Graphite containing coatings aimed for supercapacitors

Ann-Christine Engström
Abstract
The objective in this study was to investigate the possibilities to coat paper-based electrodes for supercapacitors. The low solid content in coating colours containing graphite can bring difficulties when coating on paper. For this purpose different coating colours were prepared and compared. Rheology, coating performance, visual appearance of the final coatings and the electronic capacity was investigated in both laboratory and a pilot trial. The study has shown that it was possible to produce solid electrodes by laboratory coatings but there are several factors influencing the coating results. The most important was the impact of decreased solid contents of the coating formulation in a pilot trial which caused both severe wrinkles and insufficient drying of the coated paper.

It was found that an addition 10% nanofibrillated cellulose (NFC) improved the dry coating with apparent fewer streaks and cracks. The NFC addition gives a homogenous coating colour with somewhat decreased viscosity. The reason for this is unknown but the nanofibrillic network seems to interact with the homogenized graphite. Furthermore the NFC addition improved the capacitance of the final electrode.

It is recommended to investigate further possible chemical or chemical techniques for increasing the solid content in the coating formulation.

Keywords: Supercapacitor, electric double-layer capacitor, coated paper, coating, rheology, graphite, graphene.
Acknowledgements / Foreword

I would like to thank the people working within the KEPS (Kinetic Energy Storage in Paper-Based Supercapacitors) project at the Mid Sweden University (Miun). Especially my closest project members Sven Forsberg, Britta Andres and Nicklas Blomquist who have been giving useful tips, a lot of knowledge and a nice and positive attitude.

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**Terminology / Notation**

**Acronyms/Abbreviations**

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<th>Description</th>
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<tr>
<td>EDLC</td>
<td>Electrical double layer capacitors</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared radiation</td>
</tr>
<tr>
<td>KEPS</td>
<td>Kinetic Energy Storage in Paper-Based Supercapacitors</td>
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<tr>
<td>Miun</td>
<td>Mid Sweden University</td>
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<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
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<tr>
<td>NFC</td>
<td>Nanofibrillated cellulose</td>
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<tr>
<td>PAA</td>
<td>Poly acrylic acid</td>
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<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>RGO</td>
<td>Graphene oxide</td>
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<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
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<td>SWNT</td>
<td>Single-walled nanotubes</td>
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1 Introduction

Finding smart and efficient energy systems are necessary in our society. An important part of these systems are the energy storage capacity. Also the environmental and economical aspects are important driving forces in this research area. Supercapacitors were invented during the 1950’s but did not find any extensive utilization until late 1990’s, at the time mainly as computer memory backup [1]. Supercapacitors are specially designed to handle high specific power. Another benefit is the fast charging compared to batteries and that they do not lose storage capability over time. Supercapacitors can perform numerous charge/discharge cycles without losing the energy storage capability [2].

By coating nanographite on paper, electrodes can be produced which can be mounted together to form a supercapacitor. In this work different coating formulations were investigated by measuring physical properties and their influence on the final coating result. It is important to produce durable electrodes with high electronic capacity. This means that the coatings must withstand a reel to reel coating process but also be durable in the supercapacitor.

1.1 Background and problem motivation

The work with supercapacitors was initiated in the Paper Four and the EnergyWise project at the Mid Sweden University. The development of supercapacitors for vehicles started in the KEPS (Kinetic Energy Storage in Paper-Based Supercapacitors) project in 2013. The approach to prepare environmental friendly supercapacitors at a low cost is new and unique in many ways. This supercapacitor consists basically of homogenized graphite coated paper placed in a water based electrolyte solution. The manufacturing of these electrodes would be cost-efficient if implemented in a conventional paper production of coated papers. The end-use of the supercapacitor in the KEPS-project is to recycle energy when braking a car. Within the project graphite/graphene-based electrodes have been successfully tried out parallel with preparation methods for homogenizing graphite [3, 4, 5]. Coating tests have been performed in the project but both the coating and drying gave insufficient result and were difficult to perform. It was obvious that more work was needed to improve the coating performance. For this purpose this work comprises both coating colour characterization in the laboratory and a pilot coating trial.
1.2 Overall aim / High-level problem statement
The overall aim was to investigate the possibilities to coat paper-based electrodes for supercapacitors in large-scale production. This comprised work in finding appropriate coating formulations, coating characterization methods and useful coating techniques.

1.3 Scope
The work consisted of three separate studies, two laboratory studies followed by a pilot trial. In the initial study fundamental rheological studies was performed. In the second study coating colour solid contents, different additions of nanofibrillated cellulose (NFC) were investigated by rheology measurements and final coating appearance. The third study was a pilot study which was performed for testing slot-die coating and reel to reel coating for producing large amounts of paper-based electrodes.

1.4 Concrete and verifiable goals / Detailed problem statement
The work consisted of evaluations of coating colour preparation, coating performance and the final coating quality.

The main problem by coating graphite based electrodes is the low solids received in the coating colour preparation. This is due to the solid state of matter regarding graphite which must be diluted to concentrations below 12-10% for reaching a suitable flow behavior in the coating process, see Image 1.1. The impact of the solid content and also the effect of an NFC addition to the coating colour needed to be more investigated.

Image 1.1 Grahite of 10% consistency to the left and 15% consistency to the right.

Another issue was experienced in a previous laboratory blade coating trial which was troublesome. The blade was difficult to adjust and the impact of low solid content gave problems in drying the coating [5].
In laboratory coating the coating performance is noticed almost directly. This is shown in coating coverage, streaks or other disturbances. In reel to reel coating parameters like rheology, coating velocity, drying capacity and appearance of the coating quality is important. These properties also needed further investigations.

For preparing homogenous and stronger coatings NFC is added (See Theory part 2.4). In a previous study NFC additions of 5%, 10%, 15% and 20% were tested. An addition of 10% NFC by weight of graphite was found to be the most suitable amount regarding capacitance [4]. In order to investigate the possibility to decrease the 10% amount, an addition of 7% NFC needed to be tested. One obstacle in using NFC is the low consistency, 1-2% which when added further decreases the solid content in the coating colour.

It should be mentioned that this study covers several technical, chemical and physical areas why some subjects are less detailed and given a more general description.

