



Mechanisms of Corrosion Protection with Surface-Treated Wollastonite Pigments

This article expands the understanding of corrosion protection with calcium silicate pigments.

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For almost 20 years, treated Wollastocoats® have been used successfully in both inhibitive and barrier coatings for metal. Using unmodified calcium silicate (wollastonite) in anti-corrosive systems goes back even further, but not until the pigments were specifically engineered for this type of service did the valuable performance effects that are associated with the use of these materials become well-established tools in the design of this type of coating.

Recognition of the value of these materials is now global, a fact that is reflected in the annual growth of sales. However, there still remains some degree of confusion concerning the role of these pigments in anti-corrosive primers.

There are many aspects of the fundamental mechanisms of corrosion control with barrier and inhibitive primers. Even after 50 years of research, they remain incompletely elucidated. In spite of these limitations, this article reviews the most reasonable explanation for the action of these pigments and presents some simple formulating guide-

lines that have been developed from empirical investigation and are based on ideas for optimized utility derived from the fundamental chemistries involved.

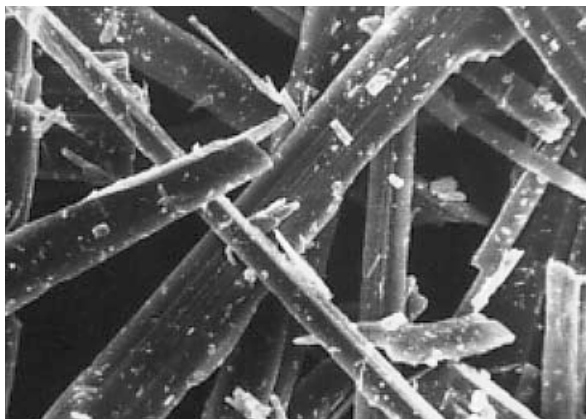
Several attributes of the pigments have direct bearing on their performance in anti-corrosive systems, including purity, acicularity, engineered reactivity and basicity.

Acicularity

Few pigments (except the organics, the attapulgite clays and certain zinc oxides) are truly acicular in nature. Wollastonite is, and this allows the pigment to be used as a reinforcing agent (see Figure 1). The reinforcing action is identical to that of shredded fiberglass in polyester and epoxy fiberglass composites, although with wollastonite, reinforcement occurs on a microscopic level. Aspect ratios of the 10-micron Wollastocoat are 3:1, and for special applications, ratios of up to 20:1 are available.¹

Moreover, the reinforcing action of wollastonite is obtained without the high oil absorption that is typical

Figure 1 / Photomicrograph of Wollastonite Pigment



of other acicular, fibrous and platy reinforcers (with their high surface areas). A 10-micron wollastonite has an oil absorption of about 30, whereas mica measures approximately 70. Consequently, wollastonite can be used in high-solids systems, where obtaining low viscosity and low volatile organic compounds (VOCs) are crucial.

High-aspect-ratio wollastonite is a coarser pigment than those that are used as bases for the treated Wollastocoat materials. High-aspect-ratio material has, however, found its own unique niches. As an asbestos replacement, it has been widely used in plastics. Certain specialty coatings, such as asphaltic roof coatings, benefit from its reinforcing action and improved resistance to cracking under ultraviolet (UV) radiation.

It can be argued that acicularity itself is not directly involved in the observed enhancement of anti-corrosive performance that comes with wollastonite pigmentation. In the field, however, there can be telling ancillary effects derived from acicularity.

Corrosion is an important secondary consequence of the deterioration of a coating's mechanical properties that is associated with UV exposure, autoxidation, crosslinking and other aging processes, especially in oxidizing systems. Brittle failure response to applied stress in the form of cracking and checking leads to an increase in the nonactivated diffusion of moisture, oxygen and ionic species through the film. Inevitably, this, along with the empirically established increasing wet adhesion that has so often been noted in films pigmented with the treated Wollastocoats, results in diminished corrosion resistance.

Purity

Purity is the aspect of New York State wollastonite that most differentiates it from other natural deposits (in China, India and Finland, for example). The New York deposit is associated with diopside and garnet and can be readily separated to provide an easily and completely beneficiated product.² The resultant pigment is chemically more homogeneous than typical wollastonites.

