



Wollastonite: A Value-added Functional Mineral



## A Specialty Mineral That Gives Improved Corrosion Protection and Durability

- AUXILIARY PIGMENT EXTENDER
- STABLE – PREVENTS DOWNWARD pH DRIFT
- IMPROVED WEATHERABILITY
- PREVENTS CRACKING AND IMPROVES SAG CONTROL
- REDUCES GLOSS

# PAINT & COATINGS



## WOLLASTOCOAT® Auxiliary Pigments

These high tech materials, known as WOLLASTOCOAT® pigments, have come a long way from simple extender applications. These calcium metasilicate products are easier to disperse and offer reduced oil absorption allowing significant elevation of the Critical Pigment Volume Concentration (CPVC), and allow substantially increased loadings without accompanying elevations in viscosity.

The use of chemically modified WOLLASTOCOAT® in metal primers has produced marked improvement in corrosion resistance and has decreased the tendency to blister. Even in non-inhibitive systems, inclusion of the WOLLASTOCOAT® family of products has improved performance by offering barrier properties.

WOLLASTOCOAT® pigments offer cost-effective, safe and successful solutions to a wide range of complex formulation problems.

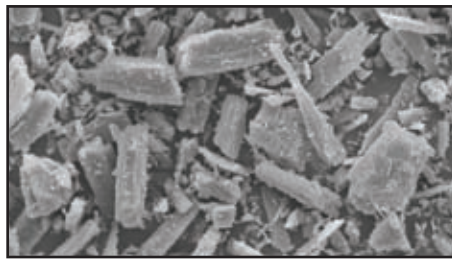
WOLLASTOCOAT®	ES	AS	WC
LONG OIL ALKYD	✓	✓✓	✓
MEDIUM AND SHORT OIL ALKYD	x	✓✓	✓
VINYL LATEX	✓✓	✓✓	✓
EPOXY AMINE AND AMIDE	✓✓	✓✓	x
COAL TAR/ASPHALTICS	✓	✓	✓✓
URETHANE/ACRYLIC & URETHANE POLYESTER	✓✓	✓	x
WATER-BASED ACRYLIC/URETHANE	✓✓	✓	N/A
VINYL CHLORIDE/ACETATE	✓✓	✓✓	✓
ACRYLIC LATEX	✓✓	✓✓	✓✓
WATER DISPERSIBLE ALKYD	x	✓	N/A
WATER EMULSIFIED ALKYD	x	✓✓	✓
WATER DISPERSIBLE EPOXY	✓✓	✓✓	N/A
ALUMINUM EPOXY MASTIC	✓✓	✓✓	N/A
UNSATURATED POLYESTER	✓	✓✓	✓✓
SATURATED POLYESTER	x	✓✓	x

✓✓ = Highly recommended    ✓ = Specific System dependant    x = Not recommended

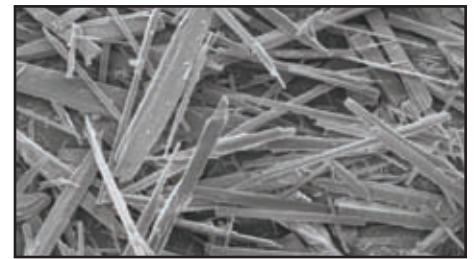
10 WOLLASTOCOAT® (750X)



NYAD® M400 (500X)



NYAD G® (100X)



WILLSBORO PRODUCTS/ TYPICAL PROPERTIES	10 WOLLASTOCOAT®	NYAD® 1250	NYAD® 400	NYAD® 325	NYAD G®
G.E. BRIGHTNESS	93	93	92	90	82
BULK DENSITY (lbs./cu.ft.) (g/cc)					
LOOSE	(41) (0.65)	(30) (0.48)	(44) (0.70)	(47) (0.75)	(25) (0.40)
TAPPED	(53) (0.85)	(50) (0.80)	(69) (1.10)	(75) (1.20)	(50) (0.80)
OIL ABSORPTION (lbs./100 lbs.)	25	27	22	21	35
HEGMAN GRIND	>6	>6	4	3	N/A
MICROTRAC D <sub>50</sub> (µm)	4	4	8	14	55
ASPECT RATIO (L/D)	3:1	3:1	3:1	4:1	15:1

WOLLASTONITE... ONE MINERAL,



## Applications

### Industrial Coatings

- Reinforce film cohesion and improves mechanical properties
- Synergism with anti-corrosion inhibitors
- Improves durability and corrosion resistance
- Chemical treatment improves homogeneity and engineered reactivity
- Reduces cracking and checking
- Enhances resistance to brittle failure
- Improves resistance to physical degradation resulting from UV radiation
- Prolongs service life of coating; especially HAR grades

### Roof Coatings, Coal Tar Coatings and Cements

- Safe alternative to asbestos and other fibers
- Partial to full replacement to cellulose fiber
- Improved film reinforcement and sag control
- High G.E. Brightness, especially beneficial for lighter or aluminum coatings
- Reduced susceptibility to UV related and mud cracking
- Improved durability and ease of application
- Improved flame and fire resistance

### Powder Coatings

- Gloss reduction
- Crack and chip resistance
- Enhanced color-fastness and moisture/corrosion resistance
- Superior reinforcing performance and "tooth" in powder primers
- Lower specific gravity than competing materials
- Heat stable, resistant to ultra-violet degradation and chemical attack
- Lower film transmission properties

PRODUCT FAMILY	PRODUCT GRADES	APPLICATION USAGE
HIGH ASPECT RATIO	NYAD G, NYAD MG, NYGLOS 12, NYGLOS M15, ASPECT 3000, NYGLOS 4W	Asbestos and cellulose replacement in roof coatings/cements • Driveway sealers • Foundation coatings • Textured coatings, • Mastics • Floor coatings • Sealers • High heat resistance powder coatings • Aliphatic polyurethane coatings
POWDER	NYAD 325, NYAD M325, NYAD MD325, NYAD 400, NYAD M400, NYAD MD400	Architectural latex paints • Trade sale coatings • Block fillers • Traffic paint • Powder coatings
FINE PARTICLE SIZE	NYAD 1250, NYAD M1250, NYAD MD1250, NYAD 5000	Metal primers • Powder coatings • Industrial coatings • Automotive finishes • Wood stains
CHEMICALLY TREATED	400 WOLLASTOCOAT, M400 WOLLASTOCOAT, MD 400 WOLLASTOCOAT, 10 WOLLASTOCOAT, M1250 WOLLASTOCOAT, MD 1250 WOLLASTOCOAT	High performance anti-corrosive coatings • Heavy duty maintenance finishes • Marine and bridge paint • Powder coatings • Aerospace

MINERA PRODUCTS/ TYPICAL PROPERTIES	M1250/MD 1250 WOLLASTOCOAT®	NYAD® M400/MD400	NYAD® M325/MD325	NYGLOS® M15	NYAD® MG
G.E. BRIGHTNESS	89	87	87	82	82
BULK DENSITY (lbs./cu.ft.) (g/cc) LOOSE TAPPED	(45) (0.72) (57) (0.91)	(41) (0.65) (62) (1.0)	(47) (0.75) (69) (1.10)	(28) (0.45) (56) (0.90)	(34) (0.55) (59) (0.95)
OIL ABSORPTION (lbs./100 lbs.)	25	24	22	30	35
HEGMAN GRIND	>6	4	3	N/A	N/A
MICROTRAC D <sub>50</sub> (µm)	4	9	12	18	23
ASPECT RATIO (L/D)	3:1	3:1	4:1	8:1	9:1

A WORLD OF APPLICATIONS



One Mineral, A World Of Applications

- State-of-the-art processing operations
- World-class chemical modification technology
- Industry leader
- World-wide distribution network
- Customer-focused global technical support
- Premium quality wollastonite

Wollastonite is a naturally occurring mineral, is non-hazardous, and is not regulated by shipping agencies. Based upon toxicological studies, there is no evidence of any significant health risks to workers.