1.5 Outline
Chapter 2 gives an overview of work related to supercapacitors, graphite, graphene as a material and possible coating techniques. This chapter also contains recent work related to industrial application in producing paper-based electrodes. Chapter 3 contains the used methods in this study. Chapter 4 presents the results and the subsequent chapter contains the conclusions of the results (Chapter 5).

1.6 Contributions
The work was performed in cooperation with the project members in the KEPS-project. Sven Forsberg who is projectleader has initiated this work. The preparation of the larger coating colour volume was done by me, Nicklas Blomquist, Sven Forsberg and Britta Andres. Nicklas Blomquist has constructed the homogenizer and together we performed the homogenization of the graphite. He has also constructed the large mixer used in the pilot trial. The evaluation of the capacitance measurements was made by Britta Andres. My contributions were the implementation of viscosity measurements on the Rheomat viscosimeter, manual laboratory coatings (RPC and blade coating) and planning of the coating trial at Kroenert. Another contribution was the implementation and manufacturing TEMPO-oxidized NFC in the laboratory at Miun.
2 Theory

2.1 Supercapacitors

Graphite containing electrodes are frequently used in supercapacitors and in scientific works this area is steadily increasing [6]. The capacitor is constructed for electrostatic storage of electrical energy in the interface between the electrode and the electrolyte in the Helmholz double layer [7]. These types of supercapacitors belong to electrochemical capacitors and are called electrical double layer capacitors, EDLC. Besides of EDLC’s there are pseudocapacitors and hybrid capacitors. EDLC’s are usually carbon or metal based and are worldwide commercially available for an expanding range of applications. The EDLC’s used in this study consists of two graphite coated electrodes with a positively and a negatively charged side attracting oppositely charged ions which are separated by a separator, see Image 2.1. The separator in this study consists of greaseproof paper. The electrode and separator are soaked in electrolyte for promoting the ion transport.

![Image 2.1. Schematic sketch of the components in an electrical double layer capacitor.](image-url)

2.2 Characteristics of graphite and graphene

Graphite is a natural carbon-based mineral which is frequently used in the industry (especially steel production). Graphite can also be used in lubricants, pencils, batteries and in products from expanded graphite which can be formed and used as heat dissipating foils etc. Graphite can be categorized into four groups based on their production and character; flake, amorphous, vein/lump, and synthetic. The flakes are flat and in size often between 1-25 mm. Amorphus graphite are finer, microcrystal flakes (0,001 mm) and vein/lump graphite are massive platy, crystalline aggregates.
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Synthetic graphite is produced from petroleum coke which in high temperature, 2500-3000°C is transformed to crystalline carbon. This graphite is usually used in electrodes, for electric arc melting of iron, steel and aluminium.

By treatment of flake graphite so called expanded synthetic graphite can be made. The process is done by intercalation and thermal shock, which exfoliates and expands the graphite flakes up to 700 times [8].

Graphite has a structure where carbon atoms lie in sheets weakly bounded to each other. Stronger covalent bonds connect the carbon atoms within each sheet, but the sheets are held together only by weak Van der Waals forces. These bounds are easily broken which make the graphite material soft [9]. Graphite has an extraordinarily low coefficient of friction under working conditions which makes it suitable as lubricant. It decreases friction and keeps the moving surface cool. Graphite is also a good conductor of heat and electricity [10]. Another property of graphite is the flotation behaviour due to its hydrophobicity. Since graphite does not require a collector flotation has become a useful process in graphite mining [11].

Graphene was discovered in 2004 by Novoselov, Geim et al. who found single two-dimensional layers of atoms with extremely strong bonds for its low weight (100 times stronger than steel). The discovery was made by placing adhesive tape on graphite and transferring the tape on a silicon wafer. This discovery gave them the Nobel Prize in Physics 2010. Graphene was also found to be an excellent conductor of heat and electricity [12].

Graphene can basically be produced in two ways, either top down or bottom-up fabrication. Top down means that the sheets are peeled off as when graphite is mechanically exfoliated. The bottom-up graphene is often made chemically as in the CVD (chemical vapor deposition) method when graphene is deposited on a substrate. Bottom-up graphene is for the time being produced in small-scale. For large-scale production the top-down method is the obvious choice.

In order to increase the electronic capacitance, graphene can be added to polymers, adhesive, oil and aqueous and non-aqueous solutions. These dispersions are advanced composites which can be used in, batteries, capacitors, as barrier materials, in coatings, inks, display materials, functional fluids, electronics and thermal devices [13].
2.3 Homogenizing graphite for supercapacitors

The graphite in this study was processed using a top down method. The graphite was diluted with water and processed in a homogenizer which exfoliates the graphite by mechanically shearing the particles in a high pressure zone. This conveys high amounts of micro- and nanosized particles with high specific area which creates small pores and enables higher conductivity in the electrodes. [14].

When mixing graphite and water a dispersing agent is necessary for separating the graphite particles. This is necessary for obtaining a homogenous solution in the homogenizer. In this study Polyacrylic acid was added which keeps the particles separated by electrostatic stabilization [15, 16]. It is important that the graphite particles are not aggregated making the slurry to thick when processed through the homogenizer.

2.4 Nanofibrillated cellulose

Nanofibrillated cellulose, NFC, can be added to the coating for promoting the bounding between the graphite particles and creating a strong material also when dried [4]. NFC is produced when disintegrating wood cellulose at a high energy input. Cellulose is present in the cell wall of the wood and consists basically of many glucose units put together to a carbohydrate, or polysaccharide [17]. About 40% of the wood is cellulose, the rest is hemicelluloses (~30%), lignin (25%) and extractives (3%). The NFC size is around 20 nm in width and the length is in the micrometer scale. Trials of producing NFC started during the 1970’s by using a homogenizer for milk separation. It was discovered that thread-like pulp particles were formed. Nowadays the mechanical disintegration is more often performed after a pre-treatment of the pulp. This conveys a more homogeneous NFC with decreased numbers of larger fibers and fibrils. As pre-treatment both mechanical and chemical methods are available. Mechanical and enzymatic pre-treatments preserve the hydrophilic surface of NFC. Chemical treatment reduces the energy input. The chemical treatments are often TEMPO-mediated oxidization, Carboxymethylation or Sodium metaperiodate followed by oxidation. These chemicals introduce charged groups to the fiber which promote delamination but also increase the swelling of the fibers [18, 19, 20].
Adding NFC to the coating colour forms a nano scaled network which not only affects the coating rheology but also enhances the strength and elasticity of the produced electrode [21]. One problem by using NFC is the high water content from the preparation caused by swelling, which slows down dewatering and contributes to a decreased solid content in the coating formulation.

