

Stabilization of High Ionic Strength Slurries Using the Synergistic Effects of a Mixed Surfactant System

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The stability of colloidal slurries is an important parameter in many industries due to problems that can arise as a result of particle settling. 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 slurries, 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 (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. For the CMP slurries investigated, the synergistic effect has been shown to be maximum for combinations of sodium dodecyl sulfate anionic surfactant and a variety of polymeric nonionic surfactants. 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. This brings about the steric stabilization of the slurry. © 2000 Academic Press

Key Words: dispersions; stabilizing agents; surfactant mixtures; chemical mechanical polishing (CMP).

INTRODUCTION

Slurry stability 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 redispersed 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 in which particle size is crucial to the process, the product 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 settling.

One example of a process in which particle size is crucial to slurry performance is the chemical mechanical polishing (CMP) industry. In the microelectronics industry, the goal has historically 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 chemical vapor deposited 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. CMP is a historically ancient technology, but there are significant differences in the present use of CMP in silicon integrated circuits manufacturing. Not only are the layers being removed by CMP very thin (usually less than 0.5 μm), but precise control of the remaining thickness, usually to within 0.01–0.05 μm , is also necessary while maintaining the integrity of the underlying structures (1).

Defects in the wafers can appear during the CMP process due to the formation of scratches, which have been determined to be caused by large particles contacting the wafer during polishing. However, the particles used in CMP slurries usually have a mean particle size of less than 0.5 μm (2), 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.

The polishing slurry provides the means by which both chemical and mechanical action is used to planarize the wafer surface. Mechanical action is accomplished by the use of abrasive particles in the slurry. The type, particle size, and concentration of abrasive material as well as slurry pH are all variables that affect the performance of the abrasive particles. The slurry achieves chemical action either by incorporating oxidizing agents or by incorporating additives that improve film dissolution, depending on the film being acted upon (3). The chemical component of the slurry, which acts isotropically on the wafer surface, is necessary because it enhances the mechanical action of the slurry. The mechanical component of the slurry must also be present to preferentially abrade material at the asperities, or high points

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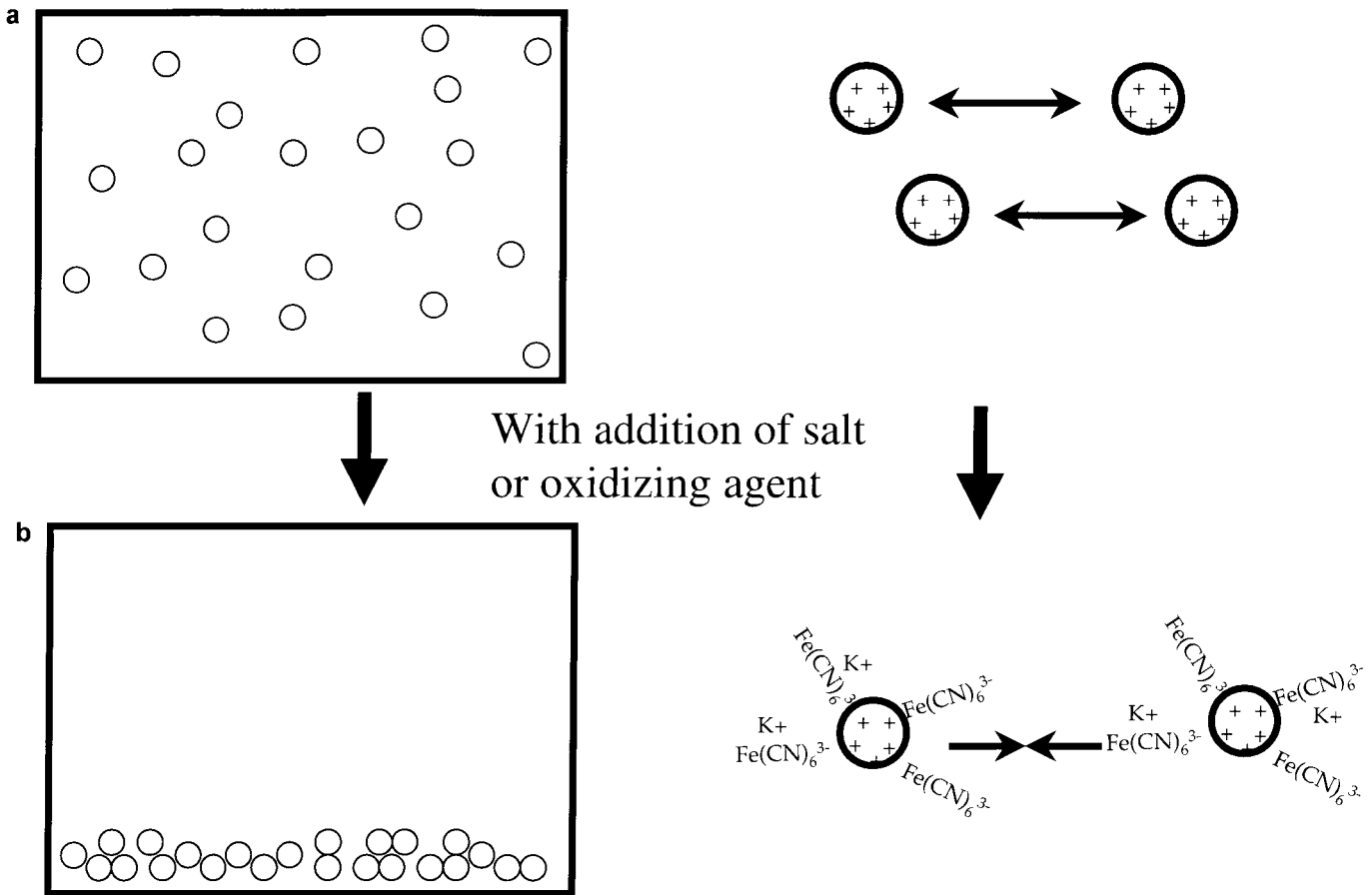