More crucial to high-performance applications is the product's surface uniformity, since this facilitates the uniformity and completeness of the subsequent surface-treatment process, which are prominent characteristics of the Wollastocoat pigments (see Figure 2).

Surface Treatment

Even refined pigments, such as the fine-particle-sized Nyad® 1250, have surfaces that are inevitably subject to many heterogeneities that are inherent in a natural product, including hot spots and cold spots, sites that can be more hydrophilic than others, sites that are more easily wet than others, and sites that have more or less affinity for the binder or water than others.

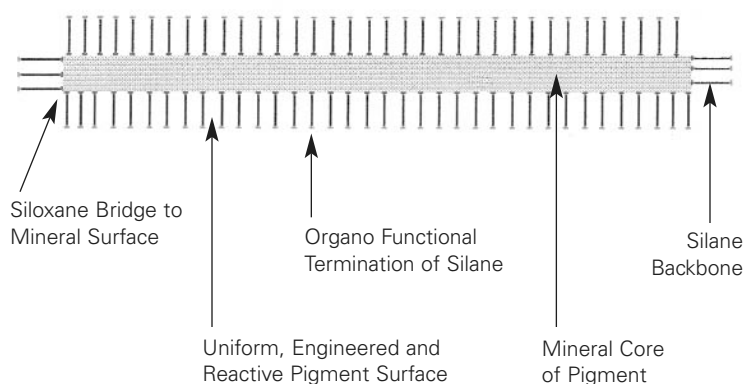
Such surface heterogeneity inevitably results in a less-than-perfect interface between the pigment and potential binders, and leads to residual voids, unwet crevices and increased opportunity for subsequent penetrants (such as water) to access the pigment surface and, through the

Figure 2 / Structure of Surface-Treated Wollastocoat

a / Unmodified



b / Silane Modified



unbound interstices, eventually the substrate.

When the surface of the pigment is engineeringly modified through treatment with a reactive silane, surface homogeneity is greatly enhanced, resulting in what is essentially an inorganic core that is shielded with a more uniform organic sheath. This is both more easily wetted by and more predictably reactive with the vehicle binder of any potential coating. Acid resistance is also improved, and the chemically secured interface between pigment and binder produces a coating film matrix in which the pigmentary interfaces are much less available to moisture and/or other film penetrants than with the unmodified pigment.

Surface modification of the engineered wollastonite pigment is performed using silane chemistry by means of a proprietary process. Wollastonite, glass and other siliceous materials have shown themselves to be uniquely suitable for treatment with the alkoxy silanes.³ In the case of wollastonite, the basic nature of the mineral catalyzes the hydrolysis of the silane alkoxy groups, and, in the presence of moisture on the pigment, a silanol condensation reaction gives rise to Si-O-Si bridges across the interface of the pigment and the treatment (see Figure 3).

When the treated pigment is applied to the uniquely hospitable particle surface during the manufacturing process, it presents a more or less aligned external organic sheath bearing organofunctional groups to the environment. The environment is the binder system into which these pigments are eventually dispersed.

While it is theoretically possible to specifically engineer mercapto, ureido and other groups onto

the molecule, two or three systems have proven most popular as treatments on wollastonites for coating applications. 10AS Wollastocoat presents reactive primary amine groups to the binder, 10ES Wollastocoat presents reactive epoxy groups. 10WC Wollastocoat is used in systems where vinyl type reactivity is possible.

It is essential, when using these pigments in coatings, to ensure that, by using complementary organic moieties on pigment and/or binder, the pigments are chemically bound (through the reactive groups on the organic sheath) into the polymeric matrix.¹ Thus, 10AS can be reacted into