2.5 Rheology in coating colours

Rheology of the coating colour is important in the industrial process and involves pumping and transporting in pipes, as well as the actual coating on the machine. This concern both the slurry and the final composed coating colour. Rheology is the flow of liquids and is affected by shape, size, density and mass fraction of the suspended particles and the viscosity of the liquid [22]. The most common rheological measurement is viscosity. Viscosity can be defined as a fluids resistance to gradual deformation by shear stress or tensile stress [23]. The viscosity is often described in an idealized situation known as the Couette flow where a fluid is trapped between one stationary plane and one moving. In a planar, laminar flow the velocity of the lower layers of the liquid will move slower than the top layer due to the friction, see Image 2.2.

The equation for describing this phenomenon is shown below.

\[ F = \mu A \frac{\partial u}{\partial y} \]

\[ F = \text{Moving force} \]
μ = Dynamic viscosity of the liquid

A = Area of the plates

\[ \frac{\partial u}{\partial y} = \text{Gradient, local shear velocity} \]

In coating colours based on pigments e.g. graphite a non-Newtonian behavior of the viscosity occurs. This means that the viscosity decreases with increasing rate of deformation, usually expressed as the shear force. In this context it means that the coatings are shear thinning [25]. Shear thinning can occur because of particle shape, loss of junctions, rearrangement of microstructure and/or breakdown of flocs. Tixotrophy is a common shear thinning property. This is shown by the shear thinning effect at increasing shear force and when the shear force stops the liquid returns to the original viscosity. The shear thinning effect starts generally instantly but the reversion of the viscosity can take longer time [26].

Dense fluids mean that solid-liquid mixtures have closely packed particles resulting in saturated pore systems [27]. Graphite has a dense structure at solid contents >15%. The hydrophobic nature, grade of packing of graphite and the water content in the coating formulation can give phase-separation. This can give a slip behavior when measuring graphite slurries by rotational viscosimeters (See 3.2 about rotational viscosimeters). This means that the concentration on the surface is lower and the bob moves faster compared to the rest of the bulk. The torque resistance is by this very low. Slipping can also occur when the rotating bob “cuts a hole” into the sample and measures very low viscosities [28].

The rheology effects in graphite suspensions are not well documented. Graphite sheet deformation, packing of particles, chemical bounding, floc behavior etc. are impossible to determine by solely rheology measurements. Furthermore the impact of the PAA and not at least the NFC addition is unknown. In the literature structure breaking behavior occurs when shearing suspensions containing soluble hydrocolloids as NFC or MFC [29]. The gel-like structure resists generally an initial low shear rate but at higher forces the viscosity decreases. By viscosity measurements this can be difficult to separate from the shear thinning effect induced by e.g. lubricating graphite or other effects in the suspension.

**2.6 Coating processes**
Possible coating technologies for electrodes are spray, slot die, gravure, metered size press, rod, reverse roll, or curtain coating particularly in reel-to-reel solutions [30].

In conventional pigment coating on paper the solid content in the coating colour is usually above 60 % by dry weight. Drying capacity is important and is related both to quality and economical aspects in the coating production. Optimized capacity regarding both dryers and energy consumption are important factors in this area.

The drying in conventional pigment coating on paper is often divided into three phases; the initial drying, the critical drying and the final drying [31]. The initial drying is important to start as quickly as possible after coating. The drying is often made by infrared radiation (IR) and air flotation dryers. The absorption of water into the paper starts immediately by capillary flow. The dryer heat conveys increased coating viscosity by water evaporation. The critical drying phase starts when the capillary forces shrinks the coating so the pigments starts to contact and the actual coating structure is formed. The final drying phase takes place when the coating layer is stable and the final moisture level is reached. These steps must be optimized since they all affect the final evenness of the coating [32].

The applied coating layer thickness in the paper industry is usually between 7-30μm. Blade coating is the most common coating technique used and the gap between the blade and the paper is usually around 15μm. This gap is in the order of magnitude of the pigments diameter which can range between 2-10μm. The particle size distribution affects both the pigments movement and position during both pumping and coating [33]. The coating thickness of electrodes in the KEPS-project aims to be around 5-10 times higher but is mainly adapted to the electronic capacitance of the supercapacitor.

The water absorption of coating onto paper occurs immediately but depends on paper-, fibre type, surface properties, various paper treatments etc.. Paper absorption occurs via diffusion transport of vapor into the pores, capillary transport of liquid into the pores, surface diffusion into the pores and liquid movement through the fibres. The most important absorption mechanism regarding greaseproof paper is fibre sorption. This paper both has absence of large surface pores and increased swelling ability due to the highly beaten fibres [34]. The water uptake releases inherent forces in the paper and affects the paper
dimension stability. The subsequent drying also influences the shape and appearance of the coated paper.

2.7 Production of paper-based electrodes

There are few industrial applications reported regarding coating paper-based electrodes. Most work has been done regarding thin graphene layers.

At the Monash University researchers claim to have found a solution similar to that used in traditional paper making. They have used graphene oxide reduced by hydrazine and ammonia to form graphene flakes. By mixing electrolyte and a solvent which evaporates, a graphene based paper was created which also carried the electrolyte [35]. As an electrochemical capacitor, this paper-like material had an energy density comparable to a lead-acid battery.

At Stanford researchers designed a paper-based supercapacitor by using Meyer rod technique to coat carbon nanotubes on a polyvinylidene fluoride (PVDF) treated paper. 10% of PVDF was diluted in Methylpyrrolidone and dropped on the paper surface. The PVDF surface treatment blocks the pores but still allows the electrolytes to wander through the paper. The single-walled nanotubs (SWNT) concentration in the water-based ink was 2 g/l (0,2%) and the dry applied coating layer was ~3 μm. In this case the advantage was that the nanoparticles would stay on the paper surface while the water in the ink was penetrated and absorbed during coating [36].

Another work approaching paper making processing was performed by researchers at the Grenoble Institute of Technology. On a pilot paper machine Li-ion battery electrodes were made by spray coating a thin layer of graphite slurry also containing carboxymethyl cellulose (CMC) and microfibrillated cellulose (MFC). One obstacle in this work was also the water content causing wrinkles why they recommended spray coating on wet paper, preferably in the wet end of the paper machine [37].

