Sedimentation-Resistant Electrorheological Fluids Based on PVAL-Coated Microballoons

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ABSTRACT: Sedimentation is often a problem in electrorheological (ER) fluids featuring solid particles suspended in a low-density hydrocarbon oil. This problem was addressed by synthesizing particles comprising silica microballoons coated with PVAL using a salt-induced coacervation process. The ER performance of the fluids based on these particles was equivalent to prototypical commercial fluids, both with respect to current leakage and shear stress under steady simple shear flow. For comparing diverse fluids as to these practical characteristics, a dimensionless ER effectiveness number, **Er,** was proposed: $\mathbf{Er} = \sigma\dot{\gamma}/EJ$ where σ is the shear stress, $\dot{\gamma}$ is the shear rate, E is the electric field, and J is the current. The resulting uniform coatings were also found to impart a degree of resistance to breakage. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 539–547, 1997

Key words: ER fluids; electrorheology; PVAL-coated microballoons; ER effectiveness number; sedimentation; attrition

INTRODUCTION

Electrorheological (ER) fluids comprising polarizable particles suspended in oil have an unusual sensitivity to electric fields, solidifying rapidly when subjected to their influence and returning to a liquid state in their absence. While this characteristic makes ER fluids valuable in various industrial applications, their long-term and quiescent application has often been limited because of problems with particle sedimentation.

To solve the sedimentation problem, researchers have proposed several methods, such as matching the density between the two phases, stabilizing particles by surfactant addition, and using high-viscosity liquids and/or small particles. An attractive approach is to make ER-active particles with a low density—low enough so they can be used in very-low-density and low-viscosity oils with low dielectric constants. Such oils not only have enhanced ER performance, but are generally less expensive and less toxic than high-density oils (e.g., halogenated hydrocarbons). Not a great deal of work has been done yet to make and study light particles. In one approach Reitz[1] made a microballoon composite, which was then ground and separated by density. The structure and shape of the powders were not addressed. Rheological characterization of the resulting ER fluid was also unavailable.

The purpose of this research was to address the sedimentation problem by using low-density particles in ER fluids. A salt coacervation technique was used to coat silica microballoons with an ER-sensitive polymer to produce particles with the desired density and an adequate ER response.

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EXPERIMENTAL

Materials

The polymer used for coating was 88% hydrolyzed poly(vinyl alcohol), an oil-resistant polymer, with an average mol wt of 22,000. The salt for coacervation was sodium sulfate. Poly(vinyl alcohol) (PVAL) and sodium sulfate were used as received. Light mineral oil from Fisher Scientific (0121-1) served as the suspending medium.

The silica microballoons used as the core material were supplied by the PQ Corporation. Because of their large variation in density, the as-received microballoons were separated by density: the fraction with densities between 0.782 and 0.866 g/cm^3 was retained. The number-average diameter of the preselected microballoons was 55 μm with a standard deviation of 20. The coating thickness was controlled to achieve a density match between the coated microballoons and the mineral oil ($\rho = 0.84$ g/cm^3 at 25°C).

Coating Process

PVAL aqueous solution (0.5%) and silica microballoons were mixed in a round-bottomed flask to obtain a homogeneous suspension. Sodium sulfate solution (20 g/100 mL water) was then added slowly using an infusion pump. Phase separation occurred in the resulting ternary mixture as the sodium sulfate concentration was increased. The amount of salt solution was a key independent variable. According to Arshady[2] the equilibrium two-phase mixture is fully reversible; but, by decreasing the pH, the separation becomes irreversible. To effect this, hydrochloric acid (38%) was added dropwise to the solution until the pH value of the solution was ~ 2. The coated microballoons were separated from the mixture by filtration, washed repeatedly with isopropanol, and dried.

A control experiment was conducted side by side following the same coating procedure, except that there was no polymer in the initial solution. The resulting microballoons were named *salt-treated* microballoons.

