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Article

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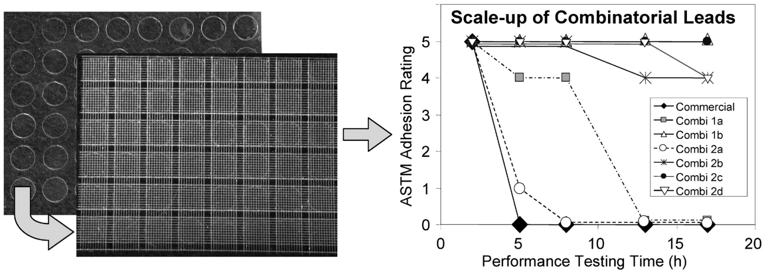

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Development of Combinatorial Chemistry Methods for Coatings: High-Throughput Adhesion Evaluation and Scale-Up of Combinatorial Leads

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Coupling of combinatorial chemistry methods with high-throughput (HT) performance testing and measurements of resulting properties has provided a powerful set of tools for the 10-fold accelerated discovery of new high-performance coating materials for automotive applications. Our approach replaces labor-intensive steps with automated systems for evaluation of adhesion of 8 × 6 arrays of coating elements that are discretely deposited on a single 9 × 12 cm plastic substrate. Performance of coatings is evaluated with respect to their resistance to adhesion loss, because this parameter is one of the primary considerations in end-use automotive applications. Our HT adhesion evaluation provides previously unavailable capabilities of high speed and reproducibility of testing by using a robotic automation, an expanded range of types of tested coatings by using the coating tagging strategy, and an improved quantitation by using high signal-to-noise automatic imaging. Upon testing, the coatings undergo changes that are impossible to quantitatively predict using existing knowledge. Using our HT methodology, we have developed several coatings leads. These HT screening results for the best coating compositions have been validated on the traditional scales of coating formulation and adhesion loss testing. These validation results have confirmed the superb performance of combinatorially developed coatings over conventional coatings on the traditional scale.

Introduction

At present, combinatorial and high-throughput (HT) methods are gaining acceptance across a wide range of materials development needs in chemistry and materials science.[1−3] Examples of materials discovered using these new techniques include catalysts, polymers, electronic materials, high-temperature superconductors, structural materials, and others. Most of these materials were discovered by measurement of their intrinsic properties. Examples of such properties of combinatorially developed materials include catalytic and mechanical properties, molecular weight, vapor uptake, resistivity, spectral emission and absorption, and others.[4−15]

However, often simple intrinsic properties of starting or final materials do not provide adequate information about materials performance. Thus, performance testing becomes critical for combinatorial experimentation with advanced materials. We have recently demonstrated the effectiveness of multilevel performance testing for weathering of polymer compositions[16] and wear abrasion of coating arrays.[17] In addition, HT performance testing has also been demonstrated in impact testing of polymers[18] and flammability and ignition testing of flame-retardant materials.[19] The testing process includes exposure of the library to an environment that imitates the end-use application and alters materials properties in a detectable manner. Upon testing, the materials undergo changes that are impossible to quantitatively predict using existing knowledge.

An important aspect of these evaluations is the correlation of HT with traditional scale results that are well-accepted in industrial applications. Often, these traditional testing methods have extensive historical databases of the performance of materials and, thus, serve as a valuable source for correlation studies of performance of combinatorial and conventional scale systems. In the development of organic coatings for automotive applications using combinatorial chemistry methodology,[20] it is important to find the performance testing methods and measurement techniques that in concert provide results that correlate well with the more conventional test and measurement methods. Our interest in the combinatorial coatings development for automotive applications lies in the discovery of materials with improved abrasion resistance, weathering performance, and adhesion.[21]

Adhesion of protective coatings is one of the important parameters in automotive and other industrial applications, such as for exterior finishes of automobile and truck bodies, appliances, and other high-quality products.[22] In principle, coating adhesion can be evaluated from the fundamental standpoint in which adhesion is viewed as a process that signifies the summation of all interfacial and intermolecular

