

---

Preparations for Microscale Studies of  
Electrorheological Behaviors of  
Nano-Silicate Particles

*Helene Rødal*  
*helenero@stud.ntnu.no*

---

December 19, 2006  
*Supervisor: Jon Otto Fossum.*  
NTNU

MASTER PROJECT AUTUMN 2006

### **Abstract**

The subject of this report is electrorheological fluids in micro scale systems. The main constituent is synthetic nano-silicate particles dissolved in different solvents. The sample droplet is placed within a gap of  $10\mu m$ . It is observed through an optical microscope coupled to a camera which is monitored by a computer. There are two solvents used here, silicon oil and turpentine. Only one sample combination gave promising results, this was turpentine and modified laponite. No electrorheological effect was observed with the silicon oil samples used here. The reason for this might be a too large viscosity, but there are also other factors to be considered. The sequel of the experimental activities that make the basis for this report will have the same subject. The goal is to find an electrorheological fluid that is suited for atomic force microscopy. It is therefore interesting to see if turpentine is a suitable electrorheological solvent. It might also be interesting to try other solvents.

# Preface

This report is a presentation of the Master Project carried out in the 9th semester of the study program of Master in Technology. It is meant as a preparation for the master thesis to be carried out in the last and 10th semester. The object of interest in this report is electrorheological fluids containing nano-silicate particles placed in a micro scale system with an electric field.

An electrorheological fluid undergoes a transition where the rheological properties change severely under application of a strong electric field. There are certain property criterias for these fluids in order for them to be electrorheological. These properties and the electrorheological phenomena will be investigated with synthetic silicate particles in a micro scale system. There are two types of electrodes presented here, one with  $10\mu m$  gap, and one with  $1\mu m$  gap. These can be used to create the electric field and induce the electrorheological response. In this report, only the one with the largest gap is used. A voltage is applied over this gap, and an electric field is thereby created. The electrode with the largest gap can be investigated by an optical microscope while the one with the shortest gap needs to be examined with an Atomic Force Microscope (AFM). This is a challenge because the AFM make certain conditions regarding the sample state. The same goes for the small electrode gap. This report presents a possible solvent for AFM microscopy, that might be suitable for an electrorheological solvent. The experiments presented here have been carried out in order to identify the type of sample that is suited for an AFM study with the  $1\mu m$  gap electrode. They are also independent experiments carried out to extract as much information as possible from the sample.

This report gives a brief introduction to the electrorheological phenomena, and presents the related experiments performed. It is meant as a preparation for further experimental activities which is going to be carried out during the Master Thesis in spring 2007. The report is divided into 6 chapters, which have the following content.

**Chapter 1** presents an introduction to the electrorheological phenomena and gives some examples where the electrorheological phenomena can be applied.

**Chapter 2** is a theory chapter that describes the electrorheological phenomena and the silicate particles. It contains two main parts. The first part describes briefly the physics behind the electrorheological transition in order to prepare the reader for the experimental results and the interpretation of these. The last part presents the properties and structure of nano-silicate particles.

**Chapter 3** presents the materials used in the experiments that have been carried out in advance of this report. After the presentation of the materials there is a section that describes the sample preparation methods used here. The next section of this chapter presents the different equipment parts used when performing an experiment. The last section describes the experimental setup.

**Chapter 4** presents the experiments performed and the results that came out of these. There are three main experiments described here. One with samples of equal volume concentration and sample preparation method. The other experiment is a search for the trigger voltage where the limit between an electrorheological effect and no effect exist. The last part of experiment is about changing the volume concentration of laponite and trying different preparation methods to find what is suited best for the type of electrode used here.

**Chapter 5** presents some concluding remarks based on the experimental results presented in the previous chapter. The last section of this chapter presents some suggestions for further experimental activities subsequent to the ones presented in this report.

**Chapter 6** is the final chapter where a short summary of this report is given.

**There are three appendices** in this report. One contains the properties of turpentine, which is used as a solvent. The second one presents the properties of Laponite RD which is a synthetic silicate that is often used in the experiments carried out for this report. The last one presents the content of the dvd following this report. This dvd contains two movies showing some experimental results of specific interest.

## Acknowledgements

First, I would like to thank my supervisor, Professor Jon Otto Fossum at NTNU, for introducing me to experimental physics and guided me when questions have arisen. Secondly, I would like to give a special thanks to Post Doc. Ahmed Gmira at NTNU who has been a great help in general, especially at introducing me to the equipment and the materials used. Finally, I would like to thank a PhD-student at IFE(Norway) named Eldrid Svåsand for informative discussions regarding our results. Another thanks is sent out to Professor Jon Andreas Støvneng at NTNU for a helpful discussion regarding my experimental results so far.

# Contents

<b>Preface</b>	<b>i</b>
Acknowledgements . . . . .	ii
<b>1 Introduction</b>	<b>1</b>
<b>2 Theory</b>	<b>2</b>
2.1 Electrorheological Fluid . . . . .	2
2.1.1 The Three Components [1] . . . . .	3
2.1.2 Origin of the ER-effect . . . . .	4
2.2 Clay Particles . . . . .	7
<b>3 Experimental</b>	<b>9</b>
3.1 Materials . . . . .	9
3.1.1 Laponite . . . . .	9
3.1.2 Solvent . . . . .	10
3.1.3 Sample Preparation . . . . .	11
3.2 Experimental Equipment . . . . .	12
3.2.1 Electrodes . . . . .	12
3.2.2 Optical Microscope . . . . .	13
3.2.3 Light Source . . . . .	15
3.2.4 Power Supply . . . . .	15
3.3 Experimental Setup . . . . .	15
<b>4 Results and Analysis</b>	<b>17</b>
4.1 Observation of the ER-effect . . . . .	17
4.2 Trigger Voltage . . . . .	22
4.3 Different Concentrations and Sample Preparation . . . . .	24
4.3.1 Silicon Oil and Laponite RD . . . . .	25
4.3.2 Turpentine and Laponite RD . . . . .	27
4.3.3 Modified Laponite . . . . .	27
4.3.4 Brief Overview . . . . .	28
<b>5 Concluding Remarks</b>	<b>29</b>
5.1 Further Plans . . . . .	33
<b>6 Summary</b>	<b>34</b>
<b>A Properties of Turpentine</b>	<b>36</b>

<b>B Laponite RD</b>	<b>39</b>
<b>C Videos of Experimental Results.</b>	<b>42</b>

# List of Figures

2.1	Formation of chains under influence of an applied electric field, E [2]. . . . .	4
2.2	Electric dipole in an external electric field [3]: a) A dipole in which the electric field exerts a torque. b)The final equilibrium state of the dipole. . . . .	5
2.3	Dipole-dipole interaction [4]. . . . .	6
2.4	Formation of chains in an electric field. The field is parallel to the chains, and the solute is Na-Fluorohectorite [5] . . . . .	6
2.5	Structure of a single laponite sheet[6]. . . . .	8
2.6	Description of the “unit-cell” of the laponite particle [7]. . . . .	8
3.1	A scetch of the electrodes [8]. a)IAME-co-IME electrode with $1\mu m$ gap. b)IAME electrode with $10\mu m$ gap. . . . .	12
3.2	Two types of electrodes coupled with wires: a)IAME-co-IME, b)IAME. . . . .	13
3.3	The extra equipment: a)Light transporter, b) Specimen table, c)Hitachi camera and d) PixelLink camera. . . . .	14
3.4	Optical microscope with an extra 2x magnification lens attached to it. . . . .	14
3.5	LCD 1500 light emitter. . . . .	15
3.6	Experimental setup. a) The total setup including all experimental parts. b)The IAME electrode on top of the specimen table underneath the extra magnification lens attached to the microscope. . . . .	16
4.1	The sample of silicon oil and Laponite RD before (a) and after (b) the electric field has been applied. The voltage of 20V was applied over the two lowest microbands. There was no observable ER-effect here. . . . .	18
4.2	The sample of silicon oil and modified laponite before (a) and after (b) the electric field has been applied.The voltage of 20V was applied over the two lowest microbands. There is no observable ER-effect here. . . . .	19
4.3	The sample of turpentine and modified laponite before (a), immediately after(b) and about 10 seconds after(c) the electric field was applied. The voltage of 20V was applied over the two lowest microbands. By comparing a) and b) one can see that there might be chain formations within the lowest gap. . . . .	20

4.4	The sample's reaction to an increasing electric field. a)5V, b)10V, c)15V, d)20V and e)> 20V. The voltage was applied over the two lowest microbands. One can see that the laponite particles assemble within the lowest gap as the applied voltage is increased.	23
4.5	The centrifuged sample of silicon oil and laponite RD before (a) and after (b) the electric field has been applied. The voltage of 20V is applied over the two lowest microbands. There is no ER-effect here. . . . .	25
4.6	Two different concentrations of laponite RD in silicon oil: 0.5vol%(a) and 3vol%(b). The pictures are taken before the electric field is applied. The voltage of 20V is applied over the two lowest microbands. There is no ER-effect here. . . . .	26
4.7	A filtrated sample of 1vol% laponite RD in silicon after application of the electric field. The voltage of 20V was applied over the two lowest microbands. There was no ER-effect here. . . . .	27
4.8	Filtrated sample of 1vol% modified laponite in turpentine after the field has been applied. The voltage of 20V was applied over the two lowest microbands. There is no ER-effect here. . . . .	28
5.1	Alignment of Laponite platelets in an applied electric field, $E$ [9].	30
5.2	A sample droplet placed upon four multibands where the applied electric field is represented by the red arrow. . . . .	31



# Chapter 1

## Introduction

The electrorheological response was discovered by Willis M. Winslow in 1949 [10][11]. He described it as a phenomena originated from electrically induced fibrillation of a solute consisting of small particles. Such solutions are called electrorheological(ER) fluids. Subsequent to this discovery, there has been severely great research on this area. The experimental background for this report is a part of this research process to learn more about the ER-fluid and the electrorheological phenomena. The experiments presented are a part of a micro scale study of the electrorheological behavior of nano-silicate particles.

The ER-fluid consist of two main parts; a solute and a solvent. When an electric field of sufficient strength is applied, the fluid undergoes a transition where the viscosity changes severely. The ER-fluid studied in this report can change from liquid state to semi-solid state. It is made up of silicon oil or turpentine as a solvent, and laponite RD or modified laponite as a solute. To apply the electric field (some of) the sample is placed between two conducting parallel plates separated by a distance  $d$ . By applying a voltage,  $V$ , over these plates, they will be oppositely charged. This results in an electric field between these two plates given by  $E = \frac{V}{d}$ . Hence, a strong applied electric field requires a high-voltage when the distance,  $d$ , is held constant.

The motivation for learning more about electrorheological fluids is not only a physicist's natural curiosity. Electrorheological fluids are also applicable in all types of systems where a large change in viscosity is beneficial. An example of where such a phenomenon can be utilized is in the industry as a mechanical interface. It can for example be used as a clutch, brake and/or damping system in vehicles [12][13], other damping systems[14], or valves and locks[13]. It can also be used in haptic<sup>1</sup> systems[16] where mechanical equipment is used to simulate tactile movement. The main disadvantage for the application of the the ER-fluid, is that it needs a strong electric field to activate the wanted transition. This means that there is need for a high voltage supply, and this is not an easily available resource, nor is it safe to use around living creatures.

---

<sup>1</sup>Pertains the sense of touch[15].

# Chapter 2

## Theory

To be able to understand the physics behind the transition which the electrorheological fluid undergoes under the influence of an external electric field, it is necessary to take a dip into the already described physics of this subject. The electrorheological phenomena is to be described in the first section of this chapter. It also presents the criterias for the physical properties of the constituents in an electrorheological fluid. The last section presents the properties of clay particles with a focus on a type of synthetic clay particles, named laponite. This type of synthetic clay is used in the experiments to be described later in this report.