In a recent lab work dispersed graphite was successfully coated on a recycled fibre based paper. The surface was pre-treated with a CMC solution for preventing water penetration. The coating thickness was around 60 μm. The coating colour consisted of dispersed graphite with sodium dodecyl sulfate (SDS), styrene-butadien latex, CMC and defoamers [38].
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3 Methodology

3.1 Material and coating techniques

Graphite (M-expanded) from Superior Graphite was used in all three studies. The graphite was diluted with deionised water to 2% concentration. The slurry was then dispersed 30 minutes with a dispersing agent, 2% poly acrylic acid (PAA, by weight of the graphite) before the homogenization. After homogenization the slurry was dewatered to a solid content of 10%. The graphite was homogenized similarly but at separate occasions. This was done in the laboratory by a homogenizer developed at the Mid Sweden University.

3.1.1 Lab study I

The initial laboratory study is based on viscosity measurements, see part 3.2. Slurries consisting of homogenized graphite diluted to 2%, 5% and 10% solid content were prepared. Parallel 2%, 5% respectively 10% graphite slurries were prepared containing 10% TEMPO-oxidized NFC (based on graphite weight) each.

3.1.2 Lab study II

The second lab study focused on NFC additions and dry content in the coating colour. The additions of NFC (%) were based on the graphite weight in the coating colour. The NFC was made at Innventia and two types with different fiber charge were used; TEMPO-oxidized- and Carboxymethylated NFC. The TEMPO-oxidized NFC had a charge of 4 mmol/g and the Carboxymethylated 0,6 mmol/g. In the study five coating colours were investigated, see Table 3.1.

Table 3.1. Coating colours investigated in the lab study.

<table>
<thead>
<tr>
<th>Coating number</th>
<th>NFC addition and type</th>
<th>Solid content in coating colour [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7% TEMPO-oxidized</td>
<td>11,8</td>
</tr>
<tr>
<td>2</td>
<td>7% Carboxymethylated</td>
<td>11,7</td>
</tr>
<tr>
<td>3</td>
<td>7% Dewatered TEMPO-oxidized</td>
<td>12,3</td>
</tr>
<tr>
<td>4</td>
<td>10% Tempo oxidized</td>
<td>10,5</td>
</tr>
<tr>
<td>5</td>
<td>10% Carboxymethylated</td>
<td>10,5</td>
</tr>
</tbody>
</table>
After mixing the coating colour components it was dispersed at 12000 rpm for 10 minutes using an IKA T25 Ultra-Turrax disperser. The rotor used was the S 25N-25F size.

The coating was performed with a RPC tester (Colour reel Printers Ltd) using the rod with a wire diameter of 1,00 mm (Standard K bar, brown) for sufficient coverage, see Image 3.1.

![Image 3.1. Laboratory coater used in lab study II.](image)

As substrate for the coatings a greaseproof paper (45 g/m², Nordic Paper) was used as.

The coated papers were dried in room temperature.

### 3.1.3 Lab study III

The third study comprised of a large-scale pilot trial for coating electrodes. Since the required coating colour amount increased from a couple of hundred ml to nearly 100 l the preparation of the coating colour was time-consuming. Both large amounts of graphite (5 kg corresponding to 5 barrels dry weight) and ~50 l NFC (1%) needed to be prepared. The large amount of NFC conveyed that TEMPO-oxidized was prepared in the laboratory at Miun.

The preparation of TEMPO-mediated oxidization of NFC followed the method described by Saito el al [39]. 100 g fully bleached soft-wood Kraft pulp was used in each batch. The pulp was diluted in a 10 l plastic bucket with de-ionized water to 2,5% consistency. 2 mmol Sodium Bromide (Merck Millipore) per g dry pulp and 0,2 mmol/g TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy, Sigma-Aldrich) was added to the pulp suspension and mixed. The suspension was left over night for properly dissolving the chemicals. The suspension was mixed and subsequently 10 mmol Sodium hypochlorite (NaClO, 14% from VWR) per g dry pulp of was added during stirring. NaClO (pH 9,5) was added and the pH in the pulp suspension was adjusted to 9,5 by NaOH (1M).
In order avoid large pH-variations, small portions of the hypochlorite was added. By this the hypochlorite addition and subsequent pH-adjustment was performed during 2-3 hours. After this the pulp was de-watered and washed thoroughly. The washed pulp was diluted to 1% consistency with deionised water and subsequently dispersed with the IKA T25 Ultra-Turrax disperser (rotor S 25N-25F) for 20 minutes. ~700-1000 ml of the pulp suspension was dispersed in each batch in order to minimize the heat developed during dispersion and also for proper mixing.

Deionised water was added for pre-wetting the dry M-expanded graphite. The graphite slurry was prepared similarly as in the previous lab studies but the mixing was performed using a larger mixer, see Image 3.2. After mixing the total volume (250 l) the slurry was continuously homogenized in one single-pass. After homogenization the slurry was dewatered on a funnel through a filter paper (Munktell Na.OO). The solid content in each de-watered filter cake varied between 6 to 11 %. After that the homogenized graphite was mixed with 50 l NFC (1% consistency) using the larger mixer. For increasing the solid content in the coating colour, 1 kg of active coal was added (0,5 kg WV-E 120, MeadWestvaco and 0,5 kg Pulsorb 208CP powder from Chemviron Carbon). The final solid content of the coating colour was 6,2%. The coating was further mixed ~30 minutes before using it on the coating machine.
The coating was performed on a pilot coating machine at Kroenert GmbH & Co KG in Hamburg. The pilot machine is called Labco, see Image 3.2. This machine is adapted for coating trials and at request different coating techniques can be tested; gravure rollers, smooth rollers, comma bars and die/curtain coaters [40]. One side was coated and the substrate was a 38 g/m² greaseproof paper (“Candor LF Svanen” from Nordic Paper).

At the end of the pilot trial an additional amount (1 kg) of active coal was added which increased the solid content to 7%. The coating was applied at A (see Image 3.3) and the coated web was transferred through a two section drying zone using hot air. In order to improve the drying efficiency an IR-dryer was moved during the trial from the end of the drying zone to the beginning. Furthermore different web speeds were tested, from 0.3 to 3 m/min, as an attempt to improve the drying efficiency by extending the time in the drying zones.