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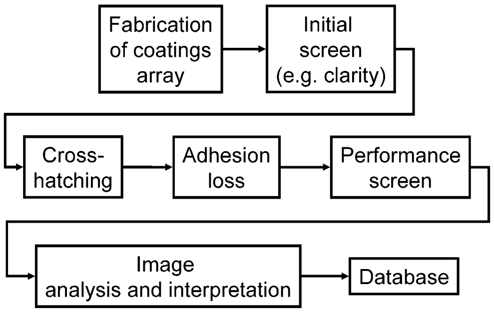

Figure 1. Methodology for HT adhesion testing of coating arrays.

forces. Fundamental effects governing adhesion include chemical, mechanical, electrostatic, and acid−base adhesion phenomena and their combination. As a result, adhesion is affected by several factors that have complex interactions. These factors include interdiffusion of materials across the substrate/coating interface, compound formation at the interface, coating and substrate morphologies, defect structures, and residual stresses. Absolute determination of these factors, their interdependence, and the resulting influence on the mechanical properties of the interfacial region is difficult to predict using known scientific principles and is the subject of ongoing research.[23,24] Thus, coating adhesion to a substrate is typically determined empirically.

Adhesion is measured using practical tools where adhesion represents the forces or work required to disrupt the adhering system. Different types of tests for evaluation of coating adhesion include the pull test,[25] peel test,[26] microscratch test,[23] supersonic water jet test,[27] stress-wave emission test,[28] crosscut test,[29] contrast analysis test,[30] and many others. The standard test methods include tape, scrape, peel, pull-off, and water immersion tests.[31,32] The adhesion loss and quantitation are performed manually by applying a crosshatch followed by visualization of the regions of coating removed from a substrate and relating the area of removed coating to the area of intact coating.[31] These adhesion loss and analysis methods have several shortcomings that make these methods inapplicable for HT screening of combinatorial libraries. These drawbacks include multiple manual steps of adhesion loss and analysis, the impossibility of reliable measurements of small changes in adhesion, the need to have a relatively large coating area for testing and measurements, difficulties in determination of the presence of a transparent coating on the substrate, difficulties in rapid measurements of multiple samples, and difficulties in measurement automation.

To address these limitations of conventional test and measurement methods of adhesion loss, we have developed HT testing, measurement, and data analysis methodology for the quantitative determination of adhesion loss of combinatorial arrays of coatings. A schematic of our HT adhesion testing methodology is illustrated in Figure 1. The approach included fabrication of coating arrays with spectroscopic tags, robotic application of an integrity-degrading step, such as a crosshatch pattern; an adhesion loss step; automatic imaging of the resulting optical properties of coating arrays; and a decision-making step. As an additional step for a prescreening of coatings, an initial evaluation can be performed, for example, a screen for clarity.[17] We implemented these developments for the routine screening applications of coating libraries with a typical throughput of ∼100 coatings a day. Finally, several coatings leads developed using these HT tools were successfully scaled up and preserved their excellent performance over conventional coatings.

Experimental Section

Preparation of Coating Libraries. Small (10-μL) volumes of various coating oligomer formulations were discretely deposited onto a 0.5-mm-thick 9 × 12-cm polycarbonate sheet using a liquid dispensing robot (Packard Instrument Co., model Multiprobe II, Meriden, CT) to produce 48-element coatings libraries as 8 × 6 arrays. The choice of polycarbonate as a substrate material for coatings was provided by the end-use application requirements. Each coating element is 10 mm in diameter and 2−5 μm thick. Each coating formulation also contained a high quantum efficiency luminophore (Lumogen F Red 300, BASF) for visualization of adhesion loss during imaging. Coating formulations were cured upon exposure to UV radiation. Further details of the library preparation are reported elsewhere.[21, 33]

