MIXED SURFACTANT SYSTEMS TO CONTROL DISPERSION STABILITY IN SEVERE ENVIRONMENTS FOR ENHANCING CHEMICAL MECHANICAL POLISHING (CMP) OF METAL SURFACES

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2000
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by

Byron Joseph Palla
I dedicate this dissertation to my father, Arthur Palla, my fiancé Lori, my sisters Debbie and Cindy, my brother Tim, and especially my late mother, Martha Palla, who would have been so proud...
ACKNOWLEDGMENTS

I would like to express my sincere thanks and appreciation to my advisor, Professor Dinesh Shah, chairman of my supervisory committee, for his support, guidance, enthusiasm, and philosophical lessons on love, life and the pursuit of happiness. May these lessons never be overlooked nor forgotten as we continue our journey. Thanks also to the other supervisory committee members, including Professors Rajiv Singh, Raj Rajagopalan, Spyros Svoronos and Chang Wong Park for their valuable time and suggestions.

I have also greatly appreciated the financial support and the collaboration opportunities provided by the Engineering Research Center (ERC) for Particle Science and Technology at the University of Florida. The opportunities to discuss research goals and directions have been the primary guidance for my research, and this dissertation is the result. I would also like to sincerely thank the ERC faculty, particularly the director Professor Brij Moudgil, for critical analysis of my research that has kept me on track through the years. I would also like to acknowledge all the undergraduate students sponsored by the ERC for their experimental contributions to this thesis: Jennifer Hite, Jason Shaw, Robel Vina, Shane Todd, Jason Shoemaker, Augustine Jeyakumar, Matthew Brinkman, Wil Companioni and Diana Widjaya (masters student). I would also like to acknowledge the members of the Goal II: Dispersion and CMP group for their guidance and stimulating discussions, particularly Bahar Basim, Joshua Adler, Uday Mahajan, Seung-Mahn Lee, Pankaj Singh, and Kimberly Christmas.
I would also like to thank my colleagues from the Department of Chemical Engineering and the Center for Surface Science and Engineering for their help and good cheers, including Dr. Alex Patist, Dr. Steve Truesdail (and Vikki), Dr. Paul Huibers, Dr. Michael Free, Dr. Rahul Bagwe, Dr. Dibakhar Dhara, James Kanicky, Linda Jacoby, Brian Burgess, and many others with whom I have had the pleasure of working.

Finally I would like to acknowledge the assistance of Dr. Bhavani Sankar from the Department of Aerospace Engineering, Mechanics and Engineering Sciences and Dr. Jose Matutes-Aquino from the Advanced Materials Research Center in Chihuahua, Mexico, for their guidance and assistance on previous projects, and also the faculty of The University of Texas at Austin and my colleagues at 3M Corporation for the knowledge and inspiration that started this quest.
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The stability of colloidal dispersions is a critical parameter in many industries such as paints and pigments, minerals processing and electronics. Particle settling is often caused by the shielding of surface charges on the particles which otherwise would prevent coagulation and subsequent settling. This is particularly a problem in high ionic strength dispersions, where large amounts of ions serve to enhance the charge shielding and compression of the electrical double layer around the particles.

This phenomenon has been investigated for industrially significant slurries used for tungsten and copper chemical mechanical polishing (W-CMP and Cu-CMP). It has been found that the effects of addition of conventional stabilizing agents (e.g. ionic
surfactants, polymers) to these high ionic strength slurries are neutralized by the electrolytes in solution. However, the synergistic combination of a properly chosen ionic and nonionic surfactant has been found to be a suitable stabilizing agent for this type of system. The stabilization observed for these mixed surfactant systems has been explained in terms of adsorption of ionic surfactant on particle surfaces and nonionic surfactant molecules penetrating the film of the ionic surfactant due to hydrocarbon chain interactions. The enhanced adsorption of nonionic surfactant in this mechanism brings about the steric stabilization of the slurry.

The factors influencing this stabilization mechanism have been examined, yielding a robust model for stabilization of chemically complex slurries. The use of a relatively hydrophobic nonionic surfactant in the mixture yields optimal stability, with increasing hydrophobicity originating from either an increase in the hydrocarbon chain length or a decrease in the length of the ethoxylated chain. The increased stability with hydrophobicity of nonionic surfactant suggests that the partitioning of nonionic surfactant out of aqueous solution is a more important factor than the enhanced steric stabilization brought about by increasing the length of the polymeric polar group. The effect of surfactant concentration is examined and shows that maximum stabilization occurs over a range of concentration, which is dependent on the chosen surfactants. The effect of ratio of ionic to nonionic surfactant is a more complex correlation, with solubility of each surfactant becoming an issue at ratios that favor that surfactant. The various factors influencing dispersion stability are verified by novel surfactant adsorption measurements for high ionic strength environments that utilize surface tension measurements and absorbance of dye into surfactant micelles.
The influence of dispersion stability on polishing performance has been correlated. First, the use of stable dispersions is found to prevent particle agglomeration. Next, the use of stable dispersions is found to have little effect on the polishing rate of blanket tungsten wafers. The surface quality (or planarization) is found to increase by adding surfactant, although it does not necessarily correlate with dispersion stability. The polishing performance is explained as due to a lubricating layer of surfactant film on the particles. Finally, the particulate contamination of polished wafers is found to decrease with added surfactant, with either single surfactants or mixtures of surfactants leading to enhanced particle removal efficiency. All of these results suggest that the use of stable dispersions and surfactant additives in CMP slurry formulations can enhance the polishing performance, particularly for metal substrates.
CHAPTER 1
INTRODUCTION

1.1 Dispersion Stability

Dispersion is a term generally applied to a system of insoluble or partially soluble solid particles dispersed in a liquid medium. Dispersion stability refers to the kinetic stability of the particles in the medium, or in other words the ability of the particles to remain “dispersed” over a relevant time scale. Dispersions are not thermodynamically stable systems except in the rare case of exact density matched phases. The relevant time scales of dispersion stability may vary from tenths of seconds to years, depending on the application [Hiemenz and Rajagopalan, 1997]. The stability of a dispersion is an issue in any industry in which settling of particles can result in poor performance. For example, if particles settle during shipment of a slurry, the product received by the consumer will appear undesirable, and often the settled particles cannot be re-dispersed by means available to the consumer. In other industries, the stability of slurries can be more susceptible to even a slight increase in mean particle size. For example, in an application where particle size is crucial to the process, the product or process can be completely changed by agglomeration of slurry particles yielding a higher mean particle size in the slurry, even if the agglomeration is not enough to cause significant visible settling.

In most industrial applications, dispersions are complex formulations of particles (sometimes multiple types) dispersed in an aqueous or organic phase, with chemical agents added to promote rheological behavior or some desired reaction or interaction with
a substrate. Dispersion stability can have a significant effect on performance, resulting in insufficient film thickness [Pineiro and Himics, 1996], poor adhesion and insufficient reactivity [Viesturs et al., 1999] amongst many other problems depending on the application.

Table 1-1. Current applications in which dispersion stability is an issue.

<table>
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<th>Stability Issues</th>
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<td>Dispersions</td>
<td>Titania with PMMA, MMA [Hegedus, 1993]; Carbon black and copper phthalocyanine in various solvents [Li, 1997]</td>
<td>Rub-up, tint strength, transparency and hue, hiding, gloss and rheology [Pineiro, 1996 and Himics, 1998]</td>
</tr>
<tr>
<td>Electronics</td>
<td>Slurries, Dispersions</td>
<td>Alumina and silica with various chemical additives for chemical mechanical polishing (CMP) [Wang, 1996]; Titania in Pb-Sn eutectic solder for surface mount technology (SMT) [Mavoori, 1998]; Powder and polymer binder in lithium-ion batteries [Kim, 1999]</td>
<td>Polish rate, surface damage and particulate contamination in CMP [Biemann, 1999]; Microstructural stability and creep resistance in SMT [Betrabet, 1992]; Discharge capacity in batteries [Kim, 1999]</td>
</tr>
<tr>
<td>General Industrial</td>
<td>Sludge</td>
<td>PCB’s, lead, oil and grease mixed with additives and water [Grube, 1990]; Fly ash (heavy metals) and sewage sludge in ocean dispersion [Young, 1997]</td>
<td>Retrieval transport and solid-liquid separations [Tingey, 1999]; Short- and long-term extraction and leaching [Grube, 1990]; Distribution, modification by organisms in ocean</td>
</tr>
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Industries in which dispersion stability is a critical issue are summarized in Table 1-1, along with some of the many terms synonymous with dispersion. Table 1-1 also lists
representative components of slurries and some of the critical issues in each industry which can be affected by dispersion stability.

An important characteristic of many of the example systems listed in Table 1-1 is that many of the dispersions are formed or are processed under severe environments. Severe environments include complex chemical environments which contribute to extreme pH or chemical reactivity conditions. Examples of these environments in Table 1-1 include acidic conditions found in the gastrointestinal tract in biotechnology applications and extreme oxidizing or dissolving conditions found in electronics applications for batteries or polishing. Another type of severe environment includes extreme pressure or temperature conditions. Examples of these environments in Table 1-1 include minerals and ceramics processing and oil refining. All of these severe environments can make the stabilization of dispersions a much more formidable challenge. This dissertation focuses on the chemically complex type of severe environment. These systems pose a challenge for the technological solution due to the effects of charge screening on the dispersed particles.

1.2 Long Range Forces in Solution

The difficulty in achieving dispersion stability in chemically complex environments can be due to either severe pH, reactivity, or high ionic strength conditions. The surface charge on particles in aqueous solution is pH dependent, and the nature of the chemical species present on particle surfaces will depend on the chemicals in solution. Likewise, stabilizing agents added to dispersions may be ineffective under extreme pH and reactivity conditions. Most importantly for the present discussion, the chemical agents present as ions in dispersions add to the ionic strength of the medium.
The effect of high ionic strength environments on dispersion stability comes about as the result of the electrical double layer developed around a charged particle in solution. The double layer refers to the electrical potential function surrounding the particle and its common division into two layers, one with rapid potential decay near the surface and the other with a more gradual decay farther from the surface. The following discussion derives expressions which govern the magnitude of the potential decay in the region farther from the surface, as derived in Adamson [1982], and then applies those expressions to high ionic strength environments.

1.2.1 Charge Screening in High Ionic Strength Dispersions

If a plane surface bearing a uniform charge density is placed in contact with a solution phase containing both positive and negative ions, the probability of finding an ion at some particular point will be proportional to the Boltzmann factor $e^{-z e \psi/kT}$, where $z$ is the valence of the ion, $e$ is the charge on the electron ($1.6021 \times 10^{-19}$ C), $k$ is the Boltzmann constant ($1.3805 \times 10^{-23}$ J/molecule (°K)), $T$ is temperature and $\psi$ is the potential at that point in solution. The integration to infinity of the net charge density ($\rho$) at any point must be equal in magnitude but opposite in sign to the surface charge density ($\sigma$) according to the equation:

$$\sigma = -\int \rho dx \quad (1.1)$$
This integration has been carried out using the additional assistance of Poisson’s equation, which relates the divergence of the gradient of the electrical potential at a given point to the charge density at that point. The treatment of a plane charged surface and the resulting diffuse double layer is due mainly to Gouy [1917] and Chapman [1913]. This treatment is simplified by the assumption that $\psi$ is now only a function of distance normal to the surface. It is convenient to define the quantities $y$ and $y_o$ as

$$y = \frac{ze\phi}{kT} \quad \text{and} \quad y_o = \frac{ze\phi_o}{kT}$$  \hspace{1cm} (1.2)

where $\psi_o$ is the potential at the surface. The solution to Equation (1.2) with the boundary conditions ($y = 0$ and $dy/dx = 0$ for $x = \equiv; y = y_o$ at $x = 0$) is

$$e^{y/2} = \frac{e^{y_o/2} + 1 + \left(e^{y_o/2} - 1\right)e^{-\kappa x}}{e^{y_o/2} + 1 - \left(e^{y_o/2} - 1\right)e^{-\kappa x}}$$ \hspace{1cm} (1.3)

where $\kappa$ has units of length$^{-1}$ and is defined by the equation

$$\kappa^2 = \frac{e^2}{\epsilon_o e k T} \sum_i n_i z_i^2$$ \hspace{1cm} (1.4)

where $\epsilon$ is the dielectric constant of the medium, $\epsilon_o$ is the permittivity of vacuum ($8.854 \times 10^{-12}$), and $n_i$ is the ion concentration.

Equation (1.3) can be simplified for the case of $y_o \perp 1$ (or, for singly charged ions and room temperature, $\psi_o \perp 25$) as

$$\psi = \psi_o e^{-\kappa x}$$ \hspace{1cm} (1.5)
The quantity $1/\kappa$ is the distance at which the potential has reached the $1/e$ fraction of its value at the surface. This quantity is instrumental in defining the potential decay of a charged surface, and is therefore often called the Debye screening length. To illustrate the importance of ionic strength on the potential decay from a charged surface, this quantity has been graphed as a function of both salt molar concentration ($c$) and counterion valency ($z$) in Figure 1-1.

![Figure 1-1. Effect of a) salt concentration and b) counterion valency on electrical potential decay from a plane charged surface according to Equation (1.3).](image)

In Figure 1-1, it is evident that both salt concentration (part a) and counterion valency (part b) have a significant effect on the electrostatic repulsion felt between two equally charged surfaces. The electrostatic repulsion then depends significantly on the ionic strength, $I$, of the solution, defined as $I=1/2\Sigma c_i z_i^2$. Hence, both ionic strength and Debye length are good indications of the extent of charge screening in a given environment.

The decreased electrostatic repulsion associated with charge screening, if significant enough, can bring about agglomeration of particle in a dispersion, as
illustrated in Figure 1-2 for high ionic strength slurries. This figure shows alumina particles, which usually have a substantial positive charge at low pHs. However, the addition of 0.1 M potassium ferricyanide, a strong oxidizing agent, shields the positive charge with the multivalent ferricyanide anions, thus causing agglomeration of particles due to van der Waals forces. The Debye length for this system has been calculated using Equation (1.4). With a surface charge of 50 mV and a counterion valency of 3, the Debye length in this system is 4.3 Å.

Figure 1-2. Illustration of the effect of salt \( \text{K}_3 \text{Fe(CN)}_6 \) oxidizing agent on the stability of dispersions of charged alumina particles: a) particles in water at pH 4, b) with addition of salt.

Figure 1-3 shows the settling behavior of slurries with and without addition of potassium ferricyanide oxidizing agent. The slurry without oxidizer (part a) is clearly stable since the white particles are dispersed throughout the cylinder. The slurry containing oxidizer (part b) is clearly unstable with all particles having settled in the 24
hours at which time this picture was taken. From Figures 1-2 and 1-3, it should now be evident that in a dispersion of charged particles, the increase in ionic strength of the medium can significantly decrease the dispersion stability.

Figure 1-3. Settling of alumina particles after addition of oxidizer, potassium ferricyanide. Slurries are 1 wt. % AKP-50 (100-300 nm) alumina particles at pH 3, 4, and 5 (left to right), allowed to settle for 24 hours.

1.2.2 Van der Waals Attractive Forces

The forces which are responsible for the agglomeration of particles under high ionic strength conditions are commonly called van der Waals forces due to the fact that it is these forces that give rise to condensation of a vapor to a liquid [Adamson, 1982]. The van der Waals forces include the sum of all electrostatic interactions between two molecules having dipole moments ($\mu,\mu$), a dipole and its induced effect on a polarizable molecule ($\mu,\alpha$), and the dispersion force between all atoms due to the polarizability of the positive nucleus with respect to the negative electrons ($\alpha,\alpha$). The energy of each of these
interactions, at the molecular level, is a function of $x^{-6}$, where $x$ is the distance of separation, and this allows all of these energies to be grouped as van der Waals forces.

The total interaction between two infinite slabs can then be obtained by a summation over all atom-atom interactions, if the forces can be assumed to be additive. This summation is made for surfaces which are large relative to the atomic diameter by a triple integration, and the summation over the second slab can be made by another integration over the depth of the second slab. The energy is then given by

$$
\varepsilon(x)_{\text{slab-slab}} = -\left(\frac{n^2 C_1}{12 \pi x^2}\right) - \left(\frac{1}{12\delta} A x^2\right)
$$

where $\varepsilon(x)$ is the potential at distance $x$, $n$ is the number of atoms per cm$^3$, $C_1$ is an integration constant, and $A$ is the Hamaker constant, which incorporates all other constants [Hamaker, 1937]. The force can then be obtained simply by calculating $d\varepsilon(x)/dx$. Due to geometry effects on the integration, the sphere-sphere interaction energy is different and is given by the equation

$$
\varepsilon(x)_{\text{sphere-sphere}} = -\frac{rA}{12x}
$$

where $r$ is the sphere radius and the interaction energy is shown to vary with $x^{-1}$.

1.2.3 DLVO Theory

The combination of the treatment of van der Waals forces between objects in a condensed medium and the electrostatic repulsion due to the electrical double layer is called DLVO theory, after its developers Derjaguin, Landau, Verwey and Overbeek [Adamson, 1982]. It can be seen from this derivation that high ionic strength of solution
can promote agglomeration. If the condition for rapid agglomeration is taken to be that no barrier exists and hence \( \varepsilon(x) = 0 \) and \( d\varepsilon(x)/dx = 0 \), then for two slabs DLVO theory predicts that the electrolyte concentration needed for agglomeration \( (n_o) \) is given by

\[
n_o = \left[ \frac{2^7A^2}{\exp(4)} \right] \left[ \frac{D^3k^5T^5\gamma^4}{e^6A^2} \right] \frac{1}{z^6}
\]  

(1.8)

where \( \gamma \) is the surface free energy per cm\(^2\) of the solid-liquid interface and all other variables are as described before [Verwey and Overbeek, 1948]. For a \( z-z \) balanced electrolyte, equivalent conditions of concentration are in the order 100 : 1.6 : 0.13 for a 1-1, 2-2 and 3-3 electrolyte, respectively. This dependence is quite close to the prediction of the well-known Schulze-Hardy rule, which states that an increase in valency of one produces an order of magnitude decrease in the concentration needed for flocculation [Langmuir, 1938].

In one of the industries mentioned in Table 1-1, the chemical environments found in dispersions can be particularly severe, and that is the chemical mechanical polishing (CMP) industry. For metal polishing, strong oxidizing agents are added at high concentrations in order to change the surface of the substrate to make polishing easier. The oxidizing agents or other salts which are added into the polishing slurries make the process particularly vulnerable to the issues concerning high ionic strength environments discussed here. The next section gives an introduction to this exciting field and the many challenges faced by researchers in this area.
1.3 Chemical Mechanical Polishing (CMP)

In the microelectronics industry, the historic goal has been to achieve increasing complexity in a smaller size device. This goal has been achieved in recent years by the implementation of multilevel processing. In order to fabricate high-performance multilevel devices, planarization of the interlayer connection metals as well as the interlayer dielectric material is essential. CMP is the preferred process by which thin films of metals and dielectric materials for multilayer integrated circuit manufacturing are planarized [Stiegerwald et al., 1996]. Figure 1-4 illustrates the processing steps involved in multilevel integrated circuit manufacturing. This processing scheme is called “damascene” processing, and it involves essentially two planarization steps, achieved by CMP, for each processing level. These steps are illustrated in part b) showing SiO$_2$ planarization and part c) showing metal CMP.

![Deposition of SiO$_2$ on Metal Circuits](image1)

![Planarization of SiO$_2$ and Etching of Interconnects](image2)

d) Repetition of Process for Additional Levels

![Deposition of Interconnect Metal and Metal CMP](image3)

![Repetition of Process for Additional Levels](image4)

Figure 1-4. Processing steps involved in multilevel integrated circuit manufacturing.
1.3.1 CMP Process Components

The CMP process generally consists of rotating a polishing media, referred to as a pad, against the wafer while polishing slurry is deposited between the pad and the wafer. The pad is used to provide support against the sample surface and to carry slurry between the sample surface and pad [Golini and Jacobs, 1991]. A schematic of the CMP process is illustrated in Figure 1-5. This figure also includes an illustration of the interaction between the wafer and slurry in tungsten CMP. This figure illustrates the movement of abrasive particles across the tungsten surface, which is simultaneously undergoing chemical conversion to tungsten oxide.

The polishing slurry provides the means by which both chemical and mechanical action is used to remove and subsequently planarize the wafer surface. Mechanical
action is accomplished by the use of abrasive particles in the slurry. Chemical action is achieved by the incorporation of chemical agents that aid in planarization into the slurry [Carr, 1990]. The chemical component of the slurry, which acts isotropically on the wafer surface, is necessary to enhance the mechanical action of the slurry. The chemical components which may be present include oxidizing agents, complexing agents, dissolution enhancing agents, corrosion inhibitors and buffering agents. However, the mechanical component of the slurry must also be present to preferentially abrade material at the asperities, or high points on the surface, thus providing the driving force for planarization [Carr, 1990].

It is both the chemical and mechanical action achieved by the slurry that achieves global planarization of the wafer surface. The chemical component of the polishing slurry, although crucial in achieving the required planarization, can also have detrimental effects on the particles used in the slurry. As discussed previously, the addition of ions to a particle slurry will decrease the electrostatic repulsion between the charged particles by shielding the charges. This decreased electrostatic repulsion, if significant enough, can bring about agglomeration of the particles.

The presence of large particles in the polishing slurry which contacting the wafer during polishing has been determined to cause defects in the wafers. However, the particles used in CMP slurries usually have a mean particle size of less than 0.5 μm [Golini and Jacobs, 1991], which is too small to cause the scratches observed on defective wafers. In addition, filtration devices are used in the input lines to the polisher which prevent particles much larger than the mean particle size from entering the polishing apparatus. Thus, the large particles that cause the observed scratches in
defective wafers are being formed during the CMP process as the result of agglomeration of small particles or chunks or pieces of debris produced by the polishing process.

In recent years, CMP has been applied to shallow trench isolation (STI) technology for deep-sub-micron processes. Poly silicon (Si), CVD Si or silicon dioxide (SiO$_2$) can be grown or deposited in the trench and planarized by a CMP process [Wang et al., 1998b]. The main area of current interest in the CMP industry is in improving methodologies for inlaid metallization applications. The two materials which have received the most attention for integration into the inlaid scheme are copper and aluminum, both of which offer significantly lower resistivities over the conventional metal, tungsten. The inlaid scheme offers greater challenges for CMP performance, primarily due to the need to provide sufficiently planar surfaces for broad topographic ranges at each metal level [Farkas et al., 1998]. Nonplanarized surface topography is a result of the fabrication process that ends up with a deposition of the film on a previously patterned surface, with a pattern generated by etching. Loss of planarity also arises during lithography due to autofocus errors, residual lens aberrations, resist thickness variations and wafer curvature associated with wafer preparations and with film stresses. [Steigerwald et al., 1996].

As can be seen from this discussion, there are many variables which can change the performance of the CMP process. Since there are many substrates which are either presently used or are candidate materials for CMP processing, there are likewise many different slurry chemistries which have been developed in order to overcome the unique challenges that each substrate presents. Within each subclass of CMP, there are also many strategies which have been taken in slurry formulation to attempt to enhance the
particular characteristics which are crucial to that subclass. For example, the issues of importance in metal CMP include planarization rate, surface quality, selectivity, dishing and erosion. The last three parameters are issues in patterned wafers, and often end up being the critical parameters influencing slurry design. Selectivity is the ratio of the polishing rate of the metal to that of the interlayer dielectric (ILD) material, which is usually silicon dioxide (SiO$_2$). Since polishing should stop once the insulating layer is reached, a high selectivity is desired in metal CMP. Another common problem in metal CMP is dishing, which refers to poor step coverage of deposited metal in etched trenches and other features. This problem is illustrated in Figure 1-6, which shows a properly polished feature with good step coverage (a), a feature which shows dishing (b) and a feature which shows erosion of the ILD material (c). As can be seen, dishing refers to a curved profile of the polished feature which is then translated to succeeding layers and can cause defects or failure. Finally, erosion of the ILD material refers to the overpolishing of insulating material near features, which results in loss of planarity near features. Erosion is enhanced by using a slurry with low selectivity towards the metal surface. Both dishing and erosion should be minimized by appropriate slurry design.

![Figure 1-6. Illustration of common problems associated with CMP of metal surfaces.](image)
1.3.2 CMP Polishing Materials and Slurry Chemistries

The successful applications of the CMP process in silicon integrated circuits (IC) has started with building multilevel (greater than 2) interconnection structures employing deposited silica (SiO$_2$) as the ILD, chemical vapor deposited (CVD) tungsten as the via fill metal, and sputtered aluminum as the planar interconnection metal [Moy et al., 1989]. Thus initial process developments in the CMP industry have focused on the CMP of SiO$_2$ and tungsten layers [Kaufman et al, 1991]. Since these developments, the use of CMP has expanded to a large variety of materials including metals (Al, Cu, Ta, Ti, TiN, W, and their alloys), insulators (SiO$_2$ and doped SiO$_2$ glasses, Si$_3$N$_4$, and polymers), and polysilicon [Steigerwald et al, 1996].

Advanced metallization schemes are required to obtain the performance benefits of scaling device dimensions into the sub-0.5 µm regime [Steigerwald et al., 1996]. Interconnect delay is a critical parameter that determines the flow of current through the IC, and it is defined by

\[ RC = \frac{\rho \varepsilon l^2}{td} \]  

(1.9)

where $RC$ is the interconnect delay, $\rho$ is the metal resistivity, $\varepsilon$ is the permittivity and $t$ is the thickness of the insulator, and $l$ and $d$ are the length and thickness of the metal line, respectively. The interconnect delay can be thus be decreased by decreasing $\rho$, $\varepsilon$, or $l$, or by increasing $d$ or $t$ [Wilson et al., 1993]. As discussed below, the use of multilevel metallization decreases line length $l$ and allows for interconnections to be scaled less aggressively than the gate level. The combination of low resistivity ($\rho$) metal, low
dielectric constant (ε) ILD, and multilevel metallization should yield high performance interconnections [Steigerwald et al., 1996].

Conventional IC metallization schemes utilize aluminum alloys, in part or in full, as the interconnection metal. While aluminum is considered a good conductor, with a resistivity of 2.66 µΩ-cm, other metals possess even lower resistivities. Table 1-2 lists several new candidates for IC metallization as well as metals currently utilized.

