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# **Characterization and performance of electrorheological fluids based on pine oils**

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## Abstract

The purpose of this work is to study the characteristics and performance of pine oil and its ester as a base fluid material for electrorheological fluids. Here, all the tested fluids had a relatively low concentration level of between 5–15% of weight. As an application for rotary machines, the electrorheological strength and phenomena were studied for keeping the working fluid in a steady position while the machine is not working.

The objective of this basic study is to give an introduction to the electrorheological fluids based on polyaniline particles and pine oil and to measure their dependencies on changes in the applied external electric field, temperature, shear rate, dynamic viscosity and concentration, and to study the influence of grinding the particles.

Based upon the results of the investigations, the following can be concluded in the case of electrorheological fluids made of polyaniline and pine oil or its ester, treated with hexane, at temperatures between 20–60°C, shear rate 40–490 1/min, electric field strength 0.5–3.5 kV/mm:

1. An increase in electric field through the fluid increases the electrorheological strength of the fluid if the concentration level is more than 5% of weight.
2. If the fluid's concentration is 5% of weight or less, the fluid does not express electrorheological phenomena.
3. In similar conditions, temperature has no or very little effect on the electrorheological phenomena.

4. The relative change in shear rate has only a small effect on the electrorheological effectiveness of the fluid if the concentration is 15% of weight or less.
5. Grinding decreases the electrorheological strength of the electrorheological fluids based on pine oils.
6. The pine oil ester is more effective as a base oil for an electrorheological fluid if the effectiveness is measured purely on the basis of maximum shear strength versus shear rate.
7. The basic idea of making an ER fluid non-hydrous and with a low concentration level was found successful, an average of over 20% increase in viscosity with a sufficient basic level of viscosity, especially if the particle concentration was 10% of weight or above and if pine oil ester was used as the carrier fluid.

# Preface

This work was carried out in the institute of Manufacturing Technology at the Technical Research Centre of Finland and in the Laboratory of Machine Design at the University of Oulu between 1996 and 1999.

I would like to express my gratitude to the Ella and Georg Ehrnrooth Foundation and to the Tekniikan Edistämissäätiö for their financial support and to VTT Manufacturing Technology for the authorization to do this work.

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Otaniemi, 18 March, 1999

Kimmo K. Mäkelä

# Contents

<b>Abstract</b> .....	<b>3</b>
<b>Preface</b> .....	<b>5</b>
<b>List of symbols</b> .....	<b>8</b>
<b>1. Introduction</b> .....	<b>9</b>
<b>2. Electrorheological fluids</b> .....	<b>14</b>
2.1 Electrorheological phenomena .....	14
2.2 Rheology .....	15
2.3 The rheology of electrorheological fluids.....	16
2.4 Electrorheological fluids .....	21
2.4.1 <i>Particles</i> .....	22
2.4.2 <i>Carrier fluids</i> .....	26
2.4.3 <i>Surfactants</i> .....	27
2.4.4 <i>Additives</i> .....	28
2.4.5 <i>ER-MR and ER-MF fluids</i> .....	30
<b>3. Test methods</b> .....	<b>31</b>
3.1 Materials.....	31
3.1.1 <i>Polyaniline</i> .....	34
3.1.2 <i>The preparation of ground particles</i> .....	35
3.1.3 <i>Fatty acid and ester carriers</i> .....	37
3.1.4 <i>Paraffinic oil carrier</i> .....	37
3.2 Experimental arrangement.....	38
<b>4. Results</b> .....	<b>41</b>
4.1 Experimental parameters .....	41
4.2 Influence of shear rate .....	42
4.3 Influence of applied external electric field .....	44
4.4 Influence of temperature.....	45
4.5 Influence of particle size and grinding .....	48
<b>5. Discussion</b> .....	<b>50</b>
<b>6. Summary and conclusions</b> .....	<b>54</b>
<b>References</b> .....	<b>57</b>

## List of symbols

$a$	Average radius of the particle
$A$	Effective area
$D$	Average distance between the centres of two particles
$E$	Electric field
$f$	Friction force
$f_d$	Dipole force between polarized particles
$F$	Force
$F_p$	Axial force between the particles
$h$	Film thickness
$k$	Boltzmann constant
$K_f$	Relative permittivity of the carrier liquid
$K_p$	Relative permittivity of the particle
$Mn$	Mason number
$N$	Number of contacts between particles in the whole system
$n$	Power-law index
$n_p$	Number of contacts per particle
$N_A$	Number of chains per unit area
$p$	Dipole moment between particles
$T$	Temperature in Kelvin
$u$	Velocity
$W_{sep}$	Force needed to separate the particles
$\beta = (K_p - K_f)/(K_p + 2K_f)$	Dielectric mismatch parameter
$\epsilon_0$	Permittivity of the free space
$\epsilon_f$	Dielectric constant of the carrier fluid
$\epsilon_p$	Dielectric constant of the particles

$\dot{\gamma}$	Shear strain rate
$\Delta$	Shear-thinning exponent
$\eta_a = \tau / \dot{\gamma}$	Apparent viscosity of the rheological fluid at the application of the electric field
$\eta_s$	Dynamic viscosity of the suspension at zero electric field
$\eta_T$	Total viscosity of the ER suspension
$\nu$	Kinematic viscosity
$\vartheta$	Sliding speed
$\phi$	Volume fraction of particles
$\chi$	Magnetic susceptibility of particles
$\theta$	Dimensionless quantity which characterizes the competition between dipolar interaction and the thermal energy
$\rho$	Density
$\tau$	Stress or strength in shear
$\tau_E$	Polarization contribution (Bingham yield stress)
$\tau_v$	Resistance to flow
$\tau_y$	Limiting yield strength



# 1. Introduction

The discovery of a small reversible change in the viscosity of glycerine, castor oil and heavy paraffin within an electric field transverse to the fluid flow was made by A. W. Duff in 1896 [1]. The formation of pearl-chains of neutral particles suspended in a medium, in a dielectric sense, differing from the particles, was observed by Priestley and Winckler in the 19th century.

Active research on electro- and magnetorheological (ER and MR) fluids started in the 1940s and resulted in the three patents of Willis M. Winslow [2,3,4]. The first patent concerning the application of ER fluids in torque transmission was granted in 1947 [2]. It was not until Winslow published the results of his investigation on how to measure the electrorheological effect with an electroviscometer in 1949 that the science of electrorheology was born [5]. The electrorheological effect is also called the Winslow-effect, after the name of the scientist who discovered it.

Both electrorheological and magnetorheological fluids consist of a carrier fluid, particles, surfactants and additives. Fluid compositions that undergo a change in apparent viscosity in the presence of a magnetic field are commonly referred to as Bingham magnetic fluids, or magnetorheological materials. Magnetorheological materials normally contain ferromagnetic or paramagnetic particles, typically larger than  $0.1\ \mu\text{m}$  but smaller than  $5\ \mu\text{m}$ , dispersed in a carrier fluid. In the presence of a magnetic field, the particles become polarized and are consequently organized into chains of particles within the fluid. The chains of particles act to increase the apparent viscosity or flow resistance of the overall material. In the absence of a magnetic field, the particles return to an unorganized or free state and the apparent viscosity or flow resistance of the overall material is correspondingly reduced. These magnetorheological materials exhibit controllable behaviour similar to that commonly observed for electrorheological materials [6]. Magnetorheological suspensions (MRS) are stable compositions of non-colloidal magnetic particles in a carrier fluid. The definition of magnetorheological fluids must be distinguished from the definition of magnetic fluids (MF), which are colloidal and do not change their viscosity under the influence of a magnetic field. Magnetic fluids, or colloidal magnetic fluids, contain particles of a smaller size ( $< 1\ \mu\text{m}$ ) than those in MR fluids. A comparison of the properties of typical ER and MR fluids is presented in Table 1.

Table 1. Comparison of properties of typical ER and MR fluids [7].

Property	ER Fluid	MR Fluid
Yield Strength (field)	2 - 5 kPa (3 - 5 kV/mm) Field limited by breakdown	50 - 100 kPa (150 - 250 kA/m) Field limited by breakdown
Viscosity (no field)	0.2 - 0.3 Pas @ 25°C	0.2 - 0.3 Pas @ 25°C
Operating Temperature	+10 - +90°C (ionic,DC) -25-+125°C(non-ionic,AC)	-40 - +150°C (limited by carrier fluid)
Current Density	2-15 mA/cm <sup>2</sup> (4kV/mm, 25°C)	can energize with permanent magnets
Specific Gravity	1 - 2.5	3 - 4
Ancillary Materials	Any (conductive surfaces)	Iron/Steel
Colour	Any, Opaque or Transparent	Brown, Black, Gray/Opaque

In order to provide a perfectly suitable ER fluid for each situation and device, the service purpose and external factors must be thoroughly investigated before designing a new fluid suspension. Features like the operating temperature, the maximum size and weight of the device, the desired yield stress and the requirements determined by a static or dynamic situation are crucial design aspects. The basic principle of behaviour of the ER particles under an applied external electric field and shear are presented in Figures 1 and 2.

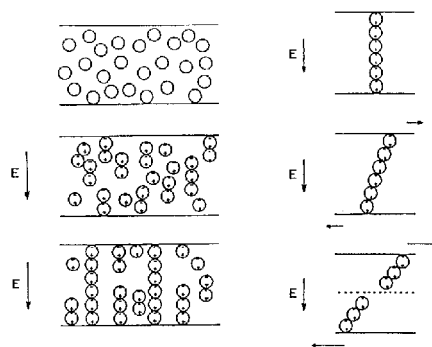


Figure 1. A picture of ER particles' behaviour in the transient process [8].

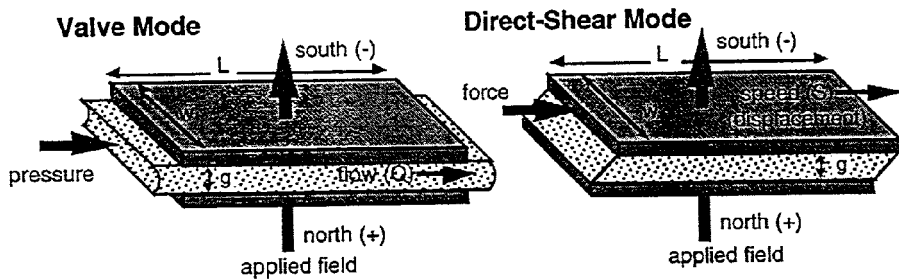


Figure 2. Basic operational modes for ER and MR fluid devices [7].

These requirements determine the particle size, the maximum volume fraction of the particles, stability characteristics, the abrasivity or the need to include surfactants or additives [9].

In electrorheological fluids, either the fluid or the particle can be the component that polarizes. The components together form a product that has the desired characteristics, which in turn fulfil the operational requirements.

The volume fraction of particles influences the yield strength of the whole suspension. The more particles in the fluid, the higher the yield strength is of the fluid. Having a maximum volume fraction of particles is not always desirable because of the effects of the suspension on the materials used in the device. In dynamic dampers, for example, the response time of the fluid and the requirement that the fluid does not cause wear of the components are much more important than the yield strength of the fluid. In clutches and rotational brakes, on the other hand, a high yield strength is crucial. In most studies, a small particle size has been found beneficial for the strength and response time of the electrorheological effect, and the tendency to cause abrasion is small [10].

Without an external electric or magnetic field, the particles are in a rotating motion inside the carrier fluid. The angular velocity and the pre-polarization

level of the particles determine how effectively the applied field induces the particles to form dipoles. The faster the dipoles regenerate, the faster the particles form chains or strings. However, although the spherical shape of the particles is good for the chain-forming speed, it is not good for the size of the contact of the particle interaction. The spherical shape of the particles also reduces the yield strength of the whole suspension [11].

