

Characterization of chemical polishing materials (monomodal and bimodal) by means of acoustic spectroscopy

Andrei S. Dukhin *, Philip J. Goetz

Dispersion Technology, 3 Hillside Avenue, Mount Kisco, NY 10549, USA

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Abstract

It is shown that acoustic spectroscopy can sense the presence of a small sub-population of large particles in a concentrated dispersion of much smaller particles. The detection limit can be as low as a single one micron particle per 100 000 particles of 100 nm size. In order to achieve this high sensitivity the acoustic spectrometer must be able to measure ultrasound attenuation with a precision of 0.01 dB/cm/MHz. It is shown that DT-1200 Acoustic Spectrometer (Dispersion Technology, NY, USA) meets this requirement over a frequency range of 3–100 MHz. A model dispersion with a known bimodal particle size distribution (PSD) was created by adding a small amount of larger particles to a stable slurry containing only small particles. Dupont Ludox™ (silica 30 nm) and Cabot SS25 (silica 63 nm) were used to represent typical chemical-mechanical polishing (CMP) slurries. Two samples of Silica Geltech silica (0.5 and 1.5 micron) were used to model the target aggregate particles. It is shown that the attenuation spectra measured with the DT-1200 has sufficient sensitivity that it can detect the larger particles at concentrations as low as 2% relative to the total solid content of the slurry (12% wt). Moreover, the bimodal PSD calculated from the attenuation spectra are consistent with the known composition of these mixed model dispersions. Importantly, a software error analysis can correctly select either a bimodal distribution or a lognormal representation of the test samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemical polishing; Model dispersion; Particle size distribution

1. Introduction

Modern chemical-mechanical polishing materials (CMP) present a new challenge for measuring techniques. Three aspects of this application cause

difficulties when using instruments based on traditional techniques. First, the particle size of a typical CMP slurry is too small for sedimentation-based instruments or electric-zone instruments. Typically, the mean size of CMP materials is approximately 100 nm with no particles, or just a few particles, larger than 500 nm. Second, the range in the size of the particles may be greater

* Corresponding author. Tel.: +1-914-2414777; Fax: +1-914-2414842.

E-mail address: dispensi@dispension.com (A.S. Dukhin)

than 1000:1 which also eliminates many classical techniques. Third, CMP systems are typically shear sensitive. Shear caused by the polishing process itself or the delivery system may cause unpredictable assembly of the smaller particles into larger aggregates. However, these aggregates may be weakly formed and easily destroyed by subsequent sonication, high shear, or dilution. Therefore, any technique which requires dilution or other sample preparation steps, may in fact destroy the very aggregates that one is attempting to quantify by measurement. We suggest that CMP systems must be characterized as is, without any dilution or sample preparation.

Acoustic spectroscopy [1–3] provides an exciting alternative to more classical methods. The technique resolves all three issues mentioned above. It is known that acoustic spectroscopy is able to characterize particles as small as 10 nm [4] and as large as 10 microns, providing at least a 1000: range. Most importantly, the technique requires no dilution and is suitable for measuring slurries, as is, up to 45% by volume [5,6]. These unique features make acoustic spectroscopy very attractive for characterizing the particle size distribution of CMP slurries.

However, there is one feature of acoustic spectroscopy which thus far has not been described sufficiently in the literature: namely the ability to characterize a bimodal PSD. Although Takeda et al [7] demonstrated that acoustic spectroscopy is able to characterize bimodal distributions of mixed alumina particles, the ultimate sensitivity in detecting one very small sub-population in combination with another dominant mode has not yet been investigated. Yet, it is just this feature, the ability to recognize a small sub-population, which is most critical for CMP studies. This paper addresses this important issue.

Unfortunately, there is no agreement in the literature as to the number of larger particles which might be allowed in a CMP slurry. We will assume for the moment that only one large particle of 1 micron size might be allowed per 100 000 small 100 nm particles. This target sensitivity corresponds to large particles amounting to 1% of the total weight of all particulates.

Of course, an acoustic spectrometer does not directly measure particle size. In fact, it measures an attenuation spectra and calculates the particle size assuming a certain model for describing the sound attenuation in terms of the physical properties of the system. It follows therefore that this target sub-population sensitivity needs to be translated into a corresponding precision and accuracy specification for the attenuation measurement. We will show that, from a theoretical standpoint, the required precision is roughly 0.01 dB/cm/MHz. The first set of experiments were performed with a single component system Dupont silica Ludox™ to confirm that DT-1200 acoustic spectrometer indeed meets this target requirement.

