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THE SLOW AND WINDING ROAD TO "ZERO" VOC

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ABSTRACT

For the last 35 years, the US coatings industry has been challenged to develop coatings systems with a lower solvent content. The initial impetus for this development was Rule 66 enacted in 1966 in California. The Federal Clean Air Act of 1970 stated that all Americans have the right to breathe clean air and that it was the responsibility of the individual states to insure the air was clean.

One of the pioneers in the development of low solvent coatings was Dr. Herbert Hönel founder of Vianova Kunstharze Graz (Austria). Dr. Hönel started the development of waterborne industrial coatings during the 1950-1955 time period¹. His concern was predominately to reduce the exposure of workers to toxic solvents.

Substantial progress has been made since these early days in the development of newer coating technologies that not only meet the performance requirements of the end user, but also reduce or eliminate solvents all together. Although many of the new technologies developed such as UV/EB, Powder Coating, Waterborne Coatings and High Solids Coatings would have made inroads into the coating market based on their own merit, they received a significant boost from increasingly stringent regulations in the USA, and also overseas.

Because of the complexities in performance, application requirements and regulatory mandates on any new coating systems, the coating industry was forced to increase its research and development expenditure to meet customer requirements. Substantial progress has been made in polymer chemistry, rheology and colloid science to be able to design polymers and coatings for these demanding requirements.

In this paper I would like to describe the progress made in the industry during the last 35 years and also address the direction the industry might go during the next few years.

Introduction

Across the world it has been recognized that man-made pollution of the environment² is a potentially serious problem for mankind. The application of coatings is one of the sources of pollution of the environment. The approaches taken in different countries to reduce solvent pollution have been varied, from ignoring the problem, denying that there is a problem, to governmental action. Some of the action taken in form of regulations and laws were based on insufficient or wrong information which led to regulations which not only delayed any meaningful action, in some cases it actually increased the problem or moved it from one area to another. It has been difficult for the industry to follow some of these mandates; this has led to a rather tortuous path that not always produced the desired results.

In different countries the emphasis to reduce the solvent content in coatings was and is driven by several concerns. Solvents in coatings not only pollute the air or water, but also present a health and safety hazard during application. Therefore, depending on the basis for concerns laws have been structured differently around the world. From laws reducing solvent exposure of workers, to laws and regulations which are predominately concerned with the environment.

The definition of VOC "volatile organic content" is different from country to country, as shown in Table 1. Countrywide regulations might be superseded with more stringent state regulations. Regulations might also be based on enduse or on volume of paint consumed. VOC is not a technical definition in many countries, but rather a legal one. In other parts of the world³ any organic compound with a certain vapor pressure or anything that will evaporate during cure is considered a VOC. The US law in regards to solvent emission⁴ has been concerned with solvents which are photochemically active and which produce ozone on UV exposure and with compounds that are Hazardous Air Pollutants (HAPs)⁵.

TABLE 1. Definition of VOC in different Countries

USA

“any organic compound that participates in atmospheric photochemical reactions except those designated by EPA as having negligible photochemical reactivity”

AUSTRALIA

organic compounds with a vapour pressure of more than 0.01 mm Hg at 21°C, and with a boiling point of less than 250°C.

EU

any organic compound having at 293.15K a vapour pressure of 0.01kPa or more, or having a corresponding volatility under the particular conditions of use

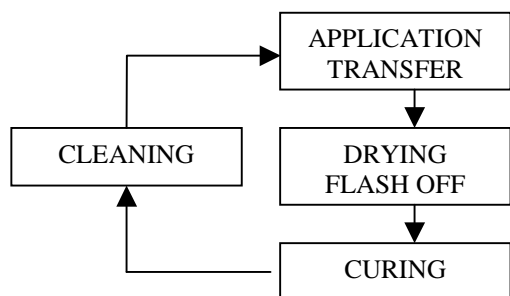


Figure 1 Life cycle of coating

Solvent evolution during the application process is only a part of the problem in the emission of solvents. For some applications the total solvent emission based on the life cycle of a product should be considered. This concern does not apply for most consumer items, where paint durability exceeds the product lifetime, but should be a consideration for industrial items and long lasting equipment such as bridges. See Figure 1

The existing method in the USA to measure the amount of VOC released from a coating system is EPA Method 24⁶. This method considers the amount of VOC generated during application and the early stage of drying or curing, but not during cure at a higher temperature.