When choosing the particle material, the importance of the desired electric and magnetic conductance properties and the possible abrasivity of the particles must be considered. In the case of an ER fluid, the conductive properties of the particles must never be the same as those of the carrier fluid [12].

The purpose of the surfactants and the additives is to support the ER effect, the speed of the reversal process and to increase the strength between the particles.

The surfactants are added either directly to the carrier fluid or as a coating on the surface of the particles. The gas dispersoid technique is usually used for the coating of the particles. The surfactants increase the conductivity of the particles and act as a buffer between the particles. Sometimes the surfactants act as an insulating material, but this is less usual [12]. Surfactants are added to ER suspensions for a variety of reasons [5,13,14,15,16,17,18,19] and can be used to tailor suspension properties. They are often used to promote colloidal stability, which is necessary to keep the particles from irreversibly flocculating, and to control the rheological properties in the absence of an electric field. Surfactants are also used to “activate” suspensions. Some suspensions display little or no ER activity unless a small amount of water or surfactant is added, while other suspensions exhibit a significantly enhanced response with activators present [17,18,19,20,21]. Enhancing ER activity with surfactants offers advantages over other approaches, such as adding water, which severely limits the allowable temperature range of operation, promotes corrosion, and also increases suspension conductivity and power consumption. Furthermore, additional independent variables (i.e., type and amount of surfactants) give flexibility in designing the desired properties, which is not possible by simply varying the materials of the disperse and continuous phases [22].

The process that the fluid undergoes when the electric or magnetic field is changed is the most important factor that must be understood for the further development of the fluids and devices based on these fluids.

The objective of this work is to characterize and describe the performance of electrorheological fluids based on pine oils. The work focuses on the examination of the influence of particle size, temperature and the volume fraction of particles on the rheological properties of an ER fluid based on polyaniline (PAN) and pine oil. Additionally, the influence of using a synthetic carrier fluid and PAN is examined as a comparison to the pine oil. The approach is to study these dependencies through rheological measurements of dynamic viscosity (shear strength) and shear rate.

## 2. Electrorheological fluids

### 2.1 Electrorheological phenomena

The electrorheological phenomena are based on particle polarization. Weiss and Carlson concluded that there are five recognized modes through which polarization of the particles in ER fluids can occur [23]. The most common of these modes, called electronic or magnetic polarization, arises from the small distortions that occur within the positive and negative charge distribution of atoms. Although the contribution of the electronic polarization to the overall polarization of the particle is small, it can directly influence the dielectric constant of the particles. Another contributory factor to the dielectric constant of the particles is the movement within the solid lattice of the charged atoms when they are exposed to an electric or magnetic field. This type of polarization, called atomic polarization, contributes to the dielectric constant of inorganic particles to a larger extent than for organic particles. The occurrence of a rotational polarization, called dipolar polarization, is possible if the particle contains atoms that have a permanent dipole. This type of particle orientation may play an important role in the polarization of macromolecules. A fourth type of polarization mechanism, called nomadic polarization, occurs through the movement of thermally generated charges in the particle over several lattice interstices. This type of molecular polarization can involve either the movement of electrons (“hypercronic”) or protons (“hyperprotonic”). It should be noted that the polarization effect induced by this nomadic mode can be quite large compared to both the electronic or atomic polarization modes. The final mode of polarization arises from the piling up or accumulation of charges at the interfaces between the particles, and is termed interfacial or Maxwell-Wagner polarization. In this mode, the charges, either ionic or electronic, are free to migrate from one side of a particle to the other. A bulk movement of charges of the described type leads to the creation of enormous dipole moments. Charge migration may occur through the actual bulk of the particle or along the exterior or interior surfaces. For a highly porous particle with a large interior surface area, the distinction between volumetric and surface conduction is not particularly crucial. Interfacial polarization generally occurs in non-homogenous systems where the different materials have different conductivities and the charges are free to move. From a macroscopic perspective, interfacial

polarization is difficult to distinguish from the intrinsic electronic or atomic polarization.

## 2.2 Rheology

Rheology is defined as the study of the relationship between the shear stress and shear strain for solid materials, and the relationship between the shear stress and the shear strain rate for liquids [24]. For liquids, this is called the science of fluidity. The fluidity of a material is usually expressed with curves. The basic terms in rheology are shear stress ( $\tau$ ), shear rate or shear strain rate ( $D$ ,  $s$  or  $\gamma$ ), dynamic viscosity ( $\eta$ ) and kinematic viscosity ( $\nu$ ). Shear stress can be calculated by dividing force ( $F$ ) by the effective area ( $A$ ) [25]:

$$\tau = \frac{F}{A} \quad (1)$$

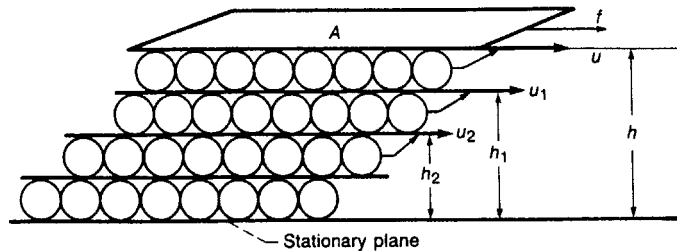


Figure 3. Physical illustration of Newton's postulate, where  $f$  is friction force,  $A$  is area,  $u$  is velocity and  $h$  is film thickness [26].

When shear stress ( $\tau$ ) and shear strain rate ( $\gamma$ ) are known, the absolute viscosity ( $\eta$ ) and the kinematic viscosity ( $\nu$ ) can be calculated [27]:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{\tau}{du / dy} \quad (2)$$

$$v = \frac{\eta}{\rho} \quad (3)$$

where  $\rho$  is density [ $\text{kg/m}^3$ ].

Equation (3) is Newton's postulate [28]. If the proportionally factor  $\eta$  is constant, i.e. independent of shear rate, the fluid is called Newtonian. However, there are fluids, such as ER fluids, which deviate from the Newtonian behaviour. For such fluids, the power law is widely used [29]:

$$\tau = K \cdot \dot{\gamma}^n \quad (4)$$

where  $K$  is the power-law coefficient and  $n$  is the power-law index.

For rheological fluids, the shear stress can also be calculated [30]:

$$\tau = \tau_E + \tau_V \quad (5)$$

where  $\tau_E$  is the effects of the applied external electric field, also called the Bingham shear stress and  $\tau_V$  is the resistance to flow without an electric field, also called the hydrodynamic or viscous component.

## 2.3 The rheology of electrorheological fluids

With electrorheological fluids' rheology, the electric field must be taken into the calculations. For example, with the shear stress from Equation (2), the force needed to separate the particles from each other, when an electric field is present, can be calculated through the polarization contribution. The shear resistance of an ER fluid reflects the combined action of polarization and viscous forces, giving for the flow stress [31]:



$$\tau = \tau_E + \eta_s \dot{\gamma} = \tau_E + \tau_V \quad (6)$$

where  $\tau_E$  is the polarization contribution, called the Bingham yield strength,  $\eta_s$  is the dynamic viscosity of the suspension at zero electric field and  $\dot{\gamma}$  is the shear strain rate [32]. Bingham materials are plastic masses that have a flow index. For Bingham plastic fluids, the Newtonian model is:

$$\tau = \tau_V + \eta \frac{du}{dy}, \text{ if } \tau > \tau_y \quad (7)$$

where  $\tau_y$  is the limiting yield stress and  $du/dy$  is the shear rate's speed gradient.

Over this index their rheological behaviour is Newtonian and under it non-Newtonian. Equation (1) expresses the plastic flow of a Bingham material. It can be developed to give the following equation for the relative viscosity  $\eta_a/\eta_s$  of an ER fluid in terms of the Mason number ( $Mn$ ), which indicates the relation between viscous force and polarization force [31]:

$$Mn = \frac{\text{Viscous force}}{\text{Polarization force}} = \frac{\eta_a \dot{\gamma}}{2\epsilon_0 K_f (\beta E)^2} = \frac{24\pi\eta_a \dot{\gamma}}{(\beta E)^2} \quad (8)$$

where  $\eta_a = \tau/\dot{\gamma}$  is the apparent viscosity of the rheological fluid at the application of the electric field,  $\epsilon_0$  the permittivity of the free space,  $K_f$  the relative permittivity of the carrier liquid,  $\beta = (K_p - K_f)/(K_p + 2K_f)$  [33] the dielectric mismatch parameter,  $K_p$  the relative permittivity of the particle, and  $E$  the electric field.

The dielectricity can be calculated through permittivity [34]:

$$K = \epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (9)$$

where  $\varepsilon_r$  is the relative permittivity, also called the suspension's total permittivity,  $\varepsilon$  is the permittivity for the whole ER suspension and  $\varepsilon_0$  is the vacuum's permittivity. The dielectricity for particles ( $K_p$ ) and for the carrier fluid ( $K_f$ ) can be calculated through the permittivity of the particles ( $\varepsilon_p$ ) and carrier fluid ( $\varepsilon_f$ ) [34]:

$$K_p = \frac{\varepsilon_p}{\varepsilon_0} \quad (10)$$

$$K_f = \frac{\varepsilon_f}{\varepsilon_0} \quad (11)$$

The Maxwell-Wagner model [35] for the polarization between contact elements defines the dielectricity for the whole ER suspension:

$$K = K_f \cdot \frac{1 + 2 \cdot \beta \cdot \phi}{1 - \beta \cdot \phi} \quad (12)$$

where  $\phi$  is the volume fraction of particles.

With the Mason number, Equation (7), the total viscosity of the ER suspension can be calculated:

$$\eta_T = \eta \cdot Mn^{-\Delta} \quad (13)$$

where  $\Delta$  is the shear-thinning exponent. The shear-thinning exponent increases when the electric field strength increases and usually for ER fluids  $0.68 < \Delta < 0.91$  [35].

The polarization contribution for ER fluids is [30,36]:

$$\tau_E = NW_{sep} = \frac{3\phi}{8\pi a^3} W_{sep} n = \phi K_f E^2 \beta \quad (14)$$

where  $N$  is the number of contacts between the particles in the whole system,  $W_{sep}$  is the force needed to separate the particles,  $a$  is the average radius of the

particles and  $n$  the number of contacts per particle, usually two. The force necessary to separate the particles when the field is present is defined as [36]:

$$W_{sep} = E_p \cdot D_p \quad (15)$$

where  $D_p$  is the average distance between the centres of two particles and  $E_p$  the electric field applied through particles. When  $F_p$  is the axial force between the particles, the force is obtained by the formula [37]:

$$F_p = \frac{37.44\pi a^6 \varepsilon_0 K_f (\beta E_p)^2}{D_p^4} e^{[14.84 - 6.16(D_p/a)]\beta^2} \quad (16)$$

The dipole force between polarized particles is [38, 39]:

$$f_d = \frac{24 \cdot \pi \cdot a^6 \cdot \varepsilon_0 \cdot K_f \cdot (E_0 \cdot \beta)^2}{D_p^4} \quad (17)$$

The relationship between these two forces is:

$$\frac{F_p}{f_d} = 1,56 \cdot e^{[14,84 - 6,16 \cdot (\frac{D_p}{a})] \cdot \beta^2}$$

The number of chains per unit area,  $N_A$ , is obtained from the formula [40]:

$$N_A = \frac{3\chi\phi}{2\pi a^2} \quad (18)$$

where  $\phi$  is the volume fraction of particles and  $\chi$  the magnetic susceptibility between particles.

