*As legislation prompts the removal of lead-based corrosion inhibitors **Peter Ciullo et al** explain why wollastonite can function as an effective supplement.*

Keeping corrosion at bay

Wollastonite is a naturally occurring calcium silicate mineral with the molecular formula $CaSiO_3$. It is known among nonmetallic industrial minerals for its combination of white color, acicular (needle-like) crystal shape and alkaline pH. The structure of wollastonite is characterised by twisted chains of silica tetrahedra connected side by side through calcium in octahedral coordination. Because of this chain structure, wollastonite grows as acicular crystals and will preserve acicularity on cleavage[1].

The high density of the calcium-linked silica chains accounts for the mineral's hardness, Mohs 4.5 to 5, low surface area, 1 to 5 m^2/g and relatively low rub-out oil absorption, 20 to 30. In contact with water, wollastonite surfaces hydrolyze to form calcium hydroxide, which accounts for the wollastonite slurry pH of 10. Wollastonite has a strong buffering effect in acid solutions due to dissociation and the release of calcium ion.

Wollastonite products are differentiated according to particle size and aspect ratio – the ratio of particle length to width. Powder grades, those most commonly used in coatings, have a low average aspect ratio of about 5:1. Standard grades are 325 mesh (4 Hegman), 400 mesh (5 Hegman) and 10 micron nominal top size (6+ Hegman).

The photomicrograph of 6+ Hegman wollastonite in Figure 1 shows that even in finely ground powder grades, substantial acicularity is retained. High aspect ratio (HAR) wollastonite grades are carefully attrition milled to ensure that the very fine, needle-like particles are preserved and recovered. HAR products have aspect ratios in the 12:1 to 20:1 range, and are used in thick build systems – texture coatings and block fillers – for mechanical strength, crack resistance and durability. Both powder and HAR grades of wollastonite are readily available with silane and organosilicone treatments to impart hydrophobicity and to improve compatibility with organic matrices.

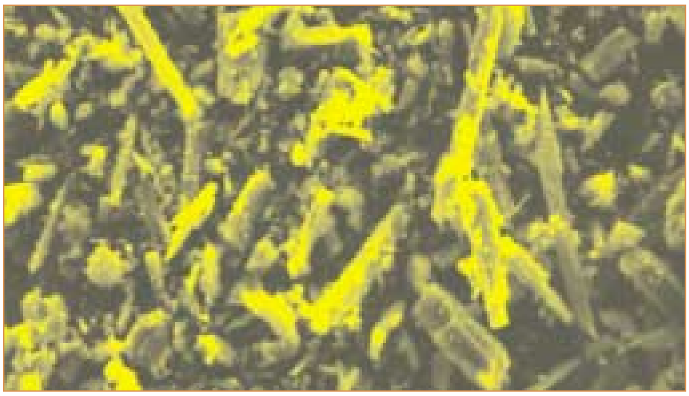

Figure 1: acicularity of 6+ hegman powder grade wollastonite (1700X)

Part A (by weight)	$ZnPO_4$ Masterbatch	Wollastonite Masterbatches
Epon 828[1]	239.0	239.0
$ZnPO_4$ JO 852[2]	540.0	0.0
Wollastonite	0.0	498.0
Bentone SD2[3]	10.3	10.3
Beetle resin 216-8[4]	13.0	13.0
MIBK	41.0	41.0
Xylene	105.8	105.8
Preblend MIBK and xylene. Add as needed for good dispersion viscosity. high speed disperse for 15 minutes. Reduce speed and add remaining solvent.		
Part B (by weight)		
Aradur 283 Hardener[5]		166.0
Mapico M214 red iron oxide[6]		100.0
325 mesh mica		45.7
Bentone SD2		1.7
Xylene		40.4
High speed disperse for 15 minutes		

Table 1: 2K Epoxy/Polyamide primer formulation

Corrosion control

Wollastonite is widely used in corrosion resistant primers. In addition to its allkalinity, wollastonite serves this function because its acicular shape effectively reinforces the coating film. This improves the film's ability to stretch and bend without breaking. Its hardness also improves film integrity by contributing to abrasion resistance.

As legislation prompted the industry move away from lead- and hexavalent chromium-based corrosion inhibitors toward the generally less efficient molybdate, borate, and phosphate alternatives, wollastonite was found to be useful for optimizing corrosion control.

One early study, for example, compared a number of functional extender pigments for their contribution to the performance of anti-corrosive epoxy metal primers. Among the nine extender pigments examined, wollastonite was preferred for improved corrosion and blistering resistance, with additional improvement derived from epoxysilane treatment of this mineral[2].

Work has also been reported on the synergy with inhibitive pigments of wollastonite surface-treated with amino and epoxy functional silanes in corrosion resistant coatings[3].

