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Technical Paper

3M™ Ceramic Microspheres in Architectural Paint

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Introduction

3M™ Ceramic Microspheres are functional additives used to enhance performance in a variety of coatings systems, including in architectural paint. 3M ceramic microspheres are dense, alkali aluminosilicate ceramic particles with predominately spherical shapes. Because of their white color and refractive index is near to that of many coatings resins, the ceramic microspheres can to be used in a wide variety of coatings applications where appearance is important. In addition, their high hardness and crush strength improve the durability of coatings. The basic properties of all grades of 3M ceramic microspheres are listed in Table 1.

Table 1: Typical Physical Properties of 3M™ Ceramic Microspheres

Properties	Value	Test Method
True Density	2.4 g/cc	
Bulk Density	1.5 g/cc	
Whiteness ("L" value in Hunter L, a, b scale)	95+	ASTM D2244
Crush Strength	4,200 kg/cm^2	
pH	9.0–12.0	ASTM E70
Hardness	6	Mohs Scale
Softening Point	1020°C	
Refractive Index	1.53	Becke Line
Dielectric Constant	3.19	
UV Light Transmission	UV Transparent down to 250 nm	
Thermal Conductivity	2.3 W/mK	

Architectural paint is the coating system in which 3M ceramic microspheres are used most. In order to provide formulators with flexibility to optimize both durability and paint appearance properties, 3M ceramic microspheres are offered in three grades, listed in Table 2. The primary difference between the grades is the effective top particle size. In this report, the durability properties – including scrubbability and burnish – of paints made with these materials are studied as a function of ceramic microsphere loading. In general, more microspheres that have a larger top size promote durability. The trade-offs for this durability are reduced gloss and rougher dried paint.

Table 2: Grades of 3M™ Ceramic Microspheres (Not for specification purposes)

Product Grade	Target Crush Strength (90% Survival) (kg/cm^2)	True Density (g/cc)	Median Particle Size (microns)	Effective Top Size (microns)
W-210	>4,200	2.4	3	12
W-410	>4,200	2.4	4	24
W-610	>4,200	2.4	10	40

Experimental Procedure

The paints in this study were made and tested in the 3M Advanced Materials Division US Paints and Coatings Application Development Lab (St. Paul, MN). The formulation was developed in house to represent current low VOC architectural paints in both formulation space and properties. The details of this formulation, modified with various levels of 3M ceramic microspheres, are given below, followed by the properties of the different paints.

Materials

The materials used in these paints and their relative amounts can be found in Table 2.1, along with a brief description of the composition of the ingredient. In order to formulate these paints consistently for each loading of 3M ceramic microspheres, the volume ratio of Minex® to Iceberg® was held to 1.5, and the ratio of Minex® to Duramite® was held at 1.0. These three ingredients were reduced compared to the initial formulation in a total volume equal to that of the 3M ceramic microspheres' volume in the new formulation. In this way, we are comparing the effect of 3M ceramic microspheres in paint to the effect of these three common paint ingredients.

Table 2.1: Ingredients and Formulation Properties

Material	Ingredient	Density (lbs/gal)	Volume %			
			Formula 1 (no ceramic microspheres)	Formula 2 (2.5 vol% CM)	Formula 3 (5 vol% CM)	Formula 4 (10 vol% CM)
Grind						
Natrosol™ 250 MHR	Cellulosic thickener	11.5	0.23	0.31	0.23	0.31
Water	Water	8.34	29.58	29.31	29.72	29.34
Tamol™ 851	Dispersant	9.9	1.07	1.05	1.06	1.05
Potassium tripolyphosphate	Buffer	21.15	0.08	0.07	0.07	0.07
Triton™ CF-10	Surfactant	8.97	0.26	0.26	0.26	0.26
Rhodaline® 643	Degasser	7.09	0.14	0.15	0.15	0.15
Skane™ M8	Biocide	8.6	0.27	0.26	0.42	0.26
Ti-Pure® R-706	TiO_2	33.4	5.53	5.50	5.49	5.50
Eagle Zinc 417	Zinc oxide	46.7	0.57	0.56	0.56	0.56
Minex® 4	Nephyline syenite	21.7	4.50	3.51	2.57	0.66
Iceberg®	Calcined kaolin clay	21.93	2.97	2.32	1.70	0.43
Duramite®	Calcium carbonate	22.7	4.30	3.52	2.45	0.66
3M™ Ceramic Microspheres	Ceramic microspheres	20	0.00	2.54	5.08	10.16
Attagel® 50	Clay	19.7	0.27	0.26	0.27	0.26
Letdown						
Rhoplex™ VSR-50	100% acrylic binder	8.8	47.08	47.20	46.81	47.13
Rhodaline® 643	Degasser	7.09	0.53	0.53	0.53	0.53
Texanol™	Coalescent	7.92	1.26	1.25	1.25	1.25
Propylene glycol	Coalescent	8.63	0.79	0.79	0.79	0.79
Acrysol™ NPR 2020	Non-ionic urethane rheology modifier	8.67	0.59	0.62	0.61	0.61
Final Paint: Total Volume (%)			100.00	100.00	100.00	100.00