It is clear from the above figure that the amount of solvent released during application of a coating is also influenced by the application method and by the transfer efficiency. See Table 2 for published information of transfer efficiencies⁷.

Table 2. Application Technologies

| Application Method | Transfer efficiency |
|--------------------------------|----------------------------|
| Manual Hand Spray | <20 |
| Plural component spray | <20 |
| HVLP guns | <40 |
| Electrostatic spray | <90 |
| Airless spray | <30 |
| Liquid carbon dioxide spray | <30 |
| Roller coating, direct reverse | >95 |
| Dip coating | >80 |
| Curtain coating | >95 |
| Flow coating | >80 |
| Electrocoating | >95 |

Against this background of many often confounding and contradictory regulations, resin and coating suppliers as well as endusers of coatings have started their slow and cumbersome progress to reduce VOC of existing coating formulations by developing new coatings systems, application technologies and often at the same time produce new coatings with superior performance.

This paper will predominately discuss the complexity in formulating low VOC coatings and the problems and limitations of different technologies to achieve a VOC free system.

Historical Background: Lower Solids Coatings and Conversion to Low VOC

Most of the industrial and architectural solvent borne coatings used before 1960 were lower solids content coatings. Coatings with a non-volatile content as low as 15-25 % were used as thermoplastic automotive topcoats. Most industrial coatings based on

alkyds, acrylics, epoxy or polyester were of low to medium solids content. The low cost of solvents, easy of application of these coatings and purchasing practices encouraged the use of these high VOC. Coatings.

There was a large resistance to the use of higher solids coatings. The introduction of hexakis(methoxymethyl)melamine (HMMM), a 100% solids crosslinker, into industrial bake coatings encountered difficulties, not only because of the need for a catalyst, but also because the formulation would not take much of a "drink of solvent". Coatings were generally purchased on a gallon basis, not considering volume solids or surface coverage. The only exception was the coil industry, which purchased on a gallon/ft²/mil basis.

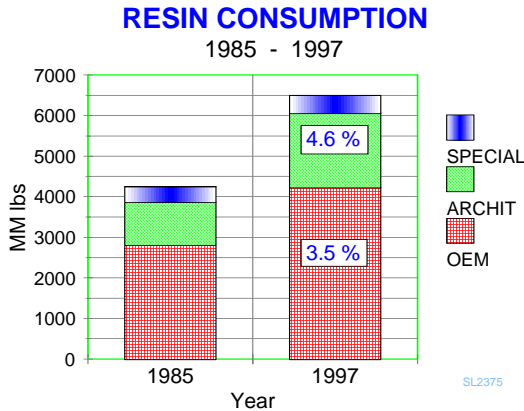


Figure 2 Resin consumption 1985-1997

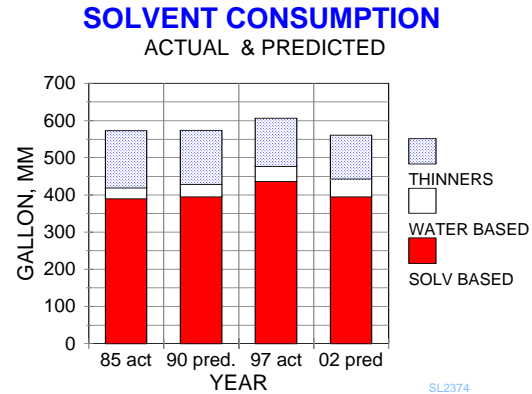


Figure 3 Solvent consumption 1985-1997

If we take a look at the growth of the coating resin market⁸ during the last 15 years (Figure 2), we see a cumulative growth of approximately 3.5 % during this time period. The solvent consumption remained essentially constant during this period (Figure 3). These numbers would indicate an average solids content of 50 % in 1985 and over 60 % in 2000.

Coating Technologies

Many new technologies have been developed during the last 30-40 years to reduce solvent emission⁹. The driving forces for these changes were not always the reduction in solvent emission, but improvements in performance or in application conditions were also major reasons for these developments. Table 3 shows a listing of current technologies and shows some of the specific problems¹⁰ that are encountered using these technologies.