For demonstration of the operation of the automated adhesion evaluation system described in this article, several coating arrays were fabricated that contained 16 different acrylate-based coating blend formulations in each array with three replicates each. These different acrylate-based coating blend formulations were obtained from Sartomer Company, Inc. (West Chester, PA) and from UCB Chemicals Corporation (Smyrna, GA). Experiments for evaluation of formulation effects were planned as a 2^4 design. The involved four factors were two types of high-function acrylates, two types of low-function acrylates, two types of UV absorbers, and two levels of these UV absorbers. These arrays also incorporated a process design of experiments (DOE) which was a 2^{3-1} design with two levels (high and low) of preheat temperature, two levels of intensity of curing UV radiation, and two levels of radiation dosage.

Adhesion Loss HT Testing. Automatic crosshatching of the coating arrays was performed using a robotic system developed in-house and illustrated in Figure 2. In this system, an $x-y$ translation stage was coupled to a z-axis positioner. The positioner was equipped with two sets of knives set at 1-mm spacing in the x and y directions, as shown in Figure 2B. An applied cutting force was automatically controlled with a force feedback mechanism to maintain a desired pressure required to cut through all the coating samples and to provide uniform and reproducible cutting conditions. As a result, cutting was performed just of the coating but not the underlying substrate. Adhesion loss was induced by periodically exposing crosshatched coating arrays to boiling water (15 min exposure) followed by rapid freezing of the array at − 25 °C. Adhesion loss was further induced by tape-pulling the delaminated coating elements. The tape pull on the array was done with 2.5-cm-wide tape that covered two rows (16 samples) at a time.

HT Adhesion Loss Measurements and Image Analysis. Determination of adhesion loss of coating arrays was performed by the automatic imaging of individual coating elements in the array, followed by the determination of

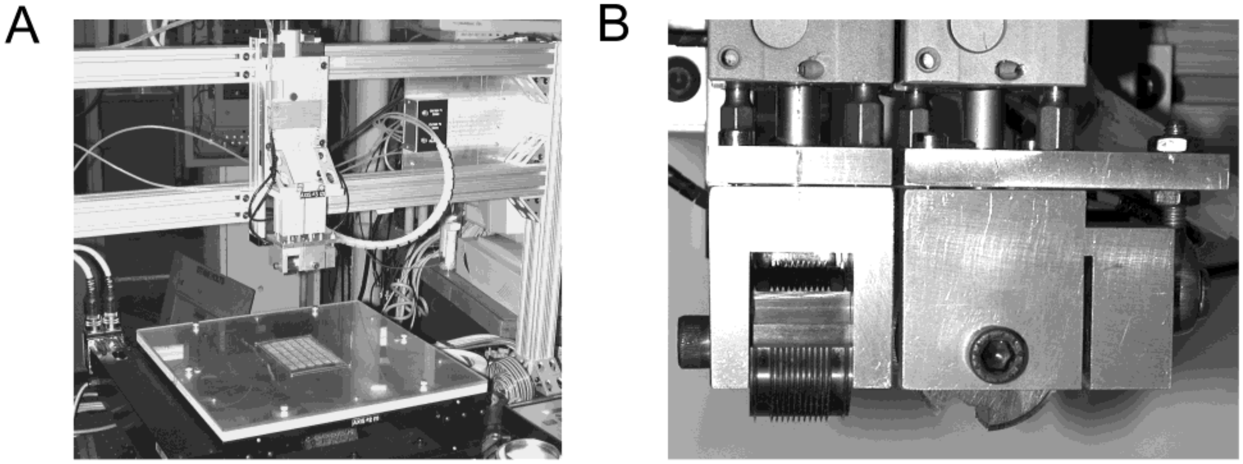

Figure 2. Robotic system built at GE Global Research for application of a crosshatch pattern onto coating arrays for adhesion testing. A, general view of the system. B, two perpendicular sets of 11 knives spaced 1 mm from each other.

