

TARGETS FOR RESIN DEVELOPMENT In the New Millennium

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INTRODUCTION

This paper was written as a “keynote” presentation for a symposium called “Resin Technology for the Next Millennium” at the International Coatings Exposition (ICE) in October 1999. It was originally published in the Proceedings and is reprinted here in revised form.

The eight other papers in this symposium all concerned low-VOC technologies: waterborne—latex and dispersion, high-solids, and UV cure. The primary objectives of the projects appear to be: cost reduction, improved product—new resins and new crosslinkers, and very low VOC.

This is a small sample, but it may represent today’s research goals in the coatings industry fairly well. All that is obviously lacking are papers on electrodeposition and powder coatings and basic research on such subjects as corrosion protection, weatherability, and rheology. It is hard to fault the objectives. No regulatory crisis is looming in the immediate future, and cost reduction and product performance improvement are the main ways to seek a competitive advantage.

If this array of objectives makes sense now, will it in the future? Not necessarily. Let’s try to look ahead. Research targets for the next five or 10 years will be considered, and then some possibilities for the more distant future will be described. But first, since coatings technology and environmental regulations are joined at the hip, we need to consider the regulatory future.

“It is unsafe for the coatings industry not to prepare for tighter restrictions.”

TO VOC OR NOT TO BE?

VOC regulation has been the primary driver of coatings technology since Rule 66 took effect in 1967. Since then, the trend has been toward tighter and tighter regulation. Extrapolation of the current trend suggests that, eventually, VOC will be virtually outlawed.

Should it be? Nobody knows. The regulations are based on the assumption that reducing VOC will reduce ozone. But, as the National Academy of Sciences pointed out in 1992,¹ the scientific basis for this assumption is shaky. Atmospheric ozone is formed by a complex sequence of reactions involving VOC, nitrogen oxides (NO_x), and UV light. Nationwide, the amounts of man-made VOC and plant-made VOC are roughly equal, but in regions with large pine and oak forests, plant-made VOC predominates. Even the EPA acknowledges that, in these regions, reducing man-made VOC may have little effect; there is already plenty of plant-made VOC to cause ozone

formation. The Great Smoky Mountains got their name before we ever heard of VOC. In regions with high plant-made VOC

levels, the best hope for reducing ozone is to drastically reduce NO_x, but that is extremely expensive. It has even been argued^{1,2} that *in some real life situations increasing emissions of some types of solvents will actually reduce ozone levels*. Can you imagine that the EPA may someday command us to emit more solvent when certain atmospheric conditions occur?

New smog chambers are being built, and perhaps they will prove adequate to develop a solid scientific under-

standing of ozone formation. We will not know for years. Better understanding may lead to surprising discontinuities in the regulatory trend. Until then, the political juggernaut that favors stricter VOC regulations will roll ahead. In December 1999, the EPA announced a 10-year schedule to sharply reduce VOC emissions by cars and light trucks. It seems likely that very strict regulations on coatings will follow because, as emissions from cars and light trucks decline, the proportion of man-made VOC that come from coatings will increase. The EPA reported³ that, in 1995, coatings and adhesives caused 11.6% of man-made VOC in the United States. Probably 9-10% came from coatings—too big a target to ignore. It is unsafe for the coatings industry not to prepare for tighter restrictions.

RESEARCH TARGETS FOR FIVE TO TEN YEARS – TOWARD ZERO VOC

We are all familiar with the generic technologies that are used to reduce or eliminate VOC. New articles about them appear almost every day. This article is limited to pointing out good targets for research and development.

Powder Coatings

Powder coatings have been commercially available since the 1950s and have been growing steadily. Worldwide production this year will be over 500,000 metric tons. It is an exciting area, but the resin technology does not change very fast. The standard generic types of resins have been around for decades. A number of new types of resins and crosslinkers are available, but they do not seem to have captured much of the market. Unless

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VOC regulations get much tighter or technology breakthroughs occur, the growth of powder coatings (currently about eight percent per year) will probably attenuate in the next five to 20 years, as appropriate applications for powder coatings are saturated. The area appears ripe for breakthroughs that could prolong or even accelerate growth.

