

Focus on Coatings R&D:

New Research Methods Creating Possibilities



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For well over 100 years, innovation has enabled the paint and coatings industry to offer novel products for new substrates, ever better products with improved performance, and products with reduced environmental impact. Despite the gains made in this time, significant gaps in knowledge and understanding remain. Research approaches such as design of experiment (DOE), high throughput experimentation (HTE), combinatorial methods (Combi), and data mining (DM) now being applied to coatings R&D aim to fill those gaps and may lead to many new opportunities for the industry.

All of these methods have been around for many years. DOE was first introduced in the early 1900s for factorial designs. Mixture designs for studying formulations were developed in the 1950s. The pharmaceutical industry has utilized combinatorial chemistry and HTE in conjunction with DOE and DM for the development of novel drugs over the past 15 years or so. It has been only recently, though, that scientists and engineers in the paint and coatings industry have begun exploring the application of these research methods to the process, ingredient, and formulations development for paints and coatings.

HIGH THROUGHPUT EXPERIMENTATION AND COMBINATORIAL METHODS

High throughput experimentation in general is very useful for speeding up discovery times for new materials and shortening time to market. HTE accelerates scientific research, especially of complex systems, by moving away from one at a time to parallel experiments. Libraries of compounds are generated, formulations are then prepared based on those libraries, and certain properties of the formulations are screened to see which ones meet a prede-

terminated criteria. Successful implementation of HTE requires well planned experiments, equipment capable of handling the materials, making the formulations and screening for properties, and software for storing and analyzing the results.

HTE offers benefits for research and synthesis, development, and process improvement. "It has real value in allowing one to explore an extensive parameter space," notes Dr. Stephanie Strazisar, senior associate scientist with Bayer MaterialScience. "Coatings in particular are well suited because there is such a large variable set—there is no shortage of components that one could consider in an experimental design," she adds. Coatings formulations are complex with numerous ingredients, according to Dr. Michael Fasolka, director of the NIST Combinatorial Methods Center at the National Institute of Standards and Technology. "In addition, applications for coatings are becoming more and more specific. Coatings now are often tailored to meet a specific set of performance criteria, and looking through this huge formulation space to find the ideal combination requires a large number of experiments."

HTE and combinatorial materials development provides information and knowledge, according to Dr. Michael J. Doyle, senior scientist with Accelrys, Inc. "Using HTE results in the development of a knowledge base and system knowledge as well. With such a large data set companies are able to get better IPR and receive much more substantive patents," he adds. Understanding, however, only comes with the use of good DOE and data mining tools. "Models and HTE go hand in glove. Serendipity and incremental knowledge are not gained by looking at a large number of flasks," Dr. Doyle states. In industry, there is significant potential for improving effi-

ciency and reducing costs. "Using a well thought out HTE approach can reduce coatings development times by an order of magnitude," says Dr. Dean C. Webster, professor of coatings and polymeric materials with North Dakota State University's Dept. of Coatings & Polymeric Materials. "Companies not only can develop coatings more quickly, but also produce better, more optimized, more robust formulations."

Like with design of experiment, quality measures such as Total Quality Management (TQM) and Six Sigma are leading people to ask where in research can variability be eliminated and productivity improved, and a high throughput approach can help achieve these goals, according to Dr. Doyle. Early adopters of HTE and combinatorial methods in the paint and coatings industry include Avery Dennison, GE, BASF, Bayer, and Symyx, to name a few.

"These companies are working to overcome the many difficulties and challenges associated with implementing a high throughput/combinatorial materials program. HTE requires a new mindset, and it is human nature to resist change. In most organizations, sharing of information is not encouraged, and in general, scientists see the knowledge that they possess as defining their value to the organization," notes Dr. Doyle. He adds that organizational protectionism is also at work, and management fears loss of power if gains in efficiency result in smaller budgets and reduced head count. Because the concept of combinatorial methods is still in the early stages of application in the coatings industry, it is also difficult to convince management that this technology should be explored.