FIG. 1. Illustration of the effect of salt (or oxidizing agent) addition on the stability of dispersions of charged alumina particles: (a) particles in water at pH 4, and (b) with addition of oxidizing agent.

on the surface, thus providing the driving force for planarization. It is both the chemical and mechanical action achieved by the slurry that provides global planarization of the wafer surface (3).

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. The addition of ions to a particle slurry will decrease the surface charge on the particles by shielding the charges. This decreased electrostatic repulsion, if significant enough, can bring about agglomeration of the particles, as illustrated in Fig. 1 for the high ionic strength slurries used in metal CMP. This figure shows alumina particles, which usually have a substantial positive charge at the low pHs used in metal CMP. However, the addition of 0.1 M potassium ferricyanide, a common oxidizing agent, shields the positive charge with the multivalent ferricyanide anions, thus causing agglomeration of particles due to van der Waals forces. Figure 2 shows the settling behavior of slurries with and without addition of potassium ferricyanide oxidizing agent. The slurry without oxidizer, on the left side of the figure, is clearly stable since the white particles are dispersed throughout the cylinder. The slurry containing oxidizer, on the right side of the figure, is

clearly unstable with all particles having settled in the 24 h after which time this picture was taken.

The present work investigates the stabilization of high ionic strength slurries such as the CMP slurries illustrated in Figs. 1 and 2. The stabilizing agents investigated are surfactants, which are known to stabilize many slurries by causing either electrostatic or steric repulsion among slurry particles (4).

MATERIALS AND METHODS

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 [$\text{K}_3\text{Fe(CN)}_6$] and iron(III) nitrate [$\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were investigated as oxidizing agents, and they were obtained from Fisher, Inc. Surfactants used were from various suppliers. Sodium dodecyl sulfate (SDS, MW = 288.38), cetyl pyridinium chloride (CPC, MW = 340.0), sodium salt of capric acid (MW = 194.2), and sodium salt of lauric acid (MW = 222.3) were obtained from Sigma Chemical Co. Hexadecyltrimethylammonium bromide (C_{16}TAB , MW = 364.46) was obtained from Fisher, Inc.

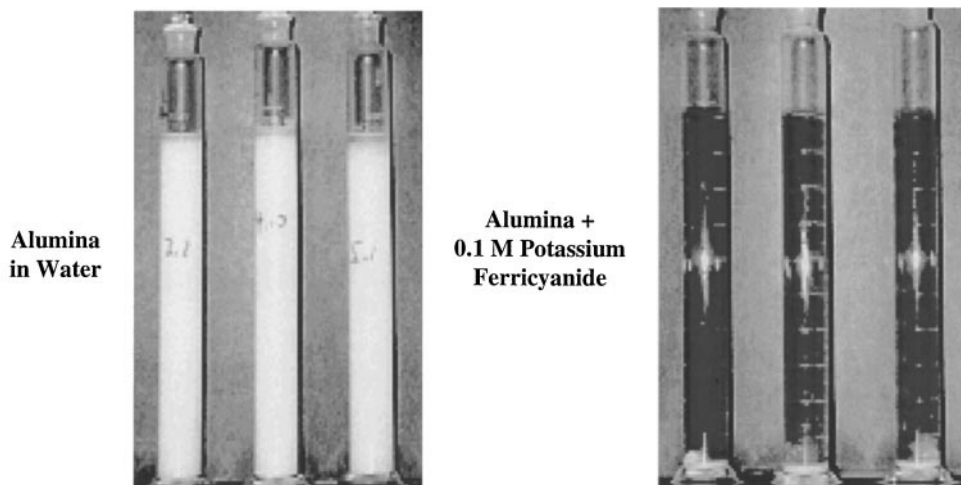


FIG. 2. Settling of alumina particles after addition of oxidizer, potassium ferricyanide. Slurries are 1 wt% AKP-50 (100–300 nm) alumina particles at pH 3, 4, and 5 (left to right), allowed to settle for 24 h.