Table 3. Newer Coating Technologies

| Technology | Major Challenges |
|----------------------------|---------------------------------------------------------|
| High Solids - Solvent free | Viscosity/solids, potlife/dry-time |
| Dispersion PVC organosol | Plasticizer migration |
| Waterborne | Co-solvents, application conditions, film thickness |
| Electrocoating | Production volume, substrate, cure temperature |
| UV/EB coating | Complex objects, pigments |
| Powder coating | Low film thickness, cure temperature, flow and leveling |

Table 3 continued

| Technology | Major Challenges |
|-------------------|-------------------------------------------|
| Hybrid | |
| Powder slurry | Waterborne and powder combined, stability |
| Powder-UV | Flow and leveling |
| UV/EB water | Appearance - cure |
| High Solids Water | Appearance, stability, applications |

Tables 4 to 8 presents in detail some of the problems encountered with these technologies. The information in these tables was obtained from Northeast Waste Management Officials' Association¹¹. These tables were edited to remove some debatable statements and assumptions about the capabilities of different technologies. The limitations of these technologies, perceived or real, require adjustments by the formulator and the end user, but they do not represent the true boundaries imposed by these different technologies.

Table 4. High Solids Coatings-Solvent free

| Advantages | Disadvantages |
|------------------------------------------------------------------------|-----------------------------------------------|
| Reduces VOC and HAP emissions | Generally requires high cure temperatures |
| Reduces inventory | Sensitive to inadequate cleaning of substrate |
| Reduces fire hazards | |
| Reduces number of spray applications to achieve a given film thickness | Is difficult to control film thickness |
| Higher crosslink density improves abrasion and mar resistance | Tacky overspray; difficult to clean |
| Compatible with conventional spray equipment | Might require paint heater in system |
| Reduces safety and odor problems | Difficult to control sagging |
| Decreases energy costs associated with reduced curing times | Has narrow "time-temperature-cure" window |
| Reduced air makeup in ovens | Cannot use in dip or flow coating |
| | Is difficult to repair |
| | Shorter pot-life than conventional coatings |

Table 5. Waterborne Coatings

| Advantages | Disadvantages |
|------------------------------------------------|----------------------------------------------------|
| Reduces VOC and HAP emissions | Has tendency to foam |
| Can use conventional application processes | Clean surface required |
| Reduces toxicity and odor | Longer drying times or increased oven temperatures |
| Is easy to clean up | Has difficulty obtaining high gloss finish |
| Reduces disposal of hazardous waste | Has difficult cleanup once coating is cured |
| Can recover and reuse some waterborne paints | Higher cost |
| | Conversion might be expensive |
| Non-hazardous waste disposal might be possible | Lower transfer efficiencies for electrostatic |
| | Increases runs and sags |
| | Requires good temperature/humidity control |
| | Heated storage |

Table 6. Electrocoating

| Advantages | Disadvantages |
|----------------------------------------------|-----------------------------------------|
| Utilizes over 90 percent of coating material | Substrate limitation |
| Uniform coating on all surfaces | Separate lines for each color |
| High production rates | High cost to install |
| Corrosion-resistant coating | Requires sophisticated maintenance |
| Low VOC and HAP emissions | Difficult coating bulky, small parts |
| Can be fully automated | Requires de-ionized water |
| | Is restricted to large volume finishing |
| | Has coating thickness limitation |
| | Requires corrosions-resistant equipment |

Table 7. Radiation Curing UV/EB

| Advantages | Disadvantages |
|-----------------------------------------------------------|--------------------------------------------------|
| Lower VOC and HAP content | Cure inhibition by pigments |
| Lower capital investment than conventional ovens | Higher RM costs for EB and UV coatings |
| Short cure time | Potential skin irritation problems with acrylate |
| Low energy costs | Shrinkage and adhesion problems with acrylate |
| Consistent performance | Curing sensitive to shape of part |
| Requires small ovens | |
| Low air movement that reduces dust and dirt contamination | |
| Easily installed/retrofitted | |
| Reduces fire and explosion hazard | |