Table 1-2. Properties of low resistivity metals (from Li et al., 1994 and Wolf and Tauber, 1986)

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Al</th>
<th>Al Alloy</th>
<th>Au</th>
<th>Cu</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (µΩ-cm)</td>
<td>1.59</td>
<td>2.66</td>
<td>3.5</td>
<td>2.35</td>
<td>1.67</td>
<td>5.65</td>
</tr>
<tr>
<td>Electromigration Resistance (at 0.5 µm)</td>
<td>Poor</td>
<td>Poor</td>
<td>Fair - Poor</td>
<td>Very Good</td>
<td>Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Corrosion Resistance</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Adhesion to SiO₂</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Si Deep Levels</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

From Table 1-2, of the metals with lower resistivity than aluminum, copper appears to be the most attractive. Copper has a resistivity only slightly greater than silver and approximately 50% lower than conventional Al alloys. Copper has a higher melting point (1356 K) than aluminum (933 K) which leads to greater electromigration resistance [Murarka, 1993]. As interconnection dimensions are scaled, the metal interconnections are required to carry greater electron current densities. Copper is expected to handle current densities of up to 5 x 10⁶ A/cm² before the onset of electromigration failure, which is over an order of magnitude higher than the current densities which Al can handle [Li et al., 1994].
According to Table 1-2, there are also several challenges with using copper metal, including the fact that copper exhibits deep levels in the silicon band gap and copper impurities in SiO$_2$ lead to leakage [Sze, 1981]. However, several materials are effective barriers to copper diffusion and their use as liner films between the copper and the silicon or SiO$_2$ will prevent degradation in the electronic properties of the silicon and SiO$_2$ [Wang, 1994]. Another challenge with copper is that it is susceptible to corrosion and therefore must be passivated. The use of corrosion inhibitors has hence been investigated for copper CMP applications [Steigerwald et al, 1996].

Table 1-3. Slurry chemistries applied to CMP applications.

<table>
<thead>
<tr>
<th>Polishing Substrate</th>
<th>Abrasive Particle</th>
<th>Chemical Agents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten</td>
<td>Alumina (Al$_2$O$_3$)</td>
<td>Potassium ferricyanide (K$_3$Fe[CN]$_6$), ferric nitrate (Fe(NO$_3$)$_3$) or potassium iodate (KIO$_3$) as oxidizing agent</td>
<td>Kaufmann, 1991</td>
</tr>
<tr>
<td>Copper</td>
<td>Alumina</td>
<td>Nitric acid (HNO$_3$) with citric acid as an inhibitor</td>
<td>Feng, 1999</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>Nitric acid (HNO$_3$) with 1H-benzotriazole (BTA) as an inhibitor</td>
<td>Stiegerwald, 1994</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>Ferric nitrate (Fe(NO$_3$)$_3$) with BTA as inhibitor</td>
<td>Luo, 1998 and Luo, 1996</td>
</tr>
<tr>
<td></td>
<td>Silica (SiO$_2$)</td>
<td>Hydrogen peroxide (H$_2$O$_2$) with citric acid and BTA as inhibitors</td>
<td>Kondo, 1998</td>
</tr>
<tr>
<td></td>
<td>Alumina or other</td>
<td>An oxidizing agent such as urea H$_2$O$_2$, a complexing agent such as ammonium oxalate or tartaric acid, and an optional surfactant</td>
<td>Kaufman, 1999 and Kaufman, 1998</td>
</tr>
<tr>
<td></td>
<td>Alumina or other</td>
<td>Oxidizing solution containing peroxides, amino acids or organic amines, and a metal or metal compound such as Cu, Co, Fe, Pb, or Ni</td>
<td>Prendergast, 1999</td>
</tr>
<tr>
<td></td>
<td>Alumina or other</td>
<td>One of the following: a hydroxylamine, ammonium persulfate, a peracetic acid or periodic acid</td>
<td>Small, 1998</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>Ammonium hydroxide (NH$_4$OH) with NaClO$_3$ as extra oxidizer and BTA as inhibitor</td>
<td>Luo, 1997</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Alumina</td>
<td>H$_2$O$_2$</td>
<td>Wrschka, 1999</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>Phosphoric acid and citric acid</td>
<td>Kuo, 2000</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>Fluoride or other halogen and citric acid as chelating agent</td>
<td>Feller, 1997</td>
</tr>
<tr>
<td>TiN (barrier layer)</td>
<td>Alumina or other</td>
<td>Urea hydrogen peroxide (oxidizer 1) and an organic acid (oxidizer 2)</td>
<td>Kaufman, 2000</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>H$_2$O$_2$ with a commercial slurry</td>
<td>Hernandez, 1999</td>
</tr>
<tr>
<td></td>
<td>Alumina or other</td>
<td>An oxidizing agent and complexing agents including a phthalate compound and a di- or tri-carboxylic acid</td>
<td>Wang, 2000 and Wang, 1998</td>
</tr>
<tr>
<td>Silica (SiO$_2$)</td>
<td>Silica</td>
<td>Ammonium hydroxide (NH$_4$OH) to adjust pH</td>
<td>Mahajan, 1999</td>
</tr>
<tr>
<td>FLARE 2.0 (low-x)</td>
<td>Zirconium oxide (ZrO$_2$)</td>
<td>None</td>
<td>Towery, 1998</td>
</tr>
</tbody>
</table>
The slurry chemistries being implemented in the present CMP market have been thoroughly reviewed and many examples are listed in Table 1-2. This table identifies the type of surface, the abrasive particles and the chemical agents incorporated along with the source. Note that the references are very recent, being primarily from the years 1999-2000. The recent research efforts in each area of the CMP industry are summarized in the following sections.

1.3.3 Tungsten CMP

Tungsten polishing (W-CMP) will be discussed first here because it is the most “conventional” metal used in CMP processes. Conventional in this sense means it has been around more than five years, has been researched thoroughly by CMP standards and is being slowly phased out and replaced by more conductive metals such as copper and aluminum. Tungsten CMP has been shown by Kaufmann et al. [1991] to proceed by oxidation of the metal surface followed by removal of the oxide by the abrasive material. Hence an oxidizing agent is incorporated in all tungsten CMP slurry chemistries used to date. The slurry chemist is assisted in tungsten CMP by the fact that tungsten not only forms a passivating oxide layer, but also that the oxide layer is a softer, easier to polish material relative to the metal. Bielmann et al. [1999a] have verified the passive layer formation on a W surface using \( \text{Al}_2\text{O}_3 \) and \( \text{K}_3\text{Fe(CN)}_6 \) slurry by electrochemical measurements. Kneer et al. [1996] have shown that the thin oxide layer formed in W-CMP is composed of both \( \text{WO}_2 \) and \( \text{WO}_3 \) phases. In a review of metal CMP processes, Yu et al. [1999] report that in the period from 1994 to 1998, defectivity, which refers to the percentage of defective wafers, and oxide erosion in W-CMP have been reduced by
factors of 20x and 5x, respectively. The colloidal stability and purity of the slurry have also been improved by using better materials and equipment.

The isoelectric point (IEP) of alumina particles in water is near pH 8.5. However, Osseo-Asare and Khan [1998] have shown that in the presence of tungstate ions removed from W wafers by CMP, the IEP of alumina shifts to lower pH values. In fact, with a tungstate ion concentration of $10^{-5}$ M, the IEP of alumina is less than 3, indicating a negatively charged surface throughout the experimental range for W-CMP. This result could have serious implications on colloidal stability and post-CMP cleaning. The defectivity performance of Cabot Corporation’s SEMI-SPERSE W2000 alumina based slurry has been investigated using atomic force microscopy (AFM) by Grumbine et al. [1998]. Although highest levels of defectivity were observed using a hard pad with high downforce, the choice of slurry was the largest factor governing the defectivity level with W2000 leaving a virtually undamaged oxide surface. The defectivity presumably reflects the damage done to the surface by slurry particles during the abrasion process.

1.3.4 Copper CMP

Copper polishing (Cu-CMP) has introduced new challenges for the CMP industry due to differences between copper and tungsten. Copper, unlike tungsten, does not form a passivating oxide layer but rather dissolves quite readily at low pH’s. As a result, inhibitors such as 1H-benzotriazole (BTA) have been introduced to copper slurry chemistries in order to control corrosion by forming a protective and stable film which can withstand chemical and thermal environments [Brusic, 1991]. Concentrations of BTA as low as 0.01 M have been found to reduce the corrosion rate of copper to near zero while not reducing the polishing rate significantly [Wang et al., 1997].
Another method that has been introduced to combat this problem has been to use less harsh chemical environments that are still capable of achieving an acceptable removal rate. The passivation regime in which copper will form an oxide layer is in the region of pH greater than 6. In this regime, oxidizing agents are added to enhance oxidation of the substrate and complexing agents may be added to enhance removal of abraded copper. The complexing agents are necessary because copper removed during the polishing process is often redeposited on the metal surface, which can cause significant defects due to lack of planarity. The use of slurries above pH 6, however, are problematic in that the selectivity to SiO₂ polishing is rather low [Carpio et al., 1995]. This is not a problem in tungsten CMP since pH’s lower than 4 combine both passivation chemistry due to the formation of an oxide layer and a high selectivity towards the SiO₂ insulating layer. Another problem with copper CMP in the oxidation regime is that the oxide layer, which may consist of CuO, Cu₂O, Cu(OH)₂ or combinations thereof, is usually porous and may not provide sufficient protection of the metallic copper from the chemical species. As a result, inhibiting layers that prevent corrosion are still added in the oxidation regime, as in the dissolution regime [Luo, 1997]. These inhibiting layers slow the dissolution rate of copper and allow the CMP process to control the polishing rate, rather than the dissolution rate.

Another challenge facing formulators is that copper is a softer material than tungsten, creating the need for using either softer abrasives or smaller, more uniform particle sizes which reduce scratching for copper CMP [Carpio et al., 1995]. Kondo et al. [1998] has proposed a model which shows that Cu-CMP proceeds according to Cu surface oxidization, oxidized layer protection by an inhibitor, polishing of the protection
layer on top of protrusions by fine abrasive, and etching of the oxide by an acidic media. This model is similar to the passivation model proposed for tungsten CMP by Kaufman et al. [1991], except that the copper model includes an inhibiting agent and the ability of the slurry to etch the oxide. The proposed silica-based polishing slurry yields a removal rate of 150 nm/min with reduced scratches. However, a large ratio of the CMP removal rate to the etching rate is required for reducing Cu dishing [Kondo et al., 1998]. Luo et al. [1998] has shown for Cu-CMP that the polish rate increases linearly with increasing downward pressure and rotational speed, but the Preston equation needs to be modified to represent the data. The inclusion of an additional velocity term representing the greater dependence of removal rate on the velocity, and a constant representing the purely chemical reactivity of the slurry, provides a satisfactory model. Although the challenges of Cu-CMP are difficult, it has been established in recent years as a viable approach for Cu metallization technology [Yu et al., 1999].

1.3.5 Aluminum CMP

Aluminum polishing (Al-CMP) is proposed to proceed much like tungsten polishing, with oxidizing agents added to the slurry to yield a surface passivated oxide layer which is removed stepwise [Wang et al., 1998c]. Hernandez et al. [1999] showed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) that the removal rate depends critically on the surface saturation of the pad with Al₂O₃ abrasive particles. Wrschka et al. [1999] showed for a H₂O₂ oxidizing agent that the oxidizing agent concentration only has a weak effect on the removal rate of Al. The Preston equation is the most frequently referenced expression for polishing rate, and it predicts that the polishing rate is directly proportional to the pressure and the linear
velocity of the pad relative to the wafer [Preston, 1927; Brown et al., 1981]. The study by Wrschka et al. [1999] fails to describe the dependence of the removal rate on pressure and velocity, and a power law function is proposed instead. An Al-CMP technology has been reported by Yu et al. [1999] to yield good defectivity and excellent patterned wafer planarity. Wang et al. [1998c] have shown using Al and alloys with Cu and Si that alloy content and grain size have an effect on removal rate. As can be seen, Al-CMP technology is more established and seems to present less challenges than Cu-CMP. Even though copper CMP is a more difficult process than aluminum CMP, the lower resistivity of copper versus aluminum makes up for the difficulties in polishing.

1.3.6 CMP of Other Metals

Polishing of a TiN barrier layer should proceed at similar rates to the primary metal, so a selectivity of close to 1 is desired in this case. Hernandez et al. [1999] found that the incorporation of hydrogen peroxide (H$_2$O$_2$) into a commercial slurry for Al-CMP dramatically increased the dissolution of TiN, as desired. Many of the slurries being investigated for copper CMP are also useful for polishing of TiN and other barrier materials.

Many investigations have also attempted to explain and improve polishing through the use of electrochemical measurements. For example, the role of metal concentration gradient in CMP has been examine by Osseo-Asare [1998] with the aid of pH-potential diagrams, also known as Pourbaix diagrams, which indicate the various phases (reactions and reaction products) that are stable in an aqueous solution at equilibrium [Pourbaix, 1975]. Process conditions have been identified that favor
mechanical polishing, etching, or polishing that is both chemical and mechanical for Cu-CMP, W-CMP and titanium CMP.

1.3.7 CMP of Silica (SiO2) and low-κ Dielectric Materials

As illustrated in Figure 1-4, CMP of the interlayer dielectric material is another important application of CMP. The conventional dielectric material is silica, which is usually polished with silica particles at a high pH in order to enhance silica dissolution [Mahajan et al., 1999]. This slurry chemistry does not yield a high ionic strength environment, and hence the instability shown in Figure 1-2 is not expected to occur in this system. This is because silica has sufficient negative charge at high pH to promote stability in these low ionic strength environments.

Table 1-4. Dielectric constants of selected candidate low-κ ILD materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric Constant (κ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.9 - 6.0</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; · F, SiO&lt;sub&gt;2&lt;/sub&gt;· B</td>
<td>3.0 - 3.9</td>
</tr>
<tr>
<td>Polymides</td>
<td>2.9 - 3.9</td>
</tr>
<tr>
<td>Fluorinated Polymides</td>
<td>2.3 - 2.8</td>
</tr>
<tr>
<td>Parylenes</td>
<td>2.3 - 2.7</td>
</tr>
<tr>
<td>Fluoro-polymers</td>
<td>1.8 - 2.2</td>
</tr>
<tr>
<td>Teflon-AF</td>
<td>1.9</td>
</tr>
<tr>
<td>Micro-porous Polymers, Aero-gels</td>
<td>1.3 - 1.7</td>
</tr>
</tbody>
</table>

Motivated by equation (1.9), strategies to reduce capacitance effects associated with shrinking design parameters include incorporating not only low resistivity metals such as copper but also insulators with low dielectric constants, or low-κ materials.
Several inorganic and organic materials are currently being investigated as low-κ materials [Pai and Ting, 1989]. Conventional SiO$_2$ deposited by CVD has a κ of between 3.9 and 6.0 depending on the H$_2$O concentration in the SiO$_2$ [Ting, 1994]. By doping the SiO$_2$ with fluorine or boron and lowering the H$_2$O content, κ may be reduced to between 3.0 and 3.9. Organic materials such as those listed in Table 1-4 exhibit even lower dielectric constants and are excellent candidates for low-κ ILD’s [Steigerwald et al., 1996].

It follows that CMP of novel low-κ ILD materials has been investigated as a processing issue. Some of the recent research in this area is highlighted in the following discussion. FLARE 2.0, a poly(arylene) ether from AlliedSignal, Inc., with a κ of 2.8, is a candidate low-κ ILD material [Towery and Fury, 1998]. Other FLARE polymers have been investigated by Hendricks and Lau [1996] and have been shown to have sufficiently high thermal and thermomechanical stability to withstand current process temperatures associated with metal deposition and annealing steps. CMP of FLARE films yield uniform, defect-free and scratch-free surfaces. A recent attempt to develop a CMP process for stacked low-κ CVD oxide films has been investigated by Hartmannsgruber et al. [2000]. The dielectric layer is composed of a low-κ, methyl-doped SiO$_2$ layer (tradename Flowfill) embedded between thin SiO$_2$ layers. A higher removal rate of the low-κ Flowfill layer in comparison to that of the cap (SiO$_2$) layer results in a significant increase in the degree of planarization. It also leads to a reduction in the polishing time required to achieve planarization of the entire wafer once the first area of the wafer is planarized, also called the overpolish time. Another low-κ material which has been
successfully planarized with a commercial CMP slurry is the spin-on SiLK resin [Kuchenmeister et al., 2000].

A study by Zhang et al. [1998a] identifies the mechanism in polymer polishing as mostly mechanical, not chemical in nature. As a result, the slurry particle size plays the major role in controlling the polish rate. Dishing in patterned wafers is minimized, as expected, by use of a hard pad surface. Hard pads do not conform to the topography on the wafer surface, hence reducing dishing effects. Another class of polymers with potential application in low-\(\kappa\) dielectric applications is the benzocyclobutenes (BCB’s). Neirynck et al. [1996] have investigated the polishing of a BCB using surfactant additives to enhance polymer dissolution, with other additives including \(\text{HNO}_3\) and BTA. It is proposed that the surfactant improves the polymer wettability by making the surface hydrophilic, hence yielding a higher dissolution rate. Other polymers which have been investigated as ILD materials with copper interconnects include divinylsiloxane and parylene-\(n\) [Price et al., 1997].

From the preceding discussion, it is evident that there are many issues in CMP which are yet to be fully addressed. Among these issues is dispersion stability, which may have a significant effect on slurry performance. The present investigation focuses on the issues concerning dispersion stability in model systems for CMP of metal surfaces.

1.4 Surfactants and Polymers as Stabilizing Agents

The work presented here focuses on dispersion stabilization and its application in CMP, so it is important to discuss the general approaches taken to stabilize dispersions. The two primary classes of molecules which are applied as stabilizing agents are
surfactants and polymers. These two classes of molecules differ, sometimes significantly, in the way in which they bring about stabilization. To illustrate this point, the use of surfactants and polymers as stabilizing agents is shown schematically in Figure 1-7.

**Figure 1-7. Illustration of surfactants and polymers as stabilizing agents on hydrophilic particles.**

Surfactants can be divided into two general types: ionic and nonionic. This designation refers to the charge on the hydrophilic head group of the surfactant. Ionic surfactants can be further categorized into cationic, anionic and zwitterionic types, with the latter referring to a molecule that has both a positive and a negative charge present on the head group. The most widely used anionic groups are sulfate (−SO₄⁻), sulfonate (−
SO₃⁻) and carboxylate (–CO₂⁻), while the most widely used cationic groups are the quaternary ammonium groups (–NR₃⁺), where R can be –CH₃, –(CH₂)nCH₃, or a variety of other alkyl groups.

1.4.1 Ionic Surfactants

As can be seen from Figure 1-7, ionic surfactants are generally used as electrostatic stabilizing agents. By adsorbing ionic surfactant onto an oppositely charged surface in sufficient quantity that a bilayer of molecules is formed due to hydrocarbon chain interactions between adjacent molecules, a layer of charged hydrophilic groups will be extending into the aqueous solution. Since these charges are opposite in sign to the surface charge, this procedure has the effect of reversing the sign of the electrical potential at some distance prior to the second layer of adsorbed ionic head groups. As a result, the long range electrostatic forces between adjacent particles will be repulsive due to the repulsion of like charges opposite in sign from the surface charge. Due to the significant number of ionic surfactant molecules which can be adsorbed on a particle in a bilayer configuration, which is limited only by the area per molecule of a tightly packed layer of the given molecule, the apparent charge of the particle can be made significant enough to produce a stable dispersion. This is true even if the initial surface charge is insufficient to electrostatically stabilize the particles, and therefore ionic surfactants can be used to stabilize particles of little or no surface charge.

1.4.2 Nonionic Surfactants

Nonionic surfactants have no charge associated with them. As a result, DLVO theory predicts that nonionic surfactants will not provide a significant repulsive barrier to agglomeration. However, nonionic surfactants have been successfully implemented as
stabilizing agents in a number of applications. This is because nonionic surfactants are a class of molecules that may act as steric stabilizing agents, which is a type of stabilization not considered by DLVO theory. Nonionic surfactants that are used as stabilizing agents are typically polymeric in nature, meaning that the hydrophilic head group of the surfactant is a hydrophilic polymer chain, and therefore they act to provide steric stabilization in the same fashion as pure polymer molecules, which will be considered in the following section.

Nonionic surfactants differ from polymers in that, in Figure 1-7, they must form a bilayer if adsorbed on a hydrophilic surface in an aqueous solution, similar to ionic surfactants. Nonionic surfactant molecules offer an advantage over polymers in that they are amphiphilic surfactant molecules and typically have a higher adsorption potential than an equal chain length polymer. The tendency of surfactant molecules to adsorb at interfaces will be discussed in more detail in the next section. The discussion of steric stabilization naturally leads to the discussion of polymers as dispersion stabilizers.

1.4.3 Polymers

Polymers can be used as stabilizing agents for dispersions as well, with the type of stabilization mechanism being steric in nature, particularly for uncharged polymers. Steric stabilization occurs due to the presence of physical barriers adsorbed on particles that prevent the particles from coming close enough to allow the van der Waals attractive forces between particles to dominate [Napper, 1970; Smitham and Napper, 1979]. The van der Waals attractive potential between two spheres has been given in Equation (1.7), and can be seen to decrease with the inverse of the separation distance. Polymers can be effective stabilizing agents only if the polymer – solvent interactions are more favorable
than the polymer – polymer interactions [Rosen, 1989]. These interactions determine the conformation of the polymer once adsorbed on a surface, and hence determine the minimum separation distance which can be achieved through the adsorbed layers.

The key to steric stabilization is to increase the closest distance of approach between particles in order to minimize van der Waals attractive forces [Tadros, 1986; Lee et al., 1986]. Without steric stabilizing agents, the closest distance of approach is limited only by the weak electrostatic forces, so the particles easily enter the strong potential well near the surface. With stabilizing agents, the attractive potential is greatly reduced at the closest distance of separation, making the barrier to agglomeration much easier to manipulate. A key modification to DLVO theory has been the estimation of so-called steric forces which come into play in a system where steric stabilization dominates. These forces then supply the repulsive barrier that prevents particle agglomeration in such sterically stabilized systems. There are at least three advantages that steric stabilization possesses over electrostatic stabilization: Its relative insensitivity to high concentrations of electrolytes; the fact that high solids dispersions display relatively low viscosities; and it is equally effective in both aqueous and nonaqueous dispersion media [Napper, 1983].

1.4.4 Applications as Stabilizing Agents

There have been numerous investigations in previous decades devoted to stabilization of particles using either surfactants or polymers. The following discussion serves to give an example of some of the research in this area, although a more thorough review is focused on the study of mixtures of surfactants as stabilizing agents in the next chapter. Numerous investigations, as discussed below, have focused on adsorption of
ionic surfactants on oppositely charged particle surfaces. Such adsorption has been studied extensively by Somasundaran and Feurstenau [1966], Gaudin and Feurstenau [1955] and Somasundaran and Kunjappu [1989], primarily for the system of sodium dodecyl sulfate (SDS) on alumina particles. The stability of silver iodide and iron (III) oxide dispersions has been found by Gotoh et al. [1998] to be dependent on both the concentration and hydrocarbon chain length of monoamino-monocarboxylic acid, a zwitterionic dispersing agent. Catalytic colloidal rhodium particles have been stabilized using a water-soluble surfactant by Larpent et al. [1991]. The stabilizing mechanism of calcite dispersions in the presence of sodium polyacrylate has been found by Rogan et al. [1994] to change from electrostatic to steric depending on the dispersant concentration. Steric stabilization by nonionic polymers at high concentrations for silica (SiO$_2$) systems has been observed by Giordano-Palmino et al. [1994]. A recent paper by Moudgil and Prakash [1998] discusses the application of polymers and surfactants as agents for selective flocculation and the parameters which influence adsorption. Another recent paper by Sjoberg et al. [1999] discusses adsorption of surfactants and polymers on stability and rheology of concentrated kaolin dispersions. As discussed, both ionic and nonionic surfactants can be effective stabilizing agents for different types of dispersions, and this class of molecules will be the subject of the remainder of this investigation. As a result, an introductory discussion into this unique class of molecules is imperative.

1.5 Surfactants in Solution

Surfactant molecules are amphiphilic in nature, meaning they have both a hydrophilic and a hydrophobic component. This characteristic is responsible for making surfactants “surface-active”, and often they are referred to as surface-active agents. This
surface activity is derived from thermodynamic considerations of the minimum free energy locations for the molecules. When placed in solution, whether polar or nonpolar, a surfactant will have a positive interaction between one of its sides and the solvent, and a negative interaction between the other side and the solvent. Although these individually solubilized surfactant molecules, termed monomers, are present in all surfactant solutions, they will quickly adsorb at lower free energy locations such as interfaces. At interfaces where a difference in hydrophobicity occurs on the two sides of the interface, surfactant molecules will adsorb with the hydrophilic side toward the more hydrophilic side of the interface. Interfaces which may have adsorbed surfactant molecules from solution include the gas-liquid interface (i.e. bubbles), the liquid-liquid interface (i.e. emulsions) and the solid-liquid interface (i.e. surfaces of particles or container walls).

Figure 1-8. Illustration of the preferential locations of surfactant molecules in solution.
The ability of surfactant molecules to adsorb at all of these interfaces is illustrated in Figure 1-8.

1.5.1 Monolayers at the Air/Liquid Interface

The adsorption of surfactant monomers in a monolayer configuration at the air/water interface, shown in Figure 1-8 as location A, has been extensively studied. The adsorption of surfactant decreases the surface tension ($\gamma$), also called the surface free energy, due to orientation of the surfactant molecules in an entropically favored configuration with hydrophilic head group towards the water and hydrophobic tail towards the air [Adamson, 1982]. The thermodynamic treatment of the variation of surface tension with interface composition has been given by Gibbs [1931], with further amplification by Guggenheim and Adam [1933]. The fundamental Gibbs equation, which relates the surface excess of the surface-active species in solution, $\Gamma_2$, to the surface tension $\gamma$ is given by

$$\Gamma_2 = -\left(\frac{a}{RT}\right)\left(\frac{d\gamma}{da}\right)$$

(1.10)

where $a$ is the activity of the solute, which is equal in dilute solutions to its concentration, $R$ is the gas constant and $T$ is the temperature. It is important to note that the adsorbed molecules of surfactant remain in equilibrium with surfactant monomers and other species in solution.
1.5.2 Micelles

Above a concentration called the critical micelle concentration (CMC), surfactant monomers will self-aggregate into structures called micelles (location B in Figure 1-8), first observed by McBain [1913]. In aqueous solution, the micelles consist of a hydrophobic core with surfactant tails associated through hydrophobic bonding, with head groups facing outward into solution. This preferred arrangement yields a lower free energy system and has been described thermodynamically as exhibiting phase equilibrium behavior [Hiemenz and Rajagopalan, 1997]. By this analysis, some minimum value of concentration $n$ is necessary before the exclusion of hydrophobic tails from the aqueous medium is effective, and once $n$ is sufficient to form micelles, any additional surfactant added to the solution goes into the micelles. A review of experimental methods for determining CMC as well as the kinetic aspects of micellar breakup and equilibrium processes has been published by Patist [1999].

