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Outlook for Zero-VOC Resins

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INTRODUCTION

This paper was written as a keynote presentation for a symposium entitled "Zero-VOC Resins" at the International Coatings Exhibition (ICE) on October 18, 2000. It was originally published in the Proceedings and is reprinted here in revised form. Zero-VOC waterborne coatings are not discussed because they were described in a separate symposium at ICE.

Sooner or later, regulations requiring near-zero VOC coatings will probably take effect in a broad range of applications. Anticipating this development, the coatings industry is working hard to develop resins that can be used in such coatings–"zero-VOC resins." The topic of zero-VOC liquid coatings is being widely discussed, as exemplified by a recent plenary lecture by Werner Blank.[1]

Approaches to zero-VOC resins can be divided into three categories:

(1) Solventless liquid coatings—vegetable oils, oligomeric binder/crosslinker combinations, moisture-curable coatings, radiation-curable coatings, and thermally initiated vinyl monomer coatings;

(2) Powder coatings—dry powders, powder slurries, and radiation-curable powder coatings;

(3) Waterborne coatings

This paper addresses only approaches 1 and 2. Approach 3 was the topic of a separate symposium in this meeting. For the plenary lecture see reference 2.

The term "zero VOC" should not be interpreted too strictly. If you look hard enough, you will find that all coatings evolve detectable VOC during and after application. It may be 100 g/L or more in the case of coatings that give off volatile by-products of crosslinking, and it may be very small amounts in the case of certain powder coatings and latexes, but it is there. An alternative term, "solventless coatings," is more precise. It covers liquid and solid coatings to which no solvent is purposefully added. Another term that is gaining favor is "liquid powder coatings."

RESINS FOR SOLVENTLESS LIQUID COATINGS

Solventless liquid coatings are not new. Vegetable oil coatings have been used for centuries[3] and probably for millennia. In the late 1960s other types of solventless coatings were developed for use as liners for storage and process vessels.[4] The main objective at that time was to reduce the risk of fire or explosion to people painting in enclosed spaces. Solventless epoxy floor and decoupage coatings were developed about the same time, perhaps earlier. Solventless polyurethane roof coatings have also been on the market for a long time. All these coatings are applied as thick films, so they can be relatively viscous as applied and resist sagging and slumping. Of course, when they are applied to floors and roofs, sagging and slumping are not a concern.

Vegetable Oils

Vegetable oils are still used today in specialized coatings ranging from artists' paints to anti-corrosive paints for rusty, oily metal. They can even be considered the original two-package (2K) coatings, if you count the oxygen in air as the second package. Yet, in accounts of high-solids and solventless coatings, they are often neglected, and the patent literature suggests that researchers are not giving this area as much attention as it probably deserves, although some excellent research has been reported.[5]

Researchers have de-emphasized vegetable oil coatings because of their well-known shortcomings. They harden slowly, they tend to yellow with age, especially indoors, and their outdoor weatherability is not nearly as good as that of contemporary acrylics and some polyesters. Another factor causing neglect may be that companies do not see a clear-cut way to earn future profits by researching vegetable oil coatings. Farmers do, and groups such as the U.S. Department of Agriculture and the United Soybean Board are working to rekindle research in this area.

Early coatings technology was concerned with making vegetable oils more viscous. For at least 600 years, artists have put oils out in the sun for several weeks or months to cause their viscosity to increase,[6] and some still practice this method. From 1900 to 1950, methods for bodying oils, primarily linseed oil, were a very important topic in coatings technology, being described in three chapters in Mattiello's classic treatise on coatings.[7-9] Why did people want to increase viscosity? The reason illustrates one of the pervasive problems with very high solids and solventless coatings—the tendency to sag or slump during application. The easiest way to solve this problem is to increase the molecular weight of the resin so you can use more solvent. Formulations with a lot of solvent and a relatively small amount of high molecular weight resin will increase sharply in viscosity as solvent evaporates. If part of the solvent evaporates quickly, the films will not sag or slump. Furthermore, the least expensive solvents are cheaper than the least expensive resins. So, until about 1950, a goal of coatings technology was to use more solvent, not less.

Presented at the 78th Annual Meeting of the Federation of Societies for Coatings Technology, on October 18, 2000, in Chicago, IL.

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In the second half of the 20th century, we reversed course and began learning how to use less solvent. Now we are thinking about eliminating it altogether. Might vegetable oils have a role to play? Quite possibly. Research is underway to modify oils and improve formulations to make them dry faster and reduce their tendency to yellow. Jamil Baghdachi, John Massingill, and others have started substantial research programs in this direction.

An intriguing possibility is to genetically modify crops to make a perfect vegetable oil for paints. Soybeans have been successfully altered so that their oil contains predominately mono-unsaturated fatty acids. The goal is to make cooking oils that are less susceptible to oxidation by air. That is no good for air dry paints; the ideal would be an oil that contains only di-unsaturated fatty acids such as linoleic acid. Di-unsaturated, conjugated fatty acids would be even better for some uses. Di-unsaturated fatty acids are generally best because saturated and mono-unsaturated fatty acids subtract from cure potential, and tri-unsaturated fatty acids are the primary culprits in yellowing. Traditional plant breeding methods have been used to develop soybeans with low levels of tri-unsaturated fatty acids, but they are intended for cooking foods, not for paint.[10] Genetic engineering methods have been used to make soybean plants that produce oils with reduced levels of saturated fatty acids. The goal was to make better edible oils, not paints. As far as I know, the genetic engineers and plant breeders have not seriously attempted to make the ideal oil for paints.