Table 8. Powder Coating

| Advantages | Disadvantages |
|------------------------------------------------------------|----------------------------------------------------|
| No solvent flash-off required | High cure temperature |
| No coatings mix room needed | Small batches expensive to manufacture |
| Minimal oven length required | Metallic powder coatings not as attractive |
| Low ventilation required | Appearance problems |
| Less floor space required | Enhances Faraday cage effect |
| VOC and HAP compliant, i.e., no solvents | Difficult to achieve thin films below 1.0-1.5 mils |
| Has good corrosion resistance | May cause powder clumping |
| High transfer efficiencies, 95-99% | Difficult to change colors |
| Saves energy | Needs cool, dry storage area |
| Requires little operator expertise | Must pretreat substrate |
| No hazardous overspray, waste sludge or contaminated water | |
| Reduces worker exposure to solvent vapors | |

Limitations of Different Low VOC Coating Technologies

The end user of coatings requires certain chemical, physical appearance and application characteristics from a coating. In the absence of these performance requirements, it would be easy to design a low VOC coating using almost any polymer

system, technology and application method. Because of the restrictions imposed by the user there are preferred technologies for each application.

High Solids Solvent Free Coatings

One of the limiting factors of applying any coating/polymer to a surface is the conversion of the polymer into a form that can be applied to a complex surface uniformly and in a very thin layer. All application processes require dissolving or dividing the polymer into particles and transferring them to the substrate. Existing application technology requires a certain liquid viscosity for the application process.

Flory has already explored the effect of molecular weight on viscosity for polyester resins¹². He found that the molecular weight of polyesters prepared by condensation polymerization follows this equation (1). This is a simplified form of the Mark Houwink equation,

$$\log \eta = A + C'M_w^{1/2} \quad (1)$$

wherein M_w is the weight average molecular weight and A and C' are constants specific for a certain polymer composition. This work clearly shows that the molecular weight (MW) of a polymer influences its viscosity and that a lower MW will give a lower viscosity. This equation does not relate any other polymer property to viscosity and since the constants are polymer specific, it does not provide any guidelines how to design low viscosity polymers or polymer solutions for high solids or solvent free coatings.

A more versatile approach is to use the relationship of glass transition temperature to solution viscosity of a polymer as expressed in the Williams, Landel and Ferry¹³ (WLF equation).

$$\ln \eta = \ln \eta_{T_r} - \frac{C_1(T-T_r)}{C_1 + (T-T_r)} + \ln \frac{\rho_r T_r}{\rho T} \quad (2)$$

In this equation, T_r represents a reference temperature, ρ_r density at T_r , with C_1 and C_2 as constants. A simplified version of the WLF equation (3) was developed by Nielsen¹⁴.

$$\log \eta_T = C - \frac{A(T-T_g)}{B + (T-T_g)} \quad (3)$$

The constants proposed by Nielsen of $C = 13.0$, $A = 17.44$ and $B = 51.6$ have not been found universally applicable for all polymers. For most high solids coating polymers, we found good agreement using these constants.

It is generally known that a reduction in molecular weight results in a reduction in the T_g of a polymer¹⁵. The decrease in T_g of an oligomer (T_{g0}) can be expressed by equation (4).

$$T_{g_0} = T_{g_{inf}} - \frac{k}{M_n} \quad (4)$$

In this equation (4) k is a constant which, depending on polymer structure, ranges from 0.2x10⁵ to 3x10⁵. For polyester oligomers, we observed a k value of about 0.3 to 0.9x10⁵. If we would like to have a polymer film with a T_g of 50°C, we can calculate the temperature that might be required to spray an oligomer of such a polymer.

Figure 4 shows the effect of lowering the MW of a polymer on its viscosity/temperature behavior. In Figures 4 and 5 we show the effect of MW, T_g of the polymer and temperature on viscosity. These results clearly indicate that it is rather easy to prepare low VOC coatings if a coating film with a very low T_g is desired. For most applications, this is not the case. Typical Knoop hardness for an acrylic/melamine clearcoat is in the area of 10-18, which corresponds to a T_g between 50 to 100.