A second set of experiments was then made to test whether the attenuation spectra changed reproducibly when a small amount of the larger particles was added to a single component slurry of small particles. Two slurries were used for the small particles: Ludox™ and Cabot SS25. Two Geltech silica with nominal sizes 0.5 and 1.5 micron were used as the model large particles. It was shown that the change in the attenuation spectra was statistically significant when the large particles amounted to at least 2% of the total weight of all particulates. Expressed another way, the detection limit for this 12% wt slurry corresponded to a sub-population which was only 0.24% wt in terms of the total sample weight, or 0.24 of large particles per 100 g of the slurry.

2. Determination of the required precision and accuracy using acoustic theory

We have set a target of detecting a large particle sub-population at concentrations above 1% wt relative to the smaller but dominant size fraction. This 1% fraction of larger particles inevitably must cause some finite change in the attenuation spectra and we should be able to predict this change using an appropriate acoustic theory. Such a theory exists and has been experimentally tested [5].

We can use this theory to first calculate the attenuation spectra for a lognormal particle size

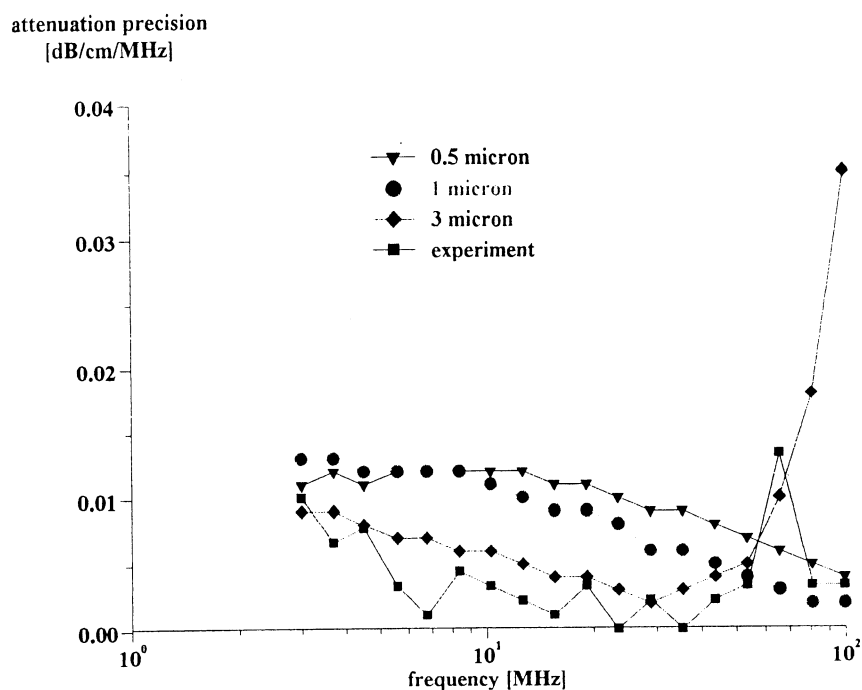


Fig. 1. Theoretical and experimental precision of the attenuation measurement. Theoretical resolution is defined as the difference between attenuation spectra corresponding to lognormal PSD with median size 50 nm and standard deviation 0.3 and bimodal distributions with 1% of solid content of large particles. Size of the large particles is shown in legend. Total solid content is 6 vol% of silica with density 2.2 g/cm³. Experimental resolution is determined based on the data from the Table 2.

distribution (PSD) of the dominant fraction of small particles. Next we can calculate the attenuation specs for a bimodal PSD corresponding to the same dominant fraction but with an added 1% sub-population of larger particles. If we then subtract these two attenuation spectra, the difference spectra can be attributed the addition of the larger particles. This difference spectra is very important, because it uniquely defines the precision and accuracy which is required to meet our target detection criteria.

These difference spectra are plotted in Fig. 1 for a slurry having a dominant mode of 50 nm, and three different sized sub-populations (0.5, 1, and 3 micron). Importantly, we observe that this difference spectra has a magnitude of about 0.01 dB/cm/MHz for each case, and therefore the acoustic spectrometer must measure attenuation with an equal or better precision and accuracy over the whole frequency range.

3. Experimental technique

For these tests we used a DT-1200 Acoustic Spectrometer developed by Dispersion Technology, Inc., NY, USA [8]. This instrument has two independent sensors: one for measuring acoustic attenuation which was employed here for determining particle size, and another for measuring electroacoustic signals from which we can calcu-

Table 1

Particle size of the initial silica samples, expected and measured acoustically

	Manufacturer	Acoustics
Ludox™	22 nm (area basis)	30 nm (weight basis)
Geltech 0.5	0.5 micron	0.65 micron
Geltech 1.5	1.5 micron	1.72 micron
Cabot SS12		63 nm
Cabot SS25		62 nm

late zeta potential. Both sensors use pulse techniques.

