Development of an Inkjet Ink to Produce Touch Sensing Surfaces

Pernilla Andersson

Luleå University of Technology
MSc Programmes in Engineering
Chemical Engineering
Department of Chemical Engineering and Geosciences
Division of Chemistry
DEVELOPMENT OF AN INKJET INK TO PRODUCE TOUCH SENSING SURFACES

Source robot hand picture: www.peratech.com

Pernilla Andersson

2010 Master Thesis for Peratech Ltd. at University of Leeds, United Kingdom.
ABSTRACT

A touch sensing material called QTC™ is currently produced by Peratech Ltd. The material is a composite with conducting particles in a polymer matrix. When a pressure is applied to the composite the conductivity rises sharply. By using this property, the QTC™ surface can tell *where* and *how much* pressure is applied onto a surface. QTC™ can be used as a 3D touch screens, sensing robot hand and so on. Currently QTC™ surfaces are produced by screen printing which is a costly technique due to the batch wise, slow and non automated process and also due to its high waste of ink.

Another method of printing conductive surfaces or pattern is inkjet printing. It is a digitally controlled deposition of ink droplets and the jetted pattern can be easily controlled by the printer software. Inkjet printing gives no or low waste and can print several inks simultaneously. The inkjet ink, compared to the screen printing paste, has to be low viscous and has to contain small particle sizes and no aggregates to avoid blocking the print head. The dispersion of particles in the inkjet ink is therefore of great importance.

In this work two types of conductive particles were used, so called K2 and K1. K2 is currently used in the QTC™ screen printing paste. K1 particles are slightly smaller but of the same type. The particle size of K2 had to be reduced to be inkjet printable and it was done with a bead mill. The products, though, did not meet the requirements for inkjet printing. The smaller K1 particles were mixed with binder, dispersing agents and additives and were then bead milled. Before printing, the inks were filtered and characterized, to make sure that they met the requirements for viscosity, surface tension and particles sizes. The printing was done with two printers, HP Deskjet 5650 and Printos P16 Digital Textile Printer and the experiments showed that the Printos printer was suited to print this ink. The touch sensing property of the printed surfaces was investigated by measuring the conductivity of the surfaces when different pressures were applied. Experiments showed that the touch sensing property could be controlled by changing the amount of binder in the ink. The developed ink could be successfully inkjet printed and was highly touch sensing.
ACKNOWLEDGEMENT

I would like to thank Professor Long Lin at University of Leeds and David Lussey at Peratech Ltd. for giving me the opportunity to do this project and for your help and encouragement. Big thanks also to you, Dr. Adam Graham, Peratech Ltd., for your help!

My grateful thanks to Lu Tian for all interesting discussions we had and also to Fengbin Wang, Ling He, Li Yuanyuan and Algys Kazlauciuinas in the labs for all help and inspiration you have given me. A friendlier lab must be hard to find! For everyday discussions and for clever ideas I thank Trevor Lambourne. I also want to thank my supervisor at LTU, Allan Holmgren, for your helpful advises and supportive attitude.

Luleå, September 2010
Pernilla Andersson
ABSTRACT

ACKNOWLEDGMENT

1. INTRODUCTION
   1.1 QTC™ material
   1.2 Printed electronics
   1.3 Inkjet
      1.3.1 Inkjet techniques – ways to create the droplets
      1.3.2 Required properties inkjet inks
   1.4 Milling of inks
      1.4.1 Bead mill - beads and milling conditions
      1.4.2 Changes in conductivity with particle size reduction and dispersion
   1.5 Dispersion of particles in a solution
      1.5.1 Forces involved in particle dispersions in liquid
      1.5.2 The role of dispersing agents
   1.6 Purpose of the project

2. EXPERIMENTAL
   2.1 Materials and equipment
      2.1.1 Materials in the inks
         2.1.1.1 Conducting powder
         2.1.1.2 Binders
         2.1.1.3 Additives and other chemicals
      2.1.2 Equipment for milling
         2.1.2.1 Bead mill and beads
         2.1.2.2 Mortar and pestle
      2.1.3 Equipment for preparation and characterization of the ink formulations
         2.1.3.1 K-bar
         2.1.3.2 Scanning electron microscopy analysis
         2.1.3.3 Touch sensing measurement device
         2.1.3.4 Viscosity and surface tension meters
      2.1.4 Filters
      2.1.5 Inkjet printers
   2.2 Experimental procedure
      2.2.1 Mixing and stirring
      2.2.2 Milling
      2.2.3 Characterization, filtration and printing
   2.3 Particle dispersion
      2.3.1 Study of the surface charge of the particles
      2.3.2 Binders influence on stability
      2.3.3 Study of dispersing agents
   2.4 Ink formulations
   2.5 Ink formulations for improved ink stability and touch sensing property
3. RESULT AND DISCUSSION

3.1 Bead mill results
   3.1.1 Milling of K2
   3.1.2 Milling of K1

3.2 Filtering
3.3 Dispersion qualities
   3.3.1 Zeta potential measurements
   3.3.2 Dispersion differences caused by binder
   3.3.3 Comparison of dispersing agents

3.4 Inkjet printing results
3.5 Ink formulations for improved ink stability and touch sensing property
3.6 Final ink

4. CONCLUSIONS

5. REFERENCES

APPENDIX 1
1. INTRODUCTION

1.1 QTC™ material

QTC™ is a composite produced by Peratech Ltd and it has a unique property of changing the conductance when it is exposed to pressure. The composite contains a polymer resin and conductive particles. The shapes of the particles are sharp projections or needles. The conductance is achieved by the tunnelling effect which means that the particles are not in direct contact with each other, the electricity carriers “jump” a small distance from particle to particle to let the electricity flow. This mechanism enables the material to be an insulator when it is at rest and conduct when compressed because the distances between particles become small enough for the tunnelling effect to take place [1]. Compared with similar material, for example those in used typically in touch screens, QTC™ can not only tell where the pressure is applied, it can also tell how much pressure is applied, see Fig. 1 [1]. QTC™ can be applied in many different products for example Samsungs Navikey used in mobile phone for a 3D input interface [2], tactile sensors in robot hands used by NASA [3], sensing car chairs, sport equipment and so on. QTC™ is currently produced as a paste and printed with screen printing.