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.⁴

The holy grail target for powder coatings is automotive OEM. Powder coatings are well established for various parts and for body primers. Massive efforts are underway in the U.S. and in Europe to develop technology for auto body clearcoats. BMW is coating production cars with powder in Europe,⁵ and a pilot line has been operating in an auto plant in Michigan for some time. The technical problems include elimination of dirt contamination, assuring 10-year weatherability, and 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. Optimistic, but very general, reports have been published.⁶ Details of the technical effort are shrouded in secrecy. Technical success or failure will depend mostly on the interactive efforts of resin chemists, coating formulators, and application process engineers. Whatever technical progress has been made, widespread adoption may depend as much on political as on technical developments.

Powder looks like an area where there is a good opportunity for innovation. For example, how about a robot that could solve the appearance

problems by sanding and polishing the entire car body automatically? One robot that can sand (but not polish) an entire care body is already used in production. Redesign of the powder

resins would almost surely be needed to make it work. Could powder stability prob-

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lems 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 CO₂⁷ or new methods to produce uniform particle size powders. Each innovation will require adjustment of the resins and formulations.

A variation on this theme is to use slurries of powder in water as automotive clearcoats. This method is used commercially by Daimler-Chrysler in Europe, and published reports have been optimistic, though general. Rheology control during application may be a key problem.

Solventless Liquid Coatings

Solvent-free (though not necessarily zero-VOC) crosslinkable coatings are used today, mostly on horizontal surfaces like roofs and floors. And, of course, most radiation-curable coatings are solventless. Technology exists or is within reach to make thermally cured solventless coatings with film properties that are probably acceptable for a broad variety of end uses.⁸ The main technical problem is application. Solventless coatings sag when applied to vertical surfaces. It is difficult to formulate them with good sag resistance, although some progress with additives and formulation methods has been made in recent years. It is also probably impossible to formulate them at a usable viscosity with high pigment loadings (above, say, 20 or 25 PVC).

Working together, good resin designers, formulators, and engineers can probably make solventless coatings work. Considerable research on polymer design, formulation, and equipment has identified ways to address the sagging problems, and

solutions are in sight. But, to develop a breakthrough commercial product and establish it in the market can cost 100 times more than the underlying research. Until regulations requiring near-zero VOC are scheduled, few companies will invest the money to complete development. The formulation and engineering problems are devilishly hard.

Here's a question: If the resources that have been put into developing powder auto clearcoats had been put into developing solventless liquid auto clearcoats, how far along would we be?

Waterborne Coatings

Waterborne has been the most popular approach to VOC reduction. The question is, how well will it work for near-zero VOC? Most of today's waterborne coatings generate substantial VOC from coupling solvents, coalescents, freeze-thaw stabilizers, and crosslinking by-products. For some applications, it is clearly possible to almost eliminate the VOC; architectural paints with essentially no VOC are on the market. But, in many industrial applications it has proven difficult. For example, waterborne auto basecoats contain substantial amounts of solvent and it has proven extremely difficult to reduce solvent levels while meeting all required application, appearance, and film performance requirements. This may be the best area for innovative resin research in the next 10 years or so.

Approaches to the problem can be classed as:

- Latex polymers made by emulsion polymerization.
- Solvent-free emulsions or dispersions of conventional resin types—alkyds, epoxies, polyurethanes, etc. made by other means. This category could include the powder-in-water slurries mentioned previously.

If I had to bet on one approach, it would be latexes. Seemingly, the industry agrees—half the papers in this symposium concerned new developments in latexes.

Countless variations of composition and morphology of latex particles can be made. In addition to straightforward latexes, those with core-share, surface modified, and multi-lobed morphologies are commonplace today. Formulators can multiply the possibilities by blending different latexes and by blending latexes and water-reducible resins.

Latexes have secured more than 75% of the market for architectural paints, where the film properties are generally adequate without crosslinking. It has proved more challenging to develop latexes for most industrial and special purpose applications. Essential problems are the difficulty of getting high gloss and latex particles to form films that are hard and tough enough for industrial coatings, especially if the use of volatile coalescing aids is ruled out. Most industrial coatings must be crosslinked or have a glass transition temperature (T_g) higher than room temperature, or both. Since latexes only coalesce well at temperatures below T_g , crosslinking appears to be the best bet.

