Mixing and Handling Challenges of Next-Generation CMP Slurries

Most modern slurry formulations are being pushed hard by two competing forces – improved affordability and critical process performance – which have resulted in products which are both lower in abrasive content and higher in chemical complexity. To achieve reduced POU (point of use) costs, slurries are being formulated as either high solids/high dilution ratio concentrates or as very low solids/ready to use versions. Achieving these high performance requirements in current and upcoming process nodes also requires a very complex mix of organic and inorganic compounds in slurry formulations. The combination of these factors results in products that, in some cases, have very particular mixing and handling requirements.

Traditional slurries have always needed to be re-homogenized after a period of time in storage, due to the stratification or settling of the abrasive content. Suspended solids are stabilized in solution as much as possible, but different types of abrasives and chemical packages naturally exhibit different levels of stratification over time. Once this occurs, the difference in concentration of both abrasives and chemistry between the bottom and top of a storage container can easily be great enough to cause variations in polishing performance if the material is withdrawn from the container without being pre-mixed.

Typically, slurries are withdrawn from a drum or a tote using an inserted dip tube which is connected to a corresponding dispense head that is attached to the slurry feed line to the distribution system. The feed dip tube extends to near the bottom of the container, so material is withdrawn from that location first. Without pre-mixing, the slurry may have some or all of its abrasive content at the bottom, resulting in initial mix batches with higher solids from a new drum, and progressively lower solids from subsequent batches as the drum is drained. The variation in solids gives a “saw tooth” result when charted, with drum changes separating the “teeth”. It should be noted that not just polishing removal rates can be affected by this. Some slurry formulations have chemical components that sequester themselves preferentially with the particle which may be critical to achieving desired polishing performance and other polishing parameters like planarity, erosion and uniformity can also be affected.

Slurry shelf life is measured in terms of months, up to a year for most slurries. The effects of stratification and settling become more and more of a concern as a slurry ages. To fully characterize the behavior of a slurry over time, detailed shelf life and aging studies are needed to evaluate the mixing requirements needed to re-homogenize the slurry at different ages to maximize shelf life. This testing is used to determine the individual pre-mixing recommendations that are made for a slurry. Both pump recirculation and mechanical agitation are popular methods of pre-mixing slurry prior to use, and this is where issues can arise with many new slurry formulations.
Shear Sensitivity

Shear force is the strain produced by opposing forces acting on the layers or components of an object. In slurry the shear force caused by mixing or filtration can impact how the components of the slurry behave. The most negative impact is when shear makes the particle agglomerate with itself or other slurry components, causing the slurry to thicken (or gel) or increases settling of the particle out of slurry. How sensitive a particular slurry is to shear greatly impacts proper handling of the product. The effects of gelling can be seen in premature filter plugging and possibly in an increase in defects during polishing.

Shear Sensitivity Issues
- Sensitivity by particle type (most to least) – fumed silica, treated particle (any), colloidal silica, alumina, ceria
- Higher solids are more sensitive than lower solids
- Some chemical components in a slurry (e.g. surfactants, polymers) may be more sensitive than their accompanying abrasive

Slurry Types

There are two broad categories of slurries for mixing and handling considerations: stratifying and settling. Each of these can be further separated into foaming and non-foaming sub groups. The methods required to pre-mix these different types of slurry are determined by the particular requirements of the slurry and the limitations of manpower and equipment available in the sub Fab.

Categorizing Slurries
- High solids (concentrate) vs. low solids (POU)
- Shear sensitive vs. shear insensitive
- Stratifying vs. settling
- Foaming vs. non-foaming

Older, predominately mechanically-driven CMP slurries mostly fall into the main category of either stratifying or settling. Very few exhibit any foaming behavior, due to their limited organic content. Generally, over time silica slurries are more likely to stratify while alumina or ceria slurries are more likely to settle. However, modern particle types and higher abrasive content in concentrated slurries can have differing effects on particle stability over time. There are some very stable alumina slurries and some very unstable silica slurries, so assumptions should not be made based on historical behavior. Newer slurries of ALL abrasive types are also much more likely to have increased numbers and types of organic compounds in their formulation, making them much more prone to foaming under conditions where splashing or air entrainment into the slurry occurs.
Stratifying slurries exhibit low to moderate levels of abrasive concentration gradients from the top to the bottom of the container. They do not settle to any significant degree, and they are relatively easy to re-homogenize with either pump recirculation or light mechanical agitation. In the standard case, separate feed and return dip tubes/dispense heads can be used with pump recirculation to homogenize the solids concentration in the drum quickly – normally one turnover of recirculation is recommended (a turnover is the amount of time required to fully withdraw and replace the volume of a container at a given flow rate). For stratifying, non-foaming slurries; a single appropriately designed feed/return dip tube and dispense head can be used instead of separate ones. However, this can result in issues with drying abrasive inside the drum if slurry usage is particularly low, so proper humidification of the headspace in the drum is recommended.

Stratifying slurries that foam require separate full length dip tubes to be installed. This avoids conditions where the slurry is allowed to fall back to solution level from the return side. Without a full length dip tube, as a drum empties the distance the returning slurry falls increases, resulting in more splashing and air entrainment. Since this is the driving cause of foaming during drum recirculation, avoiding this condition is of paramount importance. Dealing with foam once it has been formed is very difficult, and can have a number of negative effects on both the slurry and equipment in the SDS (slurry distribution system). It is preferable to prevent foaming from occurring in the first place, if possible.