The critical value, which defines the state of the fluid, can be calculated by [41]:

$$E_{c1} = \sqrt{\frac{8 \cdot k \cdot T}{\beta^2 \cdot \epsilon_f \cdot a^3 \cdot \theta_1}} \quad \text{and} \quad E_{c2} = \sqrt{\frac{8 \cdot k \cdot T}{\beta^2 \cdot \epsilon_f \cdot a^3 \cdot \theta_2}} \quad (19)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature in Kelvin and  $\theta$  is a dimensionless quantity that characterizes the competition between the dipolar interaction and the thermal energy. When the applied electric field  $E < E_{c2}$ , the system is in a liquid state. When  $E_{c2} < E < E_{c1}$ , the ER system is similar to nematic liquid crystal, which has ordering in the field direction but no ordering in the directions perpendicular to the field. When  $E_{c1} < E$ , the system is in a solid state.  $\theta$  can be calculated [41]:

$$\theta = \frac{k \cdot T \cdot 4a^2 \cdot \epsilon_f}{p^2} \quad (20)$$

where  $p$  is the dipole moment between particles [41]:

$$p = \beta \cdot a^3 \cdot \epsilon_f \cdot E \quad (21)$$

When the ER fluid is under a constant electric field, there are two critical temperatures [41],

$$T_{c1} = \frac{\beta^2 \cdot a^3 \cdot \epsilon_f \cdot E^2 \cdot \theta_1}{8 \cdot k} \quad \text{and} \quad T_{c2} = \frac{\beta^2 \cdot a^3 \cdot \epsilon_f \cdot E^2 \cdot \theta_2}{8 \cdot k} \quad (22)$$

if the dielectric constants  $\epsilon_f$  and  $\epsilon_p$  have little change in the temperature range under consideration. When  $T > T_{c2}$ , the ER system is liquid. When  $T_{c2} > T > T_{c1}$ , the ER system is similar to the nematic crystal state. When  $T < T_{c1}$ , the ER system is in a solid state.

In addition to the mechanical changes that appear when an electric or magnetic field is applied, the physical, magnetic, electrical, optical, acoustic and thermal properties that the particles, the fluid, the surfactants and the additives have may show an influence.

## 2.4 Electrorheological fluids

Electrorheological fluids or electrorheological suspensions consist of particles and carrier fluid and possible additives and/or surfactants. In electrorheological fluids, either the fluid or the particle can be the component that polarizes. The components together form a product, having the desired characteristics, which in turn conform to the operational requirements. An electrorheological fluid can also act combined with a magnetorheological fluid as a so-called ER-MR fluid.

An ER fluid is typically a dispersion of electrically polarizable particles in an oil of low dielectric constant. The dielectric mismatch between the particles and continuous phase gives rise to the ER effect. Based on the ability to tailor the electrical properties of polymers, these have emerged as an important class of ER materials. ER fluids demonstrate orders of magnitude increases in apparent viscosity over milliseconds [37,42] when an electric field, requiring a few watts of power, is applied. This fast, strong and reversible gelation provides a novel mechanism for the control of vibration and transfer of energy. Specifically, electrorheology allows for simple and efficient electromechanical interfaces [42].

The ER effect of suspensions containing particles of a non-semiconducting character is usually conditioned by hydrophilic additives that activate the particle surface and cause the particle polarizability. Mainly water is often used for the activation of both inorganic and organic dispersed phases. Surfactants and other polar liquids as additives are proposed too. Many results demonstrate that the presence of water is not always necessary, and even the dispersion of

dry particles of non-conducting material, such as calcium carbonate displays a distinct ER behaviour, which may well be increased by a suitable modification of the particle surface by silane sorption [43].

Bingham-type behaviour can be utilized only for a few explained cases of ER phenomena, in particular those consisting of fluids with a relatively low dielectric constant. In the light of the polarization capabilities of the particle-liquid system, it is shown that there exists an optimal value of the parameter  $\beta$  [37] (the particle dipole coefficient) for which the ER effect is the most intense. Some of the experiments performed open the possibility of exploring some related interesting phenomena, such as the influence of surface structure of the particles, the use of combined systems, in which the inhomogeneities in terms of relative polarizability among different constituents can be advantageously employed [44].

### 2.4.1 Particles

The volume fraction of particles influences the yield strength of the whole suspension. The more particles there are in the fluid, the higher the yield strength of the fluid. Having a maximum volume fraction of particles is not always desirable because of the effects of the suspension on the materials used in the device. In dynamic dampers, for example, the response time of the fluid and the requirement of having a fluid that does not cause wear on the construction are much more important than the yield strength of the fluid. On the other hand, in clutches and rotational brakes, a high yield strength is crucial. In most studies, a small particle size has been found beneficial for the strength and response time of the electrorheological effect, and its tendency to cause abrasion is small [12].

In respect of the particles in electro- and magnetorheological fluids and the theoretical approach and the calculations, the following assumptions are made [11]:

- The particles are spherical and all of the same size;
- The electrostatic interaction is the dominant interaction, i.e. all other interactions are ignored (in MRs the magnetic interaction of particles);

- The polarization is identical in every particle of an array;
- Complete and perfectly straight chains of particles span over the electrode (or magnetic pole) gap;
- When the array is sheared, the rate is so low that a static or quasi-static state exists;
- The separation of the particles during shearing is identical for all the particles involved.

Without an external electric or magnetic field, the particles are in a rotary motion inside the carrier fluid. The angular velocity and the pre-polarization level of the particles determine how effectively the applied field induces particles to form dipoles. The faster the dipoles regenerate, the faster the particles form chains or strings. However, although the round shape of particles is good for the chain-forming speed, it is not good for the size of the contact of the particle interaction. The round shape of the particles also reduces the yield strength of the whole suspension [9].

The ER effect can be enhanced by increasing the particle concentration in the ER fluid. A denser particle concentration produces more particle chains and greater shear stress. Since the particle concentration should be limited so that the sample fluid does not gel, the attractive force between particles that forms the particle chains must be strengthened in order to get a large ER effect. The strength of a particle chain depends on the interactive force between neighbouring particles, which varies with the applied electric field, the surface conductivity of the particles, particle shape, and particle size.

The shear stress is proportional to the square of the applied voltage, and current through the ER fluid is proportional to the fourth power of the applied voltage. The thickening of the particle chain and greater shear stress results from increasing the current. An ER fluid requires the particles to have some conductivity. Since the appropriate conductivity of particles brings large apparent permittivity, increasing the conductivity of the (polymer) particles may enhance an ER fluid without water. In order to control the surface conductivity of the particles, a conductive polymer (polyaniline, etc.) can be coated on the

particle surface. The increase in the surface conductivity of the particles enhances the ER effect. However, too much current can flow through the particle surface, so it is important to find the optimum value of the surface conductivity for each ER effect [45].

Some results suggest that the ER response can be significantly enhanced by the addition of small amounts of proteins to the suspensions. These results suggest a promising future; proteins are designed by nature to be polarizable, many are plentiful and inexpensive, and many more can be synthesized by a variety of modern techniques to possess desirable attributes. Possible problems lie in protein denaturation and that the migration polarization mechanism can inherently produce suspension conductivity, which, if excessive, would be detrimental to applications. The possible proteins that could be used in ER suspensions are, for example:  $\beta$ -lactoglobulin,  $\alpha$ -lactalbumin, bovine albumin,  $\alpha$ -casein,  $\kappa$ -casein, chicken albumin and soy protein mixtures [46]. Examples of particles used in ER fluids are presented in Table 2.

When choosing the particle material, the importance of the desired electric and magnetic conductance properties and the possible abrasivity of the particles must be considered. In the case of an ER fluid, the conductive properties of particles must never be the same as those of the carrier fluid!



*Table 2. Examples of particles used in ER fluids [47–75].*

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Examples of particles used in ER fluids

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alfa-silica	maleic anhydride
alginic acid	mannitol
alumina	metallic semiconductors
alumina silica mixtures	methoxyphenylimidoperylene
aluminium oleate	methyl acrylate
aluminum octoate	methyl methacrylate
aluminum stearate	microcel-C
azaporhin systems	microcrystalline cellulose
barium titanate	micronized mica
boron	monosaccharides
cadmiumsulphidephosphor	molecular sieves
calcium stearate	N-vinylpyrrolidole
carbon	nylon powder
cellulose	olefins
ceramics	onyx quartz
charcoal	phenolformaldehyde polymers
chloride	phthalocyanine
colloidal kaolin clay	polystyrene polymers
colloidal silica	porhin
crystalline D-sorbitol	phosphototungstomolybic acid
diallylether	polymethacrylate mixtures
dimethyl hydontoin resin	polyvinyl alcohols
diethylcarbocyanineiodide	pyrogenic silica
diphenylt hiazole-anthraquinone	quartz
divinylbenzene	rottenstone
dyes	rubber
electrolyte modified starch	substituted quinacridone
flavanthrone	sephadex ion-exchange resin
flint	silica aerogel
flour	silica gel
gelatine	silica xerogel
glass	silicone ionomers
copper phthalocyanine	sorbitol
graphite fibres	starch
gypsum	teflon
lauryl pyridinium	toners
lead oxide	water-saturated silica
limestone	white bentonite

lithium polymethacrylate  
lithium stearate  
magnesium silicate  
maleic acid

zinc oxide  
zinc sulphidephosphor  
zinc stearate  
wax

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### 2.4.2 Carrier fluids

From previous studies it has been found that the minimum requirement for a carrier fluid to be used in an ER fluid is that it must be hydrophobic, i.e., totally immiscible with water. Experimental evidence strongly suggests that the ER effect is due to water absorbed into the solid particles. However, not all hydrophobic liquids are equally suitable for use in ER fluids. The desirable features of a carrier fluid for use in an ER fluid are [76]:

- The carrier fluid must make as active an ER fluid as possible. The activity (i.e. the extent of the change in flow properties brought about by application of an electric field) of ER fluids made with the same solid but with different carrier fluids varies markedly.
- The density of the carrier fluid should be as close as possible to that of the solid, to prevent settling out of the latter. The density of the solid used in most ER fluids at present is about  $1\,400\text{ kg/m}^3$ , and this should be regarded as an approximate target for the density of the carrier fluid.
- The carrier fluid should be chemically stable under the specific circumstances the ER fluid is exposed to, so that the material has a long service and shelf life.
- The carrier fluid should have a wide liquid-phase temperature range, i.e., a low freezing point and a high boiling point.
- The carrier fluid should not be flammable, or at least it should only burn with difficulty.
- The carrier fluid should have a low viscosity, so that the no-field viscosity of the ER fluid is low.
- The carrier fluid should not attack ordinary engineering materials. Relatively few liquids are likely to attack metals in normal use, but many fluids will attack plastics, particularly elastomers used in oil

seals. This is clearly an undesirable feature for a fluid intended for use in engineering.

- The carrier fluid as such should be an effective lubricant.
- The carrier fluid should not have any adverse biological effects.
- Ideally, the carrier fluid should be odourless; there is a natural suspicion among potential users towards fluids with unfamiliar smells, and many people are very sensitive to odours.

Examples of carrier fluids used in ER suspensions are presented in Table 3.