Paint Preparation

The paints are made in two steps: the grind and the letdown. In the first step, the grind, the water, dispersant, buffer, surfactant and degasser are mixed together at a low speed (700 rpm) with a 1" Cowles blade used for grinding in an 800 mL beaker. The cellulosic thickener and liquid ingredients are added to the water and dissolved thoroughly. Next, dry powders, including titanium dioxide, zinc oxide, calcium carbonate, nephyline syenite, calcined kaolin clay, 3M™ Ceramic Microspheres and clay, are mixed together with a wooden stick and added slowly to the water solution. As the powders are added, the speed of the mixer is increased to pull the powders into the solution efficiently as the viscosity increases. Once all the powders are added and wet, the Dispermat® mixer is turned up to a speed of 3600 rpm. This is the grind stage, and it continues for 20 minutes. At the end of the stage, two samples are taken for the Hegman gage. This gage quantifies the fineness of grind and also allows a qualitative assessment of the presence or absence of agglomerations. The plate is read according to ASTM D1210.

While the grind is being mixed, the letdown mixture is weighed and mixed on a three-paddle Stir-Pak™ mixer at low speed. The ingredients in the letdown include the acrylic binder and the two coalescents. This mixture is stirred for at least 10 minutes.

Once the Hegman grind number is measured, the grind mixture is added to the letdown, and the speed on the Stir-Pak™ mixer is increased to form a shallow vortex. The letdown and grind are mixed for at least 10 minutes. Then, the polyurethane thickener is added until a viscosity of 95-100 Krebs units is reached. Finally, the degasser is added and mixed for at least 10 minutes. The finished paint is allowed to sit for at least 20 minutes, and the viscosity is measured.

Paint Testing

Scrub and burnish panels are drawn down with a 7 mm draw down bar on Leneta PVC scrub panels in duplicate for each test. These panels are allowed to dry for at least seven days in the horizontal position prior to testing.

Opacity is measured by a contrast ratio method in which a ColorFlex™ EZ Spectrophotomer is used to determine the Y, or lightness, color value on the black and white portions of the 3B Leneta chart. The opacity is calculated according to the following equation:

$$\textit{Opacity (y)} = \frac{\textit{Black backing (y)}}{\textit{White backing (y)}} \times 100$$

Scrub testing is conducted according to ASTM D2486 Test Method A with the following modifications. A shim of 0.5 mm is used rather than 0.25 mm. A non-scratch Scotch-Brite™ Pad is attached to the bottom of the brush, and standard abrasive scrubbing media is used. This test was conducted with an Elcometer™ (Model 1720) abrasion tester. The numbers reported are an average of four tests run on two panels with two tests per panel.

Burnish resistance testing is conducted according to ASTM D6735 with the following modifications. The gauze-wrapped wooden block is weighted with a 600 g weight. The block is passed over the painted surface 100 times. Then, the gloss at 60° and 85° is measured and recorded from three places on the panel. The gloss method used as part of the burnish test is conducted according to ASTM D523. The change in gloss is calculated by the following equation:

$$\textit{\% change} = \frac{\textit{final } 85° \textit{ gloss} - \textit{initial } 85° \textit{ gloss}}{\textit{initial } 85° \textit{ gloss}}$$

Results and Discussion

The results for this study give a comparison of the three grades of 3M™ Ceramic Microspheres in a flat architectural paint formulation compared to a control formulation in which the volume occupied by microspheres is filled with a mixture of Minex®, Duramite® and calcined kaolin clay. This control paint is taken to be 0% microspheres on the following graphs.

Hegman Gage

Significant differences between the grind mixtures of the three grades are apparent at the grind stage. In Figure 3.1, the Hegman gage number is plotted versus the volume fraction of ceramic microspheres in the film for the three grades and the control sample. The grind number increases as 3M ceramic microspheres W-210 and W-410 are added to the grind and Minex®, Duramite® and calcined kaolin clay are removed. Adding 3M ceramic microspheres W-610 to the grind mixture slightly decreases the Hegman grind number.

