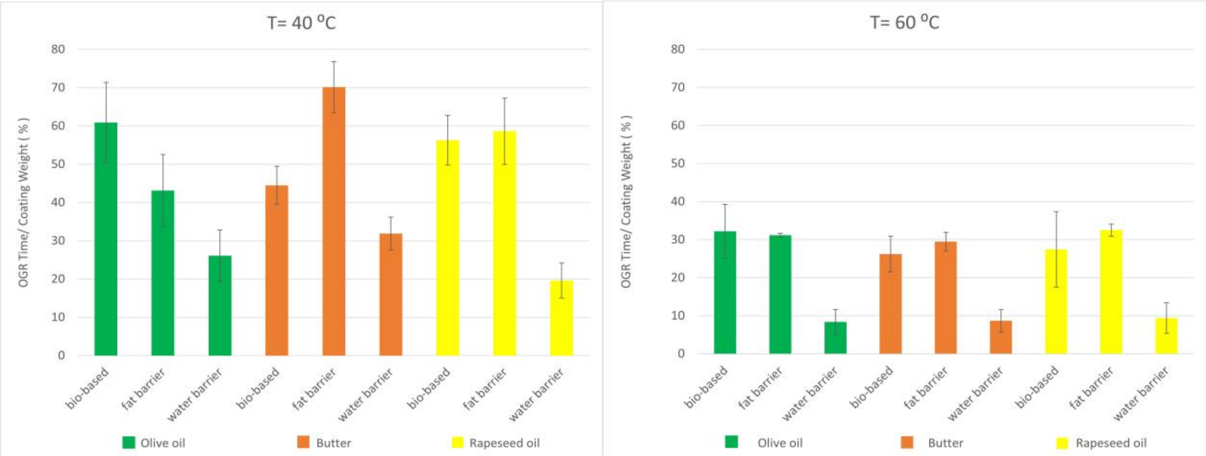


*Figure 11. The average OGR time by coating weight of three oil reagents at two temperatures.*

## 5.6 Reference methods

The result of the test methods is collected in Table 12. According to the oleic acid test result, bio-based and fat barriers are the poorest barriers. This is contradicted by the KIT-test and ASTM- F 119, which shows the fat barrier has good grease resistance and the water barrier is the poorest barrier against grease. Incorrect results of the oleic acid test may depend on the higher coating weight of the paper substrate.

*Table 12. Result of reference methods.*

| Criteria | Reagent | Temperature/ time | Bio-based barrier | Fat barrier | Water barrier |
|---|---|---|---|---|---|
| KIT-number | Castor oil, Toluene, *N*-heptane | 15 s | 10 | 12 | 8 |
| Oleic acid test value | Castor oil, Oleic acid, Octanoic acid | 6 min at 60 °C | 3 | 3 | 5-7 |