There are many technical challenges as well. "Coatings formulations require multi-tiered, multi-step processing routes to combine the components properly. So, when you think about making multivari-

ate libraries for HTE of coatings, your fabrication route must reflect this complex processing. In addition, you must develop means to measure formulations performance in a high throughput approach. If you don't have high throughput measurement methods to screen them, the libraries by themselves do

High throughput experimentation continues to be the focus of international coatings conferences. HTE for polymers and materials has been discussed at programs sponsored by the American Chemical Society, Materials Research Society, and others. Upcoming programs include the following:

Research Methods in the 21st Century: A Toolkit for Competitive Advantage

Sponsored by Federation of Societies for Coatings Technology
May 18–20, 2005
New Orleans Marriott
New Orleans, LA

(Includes high throughput experimentation, DOE, data mining, and combinatorial methods)
www.coatingstech.org

2005 Gordon Research Conference on Coatings and Films

July 10–14, 2005
Colby Sawyer College
New London, NH

(Includes high throughput screening, nanocomposites, and unconventional applications of UV curing)
www.grc.org

2005 Gordon Research Conference on Combinatorial and High Throughput Materials Science

August 14–19, 2005
Queen's College, Oxford, UK
www.grc.org

not offer much advantage to researchers," explains Dr. Fasolka. Many of these analytical tools have not yet been designed for HTE with materials. "The diverse spectrum of functionalities in materials represents a significant challenge in high-throughput characterization, often involving development of novel measurement instrumentation," adds Dr. Radislav A. Potyrailo, an analytical chemist and project leader with GE Global Research Center. Professor Webster also notes that the initial investment, if using fully automated workflow, can be quite high, whether building or acquiring systems for carrying out the experiments and analyzing them. Scale up can also be an issue, notes Dr. Doyle. Typically compound libraries are made on a very small scale, and processing conditions are not considered. Handling all of the data can be an issue as well, although advances in DOE and data mining are beginning to address these issues.

Headway has been made over the last five years in addressing the handling and measuring aspects of the HTE/combinatorial approach to coatings R&D. Companies such as Bayer and BASF have focused their efforts on developing robotics systems that can formulate and mix an array of samples in little vials, making libraries in a rapid manner. General Electric and Avery Dennison developed new methods of robotic deposition, curing, and property screening of multiple discrete coating formulations onto plastic and other substrates. NIST has focused on development of libraries using a gradient approach, where formulation mixtures are prepared using a pumping and dispensing system that changes quantities continuously. "No matter what method is chosen for preparing the library, validation measurements are necessary to confirm reliability," says Dr. Fasolka.

It is also necessary to establish a correlation between the data generated in a high throughput experiment with existing measurements made according to generally accepted industry standards. "Tests automatically conducted on a small scale by robots must be correlated to traditional macroscale tests," says Dr. Potyrailo. "These new methods won't have any value if customers are not satisfied that the results are legitimate. In other words, experiments completed on a combinatorial scale must be validated on a conventional scale."

For physical tests, speed remains an issue because some type of physical contact must occur. Hysitron is a company that conducts high throughput nanoindentation evaluations for the coatings industry. Nanoindentation involves measurement of the forces encountered by a sharp diamond tip of known geometry as it encounters a thin film sample. Modeling is used to predict properties such as hardness, modulus, and yield strength. "Speed is still a challenge. While there have been some attempts to do nanoindentation

testing in parallel, it is still much easier to work with samples in a serial manner," says Dr. Oden Warren, director of R&D for Hysitron. Currently it takes about two minutes per sample. "There also needs to be more education in the industry on the Combi aspect of HT nanoindentation," adds Hysitron's director of sales and marketing Dr. James Burkstrand. "The coatings industry is rather conservative and tends to adopt newer technologies a little more slowly than other market sectors."

Despite its conservative nature, the paint and coatings industry has been showing increasing interest in HTE and Combi methods for conducting R&D. Several academic groups have implemented programs as well. Professor Douglas A. Wicks' group at The University of Southern Mississippi uses HTE methods to study complex interactions of additives in coatings formulations. Their method development derives a lot of its inspiration from work done in the pharmaceutical industry. Using the tools of microbiology in conjunction with automated liquid handling and fluorescence spectroscopy, the students in the group are investigating latex spoilage, biodegradation of coatings, and thermal degradation of coatings resins such as PVC.

