Why organic coatings stratify

Challenges and opportunities of locally varying coating properties

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During film formation, specific coating ingredients develop local gradients in concentration, depleting some regions and enriching others. Often, this is considered a nuisance - but such effects may also be deliberately used to design highly effective coating systems.

If there is a stimulus, there is a response. This is what biological organisms do: they are stimulus-driven. When plants are exposed to the sunlight, they convert the electromagnetic radiation of the sun through photochemical reactions into their growth. For all we know, coatings only degrade upon exposure to sunlight and the implications of this are costly. Can coatings be responsive, or can they be designed in such a way that they can be response-driven? If so, how? Can we design and develop organic coatings that last longer and serve certain response-driven functions? What response-driven functions? For example, when exposed to water, coatings may exhibit repelling properties, or if desirable, absorb moisture.

Learning from nature

In biological systems such as plant stems and bones, gradients in microstructure and porosity are very common. For example, the strongest elements often are found in regions that experience the highest stresses. In coatings, however, the local variation of composition, structure, and other features is relatively new. Such multi-component systems exhibit a variety of fascinating properties, depending on their chemical composition and the compatibility of individual components, on processing and film formation conditions, and on their environment. Ultimately, they may exhibit stratified morphologies. As an analogy, the gradual changes in the elastic properties of sands, soils, and rocks of the Earth's surface influence the settlement and stability of structural formations, plate tectonics, and other properties. Learning from nature, coatings scientists increasingly aim to engineer polymeric systems in a similar way, to design coatings that are more damage resistant than traditional homogenous films.

Although it has been recognized about a decade ago that compositional gradients at or below the surface, or near the coating-substrate interface, can alter a number of properties, relatively small progress has been made to take advantage of this unique phenomenon. For example, a simple melamine/polyester coating may exhibit a varying stain resistance, depending on the ability of melamine to form self-condensed structures near the surface. As the melamine content near the surface increases, the stain resistance also increases, and these quantities are a function of film thickness (see Figure 1).

This process can easily be controlled by neutralizing amines used in these systems. For example, stratification can be controlled by dimethylaminomethylamine (DMEA), which causes melamine molecules to self-condense as a result of fast DMEA volatilization at the film-air interface, subsequently increasing acidity and giving rise to melamine condensation [1]. The stain resistance increases because melamine crosslink near the surface. It should be noted that other variables such as OHV content or the degree of polyester branching do not have a similarly pronounced effect as volatile or non-volatile bases.

Fundamental understanding of effects is necessary

There are other examples of minute chemical or physical stimulus-response changes that may serve to develop interesting coatings properties. However, they can usually only be exploited for desirable properties if we understand the origin of their behavior. If we do not, the same effects may become a costly problem. This is why an understanding of the molecular origin of such effects is important. While the examples above illustrate how chemical design of coating formulations may alter the film surface properties, there are also other factors that may provide opportunities for altering surface properties. Let us identify such other factors, which may control the stratification of individual components and ultimately alter the interfacial properties, e.g. adhesion.

Example: Surfactants and adhesion

It is well known that latex emulsions are not used to coat metal surfaces, and there are good reasons for that. Aside from a low glass transition temperature, most latex emulsions contain a number of components that are sur-
face active. Surfactant molecules are one of them. About 1 with of surfactants is considered a reasonable concentration in an emulsion system. However, if for some reason the surfactant molecules are driven to a specific film region, their local concentration levels will differ from that - some regions will be lower, but other regions excessively higher in concentration. The surfactant distribution across the film thickness becomes non-uniform - and there are numerous forces that may contribute to this effect. For example, when water evaporates, surfactant molecules can be driven to the film-air interface, thus affecting many surface properties. Contrary to this, during film formation the same surfactant molecules are capable of compensating the excess of interfacial energy at the film-substrate interface. This may cause surfactant molecules to migrate to the film-substrate interface. In the early 90s, this behavior was observed for emulsions such as ethyl acrylate/methacrylic acid (EA/MAA) [2] and styrene-butyl acrylate (Styln-BA) [3], and so in others. Interestingly enough, surfactants could be driven either to the surface (by evaporation), or to the film-substrate interface, depending on the substrate-coating interfacial energy. On metallic substrates, for example, which show high surface tension, surfactants may preferentially migrate to the coating-substrate interface, causing adhesion problems. It takes only a monolayer of surfactant molecules at the film-substrate interface to affect adhesion, particularly if the surfactant molecules are water-soluble. Traces of water will dissolve the surfactant layers, thus destroying the interface, ultimately leading to adhesion failure. However, one could also take advantage of this phenomenon, and design an emulsion system with surfactant molecules that act as adhesion promoters, thus enhancing the adhesion of latex films. This opens up numerous opportunities.

Bring additives to regions where they are most effective

A different route must be taken for pressure sensitive adhesives such as Styln-BA, where the mobility of the surfactants must be suppressed to extend the lifetime of the adhesives. The inherent diffusion of surfactants or other additives to interfacial regions will result in the loss of adhesive properties with time. In general, not only surfactants are susceptible to mobility. Almost any unattached entity placed into a coating formulation may migrate, and the degree of mobility will be determined by its compatibility with other components, the physico-chemical properties of the interfacial regions, and the film formation conditions. Although this ability of individual components to migrate is of course a major concern in the development and control of coatings properties, there are also new approaches. For example, additives should be most effective in coating regions where they bring about desirable properties. Specifically, adhesion promoters will be more effective near the film-substrate interface, whereas UV absorbers should be located near the surface exposed to the ultraviolet radiation. The challenge is to design and formulate coatings in such a way that individual components will have a desirable and meaningful spatial distribution. An example is the stratification of commercially available A-B-A block and random copolymers of silicone and poly(ether) components of additives in acrylic-isocyanate and acrylic-melamine coatings [4]. Depending upon their compatibility with the polymer matrix and the effect of other external factors such as surface tension, the additives may modify, thus leading to desirable surface and interfacial properties.

Different pigments - different formulation

Let us take this concept one step further. When inorganic pigments are placed into organic coatings, pigment particles will adsorb or repel resins and crosslinkers, and other components, depending on the nature of their surfaces. Again, this will be dictated by surface and interfacial properties. For example, resins containing carbon black pigments will exhibit entirely different characteristics than the same resins pigmented with titanium dioxide. One consequence of this is the well-known adhesion problem of carbon black containing coating systems on plastics. Incidentally, changing the same resins/crosslinker ratio is commonly practiced, but it should be realized that the consequences must be detrimental. Thus, when clear polyester/or epoxy powder coatings are formulated at 40/60 ratios, the same ratio is applied regardless of the pigment being used. But particularly functionalized pigments with reactive surface groups may serve as crosslinkers themselves, or react with crosslinkers. Consequently, the stoichiometry of the entire formulation and thus its properties will change. For instance, good adhesion, but poor mechanical properties may be achieved.

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