Microballoon Characterization

Coating Uniformity

The uniformity of the PVAL on the microballoons was determined by placing uncoated and coated microballoons in a sealed jar containing iodine vapor. Normally iodine can dye only organic surfaces, but this was checked by including neat PVAL powders, sodium sulfate crystals, and salt-treated microballoons in the jar. The dyeing process lasted ~ 10 h. The materials dyed materials were observed under an optical microscope.

Particle Density

The "sink-swim" method was invoked to measure the density of the microballoons. Accordingly, the sinkers were compacted by centrifugation, separated, dried, and weighed. The choice of the liquid for the "sink-swim" method is of extreme importance. A mixture of two liquids is attractive; the density can be changed by varying the volume ratio of the two liquids. The liquids must both be strong nonsolvents of PVAL to avoid swelling, and of suitable densities so that mixtures will fall into the desired density range. Heptane ($\rho = 0.681$ g/cm^3 at 25°C)[3] and toluene ($\rho = 0.864$ g/cm^3 25°C)[3] were chosen accordingly. There is a drawback to liquid mixtures; if one liquid is imbibed by the PVAL slightly more than the other, a systematic error will result, which can be difficult to resolve. By test, we ascertained that the maximum systematic error could be no more than 0.0001 g/cm^3.

Density measurement of the toluene-heptane mixtures was conducted using pycnometers at room temperature (25°C). A linear relationship was found between the density of the mixture and toluene volume fraction, which was defined as the volume ratio of the toluene to the sum of the unmixed toluene and heptane.

Moisture and Sodium Analyses

The moisture content of the particulate phase is an important parameter for an ER fluid. Before electrorheological tests, the uncoated and coated microballoons were heated at 50°C under vacuum overnight, a mild drying condition. Part of the heated microballoons were used to check the moisture content using a Fisher Moisture Analyzer operating at 70°C. Higher temperatures were found to cause dehydration of the PVAL, which is a limitation of this coating.

As the coating process involves sodium sulfate solution, it is appropriate to conduct sodium analysis on the uncoated, coated, and salt-treated microballoons. The results of sodium analysis could then be used to resolve the salt contribution to the ER performance. The sodium analysis was performed using atomic absorption (AA).

Mechanical Attrition Test

When used in practical devices, the microballoons should feature good resistance to breakage. An attrition test was performed by stirring suspensions of microballoons in mineral oil using a four-bladed steel blender. Tests were conducted under two different rotor speeds, 270 and 420 rad/s, for up to 10 h. The microballoons were then recovered and washed. Broken microballoons, if any, were collected by suspending the microballoons in di(ethylene glycol).

Particle Sedimentation

Direct observation of sedimentation was conducted using a 30 wt % suspension of coated microballoons. Two commercial fluids, AFS and Rheobay, were also observed under the same conditions. Both commercial ER fluids gradually formed two layers: a very thin, liquid layer on the top and a thicker one packed with particles at the bottom. The height of the particle-rich layer was measured as a function of time.

Electrorheological Measurements

Electrorheological measurements were conducted on a Rheometrics System 4. A parallel-plate configuration was used to provide a uniform electrical field across the ER fluid. The two plates were insulated from the rest of the system with posts made from nylon and machinable glass on the top and bottom, respectively. The edges of the plates were rounded to reduce electrical field enhancement at the edges.[4] Shear stress at the plate edge was calculated from the torque using the Newtonian equations.

High voltage was supplied by a Model 205A-05R Bertan Voltage Generator. Electric current going through the ER fluid was measured using a Keithley 196 system DMM meter.

Prior to the ER measurements, the coated and uncoated microballoons were heated at 50°C under vacuum overnight. The dried microballoons were then mixed with molecular-sieve-dried mineral oil to form ER fluids with known particle contents. The resulting ER fluids were sealed in laboratory vials until tested.

RESULTS AND DISCUSSION

Coating Uniformity

The color of the dyed coated microballoon was brown, and this color appeared to be uniform, although at higher magnification a slightly wavy texture was observed with a length scale of ~ 5 μm. The uncoated and salt-treated microballoons showed no color. The PVAL powders dyed dark brown, while the sodium sulfate crystals showed no change. Comparing the color change of the microballoons with these reference materials supported the conclusion that the microballoons were coated uniformly with PVAL.