Given better oils and better formulations, it should be possible to make solventless vegetable oil coatings that are serviceable in a number of applications. Such coatings would be derived from renewable resources, and they are potentially economical. Sagging and slumping problems could be addressed with use of thixotropic pigments.

Oligomeric Binder/Crosslinker Combinations

A lot of progress has been made in developing the basic technology for solventless baked coatings. Because they are intended for the kinds of industrial (OEM) applications that use powder coatings, they can be called "liquid powder coatings." Actually, the two technologies may turn out to be complimentary, with powders being more attractive for situations where long runs of a single color are desired, and liquids being more economical for small operations or for large ones where frequent color changes or lower baking temperatures are required. Several technical approaches to solventless enamels are conceivable; here I will describe one approach in detail to illustrate what is possible.

High-solids and, by extension, solventless liquid coatings have been among my main research interests for years. This interest was triggered by being responsible for the development of low-VOC liquid and powder coatings in the late 1960s and early 1970s. At that time, waterborne was the favored approach. It took a lot of effort to get the polymer chemistry for waterborne to work well, but that turned out to be the easy part of the job. The hard part was manufacturing the coatings and applying them. I have vivid memories of trying to spray refrigerator cases with an experimental waterborne coating in a plant where it was cool and extremely humid at 6:00 am and hot and relatively dry by 2:00 pm. The paint was dripping off the cases early in the morning, and it looked like sandpaper by afternoon. Such experiences (unfortunately, there were more than one) led to the serious consideration of high-solids coatings. At the time it appeared that the polymer synthesis and paint formulation challenges might be greater, but the application engineering problems might turn out to be easier. At least we would not have to struggle with variations in humidity.

Table 1—Viscosity and T_g of Oligoester Diols Made from Different Diols

$$HO{-}B{-}(OOC{-}A{-}COO{-}B{-})_x{-}OH$$
$$A = -(CH_2)_3-,\ -(CH_2)_4-,\ -(CH_2)_7- \quad B = \text{Diol residue}$$

DSC Diol	M_n	mPa•s, 25°C	Viscosity T_g, °C
Linear			
1,4-Butanediol	520	590	-83
1,4-Butanediol	670	760	-79
Diethylene glycol	540	550	-68
Diethylene glycol	610	710	-65
One methyl group			
1,3-Butane diol	560	1060	-64
1,3-Butane diol	690	1450	-61
Two methyl groups			
Neopentyl glycol	560	1430	-64

John Gardon has said that the development of high-solids coating technology to its current, excellent level is one of the outstanding accomplishments of coatings scientists and engineers. Many groups, mostly in industry, contributed to this accomplishment. In academia, part of our role is to try to look ahead to the next new thing. The study of solventless liquid coatings based on synthetic polymers dates back several decades in industrial and academic laboratories. I was very fortunate during the 1980s and 1990s to have excellent collaborators and supporters at Exxon (now ExxonMobil) Chemical Company and excellent students and associates to work on the problems. I will describe where this effort has led and try to foresee its future.

Today's technology enables formulation and application of high quality, very low-VOC enamels for a wide variety of applications. The technology resources include:

- Sophisticated methods for synthesizing low-viscosity oligomeric resins and crosslinkers.
- Formulating methods that minimize VOC including new reactive diluent resins and that control sagging and slumping.
- Use of exempt solvents, of supercritical CO_2, and more recently, of water, to reduce viscosity.
- Application equipment that makes it possible to control temperature of the coatings and to precisely mix two-component coatings as they are applied.

The topic here is resins, and resins that enable special formulating methods. Application hardware is not described, but its importance in the broader scheme can hardly be overstated.

It is my basic premise that, if all the resources are properly combined, it should be feasible to make solventless liquid coatings work well in many end uses. It is not an easy job—many details specific to each application will need to be worked out, but it appears possible.

There are many ways to approach the problem of making solventless liquid coatings. As an example, we will focus on a technology that employs two types of resins: Oligoester diol resins with viscosities as low as 300 mPa•s at 25°C and a relatively new type of reactive diluent resin. These resins can be used separately, but for solventless coatings they are particularly useful when used together. They are used with conventional crosslinkers, including melamine-formaldehyde (MF) and polyisocyanate (PI) resins. With MF resins the coatings may be solventless, but they generate appreciable VOC because the crosslinking reaction generates volatile by-products. With PI crosslinkers, it is possible to make coatings that are almost zero-VOC.

OLIGOESTER DIOLS: The classic dilemma in producing low-VOC oligoester diols was demonstrated by Belote and Blount[11] in 1981. The problem is that synthesis of very low molecular weight oligoesters by conventional means leaves a substantial proportion of unreacted monomers and other volatile material in the resin. To the extent that this material volatilizes during film formation, it must be counted as part of the VOC. Belote and Blount estimated that M_n of 800 to 1000 was optimal for making high-solids coatings. According to their results, reducing M_n much below 800 was fruitless, since VOC actually began to go up even though less solvent was required. But, M_n of 800 gave resins with viscosities far too high for use in solventless coatings, especially with the monomer combinations commonly used 20 years ago.

