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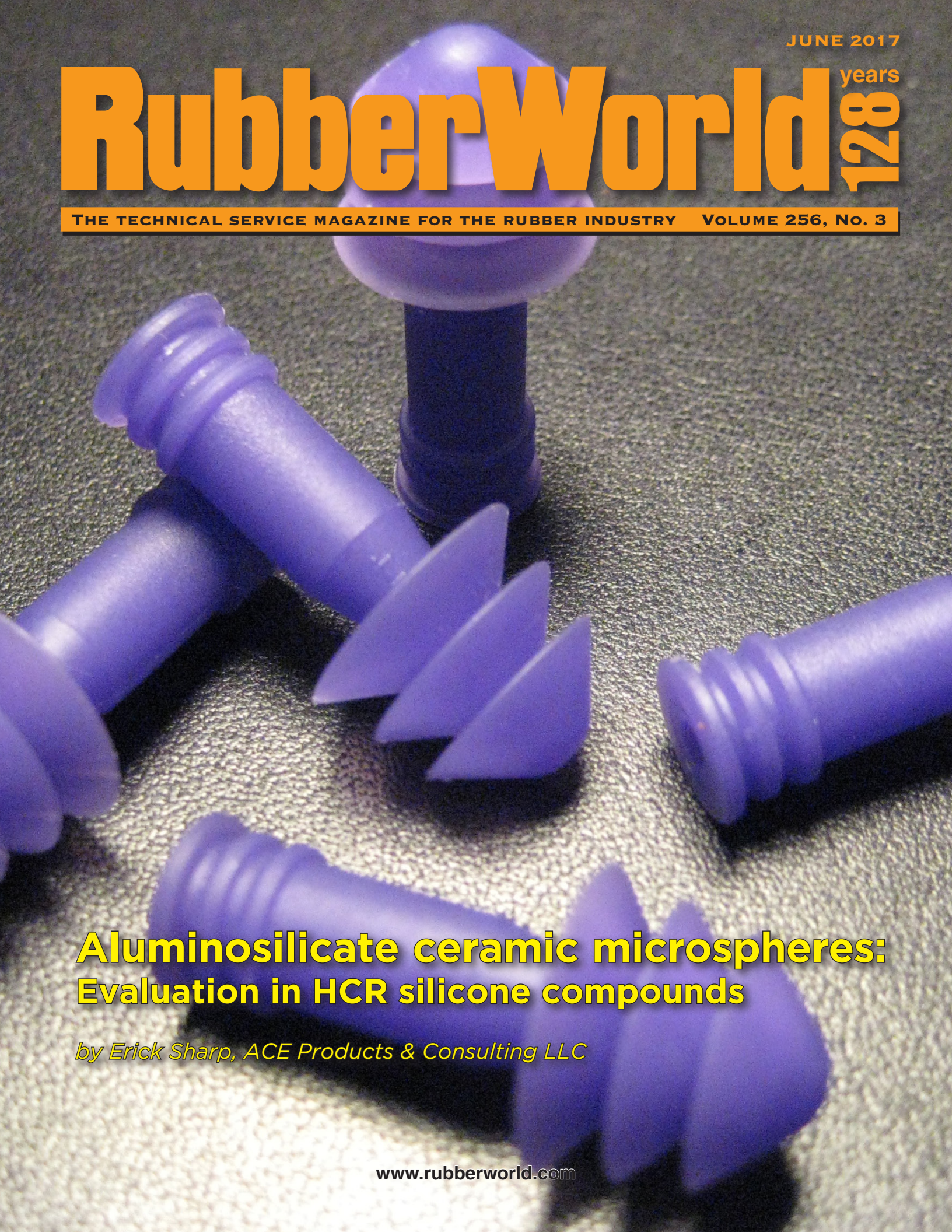

## Aluminosilicate ceramic microspheres: Evaluation in HCR silicone compounds

*by Erick Sharp, ACE Products & Consulting LLC*

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# Evaluating aluminosilicate ceramic microspheres in HCR silicone compounds