Figure 3 / Wollastocoat Reactions in Manufacture and Use

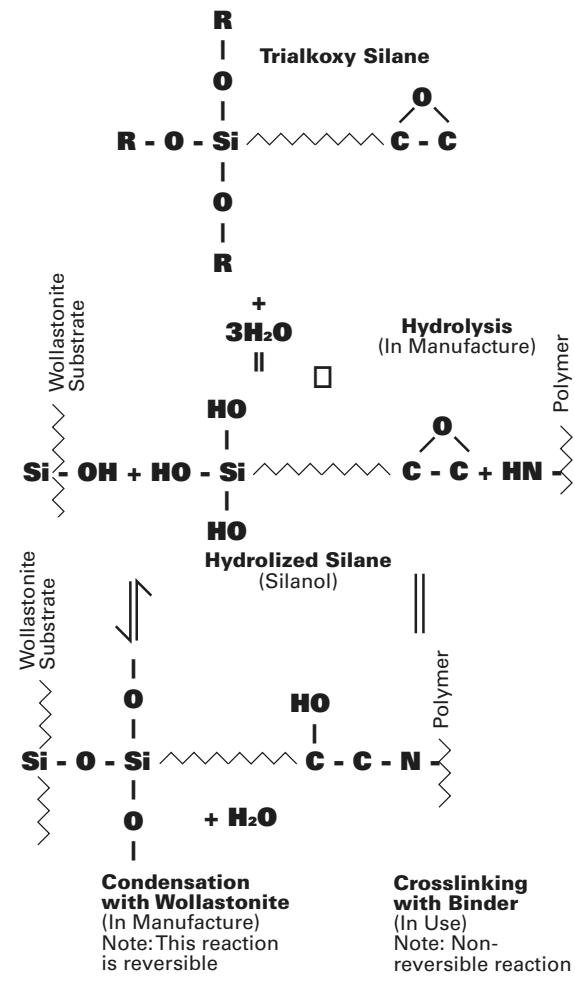


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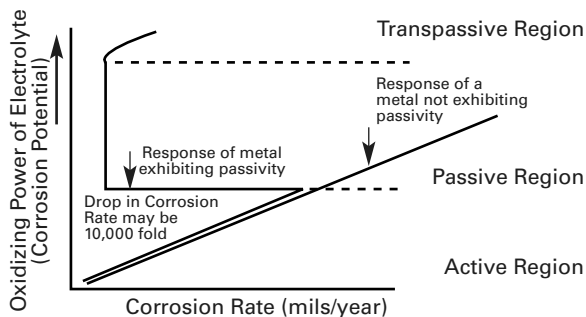
polymeric composites that have groups that are reactive with amines (epoxies, urethanes, alkyds, polyesters and amino-formaldehyde-based systems), while the 10ES must be used with amines, amides and urethanes.

It is interesting to note that the 10ES should not be used with alkyd systems. This restriction includes oil-modified urethanes, epoxy esters and other oxidizing systems. The result of such misuse is the system's tendency to "feed," which incurs an increase in viscosity shortly after mixing and in early storage. The problem is most severe in shorter oil systems. 10WC is most optimally used in systems such as unsaturated polyesters, vinyl esters and acrylics. The 10AS seems to work well in acrylic-based latex systems.

Basicity

The basicity of wollastonite is perhaps the most important aspect of the pigment where corrosion resistance is

Figure 4 / Effect of Oxidizing Power of Electrolyte (Corrosion Potential) on Corrosion Rate with Passivating and Nonpassivating Metals



concerned. Even the untreated material, Nyad 1250, works remarkably well in many systems, including Maincoat PR-71 (Rohm & Haas) and Zeneca's XA-6085. The same pigment is also used in polyurethane and epoxy primers, where pricing constrictions prohibit the use of the more efficient, though more expensive, Wollastocoats.

Wollastonite is basic without being excessively soluble, a characteristic that is invaluable for use in anti-corrosive coatings. Table 1 illustrates the pigment's solubility characteristics against typical values of many common inhibitive pigments. Wollastonite is not, however, a corrosion-inhibiting pigment in the classical sense, although its value as an auxiliary pigment used in combination with almost any other inhibitor has been well-established by experiments.⁴

To understand the way wollastonite functions in these coatings, passivity and corrosion control by inhibiting moieties must be reviewed.

