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ADDITIVES FOR HIGH SOLIDS AND WATER-BORNE COATINGS

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ABSTRACT

Higher solids and waterborne coatings have introduced new dimensions of complexity into the formulation of coating systems. Some of the old and proven tools and experiences used in formulating lower solids coatings cannot be used anymore with higher solids and waterborne coatings. Both higher solids and waterborne coatings are prone to surface defects due to high surface tension and excessive flow during the application and curing process. The rheology of waterborne coatings in most instances is non-Newtonian, creating special problems with some application processes. High solids coatings, due to their low viscosity, are prone to sag and flow before crosslinking has taken place. Higher solids coatings also require a higher concentration of functional groups which create problems in stability and cure response. All these problems has created a demand for new additives as well as many new opportunities for the additive manufacturer. We plan to give an overview of the additives used in high solids coatings and specifically address new developments in catalysts and reactive diluents for high solids coatings.

INTRODUCTION

The event of low VOC coatings has made the life of the coating formulator significantly more difficult. Many of the tools available in the formulation of low solids coatings, are suddenly not appropriate. The solvent choice in high solids coatings is more restricted, some solvents cannot be used at all and many resin choices or formulation methods are not possible. High solids coatings and water-borne coatings, although they appear to be completely different in nature, present some common challenges for the formulator. Some of these challenges are to be solved by the resin chemist in the design of backbone resins and crosslinking systems, some other challenges are to be addressed by the additive manufacturer. Clearly these systems are a fertile ground for improvements and potential innovations. Additives present an important tool to solve some of the application and coating problems.

Coatings is a science which deals with surfaces, and interfaces, e.g. coating/air, substrate/coating and coating matrix/pigments or fillers. For most of these interfaces wetting or low surface tension is required. Most of the metal oxide surfaces we coat are high energy surfaces, therefore, theoretically they should be easy to coat with an aqueous or a solvent solution of a polymer. Practically, we live in a contaminated world, where low surface tension and variations in surface tension are the norm. Water as a diluent has a surface tension of 72.5 dynes/cm, compared to 25-30 dynes/cm for organic hydrocarbons or other organic compounds. Polar resins used in high solids coatings have also an increased surface tension compared to their higher MW lower functional analogs. Water-borne and high solids coatings are therefore both troublesome coatings if they have to be applied over contaminated or low surface tension substrates.

Besides surface tension the rheology of a coating during storage, application and film formation is an important factor on how a coating system can be practically applied. This is an area where high solids and water-borne coatings are substantially different and also different from lower solids coatings. Most water-borne coatings are dispersed systems and their rheology is normally non-Newtonian and shear thinning. High solids coatings on the other hand are based on low molecular weight resins and their flow behavior is close to Newtonian. One major difference between low and high solids coatings is film formation. Low solids coatings are prepared from polymers of sufficient MW that only physical drying, i.e. evaporation of the solvent, can produce an acceptable film. Crosslinking can then be used to further enhance the film properties.

Because of the low molecular weight of the polymers, high solids coatings are still liquid after solvent evaporation, and a considerable degree of conversion of the functional groups is required to achieve film properties for handling. The polymers used in high solids coatings require a higher concentration of functional groups to achieve an adequate crosslinking density. To achieve film properties within a reasonable amount of time, higher crosslink rates are required compared to low solids coatings. This increased reaction speed also reduces the potlife of the high solids coating. In some systems control of stability and reactivity can be achieved with properly selected catalysts.

The film formation of water-borne coatings is quite different from low solids and high solids coatings. Almost all water-borne coatings, emulsions, dispersion or "water-soluble polymers" consist of polymer particles which are made water-dispersible either by means of an external surfactant or functional groups attached to the polymer. The particle size¹ determines the appearance of the water-borne resin and how it is classified. Film formation depends on the Tg of the polymer², the distribution of functional groups on the polymer and on the other additives in the system. For the coating formulator the challenge exist to convert this heterogeneous dispersion into an homogenous film³. Additives from coalescence aids⁴, reactive diluents to dispersants play a critical role in this process. For industrial applications, methods have to be developed to overcome some of the water resistance problems inherent in a system which contains water solubilizing sites. Crosslinking of water-borne industrial coatings is one of the approaches for overcoming the effect of water sensitive sites and film heterogeneity.