Tween 80 (MW = 1309.69) and dodecyltrimethylammonium bromide (C_{12} TAB, MW = 308.34) were obtained from Acros, Inc. Triton X-100 (MW = 646) was obtained from Aldrich, Inc. Tween 20, Tween 40, and Tween 60 (MW = 1228, 1284, and 1311.7, respectively) and Symperonic A4, A7, A11, and A20 (MW = 390, 522, 698, and 1094, respectively) were obtained from ICI Surfactants. Hexyl sodium sulfate (MW = 204.22), decyl sodium sulfate (MW = 260.32), and hexadecyl sodium sulfate (MW = 344.49) were obtained from Eastman Kodak Co. Ultrapure water was obtained from a Milli-Q Gradient A10 filtration system supplied by Millipore Corp.

Slurries were prepared by first dissolving surfactants (cationic, anionic, nonionic, or mixtures) in water. Alumina particles in a concentration of 10 wt% were then added into the slurries and the pH was adjusted to a value lower than 4. 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 be most successful commercially when used in this pH range (5).

Slurry stability was characterized by sedimentation tests. Sedimentation tests were used to obtain settling comparisons and were performed by thoroughly dispersing the slurries prior to pouring them in graduated cylinders. The level of clear liquid above dispersed slurry was monitored for a total of 70 mL of slurry as a function of time to obtain settling data. Two cylinders were prepared of each slurry and settling data reported are the average values.

Static surface tension measurements were made using a Rosano surface tensiometer made by Biolar Corp. Surface tension measurements were made in air using the Wilhelmy plate method (6) with a 10×20 -mm platinum plate, allowed to equilibrate in solution for 60 s before a measurement was taken. Slurries were centrifuged to obtain supernatants for surface tension measurements using a Sorvall RC-5B refrigerated superspeed centrifuge operating at 10,000 rpm.

RESULTS

Effects of Addition of Ionic or Nonionic Surfactants on Slurry Stability

The effect of addition of either ionic or nonionic surfactants to high ionic strength slurries is illustrated in Fig. 3. The shielding of surface charges on the particles due to the high ionic strength allows the adsorption of highly surface active cationic or anionic surfactants. These surfactants may form a bilayer due to hydrophobic chain interactions, but this depends on the surfactant. Common ionic surfactants that have no polymeric component typically 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 particles will agglomerate and settle. Most nonionic surfactants are polymeric in nature and hence stabilize slurries by adsorbing on the particles and causing steric repulsion. This stabilization mechanism should be significant, even in high ionic strength slurries. However, most nonionic surfactants do not adsorb significantly on alumina surfaces under high ionic strength conditions, and hence would not be expected to stabilize these slurries.

These theories are verified using sedimentation tests in Figs. 4 and 5. In Fig. 4, the addition of surfactant to a low ionic strength slurry containing 0.001 M potassium ferricyanide ($K_3Fe(CN)_6$) is investigated. The slurry with no surfactant verifies that these slurries are unstable, even with a low amount of salt added. This result is expected from the Schultze–Hardy rule since the trivalent anion is the counterion to the positively charged alumina particles. 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.