#### NORTH AMERICAN OPERATION

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ISO 9001/14001 CERTIFIED

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## Purity and Acicularity

The deposits mined by NYCO in Willsboro, New York and in Mexico's Sonoran desert are unique for their purity and acicularity.

Wollastonite is the only pure white extender that is acicular in shape with aspect ratios ranging from 3:1 to 20:1. This high acicularity is of considerable value in the cohesive reinforcement of coating films. This, in turn, has led to coatings with better mechanical strength and weathering for improved resistance to cracking and checking.

## Added Alkalinity

Wollastonite's pH of 9.9 along with its property of maintaining an alkaline pH in long-term storage make it a logical choice for use in paints to ensure better stability and maintenance of viscosity.

Wollastonite, due to its unique chemistry in combination with its particle shape, has a synergistic effect with anticorrosion inhibitors in industrial coatings. In architectural coatings, wollastonite-based formulations have better initial brightness and color than paints made with other extenders, as well as reduced sheen with better burnish resistance.

TYPICAL PROPERTIES	VALUE
APPEARANCE	WHITE
MORPHOLOGY	ACICULAR
MOLECULAR WEIGHT	116
SPECIFIC GRAVITY	2.9
REFRACTIVE INDEX	1.63
pH (10% SLURRY)	9.9
WATER SOLUBILITY (g/100cc)	0.0095
DENSITY (lbs./cu.ft.)	181
BULKING VALUE (gal./lbs.)	0.0413
MOHS HARDNESS	4.5
COEFFICIENT OF EXPANSION (mm/mm/°C)	$6.5 \times 10^{-6}$
MELTING POINT (°C) - theoretical	1540
MELTING POINT (°C) - by ASTM D1857	1410

CHEMICAL COMPOSITION: CaSiO <sub>3</sub>			
COMPONENT	MEXICO (MD) TYPICAL VALUE (%)	MEXICO (M) TYPICAL VALUE (%)	NEW YORK TYPICAL VALUE (%)
CaO	45.72	44.94	46.36
SiO <sub>2</sub>	46.52	52.94	51.60
Fe <sub>2</sub> O <sub>3</sub>	0.25	0.28	0.77
Al <sub>2</sub> O <sub>3</sub>	0.25	0.30	0.40
MnO	0.02	0.04	0.15
MgO	0.71	0.75	0.15
TiO <sub>2</sub>	0.05	0.05	0.05
K <sub>2</sub> O	0.20	0.23	0.02
Wt. Loss (1000°C)	6.30	0.47	0.50



**One Mineral, A World Of Applications**

# The Evolution of Calcium Metasilicate in Paint and Coatings

By Clive H. Hare  
Clive H. Hare Inc.  
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Effective March 1, 1994, the WOLLASTOKUP® trade name was discontinued and replaced with WOLLASTOCOAT®, a registered trademark of NYCO Minerals, Inc. No modifications were made to the products.

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# The Evolution of Calcium Metasilicate In Paint and Coatings

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Naturally occurring calcium metasilicate, or wollastonite, is a relatively new mineral in the coatings industry. The first industrial use of the product was in the early 1930s in the production of mineral wool insulation. In the 1940s, there are reports of its use in welding rods, but not until the 1950s, when more widespread uses in ceramics developed, did volume reach important levels. Today, specialized grades are widely employed in mineral-filled and mineral-glass-filled polymer composites, plastics and elastomers, in ceramics, bonded abrasives, acoustical and wall-board materials and insulation.

The use of the material in coatings also began in the early 1950s, when a range of high-grade materials of excellent color derived from a high-purity deposit in Willsboro, N.Y., first became available.

## Nature of Wollastonite Ore

While calcium metasilicate is found in various parts of the world (China, India, Finland, California and New York State), significant differences in the products exist from source to source. These differences are partly related to the type and level of associated mineral contamination, and more importantly, the level of metamorphism of the sediments and the volcanic and/or meteoric water migration through the ore body.<sup>1</sup> Local variations in temperature and pressure that occurred during metamorphism of the sediment are known to have affected both crystal formation and acicularity, resulting in products ranging from powders to high-aspect-ratio crystalline. The deposit mined at Willsboro is unique in both its purity and acicularity. The ore contains garnet and diopside as

**Table I. Calcium Metasilicate — Physical Properties**

Chemical formula	CaSiO <sub>3</sub>
	CaO.SiO <sub>2</sub>
Molecular weight	116
Appearance	White Powder
Particle shape	Acicular
Refractive index	1.63
Specific gravity	2.9
Weight/gal. (lbs./U.S. gal.)	24.17
Bulking value (U.S. gals./lb.)	0.0413
Oil absorption (gm/100 gms oil)	
Unmodified	28-33
Wollastokup	20-25
pH of 10 percent slurry in water	8-10
Hardness (Mohs)	4.5
Water solubility (gms/100cm <sup>3</sup> )	0.0095
Melting point (°C)	1500
Coefficient of thermal expansion (mm/°C)	6.5x10 <sup>6</sup>
Moisture content (percent)	0.5

associated minerals, which may be magnetically removed to produce a 97-98 percent beneficiated product, free of calcite (calcium carbonate) often associated with other major deposits of calcium metasilicate and which is virtually impossible to separate cost effectively.

Materials derived from the New York source were rapidly adopted by the coatings industry as extenders and fillers for a variety of coatings, and by the late '60s, sales were increasing at a rate of 10 percent per year.

## Wollastonite as Extender

The crude extender had a number of unique properties, as shown in Table I, which lent it to applications by a paint industry that in the early

'50s was evolving into the technically complex and diversified scientific sub-section of the general chemical industry it is today.

Wollastonite was the only pure white extender that is acicular in shape. Aspect ratios ranging from 20:1 to 3:1 are now possible, depending upon grade. Acicularity was realized to be of considerable value in the cohesive reinforcement of coating films. This, in turn, led to coatings having better mechanical strength and improved durability and weathering for improved resistance to such age-related defects as cracking and checking. In addition, acicularity allowed its use as a partial replacement for other less desirable fibrous reinforcers such as the toxic asbestos, which since the 1970s has gradually been replaced.

Slurries of the pigment in water showed a pH of 9.9 and this property could also be utilized in many of the newly emerging latex paints, which required an effective alkaline buffer preventing pH drift and deteriorating stability, especially where acidic pigments such as china clay and thermo-optical aluminum silicate pigment systems were employed. In a 1979 study, Englehard<sup>2</sup> found that unlike other alkaline extenders (calcium carbonate, magnesium silicate and nephylene syenite), only wollastonite, when used as a pigment in latex paint, maintained an alkaline pH in long-term storage. This ensured better long-term stability and good maintenance of viscosity, allowing the elimination of ammonia and/or other amines in some latex paint formulations. It was also soon discovered that the alkalinity of the pigment could be effectively used to eliminate can corrosion at seams, rims, etc., when wollastonite was



polymers. The treated product is also far more homogeneous.

By manipulating the composition of the organic, it became possible to introduce functional groups into the outer surface of the organic shell of the pigment. These groups could then be used in subsequent reactions with complementary moieties in the polymer and lead to the establishment of primary valency bonded linkages between the treatment and the polymer, as shown in Figure 2. In this way, the pigment/polymer interface, most usually held together via simple secondary valency linkages (hydrogen bonds, Van der Waals forces, etc.) is replaced by a primary valency bonded interface in which both polymer and mineral are held together via chemically bonded bridges. The technique, leading to much greater interfacial security, produced a revolution in the utility of pigments by the plastics industry.