*Table 3. Examples of carrier fluids used in ER suspensions [47–74].*

Examples of carrier fluids used in ER suspensions	
aldehydes	grease
aliphatic esters	ketones
aroclor	kerosene
carbon tetrachloride	linseed oil
castor oil	liquid paraffin
chlorobenzene	mineral oil
diphenyl alkanes	nitrobenzene
chloroform	olefins
cottonseed oil	olive oil
di-2-ethylhexyl adipate	ortho-chlorotoluene
dibutyl sebacate	polyalkylene glycols
dielectric oils	polychlorinated biphenyls
different types of ethers	polychlorotrifluoroethylene
diphenyl ethers	resin oil
diphenyl sulphoxides	silicone oils
diphenyl sulphones	transformer oil
fluorinated hydrocarbons	trifluorovinyl chloride
fluorinated polymers	white oils
fluorolube	xylene
fluorosilicones	

### 2.4.3 Surfactants

The purpose of the surfactants and the additives is to support the ER effect, the speed of the reversal process and to increase the strength between the particles.

The surfactants are added, either directly to the carrier fluid, or as a coating on the surface of the particles. The gas dispersoid technique is usually used for coating the particles. The surfactants increase the conductivity of the particles and they act as a buffer between the particles. Sometimes the surfactants act as an insulating material, but this is less usual.

Some examples of surfactants used in ER fluids are presented in Table 4.

*Table 4. Examples of surfactants used in ER fluids [47–74].*

Examples of surfactants used in ER fluids	
block copymers	glycerol monooleates
borax	hydrocarbon polymers
dodecyl alcohol	lead naphthenate
fatty acids	metal hydrates
fatty amines	octyl alcohol
glyserol	sodium oleate
glyserol esters	tin oxide

#### 2.4.4 Additives

Additives influence the carrier fluid by improving or weakening the electric conductivity of the particle material or that of the carrier fluid. Usually the purpose of the additives is to improve the flow properties of the base material and thus promote the chaining of the particles when the suspension is subjected to the electric field. Otherwise, the purpose of using additives is the same as for using surfactants.

Examples of additives used in ER fluids are presented in Table 5.

*Table 5. Examples of additives used in ER fluids [47–74].*

<u>Examples of additives used in ER fluids</u>	
acetates	lactic acid
acetic acid	LiCl
alcohols	malic acid
aliphatic compounds	malonic acid
amines	metal chlorides
ammonium ion	mono-ethyl ether
butylamine	morpholine
calcium hydroxide	NaCl
diethylene glycol	NaOH
fluorides	octanoic acid
formic acid	oxalic acid
glycerine	pyruvic acid
hexylamine	trichloroacetic acid
KCl	water
KOH	

Water is the most common additive to ER fluid compositions [47].

The estimated characteristics of an ER fluid according to recently investigated devices could be summarized as follows (Table 6) [77]:

*Table 6. Preferred characteristics of a typical ER fluid [77]:*

<u>PROPERTY</u>	<u>MAGNITUDE</u>
zero field viscosity	1 Pas
current density	$< 10 \mu \text{ A/cm}^2$ at 3.5 kV/mm
yield strength	4–15 Pa
working temperature	240–420 K

### 2.4.5 ER-MR and ER-MF fluids

An interesting solution is to combine the properties of magnetic fluids (MF) and ER fluids. In studies, it has been found that, when the MF/ER fluid is altered to both an electric and magnetic field, the maximum shear stress is twice bigger than when the fluid is altered only to an electric field. Examples of this phenomenon can be found in Fujita's et al. patent [78] and in Sasaki's et al. patent [65].

The principle of using the electro-magneto-rheological (EMR) effect is based on the application of superimposed electric and magnetic fields to a fluid; the direction and/or strength of each field can be independently regulated. In practice, it is easier to change the direction of the magnetic field rather than that of the electric field because the magnetic field can be applied without direct contact between magnetic coils and the fluid, whereas the electrodes should contact the fluid for electric field application [75]. The magnetic field is usually used mainly to help decrease the sedimentation of dispersed particles. The effect of a magnetic field is significant if the field direction is maintained homogenous, because the particle orientation and resulting cluster structure can be controlled by external field conditions [79]. The magnetic field can also be used for holding the fluid still while the apparatus is not working. The difference between ER-MR and ER-MF fluids is that in ER-MF fluids at least some of the particles are smaller than 1  $\mu\text{m}$ , see also Chapter 1 - Introduction.

When looking at articles and patents between 1995 and 1996, two materials in ER suspensions are prominent: zeolite and polymers (especially polyaniline). With base stocks, also called carrier fluids, silicone oil is the most widely used option. According to future expectations, the combining of MF and ER fluids would have possibilities beyond those of ER fluids researched so far [80–91].

## 3. Test methods

### 3.1 Materials

The purpose of this work was to study the characteristics and performance of an ER fluid that has a low concentration level of particles in an environmentally friendly carrier fluid. The characterization was done by comparing the properties of different concentration levels of particles, with or without grinding, in the temperature area of a normal rotary machine, i.e., at a working temperature of 20–60°C at shear rates of between 40–490 1/min with an applied external electric field of between 0–3.5 kV/mm. In earlier literature, studies were usually made by characterizing one or two properties (particle size, influence of additive, surfactant, particle shape, water etc.) or one or two different parameters (shear rate, shear strength, temperature, viscosity, reaction time etc.). The other significant difference to the earlier studies was the use of pine oil and the low concentration level of particles. The basic principle was to make the suspension non-hydrous [17, 18, 22, 23, 47, 77, 107, 108, 114], so that further developed suspensions could be made to work at temperatures above 90°C. A low concentration level means that the ER fluid has possibilities of gaining a higher shear strength level [15, 20, 23, 40, 47, 83] and can work in a wider area of applications, especially in high-pressure applications [104, 106, 112, 113]. By combining the appropriate treatment and surfactant, the non-hydrous ER fluid can gain a longer lifetime [47, 108, 114]. Making an ER fluid that has good properties and lifetime according to these demands puts a great pressure on choosing the correct particle and possible additive and/or surfactant. Pine oil was chosen for the carrier fluid because there was no previous knowledge of using pine oil as a carrier fluid for an ER suspension.

A short series of tests were made for choosing the appropriate particle for the ER fluid. The test arrangement was made and carried out in co-operation with Mr. Jouni Enqvist from VTT Chemical Technology.

When polarizable particles containing oil are placed between two electrodes and an external electric field is applied through this suspension, the fluidity of the suspension decreases according to the strength of the electric field. The electric field sets off the polarization so that the centroid of positive and negative charge

is clearly appeared. The electric attraction between the surfaces of the different electrodes forces the particles to create a three-dimensional chain, fibrous and net-like structures between the electrodes. When electric field is increased to the solidification point of the suspension, the compounded fibrous nets block the flow of the fluid. When the electric field is removed, the polarization disappears and the suspension is liquefied. The liquid-solid-liquid reaction takes place within 4–10 milliseconds.

There are at least three different mechanisms by which the particles can bond to each other: electric double-layer polarization, polarization through the ions of the water layer and polarization in the particle structure itself. The first two are phenomena in the interface of the particles and oil. The third one is formed by the particles in different ways:

- 1) polarizing electrons from the cloud of atoms;
- 2) movement of the net-charged atoms to the particles' crystal lattice;
- 3) constant dipoles polarizing, especially with the polymer particles;
- 4) the charges created by the heat drifting to the grid interstices, and/or
- 5) the charges that accumulate on the surfaces of the particles moving along the surface of the particle or through the cavity structure at the interface in between the two material particles.

The appropriate particle can be chosen by investigating the particle chaining, vortex movement of the particles, particle charging and particle-particle interactions under the applied external electric field with a microscope. The test for selecting those particles that had the maximum interaction at low electric field densities was carried out with an electric field of between 0–1 kV/mm. A schematic picture of the test arrangement is shown in Figure 4.

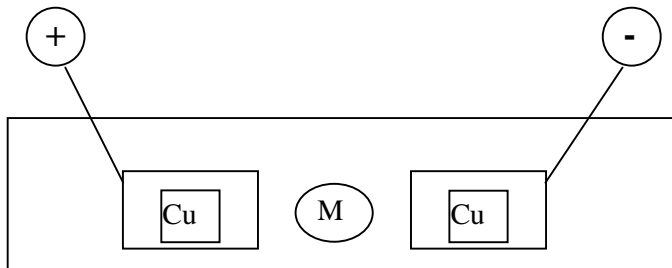


Figure 4. Schematic picture of the test arrangement. + means positive charge, - negative charge, Cu copper electrode, and M microscope.



The prepared ER fluids for the particle selection tests were:

- starch – silicon oil
- starch – sunflower oil
- silica – paraffin oil
- silica – sunflower oil - paraffin oil
- glass balls – paraffin oil
- glass balls – sunflower oil
- glass balls – silicon oil
- polyaniline – paraffin oil
- polyaniline – sunflower oil
- polyaniline – silicon oil.

The test results clearly showed that, from the particles tested, polyaniline was the most active particle and therefore the most suitable particle for an ER fluid.

In selecting the particle to be used, the most important factors were conductivity, non-abrasivity, mechanical and electrical stability, and the effect and availability of the material. Polyaniline (PAN) was chosen because polyaniline has good electrical and mechanical properties [92–94]. PAN is also highly conductive [96], is not abrasive and therefore it can be used in applications where there are surfaces in relative motion to each other. PAN is commonly known and it is commercially widely available. According to the literature study, PAN was found to best fulfil the desired properties. The particle used in all suspensions was polyaniline. All the values in Chapter 3 include the calculated or measured mean value and the calculated, measured or approximated maximal standard deviation.

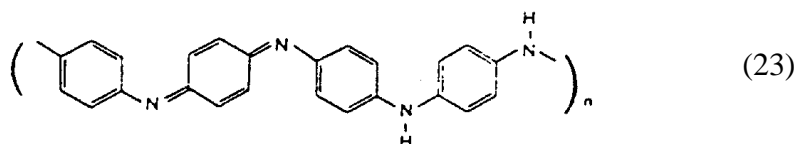
The measured density of the polyaniline was  $1.30 \pm 0.2$  g/ml. The measured average size of the particles was  $45 \pm 15$   $\mu\text{m}$  before grinding and  $3 \pm 2$   $\mu\text{m}$  after 2 hours' grinding with a ball mill. The particle sizes were measured using optical spectroscopy and an automatic particle counter. The measurements were taken twice at a temperature of  $22 \pm 0.5^\circ\text{C}$ . Automatic particle counter measurements were made according to the ISO 4406 standard. The error

margin in the measurements of density, particle size and temperature was maximally 5%, presented as standard deviation from the results. The base polyaniline was brown in colour.

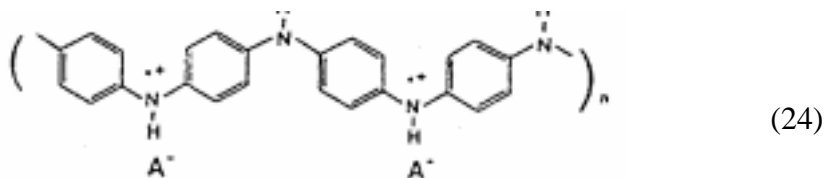
### 3.1.1 Polyaniline

Electrically conductive polymers were discovered with the invention of  $H_2SO_4$  - doped polyaniline in 1971 [92] and doped polyacetylene in 1977 [93]. One of the present research areas, of both scientific and industrial importance, is to develop electrically conductive polymers that are fusible or soluble in common solvents. For electrically conductive polyaniline (PANI), this is not a trivial question because PANI can be regarded as being a semi-rigid polymer, easily resulting in intractability. Intractability is caused by its highly aromatic nature, the interchain hydrogen bondings and the charge delocalization effects [94]. In some respects, polyaramides can be considered closely analogous materials [95].