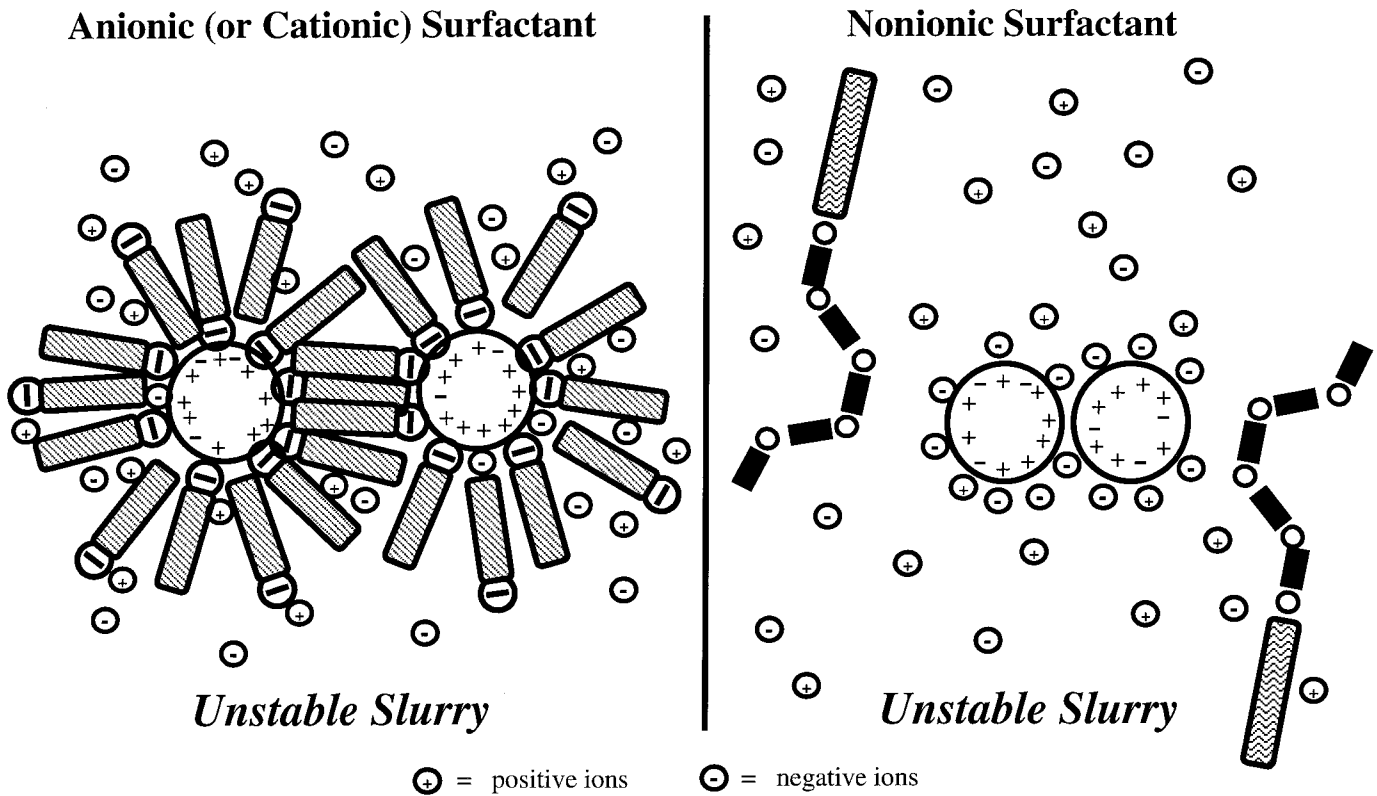


FIG. 3. Effects of ionic or nonionic surfactant addition on the stability of *high ionic strength* slurries.

These results suggest that both cationic and anionic surfactants can adsorb on these particles. The stabilization of these slurries is expected to be due to a combination of factors. At this low ionic strength, some degree of electrostatic repulsion is present between surfactant bilayers on adjacent particles, adding a contribution to a repulsive barrier to agglomeration. The adsorbed layer of ionic surfactant also adds, to some degree, a steric component to a repulsive barrier. The adsorbed layer of surfactant

will assist in keeping the particles at a greater separation distance, which in turn decreases attractive forces between particles. A combination of both the electrostatic and steric components to stabilization are responsible for stabilizing the slurries in this case. The addition of nonionic surfactant (Triton X-100) does not stabilize the slurry under these conditions. Other nonionic surfactants investigated, including Tween 80, Tween 20, and Symperonic A7, show similar results. These results show

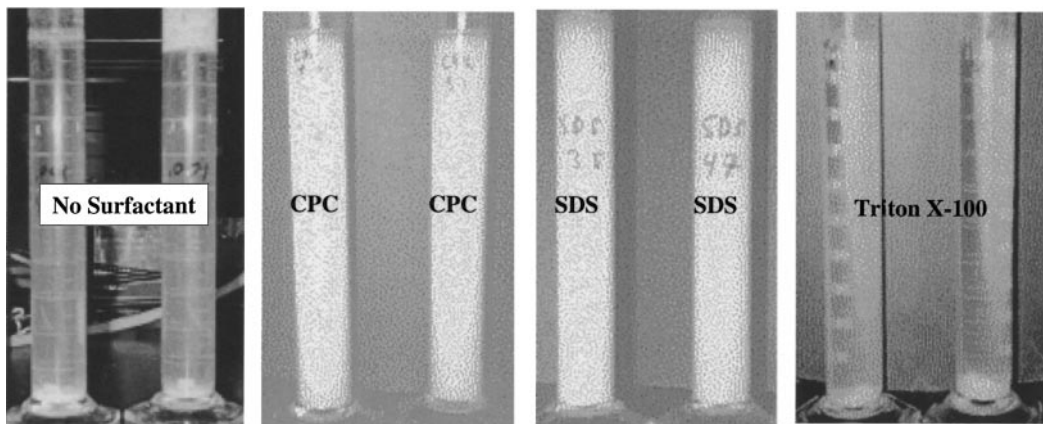


FIG. 4. Effects of ionic or nonionic surfactant addition on a *low ionic strength* slurry containing 0.001 M potassium ferricyanide oxidizing agent. The slurries are 1 wt% AKP-50 alumina at pH 4 with 10 mM surfactant added. The photographs were taken after 24 h of settling.

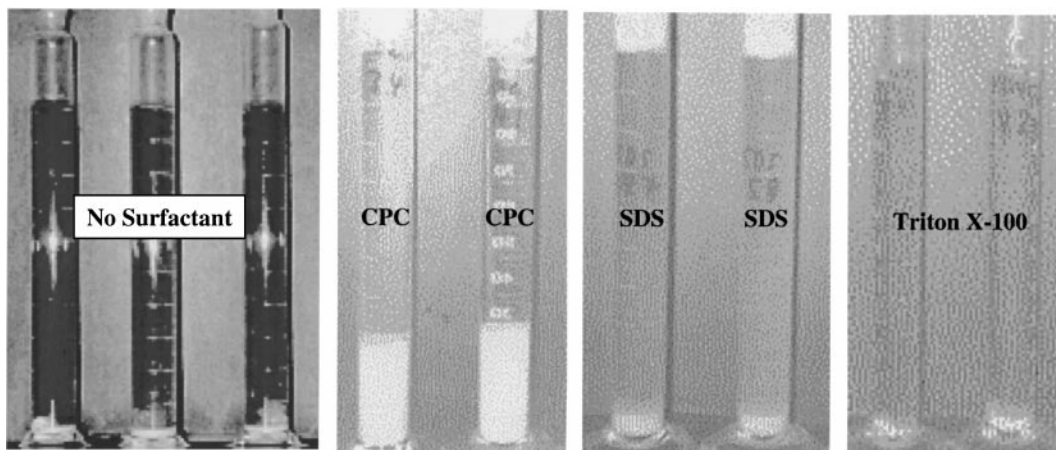


FIG. 5. Effects of ionic or nonionic surfactant addition on a high ionic strength slurry containing 0.1 M potassium ferricyanide oxidizing agent. The slurries are 1 wt% AKP-50 alumina at pH 4 with 10 mM surfactant added. The photographs were taken after 24 h of settling.