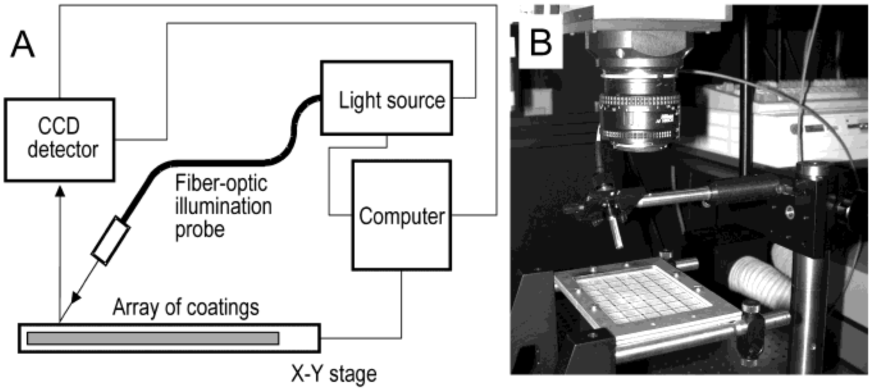

Figure 3. Automated imaging system for quantitation of adhesion loss in coating elements in a combinatorial array. A, schematic of the system. B, Photo of the imaging detector and the coating array positioned for imaging.

regions with removed coatings. Image acquisition from the coating arrays was performed using an imaging system depicted in Figure 3. This system included an $x-y$ translation stage, a light source, an imaging detector, and an associated computer to provide control of image acquisition and movement of the translation stage. The light source (532-nm compact Nd:YAG laser, Nanolase, France) was coupled to an optical fiber to uniformly illuminate a single coating at a time. The detector (ICCD camera, Andor Technologies) was operated in two modes for reflected light or fluorescence imaging. Upon operation in the reflected-light mode, a sequence of images from coating elements was collected for determination of crosshatch patterns. Upon operation in the fluorescence imaging mode, a sequence of images from coating elements was collected for determination of adhesion loss. The $x-y$ stage control, image acquisition and analysis were achieved with a computer using a program written in LabVIEW (National Instruments, Austin, TX). IMAQ Vision Builder and Advanced IMAQ Vision from National Instruments (Austin, TX) were used for development of image analysis algorithms.

Results and Discussion

Approach for HT Adhesion Testing of Transparent Coatings. Our HT adhesion testing methodology adapts the principles of a well-accepted method[31] but provides previously unavailable capabilities of high speed and reproducibility through a robotic automation, an expanded range of types of tested coatings through the coating tagging strategy, and an improved quantitation through high signal-to-noise automatic imaging. In the well-accepted manual method, adhesion loss and quantitation are performed one coating at a time by a manual application of a crosshatch pattern onto the surface of the coating followed by water soak, tape pull, and visualization of the regions of coating removed from a substrate. Ranking of coating adhesion is done by relating the area of removed coating to the area of intact coating.[31] This standard method has a large historical database on the adhesion loss determinations;[34] thus, it was adapted for the HT coatings evaluation.

One of the requirements for determination of coating adhesion loss included quantifying removal of transparent coating regions on a transparent substrate with high measurement reproducibility. To quantify the loss of a transparent coating on a transparent substrate, a liquid coating formulation was doped with an inert dye at a low concentration. Thus, measurements of coating removal were easily performed.[35] After the adhesion test was performed, the coating was illuminated with a wavelength of radiation at which the color or fluorescence of the dye in the coating was visible with an optical detector. Figure 4 illustrates our initial demonstration of this detection concept.