Where the primary valency linkage to the pigment is a siloxane group, derived from silane treatments, an additional advantage is derived from a certain amount of bonding reversibility that is believed to exist<sup>6</sup>. In this case, the reaction between the silanol groups on the pigment surface and the treatment is an equilibrium reaction, and, in the presence of surface water, the siloxane bonds are thought to temporarily break and rapidly reform, causing the treatment film to slip along the surface of the mineral under stress. In bound polymeric compositions (as well as coatings) the dynamic equilibrium that this slippage allows provides a unique stress-relief mechanism leading to the dissipation of internal and external stresses that build up in a bound system as the system cures and/or responds to environmental demands (temperatures and humidity differentials for example). Such built-in stress attenuation inevitably leads not only to improved physical properties in all polymer bound mineral filled systems (including paint films) but to improved resistance to aging.

The net result in practical polymer composites was a reduced sensitivity to water and corrosives, improved processing and flow and upgraded physicals (enhanced compressive strength, high flexural modulus, and better dimensional stability), as well as better electrical insulating properties and higher heat distortion temperatures.

It was not surprising that proto-

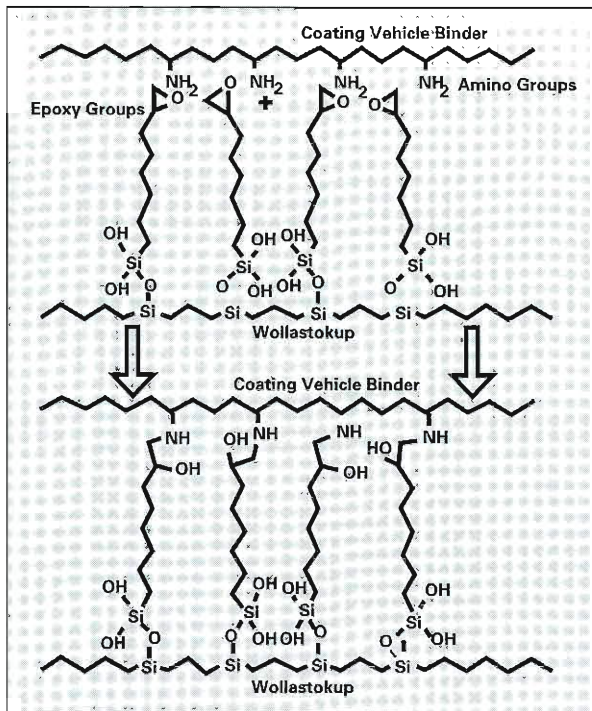


FIGURE 2. Reaction of silane treated Wollastokup with coating vehicle binder.

type materials of this kind eventually found their way into surface coatings, where they immediately demonstrated significant value, not only via enhanced levels of reinforcement, but in dramatically improved blistering resistance and underfilm corrosion resistance of paints used over active steel surfaces.

### Surface Engineered Calcium Metasilicates in Coatings

Further refinements of the same concept, made possible by an active research and development program that still continues, eventually produced a family of functionalized pigments specifically designed and produced for use by the coatings industry. These high-tech materials, today known as the Wollastokup pigments, have progressed a long way from their simple extender grade progenitors. The coating grade materials again carried specific organically reactive shells that lent it to applications in epoxies, urethanes, alkyds and polyesters, in a manner analogous to the application of the plastic grade materials in polymer grade composites.

In coatings, the advantages seen in the early work with plastic grades were again realized. In view of the mixed results from early attempts to employ coupling agents by direct integral blending techniques in coatings, these results were encouraging.

Silanes, titanates, zirconium aluminates and other coupling agents that made up the organic shell of the Wollas-

tokup had, for some years, been available to the coatings industry and used directly by formulators to doctor coating vehicles in attempts to improve the adhesion of the coatings and the wettability of pigments. Results with this integral blending approach had been spotty at best. The disparity in the results from integral blending modification of coatings and the indirect introduction of the materials as treatments on pigments was undoubtedly related to a reduced mobility of the inorganically reactive moiety when the treatment was already bound (via its organically reactive sites) to the high-molecular-weight coating vehicle.

The reduced mobility resulted in hindered access of the coupling agent to the pigment surface and less efficient wetting. This, in turn, produced no better than the partial establishment of the primary valency bonded interface between the pigment and the vehicle. In the use of such coupling agents, the general rule for maximum efficiency is to preserve the mobility of the coupling agent so that the inorganic interface is secured first.

Compared to the utilitarian extender, the new metasilicate pigments were easier to wet and had substantially reduced oil absorption, in spite of the greater surface area of their finer particle size base (23 grams/100 grams for 10AS Wollastokup, as opposed to 30 grams/100 grams for the non-treated base Nyad 1250). This produced significant elevations of the CPVC, and allowed substantially increased loadings without accompanying elevations in viscosity, or the introduction of film porosity. At this time, when VOC reductions and high-solids formulations are of paramount importance to coating formulators, these attributes are highly desirable features for any pigment.

The contribution of the pigment to anti-corrosive metal primers of all types, and particularly to high performance coatings for long-term protection of steel structures, was, from the first, realized to be substantial. Early studies<sup>7,8</sup> in many vehicle systems (epoxies, alkyds, urethanes, vinyls, acrylics, etc.) showed that the inclusion of appropriately engineered Wollastokup pigments into conventional inhibitive metal primers produced marked improvement in the salt spray resistance of such coatings, decreasing the tendency of such films to blister and the underfilm metal to corrode. In many cases, it



was found that the PVC window at which optimum corrosion resistance was achieved was significantly widened when the treated silicate was employed along with the conventional inhibitive pigment, compared to the allowable window in non-Wollastokup-modified systems (see Figure 3). The effects were seen in coatings inhibited with toxic inhibitors such as zinc, strontium and basic lead silico chromate inhibited systems, and particularly in the case of systems inhibited with non-toxic inhibitors. Wollastokups have been found to be effective auxiliary pigments in inhibited primer systems pigmented with a variety of phosphates, phosphites, phosphosilicates, borates, borosilicates, molybdates and others.

Even in non-inhibitive systems, inclusion of the Wollastokups has wrought substantial improvement in performance (10ES Wollastokup is now used in non-inhibited aluminized epoxy mastics and it has been employed to upgrade the performance of coal tar epoxy films).

The extent of Wollastokup contribution to anti-corrosive metal primers was unexpected, even to experienced formulators, and has spawned significant amounts of research over the last decade. In combination with primary inhibitors, it was found that a degree of performance could be realized that could not be achieved with either inhibitor used alone or Wollastokup used alone.<sup>9</sup> This type of synergism has been demonstrated in alkyds, epoxies and urethanes with a wide spectrum of different inhibitors. Ratios of inhibitor to Wollastokup, at which the effect has been noted are varied, but combinations generally range from 3:1 to 1:3 by volume (see Figure 4). As the Wollastokups are considerably less expensive than conventional corrosion inhibitive pigments, such combinations have allowed considerable savings in raw material price and improved cost effectiveness (see Figure 5).

### Possible Mechanisms of Wollastokup Inhibition

In some binders (water based urethane/acrylics), synergistic effects were not noted to the same extent when Wollastokup

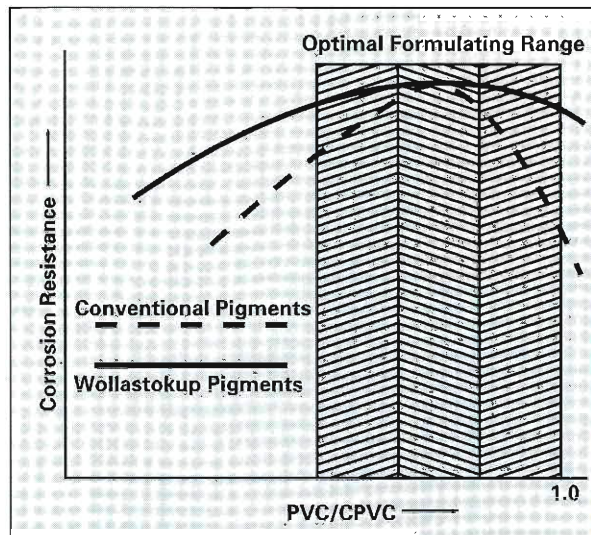


FIGURE 3. Optimal formulating window for corrosion-resistant metal primers.