3 REASONS TO AVOID FOAMING IN CMP SLURRY

- Foam can pull organic components from slurry, altering their desired concentration when slurry is introduced to the distribution system.
- Foam is prone to drying, which allows it to entrain organic particles. These particles can adhere to dispense heads and dip tubes, break off and get carried into the distribution system, where they can cause polishing defects.
- Foam can distort readings of non-contact level sensors. When liquid levels in drums are high, this can cause artificial readings that set off overfill sensors. At low levels, inaccurate level measurements can result in “starving” the distribution system, causing damage to equipment.
Two other options exist for stratifying slurries that foam. The first uses a combination single-feed only dip tube and dispense head in one drum opening, with a mechanical mixer in the other drum opening, to provide the initial recirculation. To minimize foaming, it is important to avoid splashing and air entrainment. The mixer speed needs to be controlled and the mixer must remain below the level that can form a vortex in the slurry drum. The mixer needs to be shut off before the slurry level reaches the impeller blades. The second method would be to use offline mechanical agitation to pre-mix the drum and then later connect it in a feed-only configuration.

The second main category of slurries has abrasives that actually settle over time during their shelf life and form a layer on the bottom of the shipping container. This accumulation varies widely in its consistency, from a soft, fluffy and easily re-dispersed mass to a sticky or silt-like accumulation that can be quite difficult to re-suspend. The abrasive and chemistry of the slurry determine which form this buildup will take, and the methods required to handle it vary. For soft settling, the slurry can typically be handled like a stratifying slurry, although extra recirculation time over and above a single turnover may be necessary. For the sticky, silt-like accumulation, more aggressive recirculation is required to ensure the abrasives are all thoroughly re-homogenized into the slurry before use.
Mechanical Agitation

To re-homogenize a heavy settling slurry in a reasonable amount of time, a mechanical agitator is required. Normally, the types of slurry that settle are not shear sensitive, so an aggressive mixer speed and prop type can be used. Typically a speed of 1500+ rpm and an A310 “turbine” style prop are recommended. The A310 prop’s design provides a very axial, high-speed flow to the slurry, pushing down and across the bottom of the shipping container to effectively move and break up the abrasive. Often the amount of mixing required will be substantially increased when older slurries are used, so minimizing the shelf life of these slurries is recommended, if possible.
The normal container connection to the SDS with settling slurries has one opening dedicated to the mixer shaft and the other to the dip tube for slurry removal and possible recirculation. An important point to remember is not to use the single feed and return if the slurry is prone to foaming. Some slurries can generate prodigious amounts of foam from the splashing caused by even 4 to 5 inches of drop from the return side of a feed/return dispense head to the solution surface. Foaming increases in severity as the container empties and the returning slurry has progressively longer and longer drops to solution level. For this reason, it is strongly advisable to avoid using a feed/return design dispense head and dip tube for foaming slurries.

Because of this limitation, the only viable methods of connecting a container to the SDS are to use a single feed only dispense head/dip tube in one opening and the mixer in the other, or to switch to offline mechanical mixing and use separate feed and return connections in the two openings. Please note, it is also possible in some extreme cases with extremely heavy or unstable abrasives that pump recirculation will **not** be sufficient to keep the abrasives from re-stratifying and settling, so the latter option may not be viable. In this situation, abrasive settling in the transfer lines will also be a concern, so mixing and transferring the entire container all at once into a holding tank with continuous mechanical agitation may be required.

**Particle Size Issues**

Another issue that might be encountered with some slurries is a change in the measured particle size distribution (PSD) or increases in large particle counts (LPCs) of aged slurry after it has been re-homogenized. This can result from the macroscopic breakup of the agglomerated abrasive that does not completely drive the microscopic dissociation all the way back to individual primary particles. In cases where the pre-mixing was incomplete, this can result in premature filter plugging as the agglomerates are captured either in the SDS loop or at POU. In most cases additional shear in the SDS will continue to drive the LPCs down over time, but increasing the pre-mixing in the shipping container is recommended to avoid this problem altogether. It is rare this will translate into polishing defects, as the POU filters should be sized appropriately to protect against this; however, it can cause operational problems and maintenance headaches. Normally, mixing and handling recommendations are made with a recommended time that is very conservative in order to overshoot the minimum requirement by a comfortable margin, but this also may result in a slurry’s recommended shelf life being restricted to 6 month or even as low as 3 months.
With each new generation of semiconductor polishing requiring ever more stringent performance with lower defect tolerance, it is critical to ensure slurry is handled properly to realize the full benefits of its designed-in performance. With the increasing slurry formulation complexity necessary to meet these requirements, it is crucial slurry be handled properly throughout the SDS to provide a stable, repeatable slurry to the polisher. If the slurry isn't properly pre-mixed prior to removal from the shipping container, this already difficult and challenging process becomes almost impossible, so extra care and attention to mixing and handling is essential.

**CABOT MICROELECTRONICS’ GOOD PRACTICE**

- CMC conducts foaming evaluations for all new CMP slurries to determine the level and persistency of foaming.
- We carefully consider the absolute need for foam-inducing organic components in every slurry formulation.
- We provide detailed handling procedures in CMP slurry mixing and handling documents to minimize foaming.

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*Mixing & Handling informational videos and infographics can be found on Cabot Microelectronics’ corporate website at the following url:*