The acoustic sensor measures the attenuation spectra by means of two piezoelectric transducers. The gap between the transmitter and receiver is variable in software controlled steps. In default, it change from 0.15 mm up to 20 mm in 21 logarithmic steps. The frequency of transmitted pulse changes in steps a well. In default, it changes from 3 to 100 MHz in 18 logarithmic steps. The number of pulses collected for each gap and each frequency is software controlled in order to reach a target signal-to-noise ratio for each point on the selected gap/frequency grid.

The acoustic sensor also measures the group sound speed at a chosen frequency using the change transit time of the pulse versus the gap. The instrument automatically adjusts the pulse sampling depending on the value of the sound speed, which is necessary to eliminate artifacts such as excess attenuation at low frequencies.

A single attenuation spectra is measured using default conditions in about 5 min. The user can speed up measurement by changing setup parameters, and successive measurements on the same sample are always faster as the software automatically discards unproductive points on the gap/frequency grid.

An analysis program calculates the particle size distribution from attenuation spectra. It uses an error analysis in order to determine whether a lognormal, bimodal, or modified lognormal [9] particle size distribution best fits the experimental data. The goal of the analysis program is to find that PSD which minimizes the difference between the attenuation spectra predicted by theory and that measured experimentally.

The precision and accuracy of the acoustic spectrometer has been tested with several different model systems [3]. The precision and accuracy of the particle size measurement is about 1%.

The total required sample volume is about 100 ml. A magnetic stirrer prevents sedimentation and provides mixing of reagents during titration. The instrument also provides conductivity, pH, and temperature probes, as well as digitally con-

trolled burettes for dispensing chemical reagents during automated titration.

4. Materials

We used altogether four silica materials. Two small sized particles were used, namely Dupont Ludox™ (50% wt) and Cabot SS25 (25% wt). Two larger sized particles were employed, namely Geltec 0.5 micron and Geltech 1.5 micron. We assumed a density of 2.1 g/cm³ for all silica particles.

Slurries were prepared at 12% wt for each material as follows.

The Ludox™ was supplied as a 50% wt slurry which was diluted to 12% wt with 0.01 M KCl solution resulting in a sample pH of 9.3.

The Geltech samples were supplied as a dry powder, which was dispersed in 0.01 M KCl solution and adjusted to pH 9.6 with KOH. The dispersion was repeatedly sonicated, stirred, and allowed to equilibrate for 5 h before being measured.

The Cabot SS25 silica was diluted to 12% wt with 0.01 M KCl.

Table 1 presents particle size data provided by the manufacturer for each of these samples.

5. Experimental protocol

The goals of the experiment were met in three steps:

1. Reproducibility: The objective was to prove that the DT-1200 Acoustic Spectrometer able to measure the attenuation spectra with the required precision of 0.01 dB/cm/MHz. To prove this we measured five different fillings of the same 12% wt silica Ludox™. Each filling was measured nine times. A statistical analysis of the measured attenuation spectra yielded average variation of the attenuation measurement over the frequency range from 3 to 100 MHz.
2. Accuracy: The goal here was to prove that acoustic spectroscopy can characterize the particle size with sufficient accuracy. To achieve