![Illustration of the touch sensing property of the QTC™ material.](http://www.peratech.com)

Figure 1. Illustration of the touch sensing property of the QTC™ material.
Source: www.peratech.com
1.2 Printed electronics

The method of creating electrical devices by printing is called printed electronics. The pastes or inks contain conductive particles or conductive polymers and are printed onto the substrate creating the desirable conductive pattern. The applications are for example printed batteries, transistors, chemical sensors and solar cells [4,5,6]. The market for printed electronics is expected to grow fast in the next years and was estimated at $1.2 billion in 2007 and is expected to be at $48.2 billion by 2017 [7]. These data refer ‘printed electronics’ to include organic, inorganic, and composite materials. Many companies are working with conductive inks however most of them are focusing on screen printing inks. To print conductive ink with inkjet technique is relatively new and considered to be in an early stage of development and only a few companies have commercially available conducting inkjet inks [7].

1.3 Inkjet

Inkjet printers create patterns or images by jetting ink droplets onto the substrate through small holes in the printing head called nozzles. Inkjet has many advantages against other common printing techniques,

- It is a low cost technique due to low waste of the often expensive ink.
- Inkjet is automatic and digitally controllable.
- The printing process is quick due to the continuous process (compared with screen printing which produces surfaces batch wise).
- Several fluids can be printed simultaneously. For printed electronics this enables a pattern of different surfaces that can be insulators or conductors, all in a continuous print.
- Inkjet printing is flexible. Each printing can create a new pattern easily by controlling the ink deposition by the software.
- The precision of deposition of the thinly ink droplets enables a high resolution pattern.
- More environment friendly and cleaner due to its low waste.
These advantages for inkjet printing technique make it easy to understand the rising interest of inkjet printing.

**1.3.1 Inkjet techniques – ways to create the droplets**

The droplets can be created by the inkjet printers for example by the using of heat or pressure. The thermal method is creating the droplet by rapidly heating up the ink by the nozzle which causes the ink to evaporate and the increased volume of the ink vapour forces a droplet of ink through the nozzle. Other printers press droplets through the nozzles in different ways. An example is the piezoelectric printers. The ink is filled in a chamber near the nozzles where also a piezo crystal is placed. By applying a voltage, the piezo crystal changes shape and create a pressure pulse that forces the droplet through the nozzle [8].

**1.3.2 Required properties of inkjet inks**

An inkjet ink has to meet many requirements to be printable. To avoid blockage of the small inkjet nozzles, the particles in an inkjet ink have to be small, commonly in submicron range [6,9-11]. Because the high frequency of droplets jetted out of the nozzles, the viscosity has to be low to make sure that the ink is refilled properly to the nozzles. Depending on the printer used the viscosity should be 1-25 cP [7]. The surface tension of the ink should be 25-35 mN/m [7] to make sure that the ink doesn’t leak from the printing head and give droplets that are wetting the substrate. If a thermal inkjet printer is used, the ink also must stand heat. According to previous reports, inks containing polymers are commonly printed with piezoelectric printers [9,12,13].

The common procedure of creating an inkjet ink is as follow [5,9]:

- Mixing the ingredients
- Milling
- Filtering
- Printing

Depending on the nozzle sizes in the print head the requirements for particle sizes in the ink will vary. As a general rule the particle sizes should be at least 100 times smaller than the nozzle [14] and the nozzles are normally between 9 and 50 µm [9,15-17] in diameter. There are some exceptions using commercial print head sizes up to 170 µm from Xaar [18] and
prototypes up to 410 µm by E.Q. Li et al. [19] and K. C Fan [20]. In many applications for example graphic printing, a small nozzle is desired to increase the resolution of the print.

1.4 Milling of inks

The particles or pigments tend to be in form of aggregates when mixed in a liquid Fig. 2 A. By using a mill a better dispersion can be achieved. A typical milling process can be divided into steps, initial wetting Fig. 2B, break up the aggregates Fig. 2C and breaking down of the primary particles, see Fig. 2D [21,22].

![Figure 2. Illustration of a typical milling process.](image)

Depending on applications of the mixture and the size of the primary particles, the aim of the milling will differ. For example, for inks with relatively small primary particles the aim of the milling can be to separate the particles [4,9,23] Fig. 2C. However, if the particles are too big, the aim of the milling can be to break down the primary particles to avoid printing problems [11] Fig. 2D. Milling particles near submicron size or lower can be done with ball or bead mills [4,5,11,24]. In the following chapter the bead milling process will be briefly explained.

1.4.1 Bead mill - beads and milling conditions

A bead mill consists of a milling chamber partly filled with beads and a rotating feed screw that forces the ink flow through the bead filled chamber. On the other side of the chamber a mesh is separating bead from ink and the ink is directed into recycling pipelines back to the feed screw. The beads used in bead mills are commonly made of silica glass, alumina or zirconia [24-26]. The sizes of the beads are important to achieve the right particle sizes. If the beads are too small they will not be able to break down the fed particles. If the beads are too big, the end product will be smaller. A ratio of media bead size to the median size of a feed
should be 150-200 [26]. Also the density of the beads is of importance and at lower speed the product sizes will be smaller and at higher speed lighter beads will mill more efficient [26].

To get an efficient milling the viscosity of the milled mixture cannot be too high. This can be avoided by using lower concentration of feed and/or using dispersant agents in the mixture [27]. Common additives to improve the dispersion and lower the viscosity are polyvinyl acid, polyvinyl alcohol, and copolymer of acrylamine and acrylic acid [28].