*by Erick Sharp, ACE Products & Consulting LLC*

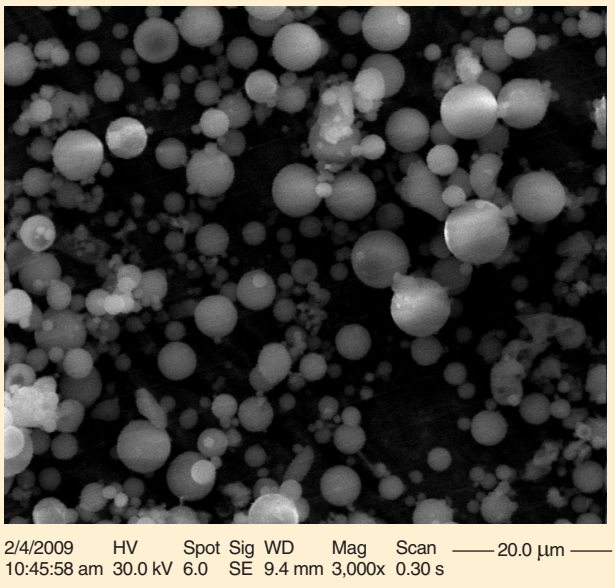
Dispersix is a growing family of hybrid inorganic-organic microspheres that deliver breakthrough gains in productivity for silica-reinforced HCR compounds. Dispersix products are optimized for HCR silicone cure chemistry, and are suitable for opaque, non-white silicone compounds. Dispersix ASC provides value-added property gains without significant changes in hardness, modulus, scorch and Mooney viscosity. Dispersix is manufactured by Spherix Mineral Products (a SEFA Group company).

**Raw material source**

Dispersix aluminosilicate ceramic microspheres are reclaimed and processed through a high temperature staged turbulent air reaction (figure 1). This patented process was pioneered by the SEFA Group. The pure microspheres are then size classified to a D50 of 3 microns (figure 2). The microspheres for the Dispersix line are functionalized by surface treatments engineered for performance enhancements in HCR silicone.

**Figure 1 - the Sefa Group's STAR (staged turbulent air reaction) plant in Winyah, SC**

**Figure 2 - microscopy of aluminosilicate ceramic microspheres**




**Product performance**

Dispersix has been shown to provide processing and dispersion advantages in the mixing of HCR silicone. This is generated from a mechanical "ball bearing effect" using the microspheres (figure 3). It also provides downstream processing advantages in molding and extrusion processes. These processing advantages are provided without any negative impact on physical properties of the compound. Often, Dispersix has provided a positive impact on properties such as tear and compression set. Dispersix also helps to reduce fly loss of silica materials.

**Recommended usage levels**

The recommended starting point in an HCR silicone formulation is 5 phr. This would be on top of an existing formulation and not in place of a filler or other material. The optimal loading generally ranges between the 5 phr and 10 phr level. Loadings less than 5 phr tend not to show any changes. Once you get above 10 phr on top of a formulation, you start to battle with viscosity, and specific gravity increases.

**Description of experiment**

Two comparison studies were performed to measure any advantages that Dispersix might provide. The primary function of Dispersix is to help with filler incorporation and dispersion. Therefore, both formulations selected require filler loadings.

**Formulations and raw materials**

*Formulation A*

The first formulation selected for comparison is a 70 durometer general purpose molding compound (table 1). This compound contains both precipitated silica, Promisil, and a ground quartz, Min-U-Sil 10. Both provide a different shear dynamic in the mixing process.

**Figure 3 -visual of ball bearing effect created by the microspheres**

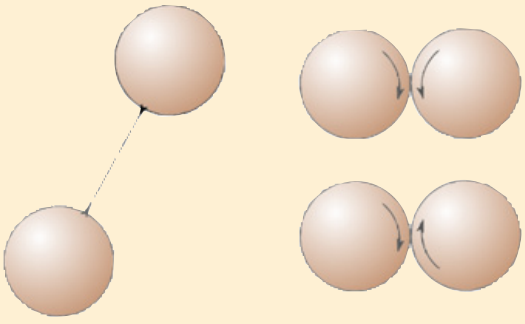


**Table 1 - formulation A**

| *Raw material* | *Raw material description* | *phr* |
|---|---|---|
| Xiameter RBB-2000-35 | 35 durometer silicone base | 50 |
| Xiameter RBG-0901 | Silicone gum | 50 |
| Promisil | Precipitated silica | 20 |
| Min-U-Sil 10 | Ground quartz | 63 |
| ACE-SD-DBPH | DBPH peroxide 50% (silicone) | 1 |
| Kri-Color black 1206 | Black pigment | 0.5 |
| *Dispersix addition for comparison batch* | | |
| Dispersix 4PC-2H | Aluminosilicate ceramic (ASC) microspheres | 5 |

**Table 2 - formulation B**

| *Raw material* | *Raw material description* | *phr* |
|---|---|---|
| Cenusil 40 | 40 durometer HTV base | 100 |
| HiSil 233 | Precipitated silica | 30 |
| ACE-SD-DBPH | DBPH peroxide 50% (silicone) | 1.5 |
| Kri-Color black 1206 | Black pigment | 0.5 |
| *Dispersix addition for comparison batch* | | |
| Dispersix 4PC-2H | Aluminosilicate ceramic (ASC) microspheres | 5 |

The precipitated silica has a smaller particle size, ranging from 14 to 15 d50 µm, but high surface area, 130 to 150 BET ($m^2/g$). Additionally, it has a cluster or chain particle structure. These characteristics allow it to build structure when incorporated into HCR silicone. The high surface area provides more area for the polymer to wet out. The smaller particle size and chain structure results in agglomeration of the individual particles.