In the intervening 20 years, coatings technologists have been learning to resolve this dilemma. A number of compositional and process refinements improved the situation somewhat, allowing gradual reductions of VOC. One approach, which has met with commercial success, is to prepare a low M_n oligoester by conventional means and then use a wiped-film evaporator to remove most of the volatiles from it. Another is to use unsymmetrical diols and two-stage processing[12] to reduce viscosity.

In the early 1990s my research group began a systematic investigation of how composition affects viscosity of oligoester diols.[13] We found that linear monomer molecules, such as $HO(CH_2)_nOH$ and $HOOC(CH_2)_xCOOH$, give oligomers with the lowest viscosities. Non-linearity, e.g., methyl side groups, increases viscosity. It can result from branching caused by the addition of tri- or tetra-functional monomer or even by use of monomers that had side chains as small as methyl groups. For example, the viscosity of a resin prepared from aliphatic diacids and neopentyl glycol (with two methyl groups per monomer molecule) was more than twice as high as that of a closely similar resin prepared from the same diacids and 1,4-butanediol. The results are summarized in *Table* 1, which illustrates the substantial effect of branching. Differences in the glass transition temperature (T_g) do not appear to explain the viscosity differences.

Table 2—Relative Rates of Reactions Involved in Polyester Synthesis, Elevated Temperature

Type of Reaction	No Catalyst	Catalyst
Esterification	fast	faster
Hydrolysis	very slow	faster
Transesterification	very slow	faster

Linear oligomeric diols tend to be crystalline, making application very difficult. Melting points can be reduced to manageable levels by incorporating small amounts of branched monomers and by mixing ingredients. On the plus side, there is evidence, weak so far, that linear structures may yield crosslinked enamels with liquid crystalline characteristics, possibly opening a door to properties that can not be achieved with amorphous materials.[14]

While my students and post-docs were seeking the lowest viscosity compositions, our collaborators at Exxon were working on processes. The late Bill Wellman, Albert Yezrielev, and others developed new methods of making polyesters.[15] They took advantage of the fact that esterification reactions are self-catalyzing, but rates of hydrolysis of esters and transesterification are very low in the absence of catalyst. The situation is summarized in *Table* 2.

It is common to use catalysts, often organotin or organotitanium compounds, to accelerate synthesis of polyesters and oligoesters. As a result, all the reactions are reversible, and the process moves toward a thermodynamic equilibrium of compositions, although the equilibrium is shifted by removal of water during the process. If no catalyst is added, however, the esterification reaction proceeds at a production-feasible rate (providing an excess of one reactant or the other is used), but the rates of hydrolysis and transesterification reactions are almost undetectable. Thus, the ester forming reaction is essentially irreversible, and the product composition is kinetically controlled. The products are so resistant to hydrolysis that unreacted monomers can be removed by steam sparging at 200°C without affecting the distribution of esters in the product.

Sometimes one wants to use diesters, rather than diacids, as a starting material. In this case, an organotitanium catalyst is used, and the initial product composition is thermodynamically controlled. Water is then added to destroy the catalyst, and unreacted monomers (usually excess diols) are removed by steam sparging. The result is almost exactly the same as if a wiped film evaporator is used to remove unreacted monomers, but steam sparging is potentially much less expensive.

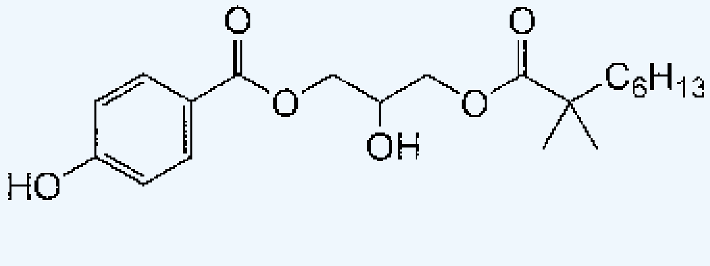
The patents[15] describing this process give dozens of examples of how it works. One example shows preparation of neopentyl glycol adipate by a direct esterification process followed by steam sparging at 160 or 200°C to remove excess neopentyl glycol. Viscosity of the products was 1400 to 2050 mPa•s, depending on the amount of excess neopentyl glycol used at the start. Viscosity of a conventionally prepared neopentyl glycol adipate was 3700 mPa•s. The acid number was 5 mg KOH/g resin and did not increase during steam sparging.

Now, putting together the best compositions for low viscosity with the

Table 3—Low Viscosity Polyester Diols

					GPC		
Diol[a]	Diacid[b]	Diol/Diacid	NVM	Viscosity (mPa•s)	M_n	M_w	Disp.
1,2-PG	SEB	3	100	437	490	626	1.27
1,3-BD	AD	3	99.9	333	385	455	1.18
1,2-BD	AD	3	100	429	403	484	1.20
1,3-PG	SU	3	100	448	325	390	1.20
1,3-BD	SU	3	99.7	666	347	405	1.17

(a) Diols: 1,2-PG = 1,2-propanediol; 1,3-BD = 1,3-butanediol; 1,2-BD = 1,2-butanediol; 1,2-PG = 1,3-propanediol
(b) Diacids: SEB = sebacic; SU = succinic; AD = adipic



PHEA

Figure 1—Phenolic ester alcohol (PHEA) reactive diluent.

best processes, the Exxon workers made a number of very low viscosity oligoesters. A sampling is given in *Table* 3. These materials were made by a transesterification process followed by steam sparging. Note that the polydispersity (M_w/M_n) is around 1.2, substantially lower than would be obtained with conventional processing.