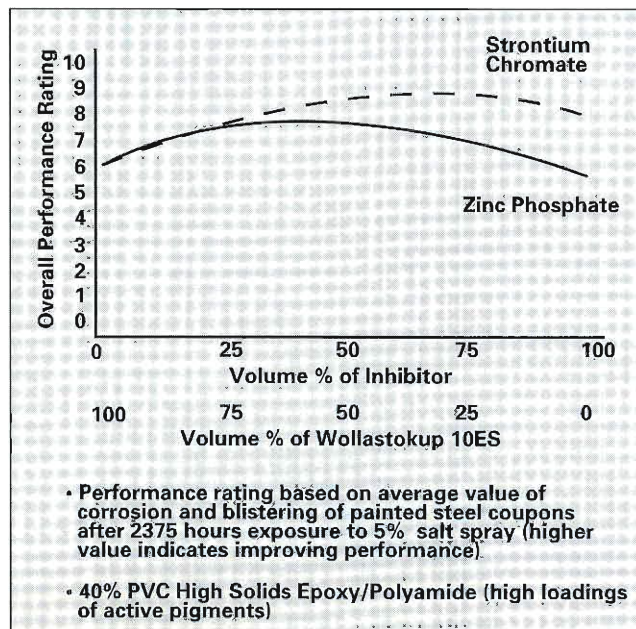


FIGURE 4. Effect of Wollastokup/inhibitor ratio on performance of finished primer.

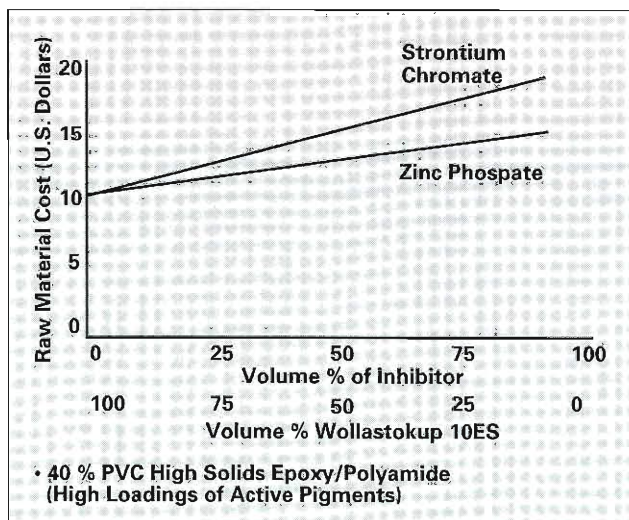


FIGURE 5. Effect of Wollastokup/inhibitor ratio on raw material cost of finished primer.

was employed with the basic molybdates, and this may be a key to the mechanism underlying this type of performance.

Similar observations had been noted several years ago when zinc oxide and magnesium oxide were used to modify a range of different inhibitors in an alkyd primer. In this case, while such modification effectively raised the levels of protection achieved with simple molybdate salts (zinc, calcium and strontium molybdate) in fresh and salt water environments, neither modifier substantially elevated the performance of similar primers pigmented with basic zinc molybdate.<sup>10</sup> In another study, where zinc oxide was found to improve the performance of a

range of simple chromates (calcium, strontium and barium chromates), zinc tetroxy chromate (basic zinc chromate) was extracted from leachants of the dry films.<sup>11</sup> Speculation of the in-situ formation of complex basic inhibitors of improved activity was made, although the simple pH modification of the interfacial environment remains an equally persuasive explanation of these phenomena. Clearly the basicity conveyed by these auxiliary pigments played a significant part in the improved performance attributes of these systems.

It has long been realized that inhibitors such as chromates are more effective in a basic environment than in an acidic one. In many fresh water boiler systems, pH adjustments alone are employed to control corrosion, although pH levels are generally higher than those provided by calcium silicate.<sup>12</sup> The ability of extender grade wollastonite to inhibit in-can corrosion and nailhead corrosion in latex paints, however, has been noted earlier. Certainly, tests have shown that extracts of calcium silicate pigmented epoxies are somewhat more basic than extracts of similar primers pigmented with other pigments, as shown in Table II. The ability of calcium silicate to buffer the

coating and maintain the interfacial environment at an alkaline pH would, therefore, seem a likely aspect of the underlying mechanism of synergism noted between inhibitive pigments and calcium metasilicate. In an alkaline environment, the primary inhibitive system is able to do its job more easily and better resist depassivation by chloride, sulfate and other moieties which tend to make inhibition more difficult by competing with the inhibitor for adsorption onto the metal. It has been shown that threshold levels of inhibitor necessary to achieve passivation in the presence of chlorides is reduced as pH is increased. It seems likely, therefore, that levels of primary inhibitor giving a specific degree of protection in non-calcium silicate systems might give more protection when calcium silicate was present. On the other hand, calcium silicate alone is not able to provide the same level of corrosion protection, and combinations show the peak performance profile so often seen in practical experiments with this type of system (see Figure 4). It is also possible that calcium silicate may inhibit steel corrosion itself by other mechanisms. Sodium silicate is a scaling inhibitor used in fresh and low salinity water systems, inducing precipitate formation over both anode and cathode areas. While calcium ions are said to interfere with the deposition of such precipitates, these difficulties are resolved by the addition of soluble phosphate. Carefully balanced mixtures of calcium and phosphate (10 ppm calcium carbonate: 12 ppm sodium hexamethyl phosphate) are used to inhibit fresh water systems (where the presence of calcium ions are found essential to phosphate inhibition<sup>13</sup>).

Yet basicity and/or the deposition of precipitates, are not the entire key to the contribution of Wollastokup to anti-corrosive coatings. Were this to be the case, extender grade pigments and certainly the 10 micron base (Nyad 1250) from which the Wollastokups are prepared, would give the same level of performance as do the chemically engineered Wollastokups. Nor would the level of performance obtained with different pigments (bearing different treatments) in the same vehicle system vary so markedly.

The answer seems most likely related to the more intimately bonded interface that exists between the Wollastokup and the binder, which results from the molecular engineering of the pigment surface. Improved chemically bonded interfaces of this type inevitably make the interstitial migration of water into and through

**Table II. pH of Water Extracts From Aged Films of Epoxy/Polyamide Metal Primers**

Variations with Pigmentation	
Pigmentation	pH
Zinc phosphate	7.0
Silica	6.3
Nyad 1250	7.7
10ES Wollastokup	7.6
10WC Wollastokup	7.4

**Table III. Moisture Vapor Transmission Rates Through Epoxy/Polyamide Films**

Variations with Pigmentation	
Pigmentation	MVT
(mg/cm <sup>2</sup> .mm 24 hrs.)	
Zinc phosphate	0.0019
Silica	0.0018
Nyad 1250	0.0020
10ES Wollastokup	0.0011
10WC Wollastokup	0.0020

the film more difficult. Indeed moisture vapor transmission data (see Table III) show epoxy/polyamide primers pigmented with Wollastokup pigments have lower permeability to water than do identical primers based on phosphates and/or silica pigment systems. Where water permeability is decreased, the accumulation of water at the primer/metal interface is inevitably reduced and the negative effects of such accumulation on the wet adhesion of the system are diminished. Chloride ion permeability (always lower than water permeability in films of PVCs below the CPVC) is consequently reduced, and this results in a decreased opportunity for depassivation. As inhibitive ions are derived from within the film, not from the environment as are the depassivators, a ratio of inhibitor to depassivator is favorably enhanced and this further increases the opportunity for adequate corrosion resistance with lower levels of inhibitor.