that the nonionic surfactants do not adsorb significantly on the alumina particles under these low ionic strength conditions.

Figure 5 investigates the addition of the same surfactants to high ionic strength slurries 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 addition of cationic surfactant (CPC) shows some stabilization of the slurry as shown by the large layer of white particles in the cylinders, but this slurry still contains agglomerated particles which have settled considerably. The addition of anionic surfactant (SDS) and nonionic surfactant (Triton X-100) shows 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 (Fig. 4). These results have been verified using other cationic, anionic, and nonionic surfactants.

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 have been prepared at pH 4 using 0.1 M potassium ferricyanide oxidizing agent. SDS, CPC, and Tween 80 surfactants have been added at a concentration of 20 mM prior to dilution. However, the solubility limit of SDS has been determined to be near 0.2 mM and that of CPC has been determined to be near 0.02 mM in 0.1 M potassium ferricyanide. As a result, these are the effective concentrations of SDS and CPC in the slurries, as prepared. All remaining SDS and CPC precipitates out of solution and does not affect the surface activity of these slurries. 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 Fig. 6, 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

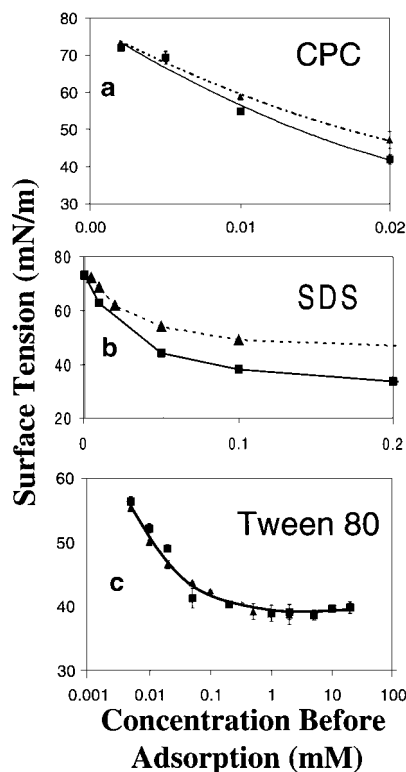


FIG. 6. Surface tension of solutions with (\blacktriangle) and without (\blacksquare) alumina particles added, as a function of surfactant concentration achieved through dilution with water. Surfactants are (a) CPC, (b) SDS, and (c) Tween 80.