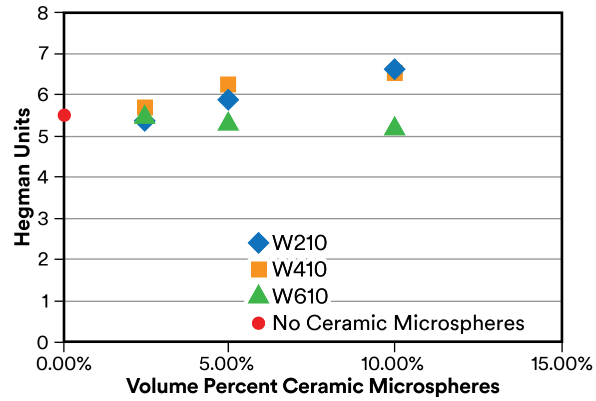

Figure 3.1: Fineness of Grind

These trends may be understood by considering the particle size of the materials that the 3M ceramic microspheres replace. The Duramite®[1] and the Minex®[2] both have larger median particle sizes than grades W-210 and W-410, but smaller median particle sizes than W-610. Thus, the Hegman grind number increases when W-210 and W-410 are substituted into the formulation because large particles are removed. By contrast, W-610 has a slightly larger median particle size on average than the Minex® and Duramite® particles it replaces. Thus, the Hegman number decreases as W-610 is added. In addition to the relative particle sizes of the fillers in this formulation, these results show that all grades of 3M ceramic microspheres are dispersible to a Hegman grind number greater than 5 and do not contain large numbers of large particles or agglomerates.

Gloss

Gloss is a difficult property to predict for complex formulations such as paint. Often, a formulation will have to be adjusted when new materials are added to correct the gloss. For consumers, gloss, along with color, is one of the basic properties considered when buying paint. Glossier paint is easier to clean but does not hide imperfections in the walls. Flat paint, on the other hand, is more forgiving of surface preparation and painting technique but is not as easy to clean. In Figure 3.3, the 85° gloss for these ten paints is plotted versus volume percent of 3M ceramic microspheres in the formulation. Much like for the Hegman grind numbers, the trends in gloss with increasing ceramic microsphere content depend on the grade of the ceramic microsphere. Adding 3M ceramic microspheres W-210 to this formulation increases the gloss. Adding grade W-410 does not change the gloss. Adding grade W-610 to the formulation decreases the gloss.

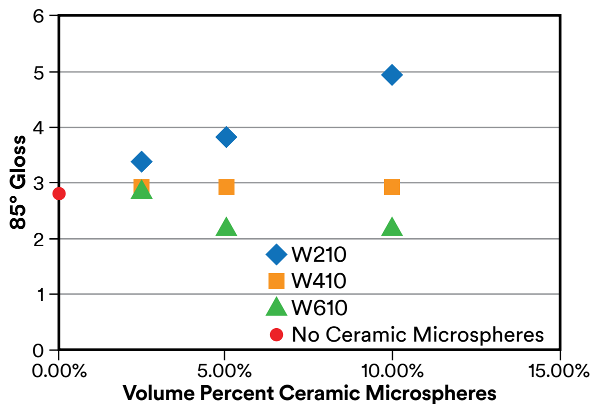

Figure 3.3: Gloss of dried paint films containing 3M™ Ceramic Microspheres

These trends in the gloss of the dried paint film can again be understood by considering the formulation strategy. Replacing large Duramite® and Minex® particles with smaller W-210 microspheres increases the gloss because fewer particles stick through the surface of the film to scatter light. Conversely, grade W-610 decreases gloss because the particles are larger, on average, than the particles they are replacing, so the surface is rougher and less glossy. In this formulation, grade W-410 does not change the gloss appreciably.

The ability of 3M™ Ceramic Microspheres to change the gloss three points at a 10% loading is significant to both the paint manufacturer and the consumer. For the paint manufacturer, the ceramic microsphere product line allows ease of formulation because the different grades of microspheres can be used to control the gloss at the same loading without the need to reformulate extensively. For the consumer, this means that the additional benefits of 3M ceramic microspheres can be gained in paints with different gloss levels.

Burnish Resistance

Burnish is the change in gloss after the panel is rubbed with a cotton cloth. This test is designed to simulate furniture rubbing against a wall, which often leaves a glossy mark. Burnish resistance is especially important for flat paint with high filler loadings, for which the filler particles on the surface are easily removed, increasing the gloss. A lower burnish number is desired. In Figure 3.4 the results of this test are shown. The durability of formulations with 3M ceramic microspheres is apparent, with all formulations containing ceramic microspheres having significantly lower burnish than the formulation without ceramic microspheres.