![Diagram of micelle formation](image)

Fast relaxation time, microseconds

![Diagram of micelle breakup](image)

Slow relaxation time, milliseconds to minutes

Figure 1-9. Mechanisms for the two relaxation times, $\tau_1$ and $\tau_2$, involved in a surfactant solution above CMC.
Micelles are dynamic structures that have two relaxation processes associated with them. First, there is a fast relaxation process referred to as $\tau_1$, which is associated with the fast exchange of monomers between micelles and the surrounding bulk phase. Second, there is a slow relaxation process referred to as $\tau_2$ which is attributed to the micelle formation and dissolution process [Patist, 1999]. Figure 1-9 shows the two characteristic relaxation times $\tau_1$ and $\tau_2$ associated with micellar solutions (from Patist, 1999).

Micellar relaxation kinetics show dependence on temperature, pressure and concentration and have been studied by various techniques such as stopped-flow, temperature-jump, pressure-jump and ultrasonic absorption [James et al., 1977; Hoffman et al., 1976; Kato et al., 1995; Tondre et al., 1975]. The stability of micelles, as determined by measurement of $\tau_2$, has been found to correlate with a number of technological processes, including foamability, wetting time of textiles, bubble volume, emulsion droplet size and solubilization rate of benzene [Shah, 1998]. The micellar stability of sodium dodecyl sulfate (SDS) solutions has been determined by Lessner et al. [1981] and Oh et al. [1993] using pressure-jump with electrical conductivity detection. This technique is described in detail by Huibers et al. [1996]. The maximum stability of micelles has been found to correlate with lower foamability, larger single bubble volumes, minimum frequency of bubble generation, and maximum single film stability [Oh and Shah, 1991; Oh et al., 1992; Patel et al., 1996]. The correlation of micellar stability, $\tau_2$, to dispersion stability is an important consideration, and its implications are discussed in the recommendations for future research in Chapter 7.
1.5.3 Adsorption of Surfactant on Particles

As can be seen in Figure 1-8, surfactant molecules will adsorb at interfaces present in solution, particularly if there is a driving force (e.g. hydrophobic forces or electrostatic forces) of some type to put the surfactant at the interface. This driving force is generally the difference in hydrophobicity across the interface, as in the air-water interface, where surfactants can orient in a way which minimizes the free energy of the system. In aqueous solutions, surfactants will adsorb due to this driving force on hydrophobic particles with the surfactant tail towards the particle (location C in Figure 1-8). This configuration, which makes the particle more hydrophilic, can be used to stabilize hydrophobic particles which would otherwise agglomerate.

On the other hand, many types of particles are too hydrophilic to promote this type of driving force. In this case, the hydrophilic head group of the surfactant can adsorb on the particles if there is an electrostatic attraction caused by opposite charges. In this case, a single layer of surfactant will make the particles hydrophobic, which will promote agglomeration (location D in Figure 1-8). However, hydrophobic bonding can attract more surfactant to a fully covered interface, causing a second layer of surfactant to adsorb with tails towards the surface. By this configuration, a bilayer of surfactant molecules minimizes the free energy of the system by excluding a significant number of hydrophobic tails in contact with water from the solution as well as from the surface (location E in Figure 1-8).

The concentration at which surfactant aggregates begin to form on a particle surface, deemed the critical aggregate concentration (CAC), is often orders of magnitude lower than the bulk counterpart, the CMC. These aggregates have been termed hemimicelles [Gaudin and Fuerstenau, 1955], admicelles [Cases et. al., 1985] and
soloids [Somasundaran and Kunjappu, 1989], and they may differ significantly in nature from their bulk counterparts. Figure 1-10, from Somasundaran and Krishnakumar [1997] illustrates the various stages of aggregate growth of surfactant on a particle surface. In this example, an anionic surfactant (sodium dodecyl sulfonate) is adsorbing onto a positively charged alumina surface, with the adsorption density as a function of surfactant concentration shown as the solid line. Similar isotherms have been reported in literature for ionic surfactants adsorbing on oppositely charged surfaces.

![Figure 1-10. Stages of aggregation of adsorbed ionic surfactant on oppositely charged particle surfaces, showing reverse orientation model (left) and bilayer model (right) (from [Somasundaran and Krishnakumar, 1997]).](image)

The four stages illustrated are represented on the solid line as stages I, II, III and IV, and the corresponding state of aggregation is shown schematically for both the reverse orientation model and the bilayer model. The CAC on this figure is at the
boundary between regions I and II. As shown, the aggregates grow in size and number rapidly in region II, then the growth slows in region III as the surface approaches saturation. Region IV then represents a full bilayer of adsorbed surfactant. This type of aggregation of surfactants on surfaces has been reported as well for nonionic surfactant adsorption, although concentrations are much lower for nonionic surfactants due to a lack of electrostatic repulsion between head groups [Giordano-Palmino et al., 1994].

1.6 Rationale of the Proposed Research

This investigation focuses on the issues affecting dispersion stability in severe environments. From preceding discussions, it can be seen that this is an issue of great interest in current industry. The use of surfactants and polymers as stabilizing agents has been introduced in this chapter, and the use of mixtures of these surfactants as stabilizing agents will be considered in Chapter 2. The mechanism of stabilization is discussed in this chapter in detail, along with literature that supports the molecular mechanism. Chapter 3 then goes beyond the current knowledge base and investigates the effects of various molecular factors on dispersion stability using the proposed mechanism. The effects of surfactant choice, concentration, and the ratio of surfactants in the mixture are all considered in this chapter. In order to verify that the stabilization mechanism and some of the nuances in the data are justified, the adsorption of surfactant is determined for various mixed systems in severe environments in Chapter 4. This determination involves the use of novel techniques for high ionic strength environments.

The remainder of this work is intended to assess the relevance of the stabilization mechanism presented to the primary application for which the model dispersions are intended, CMP. Since abrasive particle size is known to be a major factor governing
many of the parameters in the CMP process, Chapter 5 is focused on correlating the dispersion stability to the particle size of the slurry particles. This chapter includes a comparison of available techniques for particle sizing in severe environments as well as verification of the results for many different systems. Finally, the effect of dispersion stabilization using mixed surfactant systems on CMP polishing performance is ascertained in Chapter 6. These results determine if the stability of the slurry influences the important output parameters such as polishing rate, surface quality and particulate contamination of the polished wafer. The implications of the entire investigation are then considered in Chapter 7, along with suggestions for future directions to continue the growth of knowledge in the dispersion area.
CHAPTER 2
STABILIZATION OF HIGH IONIC STRENGTH DISPERSIONS USING THE SYNERGISTIC BEHAVIOR OF A MIXED SURFACANT SYSTEM

2.1 Synergistic Behavior of Surfactant Mixtures

As discussed in Chapter 1, surfactants can stabilize dispersions through either electrostatic or steric effects or some combination of both. In some instances, mixtures of surfactants can show some synergistic behavior which may be beneficial for stabilization purposes, particularly in cases where single surfactants do not perform well. This synergistic behavior is typically brought about by the interaction between different types of surfactant molecules, which provides a driving force for the mixtures to form mixed aggregates or structures, as in mixed monolayers, mixed bilayers or mixed micelles. These mixed structures can often have a more fluid-like or solid-like behavior than either of their single surfactant aggregates.

Mixed surfactant systems and mixtures of surfactants and polymers have been investigated as stabilizing agents for dispersions by a number of investigators, discussed below. Often the synergistic effect of the mixed systems has been shown to be due to the enhanced adsorption from the mixture of a weakly adsorbing component. For example, sodium p-octylbenzenesulfonate adsorbs three orders of magnitude more than C_{12}E_8 on alumina. However, when adsorption is conducted from a 1:1 mixture of these surfactants the ethoxylated alcohol has been observed by Somasundaran et al. [1992] to adsorb to a greater extent than the sulfonate. The explanation for this phenomenon is that the...
adsorption of the sulfonate provides a sufficient number of hydrophobic sites for the solloid-type adsorption of the ethoxylated alcohol. Similar results have been observed for SDS and C_{12}EO_8 [Somasundaran et al., 1992].

Another example of this phenomenon has been observed in the case of adsorption of tetradecyl trimethyl ammonium chloride (TTAC) cationic surfactant and pentadecylethoxylated nonyl phenol (NP-15) nonionic surfactant on alumina. The NP-15 does not adsorb on alumina by itself, but in the mixture with strongly adsorbing TTAC, the NP-15 does adsorb significantly and also enhances TTAC adsorption [Huang et al., 1996]. In Na-kaolinite dispersions, nonionic surfactants adsorb to a greater extent than ionic surfactants. The presence of nonionic surfactant in a mixture with either anionic or cationic surfactant has been found by Xu et al. [1991] to greatly enhance the adsorption of the ionic surfactant. Hydrocarbon chain interaction between adsorbed nonionic surfactant and ionic surfactant in solution has been proposed to be responsible for the enhanced adsorption. As seen from these examples, the enhanced adsorption of a weakly adsorbing component is due to its ability to adsorb in a reverse orientation. The strong hydrophobic chain interactions are then the driving force behind the adsorption of that component.

Different effects on dispersion stability have been observed with adsorption of mixtures of a surfactant and a polymer on particles. The adsorption of polyethylene oxide (PEO) and cationic surfactant dodecyltrimethylammonium bromide (DTAB) on silica has been shown by Esumi et al. [1998] to exhibit competitive adsorption between the two species. The amount of PEO adsorbed decreases with increasing surfactant concentration, while that of the surfactant increases with surfactant concentration but was
lower in the presence of PEO than in the absence of PEO. Similar competitive adsorption effects have been observed by Esumi and Matsui [1993] using mixtures of polyvinylpyrrolidone (PVP) and poly(dimethyldiallylammonium chloride) (PDC) adsorbed on silica. The adsorption of PVP is almost unchanged with increasing concentration of PVP, while the adsorption of PDC decreases with increasing PVP concentration. The results have been correlated to adsorbed polymer conformation on the particle. Simultaneous adsorption of PVP and either lithium dodecyl sulfate (LiDS) or lithium perfluorooctanesulfonate (LiFOS) anionic surfactant on alumina has been studied by Otsuka and Esumi [1994]. In the binary PVP-LiDS system, the adsorption of PVP increases remarkably due to the presence of LiDS at low LiDS concentration, followed by a decrease at high LiDS concentration. A similar trend is observed in the PVP-LiFOS system. The adsorption results have been correlated with dispersion stability for this system. Finally, the adsorption of hydroxyethylcellulose (HEC) or hydrophobically modified HEC (HMHEC) together with SDS on alumina has been investigated by Yamanaka and Esumi [1997]. The adsorption of HEC increases due to the presence of SDS, while the amount of adsorbed SDS is unaffected by the presence of HEC. Similar results have been obtained for the SDS-HMHEC system.

As can be seen from these investigations, mixtures of surfactants and polymers can significantly enhance or reduce adsorption of either component. However, the ability of a carefully chosen ionic and nonionic surfactant mixture to synergistically stabilize dispersions has been demonstrated in the discussion above. The application of ionic and nonionic surfactant mixtures to stabilization of model slurries for CMP will be
investigated in this chapter after a discussion of single surfactant adsorption in severe environments.

2.2 Methods for Sedimentation Experiments

Sedimentation experiments are used in this investigation and in the following chapter to investigate dispersion stability. The sedimentation method involves preparing a dispersion and allowing it to sediment undisturbed under gravity in a long vertical column such as a graduated cylinder (e.g. 100 mL volume) while monitoring the height of the dispersed phase. Both the dispersion preparation method and the monitoring procedure are variables which are addressed in the following section. This method has been used conventionally as one of the primary means of determining stability in systems where destabilization occurs on macroscopic time scales and within a reasonable amount of time for measurement (e.g. in 1 hour up to 30 days). The advantages of using sedimentation over alternative techniques include the ability to directly observe the entire sedimenting layer, which allows the experimentalist to observe any unusual changes in sedimentation behavior as a whole. The other advantage of sedimentation is that complete data is taken as a function of time, thus allowing any unusual kinetic behavior to be observed. One can also visually determine the volume of sedimented particles at the bottom of the cylinder.

A complementary technique for observing dispersion stability is centrifugation, in which the dispersion is allowed to sediment under centrifugal forces greater than gravity [Coelfen, 1998; Gafford, 1985]. The basic concepts of this technique are the same and allow for faster observation of dispersions which settle very slowly under gravity, but the technique does not allow for observation of unusual settling behavior during the
sedimentation process. Other methods for determining dispersion stability involve light transmittance measurements [Hyde, 1978]. These techniques allow for exact quantification of stability data through the use of a turbidity parameter, yet the data is taken at only one place and at one time during the experiment. For turbidity data to be as useful as a complete set of sedimentation data, the data must be taken at points located throughout the holding container and as a function of time.

2.2.1 Method of Dispersion Preparation

For the following investigation, all materials were used without further purification. The slurry particles used in this study were high purity AKP-50 α-alumina particles with particle size of 100-300 nm obtained from Sumitomo Chemical Co., Ltd. Potassium ferricyanide and iron (III) nitrate were investigated as oxidizing agents, and they were obtained from Fisher, Inc. Surfactants used were from various suppliers. Sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC), sodium salt of capric acid and sodium salt of lauric acid were obtained from Sigma Chemical Co. Hexadecyltrimethylammonium bromide (C\textsubscript{16}TAB) was obtained from Fisher, Inc. Dodecyltrimethylammonium bromide (C\textsubscript{12}TAB) was obtained from Acros, Inc. Triton X-100 was obtained from Aldrich, Inc. Tween 20, Tween 40, Tween 60, Tween 80 and Symperonic A4, A7, A11 and A20 were obtained from ICI Surfactants. Decyl sodium sulfate and hexadecyl sodium sulfate were obtained from Eastman Kodak Co. Ultrapure water was obtained from a Milli-Q Gradient A10 filtration system supplied by Millipore Corp.

Dispersions were prepared by first dissolving surfactants (cationic, anionic, or nonionic) or mixtures of surfactants in the desired concentrations in water. Alumina
particles in a concentration of 10 wt. % were then added into the surfactant solution and the pH was adjusted to a value less than 4. In order to attempt to break up agglomerates that form either in the particle preparation process or when dry particles are stored in air (in plastic containers) for long periods of time, the dispersions were then sonicated for 30 minutes. The oxidizing agent was then added and the pH was carefully readjusted to a value between 3.5 and 4.0. This pH range was used in order to model CMP slurries used for tungsten polishing, which have been shown to have a high selectivity of tungsten over silicon dioxide in this range [Kaufmann, 1991].

2.2.2 Method of Sedimentation Characterization

Dispersion stability was then characterized by sedimentation testing. Sedimentation experiments were performed by thoroughly dispersing the slurries prior to pouring them into 100 mL graduated cylinders, where they were then undisturbed throughout the length of the experiment. Room temperature was maintained at 25±1°C throughout the experiment time. The amount of settled slurry as well as the sediment height was recorded over time and the results converted to fractional volume to normalize the results. The amount of settled slurry was determined as the sum of 1) the amount of clear liquid on top and 2) a fraction of the amount of cloudy layer below the clear liquid. The cloudy layer was the transition region between fully dispersed slurry and clear liquid. Examples of this calculation procedure for total settled volume are given in Figure 2-1 in order to make the procedure more clear. The fractions used for conversion of the cloudy layer to the clear liquid equivalent are given in Table 2-1. These fractions (f) are used to calculate the total settled volume in the examples in Figure 2-1.
Figure 2-1. Examples of sedimentation experiments along with the total settled volume determined using the procedure outlined below (f = fraction settled as defined in Table 2-1).

In Figure 2-1, the slurry on the left is an example of the simplest type of settling to quantify. In this figure, 20 mL of clear liquid is on top of slurry that is fully dispersed, making the total settled volume 20 mL. This type of characterization procedure is commonly used to obtain a single parameter for settling called the initial settling rate, which is the rate of settling extrapolated to time 0. As can be seen by the other example slurries in Figure 2-1, however, this method does not always give a clear picture of the settling results. The slurries in the middle and on the right in Figure 2-1 are clearly less stable than the slurry on the left, and yet the above method would give the same settled amount for each of these slurries. In response to this problem with the characterization method, the fractions used to calculate total settled volume for the cloudy to hazy layers have been developed in Table 2-1.
Table 2-1. Fractions used for determination of total settled volume based on degree of cloudiness in sedimentation experiments.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Range of Absorbance Values</th>
<th>Fraction Settled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very cloudy</td>
<td>2.0 - 3.0 AU</td>
<td>0.1</td>
</tr>
<tr>
<td>Cloudy</td>
<td>1.0 - 2.0 AU</td>
<td>0.3</td>
</tr>
<tr>
<td>Hazy</td>
<td>0.3 - 1.0 AU</td>
<td>0.6</td>
</tr>
<tr>
<td>Slightly hazy</td>
<td>0.1 - 0.3 AU</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The slurry in the middle in Figure 2-1 has the same level of clear liquid (20 mL) as the slurry on the left, but below this clear layer is a layer of slurry that is cloudy but not fully dispersed. In order to quantify the degree of opacity in this type of situation, the scale in Table 2-1 for the different levels of opacity has been developed. The different levels are arbitrarily assigned (there easily could be 10 different levels instead of the 4 levels indicated) and the fractions used are also arbitrary, although they indicate the degree of settling based on experience with sedimentation results. In order to calculate the total settled volume for the slurry in the middle of Figure 2-1, the fraction for the cloudy layer ($f=0.3$) is multiplied by the volume of that layer (40 mL). This makes the total settled volume for this slurry $20 + 40(0.3) = 32$ mL. For the slurry on the right, the slightly hazy layer under the clear liquid layer is assigned a fraction of 0.8 to take into account the fact that the slurry is almost fully settled in this region. The region below the slightly hazy layer is also not fully dispersed, so it is classified as a very cloudy layer and gets assigned a fraction of 0.1, taking into account the fact that this layer is almost fully dispersed. The total settled volume for the slurry on the right in Figure 2-1 is then calculated to be $20 + 20(0.8) + 40(0.1) = 40$ mL. This slurry is therefore assigned the same total settled volume as a slurry with 40 mL of clear liquid atop a fully dispersed slurry. The three slurries in Figure 2-1 are then placed in the proper relative order in
terms of their settling behavior shown. Using the method outlined above, all slurry that is
settled is taken into account in this investigation, and not just the fully settled layer of
clear liquid. Although this method has arbitrarily assigned values for the different levels
of opacity, the settling data obtained with this method is shown in Chapter 3 to correlate
well with the hydrophobicity of the nonionic surfactant, indicating the validity of the
method. Two cylinders were prepared of each slurry and settling data reported is the
average value.

2.3 Effects of Addition of Ionic or Nonionic Surfactants on Slurry Stability

The simplest methodology for stabilizing dispersions using surfactants is through
the addition of single surfactants. When an ionic or nonionic surfactant stabilizing agent
is added alone to a dispersion in a high ionic strength environment, the expected effect on
the dispersed particles is illustrated in Figure 2-2.

Figure 2-2. Illustration of the effect of single ionic or nonionic surfactant addition on
the stability of high ionic strength slurries.
This figure illustrates particles with a net positive charge (e.g. alumina) after addition of either anionic surfactant or ethoxylated nonionic surfactant. The explanation of the expected effects is in the following discussion.

2.3.1 Ionic Surfactants

The shielding of surface charges on the particles due to the large number of ions does not prevent the adsorption of oppositely charged ionic surfactant. The charged sites on the particles still act as anchoring sites for the ionic surfactant head groups, even in the high ionic strength environment. In fact, since the surface charge represents a net charge, there will still be negative sites where surfactant with a positive sign (same sign as the surface charge) can adsorb, but these negative sites will be fewer in number than positive sites, resulting in a lower adsorption density of cationic surfactant. Adsorbed ionic surfactants may form a bilayer due to hydrophobic chain interactions, but this depends on the surfactant. As discussed in Chapter 1, ionic surfactants that have no polymeric component primarily stabilize slurries by increasing surface charge and hence causing electrostatic repulsion. However, in high ionic strength slurries, even the charges placed on the surface by adsorption of ionic surfactant are shielded by the ions in the slurry and the hence electrostatic repulsion will not be effective. Another way of stating this is that in high ionic strength environments the Debye length, $1/\kappa$, is so small that van der Waals attractive forces will predominate and cause particle agglomeration, practically regardless of the concentration of surfactant placed on the surface.

The adsorbed ionic surfactants do, however, have a steric component to stabilization that can be effective. The adsorbed surfactants do present a physical barrier to approach, hence reducing the effect of van der Waals forces. This effect was found to
be significant in systems of cetyl trimethylammonium bromide (CTAB) cationic surfactant adsorbed on negatively charged silica (SiO$_2$) surfaces by Singh et al. [2000]. In this system, with 0.1 M NaCl providing a high ionic strength environment, significant CTAB adsorption was found to stabilize these slurries, presumably due to steric effects since electrostatic effects should be minimal in this system. This study verifies that steric effects can have a significant contribution even in systems of nonpolymeric ionic surfactants. However, in the present investigation, the van der Waals attraction between alumina particles is much greater than that between silica particles. This can be seen by the difference in non-retarded Hamaker constant for the two materials interacting across vacuum (air), which is $14 \times 10^{-20}$ J for alumina [Velamakanni et al., 1994] and about $6.3 \times 10^{-20}$ J for silica [Israelachvili, 1992]. The greater van der Waals attraction for alumina means that the steric layer needed to stabilize these particles will be larger than that in the silica system, and hence common ionic surfactants will not be sufficient to provide this layer.

2.3.2 Nonionic Surfactants

The polar group in most nonionic surfactants is polymeric in nature and hence causes stabilization of slurries by causing steric repulsion between particles. This stabilization mechanism should be significant, even in high ionic strength slurries. Although the polymer conformation may be slightly different under high ionic strength conditions, this difference should not be significant enough to cause the steric stabilization effects to change. In aqueous environments, the most common nonionic surfactants used for stabilization are of the poly(oxyethylene) (PEO) variety. This is because PEO polymer chains are very hydrophilic in nature and therefore tend to extend
into aqueous solution and not coil at the surface. In this way, ethoxylated nonionic surfactants have been shown to stabilize numerous aqueous dispersions, even under high ionic strength conditions [Rosen, 1989]. However, numerous studies have shown that PEO has a very low adsorption density on alumina [Somasundaran and Krishnakumar, 1997]. Since nonionic surfactants must adsorb on alumina with the head group towards the surface since alumina is a hydrophilic particle, ethoxylated nonionic surfactants likewise do not adsorb significantly on alumina surfaces and hence would not be expected to stabilize these slurries.

2.3.3 Verification by Sedimentation Experiments

The theories of ionic and nonionic surfactant adsorption presented above have been verified using sedimentation experiments in Figures 2-3 and 2-4. In Figure 2-3, the addition of surfactant to a low ionic strength slurry containing 0.001 M potassium ferricyanide (K₃Fe(CN)₆) is investigated.

Figure 2-3. The effects of ionic or nonionic surfactant addition on a low ionic strength slurry containing 0.001 M potassium ferricyanide oxidizing agent. The slurries are 1 wt. % AKP-50 alumina at pH 4 with 10 mM surfactant added. The photographs were taken after 24 hours of settling.
In this figure, the control sample with no surfactant added shows instability, verifying that the electrostatic repulsion between particles has been screened even under low ionic strength conditions. Cationic, nonionic and anionic surfactants in a concentration of 10 mM each have been added to these slurries to investigate stabilization. Adding either cationic surfactant (CPC) or anionic surfactant (SDS) stabilizes the slurries, which are unstable when no surfactant is added. This is shown by the white alumina particles being dispersed throughout the slurry. These results verify that both cationic and anionic surfactants can adsorb on these particles. At this low ionic strength, the Debye length ($1/\kappa$) of the system is sufficiently large that ionic surfactant can have an effect on stabilization. This effect is presumably a combination of both steric and electrostatic effects from the adsorbed layer of ionic surfactant.

The addition of nonionic surfactant (Triton X-100) does not stabilize the slurry in Figure 2-3 under these conditions. Other nonionic surfactants investigated, including Tween 80, Tween 20 and Symperonic A7 show similar results. The lack of stability in these systems is presumably due to insufficient or lack of adsorption of nonionic surfactant on the alumina particles.

Figure 2-4 investigates the addition of the same surfactants to high ionic strength dispersions containing 0.1 M potassium ferricyanide. This amount of potassium ferricyanide is commonly used to achieve the required amount of oxidation of tungsten or copper surfaces in metal CMP slurries. Under these conditions, the control sample with no surfactant remains unstable. The addition of cationic surfactant (CPC) shows a higher fractional volume than the other surfactants, but this is presumably due to very rapid
settling of the slurry and formation of loose agglomerates between particles, resulting in a loose packing efficiency.

![Image](image_url)

Figure 2-4. The effects of ionic or nonionic surfactant addition on a high ionic strength slurry containing 0.1 M potassium ferricyanide oxidizing agent. The slurries are 1 wt. % AKP-50 alumina at pH 4 with 10 mM surfactant added. The photographs were taken after 24 hours of settling.

The addition of anionic surfactant (SDS) and nonionic surfactant (Triton X-100) show no significant stabilization of the slurries under these conditions. The high ionic strength of these slurries prevents the cationic or anionic surfactants from stabilizing the slurries electrostatically. The nonionic surfactant does not appear to adsorb on the particles under these conditions, as is the case in the low ionic strength environment (Figure 2-3). These results have been verified using other cationic, anionic and nonionic surfactants.

2.3.4 Adsorption Verification by Surface Tension Measurements

Static surface tension measurements were made using a Rosano surface tensiometer made by Biolar Corporation. Surface tension measurements were made in
air using the Wilhelmy plate method [Becher, 1965] with a 10 x 20 mm platinum plate, allowed to equilibrate in solution for 60 seconds before taking a measurement. Slurries were centrifuged to obtain supernatants for surface tension measurements using a Sorvall RC-5B refrigerated superspeed centrifuge operating at 10000 rpm.

The adsorption of ionic and nonionic surfactants has also been investigated using static surface tension measurements. By comparing the surface tension of surfactant solutions to that of the supernatant solutions after surfactant adsorption on particles, adsorption of surfactant can be determined. For these measurements, 10 wt. % AKP-50 particle slurries were prepared at pH 4 using 0.1 M potassium ferricyanide oxidizing agent. SDS, CPC and Tween 80 surfactants were added at a concentration of 20 mM prior to dilution. The slurries were centrifuged and the supernatants compared to the same three solutions before addition of particles. The solutions were diluted several times with water and the surface tension at each dilution was measured. The results are given in Figure 2-5, which shows the surface tension as a function of surfactant concentration for all three surfactant solutions before and after adsorption of surfactant on particles.