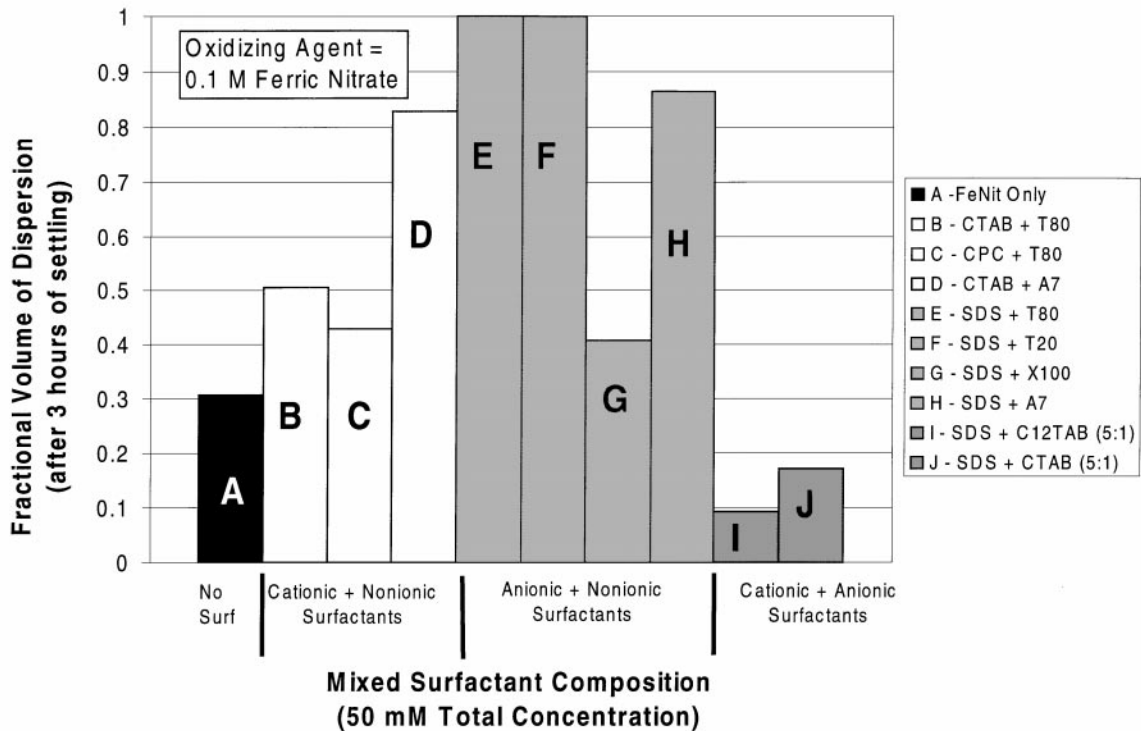


FIG. 7. Sedimentation results of 0.1 M $\text{Fe}(\text{NO}_3)_3$ slurries with mixtures of surfactants added.

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 Figs. 6a and 6b, 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. Figure 6c 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.

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. Surfactant synergism often leads to enhanced surfactant effects, such as slurry stabilization. Other authors have reported synergistic effects of mixed surfactant systems as stabilizing agents (7–13). Xu *et al.* (7) report that when mixtures of ionic and PEO-type nonionic surfactant are adsorbed on kaolinite, the adsorption of nonionic surfactant is enhanced due to hydrocarbon chain interactions between surfactants. The effects

of addition of surfactant mixtures on stabilization of high ionic strength slurries are shown in Figs. 7 and 8. These figures show the results of sedimentation tests on 10 wt% AKP-50 (100–300 nm) alumina slurries containing 0.1 M oxidizing agent. The 10 wt% solids loading is within the range of most commercial CMP slurries, which vary from 5 to 20 wt% solids loading. 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 (14, 15). 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 7 shows the sedimentation behavior of slurries containing 0.1 M ferric nitrate ($\text{Fe}[\text{NO}_3]_3$), 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 value 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 Fig. 7, the instability of slurries with no surfactant stabilizing agents added is once again verified by the ferric nitrate

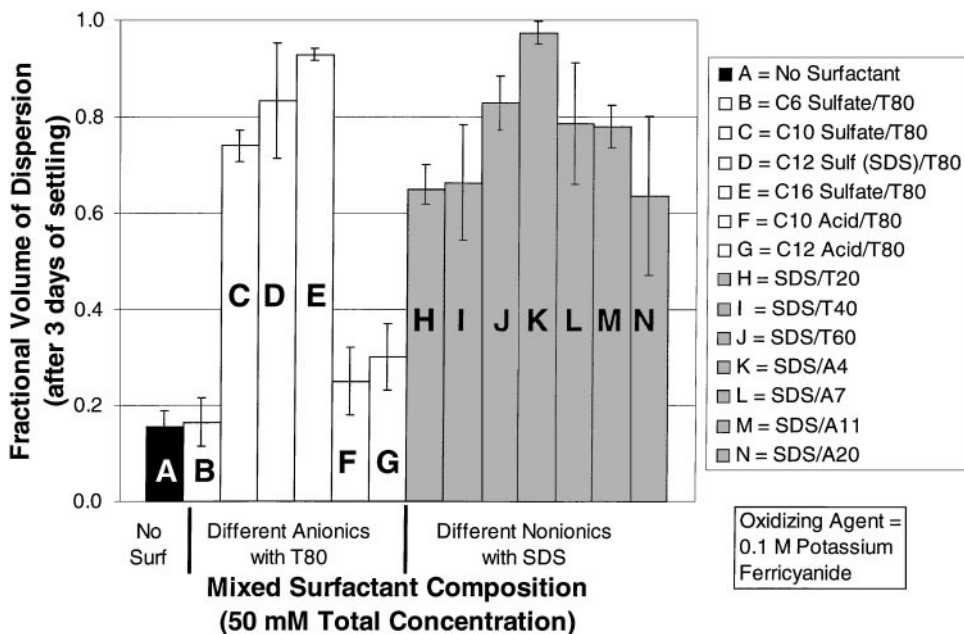


FIG. 8. Sedimentation results of 0.1 M $K_3Fe(CN)_6$ slurries with mixtures of anionic and nonionic surfactants added.

only (FeNit only) results, which show that after only 3 h of settling 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 a fully stabilized slurry after 3 h. 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 result in precipitation due to electrostatic interaction between surfactants. Figure 7 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 8 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 acids. Four chain lengths of sodium sulfate surfactants were investigated, including chain lengths of 6, 10, 12, and 16 for samples B, C, D, and E, respectively. These samples show a general