Enormous effort has gone into developing crosslinkable latexes for several decades. They are used commercially in many applications, but large-scale commercial success has been elusive. All I can say is "try harder." An appealing approach to very low VOC waterborne coatings is to use relatively low T_g latexes that can coalesce well without coalescing solvents and subsequently build film properties by crosslinking. The patent literature shows that a number of research groups have been working in this direction. However, as long as VOC regulations for industrial coatings permit use of substantial levels of coalescing solvents, the major thrust will be toward latexes that depend on coalescing solvents for film formation.

Latexes in baked coatings can be crosslinked with aminoplast resins, alkoxy silanes, blocked isocyanates, epoxy resins, and many other crosslinkers. The biggest challenge is latexes for non-bake ("air-dry") and low temperature bake ("force-dry") coatings. Here aziridine and carbodiimide crosslinkers are used in some applications. Many other possibilities have been studied. Among the most intriguing is the possibility of building autooxidizable structures into the latex so it can cure after coalescence by reaction with oxygen, similarly to the way drying oils and alkyd resins cure. This is tricky because most autooxidizable monomers will interfere with the polymerization required to make the latex. A number of patents describe ways to get around the problem.⁹ Perhaps this approach is being used commercially, but I cannot confirm it.

Emulsions and dispersions are commercially successful in a variety of applications, and the technology is

being developed further. One intriguing possibility is to use emulsions of alkyd resins as binders for trade sales paint. In principle, they could perform well in primers and in glossy enamels and varnishes. Alkyd emulsion technology is being developed mainly in Europe, where glossy alkyd architectural paints are popular. Resin suppliers are bringing the technology to the U.S. Many patents and several papers about it have appeared,¹⁰ but it is hard to deduce from them exactly how the technology is accomplished. This is probably a fruitful area for further research.

RESEARCH TARGETS FOR THE MORE DISTANT FUTURE

Predictions of the future are usually wrong. Anecdotal evidence for this statement can be found in an entertaining book by Cerf and Navasky.¹¹ The whole book is a list of wildly mistaken predictions by leading experts, for example:

- "Radio has no future." (Lord Kelvin, 1897)
- "The radio craze...will die out in time." (Edison, 1922)
- "...commercially and financially I consider it (television) an impossibility..." (Lee DeForest, 1926; DeForest was one of the pioneers of radio)
- "I think there is a world market for about five computers." (Thomas J. Watson, Chairman of IBM, 1943)

A recent book by Sherden¹² analyzes predictions of various kinds and reaches a surprising conclusion: The most reliable predictions come from the weatherman. According to Sherden, all other predictions of the future are worse.

Am I making predictions? Sort of. But, my main intent is to point out a few of the many exciting possibilities. I will start by discussing the almost unimaginable complexity of today's coating resins and look at two ways to deal with it—to live with it better or to control it. Then I will discuss polymer surfaces, which we are only starting to understand even though they influence many key coating properties.

Molecular Homogeneity, and Do We Need It?

In the late 1950s and early 1960s, General Motors cars were painted with

acrylic lacquers based on a homopolymer, poly(methyl methacrylate). Most resin chemists would regard this as a very straightforward resin, quite simple by today's standards. Actually, this straightforward polymer is incredibly complex. A car painted with poly(methyl methacrylate) lacquer carried over 10^{22} molecules of PMMA, and, disregarding low molecular weight material, *no two molecules were exactly alike*. The PMMA had a number average molecular weight (M_n) of around 40,000 and a weight average molecular weight (M_w) of about 80,000 to 90,000. Let's take a look at this simple polymer. Polymer chemists often think that a polymer with $M_n = 40,000$ and $M_w/M_n = 2.2$ has a fairly narrow polydispersity, but the distribution of molecular weights is actually very broad. Such a polymer contains molecules with molecular weights of a few hundred up into the millions—tens of thousands of different molecular weights. And that is just the "pure" straight chain molecules with the same end groups. Impurities in the monomer and chain transfer processes will lead to other molecules that are branched or have pieces of solvent molecules or other impurities attached. By now we are probably up into the quadrillions of possible different molecules, but that is just the beginning. One single PMMA molecule with a molecular weight of 100,000 has 2^{999} different possible stereoisomeric structures, so the sources of complexity already mentioned are multiplied by 2^{999} .