### Guidelines for Use of the Wollastokup Pigments

#### • In Non-Aqueous-Based Coatings

If there remains uncertainty as to the exact mechanism (or mechanisms) that underlie the contribution these pigments have made to anti-corrosive coating systems, there can be no question that these materials represent a new step forward in the progression of pigment technology. Not unreasonably, their successful application demands a new level of expertise on the part of the coating formulator.

With the introduction of grades

bearing specific functionality, the application of such pigments in coating systems becomes more specific if optimum realization of the pigments' potential contribution to the coating is to be attained. Although this is often a simple matter of mating the reactive groups on the pigment with those on the vehicle system so that the pigment becomes chemically bonded into the polymeric matrix, there are other considerations, particularly in two-pack systems such as epoxies and polyurethanes.

The pigmentation of an epoxy resin with a pigment having an epoxidized surface (e.g. 10ES Wollastokup) will only result in the assimilation of the pigment into the polymer matrix after the curing agent (which will react with the epoxy group on the pigment) is added. While such a procedure will certainly result in some of the epoxy not being converted and absorbed into the polymeric matrix, more complete association might result from the pigmentation of the same epoxy with a pigment bearing amine hydrogens (e.g. 10AS Wollastokup) which could react with the epoxy resin during and just after manufacture. In the first case, the most likely model is one in which the available amine is shared between pigment and vehicle. Not only must the pigment compete with the epoxy resin for curing agent, but as vehicular crosslinking proceeds, so polymer mobility is reduced and access of groups on the polymer to complementary groups on the pigment surface is progressively reduced. Depending on the relative reaction rates between the selected curing agent, the oxirane groups on the resin and the same curing agent with the oxirane groups on the pigment, the matrix could vary from one in which there is complete assimilation of the pigment to a situation involving little true chemical bonding between pigment and vehicle. In the second case, the pigmentary requirements are satisfied before the epoxy polymer is introduced into the system. The polymer remains fluid, and, without the limiting effects of simultaneous polymeric crosslinking, assimilation of the pigment into the polymer is far more complete. Again, the system's mobility has been preserved until the interfacial reaction (this time between the organic shell and the paint binder) is secured.

While the downside of the latter approach could be some instability or increased viscosity in the Wollastokup-pigmented component, these effects are usually found to be minimal.

More serious can be the effects of such groups and/or the pigment itself

on the catalysis of certain reactions, and therefore the pot life and dry time of the combined paint. Where catalytic effects are possible, determination of optimum loading levels are influenced not only by performance requirements, but by the changes in reaction kinetics that can occur. The use of amine terminated pigments (10AS Wollastokup) in certain urethane polyols (hydroxylated acrylics and polyesters), for example, could be expected to increase the ultimate reactivity of these components with the isocyanate component of the formulation. In this case, selection of the Wollastokup pigment and/or the blend of Wollastokup pigments and their loadings must be carefully adjusted in order to optimize the overall properties of the composition. One would never attempt to pigment an isocyanate component with the amine functional 10AS Wollastokup.

The epoxy-terminated pigment, 10ES Wollastokup, has also been found to produce significant increase in the viscosity of alkyds (most severely in short oil alkyds) where the 10AS and 10WC pigments may be used without such instability.

All vehicles of high acid number will tend to be reactive with all calcium metasilicate (treated or not) because of the minerals' inherent basicity. This applies not only to alkyds, but to carboxylated vinyls, acrylics and polyesters. The extent of such reactivity will vary with loading levels and the type of treatment, as well as the type and acid number of the vehicle, and the solvent system used (non-polar solvents will be less problematic than a polar solvent). Formulations of this type will require careful balancing of all ingredients, if stability during manufacture and storage is to be preserved. Nonetheless, it can be preserved, and functioning systems with these vehicles can be achieved.

#### • Aqueous Based Coatings

The same general guidelines concerning the use of Wollastokups in non-water-based coatings apply to those used in water-based coatings, also. However, in water, the effects of the pigment become more complex because of their basicity and tendency to produce divalent calcium cations in solution. This affects both reaction kinetics and stability (in single as well as multi-component coatings). In water, the catalytic effects of a basic pigment will be more marked, and divalent calcium cations will tend to both neutralize the carboxylic groups of vehicles such as water-based alkyds, epoxy esters and water soluble acrylics, and depress the protective electrical double layers that

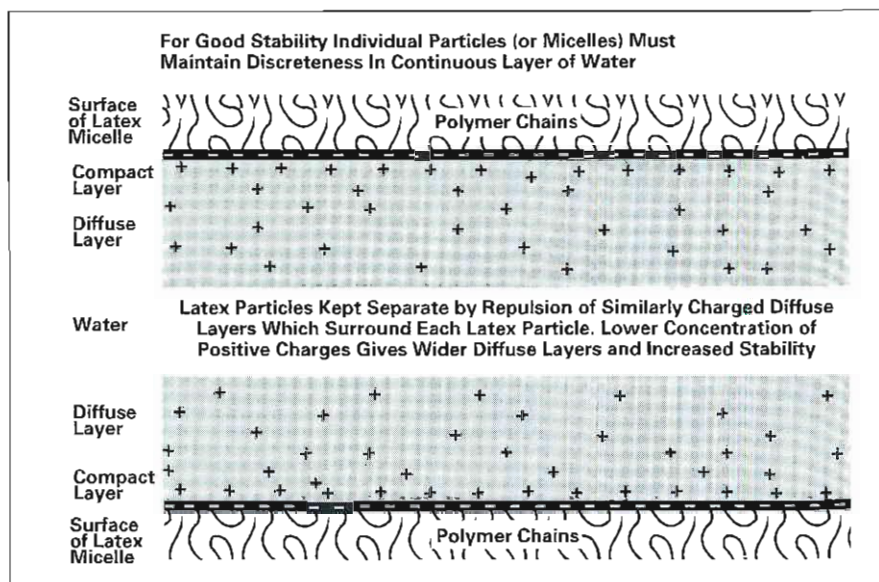


FIGURE 6A. Latex stability electrical double layer effect.

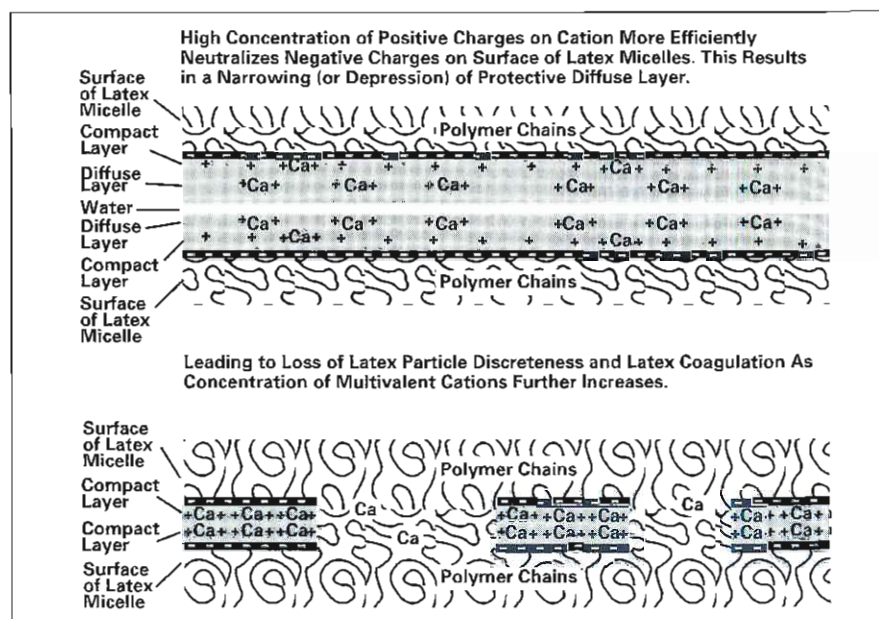


FIGURE 6B. Destabilization (coagulation) of latex effect of multivalent cations on depression of double layer.

stabilize most latex polymers. Here again, therefore, the placement of pigment and control of usage levels become most important.