In the coating trial the slot-die technique was used, see Image 3.3. By this technique the coating colour is pressed through a slot and transferred to the moving web. This technique has many advantages but the main reason was the possibility to easily coat thick layers. Kroenert also expressed that they had good experience in coating electrode materials by this technique.
Since there was problem when coating the paper with the pilot machine, manual coating was performed in the laboratory at Miun. For increasing the coating thickness the coating was done using a blade instead of the rod bars with the RPC coater. The coating was drawn on a vacuum table holding the paper stable, see Image 3.4. The applied coat weight was ~65 g and the coating thickness around 300 μm. The drying was performed in room temperature combined with an air-fan for approximately 24 hours due to the low solid content of the coating colour.

![Image 3.4. The slot-die technique (globalsolartechnology.com)](image)

### 3.2 Lab measurements

Rheology was evaluated by viscosity measurements. For characterising rheological behaviour of pigment slurries and coating colours more than one instrument is needed. As see in Image 3.5 different viscosimeters are used for measuring different viscosity levels in the process [41]. The instrument used in this study was a Rheomat RM180 (Mettler Toledo) which covers viscosities from 6,5-3230 s⁻¹. This corresponds to viscosities when pumping and mixing the coating colour. This also covers the initial range of the shear rates when using coating techniques as dip or roll coating. The viscosities when coating paper in a conventional blade
coating process correspond to shear rates from 20-40 000 $s^{-1}$. For slot die coating the shear rate range is around 3000-100 000 $s^{-1}$.

Image 3.6. Shear rates typical for the coating process.

The Rheomat RM180 instrument is a rotational viscometer using concentric cylinders according to the DIN 53019 standard determination of apparent viscosity. Rotational viscosimeters measure the torque required to rotate a bob at a known speed in a stational fluid containing cup [42]. In Image 3.6 a schematic description can be seen. Different measuring systems were used in the measurements due to the viscosity range of the fluids. Measuring system 11 (measuring tube plus bob 1) was used on the graphite slurries and measuring system 33 were used on the coating colours. The shear rate range was 6,5-1291 s-1 ranging up 8 measuring points to 1291 s-1 and subsequent back down to 6,5 s-1. The temperature in the measurements was 20°C.

Image 3.7. Measuring principle of the rotational viscosimeter (eCourse [43])

The viscosity measured in rotational viscosimeters follows the Couette geometry (See Theory chapter; 2.5). This measurement is suitable for fluids with low and moderately high viscosities and not for pastes or suspensions containing large particles [25]. The viscosity is calculated from the shear stress and shear rate by the following equations [44]:
Shear rate (sec\(^{-1}\)) \[ \dot{\gamma} = \frac{2\omega R_0^2 R_i^2}{x^2 (R_0^2 - R_i^2)} \]

Shear Stress (dynes/cm\(^2\)) \[ \tau = \frac{T}{2\pi R_i^2 L} \]

Viscosity \[ \eta = \frac{\tau}{\dot{\gamma}} \]

Definitions: 
- \( \omega \) = angular velocity of spindle
- \( R_0 \) = radius of container
- \( R_i \) = radius of spindle
- \( x \) = radius at which shear rate is being measured
- \( T \) = torque input by instrument
- \( L \) = effective length of spindle

For evaluating the electrodes capacitance measurements are used. These measurements were made in a test cell built at the Mid Sweden University. Two squared electrodes of 8.41 cm\(^2\) each were cut out from a dried, filtered sample of the coating colour. As separator a greaseproof paper (45 g/m\(^2\)) was placed in between the electrodes. These were soaked in electrolyte solution (1 M Na\(_2\)SO\(_4\)) and pressed between two metal plates. The measurements were performed by charging and discharging the cell for 24 h in order to evaluate the capacitance performance. At constant current the voltage variations versus time was measured. A discharge current was 0.1 A/g which refers to current per mass of one electrode. The capacitance, \( C \) was determined from the discharge curves, see calculation below.

\[ C = \frac{I}{\partial V} \frac{\partial t}{\partial V} \]

\( I \) is the discharge current, \( \partial t \) the discharge time and \( \partial V \) the voltage difference.

The sheet-resistance measurements were performed using a Hewlett-Packard 3457A multimeter. A four-point probe was used and the samples were pre-conditioned in 23°C and 50% (relative humidity) for 30 minutes before measuring.

Cracks in the coated electrode material convey decreased electronic capacity. Since no method for specifically detecting cracks was available
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the samples were evaluated by visual and tactile perception. The coated papers were visually examined both regarding cracks and coating coverage. The surface solidness of the graphite coating was tested by touching the coatings with the finger and observing if the surface released black graphite (see Result part 4.2.2).
4 Results / Discussion

4.1 Lab study I

4.1.1 Rheology studies

Initially slurries containing solely homogenized graphite, PAA and water were investigated. Viscosity was measured on the 2%, 5% and 10% graphite slurries, see Figure 4.1 and in detail 4.2. The shear rate points (x-axis) increases from 6,5 to 1291 (s-1) and decreases back to 6,5. The diagrams show the viscosity at each shear point. The slurries show different rheological behavior. The 2% slurry had the lowest viscosity. The 5% slurry had significantly higher values which likely are connected to the increased solid content. The 10% slurry showed however lower viscosity values by shearing. The reason for this is unknown. One hypothesis is that the higher solids gave a slip effect in the viscosity measurements due to lubrication in the more dense graphite suspension. This lubrication effects likely did not occur in the viscosity measurement of the 5% slurry when the slurry was more diluted.

![Viscosity diagram](image)

Figure 4.1 Viscosity diagram of 2%, 5% and 10% solid contents in the graphite slurries.
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2014-10-06

Figure 4.2 Detailed diagram of 2%, 5% and 10% solid contents in the graphite slurries.

The impact of an NFC addition to the 5% slurry was investigated, see Figure 4.3 and 4.4. The diagram shows two slurries of which one contains TEMPO-oxidized NFC (10% by graphite weight). One result was the significantly higher viscosity observed at the initial shear point for the NFC containing slurry. This is likely due to the gel-like character of NFC caused by swelling which thickens the slurry. At shearing generally lower viscosities were obtained in the NFC containing slurry compared to the slurry without NFC. The decreased viscosity can be explained by the NFC structure releasing internally trapped water when the shear forces increases [29]. Another explanation can be rupture in the flocculated network in NFC which would give a more shear thinning effect.
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Figure 4.3. Viscosity curves of 5% slurries and impact of 10% NFC content.