Polyaniline is one of the most promising conductive polymers due to its straightforward polymerization and excellent chemical stability combined with relatively high levels of conductivity [96]. The so-called emeraldine base (EB) form of PANI used in these tests is half-oxidized and thus consists of phenylenediamine and quinoid diimine units:



Emeraldine base is insulating, but its iminic nitrogen sites can be protonated by strong acids to form an acid-base complex [96]. This electrically conductive form is called emeraldine salt. A fully protonated conductive complex is formed when ca. 0.5 mol of protonic acid,  $A^- H^+$ , per mol of PhN repeat unit of PANI is used:



Emeraldine base is soluble only in N-methylpyrrolidone (NMP), selected amines, concentrated sulphuric acid, and other strong acids [93–99]. Emeraldine salt is even more intractable. An example of the reversible oxidation reduction process as the cyclic voltammogram for polyaniline is shown in Figure 5.

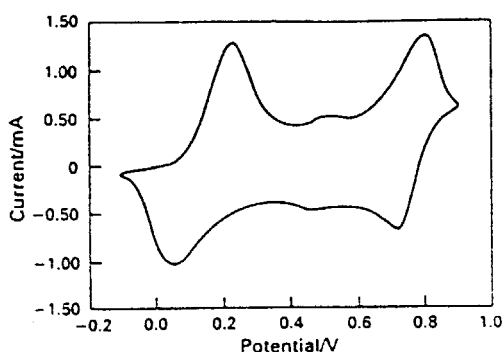


Figure 5. Cyclic voltammogram of polyaniline (HCl) on a 2 mm platinum disk electrode at 100 mV/s in 1 mol/l HCl (pH = 0) [100].

### 3.1.2 The preparation of ground particles

In making such a complex medium as an electrorheological fluid, several problems are encountered. Firstly, it is necessary to obtain electrically conductive particles whose size is almost the same. Secondly, the particles must also usually be coated with a layer of stabilizer molecules. Finally, the stabilizer must not only prevent the particles from aggregating, but also provide the formation of an electrically conductive particle solution in a carrier fluid. Once these problems are overcome, an electrorheological fluid can be manufactured, which is stable in the presence of gravitational, centrifugal, and electric fields, exhibits strong electric properties, and behaves in many respects as a homogenous continuum. Particles of the desired size may be obtained by different methods, like grinding, condensation and precipitation. The preparation and grinding of the particles that were used was performed using a ball mill because a ball mill allows the use of surface-active chemicals during

milling. In optimal conditions, this means that the mill fills with balls by up to 30–40% of its volume, and with dispersed material by 20%. Grinding can take place in the presence of a carrier fluid, and a stabilizer ensures that sufficiently fine particles are obtained whilst simultaneously ensuring the stability of the system. First,  $10 \pm 0.3$  grams of polyaniline particles were milled with  $20 \pm 0.5$  millilitres of acetone and coalacidice using a Fritsch centrifugal ball mill (type: pulverisette 6) for 1.5 hours at speed 2. The suspension was then air-dried overnight and its weight was then measured. The total mass of the suspension after drying was  $10.8 \pm 0.3$  grams. Next, 5%, 10% and 15% suspensions were made in pine oil, and the suspensions were shaken for 20 minutes in an ultrasonic washer and 20 minutes by hand. The milling and shaking times were kept accurately. The ball milling was performed three times and the total weight of dried and ground PAN was  $30 \pm 1$  grams.

Six different types of ER fluids were chosen; three based on natural, biodegradable pine oil, and three based on synthetic pine oil. The densities of the carrier fluids are presented in Table 7.

*Table 7. The mean values of carrier fluid densities and Brookfield dynamic viscosities at 25° C.*

Sample	Concentration		Carrier Fluid	
	(wt %)	Base oil	Density [g/cm]	Dynamic viscosity [mPas]
PO5	5	pine oil	0.904	23
POE5	5	pine oils ester	0.924	110
PO10	10	pine oil	0.904	23
POE10	10	pine oils ester	0.924	110
PO15	15	pine oil	0.904	23
POE15	15	pine oils ester	0.924	110

The ER suspensions were prepared as follows.

### **3.1.3 Fatty acid and ester carriers**

The choice of a dispersion medium, on the basis of which an electrorheological fluid is prepared, is specified by the purpose and place of its use. The preparation of a stable suspension has its specificity in each case according to the choice of stabilizer, optimization of the stabilizer base ratio, conversion of a dispersed phase from one type of a medium into another. A 30–60  $\mu\text{m}$  PAN fraction was prepared by sieving out the smaller and larger particles. The particles were suspended in oils and sonicated for 20 min.

### **3.1.4 Paraffinic oil carrier**

The size of electrically conductive particles must be sufficiently small, since the stability of an electrorheological fluid as a system is ensured by preventing agglomeration and precipitation. This is achieved by decreasing the particle size. The stabilizer and/or surface-active chemical must prevent particles from aggregating. To this end, long-chain molecules (polymers or surfactants) are used with functional groups (OOH,  $\text{H}_2\text{OH}$ ,  $\text{H}_2\text{NH}_2$ , and so on). In making the suspensions studied in this thesis, the stabilizer and surface-active chemical were chosen to be the same, because the stabilizers and surface-active chemicals had the same desired properties. A stabilizer was chosen so that its molecules interacted with the electrically conductive particles, via the bond of a functional group, to form a tightly bonded monomolecular layer around the particles. The choice of stabilizer for each particular application presents a rather difficult problem, and this is usually settled experimentally. In experimental studies on the use of methacrylate, petroleumsulphonate and hexane treatments, hexane was found to have the best chemical stability with the combination of pine oil and polyaniline. An emeraldine form of PAN with a wide particle distribution of over 100  $\mu\text{m}$  was ball-milled for about 2 hours down to a 1–5  $\mu\text{m}$  size. Eighty per cent of the particles were of the size of 1–2  $\mu\text{m}$ . The particles were coated by making suspensions in 2 % hexane solutions of two different surface-active chemicals. The dispersions were concentrated by a rotavapor and a paraffinic oil carrier was added.

### 3.2 Experimental Arrangement

The test apparatus for the investigations of the ER and MR effects included a Haake VT 500 viscosimeter, a Haake DC 5 heating circulator, a Canon BN 100C computer, an RS branch box CAS-4, an RS-DA converter, a voltage supply unit for the viscosimeter, a high-voltage supply unit for ER fluid measurements and a DC current supply unit for the MR fluid measurements. A schematic picture of the test arrangement is shown in Figure 6.

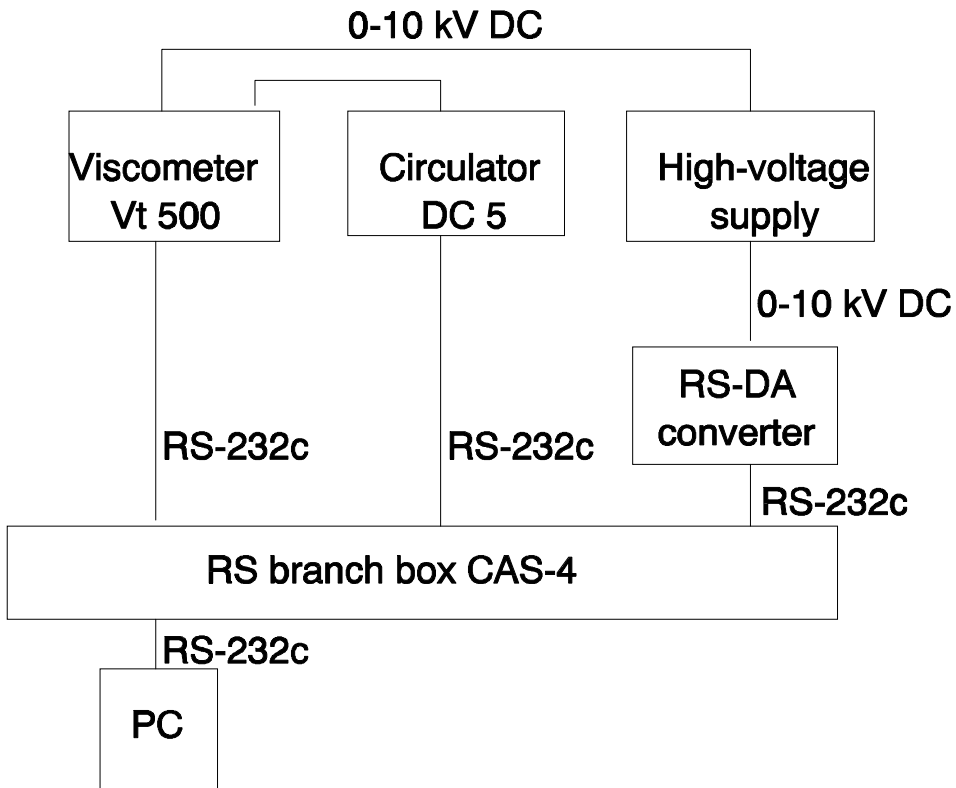


Figure 6. Schematic picture of the test arrangement.

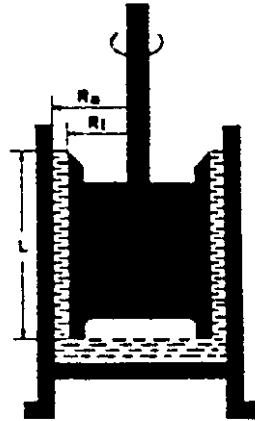
The VT 500 viscosimeter (see Figure 7) is a rotational viscosimeter that measures the viscosity of fluid substances (oils, polymer solutions, varnishes, ceramic slips, slurries, etc.) or pastes (creams, lotions, food, PVC plastisols, etc.). It is a Searle-type rotational viscosimeter, where the resistance to flow of the test substances is measured as a function of speed (= the shear strain rate).

The viscosity of the sample is calculated from the torque measured, the speed selected and the geometry of the sensor system. The technical limits of the viscosimeter are: speed range 2–500 rpm, torque range 0–2 Ncm, temperature range -30–+200°C [101]. The measurement temperature was controlled with the aid of the DC 5 heating circulator where the heating fluid flows around the Pt100 sensor system. According to the manufacturer of the viscometer [101], the variation of the torque was  $\pm 0.5\%$  of the maximum value and that of speed was less than  $\pm 0.5\%$  of the displayed value. The variation values fell within those prescribed by the ISO 3219 standard. The measurement uncertainty for temperature was at  $20^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  and at  $40^{\circ}\text{C} \pm 0.3^{\circ}\text{C}$ . The certificate of calibration for the temperature was issued by The Centre for Metrology and Accreditation of Finland.



*Figure 7. Picture of the viscosimeter.*

The ER fluid measurements were taken using an MV1-ER sensor system (Figure 8), built by the manufacturer of the viscosimeter. A computer program was used to control the measurements and for storing the measured data into files. The input data used for each measurement series were the electrical field intensity, the rotational speeds and measurement temperatures. The computer program and the high-voltage/RS-Da converter arrangement were designed and built by VTT Manufacturing Technology. The input voltage for high-voltage supply was 24 volts d.c.  $\pm 10\%$  at 6A. The measured ripple at full load was better than 0.1% peak to peak. The measured variation of the high-voltage supply had a line regulation of less than 0.1% for the input changes of 1 volt and a load regulation of less than 0.1% for the load changes from 10% to the measured maximum voltage.



*Figure 8. Picture of the sensor system MV-1-ER used in testing. The inner cylinder radius  $R_i$  is 20.04 mm, outer cylinder radius  $R$  is 21.0 mm, the gap width 0.96 mm and the sample volume  $38.0 \text{ cm}^3$ . The variation, described as standard deviation, in radius, gap, sample volume and roundness is less than 1% of the value. The variation measurements were performed by an accredited measurement laboratory in VTT Manufacturing Technology.*

The possible variations in results may be due to human errors, for example insufficient mixing of the suspension. Other possible sources of variations are the possible changes in the manufacturing of the suspensions, as well as improper cleaning of the measurement sensor system MV-1-ER. Effect of errors in the actual measurement system are considered to have less effect on the results due to active calibration.