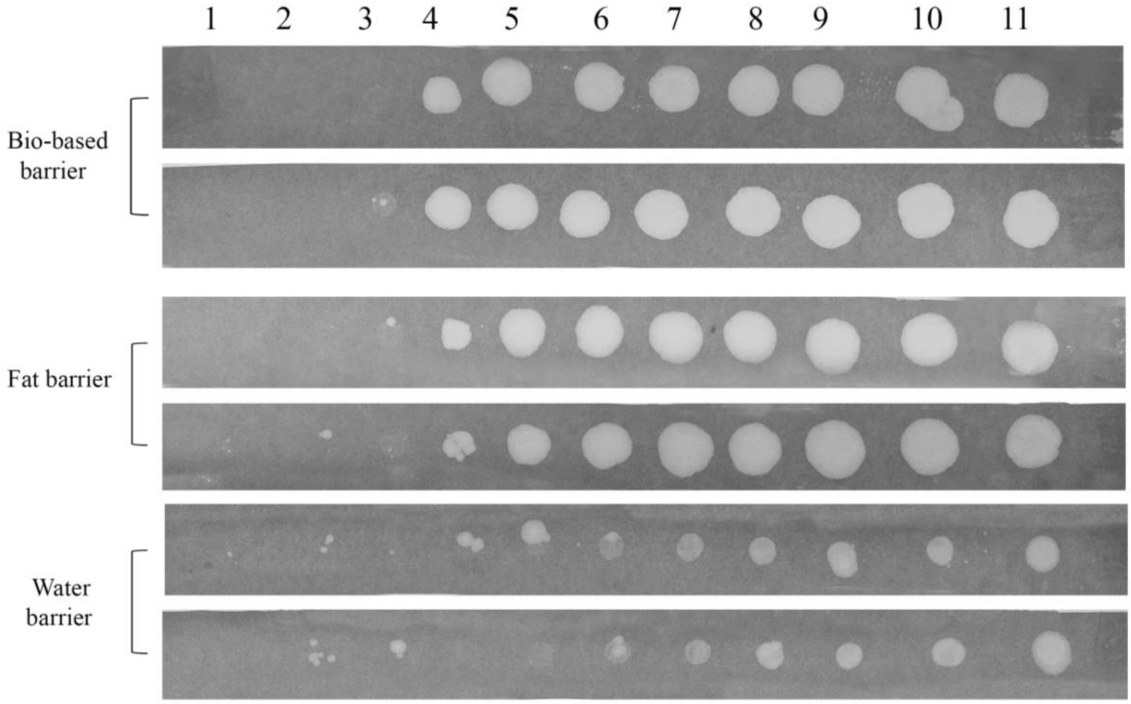


*Figure 12. Evaluation of grease resistance effectiveness of coated paper substrates using Oleic acid test.*

## 6. Conclusion

The modified ASTM- F119 method shows potential for evaluating grease resistance of different barriers using realistic oils. In this project, the observation continued for 8 hours in contradistinction to the standard test, where the observation is interrupted after the detection of the smallest little sign of oil on the glass plate. A longer inspection time makes it possible to observe the oil reagent’s behavior and define the OGR time according to the objectives and needs of customers in the paper industry.

The oil and grease penetration time can be shortened by changing the parameters like temperature, amount of oil and pressure, specifically at a lower temperature. The effect of temperature on shorter penetration time and more visible oil traces is more pronounced than other parameters. A higher temperature increases the flow rate of oil reagents into the paper substrates. The objective of this project has not been to determine the OGR time precisely. To achieve a certain estimation of oil penetration, it is needed that the barriers with low grease resistance are observed more regularly than barriers with higher grease resistance at 60 °C.

Results from the present study indicate that ASTM- F119 method correlates to KIT-test for all tested barriers but not necessarily for all types of oil reagents. Finally, ASTM F- 119 can be used to compare the barrier’s grease resistance effectiveness and estimate the OGR time of oil reagents.