Passivity

Steel is one of several metals that exhibits passivity, which is a condition wherein a metal that is usually very reactive with the corrosive environment suddenly shows an unexpected lack of reactivity (see Figure 4). With most corroding metals, as the oxidizing power of the electrolyte is increased, the rate of corrosion increases.⁵ With metals that exhibit passivity, this is only true to a point, because as the oxidizing power of the electrolyte reaches a specific level, suddenly corrosion drops dramatically. In spite of further increases in the oxidizing power of the electrolyte, there is no further increase in the rate of attack. It is, therefore, useful in corrosion control to ensure that any electrolyte that accesses the metal beneath the film is of sufficient oxidizing power to favor establishing passivity.

Effect of Oxygen and Oxidizing Agents

Theoretically, passivity can be established solely by oxygenating the electrolyte if that much oxygen could be dissolved in water. This is not possible, and no more than about 6 mls of oxygen per liter will dissolve in water at a neutral pH.⁶ As seen in Figure 5, approximately 20 mls of oxygen is needed to establish passivity. Thus, it is common for corrosion engineers to add oxidizing agents, such as chromates and molybdates, to the interfacial electrolyte against the steel surface. When dissolved in water, these oxidizing agents will increase the electrolyte's oxidizing power sufficiently to establish a passive state in the metal, even at low oxygen levels.

In the hands of paint formulators, materials that produce oxidizing chromate and molybdate ions are included in the primer films as inhibitive pigments. Dissolving into water as they access and move through the film, these ions, which are released by the pigment, modify the

Table 1 / Water Solubility of Wollastonite

Pigment	g/100cm ³
Wollastonite	0.0095
Zinc Yellow	0.1
Strontium Chromate	0.05
Zinc Phosphate	0.00003
Basic Lead Silico Chromate	0.01
Aluminum Tripolyphosphate	1.0
Calcium Borosilicate	0.35
Barium Metaborate	0.3
Basic Zinc Chromate (Zinc Tetroxychromate)	0.01

Figure 5 / Effect of Dissolved Oxygen Concentration in Water on the Rate of Corrosion of Steel at pH 7 and pH 10 (at 25°C)

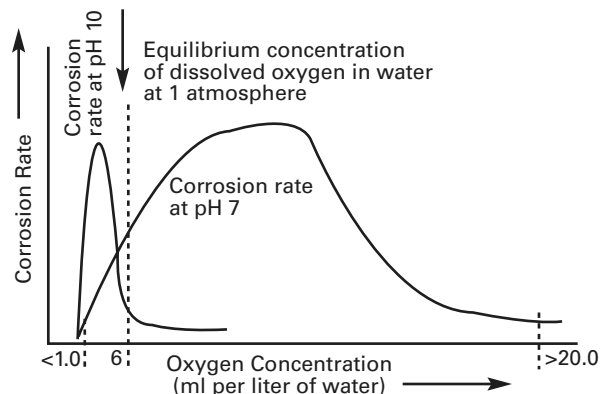
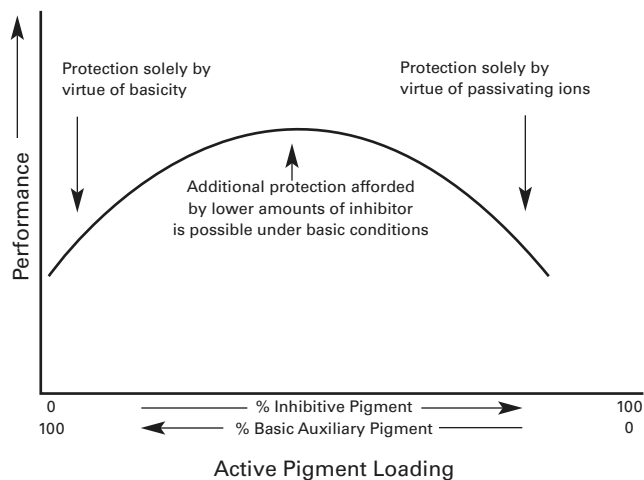


Figure 6 / Synergism of Wollastocoat Inhibitor Systems in Inhibitive Metal Primers

interface as they reach the metal. Other inhibitors that are not oxidizing agents appear to require the simultaneous presence of some oxygen to induce passivity.⁷