PREPARATION OF PAINT

Most of the coating systems used are pigmented. The dispersion of pigments and other insoluble additives presents one of the most complicated steps during the paint preparation process. The composition of the grinding paste is not only a function of the solvent, pigment and binder composition, but it also depends on the grinding method and on the performance requirements of the coating. The requirements for an automotive basecoat for example are substantially different from an industrial coating or a maintenance paint. High solids coatings are especially in need of pigment dispersants. The low molecular weight of high solids polymers is insufficient in stabilizing any pigment from flocculating. The adsorbed layer of resin does not permit any steric stabilization.

Many high acid number water-borne resins⁵ are excellent dispersants for pigments and do not require any other additives. High acid number acrylic resins are often used as dispersants. For low acid number emulsions or dispersions on the other hand the addition of surfactant is required to disperse a pigment. The pigment is often dispersed in the absence of the binder resin. Some dispersions do not have the shear stability to be used as a dispersion medium. The selection of an additive used during dispersion depends on dispersion method, end-use application, performance requirement and the composition of the coating. (Table 1)

Additive selection depends to a large extent on what components have to be added to the paint and on the interaction of all components. (Table 2)

TABLE 1 GRIND FORMULATION

Additives	Function	Chemical Composition
Deaerators, Defoamers, Antifoams	Removes air entrapped during pigment dispersion	mineral oil, silicones, waxes, silica and fatty acids
Dispersants, Emulsifiers, Surfactants	Lowers surface tension, adsorbs on pigment, steric stabilization	Nonionic, anionic surfactant, block polymer, polycarboxylate
Stabilizers	pH control, adjustment	Amines, base

TABLE 2 COMPONENTS OF A PAINT AND WHEN THEY MIGHT BE ADDED

Components in Grinding Paste. Antisettling agents, antislip agents antistats, binders, corrosion inhibitors, extenders, flame retardant, flatting agents, lubricants, marproofing agents, pigments & colorants, solvents, stabilizers, thickeners, water repellents, waxes

Components in Let Down. Antiskinning agents, binders, catalysts and driers, coalescing agents, corrosion inhibitors, coupling agents, crosslinking agents, flame retardant, flow control agents, lubricants, plasticizers, solvents, stabilizers, thickeners, UV absorbers and stabilizers, water repellents, tints.

APPLICATION PROCESS

Government restrictions on the amount of volatile organic content (VOC) in organic coatings has brought major changes to the coating systems and the application methods used. Additional changes to coating systems have been created due to concern about workers safety and health. The overall goal is to make a coating operation as safe as possible for the workers and also reduce the amount of pollution to the environment.

The application process itself places certain requirements on a coating system. Viscosity of the coating, not only the viscosity at low shear rate but also high shear viscosity or elongation viscosity play a major role on how a coating flows through the spray nozzle and how a coating atomizes. After application the coating system is supposed to flow and level. At the same time the coating system is supposed to resist sagging up to a certain film thickness.

The polymers used in high solids coatings are usually Newtonian in flow behavior, after pigmentation the rheology changes to a pseudo plastic or thixotropic flow. Because of the low solvent content of high solids coatings the increase in viscosity of the coating after application is usually not enough to provide sag resistance. If the coating is being baked, further reduction in viscosity takes place before an increase in viscosity results from crosslinking. High solids coatings therefore depend on additives to achieve non-Newtonian behavior. For maximum leveling and long term stability or to reduced

settling a thixotropic flow behavior is desired. There are many different additives available which set up a temporary network due to physical effects or hydrogen bonding and create a structure between particles which is shear sensitive. During shearing this structure breaks down and readily reforms. Depending on the time frame of reforming the structure the system is either pseudo plastic (immediate) or thixotropic (long). These additives can be inorganic particles such as organo clays or silicates, or they can be organic particles such as hydrogenated castor oil, polyamide or polyurea, or they can be a finely dispersed polymer (microgel). The incorporation method has a significant effect on the performance of the rheology control agent. Shear or heat might be required for the incorporation, although too high shear or heat can destroy the effectiveness of the additive. Many of the additives which function because of hydrogen bonding have an upper limit in temperature which also depends on the solvent composition. Water-borne coatings usually display a non-Newtonian⁶, mostly pseudo plastic flow behavior.