Then things started to get complicated. Copolymers were introduced. Mixing monomers exponentially increases the number of possible molecules. We began using crosslinked enamels to paint cars. Acrylic copolymers are crosslinked with melamine-formaldehyde resins, polyisocyanate resins, or polyacids. Sometimes siloxane crosslinking is involved as well. With the possible exception of the polyacids, the crosslinkers are all mixtures. Complexity is increased by the use of copolymers made from mixtures of three to six monomers and sometimes more. It is true that lower molecular weight acrylics are used, reducing the possible number of stereoisomers to the range 2^{10} to 2^{250} before crosslinking starts. But, this reduction in complexity disappears after the resins are crosslinked. Furthermore, the coatings tend to stratify (more about that later) so there is a range of different compositions from the top to the bottom of the film.

Ideally, a crosslinked polymer is all one big molecule, but what a complicated molecule it is!

What about other types of coatings resins? Alkyds, vinyls, and silicones are extremely complex mixtures of molecules. Polyesters and epoxies can be a little simpler, but still very complex.

Why do coatings formulators invariably select polymers that are complex mixtures? Mainly because they cannot crystallize. They are amorphous. Relatively simple, partly crystalline polymers such as nylon and polyethylene are of little use in coatings, but the complex polymers we use in coatings are extremely difficult to understand at the molecular level. That is why resin design and coatings formulation continue to be part science, part art, and part craft.

This complexity presents two kinds of opportunities. Either we can improve our ability to deal with complex mixtures of polymers or we can learn to precisely synthesize purer, less complex polymers that do exactly what we want them to. I think both approaches have excellent potential.

Dealing with Complex Mixtures

COMPUTER MODELING: Some physicists and mathematicians do their work for the joy of it and modest pay. Others hope to get rich. The latter group has developed computer models for the stock and bond markets. Huge amounts of historic data are fed to the computer; it searches for patterns and develops a model, perhaps with human assistance. As the model is used, the computer acquires more data and refines the model, correcting tendencies to make mistakes. Once the model is refined, no human judgement is used—the computer is the boss. It may not always be right, but it is always the boss. I do not know how well these computerized investment schemes actually do in practice, but I suspect it will be very hard for an old-fashioned trader to compete with them in the future, if it is not already. Other researchers (perhaps those who are content with modest pay) are trying to model extremely complex systems like the weather. If you can model the weather, you should be able to model paint. Of course, efforts to model the weather are still in a primitive state, but we are talking 1,000 years.

As I understand computer modeling, you feed every measurable

variable and outcome into the computer, and it predicts the next outcome and/or tells you how to come as close as possible to a desired outcome. As it learns more and more about your system, its predictions get better and better. The computer does not need to understand what is

happening at the molecular level to make valuable predictions. This

approach is already used in coatings. David Bauer described a time-to-failure model for auto paint based on field experience, empirical testing, and knowledge of the chemistry and physics of failure.¹³ Research on computerized formulation is underway, for example, in Gordon Bierwagen's group at North Dakota State University.

COMBINATORIAL CHEMISTRY: How can we get the data to feed the computer? Combinatorial chemistry may be a way. It involves making computer-linked machines that do a large number of experiments automatically and digest the data. Pharmaceutical companies have used combinatorial chemistry for years to screen large numbers of compositions and formulations, and it has contributed substantially to drug discovery.¹⁴ Systems that can screen 100,000 compositions in a single run are about to become available.¹⁵ The computer can find the needle in the haystack, or at least it can say what part of the haystack to look in.

Now, imagine a robot that automatically makes dozens of acrylic polymer samples with narrow gradations of composition and measures their molecular weights at a rate of one sample a minute. Far-fetched? Not at all, it already exists. Nielsen et al.¹⁶ built a machine that automatically synthesizes "libraries" of 48 to 140 different, but related, acrylic polymers in reactors holding 0.1 to 20 mL. They developed chromatographic and light scattering methods to characterize the products in 40-120 sec. They used the data to optimize polymerization conditions.

Going further, imagine another robot that prepares coatings from these samples and deposits them precisely on a panel, perhaps 64 different compositions in small squares or streaks on a single panel. The coatings are then tested, exposed or otherwise abused, and tested again. Variations due to panel location within the bake oven and testing device would be mini-

be a simple matter. Robots are also used to do the testing. The results automatically go to a computer that digests the data and gradually learns how to become the boss. As far as I know, the paint making and paint testing robots do not exist, but they

"Will We Ever Be as Smart as Silkworms and Algae?"

could surely be developed. Testing is always a headache in

coatings development and may be the biggest obstacle. However, there are test methods that can produce a lot of information about a paint specimen in seconds. For example, automated infrared testing devices that assess the purity of the disks from which computer chips will be made could be adapted to record IR spectra of coating films. Devices that can quickly measure the mechanical characteristics of paint surfaces are adaptable to automation. Perhaps electrical methods could test crosslinking and characteristics related to corrosion resistance.