# 4. Results

## 4.1 Experimental parameters

All the results are presented as the average of five acceptable and comparable results. In all cases, the measurement was accepted if, and only if, the measurement accuracy of the result was within  $\pm 5\%$  (described as standard deviation). If the measurement was unacceptable or failed for various reasons, the measurement was done again. The most common reason for failed measurement was human error, for example, giving false computer commands. In some measurements, the strength of the ER fluid was higher than the maximal torque of the viscometer at the shear rate of 490 1/min (Figures 9, 10 and 11). All the results are comparable only with the fluids' suspensions, made as described in Chapter 3.1 and Table 8, and with similar values and conditions described in Chapter 3.2. The abbreviations' contents of the tested fluids are presented in Table 8.

*Table 8. The explanations of abbreviations, where ground means ground in a ball mill for 2 hours.*

Abbreviation	Content of the tested fluid
PO5	Pine oil with 5% of weight PAN
POE5	Pine oils ester with 5% of weight PAN
PO10	Pine oil with 10% of weight PAN
POE10	Pine oils ester with 10% of weight PAN
PO10G	Pine oil with 10% of weight PAN, ground
POE10G	Pine oils ester with 10% of weight PAN, ground
PO15	Pine oil with 15% of weight PAN
POE15G	Pine oils ester with 15% of weight PAN, ground

The change in dynamic viscosity according to the shear rate at electric field densities of 0.5 kV/mm, 2.0 kV/mm and 3.5 kV/mm and at a temperature of 40°C are presented in Figures 9, 10 and 11. The changes in dynamic viscosity according to the applied external electric field at temperatures of 20°C, 40°C and 60°C are presented in Figures 12, 13 and 14. The changes in dynamic

viscosity according to the temperature at applied external electric field densities of 0.5 kV/mm, 2.0 kV/mm and 3.5 kV/mm and at a shear rate of 240 1/min are presented in Figures 15, 16, and 17. The percentage change in dynamic viscosity according to the applied external electric field at a shear rate of 240 1/min and at a temperature of 40°C is presented in Figure 19. The percentage change in dynamic viscosity according to the applied external field at a shear rate of 240 1/min and temperature of 40°C are presented in Table 9. The influence of particle volume concentration on the dynamic viscosity according to the applied external electric field at 240 1/min and 40°C are presented in Figures 20 and 21.

## 4.2 Influence of shear rate

With the shear rate measurements it was observed that the results are logical according to the increase in concentration and comparable to earlier results [13, 14, 15, 17, 19, 22, 31, 37, 39, 43, 47, 48, 51, 67, 68, 77, 88, 107, 110, 112].

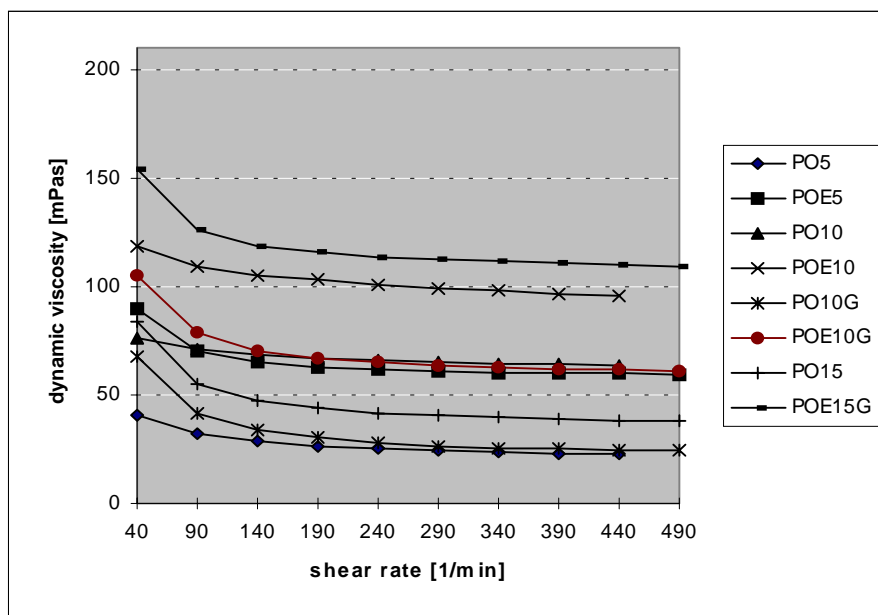


Figure 9. Dynamic viscosity according to the shear rate at electric field density of 0.5 kV/mm and temperature of 40°C.

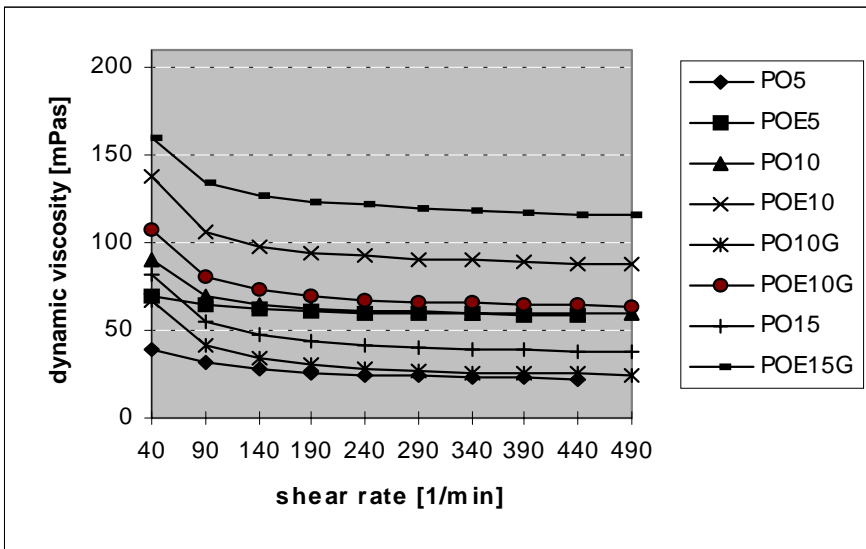


Figure 10. Dynamic viscosity according to the shear rate at electric field density of 2.0 kV/mm and temperature of 40°C.

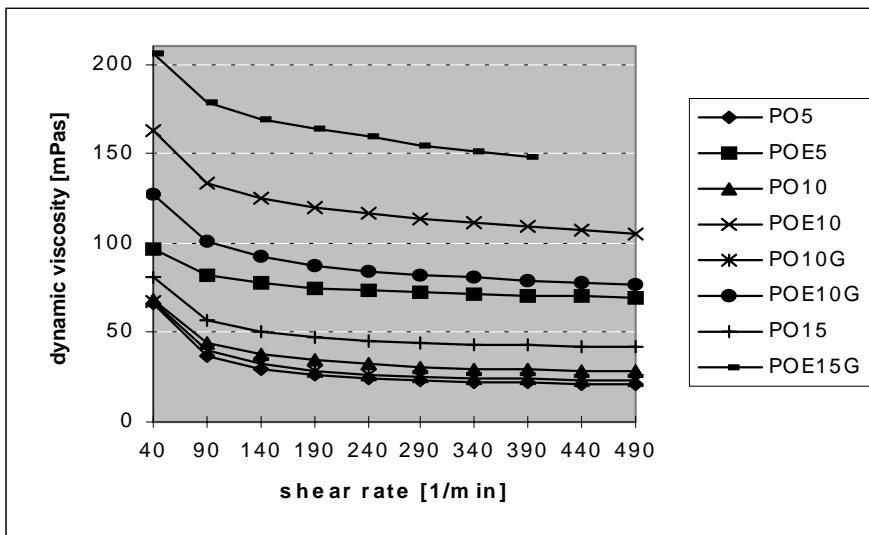


Figure 11. Dynamic viscosity according to the shear rate at electric field density of 3.5 kV/mm and temperature of 40°C.

### 4.3 Influence of applied external electric field

It was observed that the influence of the applied external electric field is very dependent on the concentration and whether the particles have been ground.

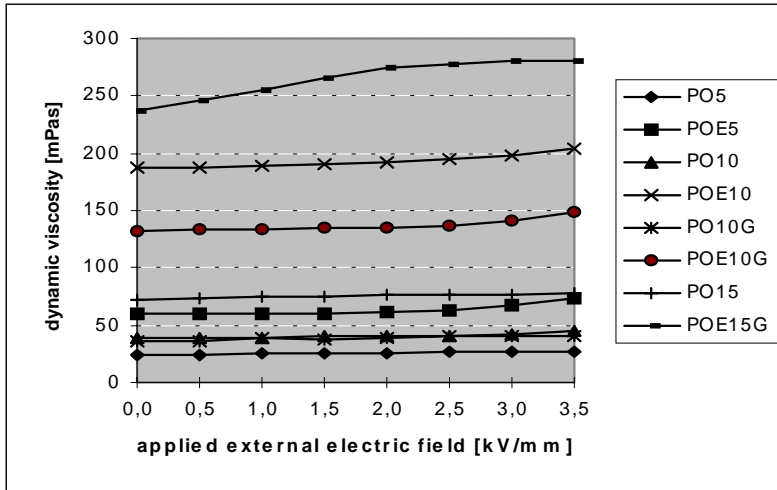


Figure 12. Dynamic viscosity according to the applied external electric field at a temperature of 20°C and shear rate of 240 1/min.

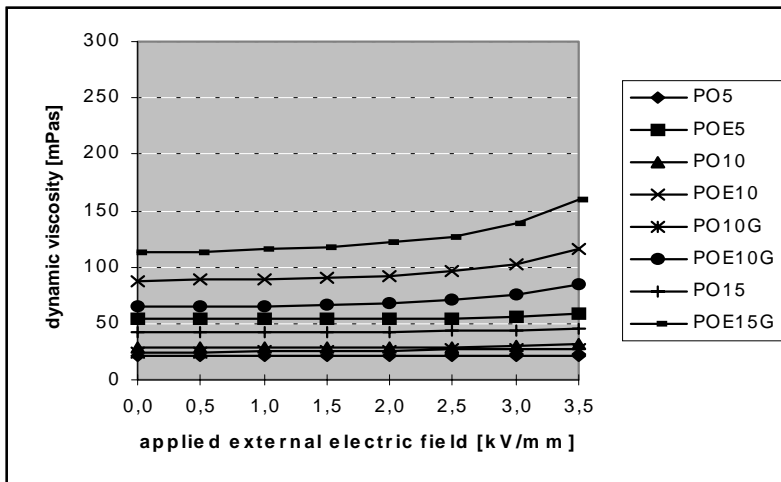


Figure 13. Dynamic viscosity according to the applied external electric field at a temperature of 40°C and shear rate of 240 1/min.

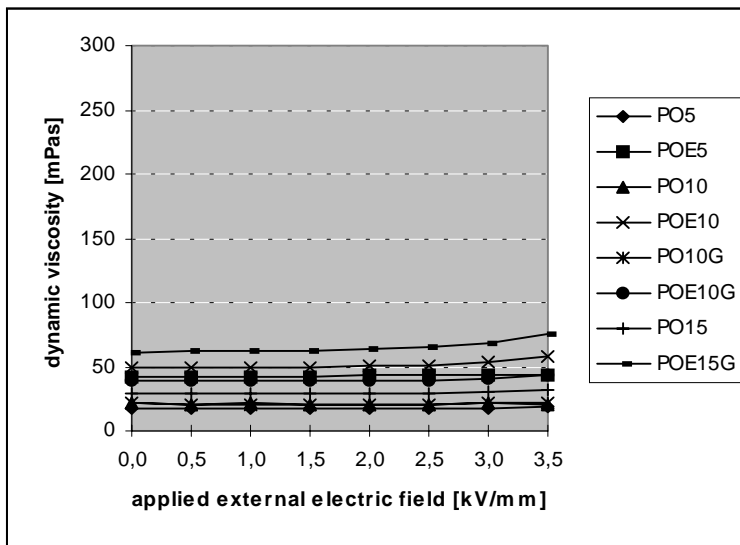


Figure 14. Dynamic viscosity according to the applied external electric field at a temperature of 60°C and shear rate of 240 1/min.