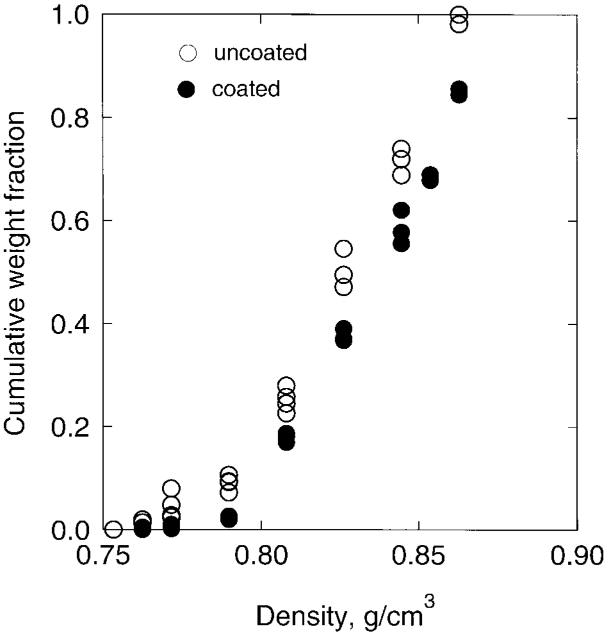

Figure 1 Density distribution of microballoons before and after coating.

Density Distribution

The plot of cumulative weight percent of the microballoons versus density is shown in Figure 1. The coating appears to shift the density distribution curve to the right, which is expected. The average density shift caused by coating is ~ 0.015 g/cm^3 for this particular measurement; the average density shift calculated by the average coating thickness (from thermogravimetric analysis) is ~ 0.010 g/cm^3, a reasonable agreement.

Moisture and Sodium Analyses

The results of the moisture analyses are listed in Table I. Reported moisture contents of ER fluids vary from $< 0.2\%$ in anhydrous systems[5] to 8% in some fluids.[6] While the moisture contents of the coated and neat microballoons used in this research were relatively low, some moisture is im-

Table I Moisture and Sodium Contents of ER Particles

Particle	Moisture Content (%)	Sodium Content[b] (%)
Uncoated	0.89 ± 0.46[a]	7.3
Salt-treated	—	17.1
Coated	1.02 ± 0.52	15.7

[a] The ± refers to the 95% confidence interval of the mean.
[b] Based on weight of microballoons.

portant for the presumed ionic polarization process.

Table I also summarizes the sodium analyses for the three kinds of microballoons. The results were based on one test on corresponding samples comprising microballoons from different batches. The sample deviation for the AA test alone is 3%. The sodium contents of the coated and salt-treated microballoons are thus indistinguishable.

Mechanical Attrition

The relationship between weight percent of nonbroken particles and stirring time is shown in Figure 2. To describe the flow conditions in the stirred suspensions, three dimensionless numbers were calculated; these are listed in Table II. The values of Reynolds number indicate that the flow under the test conditions was in the transition region between laminar and turbulent flow. The low values of the Weber number show that hydrodynamic force can not break the particles. The "Impact Number" (**Im**) was defined as the ratio of the kinetic energy possessed by a particle to the energy needed to break it. At **Im** $\ll 1$ particles are likely to bounce away from a moving surface, while at **Im** ≈ 1 the energy stored in the glass when the particle changes direction is high enough to break the glass. From the definition of the **Im,** it is evident that even a minor increase in $\varepsilon_{B,g}$ will be effective in reducing **Im** and thus reducing fracture damage. This is one important function of the coating on the microballoon.

The attrition test indicates that almost all of the coated microballoons can withstand typical impact forces. The results also suggest that the PVAL coating may increase the attrition resistance of the microballoons. The high modulus and low elongation-to-break of silica, as well as the shape and material of the blade, may also be important factors that affect the durability of the microballoons in this test. Although the microballoons probably would not survive flows between sliding surfaces, this was not checked.