1.4.2 Changes in conductivity with particle size reduction and dispersion

Often the conducting particles in inks are made of a continuous material, for example copper or carbon black spheres [9,29]. A breakage of the particles during the milling process affects the sizes but not directly the conductivity of individual particles, but for QTC™ it is different. The conductivity in QTC™ is depending on both the needle like shape of the particle [1], and the surface of the particles. The particles contain mainly an isolator and they are coated in a thin semi conductive layer. Breakage of QTC™ particles leads to both changes in the shape of the particles and to a new uncoated and non conductive surface. Because of this, breaking the primary particles used in QTC™ could cause a severe reduction in conductivity.

The conductivity of a conductive ink is dependent on how the particles are arranged in the binder matrix, see Fig. 3A-C. By breaking up aggregates the conductivity is accepted to increase because it creates paths were the electricity can flow, Fig. 3 A-B. If the dispersion is further improved, the conductivity will reduce again because the paths are lost, see Fig. 3C [29,30].
To get a touch sensing property of a material, it needs to have low conductivity in rest state and high conductivity when a force is applied. That means, for QTC™ materials a separation like Fig. 3C is desirable, unlike other conductive inks. The dispersed particles need to be encapsulated in a flexible matrix that makes the distances between particles big enough to unable the tunnelling effect. When a pressure is applied the flexible matrix let the particles come closer to each other and the distances between them become small enough for the tunnelling effect [1] and the material conducts!

1.5 Dispersion of particles in a solution

After being milled, the particles have to stay separated to make a stable dispersion. To control the dispersion of particles in a liquid, several forces have to be considered. In the following sections, these forces and prevention of flocculation will be discussed.

1.5.1 Forces involved in particle dispersions in liquid

Small particles in a solution will be affected by Brownian motion which will make them move randomly in the solution. When the particles approach each other they will attract each other due to long range van der Waals forces [31]. If the Brownian motion and van der Waals
attraction make the distance between the particles small enough it will cause coagulation or flocculation. In Fig. 4 the Gibbs energy curve is drawn depending on the distances between particles. First, at a bit longer distance between the particles there is a secondary minimum energy state which causes the particles to flocculate. If the particles can overcome the energy barrier (primary maximum) and get even closer to each other, the lowest Gibbs energy state, primary minimum, is reached and the particles are aggregated. The repulsing curve in the figure corresponds mainly to the so called electrostatic forces [32].

The electrostatic forces can be understood like the tendency of two charges of opposite sign to attract and charges with same sign to repel each other. Surfaces of particles are commonly charged and the charges can be measured and described in mV as the zeta potential. When the zeta potential values are highly negative or highly positive, the particles will repel each other and therefore make a stable dispersion, see Fig. 5. When the potential is close to zero the particles will tend to flocculate [27].
By changing pH, i.e. the amount of H+ and OH−, the charge of the surfaces can change, typical from positive charge for low pH and negative charge for high pH, see Fig. 6A-B.

The particles can also make up a stable solution if a steric barrier is preventing the particles to approach each other close enough to reach the low energy state. The steric barrier can for example be polymers adsorbed onto the surface, see Fig. 7.
If the mixture is stable because of both electrostatic and steric repulsion it is called electrosteric repulsion. It can for example be achieved by a polymer with ionic groups or neutral polymers on a charged particle.

### 1.5.2 The role of dispersing agents

Dispersing agents can give particles both an electrostatic and steric repulsion. Depending on the particles and the medium they are dispersed in, different dispersing agents will be effective in dispersing the particles.

Effective dispersants typically have a "head" and a "tail" that interacts with the particle surface and the medium in where the particles are dispersed. When the particles are hydrophobic in a polar medium the dispersant polar "head" will be directed from the surface and the hydrophobic tail will interact with the surface, see Fig. 8A. If the surface is polar, i.e. hydrophilic, the polar "head" will adsorb onto the surface with the tail directed into the dispersing medium, see Fig. 8B. If the interaction between particle and dispersant is strong the dispersing agent will adsorb onto the particles as a monolayer and if the concentration of dispersant increase as a double layer, see Figs. B1 and B2. If the interactions are weaker the dispersing agent can interact with the particles by forming micelles onto the surface, see Fig. 8B. [37]
Dispersing agents can be divided into non-ionic, cationic, anionic, and zwitterionic species. The latest mentioned are dispersing agents containing both cationic and anionic groups [38].

The polar part of non-ionic dispersants contains typically either polyether or polyhydroxyl groups. The cationic agents can have their polar part in form of a nitrogen atom, both amine and quaternary ammonium compounds are common. The amine group looses the polar character if the pH is too high and their dispersant function is lost. The quaternary ammonium compounds on the other hand are not pH sensitive. The polar head of an anionic dispersing agent is typically a carboxylate, sulfate, sulfonate or phosphate group and the counter ions are mostly sodium and potassium in case of water based dispersions. The zwitterionic dispersants contain groups of different sign and are therefore suitable for a big range of pH values. At low pH they are cationic in character and at high pH they turn to be anionic in character [39].

Previous work investigating the dispersion of coated titanium in water-based paint has shown that dispersing agents containing all three groups; amine, carboxylate, and hydroxyl, are the most efficient and the second most efficient are dispersants containing only carboxylate and hydroxyl groups [40].
The suppliers of commercial dispersing agents, for example BYK or TEGO, are not giving all the information about the chemicals. By careful reading of the official information, one can get a brief understanding of the chemicals. The amine and acid values of the dispersing agents are telling about the amount of KOH (mg) that are needed to neutralise 1 g of the chemical \[41,42\], which gives a clue to which functional groups the dispersing agent contain. Dispersants in form of salts of sodium or potassium gives typically an anionic dispersing agent in the mixture. The choice of dispersing agent is therefore hard and to find a suitable dispersing agent for a particular system, different dispersing agents may be needed to be tested experimentally.