The reactivity of base catalyzed systems such as epoxies, may be dramatically increased if the pigmentation is introduced to the water-containing epoxy component at the time of manufacture and calcium ions can subsequently accumulate in the water phase. The solubility of the basic calcium silicate in water can sharply catalyze the reaction of the epoxy and an amine (or amide) curing agent after the two components are mixed in the field. This will shorten the potlife of the system. In some cases, the basicity of a water/epoxy/Wollastokup combination (packaged together) may actually initiate the homopolymerization of certain epoxies particularly on long-

term storage and/or at high temperatures leading to gelation of the epoxy component.

Segregating the calcium silicate to the amine or amide component will prevent such homopolymerization, but if water is present in the amine or amide component, such segregation will not diminish the Wollastokup's eventual catalysis of the system on field mixing. If it becomes necessary to employ the pigment with the epoxy in such water-based systems (because of packaging, mix ratio adjustments, and/or other considerations), the aqueous phase should be confined to the curing agent in packaging, thereby eliminating the soluble base until the point of application. Here, the effects of basicity on both stability and potlife will again be minimized. A sensible rule in base-catalyzed water-based sys-

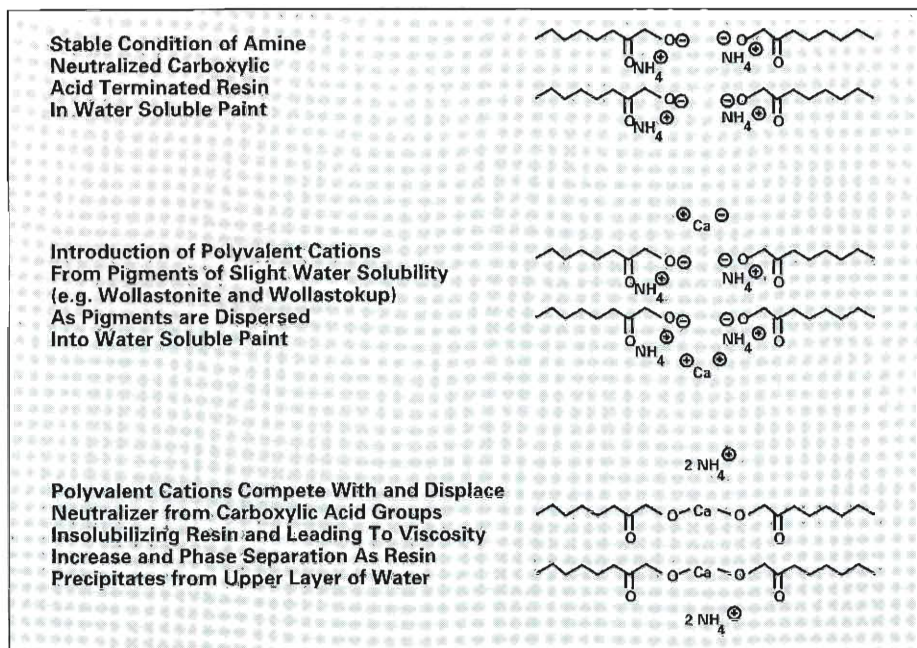


FIGURE 7. Destabilization of amine neutralized water soluble resins with polyvalent cations.

tems is to minimize the dwell time of calcium silicate in the presence of water, thereby reducing the amount of calcium ions that are in solution at the time of application.

Latex paints are stabilized by a surfactant system which produces a shield of negative charges around each latex particle and keeps the individual particles (or micelles) discrete, so maintaining the polymer dispersion (see Figure 6A). The thicker this electronic shield, the more stable the system. Positively charged cations, which neutralize the negative charges, tend to depress this shield so that it becomes thinner. If the shield becomes thin enough, it may be unable to prevent the contact of adjacent latex particles, resulting in the loss of the dispersion and the coagulation of the latex (Figure 6B). Multivalent cations, which will singularly neutralize multiple negative charges (each calcium ion in solution neutralizes two) are particularly effective in depressing the negatively charged shield. The usage level of pigments (such as Wollastokup) producing such ions must be carefully controlled if this effect is to be minimized. Again the precaution holds irrespective of the nature of the treatment.

Unfortunately, modern latex vehicles designed for use in high-performance coatings such as maintenance paints are often more leanly stabilized than conventional latex vehicles. The surfactant systems tends to remain as hydrophilic material within the dried film, and are counterproductive to good water resistance properties. Less surfactant, however, often means less stability and less tolerance for high levels of multiva-

lent cations before the protective charge shield collapses. If the Wollastokups are to be used in these systems, either levels of pigmentation must be more carefully controlled, or, in two component systems (water based epoxy/acrylics), that component bearing the pigment should be segregated from the water phase until the components are combined in the field, in order to reduce the amount of cations that get into solution.

A similar scenario applies to water-soluble systems such as alkyds, epoxy esters, acrylics, etc. Water solubility is built into these systems by means of carboxylic acid groups that are interpolymerized as part of the molecular structure. While the pendent carboxylic acid-terminated polymer is not itself soluble in water, water solubility may be easily obtained by neutralizing the acid with an amine or ammonia to produce a carboxylic acid salt. An alternative (though less commonly employed) route towards water solubility is the neutralization of an amine terminated polymer with a volatile carboxylic acid. This latter technique is used in some water-based epoxy/amine systems.

Unfortunately, when minerals produce soluble cations (particularly divalent cations) in water, and these which are used to pigment such neutralized carboxylic acid based alkyds, epoxy esters, etc., the soluble cations insolubilize the water-based resin by displacing the neutralizing amine (see Figure 7). Again, where these materials produce soluble divalent cations, one cation may displace two amine groups leading to an increase in viscosity and (if sufficient cations

are present) to a phase separation, in which the insolubilized polymer first separates as a resinous water immiscible layer beneath a supernatant layer of water.

Depending upon the degree of solubility of the pigment, its loading level, the exact make up of resin and the type of neutralization, the reaction may occur during manufacture, or later in storage. It is accelerated at elevated temperatures however both during manufacture and storage.

Pigmentation of these species with the Wollastokups is difficult, but possible, if loadings are controlled. Much depends upon the specific vehicle and neutralizer. Unfortunately, the better performing vehicles tend to be the least stable, and formulation technology may involve the judicious blending of vehicles as well as pigment types.

## Conclusion

There remains much to learn concerning these exciting new pigments, the mechanisms by which they work, and the ways in which they can creatively be employed to deliver optimum results at minimal cost. The outlook for the pigments, however, seems encouraging. Although their successful application in any given formulation can often present a unique set of challenges to the formulator, the industry appears to be meeting these challenges, perhaps spurred by the cost effectiveness of the pigments or because of their non-toxicity — certainly by the performance advantages they make possible.

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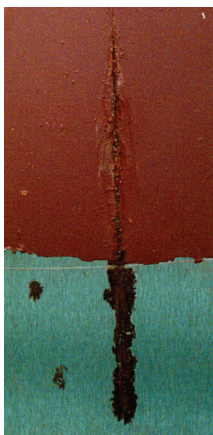
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The addition of 100% 10 AS WOLLASTOCOAT is the preferred auxiliary pigment to reduce blistering and costs versus zinc phosphate.