The surface tension of surfactant solutions decreases with concentration up to the critical micelle concentration (CMC). The adsorption of surfactant on particles will result in a lower amount of residual surfactant in the supernatants of solutions containing particles. Hence, at a given dilution, the solution with particles will have a higher surface tension than that without particles if the surfactant is adsorbing on the particles.

In Figures 2-5 a) and b), which show CPC and SDS solutions, respectively, the surface tension of solutions with particles is higher than the surface tension of solutions
without particles. These results verify that CPC and SDS adsorb on alumina particles and hence lower the concentration of surfactant in solution. However, the adsorption density of surfactant is presumably insufficient to stabilize alumina dispersions.

Figure 2-5. Surface tension of solutions before and after addition of alumina particles, as a function of surfactant concentration, achieved through dilution with water. Surfactants are a) CPC, b) SDS and c) Tween 80.

Figure 2-5 c) shows that for Tween 80 solutions, there is a negligible difference between surface tensions of solutions with and without particles. This verifies that this
nonionic surfactant does not adsorb on alumina and hence does not lower the surfactant concentration in solution.

2.4 Effects of Addition of Surfactant Mixtures on Slurry Stabilization

The addition of mixtures of cationic, anionic and nonionic surfactants to the high ionic strength metal CMP slurries has also been investigated. This has been done in order to determine if any synergistic effects of surfactant combinations are present in these slurries. The effects of addition of surfactant mixtures on stabilization of high ionic strength slurries are shown in Figures 2-6 and 2-7. These figures show the results of sedimentation tests on 10 wt. % AKP-50 (100-300 nm) alumina slurries containing 0.1 M oxidizing agent. Mixtures of two surfactants were added to these slurries at a molar ratio of 1:1, with a total surfactant concentration of 50 mM. This value was chosen because it is well above the CMC of any of the surfactants used in this study [Dahanayake, 1984; Rosen, 1982]. The CMC of SDS in water is 8.0 mM while that of ethoxylated nonionic surfactants can vary from about 0.005 mM to 0.2 mM [Patist, 2000]. More importantly, the amount of residual surfactant in these slurries after equilibrium adsorption is reached is also greater than the CMC of any of the surfactants investigated. Hence, the amount of surfactant adsorption will have reached a saturation value at the concentration used in this study, and no further stabilization effects are expected to occur at higher concentrations, unless multilayer adsorption effects are significant.
Figure 2-6. Sedimentation results of 0.1 M Fe(NO$_3$)$_3$ slurries with mixtures of surfactants added.

Figure 2-6 shows the sedimentation behavior of slurries containing 0.1 M ferric nitrate (Fe[NO$_3$]$_3$), another common oxidizing agent used in metal CMP slurries. The settling behavior is reported as fractional volume of dispersion, which is defined as the ratio of the volume of dispersed slurry remaining at a given time to the initial volume of slurry. Hence, this parameter has a value of 1.0 for stable slurries. For unstable slurries, the values of this parameter can be as low as 0.1, which represents the fractional volume of tightly packed 10 wt. % dispersions of AKP-50 particles. In Figure 2-6, the instability of slurries with no surfactant stabilizing agents added is once again verified by the ferric nitrate only (FeNit only) results, which show that after only 3 hours of settling the
fractional volume of dispersion is 0.3. The combination of cationic and nonionic surfactants gives some stabilization, but significant particle settling is still observed. The combination of anionic and nonionic surfactants shows a wide variety in extent of stabilization. In this case, the combination of SDS and either Tween 20 or Tween 80 results in fully stabilized slurry after 3 hours. The other nonionic surfactants (Triton X-100 and Symperonic A7) mixed with SDS do not significantly stabilize the slurries. For the mixtures of cationic and anionic surfactants (C_{12}TAB or C_{16}TAB and SDS), a molar ratio of 5:1 anionic:cationic surfactant was chosen because higher amounts of these cationic surfactants results in precipitation due to electrostatic interaction between surfactants. Figure 2-6 shows that the mixture of these surfactants actually results in destabilization of these slurries, since the fractional volume of dispersion is actually less than that of the slurry without surfactant.

A more detailed investigation of the effects of minor changes in surfactant type on slurry stabilization was conducted for the combination of anionic and nonionic surfactants. For this investigation, 0.1 M potassium ferricyanide was used as the oxidizing agent in order to compare the differences in stabilization behavior for surfactant mixtures in different chemical environments. Surfactant mixtures were added in a 1:1 molar ratio with a total concentration of 50 mM, as with the ferric nitrate slurries. Figure 2-7 shows the fractional volume of dispersion of these slurries after 3 days of settling. The different anionic surfactants added with Tween 80 (T80) show that sodium sulfate surfactants stabilize these slurries better than sodium salts of fatty acids. Of the chain lengths investigated, the 12-carbon chain (SDS) performed the best, with a fractional volume of dispersion near 1.
Figure 2-7. Sedimentation results of 0.1 M K$_3$Fe(CN)$_6$ slurries with mixtures of anionic and nonionic surfactants added.

The different nonionic surfactants investigated with SDS show effects of chain length on stabilization of these slurries. Tween 20, 40 and 60 are identical surfactants except that they have chain lengths of 12, 16 and 18 carbons, respectively. Tween 60 (T60) shows significantly better stability than Tween 20 (T20) or Tween 40 (T40). However, the SDS + Tween 80 (C$_{18}$ oleyl surfactant) combination still shows the best results. The Symperonic surfactants investigated are identical except that the hydrophilic polymer group length varies, with A4, A7, A11 and A20 corresponding to 4, 7, 11 and 20 ethylene oxide (EO) groups, respectively. Figure 2-7 shows that the stabilization increases with decreasing number of EO groups. This trend will be considered in great detail in the following chapter.
2.5 Explanation of Stabilization Mechanism

The stabilization of high ionic strength slurries shown in Figures 2-6 and 2-7 using the combination of SDS and either Tween 20, Tween 80, Symperonic A4 or A7 can be explained by the generic adsorption model proposed in Figure 2-8. The stabilization is shown to occur by a two step mechanism: 1) The adsorption of a strongly adsorbing ionic surfactant. 2) The adsorption by hydrocarbon chain interaction of a nonionic surfactant capable of steric stabilization.

Figure 2-8. The mechanism of high ionic strength slurry stabilization by the synergistic mixture of anionic and nonionic surfactants.
This process results in the adsorption of a mixed surfactant layer on the surface of the alumina particles. The presence of polymeric chain segments from the nonionic surfactant extending into the water results in steric repulsion when two such particles approach each other.

Although this type of stabilization has only been observed in these systems for an anionic and nonionic surfactant mixture, it is suspected that the same mechanism is possible for a cationic and nonionic surfactant system. This is because electrostatic effects are not expected to influence ionic surfactant adsorption in high ionic strength environments. Further, the adsorption of nonionic surfactant is governed in this mechanism by the interaction of the hydrocarbon chains, and these interactions should be similar for cationic and anionic surfactants.

The mechanism in Figure 2-8 only depicts one possible conformation of the adsorbed mixed surfactant layer, which in fact may be present as either a monolayer or a bilayer, as explained below. The conformation presented in this figure is a mixed monolayer conformation, in which the hydrocarbon chains of the two surfactants are lined up adjacent to each other. This type of conformation will be favored if the amount of adsorbed ionic surfactant is low enough that there are gaps between molecules that are large enough for the nonionic surfactant hydrocarbon chains to fully penetrate, as shown in the figure. The mixed monolayer conformation will result in the lowest surfactant adsorption density of any of the conformations possible in this mechanism.
Figure 2-9. Other possible conformations of stabilizing surfactant that result from the adsorption of a mixture of ionic and nonionic surfactants on particle surfaces. Conformations are a) full bilayer and b) penetrated bilayer.

Another type of conformation that the adsorbed mixed surfactant layer may prefer is a full bilayer conformation. This type of conformation is illustrated in Figure 2-9 a), which shows that in this conformation the anionic surfactant has adsorbed in a full monolayer. The nonionic surfactant then adsorbs via hydrocarbon chain interactions as a full second monolayer. This conformation results in twice as many molecules of each surfactant adsorbing on the surface than in the mixed monolayer conformation. The full bilayer conformation will be favored when there is enough anionic surfactant in solution to adsorb as a full monolayer. This conformation will result in the highest surfactant adsorption density of any of the conformations possible in this mechanism.

The final type of conformation, a penetrated bilayer, results in a surfactant adsorption density that is in between the two extremes already discussed. This type of conformation is shown in Figure 2-9 b), which shows that the hydrocarbon chains of the nonionic surfactant penetrate the monolayer of anionic surfactant adsorbed on the particle
surface, resulting in an adsorbed layer that is neither a mixed monolayer nor a complete bilayer. The degree of penetration of the nonionic surfactant will depend on the amount of space available between adsorbed anionic surfactant molecules, as well as the strength of the hydrocarbon chain interactions between adjacent molecules.

The results of Figures 2-6 and 2-7 suggest that this stabilization process is highly dependent on the choice of both ionic and nonionic surfactant. The stabilizing effect of surfactant mixtures by this mechanism is dependent on several factors, which are explained in the following chapter. This chapter has shown that mixed surfactant systems can show synergistic behavior as a stabilizing agent for dispersions. The next chapter will examine the factors that effect the stabilizing ability of a mixed ionic and nonionic surfactant system. With this knowledge, the formulator is given the ability to choose surfactants which will maximize stabilization, even in severe environments such as those considered here.
CHAPTER 3
MOLECULAR FACTORS THAT OPTIMIZE DISPERSION STABILITY USING MIXED SURFACTANT SYSTEMS AS STABILIZERS FOR DISPERSIONS IN SEVERE ENVIRONMENTS

3.1 Molecular Factors Influencing Stability of Dispersions

In this investigation, the factors which effect the stabilization mechanism shown in Figure 2-7 are investigated. Specifically, the types of surfactants which are preferred for this type of mechanism are determined, as well as the concentrations and ratios of surfactants which are necessary for the stabilization to be successful. Finally, this mechanism is applied to another slurry which utilizes chemistry for copper CMP applications, and the differences in surfactant type, concentration and ratio for optimal stability are explained.

The factors which influence the stabilization mechanism presented in Figure 2-7 have been deduced and are considered here. They are:

1) Adsorption of ionic surfactant onto alumina surface with ample surface coverage.

   As explained in Chapter 1, surfactants with sign opposite of the surface charge are expected to have a higher affinity to the surface, although the magnitude of the surface charge and heterogeneity will ultimately determine the adsorption density.

2) Partitioning of nonionic surfactant out of the aqueous phase and onto the alumina surface by hydrocarbon chain interaction with the film of ionic surfactant.

   Hydrocarbon chain interactions have been shown to be maximum for equal chain
lengths of ionic and nonionic surfactant [Shiao et al., 1997; Shiao, 1996; Patist et al., 1997]. However, the driving force for partitioning of nonionic surfactant out of the aqueous phase and onto the surface increases with increasing hydrophobicity of nonionic surfactant according to a semiquantitative extension of Traube’s rule [Traube, 1891] made by Freundlich [1926]. As a result, the adsorption affinity of the nonionic surfactant increases with long hydrocarbon chains or short hydrophilic segments of the nonionic surfactant.

3) Steric stabilization via the mixed surfactant layer on adjacent particles. This depends primarily on the ability of the hydrophilic ethylene oxide (EO) segments of the nonionic surfactant to extend into the aqueous phase upon adsorption and not tend to form flocs. As discussed in Chapter 1, steric stabilization occurs in mixed layers due to the presence of steric barriers from adsorbed nonionic molecules that prevent the particles from coming close enough to allow van der Waals attractive forces between particles to dominate [Tadros et al., 1986; Lee et al., 1986]. However, the poly(ethylene oxide) segments must not interact attractively with segments on adjacent particles to induce flocculation, causing destabilization of the slurry. The tendency for flocculation will increase as the adsorption density of polymer segments is increased [Rosen, 1989].

This investigation determines the influence of molecular factors and parameters of the surfactants used in this stabilization mechanism. The results presented in this chapter are entirely from sedimentation experiments. Although the use of this type of enhanced adsorption mechanism has been reviewed in the literature presented in Chapter 2, the investigation of detailed influences of various factors such as presented in this chapter
has not been performed to date. This investigation has even greater implications in that it investigates dispersion stability in severe environments, which is an issue in many current industries.

3.2 Nonionic Surfactants Used in This Investigation

As can be seen from the factors influencing stabilization, the nonionic surfactant plays a major role in determining the outcome in this mechanism. As a result, a large number of commercial nonionic surfactants has been investigated using sedimentation experiments. Figure 3-1 illustrates the ethoxylated nonionic surfactants used in this investigation and lists those trade names which represent each linkage. As can be seen, ethoxylated nonionic surfactants consist of a hydrocarbon chain, which may be branched, a poly(ethylene oxide) (PEO) segment as the head group and a linkage which connects the two sides of the molecule. Three types of linkages have been investigated in this chapter, including ethers, esters and sorbitans.

The sedimentation experiments have been performed using the same methodology as described in Chapter 2. All nonionic surfactants investigated, including Span 20, Span 80, Brij 30, Brij 35, Brij 52, Brij 93, Brij 97, Brij 98, Brij 700, Tween 21, Tween 80, Tween 81, Tween 85, Symperonic A4, Symperonic A7, Symperonic A11, Symperonic A50 and Myrj 45, have been obtained from ICI Surfactants, Ltd. For this investigation, dispersions of 10 wt. % AKP-50 alumina have been used at pH’s appropriate for the CMP application desired.
3.3 Optimization of Dispersion Stability Using Various Nonionic Surfactants for Tungsten CMP

In order to determine the effects of nonionic surfactant type on dispersion stability in the tungsten CMP slurry investigated primarily in Chapters 1 and 2, the same slurry has been investigated using sedimentation experiments and the nonionic surfactants listed previously. Nonionic surfactants have been divided into groups with carbon chain lengths of 12 and 18. The sedimentation results are given in Figures 3-2 and 3-3 for C_{12} and C_{18} nonionic surfactants, respectively.

As can be seen for both the C_{12} and C_{18} surfactants, there appears to be some correlation between degree of polymerization, as indicated for each series, and dispersion stability.

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**Figure 3-1.** Schematic of a general ethoxylated nonionic surfactant and details about the types used in this investigation.

<table>
<thead>
<tr>
<th>Tail Group</th>
<th>Linkages</th>
<th>Head Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12} - C_{18}</td>
<td>- O - Ether (Brij)</td>
<td>E_0 - E_{100}</td>
</tr>
<tr>
<td>C_{18} (oleate) and tri-C_{18}</td>
<td>- C - O - Ester (Symperonic, Myrj)</td>
<td>E_{11}, E_{20}, E_{23}, E_{50}, E_{100}</td>
</tr>
</tbody>
</table>

\[ C_x \text{ (Tail Group)} \quad \text{Linkages} = \quad \text{Head Group:} \quad E_y \text{ (Head Group)} \]
Figure 3-2. Sedimentation results of dispersions with 1:1 mixtures of SDS and the C_{12} nonionic surfactant indicated. Oxidizing agent is 0.1 M potassium ferricyanide. E x represents the mean number of ethoxy groups on the nonionic surfactant molecule.

Figure 3-3. Sedimentation results of dispersions with 1:1 mixtures of SDS and the C_{18} nonionic surfactant indicated. Oxidizing agent is 0.1 M potassium ferricyanide.
The most stable combinations in both Figures 3-2 and 3-3 have only 2 EO groups (E₂) on the nonionic surfactant, while the highest degree of polymerization (E₅₀ for C₁₂ and E₁₀₀ for C₁₈) results in the most unstable slurries. These two extremes show a general trend of increasing stability with decreasing degree of ethoxylation of the nonionic surfactant. Additionally, Span surfactants (E₀) are unstable in both figures. However, in both Figure 3-2 and 3-3 the Span surfactants show a substantial particle layer (F ϕ 0.4) remaining in the unstable slurries. These surfactants promote the formation of loose particle agglomerates rather than tightly packed agglomerates. As a result, the final packed volume of these slurries after settling is complete is much larger than the packed volume of other slurries that form tightly packed agglomerates. Also in Figures 3-2 and 3-3, there appears to be a significant variation with type of nonionic surfactant linkage, since for the C₁₈ surfactants, Tween 80 (sorbitan linkage) and Brij 98 (ether linkage) all are E₂₀ surfactants, but their results do not follow the same trend.

There appears to be some correlation in Figures 3-2 and 3-3 of dispersion stability with the molecular factors of the surfactant, including the carbon chain length, degree of polymerization and linkage segment. All of these parameters contribute to the overall hydrophobicity of the surfactant, which can be summed up for surfactants using the empirical hydrophile-lipophile balance (HLB) number. HLB numbers are low for hydrophobic surfactants and high for hydrophilic surfactants, and an equal hydrophobic-hydrophilic balance corresponds to a value near 10. The hydrophobicity of a nonionic surfactant is expected to be a significant factor in dispersion stability, since ultimately this factor and the surface architecture will determine the driving force for surfactant to leave the bulk and adsorb at the interface.
In order to show the effect hydrophobicity of nonionic surfactant on dispersion stability, the data in Figures 3-2 and 3-3 has been plotted in Figure 3-4 as a function of HLB number of nonionic surfactant. The surfactants are grouped in this figure according to both linkage type and chain length (C\textsubscript{12} or C\textsubscript{18}). Figure 3-4 shows that both C\textsubscript{12} and C\textsubscript{18} ethers and the esters (all C\textsubscript{12}) show a decrease in dispersion stability with an increase in HLB number of nonionic surfactant. The sorbitan surfactants remain stable at HLB numbers greater than 15, but it is expected that if it were possible to obtain very high HLB number sorbitan surfactants, they would also show a decrease in dispersion stability at higher HLB numbers.

![Figure 3-4](image-url)  
Figure 3-4. Correlation of dispersion stability with hydrophobicity of nonionic surfactant, as given by its HLB number. Data is from 50 mM 1:1 mixtures of SDS and the given nonionic surfactant adsorbed on 10 wt. % AKP-50 particles in 0.1 M K\textsubscript{3}Fe(CN)\textsubscript{6} at pH 4.
The data in Figure 3-4 shows that increasing hydrophobicity of nonionic surfactant leads to increased dispersion stability, which is contrary to general expectations. In most dispersions stabilized by steric layers, the stability should increase with increasing length of the steric stabilizing component, which is the degree of ethoxylation in the present investigation. This figure shows the reverse trend in mixed surfactant systems, in which increasing the length of the steric stabilizing layer actually contributes to a decrease in dispersion stability.

3.4 Verification of Results for Model Copper CMP Slurry

In order to determine the generality of the trends presented above, the effect of nonionic surfactant on dispersion stability was determined using similar sedimentation experiments for a type of slurry with application in copper CMP. This slurry contains primarily monovalent ions, unlike the trivalent ferricyanide ion. The slurry is composed of 10 wt. % alumina particles and 0.1 M KIO$_3$, 0.01 M KI and 0.01 M EDTA. This slurry combination has been shown to provide substantial oxidation of the copper surface due to KIO$_3$ while the corrosion is inhibited by the presence of I from KI, which forms a surface layer on Cu. Finally, the driving force for removal of copper is maximized by addition of the complexing agent EDTA [Kaufman et al., 1999].

Figure 3-5 shows the trend of dispersion stability for this copper CMP slurry with HLB number of nonionic surfactant for all of the nonionic surfactants investigated in Figure 3-4. In this figure, the surfactants are grouped according to carbon chain length ($C_{12}$ and $C_{18}$), and the $C_{12}$ surfactants are investigated at total surfactant concentrations of both 50 mM and 100 mM to observe any differences. The data in Figure 3-5 appears to be very well correlated with HLB number of nonionic surfactant. For both $C_{12}$ and $C_{18}$
surfactants, there appears to be a rapid stable – unstable transition in a range of HLB’s from 10-12. It is important to note that this stability data is presented after only 1 day of settling, indicating that the speed of settling in the unstable slurries is rapid. However, the stable slurries with HLB numbers less than 10 are fully stable after a period of 10 days, indicating a high degree of stability.

Figure 3-5. Variation in dispersion stability vs. HLB number of nonionic surfactant for a model copper CMP slurry containing 0.1 M KIO₃, 0.01 M KI and 0.01 M EDTA (Nonionic surfactants are: 1 = Span 80, 2 = Brij 93, 3 = Brij 52, 4 = Span 20, 5 = Brij 30, 6 = Symperonic A4, 7 = Tween 81, 8 = Symperonic A7, 9 = Brij 97, 10 = Tween 21, 11 = Symperonic A11, 12 = Tween 80, 13 = Brij 98, 14 = Tween 20, 15 = Brij 35, 16 = Symperonic A50, 17 = Brij 700).
The primary outlier point is a C\textsubscript{12} nonionic surfactant with an HLB number of 13.3, which yields a stable dispersion. This surfactant is Tween 21, which has a sorbitan linkage, unlike most of the C\textsubscript{12} surfactants investigated. It appears that, as in Figure 3-4, the sorbitan linkage contributes more significantly to steric stabilization at high HLB numbers than its ether or ester counterparts. The results for the dispersions at 100 mM concentration mimic those at 50 mM concentration, indicating that there is no change in stability in this concentration range. The effects of surfactant concentration on dispersion stability will be discussed in greater detail in section 3.6. The results of Figure 3-5 verify the robust nature of the stabilizing scheme presented in this investigation. The general trend of increasing dispersion stability with decreasing HLB number of nonionic surfactant holds for both the tungsten and copper CMP slurries investigated, indicating that the underlying stabilization mechanism is the same in both systems.

The results in Figure 3-5 do include the Span surfactants (E\textsubscript{0}), which produce stable slurries in contrast to the results in Figure 3-4. This is true even though the Span surfactants have 0 EO groups, and hence their hydrophilic segment is composed of only the sorbitan linkage. This contrasting element will be considered and explained in the next section after an explanation of the general trend of increasing stability with decreasing HLB number of nonionic surfactant.

3.5 Correlation of Dispersion Stability with HLB Number of Nonionic Surfactant

The trend that stands out in both Figures 3-4 and 3-5 is that increasing hydrophobicity of nonionic surfactant, with all other factors constant, brings about increasing dispersion stability. This is contrary to the popular thought that longer EO chains should provide better dispersion stability due to increasing size of the steric barrier.
to particle approach. A schematic of the environment in which a hydrophilic nonionic surfactant with a long polymer chain is present in solution is presented in Figure 3-6 a), while the same situation with a hydrophobic short chain surfactant is presented in Figure 3-6 b).

![Schematic of dispersion environment showing adsorption density differences between a) high HLB (hydrophilic) nonionic surfactant and b) low HLB (hydrophobic) nonionic surfactant.](image)

Figure 3-6. Schematic of dispersion environment showing adsorption density differences between a) high HLB (hydrophilic) nonionic surfactant and b) low HLB (hydrophobic) nonionic surfactant.

The reason for the greater degree of stabilization with the hydrophobic (low HLB) surfactant is clearly the number of surfactant molecules present on the surface. With the hydrophobic surfactant, the driving force to place monomers onto the particle surface is higher than for the more hydrophilic surfactant. As a result, the hydrophilic surfactant,
although capable of greater steric stabilization if adsorbed, does not adsorb in sufficient 
quantity to stabilize the particles. The key to understanding this stabilization mechanism 
is that there are opposing forces governing the choice of nonionic surfactant—the driving 
force to adsorb vs. the degree of polymer extension into solution once adsorbed. Clearly 
in the example slurries presented in Figures 3-4 and 3-5, the repulsive barrier is sufficient 
even with only 2 or even 0 E groups on the surface.

This leads to the discussion of the contrasting element between Figures 3-4 and 3- 
5. The Span surfactants (E\textsubscript{0}) stabilize the KIO\textsubscript{3} slurries but not the K\textsubscript{3}[Fe(CN)\textsubscript{6}] slurries. 
The reason for this observation is that in the KIO\textsubscript{3} slurries the charge screening effects 
are not as overwhelming as in the K\textsubscript{3}[Fe(CN)\textsubscript{6}] slurries. Quantitatively, the Debye length 
(1/\kappa) in electrolyte solution containing 0.1 M KIO\textsubscript{3} and 0.01 M KI is 9.17 Å, while in 
solution containing 0.1 M K\textsubscript{3}[Fe(CN)\textsubscript{6}] it is only 4.30 Å. Therefore, the alumina particles 
in KIO\textsubscript{3} dispersions experience a greater electrostatic barrier, and this combined with the 
steric barrier provided by the surfactant leads to greater dispersion stability in KIO\textsubscript{3} 
dispersions. The strongly adsorbed hydrophobic Span (E\textsubscript{0}) surfactants provide a 
sufficient steric barrier in KIO\textsubscript{3} dispersions to impart stability. The K\textsubscript{3}[Fe(CN)\textsubscript{6}] slurries, 
with a trivalent counterion, provide more complete charge screening and therefore reduce 
the electrostatic barrier to agglomeration and increase the requirements of the steric 
barrier needed. The E\textsubscript{2} or E\textsubscript{4} surfactants, however, are considerably more hydrophilic 
than the E\textsubscript{0} surfactants and possess the polymer chain necessary to provide steric 
repulsion in these slurries. Since the hydrophobicity of these surfactants is also 
sufficiently high, they provide ample surface coverage and maximum stabilization for the 
K\textsubscript{3}[Fe(CN)\textsubscript{6}] environment.
3.6 Effect of Total Surfactant Concentration on Dispersion Stability

The results in Figures 3-4 and 3-5 are for a total surfactant concentration of 50 mM, but the dispersion stability is expected to vary significantly with surfactant concentration. As a result, the surfactant concentration has been varied in sedimentation experiments presented in Figure 3-7. In this figure, the dispersions are 10 wt. % AKP-50 alumina at pH 4 with 0.1 M potassium ferricyanide and the surfactant in these systems is a mixture of SDS and the indicated nonionic surfactant in a 1:1 molar ratio.

The results in Figure 3-7 show interesting, unexpected results, particularly for the SDS/Tween 80 surfactant mixture. The data shows that, as expected, a minimum surfactant concentration is needed for stabilization, indicative of the large surface area of the particles that must be sufficiently covered with surfactant to achieve stabilization. The unexpected result is that the dispersion stability once again decreases at high concentrations of SDS/Tween 80. This result may be due to a number of factors, the first being the formation of nonionic surfactant domains or micelles lining the adjacent particles. The Tween 80 domains formed by E groups then serve as glue (adhesive) connecting the particles in a loose agglomerate or floc. This mechanism will be explained in detail in section 3.8. The other possible explanation for this result is that multilayer effects are dominant in this system, resulting in the adsorption of a third surfactant layer of either SDS or Tween 80 at high concentrations. This third layer, with hydrophobic chains extending into solution, makes the particles once again susceptible to agglomeration due to hydrophobic interactions between adjacent particles.
Figure 3-7. Sedimentation experiments showing dependence of dispersion stability on surfactant concentration in 0.1 M potassium ferricyanide slurries at pH 4.