When formulated with low viscosity MF resin crosslinkers, these diols require little or no solvent to achieve practical application viscosity. However, solventless MF resin formulations can have VOCs of 100 g/L or more because of release of methanol in the crosslinking reaction. Formulations with polyisocyanate (PI) crosslinkers can have VOCs below 10 g/L.

There are other problems: Film properties of the MF resin coatings are not very good. PI crosslinked formulations can have good properties but are expensive because the oligomers have high polyisocyanate demand.

The first of these problems was addressed by Vijay Swarup, Albert Yezrielev, Rich Ryan, and others at Exxon.[16] They developed a reactive diluent that is a phenolic ester alcohol (PHEA), *Figure* 1. It is unique among commercial reactive diluents because it adds hardness, chemical resistance, and weatherability to formulations rather than detracting from these properties.

PHEA is different from other reactive diluents because its phenol group forms cyclic (benzoxazine ring) crosslinks as shown in *Figure* 2. Formation of benzoxazines is demonstrated by model compound studies[17] and is confirmed by spectroscopic studies. Benzoxazine crosslinks enhance chemical stability and weatherability because they can be broken only by simultaneously breaking two chemical bonds, one a C–C bond. Furthermore, they add a great deal of rigidity to the crosslinked network. Thus, it becomes possible to start with "floppy," low-viscosity oligomers and end up with a tough, hard coating.

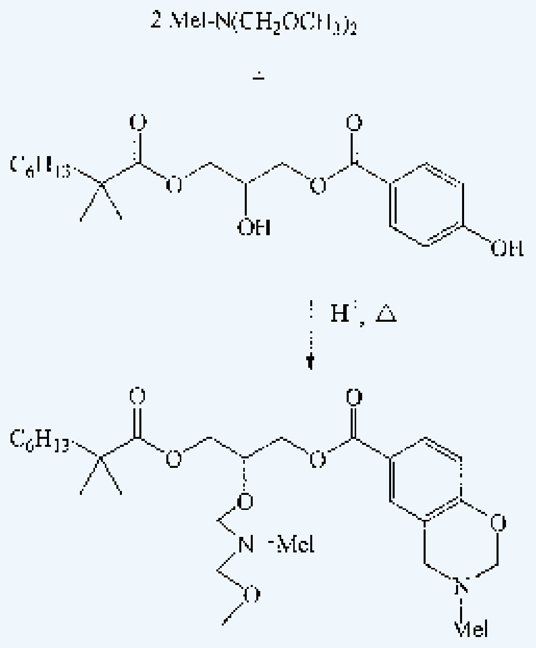


Figure 2—Reaction of PHEA with a methylolated melamine resin.

PHEA can be used in a wide variety of formulations, including conventional high-solids and water-reducible coatings. For solventless coatings, it complements the lowest viscosity oligoester diols because it adds hardness to films without excessively increasing viscosity. Thus, low-solvent and solventless coatings with excellent film mechanical properties can be formulated. In some cases, outstanding salt spray and QUV resistance have also been demonstrated.

The same principle can be applied using other phenolic reactive diluents as hardeners. For example, a diphenolic hardener can be easily made by reacting two mols of 4-hydroxybenxoic acid with one mol of neopentyl glycol.[18] Properties of solventless coatings made from a blend of this hardener with low-viscosity oligoester diols and a standard MF resin (HMMM) are shown in *Table* 4.

There is one more thing you can do. Solventless polyol/MF resin and, surprisingly, polyol/PI formulations can be thinned with small amounts of water.[13] They are hydrophilic enough that a few percent, and sometimes up to 10%, of water will dissolve in them. Viscosity is sharply reduced by even a few percent of water, as shown in *Figure* 3. This particular figure is for oligoester diol/MF formulations without hardener, but compositions with hardener behave similarly. This approach is appealing, as it does not require volatile amines as used in water-reducible formulations for success.

Sagging and slumping just after spraying and in the cure oven is a problem of high-solids coatings, and solventless liquid coatings are extremely vulnerable to sagging. The problem is usually addressed by using thixotropic additives—pigments or microgels. Another possibility is to formulate two-package systems with mixed MF and PI crosslinkers. Catalyst levels can be adjusted so that quick, partial reaction of the isocyanate "freezes" the coating in place to prevent sagging.[19]

This overview has provided a sample of the resources that can be applied to the problem of developing solventless, thermal cure coatings. To reiterate, by combining low-viscosity oligomeric resins and crosslinkers, formulating resources including new reactive diluent resins, application equipment that can reduce and control viscosity by warming the coatings, and can precisely mix two-component coatings when needed, and water reduction by exempt solvents, supercritical CO$_2$, and/or water, it should be possible to develop solventless coatings that fully satisfy the requirements for many end uses. Consider this question: What if the same level of technical effort that has been put into powder coatings during the past 40 years had been put into solventless liquids?

Resins for Moisture-Cure Coatings

Moisture-cure coatings have been around for a long time. Probably the most familiar are polyurethanes, epoxies, and silicon-containing coatings.