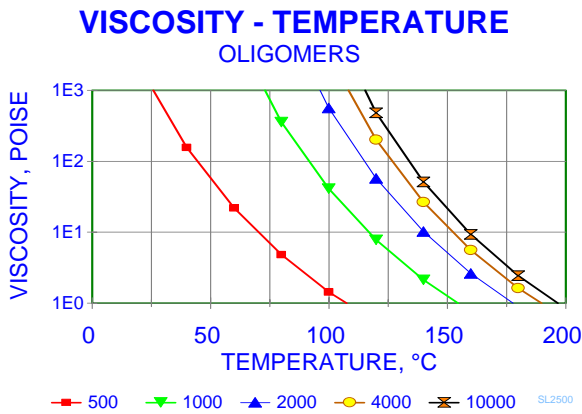


Figure 4 Viscosity -temperature of polymers

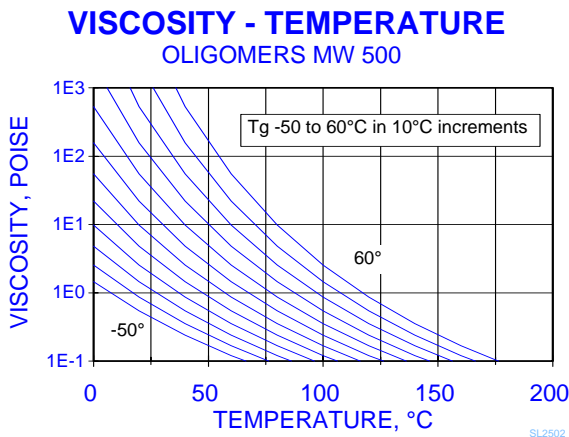


Figure 5 Viscosity-temperature as a function of T_g of oligomer

In this calculation we are using a value for k in equation (4) of 0.47x10⁵. Typical application viscosity for high solids coatings is in the range of 1-10 poise depending on application method. Therefore, none of the polymers could be sprayed at room temperature, The lowest spray temperature for an oligomer with a molecular weight of 500 would be between 60-100°C. The highest MW polymer of this series would have to be sprayed between 160-200°C.

The viscosity/temperature relationship of a series of oligomers with a molecular weight of 500 is shown in Figure 5. The T_g of the polymers that these oligomers are derived from varies from as low as -50 to 60°C in 10°C increments. The T_g of the oligomers and the viscosity were calculated using Eqs. 3 and 4 using a value for k of 0.47x10⁵. Only oligomers derived from polymers with a T_g of 0 to 20°C can be expected to be applied at room temperature.

Increasing the molecular weight of the oligomer to 1000 lowers the Tg of the oligomers to -40 to -30°C. For most coating applications, such a low Tg would produce coating films that are very soft and sticky. Polymers that produce acceptable hardness have to be applied at a temperature of between 100-125°C. This clearly illustrates how difficult it is to prepare high Tg polymers that can be applied at a reasonable viscosity. Increasing the MW to 2000, which is a reasonable range for conventional low solids polyesters, will only allow application of the lowest Tg polymer at room temperature.

Waterborne Coatings

Most of the resins used in waterborne coatings are not true solutions but rather are dispersions, emulsions or a colloidal solution¹⁶. True water-soluble polymers are used in coatings predominately as thickeners. Waterborne coating systems therefore do not follow the typical solution behavior. Loren Hill¹⁷ studied the solids-viscosity behavior of waterborne coatings and found that they follow the Mooney equation¹⁸, which would indicate the particle nature of waterborne resins. One of the major challenges with waterborne coatings has been to achieve water solubility and at the same time prepare films with excellent water resistance.

Principally two different methods are used to prepare waterborne coatings. The first method involves the synthesis of polymers in an organic solvent or in bulk and dispersing this polymer in water. Predominately anionic carboxylic acid groups neutralized with an organic base are used as water solubilizing sites. In these polymers the functional sites are randomly distributed, depending on the synthetic methods used, and the ionic groups can be in the main chain or can be end groups.

The second synthetic method used is the polymerization of the monomers in water in the presence of surfactants. This polymerization method involves mainly step growth polymerization. The functional groups of polymers prepared by this technology are often not uniformly distributed throughout the polymer particle, but rather aggregate on the surface of the particle. Table 9 shows some of the major differences between waterborne polymers prepared by the different methods.