trend of increasing stability with increasing chain length of anionic surfactant. These results are due to an increase in driving force for the anionic surfactant to partition out of the aqueous solution and onto the particle surface as the chain length and hence the hydrophobicity of the surfactant increases. The different nonionic surfactants investigated with SDS show effects of both hydrocarbon chain length and degree of polymerization on stabilization of these slurries. Tween 20, 40, and 60 (samples H, I, and J) are identical surfactants except that they have chain lengths of 12, 16, and 18 carbons, respectively. In the presence of SDS, Tween 60 (T60) imparts significantly better dispersion stability than Tween 20 (T20) or Tween 40 (T40). Tween 80 (T80) is shown with SDS in sample D, which has results comparable to those of Tween 60 (sample J). The Symperonic nonionic surfactants investigated are identical with carbon chain lengths of C_{12} , except that the number of hydrophilic ethylene oxide (EO) groups varies, with A4, A7, A11, and A20 (samples K, L, M, and N) corresponding to 4, 7, 11, and 20 EO groups, respectively. Figure 8 shows that the stabilization increases with decreasing number of EO groups. This result, along with the results of the Tween samples (H, I, and J), shows that increasing hydrophobicity of the nonionic surfactant, either by increasing the hydrocarbon chain length or by decreasing the number of EO groups, increases slurry stabilization due to greater surface activity and partitioning of nonionic surfactant out of the aqueous solution.

DISCUSSION

The stabilization of high ionic strength slurries shown in Figs. 7 and 8 resulting from the use of the combination of SDS

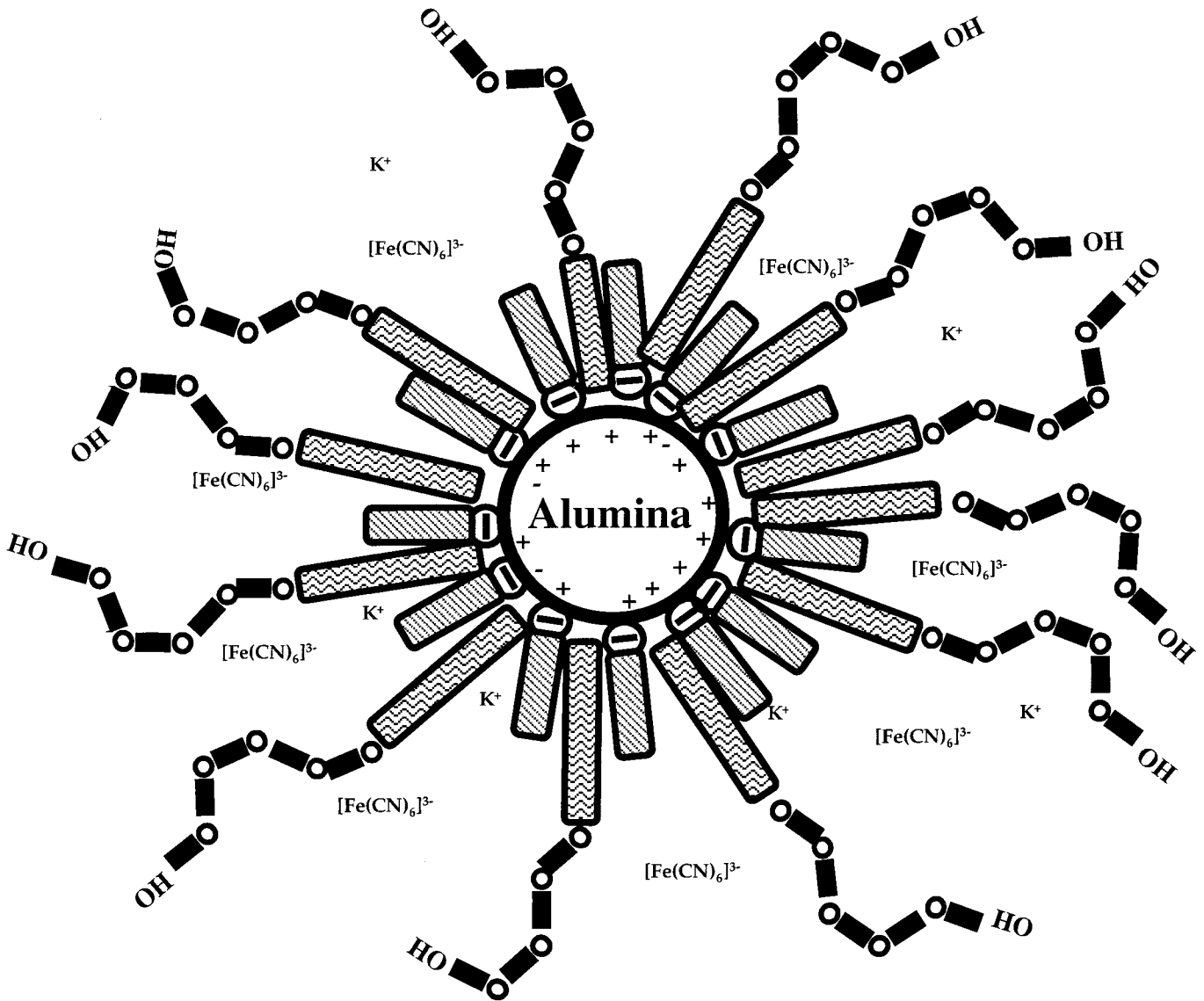


FIG. 9. Mechanism of high ionic strength slurry stabilization by the synergistic mixture of anionic and nonionic surfactants.

and either Tween 20, Tween 60, Tween 80, Symperonic A4, or Symperonic A7 can be explained by the generic adsorption model proposed in Fig. 9. The stabilization is shown to occur by a two-step mechanism: (1) the adsorption of a strongly adsorbing ionic surfactant and (2) the adsorption by hydrocarbon chain interaction of a nonionic surfactant capable of steric stabilization. This process results in the adsorption of a mixed surfactant bilayer 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 one such particle approaches another. 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 results of Figs. 7 and 8 suggest that this stabilization process is highly dependent on the choice of both ionic and nonionic surfactants. The stabilizing effect of surfactant mixtures by this mechanism is dependent on several factors, which are listed here.