The objective to getting good dispersion is to break down these agglomerates as much as possible during the mixing process and fully incorporate them into the silicone. Large agglomerates are difficult to disperse into silicone.

The ground quartz has a larger particle size, less surface area, and is platy in structure. The ground quartz also has a higher specific gravity, 2.65 ($g/cm^3$) versus 2.0 ($g/cm^3$) average for precipitated silica. The heaviness and larger particle size typically results in the ground quartz mixing into the polymer quicker than precipitated silica. The platy structure and minimal surface area, however, make it difficult to get the quartz fully incorporated into the silicone polymer. Poor incorporation of larger ground mineral fillers is often visible in a compound or a finished product. The darker the compound or product, the more visible the white filler agglomerates become.

A formulation with both types of fillers present was selected to create a larger variety of fillers for the Dispersix to break down (table 1).

*Formulation B*

The second formulation selected is an 80 durometer molding compound (table 2). This formulation contains a higher loading of the reinforcing precipitated silica. Generally, it is difficult to incorporate higher loadings of reinforcing silica and maintain processability. Processing 80 durometer HCR silicone compounds can be challenging, as well. This formulation is more simplistic in using only one polymer, one filler, a catalyst, pigment and the Dispersix (excluding the control batch).

**Variables**

The only designed variable in this experiment was the presence of the Dispersix. A possible advantage of the Dispersix was improved mixing and cycle times. To capture the potential cycle time improvement, the batches were mixed to temperature versus time. This allowed the study to compare the time to mass the batches. All other mixing and testing procedures were kept constant.

**Measured values**

Based upon the potential improvements claimed with Dispersix, the cycle time, rheology and standard physical property data were measured.

Each batch was timed from the start of the first addition in the mixer to the prompting of the mixer tilt discharge. The mixer continuously ran throughout the entire cycle. The ram was raised for additional charges, while the mixer continued to run. All charges were pre-weighed to allow for quick additions to the mixer.

Formulation B was mill mixed. The mill ran continuously as the filler was folded in. The time started with the first addition to the two-roll mill and ended when it was stripped off.

Equal RPM settings, process water temperatures and procedures were used in each comparison.

All rheology was done on an MDR 2000-P. Tests were run at 350°F for six minutes and at a 0.5° arc. Reported rheology measurements were ML, MH, Ts2, Tc50 and Tc90.

Test slabs and buttons for physical testing were cured at 355°F for five minutes. Tear testing was done using a type B die. Compression set buttons were baked at 215°C for 22 hours. They were tested using the plied method B.

**Processing method**

Formulation A was mixed on a 1.2 liter tilt body lab mixer (Mix-Max, Taiwan). Each batch started with the mixer at 18°C and dumped at 25°C. The following addition order was used (table 3). Once dumped out of the mixer, each batch was put on the mill for ten passes.

Formulation B was mixed on a 6" x 13" two-roll lab mill. Each batch started with the mill at 22°C. Once all precipitated silica was incorporated, the batch was given ten additional passes on the mill and stripped off.

**Processing comparison**

*Mixing cycle time*

The formulation A control batch mixing time was five minutes and ten seconds. The batch with the Dispersix 4PC-2H had a

**Table 3 - formulation A mix procedure**

| Stage | |
|---|---|
| 1. | Add base, gum, pigment and peroxide, and blend 30 seconds |
| 2. | Add ½ precipitated silica, Dispersix (excluded in control) |
| 3. | Add remaining precipitated silica |
| 4. | Add ½ ground quartz |
| 5. | Add remaining ground quartz |

total mix time of four minutes and 28 seconds. The Dispersix was added with the first filler addition (stage 2). That stage took longer on the Dispersix batch because of the added amount of filler going in at one time. Stage 3 was comparable to the control. Once the addition of the ground quartz started, the cycle time improvements started presenting themselves. This could be a combination of the overall high filler loading by that point and/or the type of filler. It is expected that the benefits of Dispersix increase, the higher the filler loading. As the filler loading continues to build, so will the differential improvement on cycle times (table 4). The forumation B control batch mixed in 15 minutes and 40 seconds. The batch with the Dispersix 4PC-2H mixed in 14 minutes and 15 seconds.