### 2.1 Electrorheological Fluid

ER-fluids is a subgroup of smart materials. When exposed to an external stimulus, a smart material will respond adaptively within a limited time [1]. The result of this respond is beneficial for applications and hence the name, smart materials. The external influence can be temperature, mechanical stress, magnetic or electric field etc. The ER-fluid responds to an external electric field. The ER-response can be divided into three different groups; The positive ER-effect, the negative ER-effect and the photo-electrorheological(PER) effect [1]. If the ER-fluid's rheological properties increase with applied electric field, it is termed the positive ER-effect. The negative ER-effect is when the rheological properties decrease with applied electric field. The positive and negative ER-effect of some ER-systems can be enhanced with the addition of Ultra Violet illumination. This is called the PER-effect. The effect of interest in this report is the positive ER-effect. It is characterized by a transition from liquid-like to solid-like when exposed to an electric field of sufficient strength [1][12][11]. The strength of the electric field is in the order of  $0.5 - 2kV/mm$  [11]. The response time is usually within milliseconds after the electric field has been activated [17]. The time needed to achieve maximum viscosity can be higher, and this depends on factors such as the electric field strength and the dielectric constant of the fluid. The voltage at which there is such a reaction is called the *trigger voltage*.

The transition to a solid-like state is due to chain formations within the sample. The liquid-to-solid transition indicates that there is an inner ordering of the ER-constituents which leads to a change in the rheological properties.

When the transition occurs, the viscosity can increase by a factor of up to  $10^5$  [18] but the usual magnification is about 2 to 3 orders [19]. As the electric field is turned off, the ER-fluid returns to its initial liquid state and hence this transition is reversible. The reaction of the ER-fluid depends on the external field but also by its own constituent parts. These components will be described in the following section.

### 2.1.1 The Three Components [1]

There are three main components within the ER-fluid. These are:

- the dispersed phase (liquid or solid)
- the dispersing phase (insulating liquid)
- additives (any polar material that improves the induced reaction in the manner of stability or the ER-effect)

These phases are described below.

#### The Dispersed Phase

The dispersed phase can be either liquid or solid. There are some properties that have an effect on whether or not a dispersed phase can behave electrorheologically. Physical properties such as particle size and shape, high breakdown strength since the applied electric field is high, conductivity less than  $10^{-6}S/m$  (preferred) and a large dielectric constant ( $> 10$  is preferred) have an impact on the ER-effect. The particle size is usually between  $0.1\mu m$  and  $100\mu m$ . If the particles are too small or too large, the ER-effect will diminish. For small particles the Brownian motion can dominate over the chain formations. For large particles it is expected that the ER-effect is weakened due to sedimentation. The shape of the particles influence the ER-effect because the dielectric properties of the particles depend on their shape. Ellipsoidal particles are expected to give a stronger response than spherical particles due to a stronger induced dipole moment (for ellipsoidal particles).

#### The Dispersing Phase

The dispersing phase is a non-conductive liquid or oil. The preferable physical properties are high boiling point, low viscosity, high breakdown strength, low dielectric constant and relatively high density ( $1.2g/ml$ ). The dispersing fluids can be silicone oil, paraffin or vegetable oil.

#### Additives

One can use additives to increase the ER-effect. This is polar particles adsorbed to the dispersed particles' surface. Examples of additives are water, acid, salt and surfactants.

### 2.1.2 Origin of the ER-effect

There are different models trying to explain the physics behind the transition of the ER-fluid. It is commonly accepted that the transition of the positive ER-fluid occurs due the formation of fibrillated chains along the electric field direction. This is illustrated in fig.2.1.

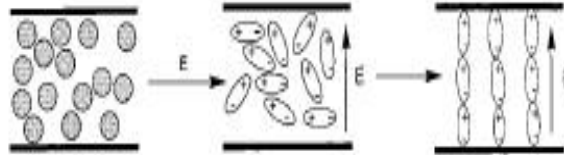


Figure 2.1: Formation of chains under influence of an applied electric field,  $E$  [2].

There are two common models that tries to explain the physical features behind the positive ER-effect. These are the polarization model and the conduction model. The polarization model regards the dielectric mismatch between the solvent and the solute as an essential factor of the ER-effect [2][20]. A greater mismatch will lead to a correspondingly larger ER-effect. This model had limitations and can not explain the ER-phenomena thoroughly enough. This forced a new model to arrive. The one of interest is the conduction model proposed by Atten [21]. It focuses on the particle interaction, but the major shortcoming of this model is that it does not consider the micro structural change of the ER-fluid during the transition. There are several other models trying to explain the origin of the ER-effect, and together they explain most of the questions arising when varying different parameters of interest. A mild description will be given here.

**The constituents of the ER-fluid** play a vital role in the degree of the ER-response. Their interaction when exposed to a strong electric field will be the basis for the coming description of the origin of the ER-effect. The ER-fluid contains small polar (conductive) colloidal particles dissolved in a non polar (non conductive) liquid. The physical properties of such a solution result in a transition from a liquid to a rigid, semi-solid state of higher viscosity when exposed to a high electric field. The degree of solidification depends (among others) on the solid volume fraction which can range from 5% to 50% [11]. The reason why the ER-fluid reacts in such a way under the influence of an external electric field, is partially due to a great mismatch between the electric conductivities of the solute and the solvent [11]. The external electric field will induce an inhomogeneous internal electric field, and correspondingly an inhomogeneous distribution of dipoles. This can induce a transition from liquid to solid state.

The ER-transition is a result of an inner ordering of the particles. The external electric field causes the positive charge center to be slightly shifted compared to the negative charge center. Hence there are electrically induced dipoles with a corresponding dipole moment. The electric field from one dipole results in

an attractive force to the other dipole charge centers of opposite charge. There is a corresponding repulsive force between the centers of same electric charge. In addition to the interaction between the other dipoles, their motion is also determined by the external electric field. When the field is applied, the dipoles will be attracted to either the cathode(positive end) or the anode(negative end) of the electric field depending on their position relative to each of these ends. The negative charge center will be attracted to the cathode, and repelled from the anode, and vice versa for the positive charge center. This causes the dipoles to align themselves so that their dipole moment is parallel to the electric field direction. This is shown in fig.2.2.

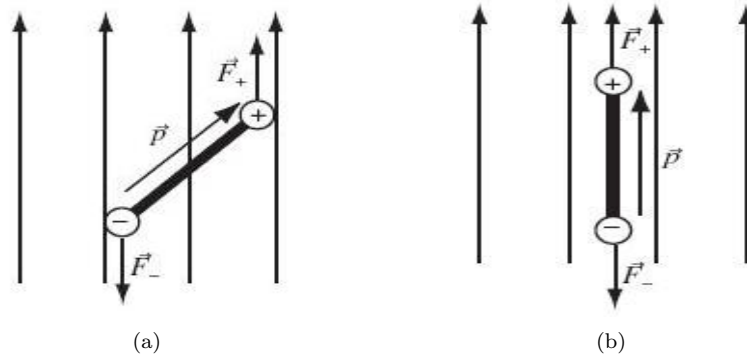


Figure 2.2: Electric dipole in an external electric field [3]: a) A dipole in which the electric field exerts a torque. b)The final equilibrium state of the dipole.

Sine the ER-fluid also consist of a non-polar fluid, the induced dipoles can move freely within this liquid and thereby get attached to the cathode or the anode of the electric field. In addition to these attractive and repulsing forces between the charge centers, there is also a repulsive force between all the dipoles. Whether two dipoles are attracted and combine, or repelled from each other, is determined by the position of one dipole relative to the other. The attracting force and the repelling force has different regions around the dipole moment, and is described in fig.2.3. As shown in this figure, there is a repulsive force in the area perpendicular to the dipole direction, and an attractive force at both ends where the charge centers are located. The dipoles will be accelerated by the electric field and may therefore move from the repelling area to the attractive area of the neighbor dipole. Hence, the dipoles can be trapped in the attractive region of an other dipole. The attractive force can therefore cause the dipoles to form chains, while the repulsive force cause the chains to align themselves relative to each other.

The electric dipole moment is aligned along the electric field direction. With the help of the attractive and repulsive forces between the dipoles there can be chain formations within the electric field. This leads to an increased inner order, and the ER-fluid ultimately undergoes a transition from a liquid to a semi-solid state. Hence, as the external electric field is increased, so does the viscosity of the sample. An example of the chain formations is given in fig. 2.4

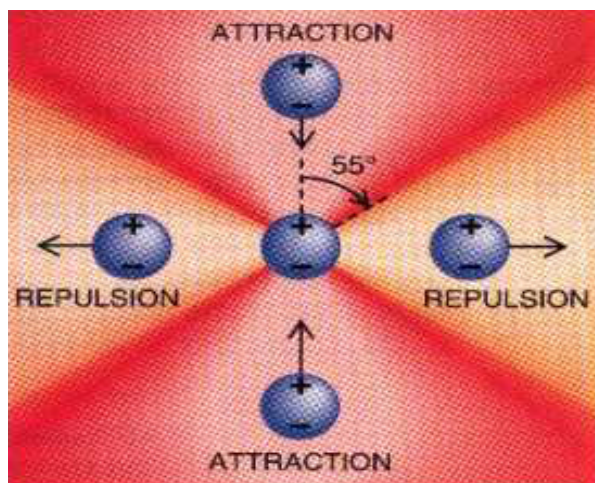


Figure 2.3: Dipole-dipole interaction [4].

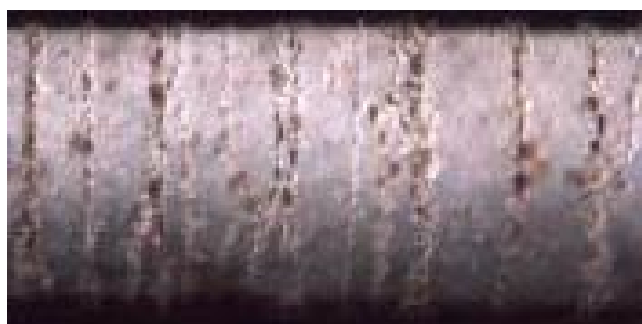


Figure 2.4: Formation of chains in an electric field. The field is parallel to the chains, and the solute is Na-Fluorohectorite [5]

## 2.2 Clay Particles

Natural clay is a rather easily accessible material in the nature. It exists as for example rocks, or quick clay which has a tendency to change to liquid-like behavior when disturbed. Clay has for example caused great avalanche disasters due to its absorption of water and loss of mineral salt, and it is a common material in the household, for example in pottery baking and as a building material. In the last few years clay has also become more interesting in experimental studies, and due to this many of the physical properties of clay particles have been investigated and explained. When used in experiments, natural clay is replaced by synthetic clay particles. In this case, Laponite. Laponite is a convenient representative for the dispersed phase in ER-fluids due to its polarisability and size[11]. Laponite minerals are layered silicates consisting of colloidal, disc shaped platelets. Each platelet has a thickness of about  $1nm$  and the diameter is about  $20 - 30nm$  [22]. The main difference between natural and synthetic clay is the size. In contrast to laponite, natural clay (and other synthetic clays) has a size in the order of micrometers, i.e. laponite particles are severely smaller. The clay platelet consist of several sheets of either tetrahedral or octahedral structure. These sub-sheets are coupled together face to face. The ratio of tetrahedral sheets to octahedral sheets may be 2:1 or 1:1. Laponite is a swelling 2:1 clay [22]. For a 2:1 clay mineral the octahedral sheet lies between two opposite tetrahedral sheets. This is shown in fig.2.5.

Laponite sheets often combine together forming aggregates. The force holding them together is due to the sharing of cations. The laponite platelets have a negative surface charge and a small positive charge at the ends. The negative surface charge is due to permanent charges and broken edges [23]. The permanent charges comes from substitution of Lithium ions with Magnesium ions. The broken edges are pH-dependent and comes from "OH" groups. The positive charge at the end is due to the restriction in spatial size. This restriction results in broken bonds leaving the edges slightly positively charged. The laponite platelet and its surface charges is depicted in fig. 2.6.

To "neutralize" the non-zero net charge at the platelet surface, the platelets share cations. This sharing of ions result in a bonding between each sheet and hence aggregation as mentioned before. The final composition is a stack of laponite platelets with cations between each interface. This sharing of cations leads to aggregation of particles which counteract the dissolving process aimed after in solutions. By replacing or isolating the cations between each laponite sheet, the physical properties of laponite particles can be changed.