Table 9. Waterborne polymers

| Characteristic | Emulsion/dispersion polymer | Polymerized in solution or bulk |
|-------------------------------------|-----------------------------------|--------------------------------------|
| Functional groups | Non-random, aggregated on surface | Random distribution on polymer chain |
| Amount of functional groups*, MEQ/g | 0 to 2 | 0.5 to 2 |
| Surfactant | Yes | No |
| Particle size, micron | 0.1-2.0 | 0.01 to 0.1 |
| Molecular weight | 10 ⁴ -10 ⁶ | 10 ³ -10 ⁴ |
| Film uniformity | Heterogeneous | Homogenous-heterogeneous |
| Film formation | Tg dependent (coalescence) | No Tg effect |
| Cosolvent | For coalescence | For dispersion-synthesis |

* Amount of functional groups required to achieve water solubility/dispersibility.

Both waterborne systems "water-soluble" or dispersed, can be prepared in the absence of solvents; therefore, they could be theoretically co-solvent free. Practical considerations often require the addition of co-solvents in waterborne coatings. Because of the particle nature of water-dispersed systems, coalescence of the particles¹⁹ can require a cosolvent. This is especially important if the polymer system has a high Tg and therefore a high film forming temperature. An additional function of the cosolvent is to improve open time, prevent skinning and change the rheology.

For "water soluble" polymers cosolvents are used in their synthesis and they also reduce the viscosity of the polymer during water addition. As in water-dispersed coatings, cosolvents can improve application characteristics and improve open time.

Although a cosolvent fulfills a function during synthesis, handling, dilution and application of a waterborne coating, it certainly defeats the purpose of creating an environmentally friendly coating. The use of a reactive cosolvent, diluents and modifiers has therefore been extensively investigated and many approaches have been found to make waterborne coatings environmentally more acceptable.

One of the challenges in designing a reactive diluent for waterborne coatings is the need to develop structures that are low in molecular weight and water-soluble. The structures should lose the water solubility after film formation, or at least not contribute to a water sensitivity of the film. In industrial coatings, this is easier accomplished since crosslinking can be used to reduce water sensitivity.

Cosolvent Replacement in Waterborne Coatings

For many applications, especially industrial waterborne coatings, the volatile cosolvent can be replaced with a reactive diluent. Table 10 lists some of the typical examples of reactive diols, which are water-soluble and reactive with a crosslinker.

Table 10 Reactive Diluents and Reactive Cosolvents

| Chemistry | Advantage - disadvantage |
|-------------------------------------------------------|-------------------------------------------|
| Non-ionic | Water sensitivity |
| Polyether polyol ²⁰ | Water sensitivity and exterior durability |
| Bisphenol A EO-PO diols ²¹ | Exterior durability |
| Urethane diols ²² (aliphatic) | Cost |
| Polyester polyol ²³ | Hydrolytic stability |
| Low molecular weight resins COOH functional | Amine |
| Melamine resins HMMM type ²⁴ | Heat cure, formaldehyde |
| Epoxy aliphatic | Not stable |
| Unsaturated compound (oxidative drying) ²⁵ | Light stability, color |

Crosslinking

Present US VOC regulations are mainly concerned with the VOC's emitted as a result of solvent evaporation and not with the total VOC emitted during the coating process. This scenario has excluded reaction volatiles that can represent a significant

amount of VOC. This does not have to be the case. There are a number of crosslinking reactions known, which either emit only water as a reaction volatile or no reaction products at all. Table 11 shows some of the crosslinking chemistries that utilize elimination or condensation reactions. Some of the condensation reactions emit water and do not present a VOC problem.

Crosslinking is known to increase the Tg of a polymer. According to L. Hill²⁶, Hardness measurements such as Knoop Hardness²⁷ depend more on the modulus E' (25°C) than the Tg. For similar type polymer systems, nevertheless, there is a direct relationship between the Tg and Knoop hardness.

A major factor in the formulation of high solids coatings is the ability to achieve a reasonable potlife and cure time for two component coatings. Because of kinetic considerations the potlife is generally short for high solids coatings and the cure time is slow. Figure 6 illustrates the problem of achieving a reasonable potlife and tack-free time for a high solids polyester crosslinked with hexamethylene diisocyanate trimer. Both potlife and tack free time show a log/log response to DBTDL catalysis.