While the mechanism is not fully known, numerous authors have described the synergistic

Pigment	$ZnPO_4$ Wollastonite	Scribe	Corrosion mm	Comments
$ZnPO_4$	100/0	X	3-4	medium blisters around scribe
		I	1-2	large blisters around scribe
Wollastonite, UN	75/25	X	1-2	large blisters around scribe
		I	2-3	large blisters around scribe
	50/50	X	1-2	no blisters
		I	<1	large blisters around scribe
	25/75	X	-	adhesion failure
		I	2-3	no blisters
	0/100	X	-	adhesion failure at 1635 hours
		I	-	adhesion failure at 1635 hours
Wollastonite, AS	75/25	X	-	adhesion failure at 1250 hours
		I	1-2	no blisters
	50/50	X	-	adhesion failure at 1635 hours
		I	<1	no blisters
	25/75	X		adhesion failure at 1250 hours
		I	1-2	no blisters
	0/100	X	-	adhesion failure at 2000 hours
		I	1-2	no blisters
Wollastonite, ES	75/25	X	<1	no blisters
		I	1-2	no blisters
	50/50	X	1-2	no blisters
		I	1-2	no blisters
	25/75	X	1-2	no blisters
		I	1-2	no blisters
	0/100	X	2-3	no blisters
		I	3-4	large blisters around scribe

Table 2: salt spray, corrosion at scribe, 2000 hours

behavior of wollastonite with the majority of primary inhibitive pigments. What is known is that when used in combination with inhibitors, wollastonite, especially the surface-treated grades, enables the inhibitive pigment to be more effective for overall corrosion protection than when the pigment is used by itself. For instance, a surface-treated wollastonite has been successfully used to improve the performance of zinc phosphate in alkyds[4].

We have evaluated the effect of 6+ Hegman (10 micrometer top size) wollastonite for contribution to corrosion control in a 2K solvent-borne epoxy/polyamide red iron oxide primer. This work comprised a ladder study of zinc phosphate with the wollastonite in untreated (UN), epoxysilane (ES) treated and aminosilane (AS) treated form.

The ratio of zinc phosphate to wollastonite ranged 100/0, 75/25, 50/50, 25/75 and 0/100. Table 1 gives the weight basis formula used.

Masterbatches of the zinc phosphate and each wollastonite were first prepared. These masterbatches were then blended as appropriate to obtain the desired zinc phosphate/wollastonite ratio. Each was then combined with Part B, and allowed to stand for one hour prior to use.

Drawdowns were made at 8 mil clearance onto Type S 48 (4"x8") steel panels from Q-Panel Company. Three of each were made. The coatings were cured at ambient conditions for 7 days prior to salt-spray testing. One panel of each type was left unscribed for gloss testing. One panel of each was scribed with a X and the other with a vertical line. Salt-spray corrosion testing was run according to ASTM B 117, with the panels removed from the cabinet after 500, 1000, 1250, 1635 and 2000 hours to measure corrosion at the scribe and 60 gloss.

Table 2 shows untreated and aminosilane treated wollastonite did not offer any benefit as a synergist with the zinc phosphate. The blends with epoxysilane treated wollastonite provided corrosion control at least equal to that of zinc phosphate alone as well as blister resistance. These blends likewise provided the best balance of gloss and gloss retention, as seen in Table 3.

Wollastonite will function as a supplement or synergist with inhibitory pigments by providing alkalinity and improving film durability. The best results are obtained by determining the optimum compatibility between the resin and the wollastonite surface. Here, epoxy functionality on the wollastonite ensured the best bonding to the epoxy/polyamide film formed from the solvent coating. PPCJ

Pigment	$ZnPO_4$: Wollastonite	Initial	2000 hours	Change
$ZnPO_4$	100/0	32	22	-10
Wollastonite UN	75/25	47	32	-15
	50/50	52	37	-15
	25/75	51	41	-10
	0/100	63	26	-37
Wollastonite AS	75/25	65	36	-29
	50/50	72	44	-28
	25/75	79	51	-28
	0/100	81	58	-33
Wollastonite ES	75/25	40	25	-15
	50/50	45	31	-14
	25/75	63	49	-14
	0/100	67	55	-12

Table 3: salt spray, 60º gloss, 2000 hours

References

1. CS Hurlbut, C Klein, *Manual of Mineralogy*, 21st Ed., John Wiley & Sons, New York, 1993
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3. Clive H Hare, 'The Evolution of Calcium Metasilicate in Paint and Coatings.' *Modern Paint and Coatings.* November 1993. Volume 83(12).
4. Clive H Hare, 'Corrosion Control Using Chromate and Phosphate Pigments.' *Paint and Coatings Industry.* August 1997.

Raw Material Sources

1. Resolution Performance Products
2. LaPorte Pigments
3. Rhodia
4. Cytec Industries
5. Vantico
6. Rockwood Pigments

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