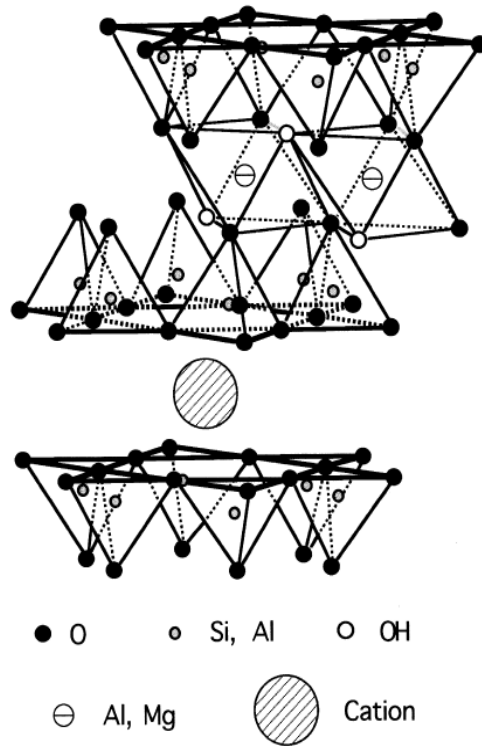


Figure 2.5: Structure of a single laponite sheet[6].

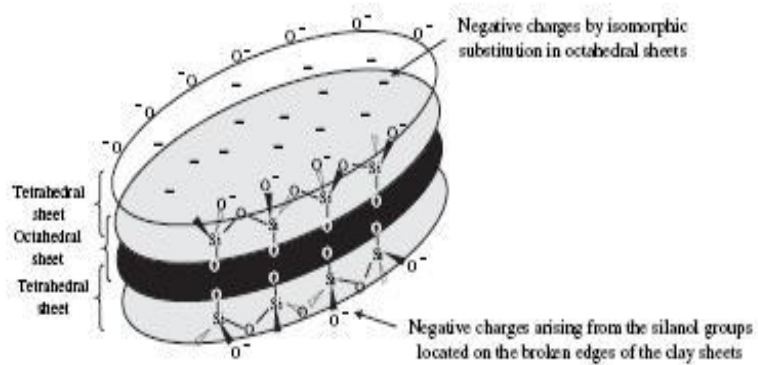


Figure 2.6: Description of the “unit-cell” of the laponite particle [7].



## Chapter 3

# Experimental

Some of the components necessary to induce a transition between liquid and solid state for an electrorheological fluid, are an external electric field of sufficient strength(see Ch 2) and a solvent and solute with a sufficient mismatch in electrical conductivity. As described in this chapter, these are the components that can trigger the positive ER-effect.

### 3.1 Materials

#### 3.1.1 Laponite

Two different types of laponite are used here. They are both produced by Rockwood. One of them is Laponite RD. The chemical composition of this type of laponite (dry basis) is as follows(see App.B):

- SiO<sub>2</sub> 59.5%
- MgO 27.5%
- Li<sub>2</sub>O 0.8%
- Na<sub>2</sub>O 2.8%

The chemical formula for Laponite RD is given by Si<sub>8</sub>Mg<sub>5.45</sub>Li<sub>0.4</sub>H<sub>4</sub>O<sub>24</sub>Na<sub>0.7</sub>[24]. This formula is not for a dry basis due to the additional H-atoms which is not given in the list above. The negative surface of the laponite RD particle contains positively charged sodium (Na<sup>+</sup>) ions. These can be shared by several laponite sheets forming aggregates. It is desired to have a solution of as small particle accumulation as possible, and therefore it would be beneficial to try to prevent aggregation. The other type of laponite used here is a surface modified laponite. It is called Alkyl Quaternary Ammonium Smectite. For this type of laponite, the sodium ions are replaced by chains of quaternary ammonium chains, which counteract the aggregation process. This is a type of additive described in Ch.2. Due to these additives, the modified laponite will disperse more easily than Laponite RD particles.

### 3.1.2 Solvent

#### Turpentine

The colloidal particles to be used are laponite particles, but the solvent might vary taking into account what type of equipment that will be used to examine the sample. The gap between the electrodes determines the size of the specimen to be examined. As the size of the specimen decreases, the equipment used to examine this will vary. The optical microscope has its limits of magnification. If the gap is too small it can't be seen well enough through the microscope. This is the case for the electrode of  $1\mu m$  gap. For this size of electrode gap, the optical microscope has to be substituted by for example an AFM. This leads to new challenges concerning the ER-fluid. When examined by an AFM, it is preferable that the examined specimen is solid. This is to avoid particle attachment to the tip of the AFM. This means that, when using the AFM, the chains should already have been formed and remain so after the electric field has been turned off. To achieve this, one can use a solvent that evaporates after the chains have occurred. This solvent must in addition fulfill the necessary requirements needed to form an ER-fluid together with laponite. For example it should have a very low conductivity (compared to laponite).

An evaporating solvent has been used before in an AMF study of magnetic colloidal particles, and the solvent in this case was isoparaffin [25]. To decide if this is a good solvent for laponite, it is necessary to know its conductivity. This, however, turned out to be very difficult. In addition, the price for isoparaffin is found to be severely high so such a solvent was declined. However, there are also other solvents that might be suitable for this purpose. Among these solvents were ethanol, isopropanol, ethyl acetate and turpentine, where turpentine was chosen. This is due to its low conductivity of about  $400pS/m$  (see App.A) and fairly convenient boiling temperature which is  $150 - 170^\circ C$  [26]. In addition it is cheap to purchase, and fairly easy to handle in small amounts. As described in Ch. 2.1 it is important that the dispersing phase has a high density and boiling point, and a low viscosity in addition to low conductivity. Compared to the oils mentioned as examples of dispersing phase, the density is lower ( $< 1.2g/ml$ , see App. A), so is the boiling point since that was intended. It is interesting to see if it is still possible to see an ER-effect despite these deviations from the ideal solvent.

#### Silicon Oil

When the sample is only examined through the optical microscope, it is not necessary for the solvent to evaporate. In this case silicon oil can be used. The silicon oil has a higher viscosity than turpentine and is commonly used as a solvent in ER-experiments. The specific type of silicon oil used is Rotitherm M150. The viscosity of this oil is  $0.1Pa \cdot s$  at 298K [27] [28] and the conductivity is  $\approx 10^{-12}S/m$  [29].

### 3.1.3 Sample Preparation

The appropriate weight of laponite is measured with a digital weight. The solvent volume is measured in milliliters with a measuring glass that has a maximum measurable volume of 50ml. Since laponite is measured by weight instead of volume, the volume fraction,  $f$ , of laponite to solvent is found by eq.(3.1),

$$f = \frac{m_s/\rho_s}{v_l} \quad (3.1)$$

where  $m_s$  and  $\rho_s$  is the weight and the density of the solid phase(laponite) respectively.  $v_l$  is the volume of the solvent(turpentine or silicon oil). The density of laponite RD is  $\rho_s = 1000kg/m^3 = 1g/ml$  (see App.B) using the relation  $1dm^3 = 1l$ . The laponite and the solvent is mixed together at ambient temperatures. The mixed sample is shaken by hand for about two to three minutes. The sample is then left alone for sedimentation of the heavier particles. This ensures that the largest accumulation of particles will fall to the bottom of the sample container, leaving the smallest ones in the upper part. The droplet to be examined is taken from the supernatant phase(upper part of the sample container) where the possibility of finding single laponite particles, or small aggregates, is largest. It is important that the particles in the droplet of interest are small because of the size of the gap in the electrode. If the particles are too large, it is impossible to see the chain formations. One can only see that the particles align themselves in the same direction as the electric field, but there is no room for more particles to form chains because the particles already fill the whole gap. By examining only small particles it is possible to see if several laponite particles form chains that are aligned along the electric field. The droplet of interest is taken out by a transfer pipette that is set to a volume of  $0.1\mu l$ .

In ch. 2 it is said that the volume concentration of colloidal particles can range between 5% and 50%, while in this case the solution contains maximum 1vol% of laponite. This is due to the size of the investigation area. The electrode gap is only of  $10\mu m$ (or less) in this case, and to be able to observe single particle movement it is necessary to keep the number of particles within the electric field at a minimum without eliminating the possibility of chain formation. If there are too few particles present around the electric field, they will most likely not interact, but only get attached to one side of the electrode gap. If this happens there can be no chain formations. In other words, there must be another laponite particle present within the range of which there is attraction between the particle dipoles. Hence, both the number of particles within the gap, and the size of these should be calibrated to give the optimum detectable result.

Another way to ensure that only small particles participate in the sample droplet of interest, is to filter the sample. If filtration is performed, this is done after mixing the constituents together. An electric pump and a filter of  $0.2\mu m$  is used. In this way, only the aggregates of size less than  $0.2\mu m$  will go through the filter paper. The filtrated sample is also left to sediment, and the supernatant phase is used for examination. An alternative to filtration is centrifugation. This is done by a centrifuge named centrifuge ISO 9001 B4i from Jouan Quality System.

## 3.2 Experimental Equipment

To be able to initialize an electrorheological effect in the sample, it has to be an electric field present. The ER-fluid is placed in an electric field of sufficient strength as described in Ch.2. This is done by electrodes with several microbands where the spacing between the microbands is in the order of micrometers. The spacing between these microbands is called a gap. This is where the sample is placed. By applying a voltage over one of these gaps, one has an electric field (see Ch.1). An optical microscope is used to observe the expected ER-effect. To preserve the response from the ER-fluid, the process is captured by a video camera coupled to the microscope. Further details about these devices is presented in this section.

### 3.2.1 Electrodes

This is a micro scale study of the ER-effect, and the size of the electrode gap is determined thereafter. It is desirable that this gap size should be between  $1\mu m$  and  $100\mu m$ . Two types of electrodes were purchased from Abtech. One model called IAME-co-IME<sup>1</sup> with a gap of  $1\mu m$ , and one model called IAME<sup>2</sup> with a gap of  $10\mu m$ . The electrodes were made of gold or platinum (two of each) on a substrate of glass. The sample is to be placed over these microbands and a voltage is applied between two of the microbands to create the electric field. These two models are shown in fig.3.1.

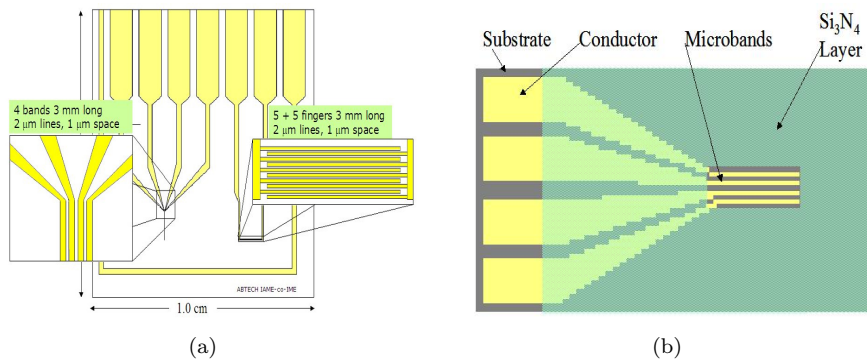


Figure 3.1: A sketch of the electrodes [8]. a) IAME-co-IME electrode with  $1\mu m$  gap. b) IAME electrode with  $10\mu m$  gap.

These have to be coupled to wires to be able to apply a voltage over one of the electrode gaps. Two sets of copper wires covered with insulating material are used, one set for each electrode. The wires have a diameter of  $0.18\text{ mm}$  and are attached to the electrode by using conducting silver paint as a glue. The final treated electrodes are pictured in fig.3.2.