TABLE 3 SPECIFIC PROPERTY OR REQUIREMENT FOR APPLICATIONS

Application method or other considerations	Rheology during application or cure, or other requirements
Roller applied coatings	Newtonian flow, viscosity 1000-10,000 cps
Environmental considerations, VOC, solvent composition,	Higher solids or water-borne coatings or other crosslinker technology
Hazards/health, flammability, toxicity	solvent selection, worker protection
Spray, hand spray, airless, electrostatic	Shear thinning, viscosity 200 cps, resistivity,
Dip/flowcoater	Newtonian
Stability requirements	Catalyst, crosslinker, stabilizer
Handling during application, pumping	Shear stability
Humidity	Control necessary for water-borne spray application
Substrate, type of metal, pretreatment, surface roughness,	Low surface tension additives to improve flow and leveling or higher MW resins.
Contamination, compatibility with other paints.	Low surface tension additives

FILM FORMATION

Film formation in high solids coatings is in many aspects substantially different from low solids coatings. In most high solids coatings the challenge lies in increasing the

MW of the polymer within a reasonable time from a low MW oligomer to a crosslinked network with properties similar to that of a film obtained from higher MW polymers. In a low solids coating utilizing higher MW polymers gel formation during crosslinking might take place at a conversion of 10-15 % of the functional groups; in a high solids coatings a conversion of 30 % of the functional groups might be required. Because of the required increase in reactivity in high solids coatings, it is difficult to balance potlife and cure response. Catalyst selection is an important part of the formulation process. Because of the more polar nature of high solids coatings film imperfections, such as cratering and crawling, pin-holing, telegraphing of substrate imperfections is a consistent problem. Additives to lower surface tension⁷, such as polyacrylates, silicones and fluoro carbons are commonly used.

Film formation in aqueous coatings is a much more interesting subject. Water-borne polymers depending on their structure⁸ can be water-soluble, dispersed or be in form of a colloidal solution. With the exception of thickening agents most water-borne polymers used as binders in coatings are hydrophobic and are made water compatible with water soluble sites or with surfactants. Film formation is a complex process of evaporation of water, diffusion of water through the partially coalesced film and diffusion of polymer chains. Most films prepared from water-borne polymers are not uniform. Additives play an important part to assist in film formation, reducing the water-sensitivity or enhancing the gloss of the formulation. During the film forming process a water-borne coating system also undergoes considerable pH change. Most amine neutralized carboxyl functional polymers are basic in pH . During film formation the pH slowly drops and eventually the pH of the film in absence of any pigments drops to 3.5-4.5. This change in pH during film formation has been one of the factors why corrosion protection in water-borne coatings has been so difficult. Most corrosion inhibitors are effective in a certain pH range. Flash rusting, "early rust", salt spray or humidity resistance all operate in a different pH region. A listing of potential film formation problems is shown in Table 4, we also show potential solutions and additives to resolve problems. Additives can only go so far to resolve film formation problems, resin, crosslinker design and selection of catalysts is often required to obtain acceptable application performance.

TABLE 4 FILM FORMATION PROBLEMS AND REMEDIES

PROBLEM	SOLUTION, ADDITIVE
Atmosphere, dry, moist, gas heated,	Humidity control, catalysis
Coalescence (water-borne)	Controlled by Tg of polymer, polymer architecture, co-solvents or reactive diluents
Flash off time, blistering	Release of solvent or diluents affected by humidity, temperature and surface active additives
Film thickness, blistering, boiling	Reaction products can lead to blistering, influence of air or moisture on reaction rates.
Flow and leveling	Viscosity (surface viscosity) and surface tension, cure speed and heat up rate controlled.
Cure profile, time, temperature, heat up time	Influences leveling, release of reaction products heterogeneity of film

FILM PROPERTIES

Often the function of a coating film is the protection of a surface, improvement in durability and appearance. In addition a coating film might also impart additional properties such as slip, mar and abrasion. Coatings have also been developed to temporarily change or protect the surface such as in photoresist.

Many of the properties of a coating film are determined by the binder, crosslinking density and also by pigments and additives. In addition the prior history of a coating, its preparation, application and condition of film formation and the substrate or substrate pretreatment have a significant effect on the film properties. Many factors are outside the control of the coating formulator. Factors influencing film properties are shown in Table 5.

TABLE 5 FACTORS INFLUENCING FILM PROPERTIES.

PROPERTY	INFLUENCED BY
Appearance (smoothness, D.O.I)	Pigment dispersion. Loading, surface smoothness
Hiding power	Pigment dispersion, refractive index, flocculation
Color	Flocculation, floating
Hardness	Degree of cure, catalyst, cure conditions,
Flexibility	Polymer and crosslinker architecture, adhesion to substrate

Table 5 continued.