*Filler incorporation*

Both the control and the Dispersix batch for formulation A mixed the filler in without much issue. The control batch did have white agglomerate specs visible to the naked eye when placed on the mill. The Dispersix batch did not exhibit these white agglomerations. The mill did not seem to break down the white agglomerations.

A small sample from the control was added back onto the mill with a tight nip setting. At a tight nip setting, the white agglomerations did break down. This small sample was to assist with understanding the processing effects and not used in testing.

The control batch for formulation B had a tough time accepting all the precipitated silica. It began to crumble towards the end of the batch. The control batch was very dry and flaky at the end.

In the Dispersix batch, the Dispersix 4PC-2H was added before the start of the precipitated silica additions. The Dispersix batch did not crumble to the pan and was able to constantly stay banded to the mill. The precipitated silica folded in quicker and in larger quantities on the Dispersix batch.

Open mill mixing of formulation B provided a good visual on how the Dispersix affected fly loss. The control batch had a lot of airborne precipitated silica above the mill and leading into the dust collector hood. This is a fairly standard result when mill mixing precipitated silica. Given new respiratory regulations, the use of and processing of silica is a growing concern in the industry. The Dispersix batch did not have the visible dust cloud of precipitated silica above the mill. The silica would ride along the nip and fold in at a regular pace with limited air pockets.

The formulation B control batch required sweeping the mill pan and re-adding the precipitated silica six times. This is silica that was added on the mill, but did not incorporate in time before making its way through to the mill pan. The Dispersix batch only required three mill pan sweeps. The silica incorporated into the silicone quicker, which reduced the amount falling to the mill pan.

*Milling*

The control for formulation A was brittle when rolling it on the mill. During the first four passes, parts of the batch would fall to the mill pan. After ten passes on the mill, the edges were still jagged.

The Dispersix batch for formulation A had smoother edges by the end of the ten passes. At no point did any of the material fall to the mill pan.

After being stripped from the mill, the Dispersix batch had a glossy look to the surface, while the control displayed a matte finish.

**Testing comparison**

*Rheology (formulation A)*

There were no significant differences in the rheology comparisons between the control and the Dispersix batch. While the Dispersix expects to provide processing improvements, it is a mechanical function rather than a viscosity modification. This is likely why there was a slight increase in the ML value on the Dispersix batch. The increase would be caused by the increased gravity of the material due to the 5 phr addition of Dispersix on top of the formulation.

The Dispersix caused negligible effect on the initial scorch rate of the compound. The Tc90 was roughly 20% faster on the Dispersix batch than on the control batch. I expect this to be a result of improved peroxide dispersion.

The differential on the MH value was within the standard margin of error (table 5).

*Rheology (formulation B)*

There was an increase in the ML value of formulation B similar to formulation A. Even though the Dispersix compound processed as though it had a lower viscosity, it tested out with a

**Table 4 - formulation A mixing times**

| *Stage* | *Control* | *Dispersix 4PC-2H* |
|---|---|---|
| 1 | 30 seconds | 30 seconds |
| 2 | 60 seconds | 68 seconds |
| 3 | 60 seconds | 60 seconds |
| 4 | 70 seconds | 45 seconds |
| 5 | 90 seconds | 65 seconds |
| Total | 5 minutes 10 seconds | 4 minutes 28 seconds |

**Table 5 - control vs. Dispersix rheology (formulation A)**

| *Test* | *Control (formulation A)* | *Dispersix 4PC-2H (formulation A)* |
|---|---|---|
| ML | 1.80 | 1.87 |
| Ts2 | 0.38 | 0.39 |
| Tc50 | 0.63 | 0.63 |
| Tc90 | 1.51 | 1.21 |
| MH | 20.05 | 19.95 |

**Table 6 - control vs. Dispersix rheology (formulation B)**

| *Test* | *Control (formulation B)* | *Dispersix 4PC-2H (formulation B)* |
|---|---|---|
| ML | 3.16 | 3.37 |
| Ts2 | 0.37 | 0.38 |
| Tc50 | 0.65 | 0.67 |
| Tc90 | 1.44 | 1.41 |
| MH | 23.57 | 24.50 |

higher ML. Also, as with formulation A, the initial scorch data showed only a minor difference between the two compounds. The Dispersix batch did have a slightly higher MH value (table 6).