"Combining HT techniques with microbiological methods has allowed us to study the interaction of industrial and experimental biocides with different components found in a latex paint," explains Professor Wicks. "To fully evaluate the interaction of these biocides with formulation variables such as surfactants, thickeners, water contaminants, and the like requires hundreds of experiments to be run. Using conventional techniques, this effort would require weeks to accomplish. Here we do it in days. The real impact of this approach will be seen in the future, as the undergraduates who now use these methods and view them as routine begin to enter the workforce."

Professor Webster's group at North Dakota State University is studying nontoxic coatings for marine applications that are made from water-stable polymers with low surface energy. The group synthesizes different polymers to make polymer libraries, creates formulations from the libraries, and does the testing. They can synthesize 24 polymers, make 96 coating formulations, and test them all in a one week period. "Using this combinatorial approach, we have been able to identify several possible new formulations and are cur-





rently working on optimizing them," says Professor Webster.

"Design of experiment helps determine the initial scope of work, while information generated from experiments laid out in the initial design is very useful for revising our experimental plan," he adds.

At Bayer Material-Science, Dr. Strazisar's HTE group works with colleagues in innovation, business development, and production groups to design better materials, respond to customer queries about formulations, and solve quality control issues in production. The group led by Dr. Richard A. Roesler, senior principle scientist at Bayer, improved productivity by 10-fold by using DOE and high throughput techniques with simple laboratory equipment.

"The experiment was designed so that 3000 vials were placed in set patterns. The vials were filled and mixed very rapidly using volumetric measurements rather than weight to control the quantities of materials. The use of a quick visual screen in conjunction with the established vial patterns also enabled rapid analysis for the exceptions. "We were able to dramatically increase productivity for a few thousand dollars (cost of the volumetric equipment)," notes Dr. Roesler. "This example demonstrates that HTE is possible within a traditional setting. People just need to think about things a little differently."

GE has applied high throughput experimentation for the development of several different types of coatings products. In one case the company worked with Avery Dennison to develop HTE automated analytical characterization tools. Avery was studying moisture and oxygen barrier coatings for flat panel displays, while GE was interested in transparent coatings for automotive applications. As a result of this collaboration, GE accelerated development of new high-performance coating materials for automotive applications by at least 10-

fold. Several cost-competitive coatings with performance equal to high cost products have been developed using this combinatorial approach. The compositions have been validated on the traditional scale for their adhesion and weathering performance. In another case, GE applied combinatorial and HTE methodologies to develop functional coatings for chemical sensors using discrete and gradient array designs. Some of these developed coatings have been tested by the U.S. Department of Energy.

The NIST Combinatorial Methods Center (www.nist.gov/combi) focuses on library fabrication and HT screening techniques particularly for polymer science. It is supported by a consortium of 21 members from industry, government, and academia, which it serves with technology transfer of developments, industrial workshops for training, national conferences, and a members' website. Industry scientists are also invited to work in the NIST labs, and the Center sends people to work at companies to help them implement technologies that NIST has developed.

"The Center fabricates libraries using gradient techniques and a new set of technologies based on microfluidics similar to the 'lab-on-a-chip' approach in biotechnology," according to Dr. Fasolka. "The challenge in implementing lab-on-a-chip methodology for coatings lies in the high viscosity and organic solvents in paint and coating systems," he says. The group has developed methods to fabricate microfluidic devices suitable for coatings formulations, and also has developed in-situ measurements that gauge formulation performance. For example, they have developed HT interfacial tension measurements for characterizing systems such as emulsions. This microfluidic system obtains measurements in several seconds, is accurate within a few percentage points, and can rapidly measure interfacial tension of a series, or library, of systematically changing fluid specimens. Dr. Fasolka's group has also designed and implemented a variety of other microscopy, spectroscopy, rheological, mechanical, and adhesion testing instrumentation useful for HTE of coating systems.