PROPERTY	INFLUENCED BY
Coefficient of friction	Surface tension, presence of a separate phase, roughness
Mar resistance, abrasion resistance	Slip, elastomeric properties of film
Gloss 60°/20°	Surface roughness, waviness
Impact resistance	Fast deformation, adhesion
Environmental resistance	Adhesion to substrate, migration of water or electrolyte, UV resistance, UV absorption
Salt spray, humidity, water immersion, exterior durability, acid etch resistance	Adhesion, PVC/CPVC
Other, specific requirements	
Defects on surface, blister, crater, sagging, color variations,	Surface tension, rate of cure, viscosity

TABLE 6 ADDITIVES USED TO IMPROVE FILM PROPERTIES

PROPERTY	ADDITIVE
Appearance (smoothness, D.O.I)	Flow leveling agents
Hiding power	Pigment dispersants
Color uniformity	Dispersant, flocculants
Hardness	Crosslinker, catalyst, stabilizer
Flexibility	Polymer modifier, adhesion promoter
Coefficient of friction	Wax, silicones, low surface tension additive
Mar resistance, abrasion resistance	Crosslinker, catalyst
Gloss 60°/20°	Flow additive, catalyst, stabilizer
Impact resistance	Polymer modifier
Environmental resistance	Corrosion inhibitor, catalyst, UV absorber
Salt spray, humidity, water immersion, exterior durability, acid etch resistance	Corrosion inhibitor, catalyst, UV absorber ,
Defects on surface, blister, crater, sagging, color variations,	Flow and leveling, low surface tension

SPECIAL CHALLENGES FOR THE COATING FORMULATOR

The development of water-borne⁹ and high solids coatings crosslinked with polyisocyanate crosslinker has created completely new challenges for the additive producer and the coating formulator. Catalysis of the isocyanate-hydroxyl reaction without catalyzing the water-isocyanate reaction is one active problem area. New catalysts¹⁰ on a non-tin basis have been developed which are selective in the hydroxyl-isocyanate reaction. These zirconium metal chelate catalysts compared to DBTDL give very little foaming in water-borne coatings and give improved crosslinking, potlife and higher gloss. For high solids coatings aluminum chelates are available which give excellent potlife and fast reactivity in the presence of a 2,4-pentanedione stabilizer. The performance profile for an ideal catalyst is shown in Table 7. Many of the requirements for an ideal catalyst are contradictory, which makes the life of the additive manufacturer more exiting and requires a good understanding of reaction mechanism of the crosslinking system.

TABLE 7 PERFORMANCE PROFILE FOR A CATALYST

Property	Ideal behavior
Potlife	No effect
Stability	Very stable
Reactivity	Highly catalytic
Chemical resistance	No reduction in resistance properties
Exterior durability	No effect
Color	No discoloration during application
Pigment interaction	No absorption
Compatibility	Compatible with all components

REACTIVE DILUENTS

Reactive diluents are used in water-borne and high solids coatings. In high solids coatings reactive diluents mainly function to increase the application solids. In addition they can also function to modify film properties such as hardness or flexibility.

In water-borne coatings reactive diluents can be used to replace co-solvents and coalescence agents. Some of the requirements for a reactive diluent are similar for high solids and water-borne coatings. An ideal reactive diluent should have a narrow molecular weight distribution, low viscosity and a compatibility with many polymers and crosslinker. For water-borne coatings a good hydrolytic stability is required. The performance profile for a diluent is shown in Table 8.

TABLE 8 PERFORMANCE PROFILE¹¹ REACTIVE DILUENT

Property	Desired Range
Molecular weight	400-800, narrow MW distribution
Functionality	2-3
Type of functional group	OH reactive with NCO, amino resin COOH reactive with epoxy, amino resin Silanol self condensation NH ₂ reactive with epoxy/NCO
Viscosity, (100 %), cps	500-5000
Tg of oligomer film after crosslinking. C°	20-50

To improve the exterior durability siloxanes¹² are used as reactive diluents, in some cases mainly to provide improved acid resistance in automotive clearcoats. Fatty acid diols¹³ are used to increase the solids content of isocyanate crosslinked coatings. As diluents for alkyd resins polyunsaturated compounds¹⁴ based on 2,7-octadienol are claimed. Diluents¹⁵ with spiro structure and with good alkali resistance are interesting examples of compounds specifically designed for high solids applications. The creation of diluents with narrow Mw distribution and a combination of two types of functional groups¹⁶, phenolic and hydroxyl, shows how this chemistry can be optimized to achieve the maximum benefit with melamine crosslinking. Reactive diluents also find a use in electrocoating¹⁷. Improvement in exterior durability and cure response in water-borne and high solids coatings is claimed¹⁸ with urethane diol structures. Polyether polyols¹⁹ based on bisphenol A or phenol formaldehyde novolak epoxy adducts can be used as low viscous modifiers for water-borne, high solids and also electrocoating.

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