So here's a prediction: sometime in the next 1,000 years, combinatorial methods will have a major influence on coating science and technology. We may even live to see it happen.

Will We Ever Be as Smart as Silkworms and Algae?

The other way to deal with complexity is to simplify it. In the case of resins, simplification would involve synthesis of polymers with precisely ordered structures. Then we could learn to make structures that have exactly the properties we need. That may seem too difficult, but some creatures that we don't think of as being very bright can already do it. Think about proteins. Proteins are polymers, often with molecular weights up to 1,000,000. They are made from 20 amino acids. They have the potential to be even more complex than coating polymers. Polymerization of just 12 of the 20 amino acids to make a protein-like polymer 300 units in length could, in theory, yield 10³⁰⁰ possible different molecules.¹⁷ That is even more complicated than poly(methyl methacrylate). *There are not enough neutrons, protons and electrons in the observable universe to make one molecule with every possible structure.*

Nature can impose order on this incredible complexity. For example, a silkworm makes a polymer with precisely structured sequences of 60 units.¹⁸

(ser-gly-ala-gly-ala-gly)₁₀

These amino acid sequences fit together to make crystalline regions. The silkworm also learned that the polymer would be too rigid if it is entirely crystalline. So, the silkworm learned to put in some amorphous segments to impart flexibility. Even blue-green algae, among the lowest forms of life, accomplish incredible feats of polymer synthesis.

Can synthetic chemists ever learn to duplicate the precision synthesis of natural polymers? A millennium is a long time, and I imagine they will some time before it ends. The effort is already underway. One of the major thrusts in polymer science research is aimed at various ways to make polymer structures more homogeneous using biomimetic methods and catalysts with encoded information.¹⁹ A recent symposium²⁰ included 65 papers on polymers that are precisely tailored for drug delivery. Research on liquid crystalline and other self-assembling polymers has been gathering momentum for more than 20 years. Methods to control the chirality of polymers during synthesis date back to Ziegler and Natta, and new advances are frequently reported. Some of today's methods are quite elegant, but they fall far, far short of the elegance with which a silkworm makes silk. In the years 2099 or 2999, people will look back on developments in the past 100 or 1,000 years. To them, today's best efforts will probably look as primitive as the age of alchemy looks to us.

I hope so. Then a world of possibilities to custom tailor resins that will perform much better than the ones we have today will open up. For example, using relatively inexpensive monomers, it should be possible to make a polymer that has superb weatherability, perhaps lasting outdoors for decades with little change. In theory, this can be accomplished just by eliminating all structures in the resin that absorb any UV light with wavelengths above about 295 nm and all structures that are vulnerable to hydrolysis under weathering conditions. This theory may be too simplistic, but it has never been properly tested. Some of today's resins, like acrylics, are already composed mainly of such structures. All you need to do is eliminate the undesired atypical structures that are formed from impurities or chemical side reactions during polymerization. That sounds easier than making silk.

Roy Bowden summed it up in 1960, when he composed *The Chemists' Prayer*:

Oh God, I fall upon my knees
And pray that all my syntheses
Will not always be inferior
To those effected by bacteria

In the next millennium his prayer will be answered.

Another possibility is use of self-assembling polymers²¹ in coatings. Self-assembling polymers include liquid crystalline polymers and others that spontaneously form structures with some degree of order that is intermediate between the amorphous and crystalline states. Order can substantially change properties, and sometimes it sharply improves them; for example, with liquid crystalline polymers, one can make coatings that are both very hard and very tough.²² The principle is well established; the obstacle is the lack of resin synthesis methods that can make inexpensive liquid crystalline resins. As methods are developed, technological breakthroughs will become possible. In recent years it has become apparent that spontaneous ordering of apparently amorphous polymers is more common than previously thought. For example, the higher *n*-alkyl methacrylates tend to form ordered structures.²³