ER Fluids Based on the Coated Microballoons

ER measurements and sedimentation observations were conducted on several suspensions of coated microballoons, as well as on two commercial ER fluids. One of the commercial ER fluids, comprising a lithium salt of poly(methacrylic acid) suspended in a halogenated hydrocarbon, was supplied by the Advanced Fluid Systems (AFS) in England. The AFS fluid had a particulate volume fraction of 35 vol %. The other ER fluid, Rheobay 3565 (Bayer), came without any compositional information, but has been reported[7] to comprise polyurethane particles suspended in silicone oil. It also had a particulate content of ~ 35 vol %, according to our measurements. Microballoon suspensions of 30 wt % and 10 wt % (~ 35 vol % and 12 vol %, respectively) were tested in this research.

Sedimentation

The progress of the sedimentation is shown in Table III. For the microballoon suspension, the particles diffused into three regions—floating on the top, dispersed in the oil, or settling on the bottom—reflecting their density distribution. In completely quiescent applications, the heavier

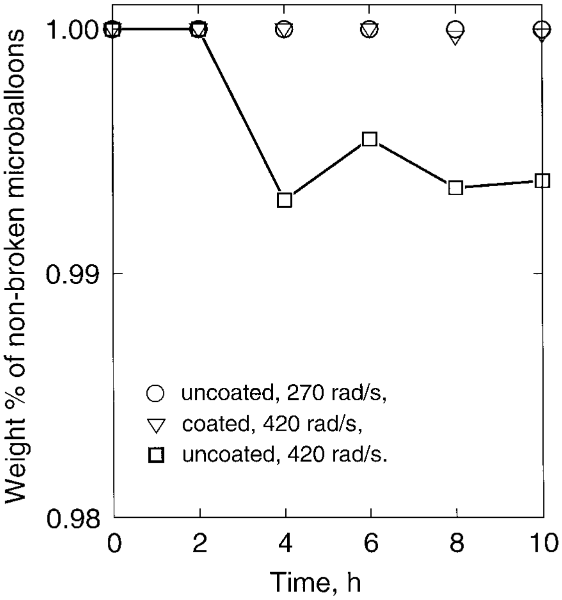

Figure 2 Mechanical attrition test results.

Table II Values of Dimensionless Numbers under Different Rotor Speeds

	Equation	Value at $\omega = 270$ rad/s	Value at $\omega = 420$ rad/s
Reynolds Number	$\mathrm{Re} = \dfrac{D^2 \omega \rho}{\eta}$	1823	2835
Weber Number	$\mathrm{We} = \dfrac{\eta \omega D_p}{\delta \sigma_{B,g}}$	$0.75 \times 10^{-6} \rightarrow 3.8 \times 10^{-6}$	$1.2 \times 10^{-6} \rightarrow 5.8 \times 10^{-6}$
Impact Number	$\mathrm{Im} = \dfrac{\rho_g \omega^2 D^2}{4 E_g \varepsilon_{B,g}}$	$0.06 \rightarrow 1.7$	$0.15 \rightarrow 4$

Symbols and values used:

D	diameter of the blade, 0.015 m
ω	angular speed of the blade, rad/s
ρ	density of the medium, i.e., light mineral oil, 840 kg/m^3
η	viscosity of the medium, 0.028 Pa s
D_p	average diameter of the particls, 55 μm
δ	average thickness of the particle shell, 5.5 μm
$\sigma_{B,g}$	tensile strength of glass, 20–100 MPa
$E_{B,g}$	modulus of glass, 73 GPa
$\varepsilon_{B,g}$	elongation-to-break of glass, $0.27 \times 10^{-3} \rightarrow 1.4 \times 10^{-3}$
ρ_g	density of glass, 2200 kg/m^3

and lighter microballoons could be used to maintain a fixed concentration of particles in the active part of the fluid, regardless of temperature.

ER Performance

The suspension of coated microballoons showed a reasonable ER response and a lower current density relative to the two commercial fluids, as shown in Figures 3 and 4, respectively. As depicted in Figure 3, the experimental fluids reached higher shear stresses at fields below 1.5 kV/mm.