The results of the other surfactant systems (SDS/Brij 93 and SDS/Symperonic A4) which are shown in Figure 3-7 do not show the same trends as the SDS/Tween 80 results. Although SDS/Brij 93 mixtures do show a minimum concentration required for stability, there is no decrease in dispersion stability at higher concentrations. However, it is important to note that Brij 93 is only slightly soluble in water due to its hydrophobicity. The solubility of Brij 93 is significantly enhanced by the presence of SDS, but there is some cloudiness present at high concentrations (µ 75 mM), indicating that the solubility limit has been reached. As a result, it is expected that the reason the SDS/Brij 93 mixtures do not become unstable at higher concentrations is that not enough Brij 93 surfactant is solubilized to cause instability at high concentrations. The
SDS/Symperonic A4 mixture is likewise less soluble than the SDS/Tween 80 mixture, so the results for this system are expected to be similar to those of the SDS/Brij 93 system, as shown in Figure 3-7.

The effects of surfactant concentration on dispersion stability have also been investigated for the copper CMP slurry consisting of 0.1 M KIO₃, 0.01 M KI and 0.01 M EDTA. It is important to note that the SDS/Tween 80 mixture does not significantly stabilize this slurry, so a direct comparison with the K₃Fe(CN)₆ slurry results is not possible. However, the effects of concentration are given in Figure 3-8 for two mixtures that have been found to provide optimum stabilization for this slurry at 50 mM concentration.

![Figure 3-8](image.png)  
**Figure 3-8.** Effect of surfactant concentration on dispersion stability in 0.1 M KIO₃, 0.01 M KI and 0.01 M EDTA slurries at pH 6.
This figure shows that both the SDS/Symperonic A4 and SDS/Tween 21 mixtures impart stability to alumina particles in the KIO₃ environment at concentrations as low as 25 mM, but at concentrations higher than 75 mM, both dispersions are clearly unstable. This result is similar to the result of the SDS/Tween 80 mixture in Figure 3-7. The SDS/Symperonic A4 mixture shows these high concentration effects in KIO₃ environment but not in K₃Fe(CN)₆ environment because the solubility of the SDS/Symperonic A4 mixture is greater in KIO₃ solution than in K₃Fe(CN)₆ solution since the prevalent ion is monovalent, not trivalent. Both mixtures of SDS/Symperonic A4 and SDS/Tween 21 in KIO₃ solution become cloudy at concentrations greater than 100 mM, indicating that the solubility limit has been reached, but not before high concentration effects cause instability of the dispersion.

The results presented in Figures 3-7 and 3-8 show that surfactant concentration is a parameter which can significantly effect dispersion stability. The results have shown the presence of a maximum in dispersion stability over a concentration range which depends upon a number of factors. The results have also shown that mixtures of surfactants will show a solubility limit that depends upon the ion concentration and valence as well as the hydrophobicity of the surfactant system. Finally, the results have shown that the solubility limit of the surfactant may keep the surfactant from dissolving at high enough concentrations to cause instability.

### 3.7 Effect of Ratio of Surfactants in Mixtures on Dispersion Stability

The final parameter regarding the surfactant mixture in the complex systems that have been investigated is the ratio of ionic to nonionic surfactant. To this point, all of the mixtures investigated have been at a 1:1 molar ratio. However, it has been shown that
ionic or nonionic surfactant alone yield unstable slurries, so there is expected to be at least two stable – unstable transitions on a plot of stability versus fraction of one component. This parameter has therefore been studied in order to make this investigation of the molecular factors influencing stabilization complete.

For the $K_3Fe(CN)_6$ chemistry, ratios of SDS:Tween 80 and SDS:Symperonic A4 have been investigated using 50 mM total surfactant and 10 wt. % AKP-50 particles. The sedimentation results are given in Figure 3-9 for these systems as a function of mole fraction of SDS in the total mixture.

![Figure 3-9](image.png)

**Figure 3-9.** The effect of ratio of surfactants on dispersion stability for slurries containing 0.1 M $K_3Fe(CN)_6$ at pH 4. Total surfactant concentration is 50 mM.

Both systems investigated are unstable when only one surfactant is used (SDS, Tween 80, or Symperonic A4 alone), as illustrated at the endpoints in Figure 3-9. The SDS/Tween
80 mixture is shown to impart stability to dispersions at mole fractions of SDS at or
greater than 0.5 and all the way up to 0.97 (corresponding to a molecular ratio of 30:1
between SDS and Tween 80). At ratios that favor Tween 80, these dispersions are
unstable. The SDS/Symperonic A4 mixture is shown to be unstable only at the endpoints
(mole fractions of 0 and 1), while it is stable throughout the range of ratios investigated.

The differences in behavior between SDS/Tween 80 and SDS/Symperonic A4
mixtures is presumably due to the inability of low ratios of SDS/Symperonic A4 to
produce nonionic surfactant domains which act as adhesive between particles. This
explanation is feasible since the mechanism, which is discussed in the next section,
depends on long hydrophilic polymer segments on the nonionic surfactant aggregating to
form the domains responsible for instability. Since Symperonic A4 is an E₄ surfactant
and Tween 80 is an E₂₀ surfactant, the tendency for Tween 80 systems to exhibit this
behavior is much greater than for Symperonic A4 systems.

The effect of ratio of surfactants in mixtures has also been investigated for the
copper CMP slurry based on KIO₃ chemistry. The results of sedimentation experiments
showing the effects of ratio of surfactants on dispersion stability are presented in Figure
3-10. Since the SDS/Tween 80 mixture does not stabilize the copper CMP slurry
significantly, only one mixture is investigated in this figure, SDS/Symperonic A4, but the
results are shown after both 2 days and 10 days of settling. The results show that for
SDS/Symperonic A4 mixtures, as with the K₃Fe(CN)₆ slurries, the dispersions are stable
almost throughout the full range of SDS mole fractions investigated, except at high mole
fractions greater than 0.9. The results after 10 days show slightly lower stability than
those after 2 days, but the dispersions are still relatively stable. Limited solubility of
SDS in high ionic strength environments is proposed to be the reason that very high ratios of SDS:A4 are unstable. The overall behavior in Figure 3-10 is very similar to the behavior of SDS/Symperonic A4 in Figure 3-9, as expected.

![Figure 3-10. The effect of ratio of surfactants on dispersion stability for slurries containing 0.1 M KIO₃, 0.01 M KI and 0.01 M EDTA.](image)

3.8 Explanation of Observed Instability in Surfactant Mixtures at High Concentrations and at Ratios Favoring Nonionic Surfactant

The results of dispersion stability as a function of concentrations and ratios of SDS/Tween 80 mixtures in Figures 3-7 and 3-9, respectively, both exhibit unexpected instability in the dispersions. Likewise, the results of dispersion stability as a function of concentration for the KIO₃ chemistry shown in Figure 3-8 shows instability at high concentrations. The results will be explained in terms of the SDS/Tween 80 system, but the same mechanism applies to other systems for the KIO₃ chemistry. The observed
instability is presumably due to a change in conformation of the adsorbed polar segments of Tween 80 in the presence of excess Tween 80. Since Tween 80 is an E\textsubscript{20} surfactant, any change in conformation of these steric stabilizing segments could lead to a change in stabilization behavior to a greater extent than the surfactants with lower degrees of ethoxylation. This is presumably the reason that the SDS/Tween 80 mixture exhibits instability in the ratio of surfactant results, but the SDS/Symperonic A4 mixture does not. Similarly, in the concentration of surfactant results, the SDS/Tween 80 mixture exhibits instability in the K\textsubscript{3}Fe(CN)\textsubscript{6} solution while the other mixtures, with lower degrees of ethoxylation, do not.

The change in conformation of adsorbed Tween 80 segments is presumably due to a greater flocculation potential between adjacent particles at higher concentrations of Tween 80. This type of flocculation, however, is of a different origin than normal flocculation, which is favored in systems using low concentrations of high molecular weight polymers that are not well solvated. High concentrations of the highly solvated Tween 80 molecules can lead to the formation of admicelles, or nonionic surfactant domains, of Tween 80 near the particle surfaces. These admicelles are aggregates of adsorbed Tween 80 and Tween 80 in bulk solution that interacts with the adsorbed molecules. When two particles surrounded by these nonionic surfactant domains approach one another, the Tween 80 molecules have a tendency to aggregate with Tween 80 molecules on the adjacent particles, causing a loose floc to form, with the region between particles having a high density of Tween 80 molecules. This type of flocculation is illustrated in Figure 3-11. The region between particles may or may not include additional Tween 80 molecules bound to the floc as shown in Figure 3-11 b). If
additional Tween 80 molecules are bound to the floc, adsorption measurements should show a high ratio of adsorbed Tween 80 to SDS, and the adsorption measurements in Chapter 4 will examine this aspect.

Figure 3-11. The proposed mechanism of induced instability in mixed surfactant systems; a) low concentrations/ratios of nonionic surfactant and b) high concentrations/ratios of nonionic surfactant.

Stable Slurry

Unstable Slurry

The results of this chapter have described the numerous factors that influence dispersion stability in mixed surfactant systems. The effects of surfactant hydrophobicity, concentration and ratio have been investigated and the trends have been explained. The next chapter will attempt to verify some of the explanations given with adsorption measurements.
CHAPTER 4
ADSORPTION OF SURFACTANTS ON PARTICLES FROM MIXED SURFACTANT SOLUTIONS IN SEVERE ENVIRONMENTS

4.1 Review of Previous Methods and Results

Adsorption of surfactant molecules on a solid surface from solution is important in controlling a variety of interfacial processes. Adsorption can be classified as physical or chemical, depending on the nature of the forces involved [Adamson, 1982]. Physical adsorption is usually weak and reversible, involves small energy changes, and is characterized by a high rate of adsorption and formation of multilayers [Parfitt and Rochester, 1983]. Chemical adsorption occurs through chemical bonding between the surfactant (adsorbate) and the atoms on the solid surface and is hence irreversible [Adamson, 1982]. It is characterized by relatively high energy changes and monolayer coverage. The adsorption density, which is the amount of surfactant (adsorbate) removed from solution by the solid/liquid interface, can be expressed as

\[
\tilde{\Gamma}_i = 2rC \exp \left( -\frac{\Delta G_{ads}^0}{RT} \right)
\]

(4.1)

where \( \Gamma_i \) is the adsorption density in the plane \( \delta \), which is the distance of closest approach of counterions to the surface, \( r \) is the effective radius of the adsorbed ions, \( C \) (mol mL\(^{-1}\)) is the bulk concentration of the surfactant (adsorbate), \( R \) is the gas constant, and \( T \) is the
absolute temperature and $\Delta G_{ads}^\circ$ is the standard free energy of adsorption [Goddard and Somasundaran, 1976]. In practice, however, the adsorption density ($\Gamma$) is measured as depletion of the surfactant (adsorbate) from the solution:

$$\bar{A} = (C_i - C_f) \frac{V}{W} \quad (4.2)$$

where $\Gamma$ (mol g$^{-1}$) is the adsorption density, $C_f$ (mol L$^{-1}$) and $C_i$ (mol L$^{-1}$) are the final and initial concentrations of the surfactant (adsorbate), $V$ (L) is the volume of solution and $W$ (g) is the mass of the adsorbent (solid particles). The adsorption density ($\Gamma$) in equation (4.2) is given in mol/g, but this quantity can easily be converted to units of mol/m$^2$ by measuring the total surface area per gram ($a_s$) of particles by the B.E.T. method [Brunauer et al., 1938]. Therefore, the adsorption density ($\Gamma'$) in mol/m$^2$ is given by $\Gamma' = \Gamma / a_s$ where $a_s$ is the surface area per gram of particles.

The determination of surfactant adsorption has been undertaken for decades as an instrumental tool in verifying adsorption mechanisms. Most of the analysis techniques currently employed measure adsorption indirectly by analyzing the amount of residual surfactant in supernatants obtained from centrifuged dispersions [Somasundaran and Krishnakumar, 1997]. The amount of adsorbed surfactant is then simply the difference between the initial amount of surfactant and the measured final amount of residual surfactant. In recent years, a number of investigations have focused on attempting to use surface analysis techniques to directly measure adsorption of surface active species. However, most of these techniques are yet to yield sufficiently quantitative results, but rather are more useful as qualitative techniques for determining composition and structural information about the adsorbed layer.
Some of the techniques used to obtain indirect adsorption measurements in solid/liquid systems include the serum displacement technique [Kronberg et al., 1981], total organic carbon (TOC), high pressure liquid chromatography (HPLC) [Xu et al., 1991], ultraviolet (UV) spectroscopy [Huang et al., 1996] and direct chemical titration techniques [Li and Rosen, 1981]. Many of these techniques encounter problems in high salt or corrosive chemical environments. TOC yields good quantitative analysis of carbon content with little regard to the exact chemical composition of the adsorbed species, and hence is readily applied to a number of surfactant systems. However, TOC also measures any other carbon-containing species in solution, such as K$_3$Fe(CN)$_6$ in the present investigation. Further, TOC catalytically oxidizes the carbon species in solution and may produce toxic HCN upon conversion of K$_3$Fe(CN)$_6$. UV spectroscopy is useful in mixed surfactant systems in that it experiences a peak for alcohol (-OH) species such as endgroups on ethoxylated nonionic surfactants. However, in the present investigation the K$_3$Fe(CN)$_6$ solution produces a strong peak throughout the UV range and hence makes this technique inapplicable. As can be seen, there are many problems with the application of common adsorption determination techniques in high ionic strength environments, and hence novel techniques have been developed in the present investigation to obtain useful data.

4.2 Novel Methods and Apparatus for High Ionic Strength Environments

The present investigation utilizes surface tension measurements and a dye absorption method in order to obtain adsorption measurements in 0.1 M K$_3$Fe(CN)$_6$ slurries for tungsten CMP, which is the same solution used in previous chapters for dispersion stability determinations. The basic premise of the two techniques mentioned
above is that they are both methods that give a precise change in a measurable property such as surface tension or dye absorption of surfactant solutions as a function of surfactant concentration. By comparing unknown residual surfactant solutions (i.e. supernatant) from dispersions to a calibration curve measured using standard (known) solutions, the amount of adsorbed surfactant can be obtained. Equation (4.2) can then be utilized to yield the adsorption density ($\Gamma$).

4.2.1 Total Adsorption Measurement

Below the CMC of a surfactant solution, the surface tension at the air/water interface decreases with surfactant concentration. The adsorption of surfactants on particles has been demonstrated in Chapter 2, but the results only demonstrated that surface tension of supernatant is higher than that before adsorption. However, it did not yield the amount of surfactant adsorbed. The same curves of surface tension versus concentration for solutions before and after adsorption can be utilized in obtaining unknown surfactant concentrations quantitatively. Since this technique requires that the unknown solution be below CMC, very large dilutions must be used to bring solutions into this concentration regime if the initial surfactant concentration is large and the CMC of the surfactant is low. This is the case in solutions containing nonionic surfactants and mixtures of ionic and nonionic surfactants, and hence this technique is only useful in the lower end of the concentration range investigated.

For higher concentrations of surfactant, the dye absorption method has been utilized. This method utilizes a dye that shows a peak shift in the visible range when shifted from a hydrophilic to a hydrophobic environment. Since surfactant micelles constitute a relatively hydrophobic environment, a number of dyes have been found to
show a peak shift due to the presence of micelles at concentrations above CMC. The micelle peak increases with increasing surfactant concentration and can hence be utilized as an adsorption measurement technique in the same fashion as the surface tension technique. As discussed in the results, Eosin-Y dye has been investigated as a possible dye for this application in solutions containing mixtures of SDS and Tween 80. This application of Eosin-Y has been successfully utilized in determining CMC’s of nonionic surfactants by Patist et al. [2000]. However, an interaction of this dye with SDS is discussed in the results and makes this dye inapplicable in this investigation. Another dye (Merocyanine 540) has therefore been utilized successfully here.

![Chemical structure of Merocyanine 540 (MC 540) anionic dye.](Image)

Merocyanine 540 (MC 540) is an anionic cyanine dye that initially garnered interest due to application as a photosensitizer. Cyanine dyes have also found application in photographic filter layers, textiles and chemotherapy [Hamer, 1963]. MC 540 has been used extensively to monitor biological membrane phenomena through the change of its spectrophotometric properties (both absorption and fluorescence) as MC 540 is bound to the membrane [Masamoto et al., 1981; Humphries and Lovejoy, 1983]. Finally, MC
540 has been applied to surfactants due to the change in affinity of the dye towards micelles, which serve as a good model for organized, well-defined hydrophobic structures [Dodin et al., 1987]. The chemical structure of MC 540 is depicted in Figure 4-1.

The absorption maxima ($\lambda_{\text{max}}$) of the MC 540 in various solvents, micelles, microemulsions, vesicles and other hydrophobic entities has been characterized [Dixit and Mackay, 1983]. A significant enhancement in both absorbance and fluorescence emission has been observed when MC 540 is present in hydrophobic entities, accompanied by a shift in $\lambda_{\text{max}}$ due to a change in polarity of the dye environment [Humphry-Baker and Gratzel, 1980]. In related experiments, $\lambda_{\text{max}}$ has been observed to shift from 533 nm to 558 nm when placed in solutions below and above CMC of SDS, respectively. The value of 533 nm is the same as the peak of the dye in water, and is due to the self-aggregation of dye monomers. No change in absorbance at 533 nm is observed for concentrations of SDS below CMC, indicating that there is no interaction between monomeric surfactant molecules or weakly organized aggregates and the dye due to Coulombic repulsion between negatively charged species. MC 540 dye has therefore been utilized in the dye absorption method for adsorption measurements of slurries containing mixtures of anionic and nonionic surfactants with metal CMP oxidizing agents.

### 4.2.2 SDS Adsorption Measurement Using a Titration Method

The adsorption characterization methods discussed in the previous section involve measurement of surface and bulk properties of surfactant solutions, namely surface tension and micelle concentration. Since mixed surfactant systems have been utilized in
the present investigation in order to stabilize dispersions in severe environments, it would be beneficial to be able to isolate adsorption of one component from mixed surfactant solutions. One particular well-established method which is useful for this purpose is a two-phase mixed indicator titration method for determining concentration of anionic surfactant, developed by Reid et al. [1967 and 1968] for the Commission Internationale d’Analyses of the Comité International des Dérivés Tensioactifs (70 Champs Elysees, Paris, France). As the name of the method indicates, this method involves two phases (aqueous and organic) and a mixed (cationic and anionic) indicator solution. The titrant is a cationic surfactant, Hyamine 1622. The reactions that form the basis for this analytical method can be formulated as shown in Figure 4-2.

Figure 4-2. Equilibria involved in the two-phase, mixed indicator titration method for anionic surfactants (from Li and Rosen, 1981).

The anionic surfactant forms a complex with the cationic indicator component, which then reacts with the titrant (Hyamine 1622) to form a colorless complex in the organic
phase. Finally, at the end point, the excess unreacted titrant forms a blue complex with the anionic indicator.

The organic phase, chloroform, may be substituted with 2:3 (v/v) chloroform:1-nitropropane in order to yield more accurate results for alkyl chains containing less than 12 carbon atoms. The effect of ionic strength on the accuracy of the method has been investigated by Li and Rosen [1981]. Cl\(^-\) at concentrations in excess of 5 x 10\(^{-3}\) M in the aqueous phase interferes with the results of the method, but Na\(^+\), Mg\(^{2+}\) and SO\(_4^{2-}\) at concentrations of up to 0.4 M do not interfere with the determination of sodium dodecanesulfonate.

4.2.3 Materials and Methods

Dispersions have been prepared as described in Chapter 2. Surfactant adsorption has been assumed to be complete within 2 hours, after which the slurries have been centrifuged in a Sorvall RC-5B refrigerated superspeed centrifuge operating at 10,000 rpm for a period of 15 minutes. The supernatants have been saved and stored at 25 ± 1 °C for adsorption measurements. Surface tension measurements have been made in air using the Wilhelmy plate method [Becher, 1965] with a 10 x 20 mm platinum plate, allowed to equilibrate in solution for 60 seconds before taking a measurement using a force transducer. The force transducer readings have been calibrated using known surface tensions of water and methanol.

For the dye absorbance measurements, Merocyanine 540 (MW 569.57) has been obtained from Acros, Inc. A dye stock solution has been prepared by making a large volume of 0.5 mM MC 540 solution and allowing it to equilibrate for at least one day. The dye has been added to solutions containing surfactant at concentrations of 0.02 mM,
which has been found to yield a maximum absorbance peak of about 2.0 AU for saturated solutions of SDS / Tween 80 mixtures. A higher MC 540 concentration of 0.05 mM yields a peak above 3.0 AU for saturated solutions, which is well into the noisy regime of the instrument, and a lower MC 540 concentration of 0.005 mM yields a relatively low maximum peak of less than 1.0 AU. The 0.02 mM MC 540 solution has been prepared by adding 0.4 mL of stock solution to 9.6 mL of surfactant solution. Dilutions of supernatants have been performed using 0.1 M K$_3$Fe(CN)$_6$ in order to keep the ionic strength of solution constant.

For the absorbance measurements, an HP 8453 UV-Vis spectrophotometer has been used in the visible range. The background absorbance with no dye addition has been subtracted for each of the measurements, in order to take into account color variations and residual particles in the supernatants. The absorbance value has been recorded at the peaks found in initial testing. For each measurement, spectra have been obtained on samples 2, 4 and 6 minutes after dye addition. The average value of the absorbance peak is reported in each case.

For the titration method for the determination of anionic surfactant, the acid mixed indicator solution has been prepared from dimidium bromide-disulphine blue indicator stock solution supplied by BDH Chemicals Ltd. This stock solution is diluted by a factor of 25 and the pH is adjusted by adding 20 mL of 2.5 M sulfuric acid, supplied by Fisher, Inc. The titrant is Hyamine 1622 (MW 448.1), also supplied by BDH Chemicals Ltd. The titration method involves adding 10 mL of acid mixed indicator solution to 10 mL of anionic surfactant solution and 15 mL of chloroform and titrating with Hyamine 1622 until the chloroform phase color changes from pink to colorless or
just slightly blue [Reid et al., 1967 and Reid et al., 1968]. Further titration leads to a blue color in the organic phase. This method gives the correct concentration of anionic surfactant regardless of the presence of nonionic surfactants, salts, or oxidizing agents investigated here.

4.3 Application of Eosin-Y Dye in Total Surfactant Adsorption Measurements

The application of Eosin-Y has been attempted in the total surfactant adsorption measurements (i.e. anionic + nonionic surfactants) by the dye absorbance method described above for mixtures of SDS/Tween 80 solutions containing 0.1 M K₃Fe(CN)₆. In order to determine the applicability of the dye (Eosin-Y), standard solutions have been prepared at various concentrations and the absorbance spectra recorded with addition of 0.02 mM MC Eosin-Y. The results are shown in Figure 4-3 a), which shows a gradual shift in the absorbance peak (λ_max) from 517 nm to 528 nm as the SDS/Tween 80 concentration is increased. The shift in λ_max is not distinct, and it occurs at concentrations that are suspected to be well above the CMC of the mixture. Also, the value of the peak absorbance stays in the range of 1.0 Absorbance Unit (AU) as the concentration increases. All of these results suggest that an interaction is occurring between Eosin-Y and the SDS/Tween 80 surfactant system.

In order to determine the specific interactions between Eosin-Y and SDS and Tween 80 individually, the UV-Vis spectra have been recorded for solutions containing SDS alone (Figure 4-3 b) and Tween 80 alone (Figure 4-3 c). The SDS alone results, taken without K₃Fe(CN)₆ due to precipitation of SDS in the presence of the salt, show
only a slight shift in $\lambda_{\text{max}}$ from 517 nm to 519 nm, and the value of the absorbance peak changes minimally with surfactant concentration.

Figure 4-3. UV-Vis spectra using 0.02 mM Eosin-Y dye and solutions containing 0.1 M $K_3\text{Fe(CN)}_6$ and varying concentrations of a) SDS + Tween 80, b) SDS only and c) Tween 80 only.
As a result, it is suggested that SDS is not interacting with the dye. The Tween 80 alone results show a much greater shift in $\lambda_{\text{max}}$ from 517 nm to 533 nm, suggesting that the results of the mixed SDS/Tween 80 system show influences of predominantly the Tween 80 species. As with the other results, the Tween 80 alone results do not show a significant increase in the absorbance peak as the surfactant concentration is increased, suggesting an interaction of Tween 80 with Eosin-Y in 0.1 M K$_3$Fe(CN)$_6$. The results of Figure 4-3 suggest that the partitioning of Eosin-Y dye occurs in mixed micelles of SDS and Tween 80 in solutions containing an oxidizing agent (e.g. K$_3$Fe(CN)$_6$). Because the peak wavelength ($\lambda_{\text{max}}$) shows a gradual shift instead of two distinct peaks (one for monomers and one for micelles), and because the peak height does not increase with micelle concentration, Eosin-Y dye is not suitable to study adsorption of anionic and nonionic surfactant mixtures on the surface of alumina particles.

4.4 The Use of Merocyanine 540 Dye to Study the Adsorption of Mixed Surfactants on Alumina Particles

Since Eosin-Y has been determined to be not suitable for this investigation, the dye MC 540 has been investigated for adsorption measurements. Due to its anionic nature, MC 540 is not suspected to interact with the anionic SDS. Figure 4-4 shows the results obtained for addition of 0.02 mM MC 540 in solutions containing SDS/Tween 80 surfactant mixture (0 – 180 mM concentrations) and 0.1 M K$_3$Fe(CN)$_6$. This figure shows a distinct shift in $\lambda_{\text{max}}$ for SDS/Tween 80 solutions from 517 nm to 563 nm at higher concentrations. The absorbance peak rises sharply between 0.1 and 1.0 mM total concentration, then levels off around 10 mM, with only a slight increase at concentrations up to 180 mM.
Figure 4-4. UV-Vis spectra for SDS/Tween 80 mixtures at the indicated concentrations (in mM), containing 0.02 mM MC 540 dye and 0.1 M K₃Fe(CN)₆.

Figure 4-5. Absorbance at 563 nm for SDS/Tween 80 solutions shown in Figure 4-4, with CMC indicated.
In order to use this data as a calibration curve for adsorption measurements, the absorbance at the micelle peak of 563 nm has been graphed in Figure 4-5. This figure shows a well-defined increase in absorbance with surfactant concentration in the range of 0.1 to 1 mmol/L of mixed surfactants. The CMC is found from this chart according to the method described by Patist [1999] as 0.090 mM, which is indicative of the micelles formed by the mixture of surfactants.

