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High Solids Coatings

Werner J. Blank
King Industries Inc.
Science Road
Norwalk, CT
USA
wblank@kingindustries.com

Introduction

VOC regulations have changed the nature of the US coating business forever. The development of high solids or solvent free coatings, water-borne and powder coatings are among the approaches taken by the coating and resin manufacturer to reduce VOC. The factors influencing the viscosity of polymer solutions are reasonably well understood. The WLF equation provides a powerful tool to link polymer structure (Tg, MW and MW distribution) to viscosity and solids content of polymers. The low MW oligomers used in high solids coating require extensive crosslinking to achieve acceptable film properties. Careful control of functionality and reactivity of the oligomers is required to obtain stability, reactivity and at the same time prevent embrittlement of the coating. The design of reactants, diluents, catalysts and other additives requires a precise balance for high solids coatings to succeed in the market place.

Historical Perspective

Since the early days of industrial coatings, solvents were used to adjust the viscosity of natural and synthetic polymers to a useful application viscosity. Flory[1] had already recognized the relationship of MW and MW distribution on the viscosity of polyester oligomers. Although the exposure to certain solvents was recognized as a health risk, relatively small incentives existed to reduce or replace solvents from coatings. The estimated consumption of solvents in coatings[2] is approximately 550×10^6 gallons. There has been a slow but steady decrease in the amount of solvents consumed in coatings since the 1980's, there has also been a slow shift from hydrocarbon solvents[3] to glycol ethers due to the movement to waterborne coatings. Some industries such as the automotive industry[4], have made tremendous progress in their conversion from low solids acrylic topcoat lacquers with a solids content as low as 15 % to higher solids coatings. Other industries such as the coil industry have invested in equipment to reduce the solvent emission by as much as 90-95 % by recycling the VOC's through the use of catalytic afterburners[5].

Environmental Regulations

Undoubtedly the primary driving force to reduce VOC has come from environmental regulations[6] which have compelled the coating industry to develop new lower solvent coating technology and has also forced the end-user to invest in new application equipment to apply these coatings. The end-user has many choices to convert his low solvent system to low VOC technology. Waterborne coatings, powder coatings and high solids coatings are the prime choices for a reduction or an elimination of VOC. High solids or solvent free coatings are one of the approaches taken to reduce the solvent content of organic coatings. The initial appeal to the coating user to convert to high solids coatings is based upon the similarities in chemistry, applications, minimum investment and performance. As progress is made in all of these areas the end-user is confronted with a confusing number of choices. Present high solids coatings are still solvent containing systems, but there are no theoretical limitations on the reduction of solvents in these coatings and a zero VOC high solids coatings appears feasible[7] for many applications.

Factors Governing the VOC of a Coating System.

The application method usually dictates the optimum rheology of a coating system for a given application. The rheology of a coating during application, flash off and cure is a function of all the formulation parameters, from resin structure and crosslinker composition, to solvents, pigments and additives used. The MW and MW distribution, functional group content and Tg of the resin components are of prime influence on VOC. The William Landel and Ferry (WLF) equation[8] encompasses all these polymer characteristics and permits the prediction of solids-viscosity behavior. Because of the low MW of typical oligomers used in high solids coatings, crosslinking is essential to achieve acceptable film properties. The low MW of the oligomers and the lower content of functional groups requires a high conversion of the functional sites to achieve an elastic effective network. Although solvents, pigmentation and additives have an influence on the rheology they also have a secondary effect on the VOC.

Resin and Crosslinking Agent Design

The ideal synthetic method for the design of high solids polymers leads to a polymer of narrow MW and a uniform distribution of functional groups[9,10]. The functional groups should be located at the end of the polymer chain leading to a network with a high content of elastic effective chains[11]. Conventional synthetic methods often do not meet these requirements. Conventional polyester synthesis by condensation reaction creates polymer chains with functional end groups, but also with a broad molecular weight distribution. Preparing low MW polyester polymers by such a method can lead to unreacted diols or other components which can contribute to volatile resin components. Ring opening reaction of cyclic lactones permits the preparation of both narrow MW polymers and functional end groups containing polymers. The preparation of acrylic polymers for high solids presents a different challenge. The incorporation of functional monomers via free radical copolymerization is a statistical process, which leads potentially to low MW chains with a reduced functional group content or no functional sites. This limitation has energized interest in other techniques such as group transfer or cationic polymerization of acrylic monomers. Neither process permits the direct incorporation of reactive sites and has not found any wide spread use in coatings. The synthesis of narrow molecular weight acrylic polymers[12] with narrow MW distribution using a cobalt chain transfer agent is now possible.