#### 4.4 Influence of temperature

It was observed that the influence of temperature, when the applied external electric field is steady, follows Newton's postulate (Figure 3).

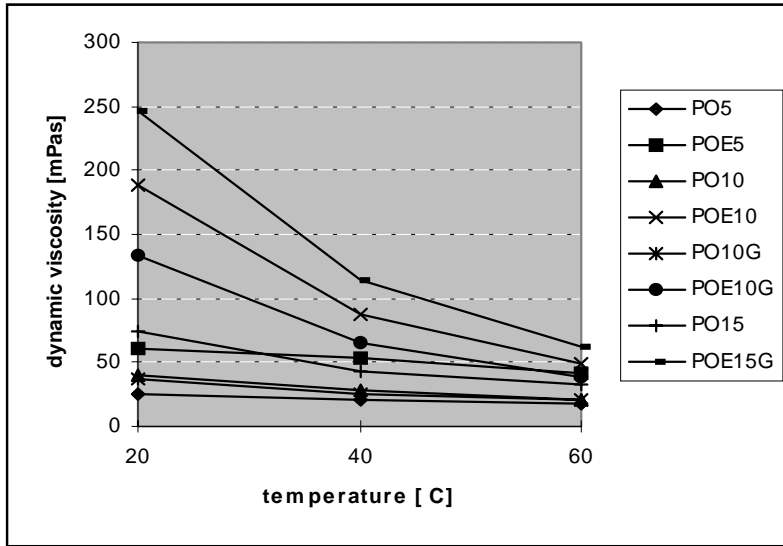


Figure 15. Dynamic viscosity according to the temperature at the applied external electric field of 0.5 kV/mm and at a shear rate of 240 1/min.

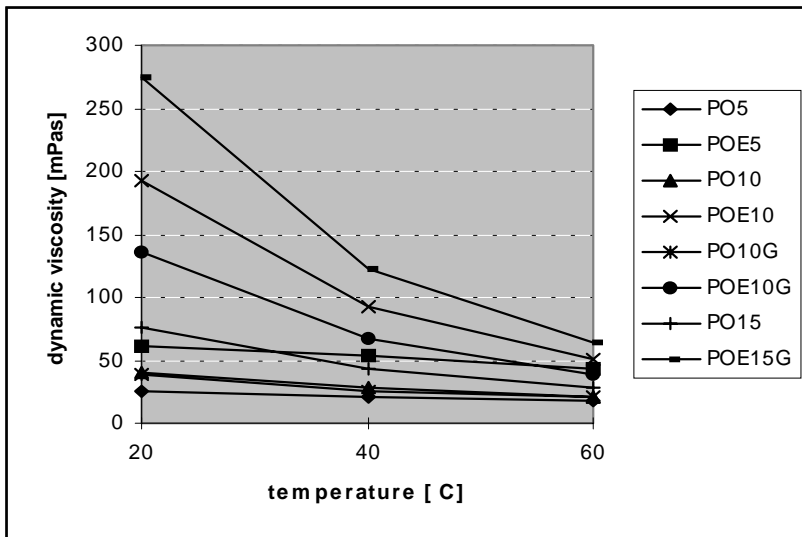


Figure 16. Dynamic viscosity according to the temperature at the applied external electric field of 2.0 kV/mm and at a shear rate of 240 1/min.

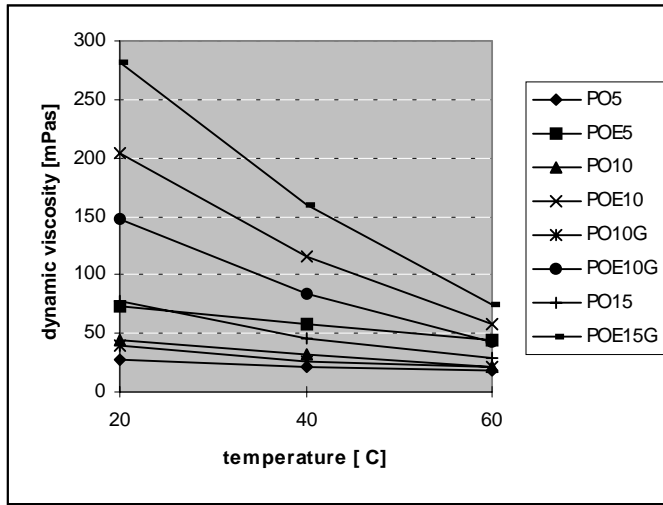


Figure 17. Dynamic viscosity according to the temperature at the applied external electric field of 3.5 kV/mm and at a shear rate of 240 1/min.

The dependencies can be clarified by looking at the results in the percentage change of viscosity. The percentage changes are presented in Table 9 and in Figure 21.

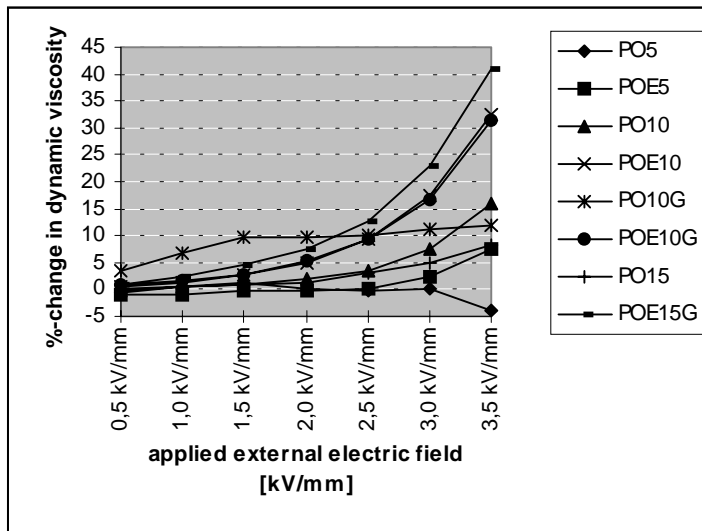


Figure 18. Change of dynamic viscosity in percentage according to the applied external electric field at a shear rate of 240 1/min and temperature of 40°C.

## 4.5 Influence of particle size and grinding

In results of the influence of particle size and grinding, the influence of grinding was observed to be different when comparing pine oil and pine oils ester.

Table 9. The percentage change in dynamic viscosity according to the applied external electric field at a shear rate of 240 1/min and temperature of 40°C.

E	Samples							
	PO5	POE5	PO10	POE10	PO10G	POE10G	PO15	POE15G
0.5 kV/mm	-0.56	-0.8	-0.09	0.67	3.54	0.76	0.17	0.85
1.0 kV/mm	0.56	-0.92	0.5	1.39	6.78	1.64	0.44	2.26
1.5 kV/mm	1.23	-0.35	0.8	2.8	9.53	2.73	0.72	4.4
2.0 kV/mm	0.22	-0.35	2.01	5.08	9.53	5.24	1.16	7.67
2.5 kV/mm	-0.11	0.23	3.35	9.39	10	9.2	2.99	12.8
3.0 kV/mm	0.33	2.29	7.46	17.33	11.1	16.73	4.87	22.85
3.5 kV/mm	-4.01	7.34	15.84	32.61	11.88	31.27	8.09	41.04

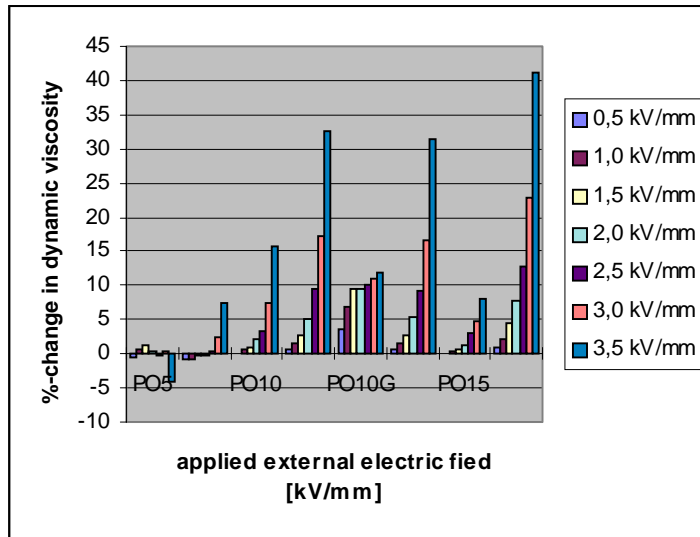


Figure 19. Change of dynamic viscosity in percentage according to the applied external electric field at a shear rate of 240 1/min and temperature of 40°C.



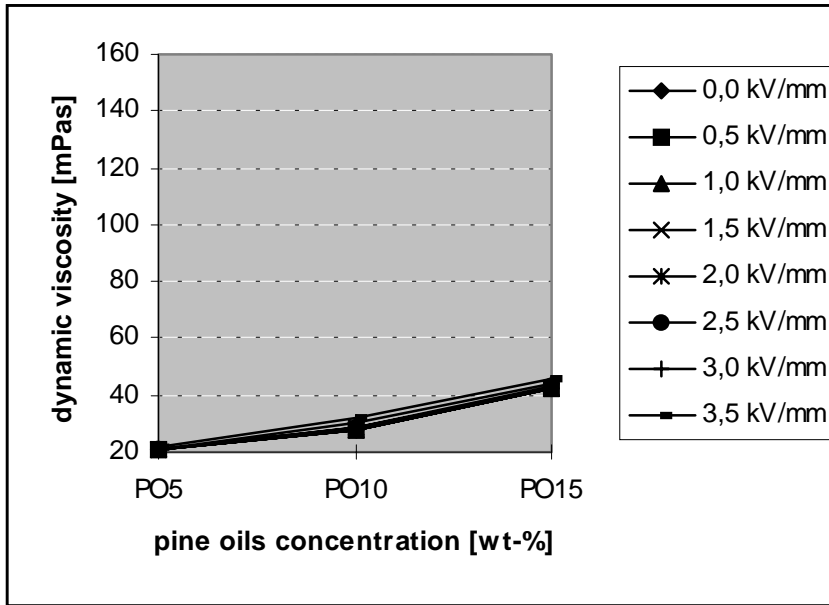


Figure 20. Viscosity as a function of volume concentration for pine oils at a shear rate of 240 1/min and temperature of 40°C.