384 Hours in 5% Salt Spray

10 AS WOLLASTOCOAT  
( 100% )

A



10 AS WOLLASTOCOAT/  
Zinc Phosphate  
( 75:25 )

B



Zinc Phosphate  
( 100% )

C



Primer	Corrosion Coated General	Corrosion Coated Scribe	Blistering Degree	Blister Size	Corrosion Stripped General	Corrosion Stripped Scribe	Overall Primer Rating Average Value
A	10	6	8	8	9	5	7.67
B	10	5	8	8	9	5	7.50
C	10	6.5	2	5	10	5	6.42

**Rating Scale**

10 = Best    0 = Worst

## Benefits of 10 WOLLASTOCOAT in Industrial Coatings

- Reinforce film cohesion and improves mechanical properties
- Synergism with anti-corrosion inhibitors
- Improves durability and corrosion resistance
- Chemical treatment improves homogeneity and engineered reactivity
- Reduces cracking and checking
- Enhances resistance to brittle failure
- Improves resistance to physical degradation resulting from UV radiation
- Prolongs service life of coating, especially in high aspect ratio grades

## Typical Properties of 10 WOLLASTOCOAT

G.E. Brightness	93
Bulk Density ( lbs./cu.ft. )/ ( g/cc )	
Loose	( 41 ) ( 0.65 )
Tapped	( 53 ) ( 0.85 )
Oil Absorption ( lbs./100 lbs.)	25
Hegman Grind	>6
Microtrac D <sub>50</sub> ( μm )	4
Aspect Ratio ( L/D )	3:1

## Procedure for Generating Panels

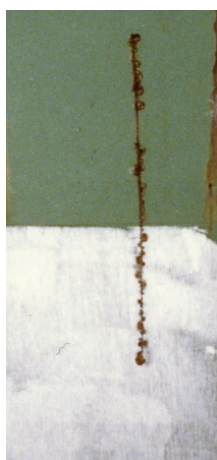
Primer films were cast on smooth MEK washed cold rolled steel Q-Panels using doctor blade techniques in films of 3±0.25 dry mills. All coated panels were allowed to age three weeks prior to testing and then scribed to the bare metal with a tungsten carbide scribing tool, backed vinyl tape and exposed for 1000 hours in 5% salt spray ( ASTM B-117 ).

**At the end of this exposure, the panels were removed from the cabinet, allowed to dry, then evaluated for general face corrosion ( rated under ASTM D-1654 ) and for blistering resistance ( both degree and size of blister ) using the numerical guide found in Federal Standard Test Method #141a Method 6461.** Evaluations were then made of the general face corrosion of the bare steel exposed, and of the bare steel in the scribe area. All six data points for each primer were then averaged ( being weighted equally ) to give an overall numerical expression for the performance value of the primer.

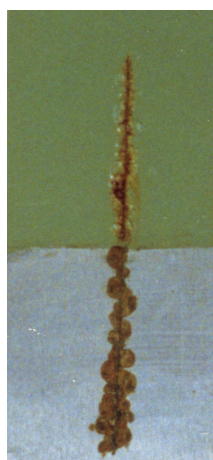
A formulation of **75:25 10 ES WOLLASTOCOAT and strontium chromate** is recommended for corrosive improvement, synergistic effects and cost savings.

600 Hours in 5% Salt Spray/17% PVC

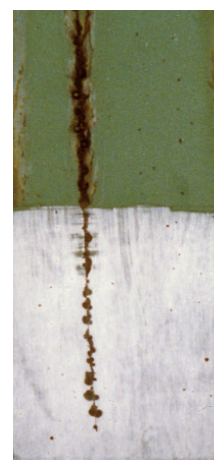
10 ES WOLLASTOCOAT/Strontium Chromate  
( 75:25 )  
A



10 ES WOLLASTOCOAT  
( 100% )  
B



Strontium Chromate  
( 100% )  
C



Primer	Corrosion Coated General	Corrosion Coated Scribe	Blistering Degree	Blister Size	Corrosion Stripped General	Corrosion Stripped Scribe	Overall Primer Rating Average Value
A	9	8	10	10	10	9	9.33
B	9	7	8	7	9.5	7	7.92
C	6.5	8	6	9	8	8.5	7.67

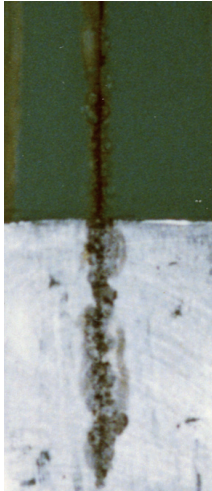
**Rating Scale**

10 = Best    0 = Worst

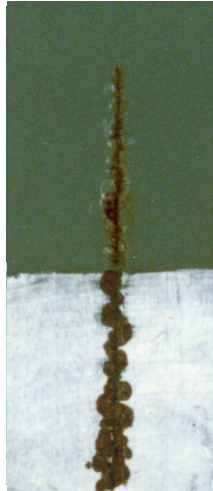
A formulation of 50:50 10 ES WOLLASTOCOAT and zinc phosphate is recommended for corrosive improvement,

**600 Hours in 5% Salt Spray/17% PVC**

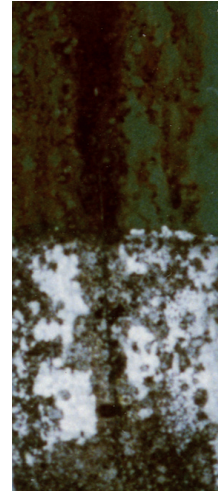
**10 ES WOLLASTOCOAT/Zinc Phosphate  
( 50:50 )  
A**



**10 ES WOLLASTOCOAT  
( 100% )  
B**



**Zinc Phosphate  
( 100% )  
C**



Primer	Corrosion Coated General	Corrosion Coated Scribe	Blistering Degree	Blister Size	Corrosion Stripped General	Corrosion Stripped Scribe	Overall Primer Rating Average Value
A	9	7	7.5	8	9.5	7	8.00
B	9	7	8	7	9.5	7	7.92
C	3	5	2	4.5	4	4	3.75

**Rating Scale**

10 = Best    0 = Worst

**Procedure for Generating Panels**

Primer films were cast on smooth MEK washed cold rolled steel Q-Panels using doctor blade techniques in films of 2±0.25 dry mills. All coated panels were allowed to age three weeks prior to testing and then scribed to the bare metal with a tungsten carbide scribing tool, backed vinyl tape and exposed for 600 hours in 5% salt spray (ASTM B-117).

At the end of this exposure, the panels were removed from the cabinet, allowed to dry, then evaluated for general face corrosion (rated under ASTM D-1654) and for blistering resistance (both degree and size of blister) using the numerical guide found in Federal Standard Test Method #141a Method 6461. Evaluations were then made of the general face corrosion of the bare steel exposed, and of the bare steel in the scribe area. All six data points for each primer were then averaged (being weighted equally) to give an overall numerical expression for the performance value of the primer.