Table III Sedimentation of Three ER Fluids

Time, Day	Fractional Height of the Particle-Rich Layer for AFS	Rheobay 3565	Suspension of Coated Microballoons
1	0.84	0.94	—[a]
3	0.69	0.88	—[a]
7	0.38	0.77	—[a]

[a] No single sedimentation layer, but three indistinct regions.

Figure 5 shows the dependence of shear stress on dc electric field for the fluids containing uncoated and coated microballoons. The effect of

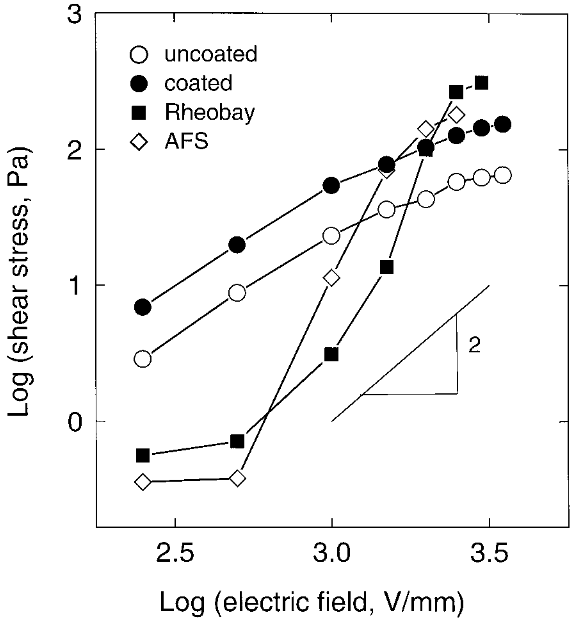

Figure 3 Comparison with commercial ER fluids: shear stress versus dc electric field.

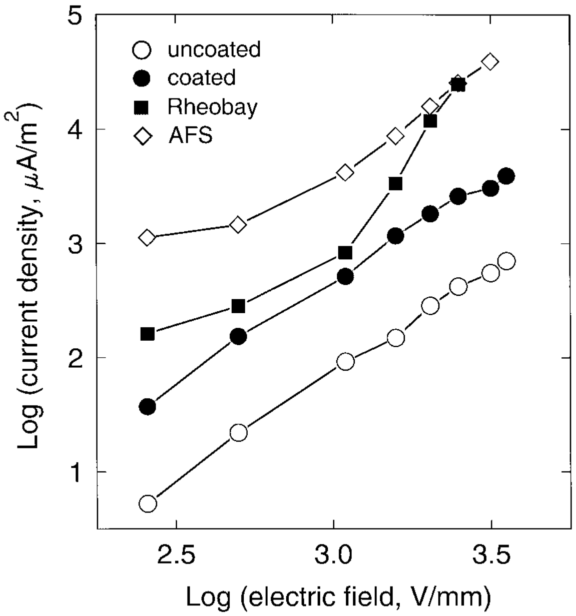

Figure 4 Comparison with commercial ER fluids: current density versus dc electric field.

electric field E on the shear stress σ often fits a power law equation[8]:

$$\sigma \propto E^n \qquad (1)$$

Here n may be fluid- and field-dependent.[8] The simplest dipole-induction theory predicts that the value of n should be 2.0. According to reported experiments, n is typically between 1 and 2.5.[9] Several explanations for the deviations from 2.0 have been reported.[8–11] Conrad and Sprecher[9] showed that the variation of n depended on the magnitude or range of the electric field: $n = 1$ at relatively high E, and $n > 2$ at low E. Another consideration is that the induced dipole moment may be not always proportional to E and may vary with the nature or moisture content of the particulate materials.[9] Conduction in the oil, as well as stress level, may also influence the value of n.[10]