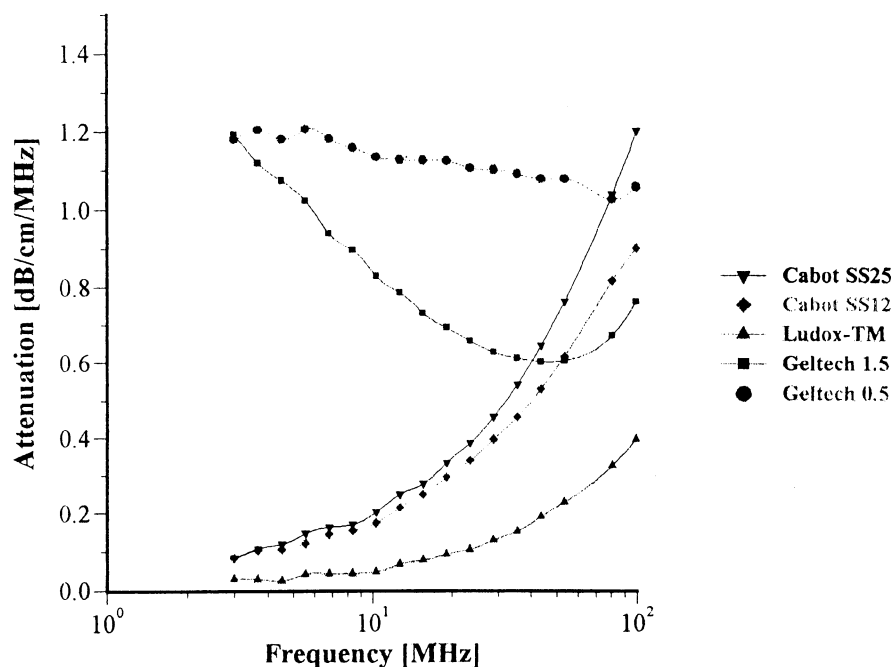


Fig. 2. Attenuation spectra measured for Ludox™ silica, Geltech 0.5 and 1.5 silica, Cabot SS, and SS12 silica. Total solid content is 12% wt except for SS25 which is 25% wt.

this goal all five silica slurries were measured individually. The measured particle size was then compared with independent information provided by the manufacture.

3. Bimodal sensitivity: This is the key step in the investigation. Model systems with bimodal PSD were prepared by mixing a small particle slurry (Ludox™ or Cabot SS12) with increasing doses of the larger particle slurries (Geltech 0.5 or Geltech 1.5). The objective was to evaluate the accuracy of the PSD calculated by the DT-1200 software for these known systems.

6. Results and discussion

The attenuation spectra obtained in the reproducibility test with the Ludox™ slurry are shown in Fig. 4. The attenuation data is also shown in Table 2 where each column corresponds to a different frequency on a log scale from 3 to 100 MHz. Importantly, we note that the small differ-

ences between the nine repeat measurements of the same sample is less than our target resolution of 0.01 dB/cm/MHz as formulated above.

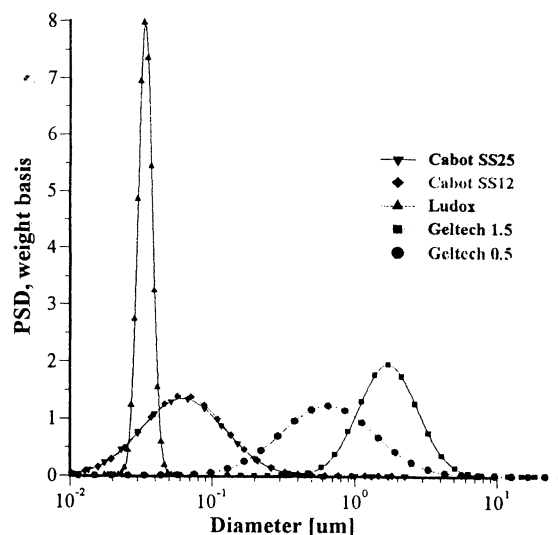


Fig. 3. Particle size distributions corresponding to the attenuation spectra from Fig. 2

Table 2
Attenuation data for Ludox™, 12% wt, measured nine times with five different loads^a

run	3	3.7	4.5	5.6	6.8	8.4	10.3	12.7	15.6	19.1	24	29	35.5	43.6	53.6	65.9	81	100
1	0.03	0.03	0.02	0.04	0.04	0.04	0.05	0.07	0.08	0.09	0.1	0.13	0.15	0.19	0.23	0.27	0.33	0.4
2	0.04	0.02	0.03	0.04	0.04	0.04	0.05	0.06	0.07	0.09	0.1	0.13	0.15	0.19	0.23	0.28	0.34	0.4
3	0.05	0.05	0.04	0.05	0.05	0.06	0.05	0.05	0.07	0.09	0.1	0.12	0.15	0.19	0.22	0.25	0.33	0.39
4	0	0.03	0.01	0.04	0.04	0.04	0.05	0.06	0.07	0.09	0.1	0.12	0.15	0.19	0.22	0.24	0.33	0.39
5	0.03	0.04	0.02	0.05	0.04	0.04	0.05	0.06	0.07	0.09	0.1	0.12	0.15	0.19	0.22	0.27	0.33	0.4
6	0.03	0.03	0.02	0.03	0.04	0.05	0.04	0.06	0.07	0.08	0.1	0.12	0.15	0.18	0.22	0.24	0.32	0.39
7	0.01	0.02	0.02	0.04	0.04	0.05	0.04	0.06	0.07	0.08	0.1	0.12	0.15	0.18	0.23	0.24	0.33	0.39
8	0.02	0.03	0	0.04	0.04	0.04	0.04	0.06	0.07	0.08	0.1	0.12	0.15	0.19	0.22	0.26	0.32	0.39
9	0.01	0.007	0.008	0.003	0.001	0.004	0.003	0.002	0.001	0.003	0	0.002	0	0.002	0.003	0.013	0.003	0.003
Deviation	0.027	0.032	0.021	0.041	0.041	0.044	0.047	0.06	0.071	0.087	0.1	0.122	0.15	0.188	0.223	0.258	0.329	0.393

^a Each column corresponds to the different frequency from 3 to 100 MHz on the logarithmic scale. First row specifies frequency in MHz. Average attenuation and average variation are shown in the last rows.