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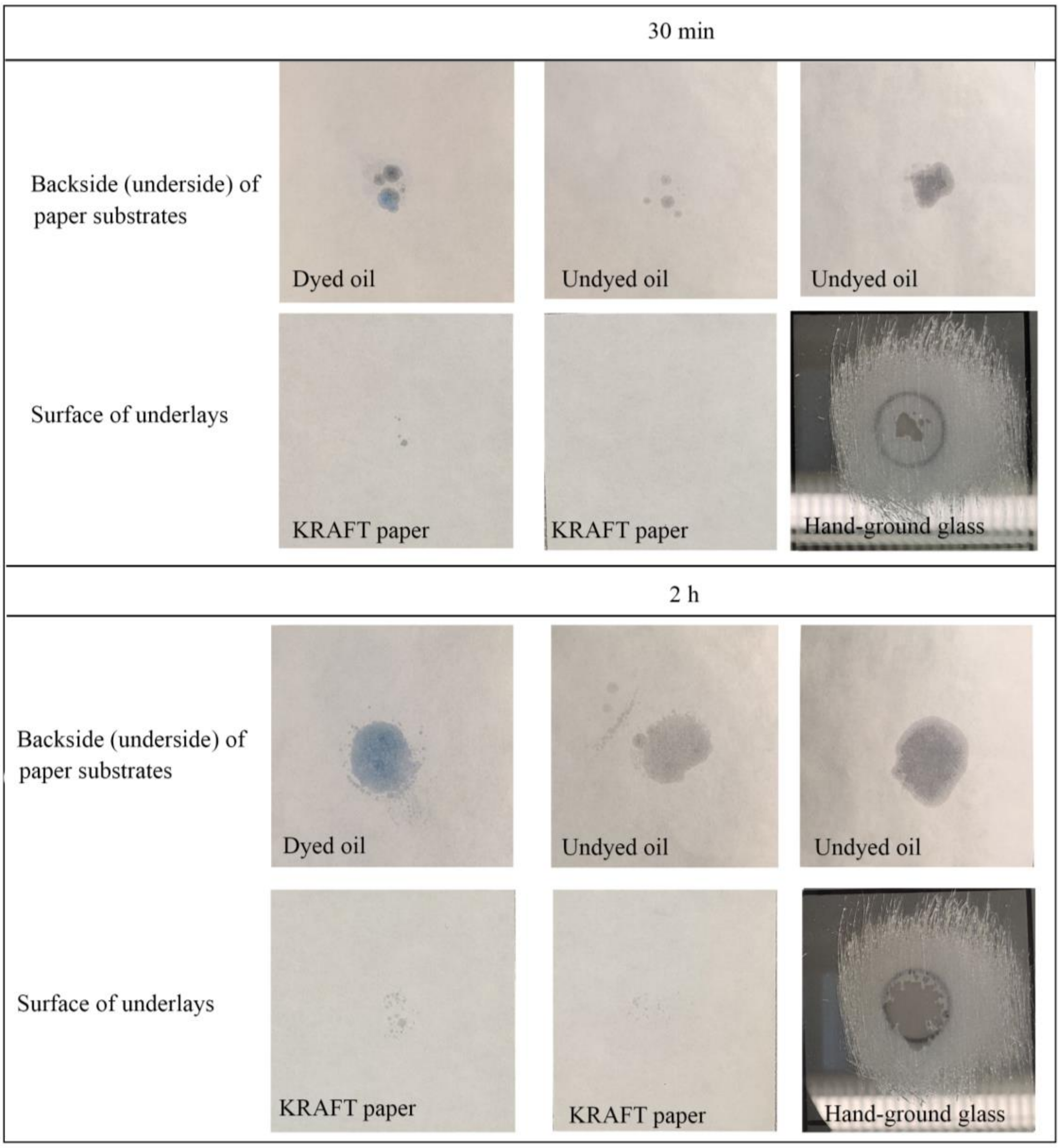
# Appendix A: Paper and hand-ground glass as underlay

Dyed and undyed rapeseed oil on the water barrier at 60 °C.



# Appendix B: Unnormalized OGR time measurement of three oil reagents

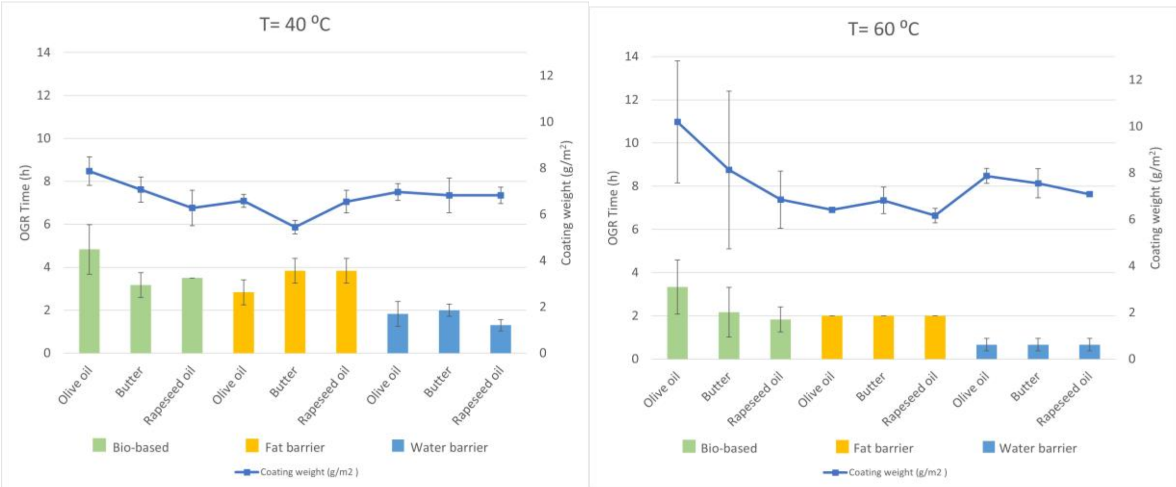



*Figure B-1: Comparison of barrier's grease resistance effectiveness at 40 °C on the left and 60 °C on the right.*