For the microballoon-based suspensions, eq. (1) was not adequate. Therefore, the shear stress (σ) dependence on electric field (E), was described with the empirical equation

$$\sigma = \frac{\sigma_\infty}{1 + \left(\dfrac{a}{E}\right)^n} \qquad (2)$$

where σ_∞, a, and n are parameters. The results are listed in Table IV; the plots are shown in Figure 5. The depiction of the field dependence of shear stress by eq. (2) is much better than that of eq. (1), as can be seen in Figure 5. However, the values of n, which should describe the scaling at low fields, were still < 2. Similar deviation was also reported in literature with fluids containing silica particles, where the discrepancy was explained in terms of a saturation of induced dipole moments on the particle surfaces.[10] Shih and Conrad[10] found that the dipole moment of glass beads exposed to an air environment with 60% relative humidity saturated at low E, while at 80% saturation was less evident. Considering that the silica microballoons used in this research were equilibrated at very low water activities, saturation of the induced dipole moment may similarly explain the deviation of n from 2.0, and one would have to go to still lower fields to find higher slopes.

Student t-tests were performed on the ratios of the three parameters in eq. (2) of corresponding 30 wt % fluids to 10 wt % ones under the null hypothesis that the average of the ratio was 1 (degrees of freedom = 3). The t values are given in Table V. The hypothesis that the true σ_∞ ratio was 3, the concentration ratio, could not be rejected. The paired ratios, coated versus uncoated, of 14.7 and 26.0, at 1 degree of freedom with a probability of error of 20%, suggest that concentration of particles has a greater-than-linear effect.[9]

Electric current passing through an ER fluid

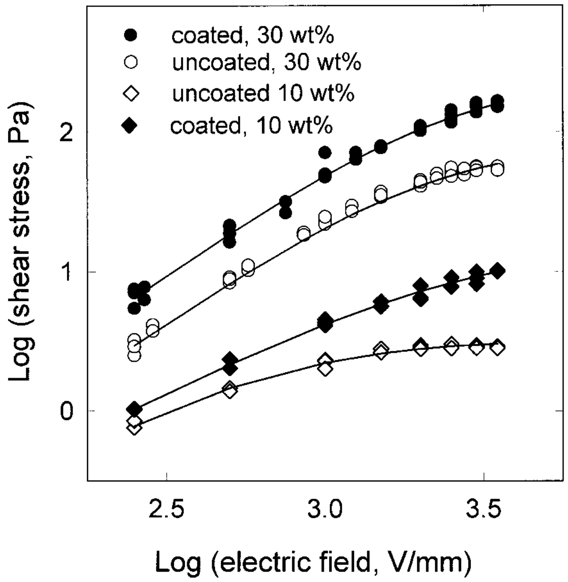

Figure 5 Shear stress dependence on dc electric field. The solid lines are fits using eq. (2) (see text).

Table IV Shear Stress Dependence on dc Electric Field for Microballoon-Based ER Fluids

Fluids	Parameter Values in Eq. (2)		
	σ_∞, Pa	a, kV	n
30 wt %, coated	246.0 ± 42.0	2.4 ± 0.5	1.58 ± 0.18[a]
30 wt %, uncoated	84.0 ± 59.0	2.1 ± 2.0	1.56 ± 0.50
10 wt %, coated	16.7 ± 1.0	2.5 ± 2.1	1.18 ± 0.60
10 wt %, uncoated	3.2 ± 0.1	0.59 ± 0.32	1.4 ± 1.3

[a] 95% confidence interval for the estimated parameter value based on fits of eq. (2) to data for ER fluids from different batches, made under the same coating conditions.

also depends on the applied electric field and the fluid. Interparticle contact and any particle chaining can provide pathways for conduction. The relationship between current density (current divided by the area) and electric field has been described by the power-law equation[9]

$$J \propto E^m \tag{3}$$

where m is usually between 1 and 5 and is found to be dependent on the field strength, the fluid, and the operating temperature.[8]

As shown in Figure 6, the suspension of coated microballoons had a higher current density than the suspension of uncoated microballoons. The current density of the microballoon-based ER fluids exhibited the characteristic non-ohmic behavior described by eq. (3); the exponents are listed in Table VI.