<sup>1</sup>Independently Addressable Microband Electrode (IAME) in combination with an Interdigitated Microsensor Electrode (IME)[8]

<sup>2</sup>Independently Addressable Microband Electrodes [8]

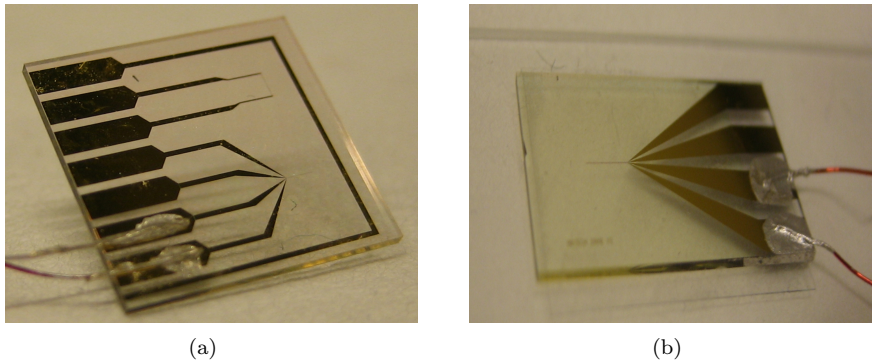


Figure 3.2: Two types of electrodes coupled with wires: a)IAME-co-IME, b)IAME.

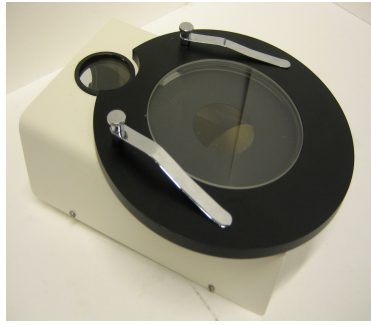
### 3.2.2 Optical Microscope

The optical microscope, Zeiss Stemi 2000-C, is used to observe the ER-fluid. This model includes a camera port to mount a camera on top of the microscope. This is to examine the sample with a computer monitor instead of through the eyepieces. The extra equipments used together with the microscope are:

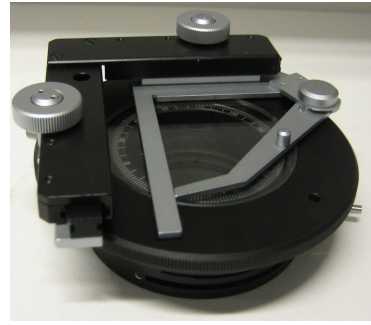
1. Extra 2x magnification lens (attached to the microscope shown in fig.3.4)
2. Light transporter (fig.3.3(a))
3. Specimen table (fig.3.3(b))
4. Hitachi camera or (fig.3.3(c))
5. PixelLink camera (fig.3.3(d))

The equipment noted in point two to five are shown in fig.3.3.

There are two different cameras that can be used(4 and 5). One is made from Hitachi(fig.3.3(c)) and coupled to the computer through a serial port and a coaxial cable. The recording interface is implemented in LabView 8.0 and called National Instruments Vision Assistant 8.0. The camera can be adjusted with the program KP-D28/D591 Remote Control. The camera can take up to 400 frames which can be stored as a video file. It is impossible to increase the number of frames because the program always end up with an error. The 400 frames correspond to a 13 second video. The other camera is named PixelLink mega pixel fire wire camera(fig.3.3(d)). The advantage with this camera is that it can be used with Windows Movie Maker, and record a much longer movie. It is not limited to number of frames, but to how much free space there is available. The user interface follows with the camera, and is named PixelLink Capture. This user interface is easier and more efficient than the VI-applet used for the Hitachi camera. The disadvantage is that the manual settings of the PixelLink camera are limited. The optical microscope is pictured in fig(3.4).



(a)



(b)



(c)



(d)

Figure 3.3: The extra equipment: a) Light transporter, b) Specimen table, c) Hitachi camera and d) PixelLink camera.



Figure 3.4: Optical microscope with an extra 2x magnification lens attached to it.

### 3.2.3 Light Source

A model from Zeiss called LCD 1500 is used as a light source. The tube directing the light is placed in one end of the light transporter described in the previous subsection. The light from this source is reflected in such a way that it goes through the sample. Some of the transmitted light goes further through the microscope lenses whereby it is captured by the camera. The light source is shown in fig.3.5.



Figure 3.5: LCD 1500 light emitter.

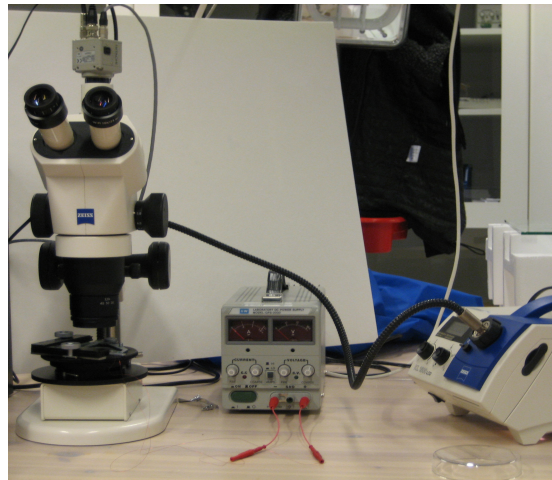
### 3.2.4 Power Supply

A laboratory DC power supply is used, with a maximum power output of 32V. This is used for the electrode with  $10\mu m$  gap. The minimum voltage output is about 3V. For the electrode with  $1\mu m$  gap it is necessary to have a more accurate voltage output in the low-voltage region. For this we use an instrument from National Instruments called DAQ Pad 6020E. This can give a voltage output between  $-10V$  and  $10V$ , with no current output. This power supply is monitored from the computer with an inbuilt program from National Instruments called Measurement and Automotation.

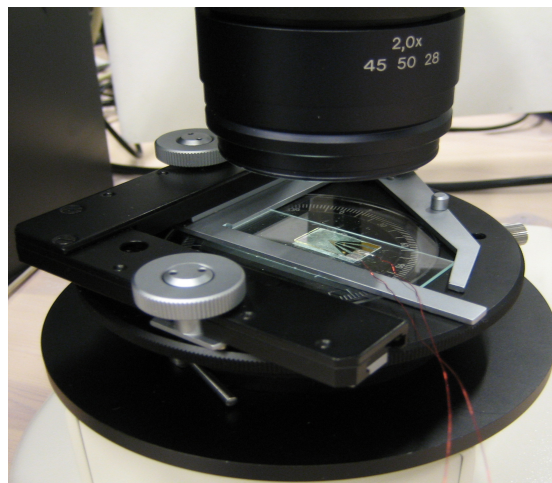
## 3.3 Experimental Setup

The electrode is attached to a glass plate with a two sided tape, and placed on a sample board with controllers to easily adjust the position of the sample. This is placed on top of a plate which directs the light, sent in from the side, through the sample and to the microscope lenses. The light source is the one described above. An extra 2x magnification lens is attached to the microscope, and a camera is mounted on top and coupled to the computer. The wires from the electrode are coupled to the voltage source through an intermediate section of different wire thickness. The applied voltage is about 20V since the gap is  $10\mu m$ . This corresponds to  $2kV/mm$  which lies in between the suitable interval

noted in Ch 2. Before an experiment is started, it is important to verify that there is actually electric contact between the electrode and the wires attached to it. This is simply done by applying a given voltage and registering the voltage over the points of attachment with a multimeter. This is done every time the wires need to be attached or reattached. A final setup is shown in fig 3.6.



(a)



(b)

Figure 3.6: Experimental setup. a) The total setup including all experimental parts. b)The IAME electrode on top of the specimen table underneath the extra magnification lens attached to the microscope.



## Chapter 4

# Results and Analysis

### 4.1 Observation of the ER-effect

The goal of this experiment was to observe whether there is chain formation and, if possible, compare the reaction of the different samples. The electrode of  $10\mu m$  gap was used. Four different types of samples was investigated with the experimental setup described in ch.3.3. These were

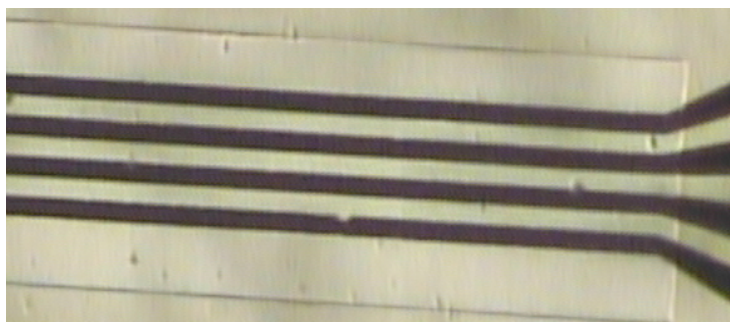
- Laponite RD and turpentine.
- Modified laponite and turpentine.
- Laponite RD and silicon oil.
- Modified laponite and silicon oil.

The concentration of colloidal particles was  $1vol\%$  for all these samples. Filtration or centrifugation was not performed, but the sample was left to sediment before use. The electrode was cleaned with acetone to remove potential dust or other contaminating material that could destroy the electric field. A droplet of  $0.1\mu l$  was placed over the gap, then a sequence of 400 frames were sampled with the Hitachi camera. A voltage of  $20V$  was applied over the gap during this video capture. This was done three times for each type of sample, leading to 12 videos where there could be signs of the ER-effect. There are four separate multibands in this electrode, and the electric field is only applied between the two lower multibands. This gap is therefore only the gap of interest and the movement of the laponite particles within this gap can be compared to the movement outside.

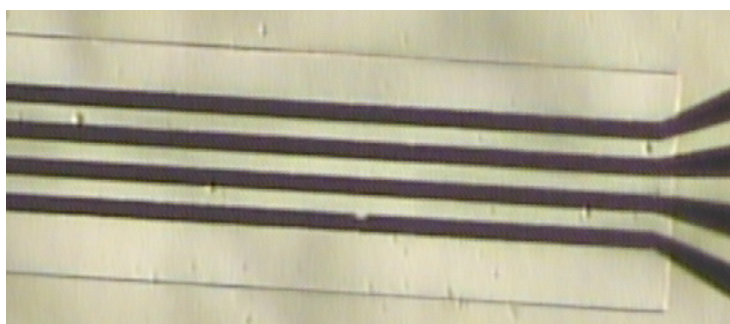
#### Results

There were four types of potential ER suspensions in this experiment, but only one sample showed an obvious reaction to the applied electric field. Whether this was chain formation or not is to be discussed later in this section. First we consider the samples where the ER-effect was not observed.

**Laponite RD dissolved in silicon oil** was one example. By regarding fig.4.1(a) and fig.4.1(b) it is obvious that there is no chain formation within the lower gap. These figures shows that there are some laponite particles that are attracted to the electrode when there is a field present, but there was no significant reaction except from this. One can therefore conclude that there is an electric field present inducing a dipole moment to the laponite particles, but there is no sign of the ER-effect whatsoever. There was the same negative result for all three tests of this sample.



(a)

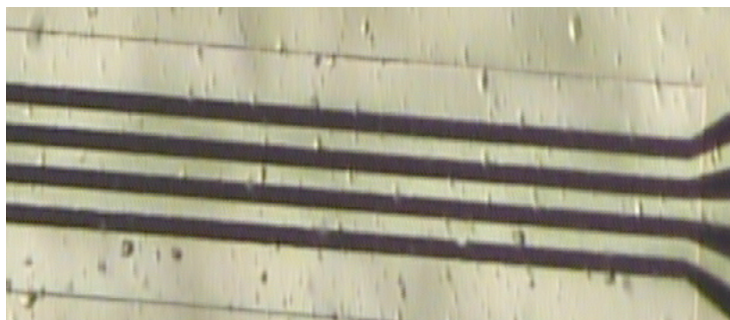


(b)

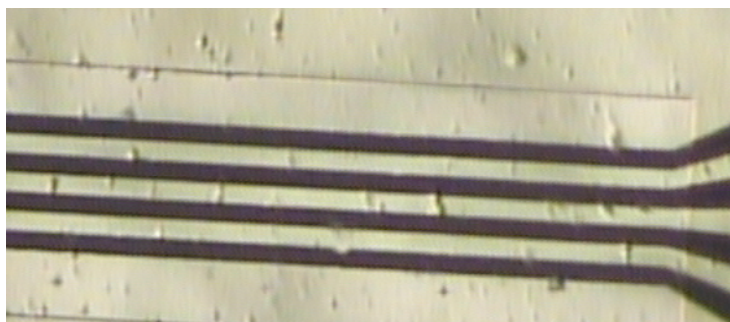
Figure 4.1: The sample of silicon oil and Laponite RD before (a) and after (b) the electric field has been applied. The voltage of 20V was applied over the two lowest microbands. There was no observable ER-effect here.