(1) The ionic surfactant chosen must adsorb with significant surface coverage. Although it has been shown in this investigation that both cationic and anionic surfactants can adsorb on alumina particles, the driving force for adsorption will depend

on the structure of the surfactant. It has been shown in Fig. 8 that increasing the hydrocarbon chain length of the ionic surfactant increases slurry stabilization by increasing the driving force for the surfactant to partition out of the aqueous phase and onto the particle surface. Also, the concentration of ionic surfactant must be sufficient to provide ample surface coverage.

(2) There must be strong hydrocarbon chain interactions between adsorbed ionic surfactant and nonionic surfactant monomers. The main influences on the strength of hydrocarbon chain interactions are the relative hydrocarbon chain lengths and the presence of steric barriers. Hydrocarbon chain interactions have been shown to be maximum for systems in which the relative hydrocarbon chain lengths are equal (16–18). However, interactions will not occur at all if steric barriers are present which interfere with one monomer's ability to orient with its hydrocarbon chain in close proximity to the other monomer. The results of Fig. 8 also suggest that in the presence of SDS or other ionic surfactants, the slurry stabilization increases as the hydrophobicity of the nonionic surfactant increases. This implies that the driving force for the nonionic surfactant to partition out of the aqueous phase and onto the film of ionic surfactant on the particle surface must be sufficiently strong.

(3) The hydrophilic EO polymer segments of the nonionic surfactant must extend significantly into the aqueous phase upon adsorption and not tend to form flocs. The tendency of an adsorbed polymer to contribute to steric stabilization depends on the relative magnitude of the polymer–polymer interaction and the polymer–solvent interaction. For the polymer group to extend into the aqueous phase, the polymer–solvent attraction must be stronger than the polymer–polymer attractive interaction, which would tend to promote a coiled conformation of the polymer. Steric stabilization occurs due to the presence of steric barriers from adsorbed nonionic molecules on particles that prevent the particles from coming close enough to allow van der Waals attractive forces between particles to dominate (4, 19, 20). Van der Waals attractive forces, also known as London dispersion forces, arise due to temporarily induced dipoles that occur in all molecules, including inert gases. The attractive potential between particles increases with the inverse of the distance between the particles to the first or second power, depending on the particle geometry (21, 22). Hence, the attractive potential decreases rapidly with an increase in distance of separation. Adsorbed EO polymer segments that extend into the aqueous phase will be much more effective for steric stabilization than polymer segments which coil close to the particle surface, since the distance of separation of particles in the former case will be kept much greater than that in the latter case. As discussed by Rosen (4), polyoxyethylene (PEO)-type nonionic surfactants are excellent dispersing agents because their highly hydrated chains extend into the aqueous phase in the form of coils that present excellent steric barriers. PEO-type nonionic surfactants adsorbed on particles are also expected to decrease the effective Hamaker constant and hence decrease the van der Waals attraction between particles. These surfactants have been shown to

provide an excellent steric barrier to particle aggregation even when the electrical double layer is compressed by large amounts of polyvalent electrolyte (23), as is the case in this investigation. This is true even though the molecular weight of PEO-type nonionic surfactants is much lower than those of many conventional polymers used for steric stabilization. However, in general the polymer segments must not interact attractively with segments on adjacent particles or flocculation will cause destabilization of the slurry. The tendency for flocculation will increase as the adsorption density of polymer segments is increased (4). Finally, the results of Fig. 8 suggest that, although a steric stabilizing layer must be present for slurry stabilization, the degree of hydrophobicity of the nonionic surfactant is a more important factor in this mechanism. The ability of a given ionic and nonionic surfactant mixture to stabilize a slurry is limited by the amount of nonionic surfactant which can partition out of aqueous solution and onto the particle surface.

If a system of ionic and nonionic surfactant stabilizing agents is chosen with these criteria in mind, the stabilization of any high ionic strength slurry is obtainable.

SUMMARY

It has been shown that high ionic strength slurries cause agglomeration of slurry particles by shielding surface charges on the particles. The addition of ionic or nonionic surfactants to model high ionic strength slurries applicable to metal CMP has been shown to have very little effect on slurry stabilization, and this result has been explained. The addition of ionic and nonionic surfactant mixtures to high ionic strength slurries has been shown to be capable of slurry stabilization. The stabilization observed by the mixed surfactant systems has been explained as the synergistic effect of adding ionic surfactant that significantly adsorbs on the alumina particles and nonionic surfactant that adsorbs due to hydrocarbon chain interactions with the film of ionic surfactant and brings about steric stabilization of the slurry. The factors influencing this stabilization mechanism have been discussed.

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