In order to determine if interactions are present between MC 540 and the individual surfactants, UV-Vis spectra have been taken for solutions containing SDS only (Figure 4-6 a) and Tween 80 only (Figure 4-6 b).

![Absorbance graphs for SDS and Tween 80](image)

**Figure 4-6.** Absorbance at \( \lambda_{\text{max}} \) for (a) SDS only solutions with no \( \text{K}_3\text{Fe(CN)}_6 \) (\( \lambda_{\text{max}} = 557 \text{ nm} \)) and (b) Tween 80 only solutions with 0.1 M \( \text{K}_3\text{Fe(CN)}_6 \) (\( \lambda_{\text{max}} = 563 \text{ nm} \)), with CMC indicated.

The results of Figure 4-6 a) and b) show distinct peak shifts and regions of sharp increase in absorbance for the micelle peak, indicating that MC 540 partitions into the micelles of either surfactant. The SDS only results, taken without \( \text{K}_3\text{Fe(CN)}_6 \) once again, show a shift in \( \lambda_{\text{max}} \) from 517 nm to 557 nm, with the micelle peak being in very close agreement with the literature value reported [Humphry-Baker and Gratzel, 1980]. The CMC of SDS is found to be 7.0 mM, which is very close to the value of 8 mM expected for pure SDS.
solutions. The differences are likely due to slight impurities in the SDS used in this investigation. The Tween 80 results (with $K_3\text{Fe(CN)}_6$) show a shift in $\lambda_{\text{max}}$ from 517 nm to 563 nm, and the resulting CMC of the solution is found to be 0.020 mM, in close agreement with the literature value of 0.028 mM for Tween 80 without $K_3\text{Fe(CN)}_6$ found by Patist et al. [2000] using Eosin-Y dye.

Since the absorbance peak of the SDS/Tween 80 mixtures (563 nm) matches that of the solutions containing Tween 80 only, the polarity of the micelles is shown to be governed by the Tween 80 component. Likewise, the CMC of the mixture (0.090 mM) is of the same order of magnitude as the CMC of Tween 80 alone (0.020 mM), which indicates that the mixed micelles are effected more by this component. The MC 540 results with the SDS/Tween 80 mixture show excellent correlation with micelle concentration and good agreement with literature, so this dye is used in the remainder of the investigation for total surfactant adsorption measurements.

**4.5 Total Surfactant Adsorption Isotherm of SDS/Tween 80 Mixture on Alumina Particles**

Now that valid methods of adsorption measurement have been described as above for use in severe environments, the application of these methods to the adsorption of SDS/Tween 80 mixture on alumina particles in 0.1 M $K_3\text{Fe(CN)}_6$ solution will be discussed. The total adsorption results compiled from both the surface tension method and the dye absorption method are given in Figure 4-7 a). This figure shows that there is very good agreement between the dye absorbance method and surface tension method, particularly at the point of overlap between the two methods. The adsorption results,
shown over a very large concentration range of 5 orders of magnitude, show a rather steady increase in adsorbed SDS/Tween 80 over the entire range.

Figure 4-7. Total adsorption isotherm of SDS/Tween 80 mixture on 10 wt. % AKP-50 alumina particles in 0.1 M K$_3$Fe(CN)$_6$ solution at pH 4: a) dye absorbance method and surface tension method and b) correlation of adsorption data with dispersion stability.
The correlation of the adsorption isotherm with dispersion stability is given in Figure 4-7 b). This figure shows the adsorption data on the left axis with the dispersion stability data from Chapter 3 on the right axis. The data is plotted against the initial surfactant concentration, not the residual concentration as in Figure 4-7 a), because the initial concentration is the relevant concentration for comparison to dispersion stability.

It should be noted that in calculating the adsorption density ($\Gamma'$), it is assumed that SDS + Tween 80 total surfactant is adsorbed at the particle surface in the same 1:1 molar ratio as it is in bulk solution. However, in order to determine the influence of changing the ratio of adsorbed surfactants on the magnitude and peak wavelength ($\lambda_{\text{max}}$) of dye absorption, solutions containing ratios of 2:1 and 1:2 SDS:Tween 80 at 50 mM total surfactant concentration have been analyzed after adding 0.02 mM MC 540 dye. The results show that $\lambda_{\text{max}}$ remains at 563 nm and the peak height does not change for the 1:2, 1:1 and 2:1 ratios SDS:Tween 80. This implies that the effect of the above assumption is minimal as long as the ratio of residual SDS to residual Tween 80 after adsorption is between 1:2 and 2:1.

4.6 SDS Adsorption Results Using the Titration Method

The two-phase mixed indicator titration method for determination of anionic surfactants described by Reid et al. [1967 and 1968] is only applicable in the sulfate concentration range of 1 – 4 mM. As a result, the mixed surfactant solutions have been diluted by a known amount in order to be in this concentration range for the measurements. The Hyamine 1622 titrant concentration used in this investigation is 2 mM, which is in the middle of the applicable range.
Figure 4-8. Verification of anionic surfactant titration method using known SDS concentrations with and without both Tween 80 (T80) and K$_3$Fe(CN)$_6$ (PoFe). Corresponding concentrations calculated assuming a 1:1 reaction between SDS and Hyamine 1622 are given above each bar.

In order to verify the applicability of the titration method to the mixed surfactant solutions containing 0.1 M K$_3$Fe(CN)$_6$ in the present investigation, standard solutions containing 1 and 4 mM SDS have been tested with and without equal amounts of Tween 80 and with and without the oxidizing agent. The results of this investigation are given in Figure 4-8. This figure shows the titration volume for each solution, along with the concentration calculated from the titration assuming a 1:1 reaction with the cationic surfactant (Hyamine 1622). As can be seen, the titration data is in close agreement with the calculated 1:1 reaction results, with each point being slightly higher due to standard titration error. The data with Tween 80 and with K$_3$Fe(CN)$_6$ is in good agreement with
the data without these components, indicating no effect of either component on the validity of the method. As a result, this method can be applied to measure SDS adsorption from the SDS/Tween 80 mixture in the presence of $K_3Fe(CN)_6$.

Figure 4-9. SDS adsorption and total surfactant adsorption on alumina particles from mixtures of SDS and Tween 80 in 0.1 M $K_3Fe(CN)_6$ at pH 4.

The results from the titration method for the same SDS/Tween 80 mixtures in 0.1 M $K_3Fe(CN)_6$ shown in Figure 4-7 are given in Figure 4-9, along with the total adsorption results from the dye absorbance method for comparison. This figure shows the adsorption density plotted against initial total surfactant concentration, since this parameter can correlate both sets of adsorption data. Note that the data in Figure 4-9 is plotted on a linear scale, not a logarithmic scale as is used in Figure 4-7, due to the smaller range of concentrations investigated. The data shows a linear increase in SDS
adsorption with concentration, while the total surfactant adsorption curve shows an increasing slope with surfactant concentration, with a 2\textsuperscript{nd} order polynomial fit to the data. This data suggests that at concentrations above 60 mM, where the dispersions become unstable as shown in Figure 4-7 b), Tween 80 is adsorbing to the surface in a greater proportion than at lower surfactant concentrations. This is shown in Figure 4-9 by the Tween 80 adsorption isotherm, which is calculated as the total adsorption (from the polynomial fit to the data) – SDS adsorption.

These results verify the mechanism presented in Figure 3-11 for instability at high concentrations of SDS/Tween 80 mixtures. The higher amount of Tween 80 adsorbed relative to SDS is adsorbed as aggregated surfactant near the surface region of particle agglomerates. This Tween 80 is effectively entrained by the formation of hydrophobic domains between the agglomerated particles, and hence is removed by the centrifugation process as adsorbed surfactant. This leads to the observed higher ratio of adsorbed Tween 80 to adsorbed SDS at high concentrations in Figure 4-9.

4.7 Comparison of Adsorption from SDS/Tween 80 and SDS/Symeronic A4 Mixture

In order to further validate the mechanism of instability at high concentrations of SDS/Tween 80 mixtures, adsorption measurements have been made on dispersions containing mixtures of SDS and Symeronic A4 (C\textsubscript{12}E\textsubscript{4}), which does not exhibit instability at high concentrations. The adsorption results are given in Figure 4-10 for both total surfactant adsorption from the dye absorbance method and SDS adsorption from the titration method. The data is plotted against initial total surfactant concentration for comparison. The data shows both total adsorption and SDS adsorption steadily increasing throughout the range of concentrations investigated, with the total adsorption
data best fit by a 2nd order polynomial equation and the SDS adsorption data best fit by a linear equation. The Symperonic A4 adsorption isotherm is calculated from the total adsorption (from the polynomial fit to the data) – SDS adsorption. The calculated Symperonic A4 adsorption is shown in this figure to increase at concentrations above 40 mM, but not as rapidly in relation to SDS adsorption as for the SDS/Tween 80 data. This implies that the ratio of nonionic surfactant adsorbed to anionic surfactant (SDS) adsorbed at high concentrations of surfactant is higher for the SDS/Tween 80 mixture than for the SDS/Symperonic A4 mixture.

Figure 4-10. Adsorption of SDS/Symperonic A4 mixture on 10 wt. % AKP-50 particles in 0.1 M $K_3Fe(CN)_6$ at pH 4.

The correlation between adsorption of SDS/Tween 80 and SDS/Symperonic A4 mixtures and dispersion stability is shown in Figure 4-11. This figure includes both total
adsorption (up to 100 mM) and SDS adsorption measurements (up to 200 mM) for both the SDS/Tween 80 and the SDS/Symperonic A4. The total adsorption results show similar trends up to 100 mM, with the adsorption density of the two mixtures at 100 mM initial concentration being almost equal. The SDS adsorption results for the two surfactant mixtures, however, give additional insight into the reason for the instability at high concentrations of SDS/Tween80 (μ 80 mM) shown in the dispersion stability results. The adsorption of SDS from the SDS/Symperonic A4 mixture is significantly greater than that from the SDS/Tween 80 mixture at concentrations above 100 mM.

![Figure 4-11](image_url)

**Figure 4-11.** Correlation of adsorption with dispersion stability for both SDS/Tween 80 and SDS/Symperonic A4 mixtures. Results include total surfactant adsorption (•), SDS adsorption (○), and dispersion stability (▲).

As a result, Figure 4-11 suggests that the differences in dispersion stability for these two systems is due to the difference in the ratio of adsorbed nonionic surfactant to
adsorbed anionic surfactant. The greater adsorption of Tween 80 relative to SDS at high concentrations of SDS/Tween 80 mixtures versus SDS/Symperonic A4 mixtures leads to the observed instability in the SDS/Tween 80 system due to the formation of Tween 80 aggregates near the surface of the alumina particles. These results further verify the mechanism of instability at high concentrations of SDS/Tween 80 mixture presented in Figure 3-11.

The results of this chapter indicate that adsorption measurements can be made in high ionic strength environments by the use of novel techniques described here that utilize characteristic properties of surfactant solutions. The dye absorption method and surface tension method have been introduced as techniques for measurement of total surfactant adsorption at concentrations above and below CMC, respectively. The adsorption results of two representative mixed surfactant systems in tungsten CMP slurry suggest that adsorption of surfactant increases throughout the range of concentrations investigated. Differences between the SDS/Tween 80 and SDS/Symperonic A4 systems have been explained in terms of changes in the relative adsorption of SDS and nonionic surfactant at high concentrations. These results have also been used to verify the mechanism for the observed instability in the SDS/Tween 80 system at high concentrations. Now that the factors influencing dispersion stability in mixed surfactant systems have been investigated and verified by adsorption measurement, the influence of dispersion stability on the principal application of these dispersions, CMP, will be investigated in the following two chapters.
CHAPTER 5
CORRELATION OF DISPERSION STABILITY TO PARTICLE SIZE MEASUREMENTS

5.1 Importance of Particle Size versus Dispersion Stability Correlation

The general trend of the CMP industry in recent years has been to use smaller and smaller particle sizes in the slurries that are being developed [Steigerwald et al., 1996]. Most slurries being developed at present use particles with a mean particle size of 0.5 µm or less. This is because, as previously discussed, in the CMP industry it is well established that the presence of large particles in the slurry is linked to increased defects on the polished wafers. Although the exact size of the particles needed to cause defects is not well established, it is generally thought that the size limit above which defects are most probable is in the range of 1 µm to 5 µm. However, most of the particles currently supplied and used in commercial slurries have fairly well characterized particle size distributions, and the upper tails (i.e. the higher particle size range) of these size distributions are seldom even close to 1 µm. Further, companies that use CMP spend a large amount of capital on slurry filters and other equipment designed to keep large particles from entering the polishing apparatus. However, it should be emphasized that the agglomeration of primary particles could lead to aggregates of considerably larger size and hence influence the defectivity of polished wafers as well as dispersion stability.
The discussion on high ionic strength dispersions in Chapter 1 explains the reason that agglomeration takes place in metal CMP slurries. Although a stabilization method has been developed and its mechanism examined in the previous chapters, there has been no verification that this stabilization method will have any effect on the polishing process under the time scales and shear forces developed in actual CMP processes. The following two chapters address this subject, with this chapter addressing the effect of the particle size of the slurries on dispersion stability. The purpose of this chapter is then to verify that stabilized dispersions do in fact prevent the particles from agglomerating.

The present study attempts to correlate the mean particle size of concentrated slurries to the stability of the slurries. In a similar study, Oumaloul et al. [1990] have found that the dispersion of alumina slurries by sodium metaphosphate is accompanied by a reduction in mean particle size of the powder. This investigation attempts to verify a similar result for a more complex system containing two surfactants and in a high ionic strength environment. The present chapter also investigates the effect of abrasive particle size on critical stabilizing surfactant concentration. In similar work, Furusawa et al. [1992] have shown that the maximum amount of polyacrylamide adsorption increases steadily with decreasing particle radius. Finally, the tendency of slurries to produce defects during CMP of interconnection metals has been addressed. Although little work has been published to date in this area, Bare and Lemke [1997] have found that the particle size distribution of CMP slurries is a valuable indicator of slurry health and its measurement can be useful in reducing slurry-related variability in the CMP process. The present investigation expands the applicability of the results of Bare and Lemke
by establishing a detailed correlation of mean particle size with dispersion stability.

5.2 Materials and Methods for Particle Size Analysis

Two sizes of alumina particles have been investigated as a function of dispersion stability. Fumed \( \gamma \)-alumina (\( \text{Al}_2\text{O}_3 \)) particles with listed mean particle size of 50 nm were obtained from Leco, Inc. High purity \( \alpha \)-alumina particles with particle size of 100-300 nm were obtained from Sumitomo Chemical Co., Ltd. Figure 5-1 clearly shows the differences in these two types of particles.

![a) Leco \( \gamma \)-alumina and b) Sumitomo AKP-50 \( \alpha \)-alumina](image)

Mean Particle Size = 0.623 \( \mu \text{m} \)
B.E.T. Surface Area = 107.57 m\(^2\)/g
Mean Particle Size = 0.393 \( \mu \text{m} \)
B.E.T. Surface Area = 10.55 m\(^2\)/g

Figure 5-1. Electron micrographs of two types of alumina particles used in particle size correlation: a) Leco \( \gamma \)-alumina and b) Sumitomo AKP-50 \( \alpha \)-alumina

For Figure 5-1, scanning electron microscopy (SEM) has been performed on dry samples after Au-Pd coating using a JEOL JSM-35CF SEM. Transmission electron microscopy (TEM) has been performed on dry samples by mounting the particles from
the dispersion on a carbon-coated copper grid using a JEOL 200CX TEM. Surface area measurements have been made using nitrogen adsorption-desorption measurements according to the B.E.T. [Brunauer et al., 1938; Gregg and Sing, 1982] method utilizing a NOVA 1200 made by Quantachrome Corp.

The TEM micrograph of Leco particles shows a very broad particle size distribution. This is because the particles are comprised of primary particles of mean size around 10 nm which have been fused into hard aggregates by the fuming process. The surface area of these particles has been verified by BET surface area measurement and is 107.57 m$^2$/g for the Leco particles. This surface area is very large and confirms that these particles are porous in nature due to the fuming process. The volume mean (or mass average) particle size measured by dynamic light scattering of the Leco particles is 0.623 µm. A large volume mean is expected for dynamic light scattering measurements of porous particles with broad particle size distributions because the volume mean will be dominated by the largest particles in the distribution.

In contrast, the SEM micrograph of AKP-50 particles shows a much narrower particle size distribution by visual observation of Figure 5-1 b). The particles are partially spherical, and the listed particle size range of 100-300 nm appears to be close to the observed size range. The BET surface area of this particle has been measured to be 10.55 m$^2$/g, which is about 10 times smaller than that for the Leco particles. The volume mean (or mass average) particle size of these slurries from dynamic light scattering measurements is 0.393 µm, which is expected from the micrograph.

Dispersions have been prepared using the same method as described in Chapter 2. The particle loading for this investigation has been kept constant at 10 wt. % with both
Leco and AKP-50 particle slurries. The surfactant system investigated is a 1:1 molar ratio mixture of SDS:Tween 80. The surfactant concentration has been varied in order to vary dispersion stability. It has further been found that varying the order of mixing of slurry components does not significantly change the settling behavior of the slurry. Similar results have been found for silica slurries by Giordano-Palmino et al. [1994].

Particle size analysis has been carried out using the Honeywell Microtrac UPA 150, a referenced dynamic light scattering apparatus. In order to perform the light scattering measurements, the slurries must be diluted. For the dilution to be performed, a portion of the prepared dispersion has been centrifuged in a Sorvall, Inc. RC-5B superspeed centrifuge at 10000 rpm for 10 minutes. The supernatant obtained for each slurry is then used as the diluant. Using this method, each slurry has been diluted by a solution containing the equilibrium concentration of surfactant and oxidizing agent. The same technique has been employed in a similar study [Giordano-Palmino et al., 1994]. The Microtrac UPA 150 has an automated dilution feature. The dilution fluid is placed in the sample cell and the slurry to be measured is added dropwise while monitoring the signal level through the software. The apparatus has a wide range of acceptable signal levels, but the signal has been kept as close to constant as possible for each sample measured in this investigation. The signal level used in this study correlates to a dilution of about 1:10 for the samples investigated.

In light scattering measurements, the viscosity of the continuous medium is a parameter that significantly effects the calculated data. As a result, the viscosity of the supernatants has been measured using a Brookfield DV-II digital cone and plate viscometer. The average viscosity from readings at 3 shear rates has then been entered in
the particle sizing software to obtain the correct particle size from light scattering data. The viscosity of the supernatants investigated in this study varies between 1 and 3 cP, as can be seen in Figure 5-2 for standard solutions of 1:1 SDS and Tween 80 up to a concentration of 0.2 M. This result verifies that the surfactants used in this investigation do not significantly raise the viscosity since they are low molecular weight additives. The viscosity of these dispersions is therefore expected to be much lower than the viscosity of slurries which use high molecular weight polymers. For CMP applications, a change in viscosity will also change the polishing ability of the slurry, so high molecular weight polymer dispersing agents should be used cautiously in this context.

Figure 5-2. Viscosity of standard solutions of SDS and Tween 80 mixtures (1:1 molar ratio) measured immediately (■) and 6 days (▲) after preparation using a Brookfield cone and plate viscometer.

For the dynamic light scattering particle sizing software, the refractive index of water has been used as the solvent refractive index, and that of alumina particles has been
used as the dispersed phase refractive index. Five-minute measurements have been repeated twice for the particle size measurements and the volume mean particle size reported in this investigation is the average value from these measurements.

One additional particle sizing technique has been employed for measuring the particle size and zeta potential in concentrated suspensions of alumina particles. This technique is the Colloidal Dynamics Acoustosizer [Hunter and O’Brien, 1997], an electroacoustic technique which uses the electrokinetic sonic amplitude (ESA) effect, in which a sound wave is generated in a colloidal system by the application of an alternating electric field. The technique measures the particle dynamic mobility, which is a complex quantity having both a magnitude and a phase angle. The measured mobility can then be transformed to particle size and zeta potential data for the particles in solution using algorithms developed by Hunter and O’Brien [1997] and O’Brien et al. [1994] which relate the ultrasonic vibration potential (UVP) to the ESA effect. The Acoustosizer has the advantage of being able to measure concentrated suspensions under shear (up to 1000 rpm) and in a broad range of ionic strengths. However, the limitation of the Acoustosizer in context of the present investigation is that the presence of an adsorbed steric stabilizing layer such as the nonionic surfactants used here has been found by Hunter [1998] to interfere with the vibration of the electrical double layer around particles, hence yielding inaccurate data in these systems. As a result, this technique has only been applied in the present investigation to the particle size and zeta potential measurement of systems without surfactant.
5.3 Particle Size of Alumina Dispersions with and without Salt

The particle size of AKP-50 (0.1 – 0.3 µm) alumina dispersions has been investigated with and without salt to check for the effect of agglomeration. The salt in this study is the strong oxidizing agent used in the dispersion studies in Chapters 2, 3 and 4 – potassium ferricyanide. For these investigations, the Colloidal Dynamics Acoustosizer has been used as the particle sizing technique due to its ability to measure particle size at high particle loading. The Acoustosizer particle size results for dispersions with and without 0.1 M salt are given in Figure 5-3.

![Figure 5-3. Acoustosizer particle size results for 10 wt. % alumina dispersions with and without 0.1 M potassium ferricyanide salt added.](image)

As can be seen in Figure 5-3, the addition of salt raises the mean particle size obtained by the Acoustosizer from about 0.1 µm to about 0.8 µm. However, the data
appears to be quite lacking in size distribution information. In most systems where agglomerated particles are present, the particle size distribution is bimodal in nature, with one peak due to the primary particles and the other due to the agglomerates. Figure 5-3 shows that the Acoustosizer data is fit to a log-normal distribution with only one mode. Although this type of distribution is expected to occur in most dispersed particle systems, it does not accurately represent a multimodal system such as the one in this investigation.

The dynamic light scattering method employed in the remainder of this chapter, the Microtrac UPA 150, is capable of measuring a multimodal distribution. As a result, the data from this technique is expected to be more informative than the Acoustosizer data. The particle size data obtained from the Microtrac UPA 150 for the same two alumina dispersions with and without salt, potassium ferricyanide, is given in Figure 5-4.

![Graphs showing particle size distribution](image)

Figure 5-4. Microtrac UPA 150 dynamic light scattering particle size results for 10 wt. % a) AKP-50 α-alumina and b) Leco γ-alumina dispersions with and without 0.1 M potassium ferricyanide salt added.

The data in Figure 5-4 is given for both sizes of particles investigated, the AKP-50, 0.2 μm alumina and the Leco 0.05 μm alumina. The mean particle size (in terms of
volume averaging) appears to be quite similar for both particle types with and without salt. Without salt, both distributions appear to be log-normal in shape with a mean in the range of 0.5 µm (values given in Figure 5-1). With salt, the distributions are multimodal with a mean in the range of 2 – 4 µm. The distribution shows three peaks for the AKP-50 particles, with a smaller peak near 0.5 µm due to the primary particles and two peaks at larger sizes (2 µm and 4 µm) due to the agglomerated particles. The distribution for the Leco particles shows a hump for the primary particles near 0.5 µm and a large peak for the agglomerated particles. It should be noted that since these are volume distributions, the agglomerated particle peaks are significantly enhanced. Distributions on a number basis for these particles would show the primary particle peak as dominant over the agglomerated particles. For the remainder of this investigation, the particle size data given will be the volume mean particle size, which refers to the mean of the above distributions, which may be multimodal. However, the volume mean is very sensitive to the presence of agglomerated particles and is therefore a good characteristic size for stability studies.

5.4 Correlation of Dispersion Stability to Particle Size

The stability of dispersions comprised of 0.1 M potassium ferricyanide oxidizing agent has been investigated as a function of surfactant concentration, with a mixture of SDS and Tween 80 (1:1) used as the surfactant. Two different particle sizes of alumina particles have been used for this investigation since the effects of surfactant concentration on slurry stability will depend on total surface area of particles.
The correlation of dispersion stability to particle size measurements using dynamic light scattering is illustrated in Figures 5-5 and 5-6 for Leco and AKP-50 alumina slurries, respectively. These figures show both the settling behavior and mean particle size of 10 wt. % alumina slurries as a function of the total surfactant concentration. The settling behavior is reported as the fractional volume of dispersion, as in Chapters 2 and 3. The mean particle size reported is the volume mean particle size of the slurries, as discussed previously.

Figure 5-5. Correlation of dispersion stability to particle size for Leco 50 nm alumina dispersions with 0.1 M potassium ferricyanide at pH 4.

Figure 5-5 shows the effects of stabilizing surfactant concentration on 10 wt. % slurries of Leco alumina particles. As shown in Figure 5-1, these particles have a very large surface area due to their small size and preparation by a fuming process. Due to the
large surface area of the particles, it is expected that a relatively large amount of surfactant is required to stabilize a slurry of Leco particles. Figure 5-5 verifies this by showing that a stable slurry is only observed for 150 mM or greater surfactant concentrations. The critical micelle concentration (CMC) of the respective surfactants has been reported to be 8.2 mM for SDS and 0.028 mM for Tween 80 [Patist, 1999], and the CMC of the 1:1 mixture of surfactants is between these two values (CMC = 0.090 mM, as shown in Chapter 4). Therefore, the amount of surfactant needed to stabilize the Leco particle slurry is very large (1667 x CMC) compared to the CMC of the surfactant mixture. Figure 5-5 also shows that the slurry stability increases monotonically with surfactant concentration for this slurry.

The particle size results in Figure 5-5 show that as the stability of the slurry increases, the mean particle size decreases. Furthermore, the particle size shown for stable slurries with surfactant concentrations of 150 mM or higher is close to that of the base particles given in Figure 5-1 (0.623 µm). These results show that the surfactant present in stable slurries prevents agglomeration of the particles. Although these particle size results are expected, it is often difficult to clearly show this correlation when using high ionic strength slurries with complex stabilizing agents due to the difficulties in obtaining precise particle size data. The data obtained by the dynamic light scattering method in the presence of salts and mixed surfactants described in this study is precise, although the data collection is tedious.

Figure 5-6 shows the effects of surfactant concentration on 10 wt. % slurries of AKP-50 alumina slurries. Figure 5-1 shows that these particles are larger than Leco particles and that they have a significantly lower surface area, so it is expected that lower
surfactant concentrations will stabilize these slurries. Figure 5-6 verifies this expectation, showing that the slurries are most stable in the range of 10 – 60 mM surfactant concentration. Note that the settling data reported in Figure 5-6 is after only 1 hour of settling. Since these particles are considerably larger than the Leco particles, they settle much more rapidly in the unstable slurries, and hence the 1 hour settling time shows the most variation in stability. However, it should also be noted that the completely stable dispersions of AKP-50 particles retain their stability even after 2 days of settling (in the surfactant concentration range of 10 – 60 mM). Above 60 mM surfactant concentration, the dispersions continue to settle further with time.