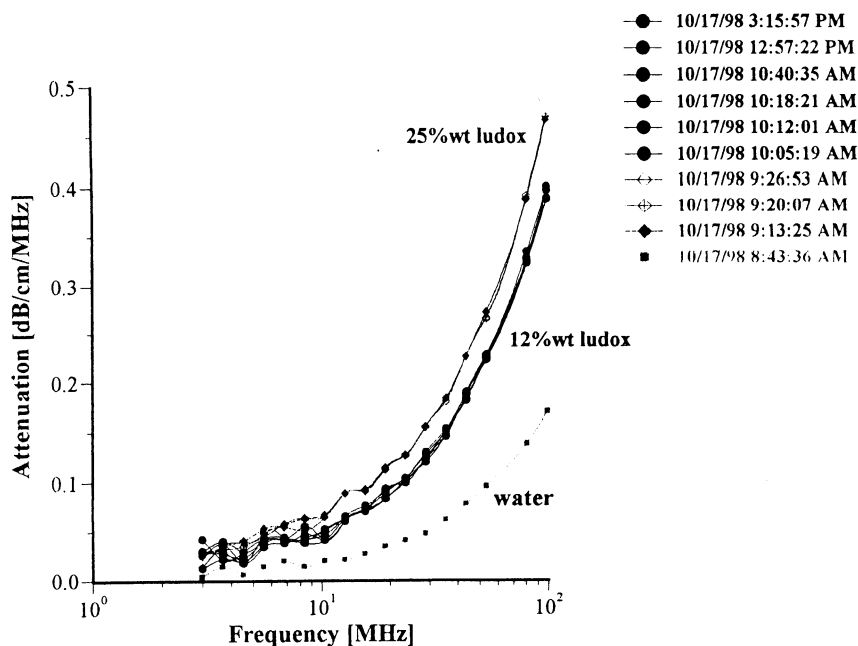


Fig. 4. Reproducibility test. Multiple attenuation spectra measured for Ludox™-50 silica with different weight fractions.

We also see that the precision in the attenuation measurement improves with frequency. It is also clear that one point at high frequency (≈ 60 MHz) is the least precise. This frequency corresponds to twice the resonant frequency of the acoustic transducers, at which point the transducers have a minimum conversion efficiency.

The experimental precision obtained in this test is also plotted in Fig. 1, together with theoretic requirement discussed earlier. It is seen that the experimental precision is much better than theoretically required for all frequencies but one. This means that the resolution of the DT-1200 attenuation measurement is sufficient for meeting the target set for PSD characterization of CMP slurries.

Another conclusion follows from the theoretical curves of Fig. 1. We note that the addition of either the 0.5 or 1 micron particles contributes additional viscous losses and results primarily in an added attenuation at low frequencies, whereas the addition of the 3 micron particles contributes additional scattering losses which results primarily in added attenuation at the higher frequencies. It

is a fortunate coincidence that this acoustic technique is particularly sensitive for distinguishing between these 'large' and relatively 'larger' particles. Qualitatively, we can say that an increase in the attenuation at the lower frequencies indicate that we are dealing with 'large' particles of about 1 micron, whereas an increase in the attenuation spectra at higher frequencies is an indication that we have even 'larger' particles exceeding 3 microns. Quantitatively, of course these calculations are made more precise by the analysis software.

The attenuation spectra for all five single component silica slurries is shown in Fig. 2 and the corresponding particle size distributions for these same samples is shown in Fig. 3. These tests allowed to compare the particle size determined by acoustic spectroscopy for the five 12% wt test slurries with independent data from the manufacturers. The values of the median size in each case is shown in Table 1. It is interesting to note that there is some difference between the acoustically measured data and that provided by the manufacturer. In large part this is related to differences in the characterization technique. For instance, the