The physical phenomena that accompany these electrochemical changes are thought to be related to the formation of dense, impermeable, monomolecular films of mixed oxides (such as chromic oxide/ferric oxide) across the anodic sites on the steel, thereby preventing iron ions from going into solution. While this seems very likely with chromates and the molybdates, other inhibitors might work in other ways and can be instrumental in the enhancement of the natural ferric-oxide layer rather than becoming themselves involved as part of the passive film.^{7,8}

It has also been reported that certain zinc-based inhibitors seem to plate zinc ions at the cathode, as well as reinforce the natural oxide layer that forms on the steel as soon as the metal is exposed.⁹ It cannot be totally dismissed that some form of calcium precipitation mechanism does not play a role in wollastonite protection.

Depassivating Salts

Many of these protective reactions can be offset by depassivating ions, such as chlorides and sulfates, that compete with the inhibitor for adsorption onto the steel.

This disrupts the passive layer so that the corrosion rate will again increase.¹⁰ There is, in fact, a crucial quantity of inhibitive ions (depending upon type) that are necessary to accomplish inhibition in the presence of a given level of depassivator, and this quantity increases more than linearly as the depassivating ion level increases (larger amounts of oxygen are required to achieve passivity in the presence of the depassivating ions).¹¹

Paint films normally do not readily allow the transmission of ionic materials through their polymeric continuum, and, as in most models, inhibitive ions are derived from within the film, and depassivating ions from without, the ratio of depassivating ion to passivating ion at the metal interface beneath the film is normally loaded in favor of inhibition.

Effect of Basicity on Inhibitive Ion/Depassivating Ion Threshold Ratio

As the pH of the electrolyte increases, the critically dissolved oxygen concentration that is necessary to achieve passivation from oxygen alone is markedly reduced. At a pH of approximately 10, the required oxygen concentration for passivation approaches the level (6 mls/liter) that is present in air-saturated water (see Figure 5). At pH levels way above 10, inhibitors are not necessary for passivation, and at pH levels between 7 and 10, less inhibitor is necessary than at pH 7. The pH of water buffered by the solubilized fraction of wollastonite slurries is approximately 10. (Under practical conditions in formulated coatings, system pH might be somewhat lower because of the effect of other components on the formulation.)

It is, however, quite clear that, in the presence of a pH-raising pigment like wollastonite, the levels of inhibitor necessary to secure passivation will be depressed, and the inhibitor/depassivator threshold ratio will be shifted so that inhibition is favored. Thus in wollastonite-containing systems, less primary inhibitor is necessary, and combinations of wollastonite and inhibitor will be synergistic, producing more efficient and more protracted inhibition than would either the inhibitor or wollastonite alone (see Figure 6).⁴ The effects have been confirmed in several empirical studies and have been reported elsewhere.^{1,4,7}

Performance in Barrier Primers

There have been many instances where Wollastocoat has produced satisfactory performance even without inhibitive pigments. It is unlikely that this effect is related to passivation alone, because the pH of wollastonite is not high enough for this to occur. While it is possible



Photo courtesy of NYCO Minerals Inc.

that some cathodic deposits might act to polarize the cathode, reducing the effects of electrolytic oxidation, it seems more likely that protection in these systems is through other mechanisms.

For the most part, these systems are all seen to be barrier-type formulations of high glass transition temperature (T_g). These protect steel by ensuring low electrolytic conductivity of the environment beneath the film and/or by depriving the cathode reaction of the necessary fuel (oxygen) to drive the corrosion reaction. Coal tar epoxies, aluminized epoxy mastics and other relatively impermeable epoxy and urethane systems have been formulated with both IOAS and IOES with considerable benefit and without any of the drawbacks that might be associated with the inclusion of even slightly soluble pigments in barrier compositions (osmotic blistering under fresh water immersion conditions and in high humidity, for example). In these systems it seems most likely, therefore, that the physiochemical effects of shape and surface reactivity add some additional reinforcement of the crosslink density of the system.