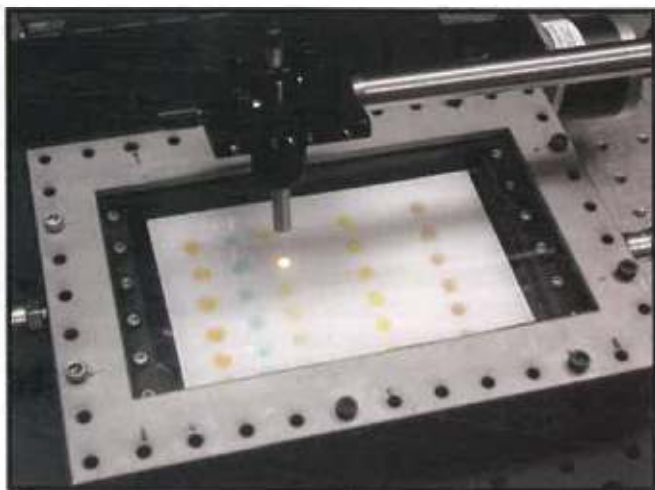
The potential power to improve efficiency and productivity, leading to better, more improved, more robust coatings formulations can be seen in these different examples. As computational tools become easier to use and ever more powerful, a greater number of people in the coatings industry will move toward the use of design of experiments, data mining, high throughput experimentation, and combinatorial methods for many different applications.

Much effort needs to be expended on developing the tools for combinatorial materials science—synthesizing, handling, mixing, measuring, and characterization—according to Professor Webster. Advances along

these lines enable more people to achieve real commercial successes with these tools, and their value to the industry will at that point become transparent. At Hysitron, the company is currently working on single test hybrid technologies that combine nanoindentation with other tests such as adhesion, stickiness, or mechanical or electrical property determination. "We hope to extend this capability to high throughput processes," says Dr. Warren. "In that way we can provide a much more significant level of information throughput. With these research tools, what the industry can achieve is only limited by imagination," adds Dr. Burkstrand.

Along those lines, Dr. Potyrailo sees HTE and combinatorial methods as being useful for the development of coatings that have advanced functionalities such as environmentally responsive coatings for sensors. "These coatings are highly complex. Combinatorial research methods already make it possible to develop these types of coatings, where such a large number of factors and interactions affect the performance of the materials," he states. Sensor materials, for example, need to exhibit high stability with respect to providing a consistent response to a given stimulus for an extended period of time under a range of conditions. If biomolecules are to be immobilized in the polymer coating, the challenges can be even more significant.

"Things are headed in the right direction, particularly in terms of getting buy-in from the industry," says Dr. Strazisar. "We must keep in mind, though, that these tools are not a panacea for all problems. We should learn from the experiences of the pharmaceutical industry and be careful about what direction we choose to follow in terms of where and how we apply these tools," she continues. The market will be the strongest driver. "These research tools will either drive



Example of robotic screening of a discrete sensor coating array for optical sensors. Photo courtesy of GE.

innovation very dramatically and in such a way as to provide a leapfrog effect, or, unfortunately, they will enable everyone to come to the same conclusions and will lead to commoditization," notes Dr. Doyle. Microsegmentation is also a possibility. With access to a large set of information about how variations within a given formula affect behaviors, companies may be able to offer a wide range of products to the marketplace for different end users and applications based on that variability.

Today, most large companies have some form of combinatorial or HTE programs in place, and many smaller companies do as well. In general the focus is on smaller R&D projects, but the leaders are looking at larger aspects of formulation. "Once more people focus on application of combinatorial and high throughput methods to formulations development, these research tools will provide a systematic way to study these complex systems, which in turn will lead to development of models for predicting their behaviors. What is now guess work will become truly scientific," says Dr. Fasolka.

DESIGN OF EXPERIMENTS AND DATA MINING

Design of experiment involves the careful planning of experiments so that an understanding can be gained about specific variables and parameters in a process or formula. A series of experiments provides a data set that is then used to create a predictive model, enabling the researcher to carry out a desirability analysis and identify the "sweet spot" for the process or formula under investigation. "The idea is to lay out the experiment so that good information is generated on what the different variables are doing to the process or formulation," says Mark Anderson, principal with Stat-Ease, Inc., a company that provides statistical software, training, and consulting, particularly on the tools of DOE. "Brainstorming is done to identify the key features that need to be evaluated, and statistics are used to generate a predictive equation," he continues.