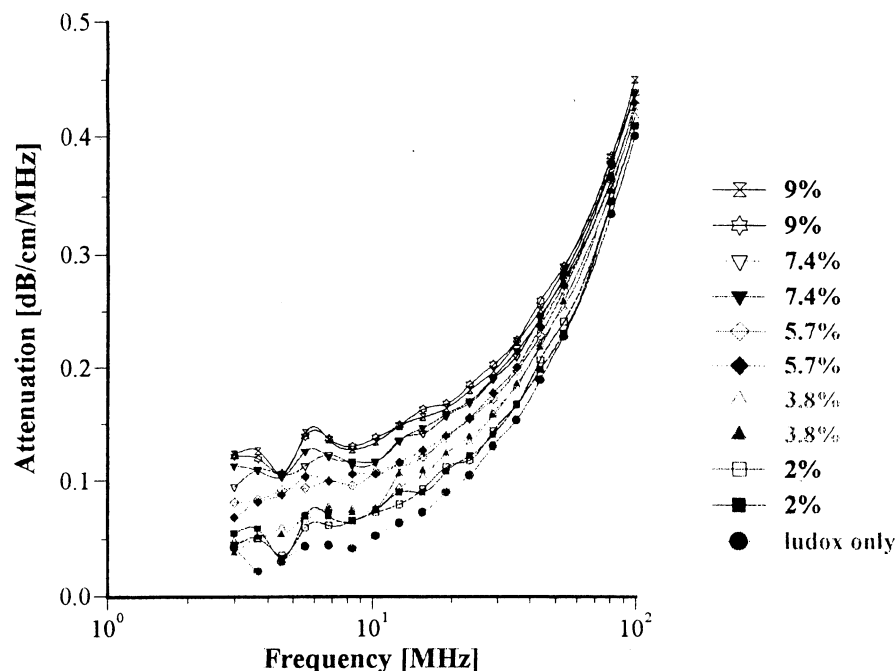


Fig. 5. Attenuation spectra measured for Ludox™-50 silica with various additions of Geltech 0.5 silica. Total solid content is 12% wt. Legend shows the fraction of the total solid content corresponding to the Geltech silica.

size of the Ludox™ slurry is determined by Dupont using a titration method. This method yields an average size on an area basis. Acoustic spectroscopy gives us a size on a weight basis, which for a polydisperse system will always be somewhat larger than an area based size. In addition acoustic spectroscopy implies some assumption about real dispersed system when particle size is being calculated from the attenuation spectra. Any measuring technique does the same. These assumptions and variation in physical properties which are involved into the calculation can cause some variation in size as well.

Successful reproducibility and reasonable agreement with other techniques then encouraged us to move to the third step which is a test of the ability to correctly determine bimodal PSD. We used Ludox™ or CMP SS12 small particles as the major component of a slurry. The Geltech 0.5 or Geltech 1.5 were used as 'large' and 'larger' particles in the minor component of the mixed slurry. In each case the minor fraction was added to the Ludox™ or the CMP SS12 systems in steps. Each

addition increased the relative amount of the larger particles by 2%. The attenuation spectra was measured twice for each mixed system in order to demonstrate reproducibility.

Figs. 5–8 give the results of these mixed system tests. It is seen that attenuation increases with increasing amounts of the 'large' or 'larger' particles. The increase in the attenuation with increasing doses of the Geltech content is in all cases significantly larger than precision of the instrument. This demonstrates that the DT-1200 data contains significant information about the small amount of large particles. The final question is to determine whether the calculated PSD calculates a correct bimodal distribution for these mixed model systems.

Table 3 gives an answer to this question. The DT-1200 always calculates a lognormal and a bimodal distribution which best fits the experimental data. These two PSD are best in the sense that the fitting error between the theoretical attenuation calculated for the best PSD and the experimental attenuation is minimized. These fitting

Table 3
 Characteristics of the larger particles (Geltech silica) calculated from the attenuation spectra of Fig. 5 and Fig. 6.

Actual Geltech content, %	Calculated for Geltech 0.5					Calculated for Geltech 1.5				
	Content, %	Larger size micron	lognormal fitting error, %	Bimodal fitting error, %	Content, %	Larger size micron	lognormal fitting error, %	Bimodal fitting error, %	Content, %	Larger size micron
9	14	0.7	14.1	7.3	11	1.6	24.5	4.4	11	1.6
9	15	0.9	10.9	8.7	12	1.7	17.7	5.5	12	1.7
7.4	8	0.9	13.6	4.5	10	1.9	17.8	6	10	1.9
7.4	12	1	15.4	7.1	10	1.9	17.3	5.4	10	1.9
5.7	7	0.9	13.8	4.3	7	1.9	17.2	4.1	7	1.9
5.7	10	1.3	12.9	7.2	6	1.6	18.5	4.7	6	1.6
3.8	4	0.9	9.5	3.7	5	1.3	18.1	3.9	5	1.3
3.8	4	0.7	12	4.3	6	1.6	16.9	3.8	6	1.6
2	4	0.6	10.8	3.6	3	1.9	12.2	2.6	3	1.9
2	5	1.2	12.2	3.7	4	1.6	12.3	3.9	4	1.6