Figure 5-6. Correlation of dispersion stability to particle size for AKP-50 100-300 nm dispersions with 0.1 M potassium ferricyanide at pH 4.
The volume mean particle size of these dispersions in Figure 5-6 is lowest in the range of surfactant concentrations (10 – 60 mM) corresponding to the most stable slurries. The mean particle size of the stable dispersions also corresponds closely to the measured value of the base particles given in Figure 5-1 (0.393 µm).

5.5 Correlation of Dispersion Stability to Surface Area of Particles

The percent coverage of a particle surface by surfactant monomers is dependent on the total area of the particle surface. This is why the amount of surfactant needed to stabilize AKP-50 particle slurries is much lower than that needed to stabilize Leco particle slurries. Figure 5-7 shows the settling behavior of the same metal CMP slurries shown in Figures 5-5 and 5-6, except that the data has been modified to show similarities between AKP-50 and Leco slurry data. Specifically, the surfactant concentration has been normalized by dividing the surfactant concentration by the total surface area in 1 gram of particles. This yields surfactant concentration / area values with units [mol / m²].

In addition, the fractional volume of dispersion data has been normalized as a parameter between 0 and 1. This is because the packing efficiency of the two particle slurries is much different due to the differences in particle size distribution. This results in the fractional volume of dispersion of the unstable 0.1 M potassium ferricyanide slurry with no stabilizing agent varying from 0.1 for AKP-50 particles to 0.7 for Leco particles. This unstable slurry value has been converted to equal 0 by the using the normalized parameter F, given by

\[ F = \frac{F_R - F_O}{1 - F_O} \]  \hspace{1cm} (5.1)
where $F$ is the normalized variable, $F_R$ is the fractional volume at the given surfactant concentration and $F_o$ is the fractional volume of an unstable slurry of particles with oxidizing agents but without any surfactant (for AKP-50, $F_o = 0.1$ and for Leco particles, $F_o = 0.7$). Finally, the mean particle size data has been normalized in a manner similar to the fractional volume of dispersion data. The measured particle size $d_R$ has been converted to a value between 0 and 1 using the formula

$$d = \frac{d_R - d_O}{d_M - d_O} \quad (5.2)$$

where $d$ is the normalized variable, $d_O$ is the mean particle size of the particles in water (without salts or surfactants) given in Figure 5-1 and $d_M$ is the maximum particle size read over the surfactant concentration range investigated.

The settling behavior of alumina slurries with two different sizes of particles shows interesting results. The sedimentation test results in Figure 5-7 show that both Leco and AKP-50 slurries show stable dispersions around the same normalized surfactant concentration, in the range of $1 – 2 \times 10^{-5}$ mol/m$^2$. The particle size results also show that a particle size near the initial particle size is achieved with a normalized surfactant concentration of $1 – 2 \times 10^{-5}$ mol/m$^2$ for both the Leco and AKP-50 slurries. Both sedimentation experiments and particle size results show similar trends for both types of alumina particles shown in Figure 5-7. It can also be concluded from this figure that 10 wt. % slurries of alumina particles in the chemical environment studied can be stabilized by a 1:1 molar ratio of SDS to Tween 80 with a surfactant concentration normalized with particle surface area of $1 – 2 \times 10^{-5}$ mol/m$^2$. This information can then be used in
determining the concentration of surfactant needed to stabilize a slurry may use different alumina particles.

Figure 5-7. Correlation of dispersion stability and particle size with surface area of the abrasive particles. Data is taken from Figures 5-5 and 5-6.

5.6 Verification of Particle Size Results with Other Systems

The correlation between dispersion stability and mean particle size measured by dynamic light scattering has been observed for other dispersions stabilized by mixed surfactant systems. In Figure 5-8, dispersion stability and mean particle size from dynamic light scattering are shown for 0.1 M Fe(NO$_3$)$_3$ slurries containing 10 wt. % AKP-50 particles at pH < 2. These are the same slurries as shown in the stabilization study in Figure 2-5. The slurries have various mixed surfactant systems added, including cationic – nonionic, anionic – nonionic and anionic – cationic systems.
Figure 5-8. Mean particle size and dispersion stability for Fe(NO₃)₃ based slurries stabilized using various mixed surfactant systems.

Figure 5-8 shows that the most stable slurries, labeled SDS+T20 and SDS+T80, have a mean particle size near the primary particle size in these dispersions of near 0.5 µm. The other dispersions are all unstable, although varying degrees of instability are shown in the settling data. The corresponding particle size data shows that, although some of these slurries have not settled significantly within the 1 hour time frame shown, they all have mean particle sizes > 1 µm.
More verification of the particle size correlation with dispersion stability is shown in Figure 5-9. This figure shows the mean particle size from dynamic light scattering of the copper CMP slurries investigated in Chapter 3. The slurries contain 10 wt. % AKP-50 alumina at pH 6 with 0.1 M KIO₃, 0.01 M KI and 0.01 M EDTA. The stabilizing agents are SDS mixed with the nonionic surfactants indicated at a 1:1 molar ratio and 50 mM total concentration. These dispersions show a very distinct stable – unstable behavior transition, and the stability is indicated above each point. Figure 5-9 shows once again decisively that the stable dispersions correspond to a mean particle size near the primary particle size. The unstable slurries, on the other hand, all show a mean
particle size of more than 2 µm. The overall size of particles is controlled by the molecular structure of surfactants used to stabilize the slurries.

5.7 Implications for Metal CMP Applications

As discussed in Chapter 1, sub-micron particle slurries for metal (e.g. copper, tungsten) chemical mechanical polishing (CMP) often have problems with agglomeration of slurry particles which has been linked to increased defects in polished wafers [Steigerwald et al., 1996]. Agglomeration of slurry particles occurs because of the large amount of ions added into metal CMP slurries to bring about the chemical aspect of the polishing. However, these ions lead to shielding of the surface charges on particles and hence cause agglomeration of primary particles. The destabilization of these slurries has been verified in this study for a typical metal CMP slurry (Figure 5-4).

The particle size of the surfactant-stabilized slurries has been measured using dynamic light scattering. It has been shown than the particle size in stable slurries is close to the initial size of the particles prior to agglomeration. This suggests that by adding stabilizing agent (e.g. mixed surfactants SDS and Tween 80) to metal CMP slurries, the number of defects on polished wafers due to agglomerated particles can be kept to a minimum. The next chapter will examine the effect of dispersion stability on CMP polishing performance, in order to determine if the effect of particle size on dispersion stability measured in this chapter has any real effect on polishing under high pressure and high shear conditions.
CHAPTER 6
A CORRELATION OF DISPERSION STABILITY TO POLISHING PERFORMANCE
OF CMP SLURRIES

6.1 Focus of the Correlation of Dispersion Stability with Polishing Performance

The final piece of information that is needed to complete this investigation is the effect of the dispersion stability on polishing performance of slurries for CMP. In Chapter 5, the particle size of the dispersions has been shown to be smaller and near that of the primary particles in dispersions stabilized by mixed surfactant systems. The aim of the present chapter is then to extend this work to a direct investigation into the effects on polishing of wafers.

As discussed previously, the number of published investigations into stabilizing dispersions for application in CMP has been rather small. In one investigation, Luo et al. [1996] has found that copper CMP slurries containing Fe(NO$_3$)$_3$ and benzotriazole (BTA) as inhibitor can be stabilized using poly(ethylene glycol) (MW=1,000,000). The settling rate is reported as the stability parameter, and adsorption isotherms of BTA on alumina particles at different pH’s are reported. The polishing rate and selectivity of Cu to SiO$_2$ polishing has also been investigated with these systems. However, the study only reports that the polishing rate varies from 150 to 1500 nm/min without details of any correlation. The present investigation has already presented the stabilization factors and mechanism in much greater detail, and in the present chapter the details of the correlation with stability will be considered in detail.

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A study more relevant to the present chapter has been conducted using SiO$_2$ CMP by Nojo et al. [1996]. However, the focus of this study is related to surfactant addition to enhance polishing performance without regard to dispersion stability, since this is not a factor in this slurry composed of CeO$_2$ particles. By adding anionic polymer as surfactant in the 2.2 – 4.5 wt. % range, it is shown using patterned wafers that dishing is reduced significantly. The slurry with surfactant decreases the polish rate gradually during planarization, providing a self-stopping mechanism which reduces overpolish and dishing. A model is proposed which shows that the surfactant forms a protective layer on SiO$_2$ which introduces a threshold value in down force which must be exceeded in order to polish according to Preston’s equation. Polish rate is shown to be much lower for blanket wafers using the slurry with surfactant.

Finally, Grumbine et al. [1998] has found that a commercial slurry, SEMISPHERE W2000 made by Cabot Corporation, has a higher colloidal stability than a control slurry made with alumina particles and ferric nitrate as oxidizing agent. Settling experiments have been carried out in this study, but only on the two slurries mentioned above. The Cabot slurry, however, provides much higher surface quality, as measured by AFM, higher polish rate, higher selectivity to SiO$_2$ polishing, and lower particulate contamination than the control Fe(NO$_3$)$_3$ slurry.

The present investigation intends to extend the results of these previous investigations. The use of low molecular weight surfactants as stabilizing agents in this investigation as opposed to polymers may significantly alter the effects of surfactant addition on polishing performance. In this case, the effects may be due to particle size changes in addition to particle morphology changes due to the adsorbed layer. Also, if a
protective layer is formed by surfactant adsorption on particles, this layer will be much smaller with addition of surfactant instead of high molecular weight polymer. This investigation will also determine the effect of surfactant addition on surface quality through direct measurement of surface morphology after polishing. A detailed study attempting to verify the effects of an adsorbed protective layer on CMP has not been conducted to date. Finally, this study includes a section devoted to the particulate contamination of wafers after CMP, which is a major concern in the post-CMP cleaning industry. The effects of addition of either stabilizing surfactants or surfactants which do not contribute to dispersion stability will be explained.

6.2 Methods for Polishing Performance Analysis

The samples used in this study are silicon wafers with a titanium nitride (TiN) adhesion layer and a tungsten (W) layer, about 0.5 μm thick, deposited by chemical vapor deposition (CVD), obtained from Sematech, Inc. The polishing slurries have been prepared as described in Chapter 2, with 10 wt. % alumina and 0.1 M potassium ferricyanide at pH 4 used as a model W-CMP slurry. Different combinations of anionic and nonionic surfactants have been added in order to vary dispersion stability throughout the experiments. Different concentrations and ratios of surfactants were used for the SDS/Tween 80 combination in order to correlate the dispersion stability studies in Chapter 3 with polishing performance.

W-CMP has been carried out using blanket tungsten-coated silicon 1-in² wafers and a Struers Rotopol 31 polisher operating at 150 rpm (linear velocity = 275 ft/min) and a pressure of 6.5 psi. Perforated IC-1000/SUBA IV stacked pads from Rodel Inc. have
been used for the polishing process. During the polishing experiments, the slurry is stirred and circulated with a peristaltic pump with a flow rate of 0.1 L/min. Pad conditioning is performed using grid-abrade diamond pad conditioners from TBW, Inc. CMP has been performed using various ionic/nonionic surfactant mixtures polished for 25 seconds. In most cases, all tungsten is removed from these wafers within 40-50 seconds.

Polishing rate is obtained from four-probe sheet resistivity measurements used to measure the W thickness. In this technique, four parallel probes are pushed against a conductive sample and the voltage drop is determined as a current is applied across the probes. The resistance, directly related to resistivity, is calculated from the voltage drop divided by the applied current. The thickness of the sample is then directly proportional to the measured resistance of the tungsten coating. The calibration of the four-probe sheet resistivity measurements was done using the thickness values obtained on an unpolished wafer from cross-section scanning electron microscopy (SEM). The thickness is then calculated for other samples using this one known point and the direct proportionality between resistivity and thickness.

A Digital Instruments Nanoscope III atomic force microscope (AFM) has been used in tapping mode to measure the surface morphology of the sample after polishing under different conditions. A 1 \( \mu \text{m}^2 \) scan size and a 3.5 Hz scan rate has been used in all measurements. The surface quality is obtained from image analysis of the surface plots obtained. The root mean square (rms) roughness has been reported as an average roughness, while the surface damage is given by the maximum height difference over the
plot ($R_{\text{max}}$). The measurement has been repeated 5 times for each wafer and the average value of the rms roughness and $R_{\text{max}}$ has been reported.

Particulate contamination results have been obtained using dip testing. For these tests, a particle concentration of 0.1 wt. % has been used in the slurries in order to facilitate manual particle counting. The procedure is to dip 1 cm$^2$ samples into stirring slurry containing potassium ferricyanide and surfactant for 1 min. The sample is then rinsed in ultrapure water for 2 min. and dried vertically in dry N$_2$. The preparation for SEM measurement is to mount the wafers using carbon paint and apply Au-Pd coat to allow viewing of the otherwise nonconductive surface. The micrographs were obtained using an accelerating voltage of 15 kV and a magnification of 1000 X. The reported particulate contamination is then the average of ten particle counts obtained across the wafer.

6.3 Effects of Dispersion Stability on Surface Quality

The use of various ionic/nonionic surfactant mixtures which have been shown to vary dispersion stability in previous chapters allows the determination of the effect of this parameter on surface quality or planarization. As discussed, AFM measurements have been made on polished tungsten wafers to determine the surface quality by rms surface roughness and $R_{\text{max}}$ calculations. Examples of surface morphology plots obtained for a) an as deposited W wafer, b) a wafer polished with slurry containing no surfactant, and c) a wafer polished with slurry containing 50 mM SDS/Tween 80 mixture are given in Figure 6-1. From these plots, it is evident that the polishing significantly reduces roughness when the unpolished wafer is compared to either of the polished wafers. Furthermore, the wafer polished with slurry containing 50 mM SDS/Tween 80 appears to
be less rough than the wafer polished with slurry containing no surfactant. The unpolished wafer has an RMS surface roughness of 21.3 nm while that of the polished wafers is 3.1 and 6.6 nm for the slurry with and without surfactant, respectively, indicating great improvement due to polishing with surfactant.

![AFM surface plots](image)

Figure 6-1. AFM surface plots obtained for a) as deposited (unpolished) tungsten wafer; and wafers polished with slurry containing b) no surfactant and c) 50 mM SDS/Tween 80 surfactant mixture. Scan size = 1 µm.

For a more quantitative investigation into this phenomenon, the results of rms surface roughness values have been correlated with dispersion stability in Figure 6-2 for slurries with a number of different ionic/nonionic surfactant mixtures added. In this
In this figure, all four combinations of ionic/nonionic surfactant investigated are stable, as shown by the stability results. This figure shows clearly that the wafers polished with stable slurries have a lower rms surface roughness value than the wafers polished with the unstable slurry. The rms roughness is reduced by a value of 30-50 % by using a stable slurry. These results may in fact be misleading in that the polishing apparatus and the model slurries tested may not be capable of reducing the roughness below the values
indicated. The increased surface quality gained by use of a stable slurry may in fact be significantly greater than what is indicated in this figure if commercial CMP facilities had been utilized. Also, these results are shown with only blanket tungsten wafers. The study by Nojo et al. [1996] discussed previously indicates that in patterned wafers, the surfactant may add the additional benefit of self-stopping and controlled dishing.

In order to determine if the surface quality improvement is affected by a change in dispersion stability, the concentration and ratio of mixtures of SDS/Tween 80 have been varied as done in Chapter 3. The rms roughness values of wafers polished with slurries containing these surfactants have been correlated with dispersion stability and are given in Figure 6-3.

Figure 6-3. Surface quality results from AFM for varying concentration and ratio of surfactants in SDS/Tween 80 mixture added to each slurry.
Figure 6-3 shows that all of the slurries with added surfactant reduce the rms surface roughness of the wafers when compared to slurry with no added surfactant. Within error, all of the slurries with surfactants give roughly the same rms surface roughness. However, the 100 mM 1:1 and 50 mM 1:4 slurries are unstable after 10 days according to the dispersion stability results. This results from the fact that in these unstable slurries, there is still considerable surfactant adsorbed onto the alumina particles, even if the surfactant does not contribute significantly to stabilization. It is proposed in a later section that this adsorbed surfactant layer changes the mechanical behavior of the particles, resulting in increased surface quality in these systems. It should be noted that the dispersions used were rather fresh and had not exhibited any significant settling. Only after 10 days, the instability shows up as shown in Figure 6-3.

### 6.4 Effects of Dispersion Stability on CMP Polishing Rate

The polishing rate has been calculated from four-probe resistivity thickness measurements on polished tungsten wafers. The polishing rate for the all of the wafers shown in Figures 6-2 and 6-3 has been calculated and is correlated with dispersion stability in Figure 6-4. Once again, the figure indicates the nonionic surfactant mixed with SDS in a 1:1 ratio, unless otherwise indicated. The Tween 80 (T80) samples also indicate total surfactant concentration (in mM) and the ratio of SDS:T80 used. Figure 6-4 shows that the use of 50 mM 1:1, 100 mM 1:1 and 50 mM 1:4 SDS/Tween 80 mixtures results in a lower polishing rate than that of the slurry with no surfactant. However, the use of 50 mM 4:1 SDS/Tween 80 mixture, SDS/Symperonic A4, SDS/Brij 52 or SDS SDS/Tween 21 mixtures results in a polishing rate approximately equal to that of the slurry with no surfactant.
Figure 6-4. Polishing rate for tungsten wafers polished with slurries containing the indicated nonionic surfactant in a mixture with SDS. Values are the average polishing rate obtained for two wafers.

This seemingly uncorrelated data actually follows expected trends if all of the factors influencing polishing rate are considered. One of these factors is the presence of the adsorbed layer of surfactant on the particles, which acts as a lubricating layer. This lubrication mechanism contributes to a lower polishing rate for the stabilized dispersions, particularly for those which have long polymer chains extending into solution, increasing the apparent lubrication mechanism. The other factor which influences the polishing rate, however, contributes to a higher polishing rate for the use of stabilized dispersions. In a rather conclusive fashion, Bielmann et al. [1999a] has found that for alumina particles of
similar phase and shape with size varying from 0.1 to 10 μm, the W polishing rate increases for the same loading with decreasing particle size. This result suggests that the W polishing mechanism may be related to the contact surface area between the particles and polished surface. The model which is used to describe the polishing is based on the contact area per particle ($A_c$):

$$A_c = 2 \cdot \delta \cdot \left(\frac{\Phi}{2}\right) \cdot \ddot{a}$$

(6.2)

where $\Phi$ = particle size and $\delta$ = penetration depth. The total contact area $A$ is then calculated from $A = \# \text{ particles} \ \exists \ A_c = C_o \ \exists \ \Phi^{-2} \ \exists A_c$, where $C_o$ is concentration, as

$$A \propto C_o^{1/3} \cdot \Phi^{-1/3}$$

(6.3)

which implies decreasing polishing rate with increasing particle size [Bielmann et al., 1999a].

These opposing forces correlate all of the data in Figure 6-4. The 50 mM 1:1 SDS/Tween 80 mixture has an $E_{20}$ ethoxylated chain extending into solution, which reduces the polish rate according to the lubrication mechanism. However, the dispersion stability is high which indicates a low particle size, and hence a higher removal rate than the 100 mM 1:1 SDS/Tween 80 mixture, which has a similar degree of lubrication. The 50 mM 1:4 SDS/Tween 80 mixture has a lower removal rate because of less SDS in the mixture for which the Tween 80 can anchor to the surface, hence less lubrication. Likewise for the 50 mM 4:1 SDS/Tween 80 mixture, which is more stable, yielding a higher removal rate, and has less Tween 80 to anchor to the surface. Finally, the
mixtures of SDS/Symperonic A4, SDS/Brij 52 and SDS/Tween 21 all produce stable dispersions, resulting in a higher removal rate. However, unlike Tween 80, these nonionic surfactants all have a degree of ethoxylation of less than 5, so the lubrication mechanism is not as dominant. This allows for a removal rate equal to or greater than that of the slurry with no surfactant. These results suggest that due to the smaller particle size in dispersions stabilized by mixed surfactant systems, the polishing rate of tungsten can be higher than that of slurry with no surfactant. This fact is true even though the surfactant provides a lubricating layer around the particles which contributes to a decreased polishing rate.

![Figure 6-5. Evidence of lubrication mechanism from polishing results of tungsten using slurry with and without SDS/Tween 80 mixture.](image)

For further verification of the lubrication mechanism, a direct comparison has been made between polishing slurries with and without surfactant as a function of
polishing time, where the surfactant is a 1:1 mixture of SDS/Tween 80, which is shown in Figure 6-4 to have a reduced polishing rate. For this investigation published by Bielmann et al. [1999b], the polishing rate is reduced overall by the use of 5 wt. % particles, and the particles are Leco 50 nm γ-alumina particles described in Chapter 5. The oxidizing agent and slurry pH is the same as used in Figure 6-4. The removed thickness of W as a function of polishing time is shown in Figure 6-5. This figure shows a linear variation in removed thickness as a function of time, with a reduction in polishing rate of about 30\% by the use of surfactant in the polishing slurry.

6.5 Lubrication Mechanism of Adsorbed Organic Layer

In the two sections above, the results have been explained as being at least in part due to the effect of a lubricating layer of adsorbed surfactant molecules around the particles. This type of mechanism has also been proposed by Nojo et al. [1996] at the beginning of this chapter for SiO$_2$ polishing. In that investigation, the use of a polymer molecule clearly showed the presence of a lubricating layer as a significant decrease in polishing rate of SiO$_2$ with increasing polymer concentration. Since dispersion stability is not an issue in that investigation, the effects are expected to be solely due to a lubrication mechanism. In the present investigation, the results of polishing rate with different ionic/nonionic surfactant mixtures as stabilizing agents have been explained as a combination of the effect of a lubrication mechanism and the effect of varying dispersion stability and hence particle size.

The effect of a lubricating layer of surfactant molecules around the particles is illustrated in Figure 6-5. This figure illustrates the difference in depth of cut (δ) produced
by abrasive particles with and without surfactant. The particles without lubricating surfactant are effectively harder and produce a greater depth of cut than the particles with adsorbed surfactant. This effect significantly changes the planarization capability of the polishing slurry, as shown in the results in Figures 6-2 and 6-3. As illustrated in these figures, even adsorbed surfactants which do not provide a strong enough repulsive barrier to enhance dispersion stability can enhance planarization via the lubrication effect.

Figure 6-6. Illustration of the lubrication mechanism of adsorbed surfactant and its effect on depth of cut (δ) and overall polishing rate.

6.6 Effect of Adsorbed Surfactant and Dispersion Stability on Particulate Contamination of Polished Wafers for Post-CMP Cleaning Applications

6.6.1 Rationale and Methodology

One of the major issues in the CMP industry is the removal of all contaminants introduced onto the wafer during the harsh polishing process. A small number of residual
particles can cause short-circuiting in the final integrated circuits, thereby reducing product yield. Particle removal from substrate surfaces is dependent upon the adhesion forces between the particles and the surface. One important consideration for CMP industries is that small particles, particularly those smaller than about 10 \( \mu \text{m} \), are more difficult to remove than larger ones because attractive forces are typically dependent on particle radius, whereas removal forces are usually dependent on the radius squared. Thus, as particle size decreases, the decay in the removal force is much more rapid than the decay in the attractive force. Many technologies are currently applied to attempt to combat the problem of particulate contamination in post-CMP cleaning, including megasonic cleaning using acoustic streaming [Busnaina et al., 1998], double-sided brush scrubbing and spin-rinse drying [Zhang et al., 1998b], along with a variety of strong cleaning solution [Wang et al., 1998a].

The presence of surfactant molecules that can present steric barriers to particle approach, even under high ionic strength conditions, may be able to significantly reduce particle adhesion to surfaces. Surfactants are already utilized in many post-CMP cleaning formulations because of their added benefit [Blackwell, 1994]. However, few studies have been published which attempt to portray the benefits of surfactant use in post-CMP cleaning. One such study has been published by Free and Shah [1998b], in which the use of cationic surfactants in W-CMP slurries has been found to decrease particulate contamination. The study utilizes Fe(NO\(_3\))\(_3\) as oxidizing agent and looks at residual particles on polished wafers using optical microscopy and rather large particles (1 \( \mu \text{m} \)). A subsequent study [Free and Shah, 1998a] explains that the effectiveness of the surfactants in reducing particulate contamination is related to their ability to adsorb
on the substrate surface. This theory is verified with contact angle measurements and spectroscopic data, particularly for cetyl pyridinium ions, which are shown to be highly effective on tungsten wafers.

The present study is modeled after this investigation, but is more fine-tuned to CMP applications and the dispersion stability aspects presented in previous chapters. The wafers in this study are dipped in stirred polishing slurry for a period of 1 minute to allow particle adsorption to occur. They are then rinsed in stirring ultrapure water for a period of 2 minutes to remove any loose particle contaminants and leave only those which are adsorbed to the surface. The polishing slurries are 10 wt. % AKP-50 alumina with 0.1 M potassium ferricyanide oxidizing agent to correlate with the dispersion stability studies in Chapters 2 and 3. The higher pH of the present slurry (pH 4) allows the use of SDS in polishing slurries, while that of the Fe(NO₃)₃ investigation (pH < 2) causes SDS to be ineffective. As described in a previous section, the dried wafers have been viewed by SEM and particle counts obtained.

6.6.2 Correlation of Dispersion Stability with Particulate Contamination

An example of SEM micrographs which have been utilized for this investigation are given in Figure 6-7. This figure compares particulate contamination pictures of wafers dipped in slurries with and without surfactants, including 10 mM SDS/Brij 52, 50 mM SDS/Symperonic A4 and 10 mM Symperonic A4 only (no SDS). The SEM micrographs are taken at 1000 X magnification with 15 kV accelerating voltage. This figure shows the type of pictures obtained, from which the alumina particles are clearly present as white dots on the dark background. From this figure, it is evident that a
significant reduction in particulate contamination can be achieved through the use of surfactant additives.

Figure 6-7. SEM micrographs of W wafers dipped in 0.1 wt. % AKP-50 alumina slurries with 0.1 M potassium ferricyanide, containing a) no surfactant; b) 10 mM SDS/Brij 52 mixture; c) 50 mM SDS/Symperonic A4 mixture; and d) 10 mM Symperonic A4 only.

A more detailed investigation of particulate contamination has been performed, and the results of particulate contamination experiments with various ionic/nonionic surfactant mixtures added to vary dispersion stability are given in Figure 6-8. As can be seen in this figure, the dispersion with no surfactant has a significant degree of surface contamination. However, most of the surfactant containing slurries significantly reduce
this contamination, with the exception of 10 mM SDS/Symperonic A4 mixture. The remainder of the mixtures result in much lower contamination, although little correlation with surfactant concentration is evident except possibly with the SDS/Tween 21 mixture.