Another kind of self-assembly involves multiple hydrogen bond formation. For example, two very inexpensive chemicals, melamine and isocyanuric acid, fit together to form structures that are held together entirely by hydrogen bonds. Each molecule forms nine hydrogen bonds and it takes a lot of energy to break them all at the same time. These structures are stable to 400°C. Derivatives of these chemicals, for example barbiturates and 2,4,6-triaminopyrimidines, can also self-assemble. They are sometimes called "techtions" or "sticky sites." They have been physically dispersed into polystyrene and poly(methyl methacrylate) to form materials with drastically changed melt rheology.²⁴ Apparently, no one has devised a way to inexpensively attach such derivatives to polymers, but when they do a new category of crosslinks with unique properties will become possible.

The associative thickeners used in latex coatings are an example of polymers that self-assemble in aqueous solution. In this case the "sticky sites" are hydrophobic segments in an

otherwise hydrophilic polymer. Similar behavior was observed with copolymers of poly(acrylamide) contain blocks of a hydrophobic monomer.²⁵

Yet another possibility is the use of nanostructured materials as components of coating resins. These are substances that are larger than most molecules but smaller than, say, most latex particles. Arbitrarily, their dimensions are on the order of 5 to 50 nm. They include spheres (large dendrimer molecules), rods, hollow tubes, and various shapes made microlithographically. An entire issue of the august journal, *Chemical Reviews*, was recently devoted to nanostructures.²⁶ Materials in this size range, for example carbon blacks and microgels, are already used in coatings. They drastically affect coating rheology and film physical properties and appearance. As the field develops, more applications in coatings can be expected. Good progress has been made toward practical synthesis of latex resins with particle diameters of 10-20 nm.²⁷ What are they good for?

Polymer Surfaces

Surfaces are hard to study. Today polymer surfaces are much less well understood than polymer bulk properties. Lacking good ways to measure surface properties, coatings scientists frequently assume (whether they realize it or not) that they are the same as bulk properties. They are not.

Theoretical calculations have demonstrated that the density of thermoplastic polymers decreases within the top few nm of the surface. If the density decreases, the freedom of molecular motion must increase and the T_g must decrease. Until recently, experimental confirmation of this prediction has been hard to get. In 1999, Kajiyama published experiments using a newly developed method called scanning viscoelastic microscopy.²⁸ This and related methods will probably become important tools in coatings science. Kajiyama measured the T_g of the outer layers of polystyrene samples with various molecular weights. As predicted by theorists, T_g near the surfaces is lower, depending on molecular weight. As the molecular weight drops below 50,000, the T_g drops below room temperature, about 75°C lower than bulk polystyrene. Similar studies of crosslinked polymers have not been reported.

Presuming that the surfaces of thermoplastic coatings, and possibly thermoset coatings, act similarly to polystyrene, coatings scientists have a lot to worry about. We do not really know what the properties of the surfaces of our coatings are, yet surface properties have a major influence on many of the most important properties of coatings—adhesion, corrosion protection, mar and stain resistance, coefficient of friction, pigment dispersion (hence color control), gloss, and probably weatherability. That is true even for coatings whose surfaces have the same composition as the bulk material. It gets even more problematic when you consider that, in most cases, the composition of the surface is probably different from the bulk composition.

Methods of studying surfaces are improving and will continue to improve. For example, Marek Urban, formerly of North Dakota State University and now at The University of Southern Mississippi, has developed spectroscopic methods that can study not only the outer surfaces of coatings but also the critical interphase where coatings adhere to the substrate. At Eastern Michigan University, Wade Shen modified a scanning probe microscope (SPM) so that it can mar surfaces of coatings under controlled conditions, characterize the severity of marring, and measure the failure mechanisms.²⁹ He plans to extend these studies with improved instrumentation. These methods have already been used to guide synthesis of resins that make better coatings. As more and better instruments become available, study of polymer surfaces appears poised for an exciting period. Coating resin designers who use the kind of information that these studies provide will stand a good chance of making breakthroughs in performance.

Prospects for Long-Range Research in Coatings

The Industrial Research Institute reports that U.S. companies increased spending on research and development (R&D) by 71% from 1994 to 1999 from \$97B to \$166B.³⁰ Japanese companies, which had taken the lead in the early

1990s, spent about \$95B in 1999. Furthermore, U.S. companies increased spending on basic research by 79% during this period to \$10.9B.