Another requirement was to apply a crosshatch pattern onto an entire array of coatings in a highly reproducible

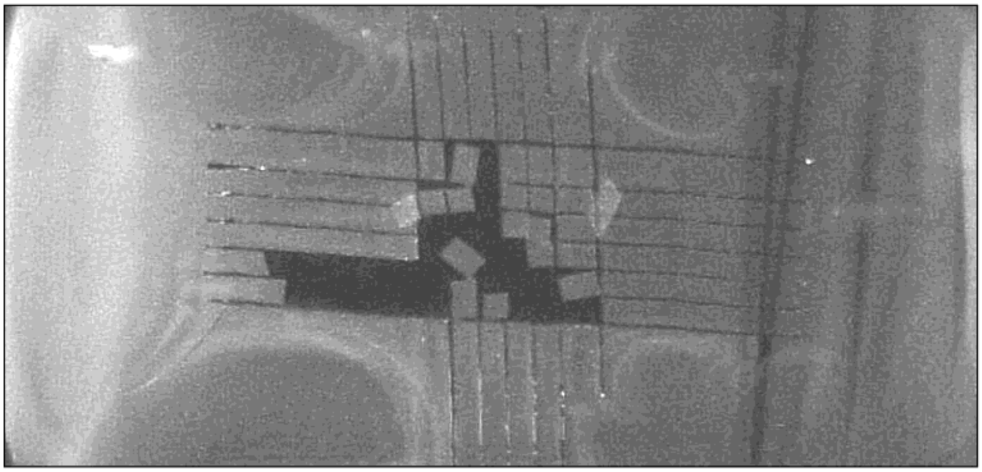

Figure 4. Initial demonstration of our detection concept based on fluorescence tagging of transparent coatings for determination of adhesion loss on transparent substrates. Fluorescence image is taken with a long-pass filter under UV excitation.

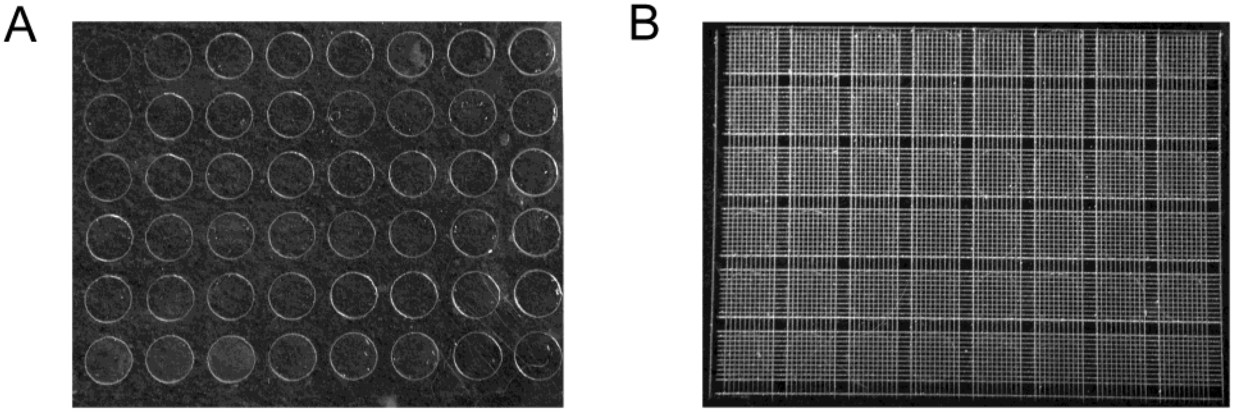

Figure 5. A general view of an array of coatings before (A) and after (B) an application of a crosshatch pattern with a robot shown in Figure 2.

automated manner because the manual crosshatch has inherent day-to-day and operator-to-operator variability. This need was met by building a robot to perform this operation shown in Figure 2. A typical coating array before and after a crosshatch shown in Figure 5 demonstrates an excellent quality of the crosshatch pattern across all coating elements in the array. Advancements were also required in the development of the adhesion-loss-inducing step that needed to be both rapid and well-correlated with the traditional (and low-throughput) adhesion loss method.