1.6 Purpose of the project

The aim of this project is to investigate the possibilities of making an inkjet ink that can produce touch sensing surfaces similar to the already available screen printed QTC\textsuperscript{TM}. Two powder sizes was used, a bigger one called K2 and a smaller one named K1. The currently produced screen printing paste contains K2. This work will investigate if it is possible to use K2 also for inkjet printing and if not, the K1 powder will be used. To achieve a touch sensing property of the surface, a binder has to be used. The type and the amount of binder suitable for a touch sensing property was investigated in this work. Further, because an inkjet ink must have small particle sizes, the developed ink has to be able to go through a small pored filter to make sure that no bigger particles reach the print head. Also, the particles in the ink are not allowed to flocculate. This project is not aiming to produce a commercial product. The long term ink stability, consistency of the conductivity values, and the replication of the ink are therefore beyond this project.
2. Experimental

2.1 Materials and equipment

2.1.1 Materials in the inks

2.1.1.1 Conducting powder
The conductive powders used in this work were acicular shaped titanium dioxide coated with a conductive layer (coating type is a company secret). Two particle sizes were tested, K2 with a particle size of approximately 0.2 µm height and 2.9 µm length and K1 with approximately 0.1 µm height and 1.6 µm length, see Fig. 9.

![Diagram of TiO2 with K1 and K2 powders](image)

Figure 9. The K2 and K1 powders with the semi conductive coating.

2.1.1.2 Binders
The binders used were;

- Cellulose, supplied by Sigma-Aldrich
- Polyethylene glycol, M_w 8000, supplied by Sigma-Aldrich
- Polyvinyl alcohol, M_w 125000, supplied by Sigma-Aldrich
- Poly(1-vinylpyrrolidone-co-styrene), 38 % emulsion in water, supplied by Sigma-Aldrich
Cellobiose is a disaccharide with the structure according to Fig. 10. It is water soluble due to its many hydroxyl groups.

![Figure 10. Molecular structure of Cellobiose.](image)

Polyethylene glycol, shorter named PEG, has been reported as a binder in inkjet ink before [13,43]. Here a long PEG is used to improve the flexibility of the printed film. PEG is a water soluble polymer with ether and hydroxyl groups, see Fig. 11.

![Figure 11. Molecular structure of PEG.](image)

Polyvinyl alcohol, $M_w$ 125000, in this report called PVA, is a water soluble polymer that makes a strong and flexible film. It is used in many applications for example to coat paper to prepare them for printing [44] and as fibres in composites to improve the strength [45].

![Figure 12. Molecular structure of PVA. The values of n and m are depending on degree of hydrolysis and polymerisation.](image)
PVA, see Fig. 12, is produced by hydrolysis of polyvinyl acetate to remove the acetate groups. In this work the PVA was 87 % hydrolysed, which means a considerable amount of acetate groups were present.

Poly(1-vinylpyrrolidone-costyrene), here named PVP-styrene, is a 38 % emulsion in water and contains particles of sizes below 0.5 µm. The pH of the emulsion is 2-5 and the viscosity is 200-800 cP according to the supplier. PVP has been used previous for encapsulate copper and gold nano particles [9,15] in inkjet ink but no reports are found for applications of the emulsion PVP-styrene. Emulsions, though, have been used in inkjet inks before [46,47].

2.1.1.3 Additives and other chemicals
Additive and other chemicals used in this work are listed below.

Dispersing agents;
- **Disperbyk 181**, supplied by BYK. Description: Alkylolammonium salt of a polyfunctional polymer with anionic/non-ionic character. Amine value 33 and acid value 33.
- **Disperbyk 190**, supplied by BYK. Description: Solution of a high molecular weight block copolymer with pigment affinic groups. Amine value – and acid value 10.
- **BYK 154**, supplied by BYK. Description: Ammoniumsalt of an acrylate copolymer. Amine value – and acid value -.
- **Dispersant 760 W**, supplied by TEGO. Description: Waterborne solution of surface active substances and polymers with groups of high pigment affinity. Amine and acid values are not mentioned.
- Dispersing couple; **Span 80**, supplied by Sigma and **Sandozin NIE**, supplied by Clariant.

Surface tension reduction additives;
- Sandozin NIE
- Ethanol, supplied by Fisher Scientific
pH regulators;
- HNO$_3$, supplied by Fisher Scientific
- NaOH, supplied by Fisher Scientific
- Triethanolamine, supplied by Alfa Aesar

Other chemicals;
- Ethylene glycol, supplied by Fluka

Span 80 is a non-ionic surfactant and is a trade name for sorbitan monooleate. It has a polar head containing hydroxyl, ester and ether groups, see Fig. 13. Span 80 has been reported useful to stabilize emulsions [48,49].

Sandozin NIE is an wetting agent used in textile, leather and paper applications for example for washing the textiles after dyeing [50,51]. It is a non-ionic alkylphenol polyglycol ether and according to supplier information, the molecular structure is assumed to be as shown in Fig. 14. It shows its polar head and a non polar tail.

Triethanolamine is a strong base that has been used before in inkjet ink [4] to regulate the pH. The basic character of triethanolamine is due to its nitrogen atom, see Fig. 15.
Commercial inkjet inks are often slightly basic, for example HP inkjet inks have pH values of 7.8-8.4 [11]. Compared with the common base KOH, triethanolamine can increase the pH in the solution without increasing the ionic strength of the solution which can cause a decrease in the zeta potential of the particles, see Section 1.5.1.