The polyurethanes use the reaction of isocyanates with water to form urea crosslinks (*Scheme* 1). A catalyst is usually used to accelerate the first step in this reaction sequence; after that, the second and third reactions are quite rapid at ambient temperature. Most commonly, the R–N=C=O group is part of a "prepolymer," an oligomer made by reacting one of the commercial isocyanates with a polyol. If properly formulated and applied, these coatings can have excellent film properties including good weatherability and outstanding abrasion and damage resistance. End uses include coatings for high-wear floors and industrial maintenance coating for bridges, tanks, concrete, etc.

The polyol that is used to make the prepolymer can be a simple diol or triol or an oligomer such as a polyester, a polyether, or a polycarbonate. One paper[20] described a new type of polyol, one that has a phenolic core and a polyether backbone. This combination gives excellent film properties and lower viscosity than conventional prepolymers. Thus, it is a step toward zero-VOC.

The epoxies often use blocked amine crosslinkers. These are di- or polyamines that (unlike conventional amine crosslinkers for epoxies) contain only primary amines that can be blocked by reaction with a ketone and removal of water to form a ketimine. The ketimine is relatively unreactive toward epoxies, but when it is exposed to water the blocking reaction reverses, liberating the amine (*Scheme* 2):

Table 4—Solventless Coatings with PE Diol/bis-Phenolic Reactive Diluent/HMMM
EPA VOC = 1^{0}6 – 111 g/L

Formulation[a]	60	60/61	60/61	60/61
HMMM; % Stoichiometric	120	100	90	65
PTSA % per binder	0.3	0.3	0.3	0.3
NVM (ATSM), %	94	94	94	93
VOC (EPA), lb/gal	0.88	0.94	0.96	0.98
NVM, 20 min @ 149°C, %	92	93	92	93
Hardness, Knoop	9	10	16	8
Hardness, pencil	4H	4H	>4H	2H
Direct impact resistance	100	100	80	100

(a) Examples from U.S. Patent 5,976,706. Baked 20 min at 149°C (300°F).

These coatings are used where the virtues of an epoxy coating—adhesion and toughness—are required. They can be good corrosion-protective primers. Ketimines are also used with polyisocyanates to make moisture-cure polyurethanes.

Familiar coatings involving silicon-containing oligomers are the "inorganic zinc-rich coatings" widely used as anticorrosive coatings in highway and marine applications. These coatings are mostly powdered zinc. The zinc is held together by crosslinking of tetraethylorthosilicate (*Scheme* 3):

The reactions are reversible, but are driven toward the crosslinked condition by evaporation of ethanol. In practice, oligomers of (EtO)$_4$Si are used for better application properties.

Similar chemistry is used to crosslink a variety of polymers, most notably in acrylic auto clearcoats. The acrylic polymer to be crosslinked bear pendant RSi(OEt)$_3$ groups. The crosslinking process is chemically very complex and has not been fully described. Presumably, an important reaction is formation of R(EtO)$_2$Si–O–Si(OEt)$_2$R crosslinks by reaction with H$_2$O followed by formation of Si–O–Si linkages. Other types of resins, such as polyurethanes, polyesters, polyolefins, and polyfluorocarbons, can be functionalized with R(OEt)$_3$ groups and crosslinked similarly.

Recent literature shows that hybrids combining more than one of these types of crosslinking are of considerable interest. Several patents (e.g., reference 21) describe moisture cure polyurethanes that are modified with RSi(OEt)$_3$ groups. The patents claim a number of benefits for the hybrids, including improved adhesion, toughness, and application characteristics. Mark Soucek and his students[22] at North Dakota State University have studied such hybrids and found attractive properties, notably improved

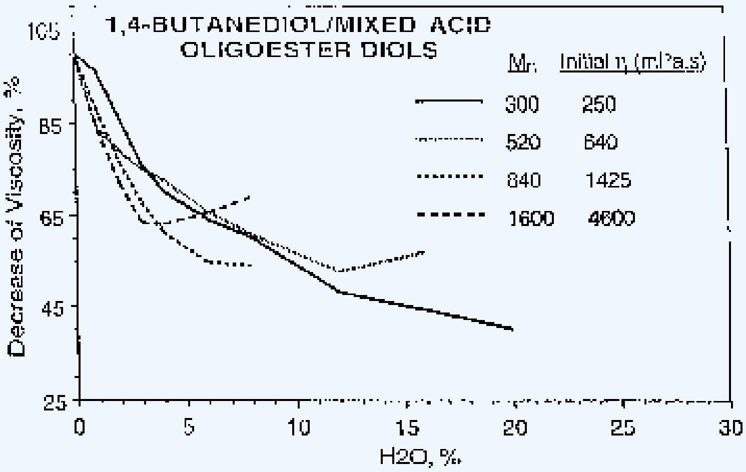


Figure 3—Viscosity reduction by thinning with water.

adhesion to metals. One can speculate that some of the $RSi(OEt)_2OH$ groups formed in the initial hydrolysis may form covalent bonds to the substrate.

The question here is: "Could these technologies be adapted for solvent-free coatings?" I think so. It is true that all, or practically all, of the moisture-cure coatings used today contain some organic solvent, but with a concerted effort it could probably be removed for many applications. As with other solventless liquid coatings, perhaps the most daunting problem is to prevent sagging. The main purpose of the solvent in current formulations is to facilitate application. Today, the isocyanate, epoxy, and silicon-containing prepolymers are deliberately synthesized at a higher viscosity than necessary for film properties to accommodate solvent so that sagging can be counteracted. To make solventless coatings, the resins will have to be made at lower viscosity and the sagging addressed by formulation or application methods (except, of course, for coatings for floors and flat roofs).