Figure 4.4. Detailed curves of 5% slurries and impact of 10% NFC content.

4.2 Lab study II

4.2.1 Rheology studies

The viscosity measurement of the five coating colours in the study is shown in Figure 4.5. The coating colour containing 7% TEMPO-oxidized
NFC with a solid content of 11.8% showed a very high initial viscosity which subsequently is sheared down to the same level as the other samples. Besides the NFC effect described in 4.1.1, this behavior can be observed in mill processes using clay or coal water slurries and can be troublesome when starting up of pumps etc. [22]. The viscosity curves in the diagram clearly show the shear thinning behavior of the coating colours. As mentioned in the theory part there a many reason for this behavior exists (See Theory part, 2.5.).

Figure 4.5. Viscosity measurements of coating colours with different TEMPO-oxidized and Carboxymethylated NFC additions and varying solid contents.

Figure 4.6 is an upscaled version of Figure 4.5. The thixotropic behaviour of the coating colours is observed. This is shown by the shear thinning effect and subsequent increase of the viscosity when the shear force decreases. Another observation is that the coating colour containing 7% carboxymethylated NFC (11.7%) and the dewatered coating with 7% TEMPO-oxidized NFC (12.3%) have no viscosity values at the lowest shear rate points. In the measurement these range points were marked “Torque to low” which means that the resistance in the liquid is too low. The reason for this is unknown but may be connected to the breaking of the components structure or increased water release as described earlier in this report.
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As seen in the diagram the difference between Carboxymethylated NFC and TEMPO-oxidized NFC was minor at the 10% addition. At lower additions, 7%, the viscosity level for the Carboxymethylated NFC coating colour was lower (see separate diagram in Figure 4.7). One hypothesis can be the lower charge of the Carboxymethylated NFC which may give weaker bonds to the homogenized graphite.

Figure 4.6. Close up of Figure 4.5.

Figure 4.7. Comparison of Carboxymethylated respectively TEMPO-oxidized NFC.
4.2.2 Perceptual studies of the coatings

The visual inspection of the samples showed clearly a connection between the 7% and the 10% addition of NFC. Despite NFC type the appearance of the coatings was affected, see Image 4.1. A lower NFC addition (7%) gave more streaks and poorer coating coverage compared to a higher (10%) addition.

Image 4.1 Surfaces of coating colour with 7% TEMPO-oxidized NFC to the left and coating colour with 10% TEMPO-oxidized to the right.

The surface strength was also affected; more graphite smudged the fingers when touching the surfaces with lower NFC content. See the compiled results from the study in Table 4.1.

Table 4.1. Characterization of the investigated coatings.

<table>
<thead>
<tr>
<th>Coating no</th>
<th>NFC addition and type (%)</th>
<th>Solid content (%)</th>
<th>Coated paper grammage (g/m²)</th>
<th>Coat weight (g)</th>
<th>Perceptual investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7% TEMPO-oxidized</td>
<td>11,8</td>
<td>59,3</td>
<td>15,8</td>
<td>Poor coverage, streaks, tactile release of graphite</td>
</tr>
<tr>
<td>2</td>
<td>7% Carboxy-methylated</td>
<td>11,7</td>
<td>58,2</td>
<td>14,7</td>
<td>More uniform coating but streaks, tactile release of graphite</td>
</tr>
<tr>
<td>3</td>
<td>7% Dewatered TEMPO-oxidized</td>
<td>12,3</td>
<td>57,2</td>
<td>13,7</td>
<td>Better coating but streaks, tactile release of graphite</td>
</tr>
<tr>
<td>4</td>
<td>10% TEMPO-oxidized</td>
<td>10,5</td>
<td>57,3</td>
<td>13,8</td>
<td>Good coating but some streaks, tactile solid surface</td>
</tr>
<tr>
<td>5</td>
<td>10% Carboxy-methylated</td>
<td>10,5</td>
<td>56,1</td>
<td>12,5</td>
<td>Good coating but some streaks, tactile solid surface</td>
</tr>
</tbody>
</table>
The visual appearance of the 7% additions of TEMPO-oxidized NFC and Carboxymethylated NFC coatings, showed equally poor results. The dewatering of the coating colour containing 7% TEMPO-oxidized NFC seemed to improve the coating appearance but the low NFC addition gave release of graphite when touching the paper surface. The coatings were improved when 10% was added and the difference was minor regarding visual coating appearance.

4.2.3 Electronic difference between coatings containing Carboxymethylated respectively TEMPO-oxidized NFC

In Figure 4.8 the capacitance measurement of the NFC 10% additions (Carboxymethylated and TEMPO-oxidized from Innventia) is presented. As observed similar capacitance values were obtained for the two NFC types. A larger difference was found in the resistance measurements of the same samples, see Figure 4.9. As seen in the diagram a larger difference in sheet resistance was found. This was also found in another study comparing Carboxymethylated and TEMPO-oxidized NFC [45]. As suggested earlier in the rheological part in this report the two NFC types may have both structural and/or chemical internal differences which for the time being are unknown.

![Capacitance measurements of coatings containing TEMPO-oxidized or Carboxymethylated NFC.](image)
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Figure 4.9 Resistance measurements of coatings containing TEMPO-oxidized or Carboxymethylated NFC.

4.3 Lab study III

The coating pilot trial was conducted on the Labco coater at Kroenert. The trial was not successful mainly because of the low solid content (6.2%) of the coating colour and the insufficient drying at the pilot machine. This conveyed that the wet coating did not dry and a high degree of wrinkles appeared, see Image 4.1. At site it was found that the drying zone was placed approximately 1.5 m after the slot-die coating. It was also found that the personnel at Kroenert had limited experience of coating on paper. The speed was lowered in order to increase the time in the drying zones. This prolonged the time before drying even more. The water which normally evaporates rapidly by IR drying was instead transported into the paper by absorption. The IR dryer was also placed after the hot air drying zone and initially burnt the paper why the heating effect was lowered. An attempt to place the IR-dryer before the heated air zones decreased the distance between the coater and the drying zone to approximately 1 m. Unfortunately this did not convey any noticeable decrease of the wrinkles. There was also a lack of supporting rolls carrying the paper web. This long open draw further increased the dimension instability of the paper. Initially the drying temperature in the first drying zone was 100°C and in the second 130°C. The temperature in the first drying zone was increased to 130°C in order
to increase the drying. At the end of the trial the temperature in both zones were increased to 150°C. None of these measures improved the drying or wrinkles appearing of the paper web. See more details about the trial in the Kroenert report in the Appendix.