**Modified laponite dissolved in silicon oil** is another example where there was no significant reaction resembling to the ER-effect. The result before and after the field had been applied is shown in fig.4.2. As for the silicon oil sample with laponite RD, there was a reaction when the field was applied. But, by considering the pictures in fig.4.2, one can see that this reaction is negligible. There was aggregation of particles within the electric field, but the reaction was not sudden and the aggregation of the laponite particles do not resemble to chains. Compared to fig.4.1 one can see that there was a lot more laponite particles present in the solution in this case. Since the concentration is the same for all solutions, this indicates that the sample had not been able to sediment enough, or that the droplet investigated had been taken from the wrong solution phase, i.e. not from the supernatant phase. The size of the particles(aggregates)

are also larger in this case than in fig.4.1. This was therefore an unsuited sample because the laponite aggregates would, at the best, only fill the electrode gap and one could not be able to verify if this was aggregation or chain formation. However, all three tests of this sample gave no indications of the ER-effect.



(a)



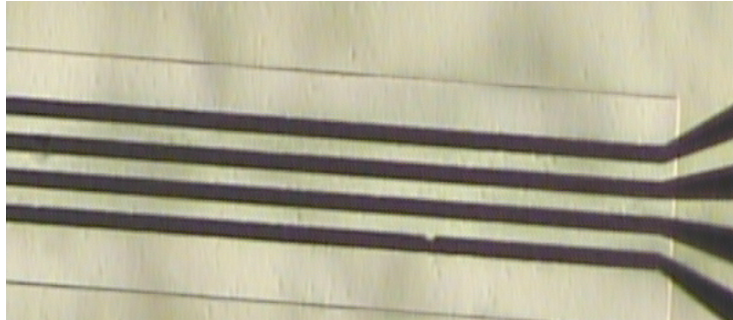
(b)

Figure 4.2: The sample of silicon oil and modified laponite before (a) and after (b) the electric field has been applied. The voltage of 20V was applied over the two lowest microbands. There is no observable ER-effect here.

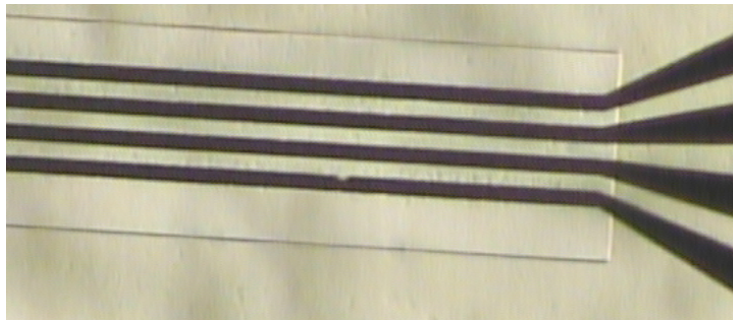
**Laponite RD dissolved in turpentine** also gave a negligible reaction to the applied electric field. As before, some of the laponite particles got attached to one of the electrodes, but there was no sign of the ER-effect.

**The one sample** that gave an interesting feedback was the sample with turpentine and modified laponite. This is shown in fig.4.3. When regarding the movie of this sample, one can see a sudden reaction when the field was applied. The laponite particles present within the electric field immediately assembled together in something that might look like chains, across the multiband gap. As the time after the field has been turned on increased, more and more laponite particles were trapped and aligned within the electric field. The reaction was the same for all three tests of this sample. A movie showing this reaction is added in App.C.

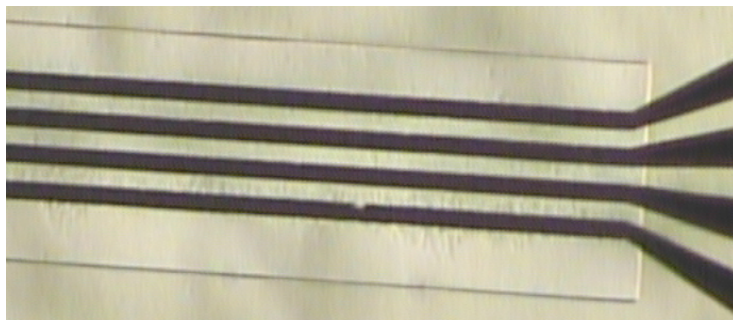
The pictures in fig.4.3 are a bit diffuse. It would be helpful if the pictures had a better focus. To be able to verify if there are chain formations present,



(a)



(b)



(c)

Figure 4.3: The sample of turpentine and modified laponite before (a), immediately after (b) and about 10 seconds after (c) the electric field was applied. The voltage of 20V was applied over the two lowest microbands. By comparing a) and b) one can see that there might be chain formations within the lowest gap.

it would also be helpful with a larger magnification. The gap of  $10\mu m$  is visible but small even with maximum magnification. Although the image quality could be better, this experiment still shows results indicating that turpentine might be fitted as a solvent in an ER-fluid.

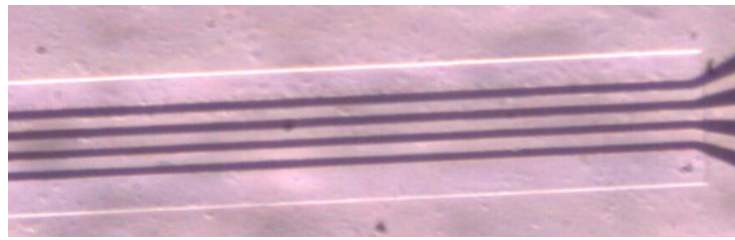
## 4.2 Trigger Voltage

It is desirable to find the trigger voltage of the sample. The trigger voltage is the minimum voltage needed to induce chain formations within the electric field. This is done by recording a movie of the sample while the voltage over the gap is increased. From the previous section we know that for an applied voltage of  $20V$  over the electrode gap, there is a sudden reaction resembling to chain formations. Therefore the trigger voltage is expected to be lower or equal to this voltage. It would be most convenient using a sample of silicon oil as a solvent, but as described in the previous section, this type of sample had a negligible reaction to the electric field. The sample used here was therefore the one with  $1vol\%$  of modified laponite in turpentine. It was the same sample as the one described in the previous section which gave a promising response. The disadvantage of using turpentine is that the recording time is limited due to evaporation. It is therefore necessary to increase the voltage fast enough so that one include as large specter of voltage as possible in one movie. This is also the reason that the PixelLink camera is used instead of the Hitachi camera. In this way the recording time is not limited to 13 seconds. Before use, the sample was shaken thoroughly by hand, and left for sedimentation. The sample droplet of  $0.1\mu l$  was taken from the supernatant phase.

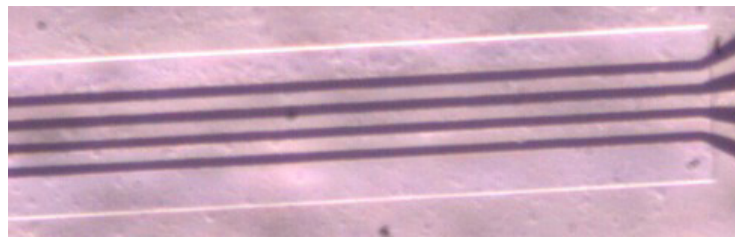
### Results

Some snapshots from the recorded movie is presented in fig.4.4.

The applied field started at a voltage of about  $3V$ . This is the lowest possible applied voltage for the voltage source used here. It was increased to about  $30V$  maximum. As can be seen from fig.4.4 there was accumulation of laponite particles within the electrode gap. What can not be seen is the acceleration of the particles when the voltage was increased. The particles started to react to the field even at a voltage of about  $5V$ (fig.4.4(a)) but there was no chain formation yet. At about  $15V$ , some particles remained within the electrode gap getting attached to one of the charged ends. As the field was increased further, more and more particles got attached to the other particles within the electrode gap. The particles outside the gap moved in circles crossing the gap. As they crossed the gap, some of them ripped away some particles within the gap. New particles entered the gap again. As the field was increased further after passing a voltage of  $20V$ , more and more particles were ripped away. The voltage was simply too high for allowing chain formations, and the particles were also too large. A movie showing this result is added in App.C It is difficult to see if there was chain formations or just accumulation of dipoles within the electrode gap. The sample should have been prepared in such a way that only small particles participated, and a less amount of particles should be present in the sample examined. In other words, the sample preparation should be adjusted so that a more convenient sample could be examined instead. In addition, the magnification should be larger to make it easier to observe the trigger voltage. An accurate value of the trigger voltage was therefore not found.



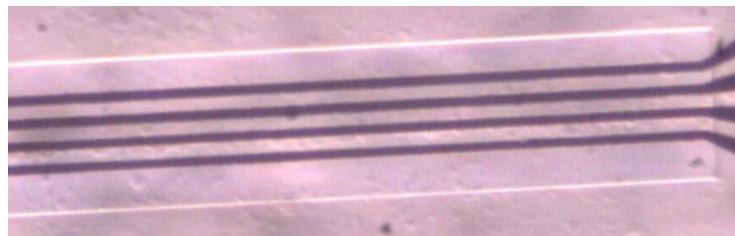
(a)



(b)



(c)



(d)



(e)

Figure 4.4: The sample's reaction to an increasing electric field. a)5V, b)10V, c)15V, d)20V and e) > 20V. The voltage was applied over the two lowest microbands. One can see that the laponite particles assemble within the lowest gap as the applied voltage is increased.

### 4.3 Different Concentrations and Sample Preparation

From section 4.1 there were indications of an ER-effect in the sample of  $1\text{vol}\%$  of modified laponite in turpentine. The other samples did not show a significant reaction to the electric field. But, one of the disadvantages of this sample was that there were too many particles present. As for the trigger voltage, where this type of sample also was used, the particles assembled within the gap, but the external ones were so accelerated that they detached the ones within the gap on their way. It would be convenient if the particles were as small as possible, and the amount of particles should be at a minimum so that we don't just fill the gap. It is desirable to find a convenient method to prepare the samples so that one could avoid aggregation. The purpose of this experiment was to try different preparation methods of the sample, like centrifugation and filtration, to see which method that lead to a well defined reaction.

From section 4.1 it is noted that no samples with silicon oil had given a response close to the ER-effect. It is also interesting to see that no samples with laponite RD gave an ER-response. Maybe the fraction of solid material to liquid was the reason, or maybe the sample should have been prepared differently than just to be left for sedimentation. In this section a set of four different concentrations of laponite RD in silicon oil were examined. The samples were centrifuged in 15 min at  $3000\text{rpm}$  before use and, as before, the droplet of interest was taken from the supernatant phase. The concentrations were  $0.5\text{vol}\%$ ,  $1\text{vol}\%$ ,  $2\text{vol}\%$  and  $3\text{vol}\%$ .

First, the two samples with the lowest concentration ( $0.5\text{vol}\%$  and  $1\text{vol}\%$ ) were prepared and examined. The samples with the higher concentration were made with the other two as a basis. The sample of  $0.5\text{vol}\%$  of laponite RD consisted of  $0.1\text{g}$  of laponite and  $20\text{ml}$  of liquid. By adding  $0.3\text{g}$  of laponite to this solution there was a total of  $0.4\text{g}$  of laponite in  $20\text{ml}$  of liquid resulting in a  $2\text{vol}\%$  sample. For the initial sample of  $1\text{vol}\%$  there was added  $0.4\text{g}$  of laponite RD after examination, giving a total of  $0.6\text{g}$  of laponite RD in  $20\text{ml}$  of liquid. This resulted in a  $3\text{vol}\%$  sample. After mixing these samples they were put in the centrifuge again. A total volume of  $0.2\mu\text{l}$  had been removed from the initial sample for use in two sets of experiments. This was regarded as negligible compared to the total volume of the sample. The uncertainty of the weight and the volume measuring cup was considered to be more significant than this fraction of volume extraction. The initial solid volume concentration was therefore regarded as reliable. The same was done for turpentine and laponite RD. But, here the volume concentration was  $0.5\text{vol}\%$  and  $2\text{vol}\%$  because the initial sample of  $1\text{vol}\%$  got contaminated. Foam arised on top of the sample after shaking it. The other sample with turpentine did not behave like this so the sample holder of the polluted sample was probably not clean enough.