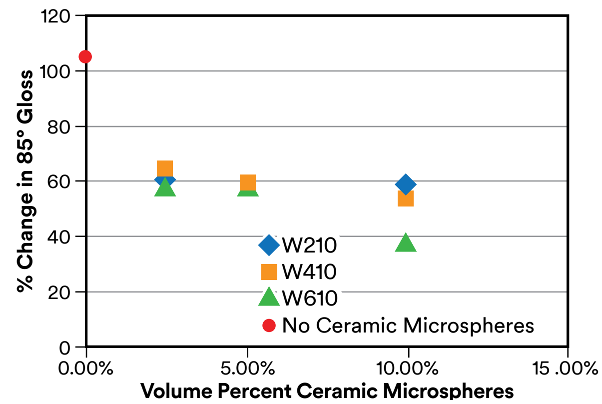

Figure 3.4: Burnish results after 100 passes

These burnish results show the ability of 3M ceramic microspheres to improve the durability of paint. The hard, round ceramic microspheres provide a tough paint film that resists removal of filler particles better than the control formulation.

Scrub Resistance

Scrub resistance is the measure of a paint film's strength against abrasion. For end-use customers, this relates to the wear and tear that paint sees when it is abraded, especially on areas such as external corners. A lower number of scrub passes until paint failure indicates weaker paint. Figure 3.5 shows the scrub resistance for the formulations in this study as a function of ceramic microsphere loading. A higher loading of 3M ceramic microspheres W-610 yields higher scrubs. For grades W-210 and W-410, 5 vol% is an optimal level. Interestingly, for both W-210 and W-610, the lowest volume percent is lower than the control formulation.

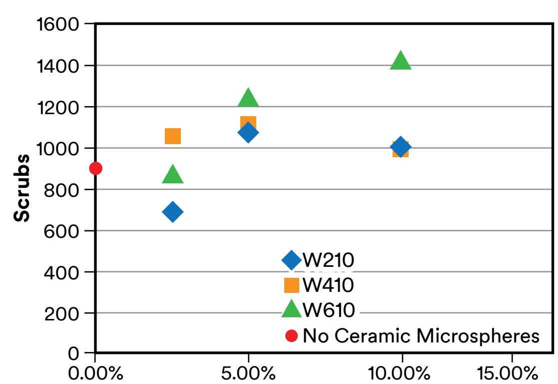

Figure 3.5: Scrub resistance

These results demonstrate the importance of optimizing the formulation. More is not always better. For grade W-210, adding a small amount to the formulation by removing some Minex®, Iceberg®, and Duramite® decreases the strength of the film significantly. This is most likely because the median size of the W-210 particles is smaller on average than the Duramite® and Minex®. Thus, the small amount of round particles does not substitute for the big, irregular particles removed. At this time, the maximum observed at 5 vol% for W-210 and W-410 is not fully understood. It most likely relates to the relative sizes of the ceramic microspheres and other fillers and how they pack.

These results emphasize the importance of doing a ladder study to optimize the formulation for a particular grade of ceramic microspheres.

Hand Feel

For architectural paints, the feel of paint to a bare hand is an important, although qualitative parameter. In a qualitative, blind comparison, in which people felt the surfaces of the film with their fingertips, the 10 vol% loading samples from all three grades of 3M™ Ceramic Microspheres were consistently ranked paints in order of smoothest (W-210) to smooth (W-410) to less smooth (W-610).

Once again, the reason for the differences in a paint property can be attributed to the different sizes of the grades of ceramic microspheres. The paint films here are deposited with a 7 mm clearance applicator leaving dried films of approximately 50 µm. The effective top-size for 3M ceramic microspheres W-610 is 40 µm. This is a significant fraction of the film thickness. Even the 10 µm median size for grade W-610 is a large fraction of the film thickness. The "feel" of paint films with grade W-610 is uniformly rough, rather than rough in certain distinct areas. This suggests that the particles are well distributed and contribute to the roughness of the film's surface.

Summary and Conclusions

In this study we have differentiated the three grades of 3M ceramic microspheres in flat architectural paints. Each grade contributes certain benefits and certain drawbacks to the overall paint formulation. These are summarized in Table 4.1 from the data presented above.

In general, more and larger microspheres provide better durability as measured by burnish and scrub resistance. However, larger particles can reduce the gloss and give a rougher "hand feel" to the dried paint. There are also exceptions to the more is better recommendation as evidenced by the optimum point for grade W-410 at 5%. All of these observations are based on the formulation here where specific ratios of three different low-cost fillers are replaced by ceramic microspheres. This formulation is a good example of the performance improvements afforded by ceramic microspheres in architectural paint.

Table 4.1: Summary Comparison of 3M™ Ceramic Microspheres W-210, W-410 and W-610

Grade	Top Size (microns)	Reduce Glossiness	Increase Glossiness	Burnish Resistance	Scrub Resistance	Hand Feel
W-210	12	-	+	++	++	Much smoother
W-410	24	=	=	++	++	Smoother
W-610	40	+	-	+++	+++	Less smooth

References

[1] http://coatings.specialchem.com/product/a-imerys-duramite. Accessed August 6, 2015.

[2] http://www.thecarycompany.com/adobe/unimin/minex-techdata.pdf. Accessed August 6, 2015.

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