Image 4.1. Appearance of the coating in the pilot Labco trial. In the picture the long open draw is visible, this gave also some wrinkles on the uncoated paper web.

As described in the methodology part the preparation of the coating colour was not optimal. The presence at the pilot trial enlightened what problems a low solid content conveys and identified which factors in the preparation affects the solid content most. Both the dewatering of the homogenized graphite slurry (250 l) was dissatisfactory and the low solid content of the NFC (1%) contributed to the low solids.

The coating colour was further evaluated by laboratory blade coating performed manually at Miun. The coating coverage was good but the low solid content in the coating colour brought unstable paper dimensions. The coated sheets were placed on a bench and could manually be stretched in all directions which prevented wrinkles. The drying was performed in room temperature which brought a drying time of approximately 24 hours. The appearance of the dry coating did not suffer from any streaks or cracks and the tactile evaluation showed no graphite release from the surface. By this it is evident that the 10% NFC addition promoted the final coating quality.

The viscosity levels of the coating colour from the pilot trial, see Figure 4.10, are comparable to the result from Lab study II. As seen in the graph the viscosity in the initial shear point was not detected due to too low torque values. This was probably due to the high water content in the coating colour which likely conveyed a phase-separation. The resistance to shearing was decreased when water from the phase-separation surrounded the measuring bob surface. This phenomenon was also observed when the coating colour was resting and a thin
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A surface of water was found. The measurement in the final shear point was also too low.

Figure 4.10. Comparison of viscosity of coating colour (containing 10% TEMPO-oxidized NFC and 6,2% solid content) used in Lab study II.

The NFC used in Lab study III was prepared at Miun. The fiber charge of this NFC is unknown and also if swelling affected the coating in the pilot trial. A test was performed to evaluate the capacitance, see Figure 4.11. In this comparison the NFC types from Innventia was compared to the Miun type. In the comparison 10% additions of TEMPO-oxidized NFC were added to the graphite slurry. As observed the specific capacitance increased when using the Miun NFC. The reason for this needs further investigations. In Figure 4.12 the sheet-resistance measurements with TEMPO-oxidized NFC both from Innventia and MIUN is compared. As seen the values were on the same level.
Figure 4.11. Specific capacitance measurements on electrodes with different NFC types.

Figure 4.11. Sheet-resistance on electrodes with TEMPO-oxidized NFC from Innventia respectively Miun.
5 Conclusions / Recommendations

This study showed that it is possible to use coating colours based on homogenized graphite for making supercapacitor electrodes. Coating colours based on homogenized graphite and a 10% TEMPO-oxidized NFC addition shows in laboratory coating qualities on a satisfactory level. There is however several factors regarding the coating performance which needs further development. The main factors have been identified as:

* Solid content and water holding in the coating colour
* Paper / water absorption
* Drying capacity in the coating process
* NFC addition and NFC type
* Impact of rheology on the coating performance

The solid content has a great impact of the coating “runnability” on coating machines which was experienced in the Kroenert pilot trial. The high water content in the coating colour brought a slow web speed to be used in order to increase the drying time. This increased the paper water absorption which affected the dimension stability of the paper and gave large wrinkles of the coated paper. This was further escalated by the insufficient drying capacity on the pilot machine. Besides the wrinkles some web brakes occurred when rolling up the paper. The pilot trial gave new ideas to be developed in the project both regarding mechanical and chemical treatment of the coating components but also for enabling a future process application. E.g. the dewatering of the homogenized graphite slurry is one problem which needs to be attended. More focus should be on finding ways to increase the solid contents in coating colour preparation, control paper/water absorption and drying efficiency during coating. Besides this careful planning and enough preparation time are necessary when performing the next large-scale coating trial.

The NFC addition had a positive impact of the final coating quality. In this study it was found that a lower NFC addition (7%) is not sufficient for reaching a good coating quality. An amount of 10% NFC improved the coating quality by effectively enhance both coating coverage and decrease cracks and stripes. Another important result was the tactile
investigation which showed that a 10% addition of NFC conveyed no graphite release from the surface. The NFC produced at Miun gave higher capacitance values compared to the NFC from Innventia. The reason for this is unknown but more measurements are needed for verifying the results. The chemical interactions between NFC and graphite is also unknown. Microscopy investigations of the electrodes may increase the comprehension but more advanced measurements are needed to fully clarify the beneficial effect from NFC. The absence of laboratory methods for characterization of the coated electrodes is important to enlighten. For the time being the electronic capacity is useful as measurement but more methods regarding material testing should be evaluated.

More studies are needed for clarifying the rheology results. Different rheological behavior was observed when increasing the graphite concentration or adding NFC. As commented in the Result part some of these results can be given hypothetical explanations but the impact on the coating properties is still unexplained. NFC seems to stabilize the coating colour but the physical and chemical effect by graphite, NFC or other chemicals used in the coating colour should be investigated more thoroughly. It is recommended to use viscosity measurements when testing new chemicals in order to increase this knowledge.
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2014-10-06


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supercapacitors-created-with-traditional-paper-making-process-rivals-lead-acid-battery-capacity


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Trial Protocol

TRIAL PROTOCOL:

Day of trials: 17.06.2014  
Place: KROENERT TC dokument2

Client: Mid Sweden University  
Comm.Nr.: 17001339

Subject: Trials on the LabCo-Machine with slot-die coating technology

Aim of the trials

The target of the trials is to apply successfully a 40 µm dry coating layer on paper respectively getting as thick layer as possible, at least 40 µm dry with a solid content between 10 and 15 % solid content. The coating material graphite is dissolved in water and regarding the particle sizes it is estimated to have a large part of nano particles but also particles on µm-level in the slurry. The slurry is shear thinning with an estimated start-up viscosity of ~500 mPas.