The results in Figure 6-8 do not correlate directly with the dispersion stability studies in Chapter 3 with 0.1 M potassium ferricyanide solution because of the lower concentration of particles (0.1 wt. %) used to facilitate viewing by SEM. The reduction in particle loading corresponds to a significant reduction in surfactant concentration needed for stabilization. This explains the reason that the 1 mM concentrations result in reduced contamination. The enhanced contamination of the 10 mM SDS/Symperonic A4 mixture is probably merely an artifact of the counting or experimentation and is not a significant result.

![Figure 6-8](image_url)

Figure 6-8. Particulate contamination of W wafers dipped in dispersions containing 1:1 mixtures of SDS and indicated nonionic surfactant, viewed by SEM.
6.6.3 Effect of Single Surfactants on Particulate Contamination

Single surfactants such as 10 mM Symperonic A4 shown in Figure 6-7 are also expected to have some effect on particulate contamination. In this case, the surfactant is not expected to adsorb on the alumina particles, so the reduced particulate contamination is due to surfactant adsorption on the wafer. The Hamaker constant of the tungsten wafer is about $20 \times 10^{-20}$ J [Visser, 1972], while that of the alumina particles is only $6.3 \times 10^{-20}$ [Israelachvili, 1992], so the driving force for adsorption of surfactant on the wafer due to van der Waals forces is much greater than on the particles. Ionic surfactants, particularly cationic surfactants, are expected to adsorb significantly on tungsten due to electrostatic interactions. Of course, anionic surfactants are expected to adsorb strongly on the positively charged alumina particles, which may also contribute to decreased particulate contamination.

The effect of addition of cationic, anionic and nonionic surfactants to 10 wt. % AKP-50 slurries containing 0.1 M potassium ferricyanide on particulate contamination is given in Figure 6-9. All surfactants have been investigated at concentrations of both 1 and 10 mM. As can be seen in the figure, all surfactants significantly reduce particulate contamination, similarly to mixed surfactant systems. Additionally, all surfactants show reduced contamination at 10 mM concentration than at 1 mM concentration. As explained before, the cationic and nonionic surfactants are expected to adsorb on the tungsten wafer, while the anionic surfactants are expected to adsorb on the alumina particles, but according to Figure 6-9, both of these mechanisms are equally effective at reducing particulate contamination. These results could lead to easier removal of the remaining particles by conventional post-CMP methods.
It is apparent from the results in this chapter that the addition of surfactant to CMP slurries can in fact significantly enhance the polishing performance of the slurries. The lubrication mechanism caused by surfactant adsorption seems to be most influential in improving planarization of tungsten. The dispersion stability does not correlate with the surface quality results obtained. However, the polishing rate results show correlation with dispersion stability due to the lower particle size in stable dispersions, as shown in Chapter 5. The polishing rate is likewise affected by the lubrication mechanism, which is more predominant in slurries containing Tween 80, an E<sub>20</sub> surfactant, than in slurries containing E<sub>2</sub> or E<sub>4</sub> surfactants. Finally, the particulate contamination results show that surfactant can adsorb on both the particles and the polishing wafer, which is the reason
that all surfactants investigated, whether alone or in mixed surfactant systems, show improved particulate contamination results over slurries with no surfactant added.
CHAPTER 7
SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Dispersion Stability in Severe Environments

Dispersions appear in many industries, including paints and pigments, pulp and paper processing, electronics, biotechnology, oil refining and general waste industries. Severe environments are encountered in many of these industries are often responsible for inconsistencies and failure in processes. It has been shown that one type of severe environment, the chemically complex and hazardous type, can contribute to agglomeration of particles in dispersions due to charge screening. The implications of the agglomeration have been discussed, and include handling issues, process reproducibility, and ultimately process failure.

The application of dispersion science to the chemical mechanical polishing (CMP) industry has been discussed. CMP is the preferred method for achieving global planarization in multilevel integrated circuits manufacturing. The process consists of rotating the substrate against a polishing pad while slurry flows in the gap. In CMP of metal surfaces, such as tungsten, copper and aluminum, oxidizing agents and other chemical additives are necessary in the polishing slurries in order to enhance the performance of the abrasive particles. These additives often contribute to particle agglomeration, which can in turn lead to defects.
In order to stabilize these and other dispersions, the two classes of molecules commonly used as stabilizing agents are surfactants and polymers. Surfactants, which are amphiphilic molecules, may act as either electrostatic or steric stabilizing agents, depending on the charge of the hydrophilic head group, while polymers act solely as steric stabilizing agents unless they are of the polyelectrolyte variety. While electrostatic stabilization is only expected to be dominant in low ionic strength environments, steric stabilization should be effective regardless of the ionic strength. Steric stabilization has been described as adsorption of molecules which prevent the particles from approaching to close enough distances to allow van der Waals attractive forces to result in agglomeration.

7.2 Stabilization of High Ionic Strength Dispersions Using the Synergistic Behavior of a Mixed Surfactant System

The use of mixed surfactant systems as stabilizing agents for dispersion in severe environments has been investigated. It has been shown that mixed systems of ionic and nonionic surfactants often show synergistic adsorption of a weakly adsorbing component due to hydrocarbon chain interactions which accompany surfactant adsorption. The addition of ionic or ethoxylated nonionic surfactants to model high ionic strength slurries applicable to metal CMP has been shown to have very little effect on slurry stabilization. This is because the ionic surfactants are ineffective electrostatic stabilizing agents under high ionic strength conditions, and ethoxylated nonionic surfactants do not adsorb significantly to the alumina surfaces investigated. The adsorption of ionic surfactants has been verified by surface tension measurements, which show a shift to higher values in
dispersion supernatants due to adsorption. By the same method, nonionic surfactant adsorption has been found to be negligible on alumina surfaces.

The addition of ionic and nonionic surfactant mixtures to high ionic strength slurries has been shown to be capable of slurry stabilization for model tungsten CMP slurries consisting of 10 wt. % AKP-50 (0.2 μm) alumina particles with 0.1 M potassium ferricyanide oxidizing agent at pH 4. For this system, mixtures of anionic and nonionic surfactant have been shown to impart stability for a period of at least 7 days. However, cationic and nonionic surfactant mixtures and cationic and anionic surfactant mixtures have been shown to not be capable of the same degree of stabilization. The stabilization observed by anionic and nonionic surfactant mixtures has been explained by a two step mechanism. The ionic surfactant significantly adsorbs on the alumina particles due to electrostatic interactions, which causes synergistic adsorption of nonionic surfactant due to hydrocarbon chain interactions with the film of ionic surfactant. This mixed bilayer then brings about steric stabilization of the slurry.

The factors influencing this stabilization mechanism have been discussed. The strong adsorption of ionic surfactant is extremely important, as verified by the stabilization of alumina dispersions by mixtures containing anionic surfactant but not cationic surfactant. The nonionic surfactant must then be capable of adsorption via hydrocarbon chain interactions with the ionic surfactant. This adsorption is governed by two factors: the ability of the nonionic surfactant to partition out of the aqueous solution, which will favor more hydrophobic nonionic surfactants, and the strength of the interactions between adjacent adsorbed molecules, which will be strongest if the chain lengths are equal. Finally, the nonionic surfactant must conform to allow steric
stabilization, which is not generally a major problem with the use of ethoxylated nonionic surfactants in aqueous solution.

7.3 Molecular Factors that Optimize Dispersion Stability Using Mixed Surfactant Systems as Stabilizers for Dispersions in Severe Environments

The molecular factors which influence this stabilization mechanism have been considered. The type of nonionic surfactant has been shown to have a major effect on the degree of stabilization by measuring sedimentation of dispersions containing numerous nonionic surfactants mixed with anionic surfactant. The results show a trend of increasing dispersion stability with decreasing HLB number of nonionic surfactant. This result is explained as due to the fact that the tendency of lower HLB (hydrophobic) nonionic surfactants to partition out of the aqueous phase and onto the particle surface is much greater than that of high HLB (hydrophilic) nonionic surfactants. This same trend has been observed for a model copper CMP slurry chemistry consisting of the same particles in a solution of 0.1 M potassium iodate, 0.01 M potassium iodide and 0.01 M EDTA complexing agent. This observation verifies the robust nature of the stabilizing scheme and its applicability to numerous environments, including severe environments.

The dependence of dispersion stability on surfactant concentration has been investigated for a number of mixed surfactant systems. The results show that a range of concentrations is capable of providing maximum stabilization, although some systems do not show instability at higher concentrations. The differences are due to the solubility of some mixtures being too low to experience the instability at high concentrations. The dependence of dispersion stability on ratio of ionic to nonionic surfactant has also been investigated. For most systems, stability is high in most regions except near the pure
component endpoints. This is not true in the sodium dodecyl sulfate (SDS) / Tween 80 system, which is unstable with ratios favoring SDS. This result is due to insufficient driving force for the relatively hydrophilic nonionic surfactant to attach to the lower number of adsorption sites created by SDS adsorption. With all of these investigations, the factors influencing robust dispersion stability by using synergistic mixtures of ionic and nonionic surfactants have been explained.

7.4 Adsorption of Surfactants on Particles from Mixed Surfactant Solutions in Severe Environments

In order to verify some of the factors considered in this stabilization scheme, adsorption measurements have been undertaken for these model CMP slurries for metal surfaces. For these measurements, novel techniques have been implemented which are useful in environments containing a large salt concentration. All of the adsorption measurements have been made by measuring the residual surfactant concentration in supernatants of dispersions stabilized by mixed surfactant systems.

The total adsorption has been measured by two techniques, one of which utilizes surface tension measurements and is applicable at concentrations below CMC, and the other of which is a dye absorption method that is applicable above CMC. Both techniques characterize surfactant concentration in high ionic strength environments by measuring parameters that change reproducibly with surfactant concentration in a range of interest. The surface tension technique utilizes the measurement of surface tension as its primary variable, while the dye absorption technique utilizes the measurement of dye absorption into micelles as its primary variable. The absorption of dye into micelles
produces a peak in the visible range which changes with micelle concentration, hence yielding results through absorbance measurements.

In order to obtain adsorption measurements of individual surfactants from the mixture in some representative systems, a titration technique has been implemented which characterizes SDS concentration directly. This technique utilizes a mixed indicator solution and a chloroform phase where the color change occurs. By using this method, the color of the chloroform phase is not influenced by the color of the salt in solution. The adsorption of nonionic surfactant can then be deduced from the total adsorption measurements.

The adsorption of the SDS / Tween 80 mixture on alumina particles in the presence of 0.1 M potassium ferricyanide has been measured by these techniques in order to obtain direct comparison with stability measurements. The adsorption isotherm shows a steady increase in adsorption density throughout the range of concentrations investigated for dispersion stability. The stability results indicate a minimum concentration needed for stabilization and a maximum concentration above which instability is present. These results suggest that multilayer adsorption effects are occurring in this system. Above a critical concentration, surfactant continues to adsorb in excess of a bilayer conformation, rendering the surface of the particle hydrophobic and hence vulnerable to agglomeration. The adsorption results hence explain the instability of dispersions containing surfactant mixtures at high concentrations.

7.5 Correlation of Dispersion Stability to Particle Size Measurements

Finally, the last two chapters discuss the implications of dispersion stability on the primary application considered in this investigation, CMP of metal surfaces. The
dispersion stability is shown to correlate precisely with mean particle size of the dispersions as measured by dynamic light scattering for a number of systems, including the model tungsten CMP and model copper CMP slurries investigated previously. The particle size of the stable dispersions is shown to be in the same range as the initial size of the particles prior to agglomeration. This result suggests that the use of stabilized dispersions can lead to a reduction of defects in CMP applications. Finally, by investigating two different sizes of particles, it has been found that the amount of surfactant needed to stabilize dispersions is directly proportional to the surface area of the particles in the dispersions.

7.6 Correlation of Dispersion Stability to Polishing Performance for CMP Applications

For further correlation of dispersion stability with CMP performance, the polishing of tungsten wafers using slurries containing a number of surfactant systems has been investigated. The surface quality of the polished wafers has been found by AFM surface roughness measurements to be significantly enhanced by the presence of mixtures of surfactants in solution. However, the use of both stable and unstable dispersions with mixed surfactant additives has been found to increase surface quality. This result has been explained as due to a lubricating effect of adsorbed surfactant layers on the particle surfaces.

The polishing rate of tungsten wafers has been found to be dependent on two factors concerning the particles: the degree of lubrication imparted by surfactant layers as well as the mean particle size of the particles in the dispersions. The polishing rate of tungsten using the same slurry has been shown in another study to decrease with increasing mean particle size, while the polishing rate of tungsten is proposed here to
decrease with increasing degree of lubrication. Hence, surfactant layers will contribute to a reduced polishing rate due to the lubrication mechanism, but the layers will also contribute to an enhanced polishing rate due to the lower mean particle size obtained in these dispersions. This explanation has been verified by investigating dispersions with varying degrees of lubrication due to varying lengths of the hydrophilic EO segments on the nonionic surfactant. The data is well correlated with the proposed explanation.

Finally, the particulate contamination of tungsten wafers polished by slurries with various surfactant additives has been investigated by SEM particle counts on dipped wafers. The particulate contamination is found to decrease significantly with surfactant additives, although not correlated with dispersion stability. In fact, single surfactant additives have been found to reduce the contamination by the same degree as mixed surfactant systems. The explanation for these results is that the surfactant can reduce particulate contamination by adsorbing on either the particles or the wafer. The adsorption of single surfactants on the wafer surface is expected to be much greater than on the particle surface for cationic and nonionic surfactants, so this adsorption is responsible for the reduced contamination in these systems. The mixed surfactant systems have already been shown to adsorb significantly on the particle surfaces, and this adsorption is expected to likewise lead to reduced particulate contamination.

Overall, the use of mixed surfactant systems has been shown in this investigation to be a robust stabilizing scheme for dispersions, even in severe environments. The factors influencing the stabilizing ability of the mixtures has been examined, yielding factors to be considered in order to obtain optimal stability when using these systems. Finally, the effect of surfactant addition on CMP polishing performance has been
investigated. The use of mixed surfactant systems contribute to both a lower mean particle size and a lubricating layer around the particles, which in turn leads to an enhanced surface quality and reduced particulate contamination in wafers polished with these systems.

7.7 Recommendations for Future Research

The understanding of the both the factors that influence stabilization using mixed surfactant systems and the effect on chemical mechanical polishing (CMP) applications is not yet complete. Recommendations for further research and development in this area are given below, and these are divided into two categories: recommendations which are high priority and should be undertaken in a short time scale, and recommendations which are intended to be long-term projects that may lead to the completion of an additional thesis or dissertation.

7.7.1 High Priority Recommendations

Effect of addition of single surfactants on tungsten CMP. Although the effect of mixed surfactant systems on polishing rate and surface quality in tungsten CMP has been investigated, it has also been shown in Chapter 6 that single surfactants as well as mixed surfactants can significantly alter the degree of particulate contamination. Single surfactants can adsorb either on the alumina particles or the tungsten wafer, and hence all types of single surfactants decrease particulate contamination. It is unknown whether these surfactants will significantly alter the surface quality or polishing rate of tungsten. Adsorbed single surfactants will provide some degree of lubrication, although with the exception of nonionic surfactants, the thickness of the organic film adsorbed on either the
particles or the wafer will be much smaller than for mixed surfactant systems. Also, in
the present investigation, the lubricating layer of surfactant presumably has been
adsorbed on both the particles and the wafer. Single surfactants are only expected to
adsorb in one location, which may also change the degree of lubrication provided by
these films.

Adsorption of single surfactants in low ionic strength environments. The
dispersion stability data for single surfactants at both low and high ionic strengths in
Chapter 2 has been used to determine that ionic surfactants adsorb to alumina particles
but nonionic surfactants do not. Furthermore, surface tension measurements have been
used to verify adsorption in high ionic strength environments. However, the
measurement of adsorption in low ionic strength environments has not been undertaken.
This measurement will determine if differences exist in the adsorption density due to
enhanced charge shielding at high ionic strengths, and it will also further verify that ionic
surfactants do adsorb under these conditions, and to what extent nonionic surfactants
adsorb.

Effect of dispersion stability on copper CMP. A logical continuation of the work
presented in Chapter 6 is to extend the correlation of dispersion stability with tungsten
CMP to copper CMP using the KIO₃-based slurry investigated in Chapter 3. These
results should follow the same trends as for tungsten CMP, but the effects of a lubricating
surfactant film on particles may be significantly enhanced in copper CMP due to the
differences between copper and tungsten. As a result, the addition of mixed surfactants
to copper CMP slurries should increase the surface quality and decrease the particulate
contamination of copper wafers. The effect on polishing rate is unpredictable, since it is
unknown whether a decrease in particle size should increase or decrease the polishing rate of copper.

**Adsorption of mixed surfactant systems with varying HLB number nonionic surfactants.** The increase in dispersion stability with increasing hydrophobicity of nonionic surfactant, presented in Chapter 3, should be verified with adsorption measurements presented in Chapter 4.

**Electrochemical determination of layer thickness in mixed surfactant systems.** As explained in Chapter 2, the mixed surfactant layer adsorbed on particles may be in the form of a mixed monolayer, a full bilayer, or a bilayer in which the second layer has penetrated the first layer to some extent. Electrochemical measurements can be used to probe the layer thickness of adsorbed films via determination of electrical conductivity. The relative layer thicknesses of films of mixed surfactants layers and the component single surfactant layers establishes the degree of penetration of one layer into the other. This fundamental study can shed light on the molecular factors influencing dispersion stability.

**Redispersion of sedimented flocs at high surfactant concentration.** The force needed to redispersed the particle agglomerates (flocs) settled at high surfactant concentration will give insight into the nature (loose or hard) and packing efficiency of the flocs. Redispersion can be measured by first diluting the dispersions in equilibrium salt solution to a concentration that can be used by dynamic light scattering. The graph of mean particle size vs. sonication time can then give the relative strength of the flocs, with the measured particle size showing a rapid decrease at the sonication time needed to break the flocs.
Stabilization of unstable flocs formed at high surfactant concentration using micelle breaking agents. If the flocs are forming at high surfactant concentrations due to the formation of nonionic surfactant domains around particles which cause agglomeration, these domains can be destabilized by the addition of a micelle breaking agent. Such agents include ethanol, urea, trichloroacetate and other species that prevent the formation of aggregates in bulk solution. Likewise, these agents can be used to break the nonionic surfactant domains formed at high concentrations of surfactant and cause high dispersion stability under these conditions. The same dispersion stability methodology used in this investigation can be utilized in the proposed investigation.

Verification of nonionic surfactant domain formation at high surfactant concentration using AFM determination of the repulsive barrier. It is proposed that the nonionic surfactant domains proposed in Figure 3-11 will form only in the presence of multiple particles that can agglomerate. As a result, an AFM force-distance curve of a single particle surface is not expected to show a significant decrease in the measured repulsive barrier height at high concentrations of surfactant due to the lack of formation of these domains. This project involves the measurement of the barrier height by AFM at concentrations above and below the concentration at which instability is shown in Chapter 3.

Comparison of rigidity of film formed on alumina particles from SDS/Symeronic A4 mixture and SDS/Tween 80 mixture. The rigidity of a film around particles can be measured using force-distance curves determined by AFM. The film formed by a surfactant mixture containing highly ethoxylated nonionic surfactant should be less rigid than that formed by a mixture containing nonionic surfactant with a low
degree of ethoxylation. As a result, a comparison of the film rigidity for the SDS/Tween 80 (E\textsubscript{20}) mixture to that of the SDS/Symperonic A4 (E\textsubscript{4}) mixture should show a significant change in the repulsive barrier height measured by AFM.

**Verification of stability of various alumina dispersion using Figure 5-8 to determine surfactant concentration.** Figure 5-7 predicts that a surfactant (SDS/Tween 80 mixture) concentration of 2 x 10\textsuperscript{-5} mol/m\textsuperscript{2} will be sufficient to stabilize any alumina dispersion if the BET surface area of the particles is known. After measuring the BET surface area of 5 different types of alumina particles, the dispersion stability at surfactant concentrations of 0.5 and 2 x 10\textsuperscript{-5} mol/m\textsuperscript{2} should be measured. Also, using one type of alumina particle, the dispersion stability for 5, 10, 15, and 20 wt. \% alumina dispersions should be characterized using surfactant concentrations of 0.5 and 2 x 10\textsuperscript{-5} mol/m\textsuperscript{2}. These results will verify the robust nature of the normalized stability diagram shown in Figure 5-7 for alumina particles in 0.1 M K\textsubscript{3}Fe(CN)\textsubscript{6}.

**Mechanism behind difference in stability of dispersions made using SDS/Tween 80 mixtures in different chemical environments.** As discussed in Chapter 3, the SDS/Tween 80 mixture stabilizes dispersions made in Fe(NO\textsubscript{3})\textsubscript{3} and K\textsubscript{3}Fe(CN)\textsubscript{6} solutions and not those made in KIO\textsubscript{3} solutions. The mechanism behind this observed difference is hypothesized to be the increased salting out effect brought about by using the multivalent salts versus the monovalent salt. Since Tween 80 is a relatively hydrophilic surfactant, it requires a significant driving force via the salting out effect to drive it to the particle surfaces. The degree of salting out effect in the various chemical environments can be shown by surface tension measurements. If the above hypothesis is true, then the surface tension of K\textsubscript{3}Fe(CN)\textsubscript{6} and Fe(NO\textsubscript{3})\textsubscript{3} solutions should be lower than that of KIO\textsubscript{3} solutions.
at the same salt concentration. The surface tension measurement will give insight into the mechanism proposed.

7.7.2 Long-term Recommendations

**Correlation of dispersion stability with the characteristics of the adsorbed surfactant layer.** Techniques such as fluorescence spectroscopy [Somasundaran et al., 1986; Chandar et al., 1987] and electron spin resonance [Waterman et al., 1986; Chandar et al., 1986] have been utilized to characterize the strength of adsorbed surfactant layers on particles. These techniques measure the micropolarity, microviscosity, and surfactant aggregation number of adsorbed layers. The variation in these parameters with dispersion stability in mixed surfactant systems should give insight into the structure of the adsorbed layers on stable particles. Other techniques may also be useful in determining the orientation of each adsorbed layer, which should be correlated with dispersion stability.

**Correlation of dispersion stability with the strength of the repulsive barrier, measured by atomic force microscopy (AFM).** The strength of the repulsive barrier established on particles in mixed surfactant systems should correlate with the dispersion stability. The measurement of the repulsive barrier using AFM can give insight into the degree of steric repulsion needed to stabilize dispersions. The variation in barrier height with ionic strength of the medium should also be beneficial, since these results will include electrostatic effects at low ionic strength. Additionally, chain length compatibility effects can be studied using the repulsive barrier height measured by AFM. Chain length compatibility has been shown to have a major influence on technological processes such as foaming and emulsification [Shiao et al., 1998]. In a mixed monolayer
configuration of surfactants, the repulsive barrier strength should be maximum for equal chain lengths of ionic and nonionic surfactant. In a full bilayer configuration of surfactants, chain length compatibility effects should be less important, and the maximum barrier height measured by AFM should be observed for the maximum hydrophobicity of nonionic surfactant.

Development of a model which can predict the degree of stabilization imparted by a chosen mixed surfactant system on a chosen particle in a given environment. Experimental design software can identify the input variables that influence output parameters while keeping the number of experimental trials to a minimum. In the industrial CMP slurries considered in the present investigation, there are an enormous number of variables which can be manipulated, and these types of systems are best modeled using experimental design techniques. The ultimate goal of the dispersion stability investigations has been to provide predictive capabilities for inexperienced users. With the multitude of dispersion stability results presented in this investigation, a modest effort to confront this problem has been attempted, but there are a considerable number of variables which have not been considered here. A model for predicting dispersion stability should be developed which includes variables relating to the particles, stabilizing agents, and the chemical environment in a given system. The relevant particle variables include particle size and polydispersity, concentration and zeta potential at the given pH. The relevant stabilizing agent variables include hydrophobicity of each surfactant, charge on ionic surfactants, concentration and ratio of surfactants. Finally the relevant chemical environment variables include the Debye parameter (κ) and pH. All of these variables
should be incorporated into an experimental design to develop a robust model for dispersion stability in mixed surfactant systems.

**Influence of micellar stability ($\tau_2$) on dispersion stability.** As discussed in Chapter 1, the stability of micelles ($\tau_2$) in a surfactant solution is a parameter that can have a significant influence on various technological processes, including foaming, detergency, wetting, emulsification and solubilization capacity [Shah, 1998]. This is because the micellar stability determines not only the hydrophobicity of the micellar core, but also the flux of monomers available for creating fresh interfaces around air bubbles and oil droplets in solution. Likewise, $\tau_2$ is expected to influence the flux of monomers available for adsorption on solid particles in a dispersion. Specifically, a high value of $\tau_2$ (on the order of seconds as opposed to milliseconds) should decrease the amount of monomer available to adsorb to the particle surface, hence decreasing dispersion stability. However, it is important to note that $\tau_2$ is a kinetic parameter, and the time scales used to reach adsorption equilibrium in the present investigation and in actual industrial applications of surfactants as dispersing agents, are normally on the order of hours or days. It is therefore unknown whether $\tau_2$ will in fact have any influence on the equilibrium adsorption density of monomers on solid particles, and this question is a subject of the proposed investigation.

There is another interesting caveat to the influence of micellar stability on dispersion stability. A number of recent investigations have identified adsorbed surfactant aggregates, including hemimicelles, full micelles and cylindrical micelles, on particles using imaging by AFM [Ducker and Wanless, 1999; Wall and Zukoski, 1999]. In the present investigation, if full micelles or hemimicelles from surfactant mixtures are
adsorbing on the alumina particles instead of a bilayer of monomers, the influence of $\tau_2$ on dispersion stability would in fact be the opposite of the case of monomer adsorption. Assuming that adsorbed micellar stability follows the same trend as bulk micellar stability, a high value of $\tau_2$ in this case would cause the adsorbed species to be maximum in strength, and would hence cause enhanced dispersion stability. As can be seen from this discussion, the correlation of dispersion stability with micellar stability ($\tau_2$) should shed light on the mechanism of surfactant adsorption in mixed surfactant systems.

**Comparison of CMP defectivity using TEM pictures.** Using TEM, carbon replicas of surfaces polished using CMP can be viewed and analyzed for both depth and concentration of scratches. This analysis will help to verify that a lubrication mechanism is responsible for the decreased surface roughness and polishing rate when the particles are coated with an organic layer. The analysis should be carried out with mixed surfactant films, single surfactant films, and polymer films placed on particles in order to fully understand the lubrication mechanism.
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BIOGRAPHICAL SKETCH

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