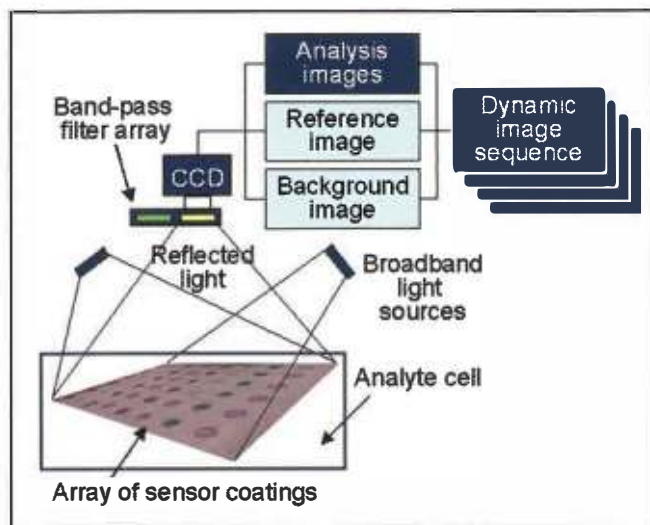
Benefits of DOE include improved productivity and efficiency and higher quality, more reliable results. Development of new materials can also be a direct result. "DOE is useful in the coatings industry as it provides a tool to allow formulators to develop products rapidly and maximizes the amount of information," says Dr. Richard Rosen, senior staff scientist with Rhodia. DOE can also be used to demonstrate that the results do not have any unnecessary variability, according to Dr. Roesler, of Bayer MaterialScience. "Scientists need to be aware that every measurement has variability in it, and running one experiment can't identify that variability. The only way to determine the variability is by running replicates, and using DOE provides the

most reliable results." The multi-functional aspect of coatings can also be addressed with DOE. "The interactions between the various components of a coating formulation must all be considered, which requires a large number of experiments," says Dr. Potyrailo. "Experimental design tools help reduce the number of experiments needed, which can save a great deal of time and money."

DOE can also be used for improving manufacturing processes. Optimization of parameters such as yield, cost, scrap, throughput, or a specific property (gloss, reflectivity, etc.) can be achieved through application of DOE analyses. In the past, the coatings industry has shied away from DOE because it required making a large number of batches, according to Dr. Peter J. Hunt, president of Productivity Management Consultants, an organization specializing in on-site training and implementation of statistically based Quality Management Systems (QMS). "We have conducted an assessment of different design options and found five that are applicable to production processes in the coatings industry. With these five designs, variable optimization and interaction effects between variables may be defined in as few as eight production runs and in no more than 16 production runs," notes Dr. Hunt. "The analyses of any one of these five designs can be done on a hand calculator. My approach is to get more people involved in process improvement, including process engineers, quality control managers, pilot plant operators, and others. This gets appropriate people involved with DOE and allows them to discover how beneficial DOE can be. They only need first to develop an intuitive understanding of DOE in general laymen's terms to utilize any one of these five designs."

In fact, a fear of statistics is one of several challenges faced by proponents of DOE. "Both chemists and chemical engineers tend to be nervous and fearful of statistics, in large part because of the way it is presented in school," says Mr. Anderson. For Dr. Rosen, providing the proper organizational structure so the chemist or engineer has the knowledge, training, support and resources necessary to design, execute, and analyze the DOE experiment is the major challenge. Dr. Roesler adds that research and formulations managers need to understand that if they invest a little up front they will get returns down the road. "The paint and coatings community also needs to publish and further communicate successful projects using DOE to generate interest among chemists and engineers," adds Dr. Rosen.

There are several examples of commercial applications of DOE in the coatings industry. Coding Products addressed customer concerns about the product life and inconsistent quality of its hot ink rollers, which are pre-inked foam rollers used to print, for example, expiration dates onto candy bar and other food wrappers.