The coating process used in this project was salt coacervation. As indicated in the sodium analysis result, the coated and salt-treated microballoons had the expected higher sodium content than the uncoated ones. As shown in Figure 7, the suspension of salt-treated microballoons did, as a result, show a higher ER response than the suspension of uncoated ones, but it was not comparable to the response of the suspension featuring PVAL-coated microballoons. Figure 8 shows the current density results for the suspensions.

Table V Student *t*-Test Results

Parameter	*t*-Value and Comment
σ_∞	4.02, 5%[a]
a	0.76, 50%
n	1.27, 30%

[a] Chance of error by rejecting the null hypothesis.

For comparing different fluids on an equal footing, we define an ER effectiveness number (**Er**) for a fluid as the ratio of viscous dissipation to electrical dissipation

$$\mathbf{Er} = \frac{\sigma\dot{\gamma}}{EJ} \tag{4}$$

where $\dot{\gamma}$ is shear rate, s^{-1}. High **Er** is favorable.

The ER number for the three fluids at a shear rate of 0.1 s^{-1} and at various shear stress levels, as listed in Table VII, suggest an advantage for the polymer coating in achieving high performance and low power consumption.

For the fluid containing coated microballoons, we hypothesize that annealing the particles in

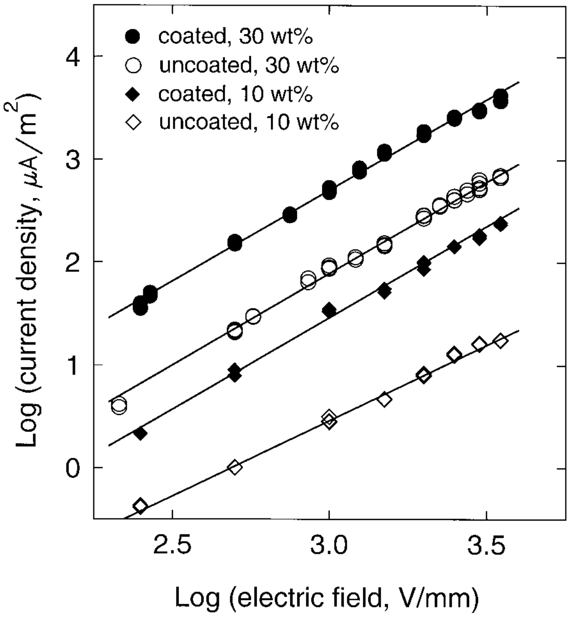

Figure 6 Current density dependence on dc electric field. The solids lines are fits using eq. (3) (see text).

Table VI Current-Density Dependence on dc Electric Field for Microballoon-Based ER Fluids

Fluid	m in $J \propto E^m$
30 wt % coated	1.77 ± 0.05[a]
30 wt % uncoated	1.81 ± 0.09
10 wt % coated	1.76 ± 0.20
10 wt % uncoated	1.47 ± 0.03

[a] 95% confidence interval for the estimated parameter value based on fits of eq. (3) to data for ER fluids from different batch, made under the same coating conditions.

mineral oil will aid in reaching higher **Er.** According to this idea, the salt will migrate toward the glass surface, while the insulating hydrophobic acetylated sequences of the PVAL will tend to migrate to the coating-oil interface. The hydroxyl groups of PVAL are hydroscopic[12] and solvating, and should encourage mobility of the Na^+ and SO_4^- ions near the surface of the glass. This layered structure should give high circumferential and low radial conductivity.

At 20% acetylation, the T_g of PVAL is ~ 20°C.[12] Thus the enhancement created by the PVAL coating may be unfavorable for ionic conduction at subambient temperatures. The dielectric constant of PVAL drops from ~ 14 to 7 as temperature drops from 31°C to −30°C, which will contribute to decreased performance at low temperature. However, the dielectric strength of PVAL can reach an incredible 1500 kV/mm at −190°C[13]; thus these coatings might endure very high fields at low temperatures, which could compensate for the lower polarizability. At high temperatures the radial conductance may be too large for practical use; at still higher temperatures (e.g., 240°C[14]) the PVAL will dehydrate.