Mayne and Mills^{12,13} have shown that corrosion in this type of system (the barrier system) can be associated with ionic permeability through heterogeneous areas of low crosslink density in otherwise nonpermeable, high-crosslinked films. Funke has postulated that, in binders having chemical reactivity with the pigment surface, the pigment can act as a crosslinking center that might augment the homogeneity of the matrix.¹⁴ Thus, in addition to physically reinforcing the rigidity of the film (because of the pigment's shape), each needle of Wollastocoat might chemically reinforce the system (presumably raising the T_g) by virtue of the chemical bonding that takes place with the vehicle through its surface treatment.

Why are such systems so resistant to osmotic blistering, when a pigment of even limited solubility is used? It seems most likely that the high crosslink density and adhesion of these high-performance systems allow insufficient water accumulation at the interface to set up osmotic centers. Under 190°F distilled-water immersion (above the T_g of the polymer) an epoxy/polyamide primer pigmented with IOES produced blisters in six days, although time to

blister was extended to two weeks using topcoats with aluminum that replaced the original titanium-dioxide (TiO₂)-pigmented finishes.

However, when the polyamide resin was replaced with a cycloaliphatic amine, which gave a system with a much higher T_g but still contained Wollastocoat, all blistering was eliminated, even though the high-temperature immersion exposure was extended to more than 10 months. From these studies it would appear that in rigid, high-T_g systems, even under the most aggressive stress, osmotic effects from Wollastocoat pigmentation are not substantial enough to produce coating failures.

Stress Relaxation Effects

High-performance thermosets, such as highly crosslinked epoxies and other systems including unsaturated polyesters and vinyl esters, are subject to high shrinkage on polymerization producing high levels of internal stress. These stresses inevitably oppose both the adhesion of the film to the substrate and the cohesion within the film itself. In strong systems such as these, internal stress is generally not great enough to

produce failure alone, but, as the stress is stored within the film as an internal strain, it severely diminishes the film's ability, after curing, to withstand the application of other tensile stresses derived from hygrothermal or external sources.

In overcoating applications, for example, where epoxy overcoats are applied over less well-adherent old oil and alkyd systems, instances of stripping are not uncommon. In these cases, tensile stress in the recoated composite is great enough to pull the recoated system (already under tensile strain before recoating) from the original interface.

Whatever its source, stress is counterproductive to any design for optimized corrosion control. Where it becomes so great as to exceed either cohesive force that maintains film integrity or adhesive force that keeps the film in place, it directly and substantially threatens protection through cracking or de-adhesion. Other effects of less extreme stress accretion are probably not as yet fully appreciated. Certainly its avoidance or mitigation can only improve system design.

A variety of devices have been proposed to mitigate these difficulties¹⁵, including the use of thinner coating

films, the use of multiple thin (as opposed to single thick) coats in recoating and/or, the use of flat, platy pigmentations (such as aluminum flake) that tend to attenuate stress by allowing more stress relief in the lateral plane of the film.

The silane-treated Wollastocoats also add a measure of stress release, especially under wet conditions. The oxane bonds formed by silanol condensation between the hydrolyzed silane and the silanol groups on the surface of the pigment are not permanent. In fact, they are very susceptible to hydrolysis in the presence of moisture, but reform even more readily.¹⁶

This dynamic equilibrium, in which the oxane bonds can continuously break and reform, provides an excellent stress relaxation device. Stress applied to the interface of the pigment and the silane bridge (and therefore the polymeric binder) can be dissipated, as this reversible dynamic equilibrium allows the silane-bonded polymer to slip along the pigment surface until a more relaxed orientation is achieved.^{17,18}

Conclusion

The pigmentation of coatings has become an increasingly exact discipline. With the replacement of traditional toxic corrosion inhibitors and the necessary preoccupation with controlling VOC and hazardous air pollutant levels, there is no room for the undisciplined approach to pigmentation that characterized early formulating practice. Careful control of such constants as PVC and CPVC is now considered essential.

Newer pigments are often deliberately engineered for specific uses. Such pigments are almost always by definition more complex in usage. The Wollastocoats are no exception, and understanding their benefits has followed the empirical realization of their effects. This article has related those formulating techniques that have evolved from empiricism to the most likely fundamental mechanisms that could underlie such usage. In this way, it is hoped to facilitate their optimal utility. ☉

For more information on wollastonite, Circle Number 160.

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