The reduction in functional group content of the backbone polymer requires either an increase in functionality[13] on the crosslinker or crosslinking reactions which lead to high conversion of functional sites and are not prone to side reactions. In the melamine resin area this chemistry already exists with hexa(methoxymethyl)melamine (HMMM) resins. HMMM offers a theoretical functionality of 6. In low solids coatings HMMM has a practical functionality of 2-3 because of steric hindrance considerations. In high solids coatings the functionality can be as high as 5. Condensation chemistry can lead to the formation of reaction products which might meet the existing letter of the law on VOC regulations, but not meet the objective of low polluting coatings. Ring opening reactions, addition and free radical reactions hold promise to delivering a true zero VOC coating. Both epoxy and isocyanate chemistry can be used to prepare coatings which do not emit volatiles during the crosslinking reaction. Free radical reactions are being used in which the free radicals are being generated by heat, decomposition of initiators by a UV source or higher energy radiation.

New Technology

Much progress has been made to convert the coating industry to lower VOC technology. Existing VOC regulations and also the declaration of certain solvents as "non-VOC" solvents is going to slow down the development of further reduction or the elimination of volatile organic compounds from coatings. Most of the advances made to meet the existing VOC regulations have been accomplished by extension of existing technology. Existing regulations provide no incentives to develop completely new technology. In my opinion incentives, possibly of a financial nature, should be created to move industry toward lower or zero VOC technology.

One of the approaches taken to achieve very low or zero VOC coatings has been the use of lower molecular weight polymers in combination with reactive diluents. Such combination give the formulation application characteristics similar to high VOC technology but substantially reduces the VOC. Going even further to zero VOC coatings will eventually require the reduction or elimination of all polymers from the formulation and a switch to oligomers or diluents as the sole reaction partners. The future for polymers in these systems will be as additives to modify the application characteristics.

Besides advances in backbone polymers improvements in crosslinking technology is also necessary. Overall, a movement from condensation chemistry to addition or ring opening reactions is expected.

Although it is relatively easy to demonstrate extremely low or no VOC high solids coatings in the laboratory, the translation of any new technology to industrial applications requires the collaboration of the resin supplier, the paint formulator, equipment supplier and end user. In many instances going beyond a certain reduction in VOC might bring little or no benefits to the environment and create such a high level of rejects, that it might actually have negative impact on the environment. Any changes in the chemistry of coatings will also require extensive testing of these coatings to demonstrate that all the performance requirements are met. Specialty enduses which require exterior durability such as automotive coatings[14] will need not only have to demonstrate performance in accelerated tests but also in actual exposure.

Additives

For many applications, going to lower VOC coatings creates severe application problems[15]. Sagging or excessive flow of the applied paint film, cratering etc. are some of the obstacles in spray applications. Sensitivity to less than perfectly cleaned surfaces is a problem for almost all applications. Lower molecular weight oligomers or diluents are higher in polar functional groups, leading to coating films which are not only low in viscosity and prone to sag, but also sensitive to crawling, cratering and to intercoat adhesion problems. Resin, crosslinker or diluent design can assist in solving some of these problems, but additives are an essential part of the equation. Rheology control agents needed to reduce sagging such as polyamides, polyureas or colloidal silica are an important part of a high solids formulation.

Silicones, fluorocarbon surfactants and acrylic polyols are being used as flow and leveling agents[16]. These additives again can create their own problems such as intercoat adhesion and humidity resistance problems.

Catalysis is another area were significant progress is being made and further improvements are necessary. High solids coatings because of the higher concentration of functional groups and because of the increased reactivity required, are in most cases not as stable as low solids coatings. For two component formulations, the potlife of the high solids formulation is often exceedingly short[17]. Catalysts have been developed[18] for high solids 2K NCO-hydroxyl coatings which give excellent potlife and good reactivity.

Because of the lower molecular weight of the reactive diluents or components used in high solids coatings, pigment flocculation may also be a problem, requiring dispersant[19] which stabilize the pigment sterically.

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