### 2.1.2 Equipment for milling

**2.1.2.1 Bead mill and beads**

A bead mill was used to disperse the particles. It was of type: MkII M250 ‘MINI’ MOTORMILL and produced by Eiger Torrance Ltd.. The mill was recommended to be fed with at least 75 ml ink, the rotational speed is recommended to be 3000-5000 rpm and the recommended bead load is 30-40 ml. The bead diameter was 1.0-1.25 mm and the beads were made of the hard material zirconia dioxide which has a density of 5.4 g/cm$^3$.

**2.1.2.2 Mortar and pestle**

Mortar and pestle were used for experiments were particle aggregates had to be broken down without adding chemicals. It was done with dry powder.
2.1.3 Equipment for preparation and characterization of the ink formulations

2.1.3.1 K-bar
K-bar is a simple method to create drawdowns of paint and inks and gives a first impression of the quality of the ink, see Fig. 16. The printed film indicate if the surface tension is suitable for the substrate and after drying the film can be characterised, for example by conductivity measurements and SEM analysis. The thickness of the film can be controlled by using different bar sizes. In this work steel bar number 1 was used for SEM analysis and 4 for conductivity measurements. The substrate was a flexible plastic film supplied by Printpack Inc.

![Figure 16. K-bar used to create drawdowns](image)

2.1.3.2 Scanning electron microscopy analysis
The samples were prepared for scanning electron microscope, SEM, by cutting pieces of the K-bar printed films and then coat them with a thin layer of platinum. The SEM was of type Leo 1530 and supplied by Gemini/ Zeiss.

2.1.3.3 Touch sensing measurement device
To measure the touch sensing properties of the printed film a special designed device, supplied from Peratech Ltd., was used. The device consists of a conductive pattern printed onto a hard plastic film and the diameter of the pattern is 1.8 cm. Copper pieces are in contact with the pattern to enable connections with extern measurement tools. To measure the conductivity of the drawdowns, the conductive side of the device was pointing down to the
film and a multimeter supplied by Extech Instruments was connected to the copper pieces on the device, illustrated in Fig. 17.

![Image of device to measure the resistivity of the printed film.](image)

**Figure 17.** Device to measure the resistivity of the printed film.

To measure the changes in resistivity with applied force, weights were placed on top of the device. A small weight of 3 grams was used as the static weight on the device during the measurements to assure that the same area was affected no matter which weight was on top of it. On the picture, Fig. 18, this 3 gram weight is lying underneath the bigger weight.

![Image of measuring equipment for touch sensing measurements.](image)

**Figure 18.** Measuring equipment for touch sensing measurements.

### 2.1.3.4 Viscosity and surface tension meters

For the viscosity and surface tension measurements Brookfield Viscometer DV-II + and Torsion balance from Torsion Balance Suppliers were used.
2.1.4 Filters

Filters papers from Wathman were used. They were two syringe filters, 0.45 µm and 1.2 µm pores, and one filter for vacuum pump usage; the cellulose filter ‘Grade 1’ specified having 11 µm pores.

2.1.5 Inkjet printers

Two inkjet printers with different techniques were used.

The first one was the HP Deskjet 5650 Inkjet printer which jets the ink with the thermal technique. The cartridge was an Office depot inkjet cartridge 367385, see Fig. 19, with unknown nozzle size. The cartridge was emptied and cleaned, and the cleaning was done with ethanol and water in an Ultrasonic bath.

![Figure 19. Cartridge used for the HP printer.](image)

The second printer was Printos P16 Digital Textile Printer, see Fig. 20, which jets with the so called valve-jet technology. A pressure pump is connected to the ink bottle and creates a pressure of around 1.5 bars to force the ink through pipelines to the printing head. In the head the nozzle are closed by valves. The valves contain of a spring and armature with a rubber seal on the top, sealing the nozzles, see Fig. 21. When printing takes place, the valve opens and ink droplets are jetted through the nozzles. The volume of the droplet is 8 – 25 nanolitres and there are 16 nozzles with the size of 100 µm. The printing head is static and the substrate
is moving to create an image. The printer requires an ink viscosity of 1-20 cP depending on the fluid type, nozzle size and jetting pressure.

Figure 20. Printos P16 Digital Textile Printer.

Figure 21. A Printos print head in pieces.
2.2 Experimental procedure

An overview of the experimental procedure is shown in Fig. 22 and the procedures are explained in details in this chapter.

2.2.1 Mixing and stirring

The binders were dissolved in water by stirring and heating and then the particles and additives, such as dispersant agents, were added.

When using dispersant agents Span 80 and Sandozin, the ink ingredients have to be mixed in a special order. The particles, Span 80 and ethanol have to be mixed by hand. Then Sandozin is added and mixed again until a well mixed paste is achieved. The particles should now be coated in two layers, first in Span 80 and secondly a layer of Sandozin to make them dispersible in water. The water, binders and other additives could then be added.
2.2.2 Milling

The milling was done from 12 min up to 5 hours. For milling times shorter than 2 hours, the main aim is to break up the agglomerates and for longer milling times, the aim is to break down primary particles. The milling speed was 3000 rpm which is equal to 6.0 m/s for this mill and the bead loading was 30 ml equal to 60 vol.% of mill chamber.

Inks done with K2 had to be milled long enough to break down primary particles and they were milled for 5 hours. Because of the length of the particles, a few times size reduction is desirable and a narrow particle size distribution. The particles were dispersed in; three different binders, ethylene glycol and water, for exact formulations see Table 2. Ethylene glycol is normally used in inks to control the evaporation rate but there are previous work showing that one also can achieve good particles size reduction by milling particles in a mixture of ethylene glycol, dispersing agents and water [44]. In this work ethylene glycol was used to study how the particles were broken down compared to when they were dispersed in a binder solution.

Inks done with K1 were milled just long enough to break up the particle aggregates and therefore the K1 inks were milled between 15 min and 1 hour.