For all the experiments described in this section a voltage of  $20\text{V}$  was applied. This voltage was applied over the lowest gap, i.e. the spacing between the two bottom multibands. The PixelLink camera was used to record the possible reaction of the sample when the field was applied.



### 4.3.1 Silicon Oil and Laponite RD

The samples were examined after centrifugation and the suspicion that none of these would give an ER-effect was confirmed. Every sample was tested twice, all giving the same result independent of the volume fraction of laponite. There was occasional movement within some of the samples, but this was seemingly independent of the electric field. Just to ensure that there actually was a field present, and no shortcuts within the circuit, the contact between the electrode and the wires was tested with a multimeter. The applied voltage was registered which proved that there in fact was an electric field present even though the particles did not seem to react to it. There is no point in showing two almost identical pictures for every sample tested. But as an example two pictures are given in fig.4.5 which shows the situation before and after the field was applied for the 1vol% sample. As can be seen from this figure, there was no visible

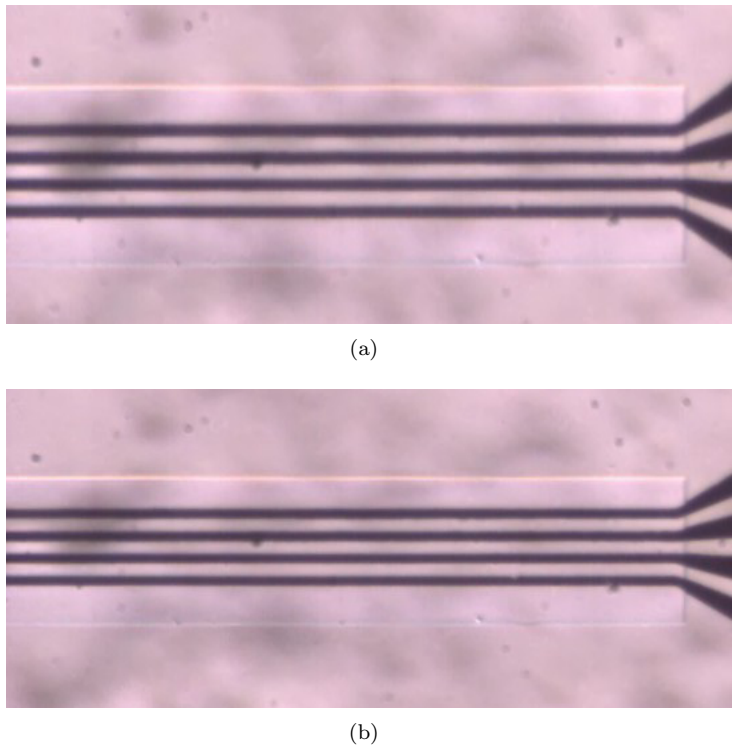
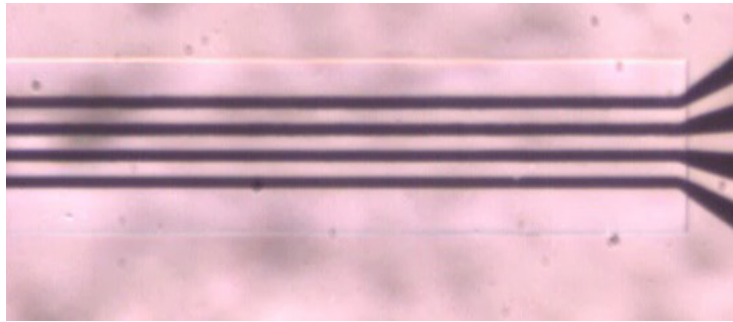


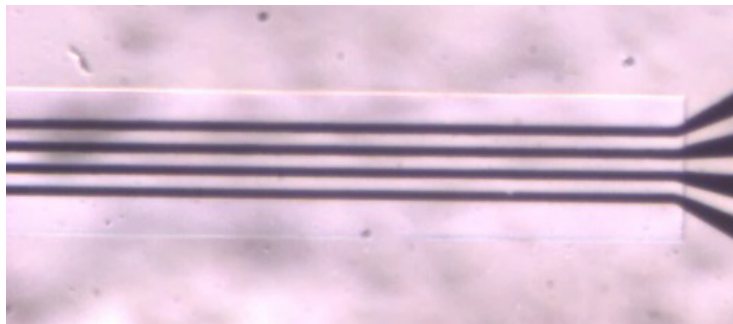
Figure 4.5: The centrifuged sample of silicon oil and laponite RD before (a) and after (b) the electric field has been applied. The voltage of 20V is applied over the two lowest microbands. There is no ER-effect here.

change within the sample after the field was applied. The larger, dark dots are impurities on the camera lens and should be discarded. But since there is no movement whatsoever, they play the same role as the sample particles. Even though the highest concentration was six times larger than the lowest one, there was no significant change in the amount of particles present in the sample. This can be seen by comparing pictures with 0.5vol% laponite and 3vol% laponite as shown in fig.4.6. This implies that centrifugating the samples lead to a change

in the effective concentration of laponite particles. Perhaps the centrifugation time and/or the centrifugation speed should be lowered to prevent this lack of particles in the supernatant phase.



(a)



(b)

Figure 4.6: Two different concentrations of laponite RD in silicon oil:  $0.5\text{vol}\%$ (a) and  $3\text{vol}\%$ (b). The pictures are taken before the electric field is applied. The voltage of  $20\text{V}$  is applied over the two lowest micro bands. There is no ER-effect here.

### Filtrated Samples

Two different concentrations of laponite RD in silicon oil were examined. One with  $0.5\text{vol}\%$  and the other with  $1\text{vol}\%$  of laponite. Neither one of these gave a significant response. The main problem with these samples was the low amount of particles present. A picture of this is shown in fig.4.7. The sample in this figure is the one with the highest volume fraction of laponite RD.

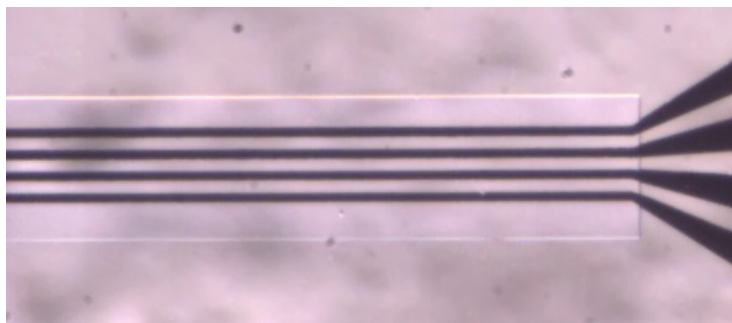


Figure 4.7: A filtrated sample of  $1\text{vol}\%$  laponite RD in silicon after application of the electric field. The voltage of  $20\text{V}$  was applied over the two lowest microbands. There was no ER-effect here.

### 4.3.2 Turpentine and Laponite RD

Two centrifugated samples of  $0.5\text{vol}\%$  and  $2\text{vol}\%$  were examined. Once again there were no observable effect within the two samples when the electric field was applied. This is because there were too few particles within the sample. If these particles are too far away from the electrode gap, they would barely be affected by the electric field within this gap. Practically no particles could be seen within the area of which there are multibands. It is therefore impossible to have dipole-dipole interaction which could lead to chain formations.

### 4.3.3 Modified Laponite

The access to the modified laponite was limited, so the initial sample of  $1\text{vol}\%$  of modified laponite in turpentine used in section 4.1 was also used here. It was first shaken and then centrifugated at a speed of  $3000\text{rpm}$  in  $15\text{min}$ . The sample was taken from the supernatant phase. There was no observable ER-effect in this sample, and the reason was probably the same as for all the other centrifugated samples, there were too few particles present close to the electrode gap where the field was applied. After the examination of the centrifugated sample, it was shaken once more before it was filtrated with a  $0.2\mu\text{m}$  filter. The amount of particles within the sample was now severely reduced. It was impossible to see any movement of laponite particles within the field. Fig.4.8 shows the filtrated sample after the electric field has been applied. There was no aggregation or chain formations, but there was a beautiful rainbow present in the upper part of the picture. The concentration of modified laponite was too low which lead to fewer particles passing through the filter. Hence the initial particle concentration should probably be increased before filtration.

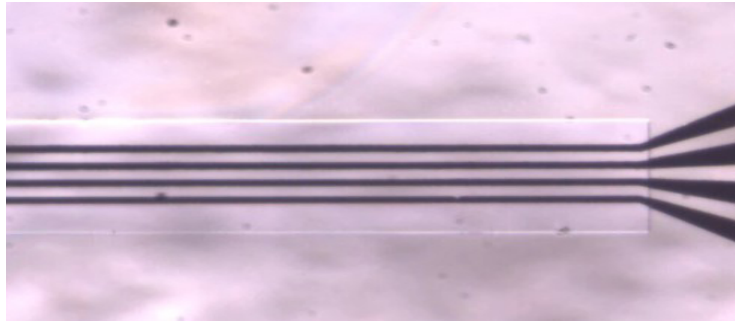


Figure 4.8: Filtrated sample of 1vol% modified laponite in turpentine after the field has been applied. The voltage of 20V was applied over the two lowest microbands. There is no ER-effect here.

#### 4.3.4 Brief Overview

Different types of samples have been prepared either by centrifugation or by filtration. None of these gave any results concerning the ER-effect. The main reason for this was thought to be the amount of laponite particles present within, or close to, the gap where the electric field was applied. For centrifugated silicon oil and laponite RD samples, four different concentrations have been tested, all with negative results. They all had too few particles present within the electric field, or in the sample droplet in general. The same conclusion could be made for the filtrated samples with the same constituents and the turpentine samples containing laponite RD particles. The same could also be said regarding the filtrated sample and the centrifugated sample of modified laponite and turpentine.

## Chapter 5

# Concluding Remarks

In order to be able to perform experiments with the  $1\mu m$  gap electrode, there had to be some research and investigation of different types of samples. This was done with the  $10\mu m$  gap electrode and observed through the optical microscope. As explained before, the  $1\mu m$  gap electrode could not be examined through the optical microscope used here. For such small systems it would be more convenient to use an Atomic Force Microscope(AFM). This requires some additional properties of the ER-solvent, leading to turpentine as a possible functional solvent since it evaporates around room temperature. The chains can therefore be investigated after the field has been applied and the turpentine fluid has evaporated. This report has presented a few experiments performed to see if turpentine is suitable as an ER-solvent and which concentration and sample preparation leads to an ideal sample where the laponite particles form chains, and not simply fill the whole gap with aggregates.

The experiments presented in Ch.4 have given some interesting results, which will be discussed in this chapter. These experiments showed that all the samples that contained silicon oil, or laponite RD, did not give an ER-effect when the electric field was applied. It is important to note that the samples who either was centrifugated or filtrated had a different problem concerning the concentration of laponite particles. To have an ER-effect there must be at least some particles within the gap. But, for some videos with such samples, one can see some movement of one or more particles. These particles should at least react to the applied field since they are dipoles. Therefore these results are still interesting, and this outcome is to be discussed here.

The only sample that gave a promising result concerning the ER-effect, was the solution of modified laponite and turpentine. The pictures revealing the response of modified laponite in turpentine(fig.4.3) indicate that there might be an ER-effect there, but the picture quality and the maximum magnification needs to be improved in order to confirm if there are chain formations within the gap.

It is interesting to see that the supposedly perfect ER-solvent, silicon oil, did not show any sign of an electrorheological response. It is well known that a solution of silicon oil and laponite is an ER-fluid[9][5], so this is not an attempt to deprive it from the electrorheological property. The main difference of the previous detected ER-effect, and the attempt to detect it here, is the gap which the sample is placed within. This is a micro scale study where a gap of  $10\mu m$  has

been used, while the previous experiments referred to here have used a gap of  $\geq 1\text{mm}$ . Different sample preparation methods like sedimentation, centrifugation or filtration have been tested out, all with the same negative result. The same goes for different concentrations of laponite (in silicon oil), ranging from  $0.5\text{vol}\%$  to  $3\text{vol}\%$ . By talking to a PhD student at IFE(Norway) named Eldrid Svåsand<sup>1</sup>, who also uses an electrode of  $10\mu\text{m}$  gap, it was revealed that also her samples with silicon oil did not show an electrorheological response. She is now working with isopropanol as a solvent and this has resulted in chain formations.