Resins for Radiation-Curable Coatings

One class of solventless coatings made from zero-VOC resins has been around for a long time: radiation-curable coatings. There are two types: (1) those that cure by free-radical initiated chain reactions, often (meth)acrylate oligomers and (2) those that are cured by cationic-initiated reactions, often epoxy or vinyl ether resins. The technology is complex and will not be treated in detail here. It has been described in many publications.[23]

The economic importance of radiation-curable coatings is enormous. Optical fibers, computer chips, printed circuits, magnetic tapes, and some high-speed printing methods depend on radiation-curable resins, and it is hard to see how the computer and telecommunications industries could have developed without them. Unfortunately for coatings technologists, these technologies are not counted as part of the mainstream coatings markets. Thus, they are outside the scope of this presentation.

In the traditional coatings markets, radiation curing has found significant, but rather limited uses. Often they are used on heat sensitive substrates—wood, plastics, and paper. Considerable volume is used to coat furniture in Europe, where the furniture is coated before it is assembled and there is a demand for glossy furniture. It has proven difficult to adapt radiation-curable coatings to North American furniture manufacturing practices. Another obstacle is the North American preference for transparent, but lower gloss, appearance, which is difficult to achieve consistently under production conditions with radiation-curable coatings.

Thermally Initiated Vinyl Monomer Coatings

Solventless coatings can be made from the same types of resins used in radiation-curable coatings, using thermal free-radical or cationic initiators instead of radiation to start the curing reaction. Solvent coatings based on this principle have been developed but are not widely used, perhaps because the coatings would generally need to be two-package coatings and would tend to be expensive. There have been many efforts to commercialize coatings that work on this principle; some failed, and a few succeeded. This type of technology is widely used in fiber-reinforced plastic applications, for example, fiberglass-polyester resins for boats, and acrylated epoxy resins for a wide variety of high-end applications. Little or no solvent is used.

When regulators begin to require zero-VOC coatings, this type of technology deserves a serious look. It can get around two of the major drawbacks of radiation-curable coatings—the difficulty of curing thick, pigmented films and the problem of coating anything that is not flat or cylindrical. It would appear possible to build in excellent film properties, as acrylated epoxies, polyurethanes, and polyesters can all be used.

POWDER COATINGS

Dry Powders

This overview will focus on thermosetting powder coatings, which account for well over 80% of the market.

Thermosetting powder coatings have been commercial since the 1950s, and have been growing steadily. Worldwide production this year will be well over 500,000 metric tons[24] valued at about \$4B.[25] In the early days (the 1960s) Europe led in developing the technology. Key early developments included epoxy resins and crosslinkers from Shell's Delft laboratory, and the introduction of electrostatic spray guns by Sames, Gema, and several other companies. The epoxy resins were similar to existing solid epoxy resins but were optimized for use in powder coatings; the original crosslinker was dicyandiamide ("dicy"); it required high cure energy, about 200°C for 20 minutes. "Modified dicy" and "catalyzed dicy" crosslinkers were introduced in the 1960s, bringing cure temperatures down. All these epoxy coatings had excellent mechanical film and anti-corrosive properties but poor weatherability. By the 1970s more weatherable, resin/crosslinker combinations appeared on the market—epoxy/polyester "hybrids," polyester/TGIC, and polyester/blocked isocyanate.

Since then, change in the basic resin technology has been evolutionary. According to Micek, the four generic resin/crosslinker types previously described still account for over 95% of the thermosetting powder coating market.[24] Of course, there have been refinements, for example, epoxy and

$$R{-}N{=}C{=}O + H_2O \rightarrow R{-}NH{-}C({=}O)OH \rightarrow R{-}NH_2 + CO_2$$
$$R{-}N{=}C{=}O + R\text{-}NH_2 \rightarrow R{-}NH{-}C({=}O){-}NH{-}R$$

Scheme 1

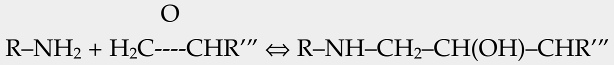
Ketimine formation:

$$R{-}NH_2 + R'R''C{=}O \Leftrightarrow R{-}N{=}C(R'R'') + H_2O$$

Ketimine unblocking:

$$R{-}N{=}C(R'R'') + H_2O \Leftrightarrow R{-}NH_2 + R'R''C{=}O$$

Reaction with an epoxy resin:



$$R{-}NH_2 + H_2C\overset{O}{\text{----}}CHR''' \Leftrightarrow R{-}NH{-}CH_2{-}CH(OH){-}CHR'''$$

Scheme 2

$$(EtO)_4Si + H_2O \Leftrightarrow (EtO)_3Si{-}O{-}Si(OEt)_3 + 2EtOH$$
$$(EtO)_3Si{-}O{-}Si(OEt)_3 + nH_2O \Leftrightarrow \text{Chain extension and crosslinking}$$

Scheme 3

polyester resins with improved flow, new blocked isocyanate crosslinkers that cure at lower temperatures[26] and uretdione (a type of self-blocked isocyanate) crosslinkers for which a number of advantages are claimed.[27] Several new classes of crosslinkers have been introduced, for example, those based on hydroxyalkyl amides[28] and aminoplasts.[29] A paper describes new crosslinkers and accelerators.[30] Historic advances have been described in more detail in an excellent review by Richart.[31]

While the resin technology was evolving slowly, commercial use of the technology has been growing fast. Various authorities estimate the growth rate of powder coatings in North America during the 1990s at 7% per year to 11% per year, not sensational growth by .com former standards but excellent for coatings. All agree that the growth rate in Europe was a bit slower because the market there had grown faster before 1990.