2.2.3 Characterization, filtration and printing

By creating drawdown with the K-bar, the inks were prepared for conductivity measurements and SEM analysis. The filtering was done with a syringe or by using a vacuum pump. The syringe filter, see Fig. 23, was used as follow; the ink was diluted and loaded in the syringe and the filter was placed onto the syringe and then the ink was pressed through the filter. The syringe filtration is an easy method to separate the bigger particles from the solution but the pressure that forces the ink through is not as high as for the vacuum pump.
The vacuum filters where used together with two filter flasks, one where the ink was fed and one as a security bottle to assure that no ink reached the vacuum pump, see Fig. 24. The filter was placed in the Buchner filter funnel and wetted with DI (deionized) water. The diluted ink (50:50, ink:water) was put in the funnel, the pump was turned on and the filtered ink could be collected from the filter flask.

To find out which filter size was suitable for select particles small enough for inkjet printing and big enough to retain the conductivity, an experiment was done. By using mortar and pestle the particles were separated and were then mixed with water and forced through three
different filter papers with pore sizes from 0.45 to 11 µm. By using the K-bar to create drawdown the conductivity could be measured and the resistivity differences caused by the filter papers became known.

Conductivity measurements were done with the weights 13 g, 103 g and 603 g. The resistivity values for screen printed QTC\textsuperscript{TM} are listed in the Table 1 and are used as reference.

Table 1. Reference values for the touch sensing surface.

<table>
<thead>
<tr>
<th>Weight [g]</th>
<th>Resistance [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1145</td>
</tr>
<tr>
<td>103</td>
<td>235</td>
</tr>
<tr>
<td>603</td>
<td>83</td>
</tr>
</tbody>
</table>

2.3 Particle dispersion

2.3.1 Study of the surface charge of the particles

The zeta-potential of powder dispersed in water with different pH was measured with Zetasizer, Malvern. The pH was regulated with HNO\textsubscript{3} and NaOH. Previous researchers have used these chemicals for this purpose [52]. The measurements were done by adding small amount of K2 powder in the different pH solutions just prior to the measurements.

2.3.2 Binders influence on stability

The binders influence on stability was observed by the stability of the inks after milling. The inks with Cellobiose, PEG and PVA were all done with the same dispersing agents and were compared. PVP-styrene inks cannot be compared because the binder is not transparent and the settling of particles is not visible enough.
2.3.3 Study of dispersing agents

The quality of dispersing agents were investigated by study the settling of the powder. After using mortar and pestle the powder together with water and different dispersing agents were put in test tubes and the settling was studied. The sample with Span 80 and Sandozin NIE had to be mixed as described in 2.2.1.

2.4 Ink formulations

A summary of the mixtures milled with K2 and K1 can be found in Table 2 and 3. In both tables the percentage are related to the weight of liquid in the mixture and the remaining percentage is DI water.

<table>
<thead>
<tr>
<th>Table 2. Milled mixtures with K2 powder.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink</td>
<td>Material</td>
</tr>
<tr>
<td>Celllobiose ink</td>
<td>Celllobiose</td>
</tr>
<tr>
<td></td>
<td>K2</td>
</tr>
<tr>
<td></td>
<td>Dispersant 760 W</td>
</tr>
<tr>
<td>PEG ink</td>
<td>PEG</td>
</tr>
<tr>
<td></td>
<td>K2</td>
</tr>
<tr>
<td></td>
<td>Dispersant 760 W</td>
</tr>
<tr>
<td>Two PVA inks</td>
<td>PVA</td>
</tr>
<tr>
<td></td>
<td>K2</td>
</tr>
<tr>
<td></td>
<td>Dispersant 760 W</td>
</tr>
<tr>
<td>Ethylene glycol mixture</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td></td>
<td>K2</td>
</tr>
<tr>
<td></td>
<td>Dispersant 760 W</td>
</tr>
<tr>
<td>Water mixture</td>
<td>K2</td>
</tr>
</tbody>
</table>

Table 3. Milled inks with K1 powder.

25
<table>
<thead>
<tr>
<th>Ink</th>
<th>Material</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA ink</td>
<td>PVA</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>K1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Dispersant 760 W</td>
<td>1</td>
</tr>
<tr>
<td>Four PVP-styrene inks</td>
<td>PVP-styrene emulsion</td>
<td>10, 20 and 60</td>
</tr>
<tr>
<td></td>
<td>K1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Additives *</td>
<td>~13</td>
</tr>
</tbody>
</table>

* Span 80, Sandozin NIE, 760 W, Ethanol, Triethanol amine

### 2.5 Ink formulations for improved ink stability and touch sensing properties

The PVP-styrene inks with different binder concentrations were done to study how the touch sensing property changed. Due to the complex procedure of using Span 80 and Sandozin, see 2.2.1, other dispersing agents was also used to try to make the mixing process easier. Triethanolamine was added after filtering to increase the pH.
3. RESULT AND DISCUSSION

3.1 Bead milling results

3.1.1 Milling of K2

5 hours of milling of the Cellobiose, PEG and PVA inks could not efficiently reduce the particle sizes. A big amount of particles seems unaffected of the milling and others are only traces of the original particles. The desirable breakage of making the particles around a third of the length was not achieved and the result was a broad particle size distribution, see Fig. 25-27. According to previous reports the type and size of the beads, and speed of the mill, should be able to mill also primary particle down to a smaller size [11]. But none of these inks could provide particle sizes small enough for inkjet printing.

Figure 25. Cellobiose ink milled 5 hours.

Figure 26. PEG ink milled 5 hours.
One of the differences of this milling compared with previous reports [27] is the high concentration of binders used here. Because of that one milling was done with a low concentration of 1 % PVA and dispersing agent but it only lead to flocculation and the milling efficiency was not improved, see Fig. 28.

The breakage of the particles after 5 hours milling with 10 weight % ethylene glycol shows a better grinding behaviour, with a narrower particle size distribution, see Fig. 29.
Ethylene glycol, with its high boiling point, makes an ink that not dries within a reasonable time. The dispersions were good enough to unable a separation of particles and solution by sedimentation. The high concentration of ethylene glycol remained and made the ink complicated to characterize.