There have been many approaches to overcome this problem. Using blocked hydroxyl groups²⁸, potlife can be substantially improved without sacrificing reactivity. Another approach is the use of a catalyst that provides delayed reaction²⁹. The use of 2,4-pentanedione to improve the potlife of a DBTDL and Al chelate stabilized formulation is shown in Figure 7.

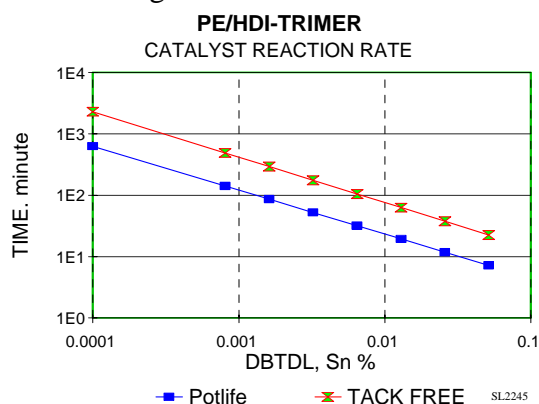


Figure 6 Potlife-tack free of 2K system

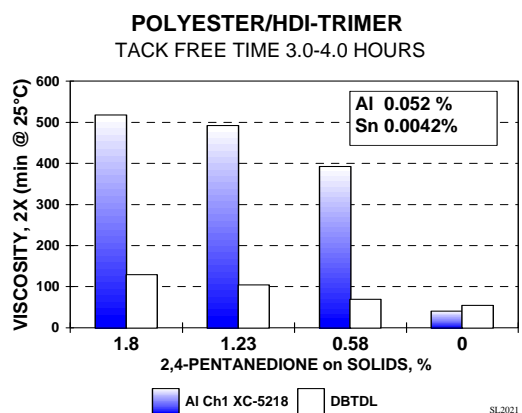


Figure 7 Potlife as a function of catalyst

Table 11 Condensation Reactions

| Chemistry | Reaction Product |
|--------------------------------------------------------------|----------------------------|
| Amino resins, melamine, urea formaldehyde ³⁰ | Alcohol, formaldehyde |
| Blocked isocyanate, ketoxime, pyrazol, alcohol ³¹ | Ketoxime, pyrazol, alcohol |
| Silane, siloxane ³² | Alcohol |
| Transesterification, Activated ester ³³ | Alcohol |
| Hydroxyethylamide -carboxyl ³⁴ | Water |
| Methylol amide, glycoluril, cyclic urea ³⁵ | Water |
| Acetoacetate - amine ³⁶ | Water |

The ring opening and addition reactions that do not produce a reaction volatile are shown in Table 12. Epoxides, cycloaliphatic and glycidyl ether are the easiest to prepare and are therefore used to a large extent. This chemistry covers cure temperatures from as low as room temperature to heat-cured systems. This chemistry can be used for self-condensation and also for reaction with hydroxyl, carboxyl or amine groups.

Table 12. Ring Opening and Addition Reactions

| Chemistry | Reactants |
|-----------------------------------------------|---------------------------------------------|
| Epoxy, Glycidyl, Cycloaliphatic ³⁷ | Self, carboxyl, hydroxyl, amine |
| Oxetane ³⁸ | Self, carboxyl |
| Uretdione ³⁹ | Hydroxyl, amine |
| Cyclic carbonate ^{40, 41} | Self, epoxy, amine |
| Azetidine ⁴² | Carboxyl |
| 2-Oxazoline ⁴³ | Carboxyl |
| Pseudourea ⁴⁴ | Self |
| Carbodiimide ⁴⁵ | Carboxyl |
| Aziridine ⁴⁶ | Carboxyl |
| Azlactone or 2-Oxazolin-5-one | Carboxyl |
| Bis cyclic urea ⁴⁷ | Hydroxyl |
| Isocyanate | Hydroxyl, amine, activated CH ⁴⁸ |
| Michael Addition ^{49, 50} | Amine, vinyl compound |

Potential for reducing VOC in High solids

From a practical standpoint some of the presently available coating technologies are already "Zero VOC" and some technologies can readily be converted to this status. Both UV and powder coatings can be formulated to be virtually pollution free. The greatest progress to be made is in waterborne and high solids coatings.