Conclusion

The trial has shown, that the paper absorbs a huge amount of water, which led to a formation of wrinkles in machine direction. This happens directly after the coating independent on the drying process. However, the following arrangements were done trying to avoid the creation of wrinkles:

- Changed convection dryer settings (temperatures),
- Changed IR dryer settings (heating power and place of heating),
- Variation of web speed
- Higher solid content of the fluid (from 7% to 14%).
- Check the influence of corona treatment on the porous structure

All arrangements brought no improvement concerning wrinkles in the product. Therefore the aim should be to increase the solid content of the material. Another option would be to coat beforehand a barrier layer on the paper to avoid any penetration of the water based slurry into the substrate.
### Process- & Material-data

#### Tab. 1: Process-Data

<table>
<thead>
<tr>
<th>Nr.</th>
<th>$h_{\text{dry}}$ [$\mu$m]</th>
<th>$U_w$ [m/min]</th>
<th>$B$ [mm]</th>
<th>Liner Nr.</th>
<th>Liquid Nr.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>as fast as possible</td>
<td>400</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

#### Tab. 2: Substrate-Data

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Type</th>
<th>$d$ [$\mu$m]</th>
<th>$W$ [mm]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Paper</td>
<td>40</td>
<td>500</td>
<td>38 g/m²</td>
</tr>
</tbody>
</table>

#### Tab. 3: Fluid-Data

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Type</th>
<th>SC [%]</th>
<th>Solvent</th>
<th>$\mu_{200}$ [mPas]</th>
<th>$\mu_{1500}$ [mPas]</th>
<th>$\rho_{d1}$ [kg/m³]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>graphite / graphene colouring colour</td>
<td>7</td>
<td>Water</td>
<td>higher, not known</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Feeding System:
- MFW ☐, MDW ☐, NIP ☐, Gear-Pump ☐ (Medium 1), Excenter-Pump ☐,
- Pressure Vessel ☒

Viscosity influence depending on shear force? – shear thinning

### Cooling:
- yes ☐, no ☒

### Filter
- yes ☐, no ☒

### Coating Technique:
- Slot-Die-Coating

### Width:
- 400 mm (slot die 500 mm width with shims)

### Slot-Die:
- Battery slot die (TSE 8244, 680 µm)

---

![Diagram](image)

**Fig. 1 Scheme of coating arrangement**

### Laminating:
- yes ☐, no ☒

### Pressure:

### Moisturing:
- yes ☐, no ☒, WEKO ☐, SteamTec ☐

### Pre-Treatment:
- Corona: yes ☒ (only trial 11), no ☒

### Drying:
- **Type of nozzle**
  - FLOATEC ☐, CONTECI ☒, CONTECII ☐

- **Floating**
  - yes ☐, no ☒

  *Additionally IR-unit behind dryer (Trials 1-5) / in front of dryer (Trials 5-11)*

- **IR Unit**
  - Type: Heraeus CB3x25 (30 kW, 400 V, 50 Hz)
### Drying- & Web-Tension Parameters

#### Tab. 4: Convection-Drying

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Typ</th>
<th>T1 [°C]</th>
<th>T2 [°C]</th>
<th>Blower,above [%]</th>
<th>Blower,below [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>RollTec</td>
<td>100</td>
<td>130</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>5, 8-11</td>
<td>RollTec</td>
<td>130</td>
<td>130</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>6-7</td>
<td>RollTec</td>
<td>150</td>
<td>150</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

#### Tab. 5: Web Tension Parameters

<table>
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<tr>
<th>Place</th>
<th>Tension [N]</th>
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</thead>
<tbody>
<tr>
<td>Unwinder</td>
<td>20</td>
</tr>
<tr>
<td>Rewinder</td>
<td>50</td>
</tr>
<tr>
<td>Coating station</td>
<td>25</td>
</tr>
<tr>
<td>Dryer</td>
<td>30</td>
</tr>
</tbody>
</table>

### Results

#### Tab. 6: Trial-Data

<table>
<thead>
<tr>
<th>Nr.</th>
<th>U [m/min]</th>
<th>Trocknung [°C]</th>
<th>IR [%]</th>
<th>Gap [µm]</th>
<th>Pressure [bar]</th>
<th>solid contend [%]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,3</td>
<td>100 /130</td>
<td>40</td>
<td>600</td>
<td>0,6</td>
<td>7</td>
<td>IR after Dryer</td>
</tr>
<tr>
<td>2</td>
<td>0,5</td>
<td>100/130</td>
<td>40</td>
<td>600</td>
<td>0,6</td>
<td>7</td>
<td>wrinkles in the substrate with coating</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>100/130</td>
<td>40</td>
<td>600</td>
<td>0,6</td>
<td>7</td>
<td>wrinkles in the substrate with coating</td>
</tr>
<tr>
<td>4</td>
<td>0,3</td>
<td>100/130</td>
<td>40</td>
<td>300</td>
<td>0,3</td>
<td>7</td>
<td>wrinkles in the substrate with coating</td>
</tr>
<tr>
<td>5</td>
<td>1,5</td>
<td>130/130</td>
<td>40</td>
<td>600</td>
<td>0,7</td>
<td>7</td>
<td>IR dryer after Coating unit!!!</td>
</tr>
<tr>
<td>6</td>
<td>1,5</td>
<td>150/150</td>
<td>45</td>
<td>600</td>
<td>0,8</td>
<td>7</td>
<td>Overdried substrate,</td>
</tr>
<tr>
<td>7</td>
<td>2,5</td>
<td>150/150</td>
<td>45</td>
<td>600</td>
<td>0,95</td>
<td>7</td>
<td>wet substrate</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>130/130</td>
<td>45</td>
<td>100</td>
<td>0,7</td>
<td>7</td>
<td>still strong wrinkles directly after the coating</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>130/130</td>
<td>45</td>
<td>100</td>
<td>0,8</td>
<td>14</td>
<td>still strong wrinkles directly after the coating</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>130/130</td>
<td>45</td>
<td>100</td>
<td>1</td>
<td>14</td>
<td>remoisture the web with water</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>130/130</td>
<td>45</td>
<td>100</td>
<td>1</td>
<td>14</td>
<td>with Corona no effects</td>
</tr>
</tbody>
</table>
Appendix

Fig. 1: Drawing of the LabCo

Fig. 2: Picture of the LabCo

Fig. 3: Coating unit
Fig. 4: Coating with slot die

Fig. 5: Coating with slot die

Fig. 6: Product in front of dryer
Fig. 7: Product inside the dryer

Fig. 8: Product under IR-Dryer (IR-Dryer behind convection dryer)

Fig. 9: Product behind IR-Dryer (IR-Dryer behind convection dryer)