L.E. SCRIVEN'S CONTRIBUTION TO THE COATINGS INDUSTRY: A BASF PERSPECTIVE

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High-resolution **S**canning **E**lectron **M**icroscopy (SEM) has developed into a powerful tool, which can visualize and elucidate the behavior of various waterborne coating systems in their dry state and with the help of a cryo-stage in their wet state. This presentation will focus on Professor Scriven's collaborative works with BASF toward better understanding the micro-structural, colloidal behavior of latex dispersions and their role in respective formulated coatings. The knowledge gained through this cooperation has been instrumental in designing several new commercial products.

Over the last 50 years the science behind emulsion polymerization and latex design has matured into an industry with a current global production capacity of 10 million metric tons (dry) per year. The role of this important coating's raw material has continued to evolve and expand due to the growing environmental and now an economical push to reduce greenhouse gases that are generated and emitted from solvent-borne applied coatings. These gases result from the decomposition of volatile organic components, which were traditionally used to help promote key performance properties (i.e. film formation and freeze-thaw (F/T) stability). As the use of VOCs becomes evermore stringent, these coatings must now be increasingly dependent on the careful design of the latex architecture to achieve the same level of performance as their solvent reliant predecessors. As a result of this paradigm shift, there have been more recent efforts to understand the fundamental nature of colloidal polymeric latex dispersions and their role in promoting performance concerning how they interact on the microscopic level with the other ingredients of

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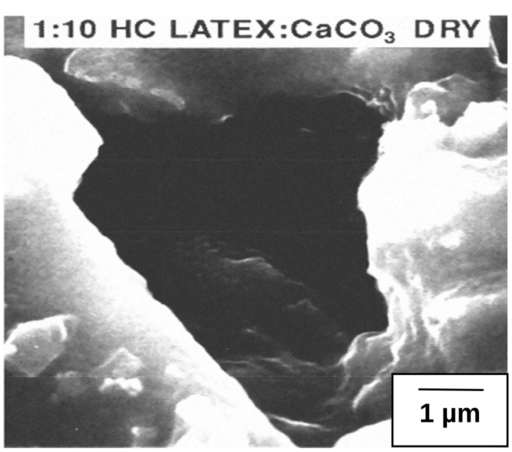
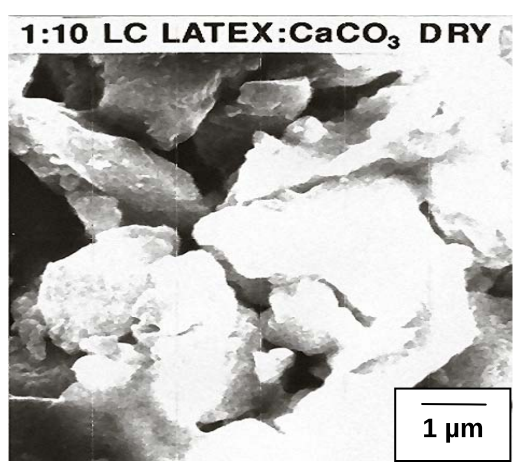
the coating formulation. The overall aim of this research is to advance the science of latex design which will result in elimination of solvent auxiliaries used in coatings formulations while maintaining or even increasing the level of binder performance.

Both conventional and cryo-SEM allow us to begin to address this goal through a qualitative assessment through obtaining micrographs or photoimages of the coatings microstructure. Cryo-SEM, in particular, further allows us to visualize the colloidal interactions in its “undisturbed” wet state. This is achieved through the use of a high pressure freezing apparatus, where the sample is rapidly frozen under high pressure (~2100 atm) and then fractured. High pressures are needed during the freezing process to prevent the formation of large ice crystals which can denature the specimen. The vitrified water on the sample surface is differentially sublimed and the sample is sputter-coated with platinum before it is analyzed to prevent charging artifacts. After the coating process the sample is examined in a SEM equipped with a cryo-stage.

One of our main motives is to better understand the phenomenon of film formation of latex dispersions and latex–filler formulated coatings. The film formation of the latex particles during the drying process of latex fillers formulations is of particular interest due its critical nature in the development of binding strength or film integrity of the dried coating. In this case the influence of ionic strength of the latex serum and the extent of carboxylation on the latex particle surface change the way latex particles consolidate with themselves and with the particles in the coatings formulation.[1] *Figure 1* shows the influence of the degree of carboxylation of the polymer latex toward forming a latex/filler film containing $CaCO_3$ particles.

Figure 1. (left) Conventional SEM Micrograph of a suspension of one part latex with a high degree of carboxylation (HC) to 10 parts $CaCO_3$. (right) Convenional SEM Micrograph of a suspension of one part latex with a low degree of carboxylation (LC) to 10 parts $CaCO_3$.