The final requirement was to provide improved quantitation of adhesion loss, because the standard method involved manual visual determination of the removed regions only with a rough gradation of coating performance by five levels that cover coating removal from 0 to 100%. In the developed HT system, this improved quantitation was achieved through the high signal-to-noise automatic imaging of the coating regions after a crosshatch with a 10×10 crosshatch pattern and determination of percent of the removed coatings with accuracy of better than 1%. The high spatial resolution of the used ICCD camera provided the required determination of loss of coating elements of <1 mm^2. Automation of quantitation was based on counting the number of removed squares or square segments. To compensate for the repositioning errors of the arrays, positions of the crosshatched squares were first automatically determined from the reflected light images and were further translated to the fluorescence image. Further, the photon-counting mode in the CCD camera was used to improve the quality of determination of removed coating regions. Figure 6 illustrates reflected light, fluorescence analogue, and fluorescence photon-counting images of a typical array element with several coating regions removed after an adhesion test. These data illustrate that the photon-counting mode dramatically improves the quality of determinations (signal-to-noise) when a coating of smaller thickness is still present on the substrate.

Optimization of HT Performance Test Conditions. Our initial studies showed that the standard adhesion loss-promoting method, such as coating exposure to boiling water followed by a tape pull, did not induce adhesion loss of the crosshatched array when the coatings had strong initial adhesion. Thus, several additional methods to accelerate adhesion testing were investigated using arrays with control (conventional) and combinatorially developed coatings. We have found that autoclaving of coating arrays at 120 °C did provide a desired adhesion loss. However, the autoclaving time to observe a reliable ranking in coating performance was 24 h. This duration of the test was clearly not very attractive for HT evaluation. In addition, the polycarbonate substrates were warped as a result of stress relaxation of the polycarbonate during the autoclaving. This dimensional

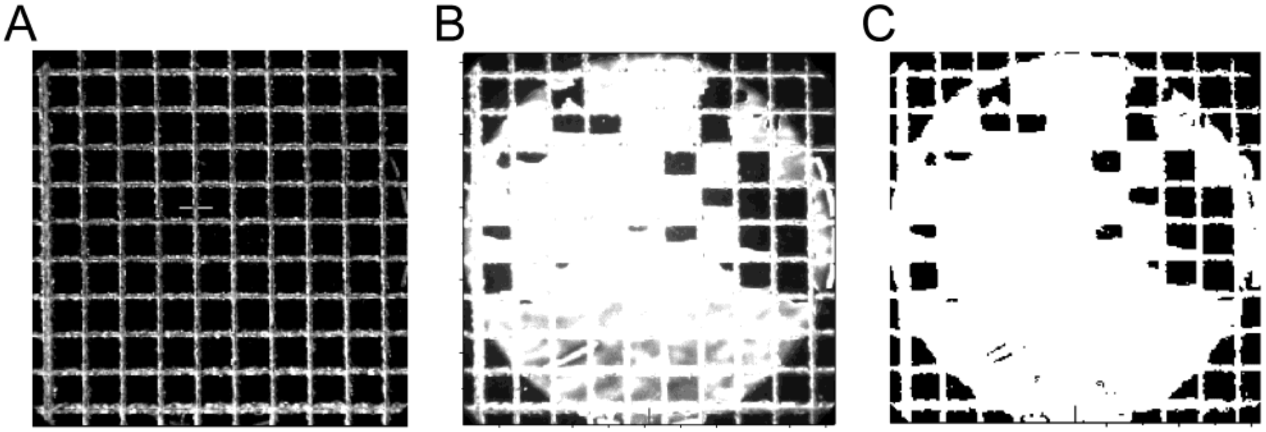

Figure 6. Reflected light (A), fluorescence analogue (B), and fluorescence photon-counting (C) images of a typical individual array element with several coating regions removed after an adhesion test. Each image of the same array element is taken with an integration time of 200 ms and accumulation of five frames.