Milling the mixture of water and K2 caused severe flocculation already after 8 minutes and after 12 minutes the milling was stopped.
3.1.2 Milling of K1

The milling of PVP-styrene ink was done 1 hour to break up aggregates and the aim was not to break down primary particles. After mixing and stirring the ink ingredients, drawdown was created to take SEM pictures. They showed how the dispersing agents encapsulated the particles, see Fig. 30. After one hour of milling they are better separated, see Fig. 31.

![Image 30](image30.png)

Figure 30. K1 particles in PVP-styrene ink before milling.

![Image 31](image31.png)

Figure 31. K1 particles in PVP-styrene ink after 1 hour milling.
### 3.2 Filtering

Filtering turned out to be a big challenge. The filtering of all K2 inks was unsuccessful; they blocked the filter, had to be diluted too much (up to 15 times) before filtering or the particle concentration was reduced too much after filtering.

The only successful filtering was done with PVP-styrene inks or water and powder only.

Powder treated in mortar and pressed through filters of sizes 0.45 µm, 1.2 µm, and 11 µm and the resistance was measured under a weight of 603 g for the printed film, see Fig. 32-34 and for the resistivity measurements see Table 4.

Figure 32. K2 particles filtered through 11 µm pores.

Figure 33. K2 particles filtered through 1.2 µm pores.
Figure 34. K2 particles filtered through 0.45 µm pores.

Table 4. Resistances versus the filter pores size used.

<table>
<thead>
<tr>
<th>Filter pore size [µm]</th>
<th>Resistance [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>1.2</td>
<td>800</td>
</tr>
<tr>
<td>0.45</td>
<td>1800</td>
</tr>
</tbody>
</table>

It was shown that both filter 0.45 µm and 1.2 µm allowed too small particles to go through; they are not conductive enough. It showed that filters with pores bigger than 1.2 µm has to be used and that filter pores of 11 µm can be used, for the sake of conductivity. To avoid the risk of blocking the nozzles two layers of 11 µm filter ‘Grade 1‘ was chosen for further filtrations.

SEM analysis of PVP-styrene ink with dispersing agents Span 80 and Sandozin filtered through two layers Grade 1 confirmed that the particles were small enough for inkjet printing, see Fig. 35.
The ink done with PVP-styrene and the dispersing agent 760 W could not be filtered. The filtering process made the ink flocculate. It is assumed that none or weak steric stabilization was achieved by the dispersing agent and the stabilisation seen in the ink before filtering was due to mainly electrostatic stabilization. This stabilization was not strong enough to stand the stresses of filtering.
3.3 Dispersion qualities

3.3.1 Zeta potential measurements

The zeta potential measurements showed that the mixture can be considered as stable, see 1.5.1, as long as the pH value is at least 7.1, see Table 5.

Table 5. Zeta potential versus pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Zeta potential [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>-18.5</td>
</tr>
<tr>
<td>4.7</td>
<td>-14.5</td>
</tr>
<tr>
<td>7.1</td>
<td>-26.7</td>
</tr>
<tr>
<td>9.9</td>
<td>-22.8</td>
</tr>
<tr>
<td>11.1</td>
<td>-26.1</td>
</tr>
</tbody>
</table>

3.3.2 Dispersion differences caused by binder

The 5 hours milled inks with Cellobiose, PEG and PVA inks showed that only PVA ink was relatively stable after 3 days, see Fig. 36. The black appearance of the Cellobiose ink is caused by contamination of carbon black from the mill. It is important to notice that the particles sizes after milling in the binders are not the same for these three inks. On one hand, the more broken the particles are, the less tendency of sedimentation due do the gravitational force is expected to be seen. On the other hand, the more new particle surface created the more hydrophobic the particles are expected to be due to the less hydrophilic titanium dioxide.

Figure 36. Ink stability in Cellobiose ink (A), PEG ink (B) and PVA ink (C).
### 3.3.3 Comparison of dispersing agents

After 72 hours of settling the ability of the dispersant agents to prevent settling is shown in Figs. 37 and 38 and the dispersing agents’ abilities to disperse this powder are listed in Table 6.

![Sample with dispersing agent](image1)

**Figure 37.** Sample with K2 and dispersant A) 181, B) 191 and C) 154.

![Sample with dispersing agent](image2)

**Figure 38.** Sample with K2 and dispersant A) 760 W, B) without dispersing agent and C) Span 80 and Sandozin.

**Table 6.** The dispersing agents abilities to disperse (ordered best to worst).

<table>
<thead>
<tr>
<th>Ability to disperse</th>
<th>Dispersion agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>Span 80 and Sandozin</td>
</tr>
<tr>
<td></td>
<td>Equal good; 190 and 760 W</td>
</tr>
<tr>
<td></td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>Ref. Water alone</td>
</tr>
<tr>
<td>Low</td>
<td>154</td>
</tr>
</tbody>
</table>

35
3.4 Inkjet printing results

Only the inks that could print a touch sensing surface with K-bar and meet the requirements according to particle size and stability, were further prepared for inkjet printing. The viscosity and surface tension were measured to assure that the inks had suitable values. These ink formulations were prepared with PVP-styrene, Span 80 and Sandozin. The concentration of binder was varied from 10 to 60 weight %

PVP-styrene with 10 weight % PVP-styrene was printed with the HP Printer as a solid area of 10 x 10 cm several times. First print resulted in a thin white image, but the amount of ink printed reduced sharply print after print. After four layers on top of each other, all the nozzles were blocked and no ink could be printed. Even careful cleaning couldn't unblock the nozzles. During the cleaning process white flakes came out from the heating area of the cartridge, which indicate that PVP-styrene is sensitive to heat and not suited for thermal inkjet printers. The thin area printed had no conductivity.