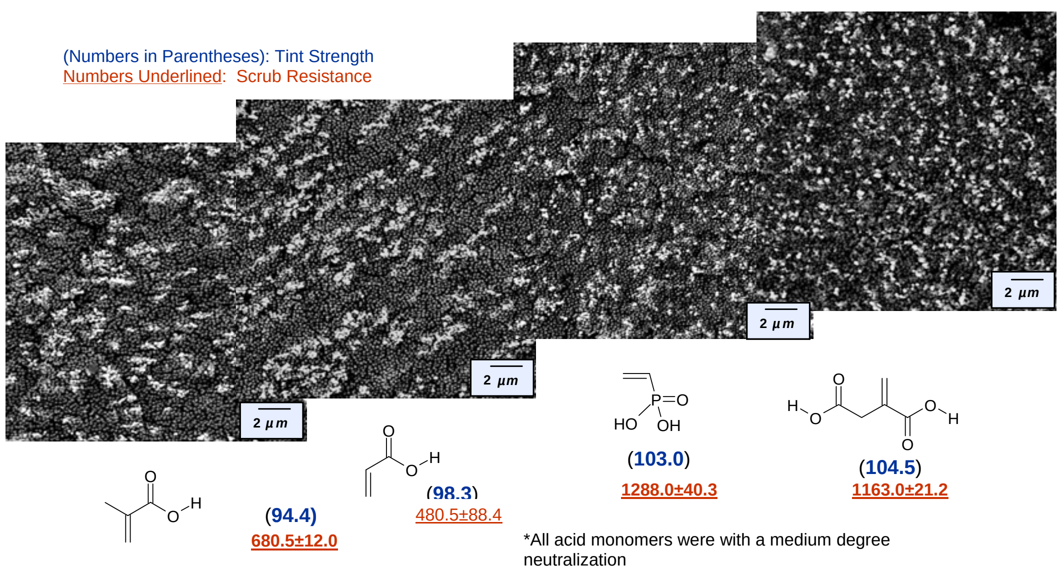




The left hand figure shows the composite containing a latex with a high degree of carboxylation, where there appears to good film integrity and inclusive coating of the $CaCO_3$ particles. The opposite is apparent in the right hand figure where the latex with a low degree of carboxylation appears not to film form readily nor coats the $CaCO_3$ particles adequately.

Additionally, we were interested in enhancing the interaction of the latex with inorganic pigments (TiO_2) of the coating in its wet state and therefore increasing the latex's TiO_2 efficiency. Through latex design we decided to vary the type of functional acid monomers used and how they were partitioned throughout the latex particle and in the latex serum.[2] Both the acid monomer type and acid monomer partitioning play crucial roles with regard to how the latex particles are orientated and interact with each other and with the pigment particles in forming strong homogeneous and durable films. Consequently, these interactions have a profound influence over such application properties as scrub resistance and tint strength. *Figure 2* shows cyro-SEM micrographs of four model latices, which contain different types of functional acid monomer (acrylic acid (AA), methacrylic acid (MAA), vinyl phosphonic acid (VPA) and itaconic acid (IA)) in mixture with TiO_2 slurries in the same proportion to what is found in a flat paint formulation.

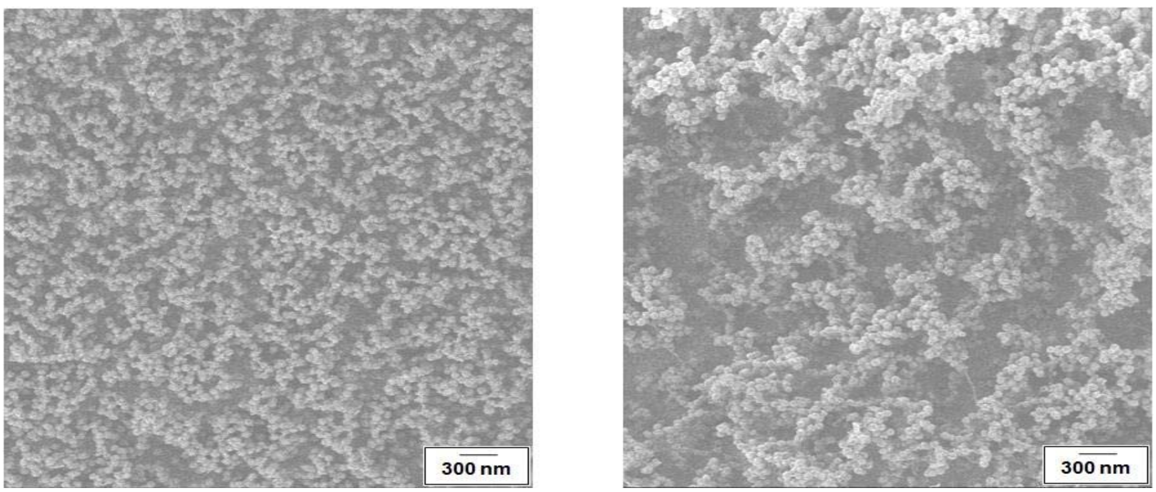
Figure 2. Influence of Acid Type on Pigment Dispersibility/Paint Film Durability and Tint Strength.



The figure shows nicely the correlation between the dispersibility of TiO_2 particles with the product performance properties of tint strength and scrub resistance. It is easily seen that AA and MAA promote TiO_2 efficiency to a lesser degree than VPA or IA.

Finally, freeze-thaw stability and consequential polymer and colloidal characteristics are also applications areas of interest that warrant further investigation.[3-5] By gaining information on the causes of destabilization or viscosity rise during the F/T processes in a F/T-unstable latex, new strategies and technologies can be developed which can promote F/T stability. *Figure 3* shows the cryo-SEM micrographs of a model latex before and after 5 freeze-thaw cycles. The image on the right shows a higher degree of particle aggregation than what is seen in the unspoiled latex sample. Consequently, after the fifth freeze-thaw cycle the viscosity of the dispersion rises by a factor of 30.

Figure 3. Cryo-SEM Micrographs of a Model Latex Before, Left, and After 5 F/T Cycles, Right.



This presentation will focus more on these areas of interest and highlight the some of the award winning papers that resulted from this cooperation.

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