In the authors opinion most of the progress to "Zero" VOC not going to come from new and revolutionary approaches, but rather by combining and optimizing of existing technologies.

In high solids coatings the inherent problem of viscosity and solids⁵¹ has been discussed earlier. The major problem centers on the ability to achieve acceptable application solids and hardness. For heat-cured systems, one of the approaches is the creation of a dispersed high Tg polymer in a low Tg matrix. Similar to a PVC organosol, such a system will have the viscosity of the low Tg continuous phase and the benefit of increased film hardness of the high Tg dispersed phase.

Other advantages can be gained from polymer architecture. Z. Wicks⁵² has shown that functional groups substantially contribute to hydrogen bonding and increase the viscosity in high solids coatings. Polymers that do not have hydrogen-bonding groups that can be crosslinked give improved hardness/nonvolatile behavior. Polymers or crosslinkers, which fall into this category, are epoxy, acetatoacetate, cyclic carbonate and isocyanate functional materials. Some of the approaches which can be taken to reduce VOC in high solids coatings are shown in Table 13.

Table 13. Approaches to reduce VOC for high solids coatings

| Approach | Details |
|-------------------------------|-------------------------------------|
| Molecular weight | <500 |
| Molecular weight distribution | Narrow |
| Functional groups amount | 2-3 per polymer chain |
| Functional groups type | End groups, no hydrogen bonding |
| Crosslinking type | Ring opening |
| Crosslinking | Creating of hydrogen bonding groups |
| Dispersion of resin | High Tg heterogenous phase |
| Reactive diluents | Narrow MW distribution |
| Water addition | Breaking of H-bonds |

Potential for reducing VOC in Waterborne Coatings

For waterborne coatings the reduction in organic amine and the replacement of the cosolvent are the major issues. The problem is different for dispersion polymers and for water soluble polymers. A large effort in polymer design has gone into preparing polymers with ever-improved properties; application of the polymer was up to the formulator. The next phase of development has to be in designing polymers with inherently improved application characteristics.

Acrylic emulsion polymers prepared in the presence of a water soluble polymer⁵³ have been shown to overcome some of the problems of film formation and application characteristics. Polymers prepared by such a process can form films above the Tg of the polymer. The rheology approaches more of a waterborne solution polymer than an emulsion. Other approaches that are being used and can be further improved upon, is the use of reactive diluents such as polyether polyols⁵⁴ or polyurethane polyols⁵⁵. Low molecular weight crosslinker can play a double role as crosslinker and coalescence aid. Acrylic emulsions have been formulated with large excess HMMM or urea-formaldehyde resins, which plays the role as crosslinker and coalescent⁵⁶.

Additives

New catalysts, flow and leveling agents, defoamers, thixotropic agents and dispersants have to be developed for new coating systems to succeed.

One of the pivotal problems in the application of two component coatings is to achieve a good combination of potlife and reactivity. Table 14 shows some of the new catalysts that have been developed for high solids or VOC free coatings.

Table 14 Catalysts

| Crosslink Chemistry | Catalyst |
|------------------------------------|-------------------------------------------|
| NCO-OH ⁵⁷ | Al chelate/2,4-pentanedione |
| NCO-OH ⁵⁸ | Bi carboxylate |
| Cycloaliphatic epoxy ⁵⁹ | Quaternary N triflate or SbF ₆ |
| Cycloaliphatic epoxy-OH | Quaternary N triflate or SbF ₆ |
| Epoxy ether -COOH ⁶⁰ | Zn complex |
| Uretdione ⁶¹ | Metal chelate |

Summary

For many coating systems and applications it is possible to reduce or eliminate VOC. This goal cannot be achieved solely by developing new coating formulations. It requires changes in application equipment, and application conditions and in most cases some investment by the end user. Low VOC technology in many instances will encompass an increase in the cost of the coating formulation. This does not necessary indicate an increase in applied cost. Higher transfer efficiency, reduced cost of curing, smaller curing ovens or reduced energy cost can compensate in many instances for the higher cost of the paint.

Acknowledgement

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