Although there are several combinations of sample preparations and laponite concentrations to be tested out in order to confirm that silicon oil does not work in such small gaps as here, there seems to be a tendency that silicon oil is not a convenient ER-solvent for this type of systems. One of the main differences between silicon oil and turpentine is the viscosity. Turpentine has a viscosity closer to water, i.e. much lower viscosity than oils. Laponite particles within a droplet of silicon oil will have more difficulty moving in any direction (compared to turpentine) due to the resistance from the oil. In other words, an increased viscosity will result in less mobility of movement for the laponite particles. The silicate platelets are aligned to the electric field as shown in fig.5.1.

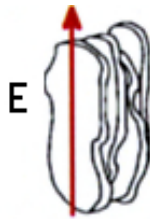


Figure 5.1: Alignment of Laponite platelets in an applied electric field,  $E$  [9].

Some of the laponite platelets end up within the  $10\mu\text{m}$  gap which has a height of only  $0.1\mu\text{m}$ [8]. One can compare the height of the multi bands with the typical diameter of the laponite platelets( $\approx 30\text{nm}$ , see Ch.2.2). In this case there is a factor of 10 in difference. For the mentioned electrodes used earlier, the height of the electrodes is in the order of millimeters. This is a factor of  $10^5$  larger than the typical diameter of the laponite sheets. In other words, there is more room for the ER-fluid within the larger gaps than it is here with the  $0.1\mu\text{m}$  high,  $10\mu\text{m}$  wide gap. When placing the droplet over the electrode gap used here, it will cover more than all the four multi bands even when using the smallest volume possible( $0.1\mu\text{l}$ ), which is what was used here. The maximum height of the droplet is larger than the height of the multi bands (this is seen when placing the droplet on top of the multi bands). Hence, some of the particles will be in the upper part of the droplet, further away from the multi bands, while others will be closer to, or within, the gap. When applying the electric field, it will be a homogeneous electric field within the two multi bands. Above these multi bands the electric field will be severely reduced.

Since the silicon droplet of laponite particles is placed over all of the multi bands, only those within this gap is accelerated and polarized by the electric field. If, for example, a laponite particle is positioned above the gap, it has

<sup>1</sup>eldrid.svaasand@ifef.no

to move down within the two multibands to be able to form chains with other dipoles. This will require a larger force than to only accelerate the particles within the gap because the distance from the homogeneous electric field is larger. One can imagine that for turpentine it is easier for the laponite particles to move within the droplet because of the gravity, and therefore they can also end up between the multibands. While, for laponite particles within a silicon droplet, it is more difficult because of the viscosity. Those who have a position above the multibands will in addition be less affected by the electric field. An example of a sample droplet on top of the four multibands is shown in fig.5.2

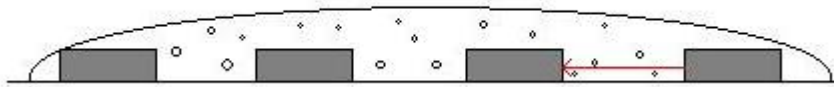


Figure 5.2: A sample droplet placed upon four multibands where the applied electric field is represented by the red arrow.

If it is the viscosity that is the problem for silicon in this case, then this could be investigated further by using solvents with different viscosity, say between turpentine and silicon oil. The viscosity of the silicon oil can only make it more force-requiring to make chain formations, but it will not make it impossible. In other words, by applying a large enough force, i.e. a high enough voltage, the particles should eventually align within the field. This is if the viscosity of the oil is a dominant reason for no chain formation. This has not been tested out in this report.

There are of course also other factors that can contribute to a lack of ER-response when using silicon oil in such small gaps. Since the conductivity of silicon oil is small but non-zero, there will be a small current within the electric field. This is also the case for turpentine. It is said that an increasing current density can lead to an increased ER-effect depending on the relaxation frequency of the fluid [30]. Maybe this is a factor that makes turpentine a better ER-solvent than silicon oil. The current created when the voltage is applied should be small to keep the electrode intact and working. If the current is too high, the multibands can get burned. To control this, it is possible to include an instrument that can measure a small current to the circuit. In this way one can measure if, or how, the current influence the behavior of the laponite particles.

In short, there are several factors that can lead to turpentine showing a more promising reaction resembling the ER-effect, than silicon oil has done so far. It can be the viscosity difference. Maybe a viscosity closer to water is more convenient in such small gaps. This can be confirmed or disproved by for example increasing the electric field further than what has been done here. This will require a different power supply. It can also be other properties like a difference in the current density as described above. Or, it can be a combination of these and other factors not described here.

Laponite RD dissolved in both solvents used here, also had a tendency not to give an ER-response. The induced dipoles would align to the field, and aggregate if possible, but there are no chain formations to be seen with this type of laponite. The main difference between the modified laponite and laponite RD is that the modified laponite has been surface treated with quaternary ammonium chains which results in an increased solubility. In other words, the modified laponite particles has a less tendency to aggregate than laponite RD particles. Since the electric field is applied over a small gap, it is definitely convenient with small aggregates to be able to see the particles movement. They can not be too small either, because that can weaken the ER-effect(see Ch.2.1).

**The preparation** method of the samples can be utterly improved. For example, since the amount of particles present in the centrifugated samples is too small, it might be an idea to try to centrifuge them at a lower velocity, or within a shorter time. If the acceleration is too high, it will only make too many of the particles end up at the bottom of the sample holder. This might be the reason that all samples, regardless of their concentration, had too few particles within the supernatant phase. There are also other preparation methods that can be tested in order to find an ideal one where the laponite particles have a more convenient size. For example the laponite aggregates can be grained into smaller pieces in order to decrease their size. After graining it could for example be filtrated or put in a centrifuge. Adding a small weight percent of water is also known to increase the ER-response[11], and the effect of this could be examined in a later occasion. Filtrating the samples also resulted in too few laponite particles within the supernatant phase. One could try to utterly increase the volume concentration of laponite to increase the amount of small particles present. Especially when using filtration, only these have a chance to participate in the sample droplet. Filtration probably also lowered the net concentration of particles. As can be seen, there are several preparation methods and combinations to be tested out, and only a small part of them have already been tested in this report.

One of the problems with the equipment used here, was that the captured video did not have a good enough resolution, and the magnification should be larger. This can be achieved by adding a lens of 10x-20x magnification instead of the extra 2x magnification lens used here. This might lower the picture quality due to scattering, so when buying such a large extra lens one should take this into consideration. A couple of lenses from Zeiss are of interest(20x magnification) and the investigation of such a lens will be continued later. The viewing point has also been the same for all experiments done here. The sample has been investigated by sending light through it from below. Maybe a light source only from above can improve the picture quality.



## 5.1 Further Plans

A further investigation of the ER-properties of turpentine (and maybe silicon) will be continued during the Master Thesis. Laponite is still the main ingredient, while the solvent may change if necessary. It would for example be interesting to try isopropanol as a solvent since the PhD-student Eldrid Svåsand got chain formations with this solvent. The disadvantage of this solvent is that it has a higher viscosity than turpentine. Maybe it is too large compared to laponite. The goal is to try to make chains within the  $1\mu m$  gap electrode and investigate it with an AFM. To be able to do this it is necessary to find the optimized sample that behaves as an ER-fluid when placed in such small gaps, and which does not fill the gap with aggregates of laponite. So far, only the modified laponite has shown a promising response and it would be interesting to continue the investigation of this type of laponite. The search for a larger magnification lens for the optical microscope will continue. Also the investigation with the  $10\mu m$  gap electrode will continue, both as a preparation for the electrode of less gap, and as a single source of information about how the ER-fluid behaves when varying different parameters. This is already started with the experiments presented here, and there are a lot of parameters such as concentration and sample preparation that can be varied in order to be able to extract more information about the sample properties.

## Chapter 6

# Summary

This report has given a theoretical introduction to electrorheology, and presented some experiments carried out in order to learn more about the electrorheological behavior of laponite particles in a micro scale system. The micro scale system used here was an electrode with four microbands with a spacing of  $10\mu m$ . The main constituent of the ER-fluid, was synthetic nano-silicate particles, named Laponite. There were two different types of laponite used here; Laponite RD and a modified type of laponite. The modified laponite had been surface treated with quaternary ammonium chains in order to make the particles dissolve more easily. Two different solvents were used, silicon oil and turpentine. Turpentine was used because it could be a suitable solvent used for AFM studies due to its relatively low boiling temperature. There is an electrode with a gap of  $1\mu m$  that is thought to be used for this at a later time. First it was necessary to find out if turpentine was a suitable ER-solvent for laponite. Laponite RD did not show any sign of an ER-response. Neither did the silicon oil with any of the synthetic clay particles. Changing concentration and/or preparation method did not make a difference. But, together with the modified laponite, there was a significant reaction indicating that there might be an ER-response. The applied voltage was  $20V$  and the volume concentration of modified laponite was 1%. It is therefore expected that turpentine might be a good ER-solvent for modified laponite particles.

Some of the samples were either centrifugated or filtrated. The particle volume concentration was from 0.5% to 3%. None of these samples had enough particles within the electrode gap after treatment to give an ER-response. There are other sample preparation methods and combinations to explore in order to find the best suited sample for such small gaps as used here. The point is that the size and number of laponite particles should be calibrated so that they don't fill the gap with aggregates. A provoking thought coming from these experiments was that even if there was a laponite particle seemingly within the gap, the reaction to it was negligible.

A PhD. student at IFE(Norway) named Eldrid Svåsand informed me that she never observed any ER-response from the samples with silicon oil. This was also observed here. The reason for this might be the high viscosity compared to laponite. This reduces the mobility of the laponite particles, and hinder the particles to diffuse to the bottom of the sample droplet. It is mainly this part of the droplet that is within the homogeneous electric field applied between

the two microbands. The height of these microbands also determine how large fraction of the sample droplet that is within the electric field. The height is only  $1000\text{\AA}$ . If the viscosity is the main problem this can be confirmed by for example increasing the applied field until there is a reaction. This was not done here. There are also other factors that can influence the ER-response, for example can an increasing current density lead to an increased ER-response.

The plan is to continue the experimental research on this area. It is interesting to continue the search for an ideal sample for this system. The goal is to find such a sample and try it with the  $1\mu\text{m}$  gap electrode and investigate the chain formations with an AFM. There are several combinations of concentrations and sample preparation methods still waiting to be tested. This can be done as a continuation of this report. There is also need for a larger magnification lens in order to be able to confirm if there was chain formations.

## Appendix A

# Properties of Turpentine

This chapter presents the specifications of turpentine given from SHELL[31]. The specific turpentine used in the experiments described in this report was not bought from Shell but it was marked as pure turpentine and hence fit the specifications given in this appendix. See next page.



## Data Sheet

**Issued:**

13-May-2005

**Product Name**

# Mineral Turpentine

**Product Code****Q7249****Asia Pacific****ANZ****Product Category****White Spirits****Description**

Mineral Turpentine is a wide boiling range, medium evaporating solvent widely used in the paint industry. Mineral Turpentine conforms to Australian Standard AS 3530.

