The Evolution of Calcium Metasilicate in Paint and Coatings

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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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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 use 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. Local variations in temperature and pressure that occurred during metamorphism of the sediments 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 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 1960s, 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 1, 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 reinforcing 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 found that unlike other alkaline extenders (calcium carbonate, magnesium silicate and nepheline 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

<table>
<thead>
<tr>
<th>Table 1. Calcium Metasilicate — Physical Properties</th>
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<tbody>
<tr>
<td>Chemical formula: CaSiO$_3$</td>
</tr>
<tr>
<td>Molecular weight: 116</td>
</tr>
<tr>
<td>Appearance: White Powder</td>
</tr>
<tr>
<td>Particle shape: Acicular</td>
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<tr>
<td>Refractive index: 1.63</td>
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<tr>
<td>Specific gravity: 2.9</td>
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<td>Weight/gal. (lbs./U.S. gal): 24.17</td>
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<tr>
<td>Bulking value: 0.0413</td>
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<td>Oil absorption (gm/100 gms oil):</td>
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<tr>
<td>Unmodified: 28.3</td>
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<tr>
<td>Wollastokup: 20.25</td>
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<td>pH of 10 percent slurry in water: 8.10</td>
</tr>
<tr>
<td>Hardness (Mohs): 4.5</td>
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<td>Water solubility (gms/100cm$^3$): 0.0095</td>
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<td>Melting point (°C): 1500</td>
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<tr>
<td>Coefficient of thermal expansion (mm/°C): 6.5x10$^6$</td>
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<td>Moisture content (percent): 0.5</td>
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</tbody>
</table>
Engineered High-Performance Calcium Metasilicate Pigments

In the late 1970s, technology was developed to produce much finer micronized grades of wollastonite having further refinements in beneficiation, sizing and quality control. Around the same time, new surface modification technology was being developed for use in specialty products designed for reinforced plastic applications, required by the automobile industry.

Wollastonite had been, for some years, employed as a reinforcing pigment in a number of proprietary filled polymer composites (thermoplastics such as nylon, thermosets such as phenolics, epoxies, polyesters and polyurethanes). In these applications, the pigments developed a considerable market. However, the highly polar, high-surface-area of the mineral and a degree of natural hydrophobicity caused some difficulties in the quality control of parts filled with the product, and led to some vulnerability to moisture and other corrosives which attacked the interface between the filler and the polymer. Loadings had to be critically controlled if impact strength and other physical properties were to be optimized. In the first instance, the new development programs were specifically directed to resolving these difficulties.

The technology was based on the establishment of improved interfaces between the polymer and the pigmentary reinforcer. It employed specialized techniques to reengineer the surface of selected grades of the wollastonite (with proprietary blends of organo silicate, zirconium and titanium based coupling agents, surfactants and other proprietary materials).

In these techniques, the inorganic end of the coupling agent is reacted with silanol groups on the pigment surface to produce a permanent primary valency linkage which effectively anchors the organic onto the surface. The organic portion of the treatment is aligned outward from the pigment, available for subsequent access by the polymeric binder. Figures 1A and 1B show the effect when silanes are employed as part of the treatment. The alkoxy groups on the silane are first hydrolyzed by the water on the pigment surface to produce silanols. These will then react with the silanol groups on the pigment surface.

It was found that the calcium silicate surface was particularly hospitable to the establishment of thin, primary valency bonded monomolecular shells of these unique materials. After treatment, the wholly inorganic surface of the pigment is transformed into one which is at least in part organic, and therefore more hospitable to wetting by specific organic
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. 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 prototypikup 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 in many vehicle systems (epoxies, alkyls, 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 nontoxic inhibitors. Wollastokups have been found to be effective auxiliary pigments in inhibited primer systems pigmented with a variety of phosphates, phosphites, phosphosilicates, borates, borates, 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.9 This type of synergism has been demonstrated in alkydes, 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 was employed with the basic molybdates, and this may be a key to the mechanism underlying this type of performance.

Similar observations have 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.10 In another study, where zinc oxide was found to improve the performance of a range of simple chromates (calcium, strontium and barium chromates), zinc tetroxychromate (basic zinc chromate) was extracted from leachants of the dry films.11 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.12 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 metaasilicate. In an alkaline environment, the primary inhibitive system is able to do its job more easily and better resist deactivation by chloride, sulfates, 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 hexamethylyldiamine phosphate) are used to inhibit fresh water systems (where the presence of calcium ions is found to be essential to phosphate inhibition).

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, the extent 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 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 PVC's 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 matching the reactive groups on the pigment with those in 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 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 complementarily 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 pigmented 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 alkyls (most severely in short oil alkyls) 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 alkyls, 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. 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 alkyls, epoxy resins and water soluble acrylics, and depress the protective electrical double layers that 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 resin. 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. 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-
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 sheath 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).

Valvulants, 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 Wollastonite) 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 leathily stabilized than conventional latex vehicles. The surfactant systems tend 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 multivalent cations before the protective charge shield collapses. If the Wollastonite is to be used in these systems, either levels of pigment must be more carefully controlled, or, in two component systems (water based epoxy/acrylics), the 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, acrylates, 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 amineminated polymer with a volatile carboxylic acid. This latter technique is used in some water-based epoxyamine 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/or 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 Wollastonite 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.

**References**

5. Literature, NYON, Willahoe, NY.