That's the good news. The bad news is that the increase occurred mainly in the fields of information and life sciences. R&D spending in materials

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science, of which coatings technology is a part, apparently did not grow very

much. Materials science remains a high priority in Japan. Judging by anecdotal reports, R&D activity in the coatings industry and its suppliers did not increase much, if at all, during this period, and basic research budgets may well have fallen. Many companies cut back on long-range research, and several major companies eliminated their research departments completely—during a period of unprecedented prosperity. There are exceptions—a few coatings and supplier companies continue to do significant research, but on the whole the trend seems unfavorable. Robert F. Brady, Jr. commented on this during his 1999 Mattiello Lecture, saying “I think Joe Mattiello would be genuinely disappointed to find the lack of emphasis on research that pervades the coatings industry today. I think he would believe that the industry has defaulted on its responsibilities for research...”³¹

The coatings industry is not alone. During the 1980s and 1990s long-range research became unfashionable in large sectors of U.S. industry, and research budgets were cut. Mergers might logically have created companies that are large enough to support substantial research efforts, but they were more often treated as an opportunity to reduce technical staff. Of course, it is not enough just to spend money; research must be well staffed and well managed to pay off. But it can pay off. A 1999 study by Sadowski and Roth,³² published by the Industrial Research Institute, identified 300 businesses as technology leaders and showed that they are more profitable and faster growing than their competitors.

Do business leaders in the coatings industry believe that there is a shortage of good research targets? If they do, I do not agree. In this paper, I tried to

show that there are plenty of good targets for resin research and development. There are also good research targets in other areas of coatings technology such as color and appearance, application equipment, testing (especially of corrosion protective coatings), and rheology. In some cases, the basic science is already done. The coatings industry can profit by adapting existing knowledge and by keeping alert for new opportunities that arise as new knowledge is created. In other cases, basic research is needed in areas especially important to coatings.

Or, possibly, the business leaders think there are good targets but lack confidence that their organizations can handle them. If so, that is a problem they should address. If they don't, some other company will. There is a real possibility that companies headquartered outside the U.S. may become the technology leaders in coatings—in some areas they already are. For example, did you know that all of the top 10 companies holding patents in one important field—blocked isocyanates—are Japanese and German companies?³³

CONCLUSION

No one can foretell the future. There are certainly many possibilities for improved resin design and many new ways to go about it. Some innovations will address problems we already know about, and others will meet challenges we cannot easily visualize. Overall, the prospects for long-range research in coatings appears excellent, but it is not clear that U.S. companies will commit the resources to retain overall leadership.

References

- (1) Committee on Tropospheric Ozone Formation and Measurement, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D.C., 1992.
- (2) Edwards, K.N. and Mislav, H.B., “Alkyd Resins,” *Polym. Mater. Sci. Eng.*, 80, 305 (1999).
- (3) Anon., *National Air Pollution Emission Trends, 1990-1995*, U.S. Environmental Protection Agency, 1998.
- (4) Graziano, F.D., “High Speed Powder Coil Coating,” *Proc. 23rd Intl. Conf. Org. Coat.*, Athens, Greece, 139, 1997.
- (5) Wimmer, W., “Powder Clearcoat: BMW Takes a Quantum Leap in