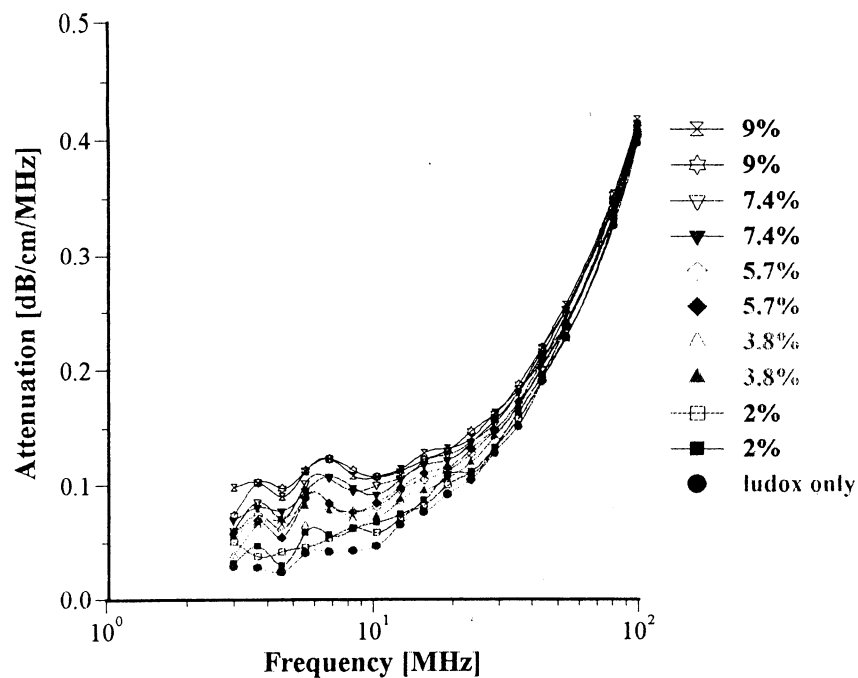


Fig. 6. Attenuation spectra measured for Ludox™-50 silica with various additions of Geltech 1.5 silica. Total solid content is 12% wt. Legend shows the fraction of the total solid content corresponding to the silica Geltech.

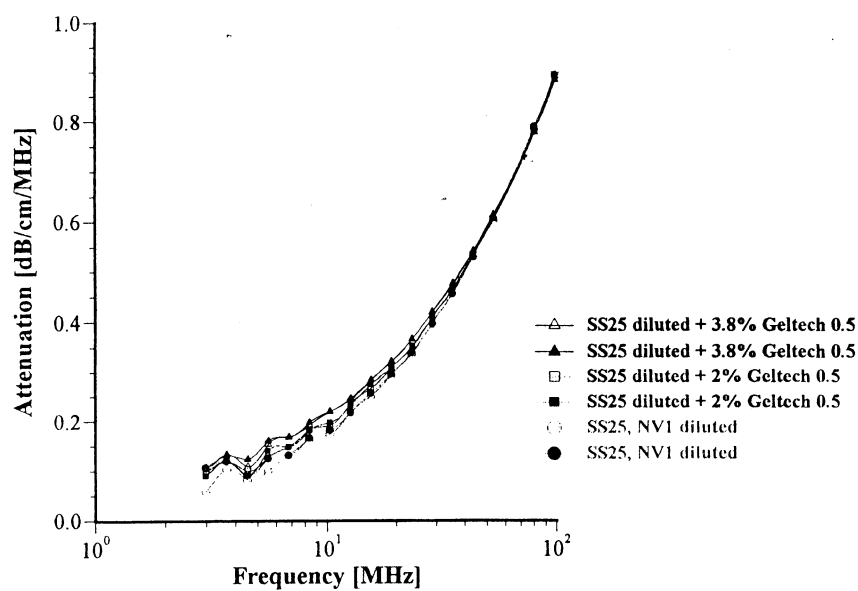


Fig. 7. Attenuation spectra measured for Cabot SS25 silica diluted down to 12% wt with various additions of Geltech 0.5 silica. Total solid content is 12% wt. Legend shows the fraction of the total solid content corresponding to the silica Geltech