How has the technology grown very nicely for the past 30 years without major earthquakes in the polymer chemistry? Success appears to have resulted from continued refinement of all the major elements of powder coating technology. New types of resins do appear from time to time, and some have found commercial application. Acrylics seem to have the most potential. They were used as early as the 1970s on monocoat powder coatings for cars produced in Japan. In this symposium a new type of acrylic resin is described,[32] an acrylic copolymer with a vinyl ester monomer. This vinyl ester is said to provide a sufficiently high T_g for powder stability, good processability, and appearance and weatherability good enough to make these resins candidates for automotive clearcoats.

While the compositions of the standard resins may not have changed much, resin manufacturing technology has improved. Equipment and process control have improved, making it possible to reduce batch-to-batch variations in molecular weight (critical to film properties and appearance) and probably to make narrower molecular weight distributions, improving flow at a given level of appearance.

Formulating technology has also improved. For example, 30 years ago most powder coatings had high gloss. Many customers wanted lower gloss or even matte finishes, but it was difficult to control gloss within an acceptable range in day-to-day production. Now, according to Richart,[33] roughly one-third of the powder coating market uses semi-gloss or lower gloss coatings. Several formulating methods have made this possible: use of fillers, careful mixing of incompatible resins, and use of mixed crosslinking chemistries that cure at different rates.[33]

Powder coating production methods have also improved. Better extruders make it possible to increase production rates and/or to achieve superior mixing, leading to more consistent properties and color.[33] Better control of grinders and classifiers provide better control of particle size distribution, enabling thinner films with more uniform appearance.[31]

Powder coating application methods have been the subject of considerable research, for example, by J.F. Hughes at Southampton.[35,36] Spray equipment manufacturers report improvements that lead to better transfer efficiency.[37] However, there remains considerable room for improvement both in basic understanding and in practice.

Taken together, these improvements make it easy to understand how powder coating has been able to grow commercially for 30 years without any single, bombshell breakthrough. The advances have been smaller, thousands of them, and they add up to more or less continuous improvement of the technology.

What about the future? Most authorities expect the worldwide growth of powder coatings to continue, but the growth rate is expected to decrease in the 2000s as appropriate applications for powder coatings approach saturation. Some expect the fastest growth to occur in the Asia-Pacific region.[25] It appears that the pattern of incremental technology improvement will continue and will be adequate to support the projected slower growth.

But, will there be major breakthroughs? They are possible, in several areas.

As Marco Wismer pointed out decades ago, breakthroughs in coatings technology often stem from breakthroughs in application technology. After a new application method is conceived, polymer chemists and the coatings formulators work with application engineers to put together a system of coating and hardware that works. Marco may have had electrodeposition coatings in mind, but powder coatings are another example. Future breakthroughs in powder will probably result from such combined efforts. For example, serious efforts are underway to develop hardware and powder coatings to replace liquid coil coatings.[38]

The holy grail target for powder coatings is automotive OEM, expecially auto body clearcoats. Powder coatings are well-established for various parts and for body primers; three million auto bodies have been coated with powder primer.[39] Substantial efforts are underway in the U.S. and in Europe to develop clearcoat technology. BMW has been coating some production cars with powder clearcoats in Europe for more than a year,[40] and GM, Ford, and DaimlerChrysler have been operating a powder clearcoat pilot line in an auto plant in Michigan for some time. A recent report[41] states that BMW now coats 3-, 5-, and 7-series bodies with powder clearcoat at a rate of over 1000 units/day. Problems that have been repeatedly cited with powder clearcoats include the difficulty of eliminating dirt contamination and of getting good, uniform appearance; good appearance requires precise film thickness control, since the orange peel of powder coatings varies with thickness much more than it does with liquid coatings. Apparently, BMW has learned to control these problems to a satisfactory level.[37] The powder clearcoat is more expensive than a 2K liquid clearcoat, but operational savings (overspray recycle, no sludge disposal) partly offset the extra cost and are said to have the potential to fully offset it. Despite optimistic, but very general, reports,[39,42] the Michigan pilot line was recently placed on standby status. Ultimate technical success or failure will depend mostly on the interactive efforts of resin chemists, coating formulators, and engineers of powder production and application equipment. One observer points to the need for more precise application equipment,[39] although BMW's experience indicates that this is possible. Whatever technical progress is made, widespread adoption may depend as much on political as on technical developments.

Where there are unsolved problems, there are opportunities for innovation. For example, how about a robot that could solve the appearance problems by sanding and polishing the entire car body automatically? A robot that can sand (but not polish) an entire car body is already used in production. Redesign of the powder resins would almost surely be needed to make it work. Could powder stability problems be solved by grinding and classifying the powder within the electrostatic spray system, perhaps at low temperature? There may also be room for innovations in powder production engineering, such as processing with supercritical CO_2[43] or new methods to produce uniform particle size powders. Each innovation will require adjustment of the resins and formulations.