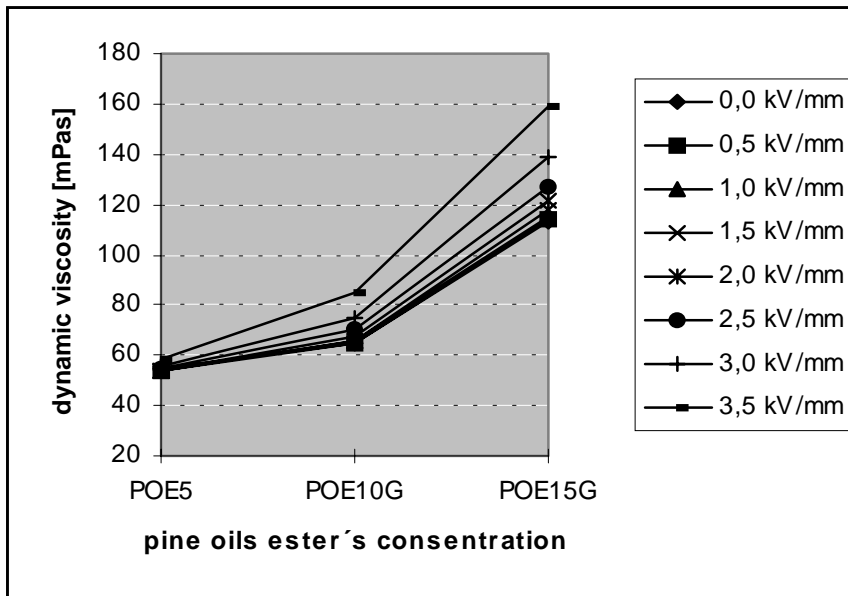


Figure 21. Viscosity as a function of volume concentration for pine oil esters at a shear rate of 240 1/min and temperature of 40°C.

## 5. Discussion

According to the results, pine oil and its ester are capable of working as a base fluid for electrorheological suspensions. Pine oil ester has higher electrorheological strength than pure pine oil, when combined with PAN particles. For ER fluids, the term efficiency means the capability of the fluid to increase its viscosity according to the applied external electric field and the dynamic strength of the ER fluid at different shear rates, temperatures and electric field strengths. For example, in Table 9 it can be seen that fluid PO10G increases its dynamic viscosity at 3.5 kV/mm 11.9% and POE10G 31.3%. From this it can be concluded that the electrorheological fluid made of pine oil ester and PAN increases its dynamic viscosity and shear strength more, according to the applied field external electric field, than the combination of pure pine oil and PAN (Figure 19). On the other hand, the increase in dynamic viscosity does not ensure the fluids capability to work as an ER fluid or at selected solution if the absolute viscosity level of a suspension is too low before applying the external electric field through the suspensions. In addition, from Table 9 it can be concluded that electrorheological fluids based on pure pine oil and polyaniline have a very small ER effect. The results of PO5 and POE5 conclude that, if the concentration level of pine oil or pine oil ester based ER suspensions is 5 wt-% and under, these fluids cannot and do not work as an ER fluid.

The change in temperature has no or very little effect on the electrorheological strength of the tested fluids (Figures 15, 16 and 17). One important factor to be considered in the future is the lifetime of the ER fluid at temperatures above 80°C. This is because of the higher temperature applications, such as paper machines. The results also show that the ER fluids' strength increases when the concentration increases (Figures 20 and 21). This can be considered normal according to the laws of fluid flow mechanics. According to the results, grinding decreases the electrorheological strength of pine-oil-based ER fluids. This can also be seen in Table 9 and Figure 19. On the other hand, grinding causes the particles to become smaller and therefore the particles are less vulnerable to brake in rotating machinery where there are mechanical forces against particles and small gaps through which the particles have to pass. Additionally, the smaller particle size through grinding is much less likely to cause wear. In generally it can be said that the design of an optimal ER fluid is a compromise

between choosing the appropriate materials, additives, surfactants and particle size for each and every situation where ER fluids are used.

In general, if the increase in viscosity is over 20% from 0 kV/mm to 3.5 kV/mm, the fluid can be considered a possible working fluid for the purposes mentioned earlier. If the percentage increase is over 20%, the fluid can still hold while the machine is not running. On the other hand, if the concentration is under 15% of weight and the average particle size is 2  $\mu\text{m}$  or less, the fluid can be believed to cause no permanent damage to the machinery while the machine is running and there is no external field present.

In earlier studies on the change in viscosity according to the applied external electric field, for example Otsubo [102], Bailey et al. [103], Nikolakopoulos et al. [104], Xu et al. [105], Spurk et al. [106], Gow et al. [107], Conrad et al. [88], Ishino et al. [108] and Stipanovic et al. [109], a similar type of increase in viscosity according to the applied external electric field was found. In Otsubo's research, the increase in viscosity was higher because of the higher concentration (35 wt-%) but the change in viscosity according to the concentration (25, 30, 35 and 40 wt-%) was similar to the results presented in this paper (Figures 9, 10, 11, 12, 13, 14 and 18). Otsubo's results are not quite comparable to the results presented in this thesis because Otsubo's fluids contained water. Bailey et al. [103] found the ER fluids to be a reversible media, which agrees with the results presented in this thesis. Compared to Nikolakopoulos et al. [104], who tested four different ER fluids at between 34.3°C and 55.8°C when the concentration was 25 wt-%, the pine-oil-based ER fluids presented in this thesis are more ER-efficient. The zero water content of the pine-oil-based ER fluids tested are also in good agreement in the ER activity and ER efficiency with earlier results (Xu et al. [105], Spurk et al. [106] and Ishino et al. [108]). On the other hand, hydration can cause ER efficiency to increase dramatically, but cause ageing [109].

The effect of concentration is very much dependent on the materials used, additives and/or surfactants and the compatibility of the materials. In this matter, the materials presented in this thesis are comparable with the suspensions presented earlier (Brooks [110], Gow et al. [107] and Uejima [111]). Gow et al. [107] studied ER suspensions based on polyaniline with a rheometer and found that the transition from fluid to solid-like behaviour occurs

over a narrow range of field strength. Compared to Gow et al., the results in this thesis show the change to be much smoother. This is because of the additive used and the nature of the carrier fluid. Gow also states that the dependence of the yield stress on volume fraction and field strength is found to be independent of particle type. This agrees with the results in this thesis (Figures 12, 13 and 14, Table 9).

The decrease in viscosity when the temperature is raised and the applied external field is not changed are also in good agreement with earlier results (Lingard et al. [112], Leek et al. [113] and Filisko et al. [114]). In Filisko's results, there is a turning point in temperature from where the relative viscosity begins to decrease. This is because of the use of the water in Filisko's ER suspension. The temperature versus increase in viscosity (Figures 15, 16 and 17) according to the field is in good agreement with the earlier results of Pialet et al. [115].

The evaluation of the influence of grinding the particles is difficult because it purely depends on the purpose on the function in which the ER fluid is supposed to work. Large particles, meaning a particle size above 10  $\mu\text{m}$ , can be used if there are no narrow gaps or if the fluid is not compressed through holes, etc. This can be generalized as the smaller the particles are, the better the ER fluid can function in a dynamic situation without harmful effects on the machine, its components or to the fluid's functionality itself. Larger particles can easily be used in, for example, fluid-composed beds or other more static situations. The development of the ER suspension is always a compromise between optimum particle size according to the effectiveness and wear properties, etc., the particles and carrier fluid's material and their effect on the other materials and mechanical parts, the relationship and the function between particle and carrier fluid material, the effective use and the amount of additives and/or surfactants etc. A summary of the results compared to three different references is presented in Table 10.

*Table 10. Comparison of impact properties on ER efficiency between measured ER fluids and three different references. Explanation: ++ very positive effect, + positive effect, x not mentioned or measured, • no effect, - negative effect.*

Property	Material or reference				
	PO	POE	Ref. 110	Ref. 112	Ref. 107
increase in electric field strength	++	++	++	++	++
additives	+	++	+	+	+
surfactants	x	x	•	-	x
increase in particle size	-	•	•	x	x
increase in particle concentration	+	•	•	x	x

Table 10 shows that the influence on electrorheological activity and on the electrorheological strength is similar between the tested fluids and the reference material. In general, the tested fluids showed good comparison between the properties of the electrorheological fluids mentioned in the references, if the concentration level of the tested fluids was 10% of weight or more. As described in references 107, 110 and 112, the increase of viscosity by 20% or more can be concluded to be sufficient for low concentration level, non-hydrous electrorheological fluids.

## 6. Summary and conclusions

According to the tests and analysis, an electrorheological suspension made out of pine oil or its ester, where polyaniline is used as an electrically conductive particle, can work properly in the conditions similar to those in this thesis. That is, if the fluid is made in the same way and with the same materials as in this thesis and if the parameters, such as temperature, shear rate and electric field strength are similar to this thesis. To make highly similar conclusions, the test arrangement must be the same. This work attempts to verify experimentally the developed electrorheological fluids based on pine oil and its ester.

It was found and verified that pine oils can be used as a carrier fluid for ER suspensions. The influence of applied external electric field was shown and its influence on the electrorheological effectiveness was discussed. When an external electric field is applied through an ER fluid, the viscosity (shear strength) of the fluid increases according to the applied external electric field. If the field strength is small compared to the fluid's properties (concentration etc.), the electrorheological phenomenon is not shown. On the other hand, if the field is too high compared to the properties of the ER fluid or to the mechanical situation (gap width etc.) the current short-circuits over the gap. The optimum external electric field strength for the ER fluids tested for this thesis was between 1 and 3.5 kV/mm when the gap was approximately 1 mm.

As a basic principle, the higher the particle concentration, the more ER-effective is the ER fluid. Depending on the materials and electric field strengths used, a maximum particle concentration for the ER effectiveness can be found. This work was concentrated on the low-concentration ER fluids and the specific use for these kinds of fluids was discussed.

The influence of temperature on the viscosity was shown to be according to the laws of thermodynamics, where [116]:

$$\log \log(\nu + 0,7) = A - B \cdot \log T \quad (25)$$

, where  $\log$  is the logarithm base 10, and A and B are dimensionless constants.

On the other hand, the results show that the effect of a rise in temperature on the viscosity can be eliminated by applying an electric field through the ER fluid. This means that, when temperature normally decreases the viscosity of the suspension, the viscosity can still be kept or raised by using an electric field applied through the ER fluid.

The influence of grinding the particles is very difficult to evaluate because of the different purposes of use of ER fluids. It was found that grinding at the level used in this work decreases ER effectiveness.

Based upon the results of the investigations, the following can be concluded in the case of electrorheological fluids made of polyaniline and pine oil or its ester, treated with hexane, at temperatures between 20–60°C, shear rate 40–490 1/min, electric field strength 0.5–3.5 kV/mm:

1. An increase in electric field through the fluid increases the electrorheological strength of the fluid if the concentration level is more than 5% of weight.
2. If the fluid's concentration is 5% of weight or less, the fluid does not express electrorheological phenomena.
3. In similar conditions, temperature has no or very little effect on the electrorheological phenomena.
4. The relative change in shear rate has only a small effect on the electrorheological effectiveness of the fluid if the concentration is 15% of weight or less.
5. Grinding decreases the electrorheological strength of the electrorheological fluids based on pine oils.
6. The pine oil ester is more effective as a base oil for an electrorheological fluid if the effectiveness is measured purely on the basis of maximum shear strength versus shear rate.

7. The basic idea of making an ER fluid non-hydrous and with a low concentration level was found successful, an average of over 20% increase in viscosity with a sufficient basic level of viscosity, especially if the particle concentration was 10% of weight or above and if pine oil ester was used as the carrier fluid.

This work has defined an environmentally friendly, non-hydrous, low-concentration level electrorheological fluid based on pine oils. The use of this combination, to my knowledge, has never been published before. This work has also discussed the simultaneous effects of temperature, shear rate, electric field strength and grinding on the rheological characteristics of an electrorheological fluid. Pine oil and its ester have been shown to be an environmentally friendly and effective carrier fluid for ER fluids. The results indicate that the further development and further production of larger amounts of ER fluids based on pine oil and its ester can be a success in the matter of developing commercially available ER fluids. The results can be exploited in the making of novel electrorheological fluids for applications where a low concentration level of particles, environmental aspects, and water free solutions are important factors.



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