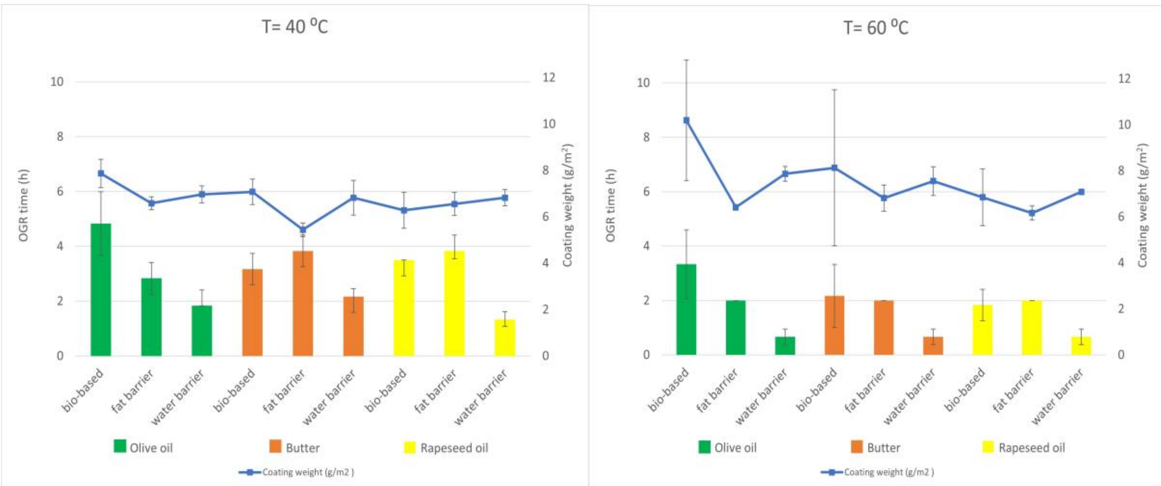
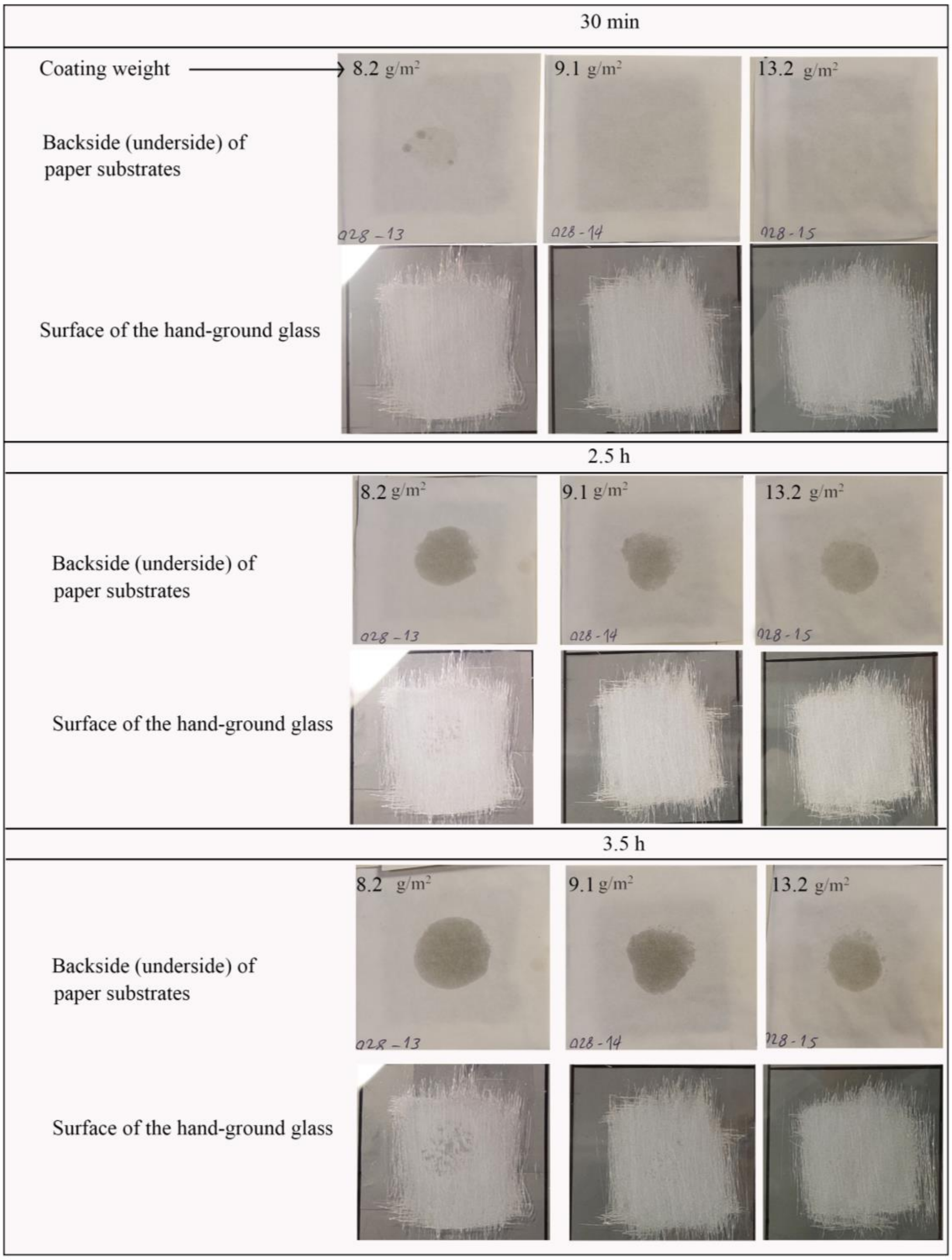
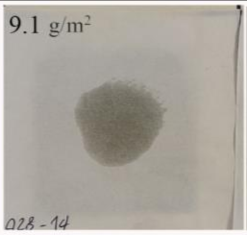
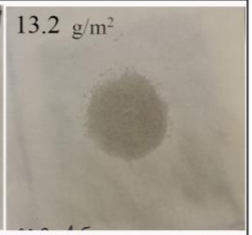
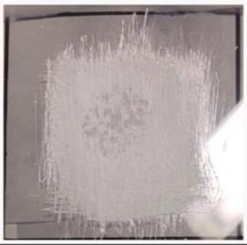
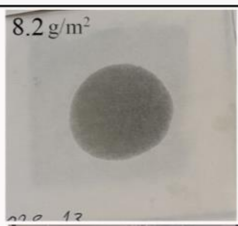
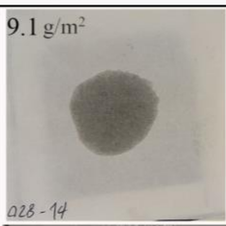
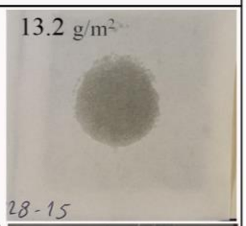
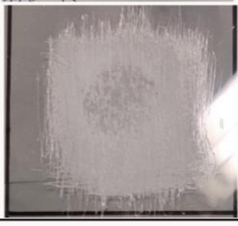
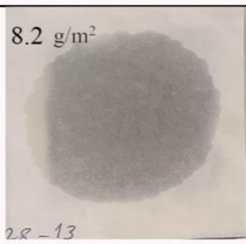
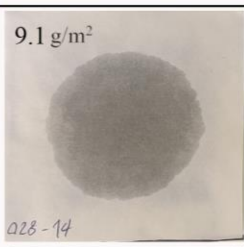
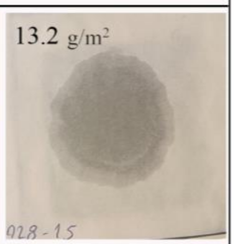
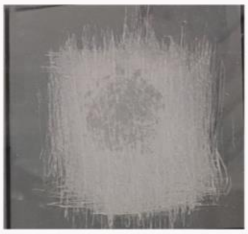



*Figure B-2: Comparison of oil reagent's average penetration time into different barriers.*

## Appendix C: ASTM F- 119 results of a triplicate test of the biobased barrier using olive oil at 60 °C from 0 - 5.5 h and 23 h



## Appendix C: ASTM F- 119 results of a triplicate of the biobased barrier using olive oil at 60 °C from 0 - 5.5 h and 23 h

| | | | |
|---|---|---|---|
| 4.5 h | | | |
| Backside (underside) of paper substrates |  |  |  |
| Surface of the hand-ground glass |  |  |  |
| 5.5 h | | | |
| Backside (underside) of paper substrates |  |  |  |
| Surface of the hand-ground glass |  |  |  |
| 23 h | | | |
| Backside (underside) of paper substrates |  |  |  |
| Surface of the hand-ground glass |  |  |  |

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