**Sales Specification**

Property	Unit	Min	Max	Method
Appearance		Cl & FFSM		Visual
Color	Saybolt	25		ASTM D156
Density @15°C	g/mL	0.800	0.820	ASTM D4052
Copper Corrosion			1	ASTM D130
Distillation, IBP	°C	145	155	ASTM D86
Distillation, 10%v	°C	150	160	ASTM D86
Distillation, 50%v	°C	160	170	ASTM D86
Distillation, 95%v	°C	180	190	ASTM D86
Distillation, FBP	°C		200	ASTM D86
Flash Point (Abel)	°C	31		IP 170
Aniline Point	°C	20	25	ASTM D611 (4)
Aniline Point (85-95%v fraction)	°C		36	ASTM D611 (4)

(1) Guaranteed, (2) Typical, (3) Report Only, (4) Guaranteed spec with typical result

<b>Typical Properties</b>	<b>Property</b>	<b>Unit</b>	<b>Method</b>	<b>Value</b>
	Color	Saybolt	ASTM D156	+29
	Odor	-	-	Marketable
	Density @15°C	kg/L	ASTM D4052	0.814
	Copper Corrosion (3hr @100°C)	-	ASTM D130	1
	Non Volatile Matter	mg/100mL	ASTM D1353	4
	Distillation, IBP	°C	ASTM D86	149
	Distillation, 10%v	°C	ASTM D86	154
	Distillation, 50%v	°C	ASTM D86	165
	Distillation, 95%v	°C	ASTM D86	185
	Distillation, FBP	°C	ASTM D86	195
	Flash Point	°C	IP 170	35
	Aniline Point (M=Mixed)	°C	ASTM D611	23
	Aniline Point (85-95%v fraction)	°C	ASTM D611	27
	Electrical Conductivity @23°C	pS/m	ASTM D2624	400
<b>Test Methods</b>	<p>Copies of copyrighted test methods can be obtained from the issuing organisations:</p> <p>American Society for Testing and Materials (ASTM) : <a href="http://www.astm.org">www.astm.org</a>  Energy Institute (IP) : <a href="http://www.energyinst.org.uk">www.energyinst.org.uk</a>  Deutsches Institut für Normung (DIN) : <a href="http://www.din.de">www.din.de</a></p> <p>Shell Method Series (SMS) methods are issued by Shell International Chemicals B.V., Shell Research and Technology Centre, Amsterdam, The Netherlands. Copies of SMS can be obtained through your local Shell Chemicals company.</p> <p>For routine quality control analyses, local test methods may be applied that are different from those mentioned in this datasheet. Such methods have been validated and can be obtained through your local Shell Chemicals company.</p>			
<b>Quality</b>	Mineral Turpentine does not contain detectable quantities of polycyclic aromatics, heavy metals or chlorinated compounds.			
<b>Storage and Handling</b>	Provided proper storage and handling precautions are taken we would expect Mineral Turpentine to be technically stable for at least 12 months. For detailed advice on Storage and Handling please refer to the Material Safety Data Sheet on <a href="http://www.shell.com/che">www.shell.com/che</a>			
<b>Hazard Information</b>	For detailed Hazard Information please refer to the Material Safety Data Sheet on <a href="http://www.shell.com/chemicals">www.shell.com/chemicals</a> .			

## Appendix B

# Laponite RD

This chapter includes the specifications for laponite RD given by the supplier i.e. Rockwood [32]. See next page.



Southern Clay Products, Inc.  
1212 Church Street  
Gonzales, TX 78629  
Phone: 800-324-2891  
Fax: 830-672-1903  
www.scprod.com

## Laponite RD

The Clear Leader

### Description

LAPONITE RD is a synthetic layered silicate. It is insoluble in water but hydrates and swells to give clear and colorless colloidal dispersions. At concentrations of 2% or greater in water, highly thixotropic gels can be produced.

### Application

Used for imparting a shear sensitive structure to a wide range of waterborne formulations. These include household and industrial surface coatings, cleansers, ceramic glazes agrochemical, oilfield and horticultural products.

### Typical Characteristic

Appearance free flowing white powder  
Bulk Density 1000 kg/m<sup>3</sup>  
Surface Area (BET) 370 m<sup>2</sup>/g  
pH (2% suspension) 9.8

Chemical Composition (dry basis)	
SiO <sub>2</sub>	59.5%
MgO	27.5%
Li <sub>2</sub> O	0.8%
Na <sub>2</sub> O	2.8%
Loss on Ignition 8.2%	

### General Specifications

Gel strength	22g min
Sieve Analysis	2% Max >250 microns
Free Moisture	10% Max

Rockwood QA Test Code  
ELP-L-1H  
ELP-L-6A  
ELP-L-5A

Specifications can be agreed to meet individual requirements.



## **Storage**

Laponite is hygroscopic and should be stored under dry conditions.

For additional information or technical assistance contact Southern Clay Products, Inc. toll free at 800-324-2891.

Disclaimer of Warranty: The information presented herein is believed to be accurate but is not to be taken as a warranty, guarantee, or representation for which we assume legal responsibility. This information does not grant permission, license, or any rights or recommendations to practice any form of proprietary intellectual property without obtaining the appropriate license or grant from the property owner. The information is offered solely for your consideration, investigation and verification, but you must determine the suitability of the product for your specific application. The purchaser assumes all risk of use of handling the material, including but not limited to transferring the material within purchaser's facilities, using the material in applications specified by the purchaser and handling any product which includes the material, whether or not in accordance with any statements made herein.

## Appendix C

# Videos of Experimental Results.

There is a dvd following this report. This dvd contains two videos. One is the recorded movie of 1vol% modified laponite in turpentine where an electric field of 20V is applied over the two lowest multibands. The experimental result is described further in Ch.4. The videofile is named 2511\_turpmodlap3. It is advised that this file is copied to a personal computer. It is a severely large and uncompressed file, and it is difficult to read it continuously due to the large amount of information. When opening this file it is probably necessary to run it a few times before there is a continuous movie without delays.

The other video is from the trigger voltage experiment. The same sample is used and further details are given in Ch.4. This movie file is called test2911, and the size is much smaller than the other movie. The applied voltage as a function of time is shown in table C.1.

Table C.1: Table of applied voltage as a function of time.

$t$	$V$
(s)	(V)
10	5
20	10
30	15
40	20

# Bibliography

- [1] Tian Hao. Electrorheological fluids. *Adv. Mater.*, 13, No. 24, December 17, 2001.
- [2] Tian Hao, Akiko Kawai, and Fumikazu Ikazaki. Mechanism of the electrorheological effect: Evidence from the conductive, dielectric and surface characteristics of water-free electrorheological fluids. *Langmuir* 14, p.1256-1262, 1998.
- [3] University of Arkansas. Chapter 8: Electric dipoles. <http://www.uark.edu/depts/physinfo/up2/guide/mat-chp-top-electricdipolecap.pdf>, Last visited Dec.18, 2006.
- [4] Jon Otto Fossum. Some thoughts about the future of complex fluids like clays. [http://folk.ntnu.no/fossumj/cpx/terminator\\\_e.html](http://folk.ntnu.no/fossumj/cpx/terminator\_e.html), Last visited Dec.18, 2006.
- [5] J. O. Fossum, Y. Méheust, K. P. S. Parmar, and D. M. Fonseca K. D. Knudsen K. J. Må løy. Intercalation-enhanced electric polarization and chain formation of nano-layered particles. *Europhysics letters* 74, p.438-444, 2006.
- [6] S. A. Solin. Clays and clay intercalation compounds: Properties and physical phenomena. *Annu. Rev. Mater. Sci.*(27), p.89-115, 1997.
- [7] Norma Negrete-Herrera, Jean-Luc Putaux, and Elodie Bourgeat-Lami. Synthesis of polymer/laponite nanocomposite latex particles via emulsion polymerization using silylated and cation-exchanged laponite clay platelets. *Progress in Solid State Chemistry* 34,p.121-137, 2006.
- [8] Inc. ABTECH scientific. Laboratory products. <http://www.abtechsci.com/labproducts.html>, Last visited Dec.18, 2006.
- [9] Kanak P.S Parmar. *Oil dispersions of nano-layered silicates in an external electric field: An experimental study*. August 2006.
- [10] W.M. Winslow. Induced fibrillation of suspensions. *Journal of Applied Physics* 20 p.1137-1141, 1949.
- [11] Alice P. Gast and Charles F. Zukoski. Electrorheological fluids as colloidal suspensions. *Advances in Colloid and Interface Science*, Vol. 30, p.153-202, 1989.

- [12] Tian Hao. Electrorheological suspensions. *Advances in colloid and interface science*, Vol.97 p.1-35, 2002.
- [13] Weijia Wen, Xianxiang Huang, and Ping Sheng. Particle size scaling of the giant electrorheological effect. *Applied Physics Letters*, Vol.85 N.2, p.299-301, 2004.
- [14] Nicos Makris, Scott A Burton, and Douglas P Taylor. Electrorheological damper with annular ducts for seismic protection applications. *Smart Mater. Struct.* 5 p.551-564., 1996.
- [15] Keith Yates Design Group. Glossary. <http://www.keithyates.com/glossary.htm#anchor517411>, Last visited Dec. 18, 2006.
- [16] Young-Min Han and Seung-Bok Choi. Force-feedback control of a spherical haptic device featuring an electrorheological fluid. *Smart Mater. Struct.* 15, p.1438-1446, 2006.
- [17] R. Nava, M. A. Ponce, L. Rejon S. Viquez, and V. M. Castano. Response time and viscosity of electrorheological fluids. *Smart Mater. Struct.* 6, p.67-75, 1997.
- [18] Wolfram Research. Electrorheological fluid. <http://scienceworld.wolfram.com/physics/ElectrorheologicalFluid.html>, Last visited Dec.18, 2006.
- [19] Seth Fraden Brandeis University Ujihta Dassanayake. Structure of electrorheological fluids. <http://www.elsie.brandeis.edu/er/index.html>, Last visited Dec.18, 2006.
- [20] L.C. Davis. Polarization forces and conductivity effects in electrorheological fluids. *J. Appl. Phys.* 72(4), p.1334-1340, 1992.
- [21] J.N. Foule, P.Atten, and N. Felici. Macroscopic model of interaction between particles in an electrorheological fluid. *Journal of Electrostatics* 33, p.103-112, 1994.
- [22] Jon Otto Fossum. Physical phenomena in clays. *Physica A* 270, p.270-277, 1999.
- [23] Norma Negrete-Herrera, Jean-Luc Putaux, and Elodie Bourgeat-Lami. Synthesis of polymer/laponite nanocomposite latex particles via emulsion polymerization using silylated and cation-exchanged laponite clay platelets. *Solid State Chemistry* (34), p.121-137, 2006.
- [24] A. Mourchid, E. Lecolier, H. Van Damme, and P. Levitz. On viscoelastic, birefringent, and swelling properties of laponite clay suspensions: Revisited phase diagram. *Langmuir*, 14, 1998.
- [25] Kevin J. Mutch, Vasileios Koutsos, and Philip J.Camp. Deposition of magnetic colloidal particles on graphite and mica surfaces driven by solvent evaporation. *Langmuir* 22, p.5611-5616, 2006.
- [26] Wikipedia. Turpentine. <http://en.wikipedia.org/w/index.php?title=Turpentine&oldid=84727214>, October 2006.

- [27] Yves Méheust, Kenneth Dahl Knudsen, and Jon Otto Fossum. Inferring orientation distributions in anisotropic powders of nano-layered crystallites from a single two-dimensional waxes image. *Journal of Applied Crystallography*, Vol.39 p.661-670, 2006.
- [28] Carl-Roth. <http://www.carl-roth.de>, Last visited Dec.18, 2006.
- [29] X. Tang, C. Wu, and H. Conrad. On the conductivity model for the electrorheological response of dielectric particles with a conducting film. *Appl. Phys.*, Vol.78 (6), 1995.
- [30] F. Ikazaki, A. Kawai, K. Uchida, T. Kawakami, K. Edamura, K. Sakurai, H. Anzai, and Y. Asako. Mechanisms of electrorheology: the effect of the dielectric property. *Appl.Phys.(31)*, p.336-347, 1998.
- [31] Shell. Mineral turpentine. [http://www.shellchemicals.com/chemicals/pdf/solvents/hydrocarbon/white\\\_spirits/mineral\\\_turpentine\\\_ap\\\_297.pdf?section=our\\\_products](http://www.shellchemicals.com/chemicals/pdf/solvents/hydrocarbon/white\_spirits/mineral\_turpentine\_ap\_297.pdf?section=our\_products), Last visited Dec.18, 2006.
- [32] Rockwood Additives Ltd. Product bulletins. [http://www.rockwoodadditives.com/product\\\_bulletins.asp](http://www.rockwoodadditives.com/product\_bulletins.asp), Last visited Dec.18, 2006.