About 10 years ago ICI/Glidden assigned a physicist, Ed Meyer, to investigate electrostatic powder spray. His report[44] concluded, in part, "There are many electrostatic phenomena associated with powder charging and charge decay that defy explanation using the conventional model of powder coating application." In other words, "it works, but it shouldn't." More recently, Hughes has affirmed that better understanding is still needed.[36] There is an opportunity here for good science that would have a big commercial impact. If physicists and polymer scientists can collaborate to better understand the relationship between powder particle composition and morphology and its electrostatic sprayability, it might be possible to make powders and guns that would greatly improve charging efficiency. That could lead to the solution of one of the major obstacles to the penetration of powder in the market—the difficulty of color change. Today, transfer efficiency is limited, and it is usually necessary for economic reasons to reclaim and reuse the powder overspray that did not go on the object to be painted. When colors are changed, the entire booth and reclamation system must be carefully cleaned. If transfer efficiency could be increased to 90% or 95%, reclamation would be unnecessary and color change would be a great deal easier. Improved understanding in this area might also help overcome the problems of powder clearcoat application to auto bodies. There the problem is not color change, but uniformity of film thickness and its influence on appearance.

These examples highlight the importance of resin chemists and engineers collaborating closely to make things work. What about possibilities for dramatic improvements in resin technology? Someday someone will probably come up with a new crosslinking chemistry that will replace the incumbents in major applications.

- One possibility is to use aminoplast resin technology. It is appealing because it is economical and gives excellent film properties in many liquid coatings. People have worked on this problem for many years, and at least one product is on the market,[29] but large-scale commercial success has been elusive. One limitation has been pinholing caused by the escape of volatiles from the crosslinking reaction. Why is that a problem with powders but not with liquids? I am not sure. It is true that powder films are often thicker than liquid films, but that can't be the whole story.
- Another possibility is to use semicrystalline, or liquid crystalline, rather than amorphous resins. Both types have the potential for much superior flow characteristics since they can be designed to become quite fluid when heated above their melting points. A series of patents has appeared on this subject, but I am unaware that the approach has been commercialized.
- An extension of this possibility is to use semicrystalline, hyperbranched resins. Such resins have extraordinary viscosity/molecular weight characteristics that should translate into excellent flow and appearance control, enabling low temperature application. A recent report[45] shows that this approach has potential.
- Over the years there has been considerable experimentation with different types of powder coating resins, for example perfluorocarbon and silicon modified polymers.[31] It has not had a big pay off yet, but the potential for major breakthroughs seems to exist.

Powder Slurries

Powder slurries are dispersions of solid powder coatings in water. They could be classified either as waterborne coatings or as powder coatings; since the chemistry is similar to that of powder coatings we will consider them here. Attempts to commercialize powder slurries date back at least to the 1970s.[46] A persistent obstacle was to control rheology for successful application.

BASF and DaimlerChrysler have worked together to develop powder slurry clearcoats. This effort has been successful, and powder slurry is used in production to clearcoat Mercedes Benz A-body units, a sort of minivan that is marketed in Europe. I have seen one A-body unit coated in this way, and its appearance was outstanding, demonstrating that the rheological problems can be overcome.

Radiation-Curable Powder Coatings

One of the principle limitations of powder coatings is the need for high bake. Thermally cured powder coatings have been developed that can cure at temperatures as low as 100°C for 30-40 min.[27] However, such coatings have severe package stability and application problems, and for most applications the practical lower limit is higher, perhaps around 130-140°C. The effect has been to limit powder coatings almost entirely to metals. Plastics, wood, and paper are generally too heat sensitive for conventional powder coatings.

A possible solution to this is to use radiation-curable powder coatings. UV radiation is generally used. Much research and development has been devoted to this subject for the past 10 years or so,[31] and it is bearing fruit. Most coatings journals have featured articles on the subject this year, for example.[45,47,48] Resin suppliers are marketing several types of resins for the purpose, including solid polyester (methacrylates) and solid maleate (fumarate?) polyesters with vinyl ether crosslinkers. These materials are package stable and are curable with UV-light at 100–110°C in just a few seconds, making them candidates for many applications on heat-sensitive substrates. One scheme calls for a continuous process in which heating with IR lamps is followed by curing with a UV source. The heat is required to melt and flow the powder coating; UV cure could be induced at lower temperatures. With refinement, the cure schedules can probably be further reduced.

CONCLUSIONS

The examples cited in this paper are only a sample of the approaches to zero-VOC resins for solventless coatings. Research on other possibilities is going on around the world. Converting to a zero-VOC coatings industry will be challenging and will require decades of concerted effort by chemists, engineers, and technologists. I think it could be done.

ACKNOWLEDGMENTS

Research at Eastern Michigan University on solventless liquid coatings was supported by Exxon (now ExxonMobil) Chemical Company. The students who benefited from this support and I are grateful for it. Furthermore, we are grateful for the opportunity to collaborate with researchers at Exxon. Students involved in the project included Dan Ford, Shou-Kuan Fu, Brad Haskell, Jun Hua, Ramachandran Subrayan, Ganghui Teng, Ganghua Teng, Xiaoying Yuan, and Suru Zhang. Collaborators at Exxon included George Knudsen, K.R. Rigopoulos, Rich Ryan, Vijay Swarup, the late Bill Wellman, and Albert Yezrielev.

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