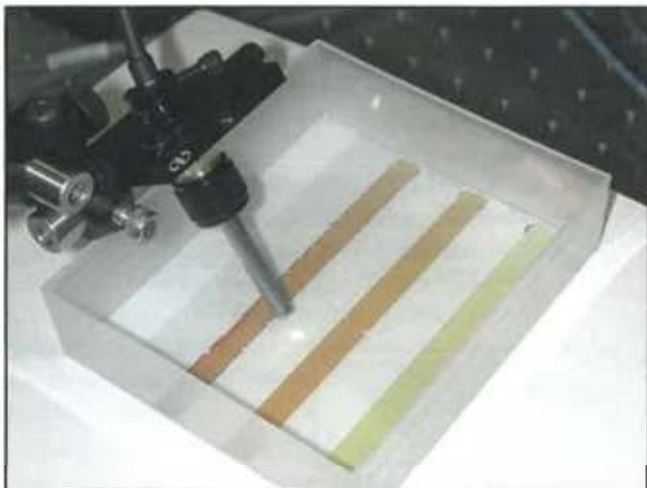


Automated analytical instrumentation developed for imaging of discrete and gradient optical sensor coating arrays. Image courtesy of GE.

End users heat the rollers, releasing ink that is available in an array of colors. The company used DOE software to dramatically improve its hot ink roller consistency and impression count. Another company, Exatec, employed DOE to determine optimal operating conditions for its proprietary in-line, plasma-deposition machine bonding abrasive-resistive layers onto silicon hard-coated polycarbonate. The company used DOE to discover how thickness varied as a function of key input factors, screening a large number of factors using the fewest number of trials that would give them precise results.

An advanced form of DOE called "response surface methods" (RSM) has also been applied to the development of coatings systems to achieve optimal performance with minimum variability, thus meeting the objectives of Six Sigma programs. According to Mr. Anderson, this approach has been utilized to eliminate variability in a powder coating operation.¹ "This example demonstrates how systematic experimentation, using sound statistical principles, can improve coating quality and make it more robust to variations in the levels of components and processing factors," he says. Akzo Coatings also used RSM to achieve an optimal balance between hardness and solids content in an acrylic automotive clear coat binder.² In addition, the statistical methods helped Akzo establish acceptable tolerances in both the resin specifications and the paint production process.

DOE has also been used to improve process operations for coatings manufacturers. According to Dr. Hunt, in one example, cycle time for product production was reduced by nearly five hours after a key step was identified as the main factor in determining that parameter. The DOE was based on four key factors,



Example of robotic screening of a gradient sensor coating array for optical sensors. Photo courtesy of GE.

each at two different levels. In another case study, factors affecting the yield of a filtration step were evaluated. The analysis showed that an interaction between solvent and water, the amount of each, and the use of agitation strongly impacted the yield. Controlling these factors led to significant improvement in isolated product yield.

Data mining tools enable researchers to gather and analyze information from various sources with the goal of discovering new meaning in the data through unveiled patterns and correlations in data sets. Computer software programs make it possible for analysis of the very large quantity of data generated in high throughput experiments. Data generated in new experiments must also be correlated and compared to historically produced results. Data mining tools make it possible to access information in database programs from different vendors.

Traditionally, companies built monolithic repositories to store data, but these systems are not very useful

because the data often is out of date when accessed, or is not the right information. Pipelining is a new way to connect data from multiple sources and also allow access by many different people. "In essence, pipelining removes the traditional centralized approach and makes the data available to anyone who can derive value from it," says Dr. Doyle. Data input from robots and comparative analyses with historical data can also be automated. As high throughput screening becomes more accepted in the coatings industry, pipelining will become more important.

"The real question that R&D people are asking is 'which experiments resulted in something different?'" says Dr. Doyle. "When you are applying high throughput methods, you need a way of filtering the data to allow people to gain value from it. That is what pipelining and data mining do." When combined together, design of experiment and data mining tools provide a way for those involved in coatings R&D to generate valuable predictive models and gain a much deeper understanding of the formulations and processes they are investigating.

"In the end," says Dr. Roesler, "the key to success in R&D is to think about a project, plan it, execute it, and then evaluate it. Design of experiments allows researchers to follow the real scientific method, which involves proposing a hypothesis and using statistics to design a set of experiments to disprove it. HTE and combinatorial methods make it possible to carry out the experimental plan, and data mining aids in the analysis of the results." **CT**

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