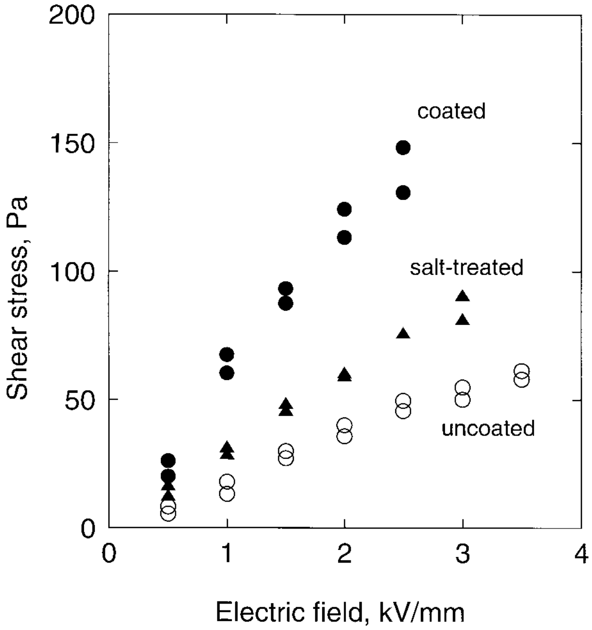

Figure 7 Comparison of the three microballoon-based ER fluids: shear stress versus dc electric field.

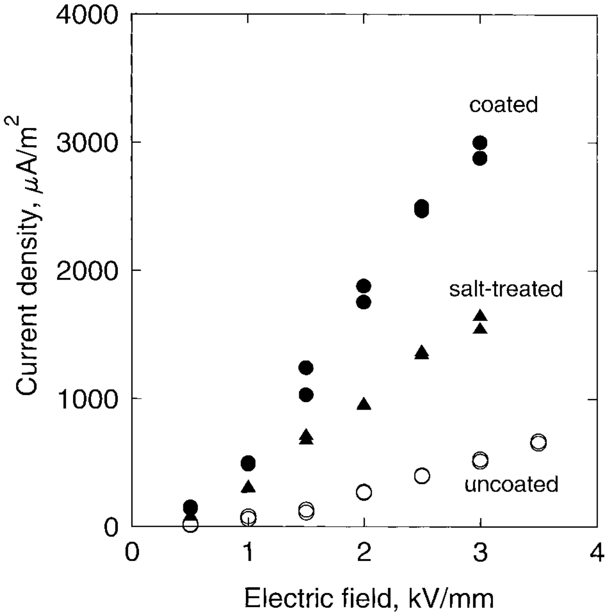

Figure 8 Comparison of the three microballoon-based ER fluids: current density versus dc electric field.

SUMMARY

By using silica microballoons, the sedimentation behavior of the resulting ER suspension differed both qualitatively and quantitatively relative to other known ER fluids in that a certain portion of the particles never settled. While this portion

Table VII ER Number (Er), at a Shear Rate of 0.1 s^{-1} for Microballoon-Based Fluids

	Values of **Er** for		
Shear Stress, Pa	Uncoated	Salt-Treated	Coated
50	0.003	0.006	0.023
75	—[a]	0.002	0.008
100	—[a]	—[a]	0.005

[a] The fluid couldn't reach the indicated shear stress under the testing conditions.

should increase with a narrower density distribution, a broader distribution will be able to compensate for the influence of temperature on the density of the suspending oil. Compared with the commercial ER fluids, the microballoon-based fluids exhibited reasonable ER performance and lower conductivity at low electric field. For comparing the practical performance of different fluids, a dimensionless group **Er** was proposed, where $\mathbf{Er} = \sigma\dot{\gamma}/EJ$ and where σ is the shear stress, $\dot{\gamma}$ is the shear rate, E is the electric field, and J is the current.

The attrition resistance of the silica microballoons was improved by coating with poly(vinyl alcohol).

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