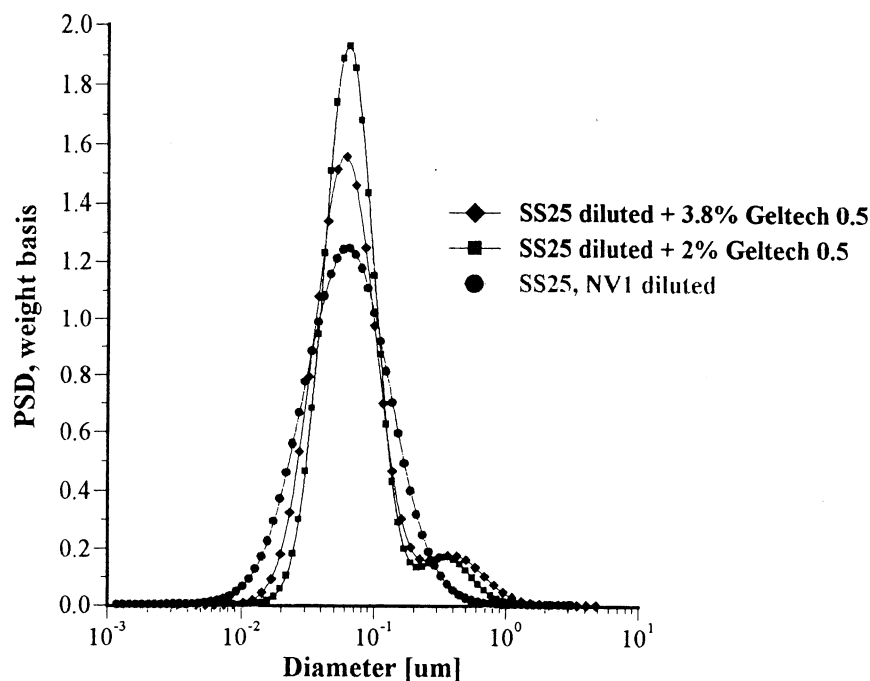


Fig. 8. Particle size distribution of Cabot SS25 silica diluted down to 12% wt with various additions of Geltech 0.5 silica. Total solid content is 12% wt. Legend shows the fraction of the total solid content corresponding to the silica Geltech.

errors are important criteria for deciding whether the lognormal or bimodal PSD is more appropriate for describing a particular sample. For instance, the PSD is judged to be bimodal only if the bimodal fit yields substantially smaller fitting error than a lognormal PSD. The value for the lognormal and bimodal fitting errors are given in Table 3. It is seen that fitting errors for the bimodal PSD is better than the lognormal for all of the mixed systems over the whole concentration range and for both the large and larger sized particles. According to the fitting errors, all PSD in the mixed Ludox–Geltech systems are bimodal, which of course is correct for these known mixed systems.

At the same time our experience tells us that this fitting error criterion alone is not a sufficient test for the bimodality of the PSD. It is always possible to obtain a better fit to a data set by allowing more degrees of freedom in the solution. A bimodal PSD provides at least four adjustable parameters for fitting the experimental attenua-

tion curve, whereas a simple lognormal PSD provides only two parameters.

The value of the larger particle content is another important parameter which must be taken into account. We have demonstrated that the precision of the DT-1200 is sufficient to detect larger particles present at concentrations larger than 2%. Therefore, the software will not claim a bimodal PSD if the content of the large particles less than 2%, even if this yields a marginally better fit. Referring to Table 3, we see that the calculated large particle content in all of the mixed Ludox™–Geltech systems is well above this 2% threshold and gives therefore an additional argument to claim a bimodal PSD for these systems. It is important that the calculated content of the large particles increases with the actual content the added Geltech particles which confirms consistency of the PSD analysis.

Figs. 7 and 8 illustrate a similar test performed with actual CMP Cabot SS slurry. It is seen that DT-1200 is again able to resolve the presence of the small added amount of Geltech particles.

7. Conclusions

We assumed that characterization of CMP slurries requires the detection of 1 particle with 1 micron diameter per 100 000 small particles with diameter 100 nm. This is equivalent to large particles having a weight equal to 2% of the total particulates in the slurry.

It is shown theoretically that in order to achieve this detection capability the Acoustic Spectrometer must be able to measure attenuation with a precision of 0.01 dB/cm/MHz within the frequency range of to 100 MHz. It is also shown that larger particles with a size below three micron contribute to the attenuation spectra mostly at low and medium frequencies whereas particles with a size above three microns show up primarily at high frequency.

Experimental reproducibility and accuracy tests show that the DT-1200 Acoustic Spectrometer meets the target detection requirement for characterizing small amounts of large particles in CMP slurries

Attenuation spectra measured using the DT-1200 reflects the presence of the added small amount of large particles. Particle size distribution calculated from these attenuation spectra are bimodal according to the suggested PSD criterion. This criterion applies fitting error analysis in order to select a proper PSE shape. It also assumes a certain constraint on the large particle content.

Content and size of the large particles calculated from attenuation spectra are in a good

agreement with a priori known amount and size of the added large particles, which shows consistency of the bimodal PSD calculated from the attenuation spectra.

Experimental tests with real CMP slurries confirms the applicability of the DT-1200 Acoustic Spectrometer for characterizing small amounts of the large particles in CMP slurries.

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