*Physical testing (formulation A)*

There was no change in the durometer results between the two batches. There was a minor increase in the specific gravity of the Dispersix batch. The Dispersix 4PC-2H has a specific gravity of 2.3 kg/m$^3$. This value is higher than the specific gravity of the control compound. Since 5 phr of the higher gravity Dispersix material was added, a slight increase in the specific gravity of the compound is to be expected.

There were minimal differences in the tensile and elongation results. The 200% modulus result was higher in the Dispersix batch.

The Dispersix batch provided significant improvement in the tear die B results, providing nearly a 30% improved value. This is due to improved dispersion of the material and the added bonds from the treated Dispersix. Combined, this improved the overall crosslink density of the compound, leading to a 10% comparative improvement in compression set (table 7).

*Formulation B*

There was a three-point increase in durometer in the Dispersix batch versus the control. Additionally, the specific gravity did not increase as much as expected when adding 5 phr of the 2.3 gravity Dispersix to the formulation. I believe the Dispersix batch incorporated more of the precipitated silica, which reduced the total amount of fly loss. The higher amount of incorporated precipitated silica resulted in a higher durometer and helped balance out the specific gravity. Given this formulation was open mill mixed, the possibility for high amounts of fly loss was greater.

**Table 7 - control vs. Dispersix physical properties (formulation A)**

| *Test* | *Control (formulation A)* | *Dispersix 4PC-2H (formulation A)* |
|---|---|---|
| Durometer A | 71 | *71* |
| Specific gravity (kg/m$^3$) | 1.409 | *1.430* |
| Tensile (psi) | 760.5 | *765.3* |
| Elongation (%) | 306 | *297.5* |
| Modulus 100% (psi) | 296.3 | *293.2* |
| Modulus 200% (psi) | 570.5 | *781.2* |
| Tear die B (ppi) | 55.75 | *71.15* |
| Compression set (%) | 14.1 | *12.7* |

**Table 8 - control vs. Dispersix physical properties (formulation B)**

| *Test* | *Control (formulation B)* | *Dispersix 4PC-2H (formulation B)* |
|---|---|---|
| Durometer A | 79 | *82* |
| Specific gravity (kg/m$^3$) | 1.193 | *1.205* |
| Tensile (psi) | 1,007.1 | *1,014.6* |
| Elongation (%) | 288 | *291.1* |
| Modulus 100% (psi) | 393.3 | *394.9* |
| Modulus 200% (psi) | 678.0 | *682.9* |
| Tear die B (ppi) | 47.11 | *54.17* |
| Compression set (%) | 46.7 | *38.5* |

Similar to the formulation A results, there were minimal differences in the tensile and elongation. Modulus at 100% and 200% showed minimal differences between the two batches. The compound with the Dispersix 4PC-2H did yield a 15% improvement in tear results.

Compression set improved nearly 18% on the Dispersix batch compared to the control batch (table 8).

**Conclusion**

The Dispersix 4PC-2H did provide mixing cycle time benefits, as expected. The mixing improvements also resulted in visibly better dispersion of the filler in the compound.

Processing of compounds on the mill was improved with the addition of the Dispersix. This was with both the mill mixing and sheeting out of the tilt mixer batches. The Dispersix did reduce the amount of fly loss on the mill mixed compound.

Rheology data were not impacted much with the addition of the Dispersix. The Tc90 showed minor acceleration, which could have been provided by the improved dispersion of the peroxides. While the Dispersix does provide processing advantages, mechanically that does not result in a lower viscosity or ML value.

Dispersix has a gravity of 2.33 kg/m$^3$. The recommended starting usage level is 5 phr on top of the formulation. If the formulation has a specific gravity lower then 2.33 kg/m$^3$, one can expect an increase in the final gravity.

Tensile and elongation were not affected by the addition of the Dispersix 4PC-2H to either formulation. Spherix Mineral Products' goal was to, at a minimum, maintain physical properties while providing the processing advantages. They achieved that objective with these two properties.

There was a substantial improvement in tear properties in both formulations. This is a result of improved crosslink density in the Dispersix compound caused by improved dispersion and the additional sites provided by the treated material. While Dispersix's primary function is a process aid, it is possible it could be used specifically to enhance tear properties.

The Dispersix did provide improvement in compression set in both formulations. The theory for this correlates with that of the tear properties improvements. It is possible that Dispersix could be used to help compounds meet stringent compression set specifications.

Overall, the Dispersix did behave as expected by the author at the beginning of this experimentation.