## NYAD® 1250 Wollastonite – A Cost Performance Additive and TiO<sub>2</sub> Enhancer for Coatings

- Cost Savings - 10-20% replacement of TiO<sub>2</sub>
- Maintains tint strength and opacity
- Improved scrub resistance
- Effective for matte finishes, controls gloss
- Advanced corrosion and blister resistance
- pH buffer
- Environmentally safe

### Opacity and Color Value Comparison - 10% Replacement of TiO<sub>2</sub> with NYAD 1250

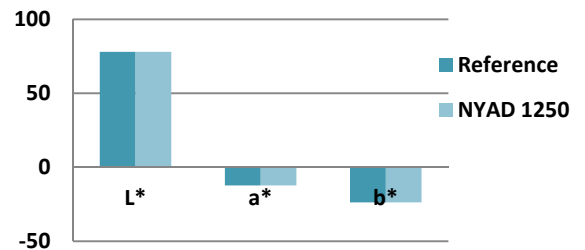
	Opacity (%)	Over Black Substrate			Over White Substrate			ΔE
		L*	a*	b*	L*	a*	b*	
<b>Reference</b>								
100 μm Wet Film Thickness	96.59	95.04	-0.79	0.93	96.32	-0.59	1.97	1.66
150 μm Wet Film Thickness	98.75	96.41	-0.75	2.08	96.88	-0.59	2.52	0.66
<b>NYAD 1250</b>								
100 μm Wet Film Thickness	96.30	95.01	-0.81	1.00	96.36	-0.63	2.07	1.73
150 μm Wet Film Thickness	98.52	96.42	-0.74	1.95	96.94	-0.59	2.45	0.75

### Starting Point Formulation Contains 14% TiO<sub>2</sub>

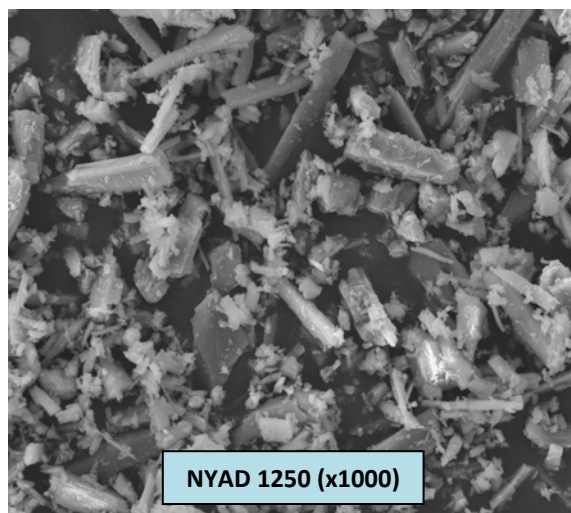
### Gloss Values - 10% Replacement of TiO<sub>2</sub> with NYAD 1250

	Gloss 20°	Gloss 60°	Gloss 85°
<b>Reference</b>			
100 μm Wet Film Thickness	1.2	2.3	5.8
150 μm Wet Film Thickness	1.3	2.4	6.7
<b>NYAD 1250</b>			
100 μm Wet Film Thickness	1.3	2.5	7.8
150 μm Wet Film Thickness	1.3	2.5	7.6

### Tinting Strength - 2% Blue Tinting Paste at 150 μm Wet Film Thickness



Typical Properties of Wollastonite	Value
Appearance	White
Morphology	Acicular
Refractive Index	1.63
Molecular Weight	116
Specific Gravity	2.9
pH (10% slurry)	9.9
Water Solubility (g/100cc)	0.0095
Density (lbs./cu.ft.)	181
Bulking Value (gal.lbs.)	0.0413
Mohs Hardness	4.5
Coefficient of Expansion (mm/mm/°C)	$6.5 \times 10^{-6}$
Melting Point (°C)	1540



NYAD 1250	Typical Values	Features of Wollastonite
G. E. Brightness	93	<ul style="list-style-type: none"> <li>• Acicular (needle-like) structure improves mechanical properties and particle shape influences gloss</li> <li>• High Refractive Index</li> <li>• Low specific gravity</li> <li>• Nonhazardous</li> <li>• Low solubility</li> <li>• Thermally stable</li> </ul>
Bulk Density		
Loose	(30) (0.48)	
Tapped	(50) (0.80)	
Oil Absorption	27	
Hegman Grind	>6	
Microtrac D <sub>50</sub>	4	
Aspect Ratio	3 :1	

\*Viscosity will drop with the replacement of TiO<sub>2</sub> with wollastonite. The replacement levels of TiO<sub>2</sub> are formulation dependent and customers are advised to test in their own formulation to determine optimal levels of replacement.

\*NYCO offers a range of wollastonite products for testing. Results will vary due to particle size and application.

This data contains general information and describes typical properties only. It is offered for use by persons qualified to determine for themselves the suitability of our products for particular purposes. No guarantee is made or liability assumed, the application of this data and the products described herein being at the sole risk of the user.

For any further information, please contact [info@nycominerals.com](mailto:info@nycominerals.com)



## NYAD® Wollastonite – A Functional Additive in Powder Coatings

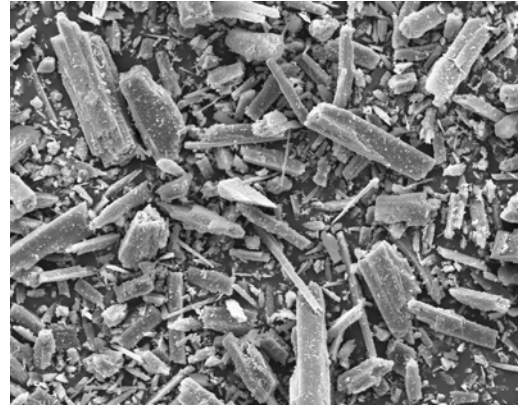
- **Corrosion Resistance**
  - The acicular structure of wollastonite improves the cohesive strength which provides improved corrosion and blister resistance.
- **Reinforcement**
  - Wollastonite acts as a reinforcing additive and promotes the retention of impact strength after prolonged exposure.
- **Moisture Resistance**
  - Pipes coated with powder are widely used in the transmission and distribution of gas. The pipes are buried in the ground and must retain adhesion, good electrical resistance and prevent corrosion over many years.
- **Gloss Control**
  - Wollastonite, especially the coarser grades, is an effective matting agent and lowers the gloss in decorative coating powders compared with other commonly used fillers.
- **Thermally Stable, High Heat Resistance**
- **Commercial Success in Varying Film Thickness and Functionality**

### Comparison Properties of Wollastonite in an Exterior Polyester/TGIC Coating Pigment: Filler Ratio is 1:3

Properties		NYAD 325	NYAD 400	NYAD 1250
Wollastonite				
Particle Size (D <sub>50</sub> )	µm	14	8	4
Gloss 60°	%	54	51	71
Corrosion Resistance	Salt Fog Hours	1000-1500	1000-1500	1725-2200
Impact Resistance	In-lbs., pass	160	160	160
Pencil Hardness				
Mar		H	H	F
Gouge		2H	H	H



Typical Properties of Wollastonite	Value
Appearance	White
Morphology	Acicular
Molecular Weight	116
Specific Gravity	2.9
Refractive Index	1.63
pH (10% slurry)	9.9
Water Solubility (g/100cc)	0.0095
Density (lbs./cu.ft.)	181
Bulking Value (gal.lbs.)	0.0413
Mohs Hardness	4.5
Coefficient of Expansion (mm/mm/°C)	6.5 x 10 <sup>-6</sup>
Melting Point (°C)	1540



**Powder Grade Wollastonite (x500)**

Product(s)	Recommendations	Features of Wollastonite
<b>NYAD® 325/M325</b> <b>NYAD® 400/M400</b> <b>NYAD® 1250/M1250</b>	<b>Functional (325, 400 Mesh)</b> <b>Decorative (325,400 or 1250 Mesh)</b>	<ul style="list-style-type: none"> <li>• Acicular (needle-like) structure improves mechanical properties and particle shape influences gloss</li> <li>• Low specific gravity</li> <li>• Nonhazardous and environmentally safe</li> <li>• Low solubility</li> </ul>
<b>NYGLOS® 8/ASPECT® 4000</b> <b>NYGLOS® 4W/ASPECT® 3000</b>	<b>High heat resistant, thicker coatings</b>	
<b>Grades used depend on coating thickness and functionality</b>	<b>Chemical modifications enhance corrosion performance</b>	

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