The same ink was also printed with Printos printer without any problems. The printed film had resistivity values listed in Table 7.

Table 7. Resistivity of inkjet printed PVP-styrene ink.

<table>
<thead>
<tr>
<th>Weight [g]</th>
<th>Resistance [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1030</td>
</tr>
<tr>
<td>103</td>
<td>224</td>
</tr>
<tr>
<td>603</td>
<td>19</td>
</tr>
</tbody>
</table>

When printing these surfaces, the printer did not deposit the droplets in a controlled pattern. The pump and surface plate that are expecting to move the substrate did not work, meaning the thickness of the surface differed and therefore also the resistivity values. The values above (Table 7) should be taken just as trend values. To get exact and reproducible values the printer has to be more controllable. The same is valid for the other resistivity tables as well.
3.5 Ink formulations for improved ink stability and touch sensing properties

The PVP-styrene inks with 10, 20 and 30 weight % binder showed a significant increase in resistivity with increasing PVP-styrene concentration, see Table 8 and Graph 1. With a binder content of 20 % the printed film had the best touch sensing property.

Table 8. Touch sensitivity for different PVP-styrene concentrations.

<table>
<thead>
<tr>
<th>PVP-styrene content [weight %]*</th>
<th>Resistance by various applied weight [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13 g</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
</tr>
<tr>
<td>20</td>
<td>6000</td>
</tr>
<tr>
<td>60</td>
<td>9000</td>
</tr>
</tbody>
</table>

* The percentages are weight percentages with respect to the total weight of liquids in the mixture before dilution.

Graph 1. Touch sensing property versus binder concentration.

For the exact formulations see Appendix 1. These measurements are done from a K-bar printed film.

PVP-styrene ink done without triethanolamine had pH values around 4. By adding triethanolamine the pH values increased to 8-9. This change in pH was desirable after
considering the zeta potential measurements performed on the particles. The addition of triethanolamine also showed a significant improvement of the stability. This improvement could be easily seen by the cleanness of the walls of the test tube, see Fig. 39.

Figure 39. Before addition of triethanolamine (to the left) and after addition (to the right).
3.6 Final ink

The results led to the final ink formulation shown in Table 9. The weight percentages are with respect to the total weight of liquids in the mixture before dilution.

Table 9. The formulation of the final ink.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Material</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final PVP-styrene ink</td>
<td>H₂O</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>PVP-styrene emulsion</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>K2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Sandozin Nie</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Triethanolamine</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The final PVP-styrene ink was low viscous, see Table 10, had a pH value of 8.4 and a surface tension of 27-29 mN/m, which make this ink suitable for inkjet printing.

Table 10. The viscosities of the ink depending on revolutions per minute.

<table>
<thead>
<tr>
<th>Revolutions per minute [rpm]</th>
<th>Viscosity [cP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>1.4</td>
</tr>
<tr>
<td>100</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The touch sensing properties was very good, compared with the reference, see Table 11 and Graph 2.

Table 11. Touch sensing properties for the inkjet ink compared with the reference values.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Resistance by various applied weight [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13 g</td>
</tr>
<tr>
<td>Inkjet ink</td>
<td>6000</td>
</tr>
<tr>
<td>Reference values</td>
<td>1145</td>
</tr>
</tbody>
</table>
Graph 2. Touch sensing property of inkjet ink compared to screen printed ink.

The ink was also put to dry onto Peratech’s tester strips, see Fig. 40, and was measured for their touch sensing properties. The strips were made of a silver and carbon pattern printed onto a rigid plastic film. Small areas (circles with diameter of 7 mm) of inkjet ink was put to dry onto some of the printed carbon areas.

The carbon circle on the other side was put into the inkjet ink and the resistivity was measured through the layers of carbon - inkjet ink - carbon by using the silver pattern. Due to the small areas of theses circles and the low weight load (maximum 100 grams) during the
measurements, the resistivity values were bigger than previous measured for this ink, see Graph 3, but the values were still as good as the currently produced QTC™.

Graph 3. Touch sensing measurement of inkjet ink on Peratech tester strips.
4. CONCLUSIONS

Based on the experimental studies carried out, the following conclusions could be drawn;

1. K2 could not be milled to make it suitable for inkjet printing.

2. K1 together with Poly(1-vinylpyrrolidone-costyrene) and dispersing agents Span 80 and Sandozin NIE made inkjet printable inks.

3. The inkjet ink could be produced by 1 hour bead milling, filtration through two layers of Wathman filter ‘Grade 1’ and printed with Printos P16 Digital Textile Printer. The ink had a viscosity just above 1 cP and a surface tension of ~30 mN/m.

4. The printed surface was highly touch sensing. From being almost an insulator (MΩ range) in rest the resistance dropped to a few kΩ under pressure.
5. References


## Appendix 1

<table>
<thead>
<tr>
<th>Ink</th>
<th>Material</th>
<th>Weight %*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP-styrene no. 1</td>
<td>H₂O</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>PVP-styrene emulsion</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>K₂</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Sandozin Nie</td>
<td>3.5</td>
</tr>
<tr>
<td>PVP-styrene no. 2</td>
<td>H₂O</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>PVP-styrene emulsion</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>K₂</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Sandozin Nie</td>
<td>3.5</td>
</tr>
<tr>
<td>PVP-styrene no. 3</td>
<td>H₂O</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>PVP-styrene emulsion</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>K₂</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Sandozin Nie</td>
<td>3.5</td>
</tr>
<tr>
<td>PVP-styrene no. 4</td>
<td>H₂O</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>PVP-styrene emulsion</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>K₂</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Sandozin Nie</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td><strong>Triethanol amine</strong></td>
<td><strong>0.1</strong></td>
</tr>
</tbody>
</table>

* The percentages are weight percentages with respect to the total weight of liquids in the mixture before dilution.