- Automobile Production Line Paints," *Powder Coat.*, 10, 19 (1999).
- (6) Galvin, P.J., "In High Gear," *Mod. Paint and Coat.*, 6 (2), 24 (1999).
- (7) Koop, P.M., *Powder Coating*, 6, 58 (1995).
- (8) Jones, F.N., "Toward Solventless Liquid Coatings," *JOURNAL OF COATINGS TECHNOLOGY*, 68, No. 852, 25 (1996).
- (9) Clark, M.D., Collins, M.J., Lopez, P., and Taylor, J.W., "Waterborne Polymers Having Pendant Allyl Groups," U.S. Patent 5 869 590 (1999).
- (10) Bergenstahl, B., Hofland, A., and Ostberg, G. "Alkyd Emulsions," in *Polymeric Materials Encyclopedia*, Salamone, J.C., (Ed.), CRC Press, Boca Raton, FL, pp. 154-160, 1996.
- (11) Cerf, C. and Navasky, V., *The Experts Speak*, Pantheon, New York, 1984.
- (12) Sherden, W., *The Fortune Sellers*, John Wiley & Sons, New York, 1997.
- (13) Bauer, D.R., "Predicting In-Service Weatherability of Automotive Coatings: A New Approach," *JOURNAL OF COATINGS TECHNOLOGY*, 69, No. 864, 85 (1997).
- (14) Terrett, N.K., *Combinatorial Chemistry*, Oxford University Press, 1998.
- (15) Archer, R., "Industrializing Drug Discovery," *Am. Lab.*, 31(14), 17 (1999).
- (16) Nielsen, R.B., Safir, A.L., Petro, M., Lee, T.S., and Huefner, P., "The Preparation and Screening of Combinatorial Polymer Libraries," *Polym. Mater. Sci. Eng.*, 80, 92 (1999).
- (17) Allcock, H.R. and Lampe, F.W. *Contemporary Polymer Chemistry*, 2nd Ed., Prentice Hall, Englewood Cliffs, NJ, p. 169, 1990.
- (18) Elias, H-G., *Mega Molecules*, Springer-Verlag, Heidelberg, p. 107, 1987.
- (19) Frechet, J.M.J., "Structural and Functional Control in Organic Polymer Synthesis: From Organic Approaches, to Catalysis, to Combinatorial Techniques," *Polym. Mater. Sci. Eng.*, 80, 494 (1999).
- (20) Various authors, *Polym. Prepr.*, 40(1), 252-368 (1999).
- (21) Eisenbach, C.D., "Novel Morphology and Structure Formation by Self-Assembly of Specially Designed Macromolecules," *Polym. Mater. Sci. Eng.*, 80, 496 (1999).
- (22) Jones, F.N., Chen, D-S., Dimian, A.F., and Wang, D., "Coatings Binders Comprising Liquid Crystalline Enhanced Polymers," U.S. Patent 5 218 045 (June 8, 1993).
- (23) Beiner, M., Schroter, K., Hempel, E., Reissig, S., and Donth, E., "Multiple Glass Transition and Nanophase Separation in Poly(*n*-alkyl methacrylate) Homopolymers," *Macromolecules*, 32, 6278-6282 (1999).
- (24) Fuchs, K., Bauer, T., Thomann, R., Wang, C., Friedrich, C., and Mulhaupt, R., "Nanostructure Formation via Association of Tectons in Amorphous Polymer Matrices," *Macromolecules*, 32, 8404-8412 (1999).
- (25) Regalado, E.J., Selb, J., and Candau, F., "Viscoelastic Behavior of Semidilute Solutions of Multisticker Polymer Chains," *Macromolecules*, 32, 8580-8588 (1999).
- (26) Various authors, *Chem. Rev.*, 99 (7), 1641-1990 (1999).
- (27) Ming, W., Jones, F.N., and Fu, S., "Synthesis of Nanosize Poly(methyl methacrylate) Microlatexes with High Polymer Content by a Modified Microemulsion Polymerization," *Polym. Bull.*, 40, 749-756 (1998).
- (28) Satomi, N., Takahara, A., and Kawaiyama, T., "Determination of Surface Glass Transition Temperature of Monodisperse Polystyrene Based on Temperature-Dependent Scanning Viscoelastic Microscopy," *Macromolecules*, 32, 4474 (1999).
- (29) Shen, W., Smith, S.M., Jones, F.N., Ji, C., Ryntz, R.A., and Everson, M.P., "Use of a Scanning Probe Microscope to Measure Marring Mechanisms and Microhardness of Crosslinked Coatings," *JOURNAL OF COATINGS TECHNOLOGY*, 69, No. 873, 123 (1997).
- (30) Broad, W.J. "U.S. Back on Top in Industrial Research," *New York Times*, December 28, 1999.
- (31) Brady, R.F. "Clean Hulls Without Poisons: Devising and Testing Nontoxic Marine Coatings," *JOURNAL OF COATINGS TECHNOLOGY*, 72, No. 900, 45 (2000).
- (32) Sadowski, M., Roth, A., http://www.onlinejournal.net/iri/RTM/1999/42/6/html/42_6_32.html.
- (33) Wicks, D.A. and Wicks, Z.W. Jr., *Prog. Org. Coat.*, 36, 148-172 (1999).