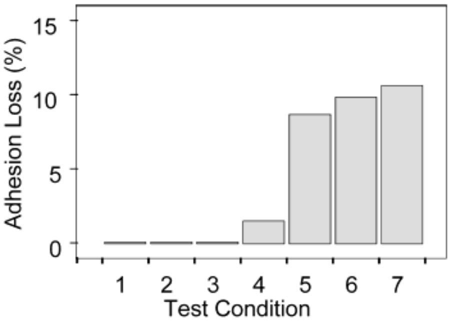

Figure 7. Summary of experiments for optimization of test conditions for adhesion loss. Test conditions: 1, deposited/cured; 2, crosshatched; 3, hot/cold water-soaked; 4, tape-pulled; 5, (hot/cold water-soaked) × 3 + tape-pulled; 6, hot water/freeze + tape-pulled; 7, (hot water/freeze) × 3 + tape-pulled. Percent adhesion loss determined taking the number of regions in the coating element as 100%.

distortion of the substrates with coating arrays made the tape pull and imaging of the entire arrays difficult.

Several alternative adhesion loss methods were evaluated further. Results of these evaluations are compared in Figure 7. These results demonstrate that a single soak cycle of the array in boiling water for 1 h followed by 1 h of soak in an ice-cold water and the tape pull provides an adhesion loss of ~2%. Upon repeating this cycle three times, adhesion loss is increased to ~8% without the occurrence of substrate warping. However, a single cycle of a boiling water and freezing at −25 °C provides an even higher adhesion loss of ~10%. More repeats of the boil−freeze cycles did not significantly increase the adhesion loss. Thus, a single boil−freeze cycle followed by a tape pull has been adopted for routine use in combinatorial screening. The time of the boil and freeze steps was further reduced because the most important aspect of these steps is the temperature shock. Thus, the boil and freeze portions of the cycle were reduced from the original 1 h each to 15 min each. Overall, a single boil/freeze cycle was adequate for reliable ranking of coatings produced in combinatorial routine screening over diverse process conditions.

Combinatorial "Factory" Operation. Upon optimization of all the parameters of the adhesion evaluation subsystems, the combinatorial coating screening process involved manufacturing, testing, and measurement of coating arrays on a daily basis.

Our "combinatorial factory" for coatings development with high adhesion performance was operated by two chemists and had a typical throughput of two 48-coating arrays/day. Operation of our "combinatorial factory" included all the steps shown in Figure 1. This throughput was slightly less than that for the development of coatings with high abrasion resistance (2−4 arrays/day)[17] because of more performance testing steps involved in adhesion screening. Nevertheless, our HT approach has led to an important productivity improvement of at least 10 times over a conventional development process of coatings with high adhesion performance, which has a typical throughput of 5 coatings/day with the same number of chemists.

Typical results of adhesion analysis of several types of 48-element coating arrays are presented in Figure 8. These arrays of coating formulations were deposited as 16 formulations per array, with three replicates of each formulation. These arrays incorporated a process DOE that was a 2^{3-1} design with two levels of preheat temperature, two levels of intensity of curing UV radiation, and two levels of radiation dosage. As seen in Figure 8, the differences in performance of adhesion of these coating formulations are provided not only by the composition of the formulations but also by the curing conditions of the coating formulations. Such dependence of performance of traditionally developed coatings on curing conditions is well-known.[22] Our current efforts are directed to the development of strategies for HT exploration of the composition−process variables−performance space of organic coatings that should result in generation of new knowledge for building more successful predictive performance models.

Scale-Up of HT Lead Coatings. As a result of the combinatorial studies, three leads were identified as potential lower-cost formulations to replace the current commercial material. These lead formulations were scaled up in GE Silicones laboratories (Waterford, NY). Followed by conventional conditions for adhesion loss evaluations, the coatings were also subjected to much more abusive adhesion tests as required by several automotive customers. The

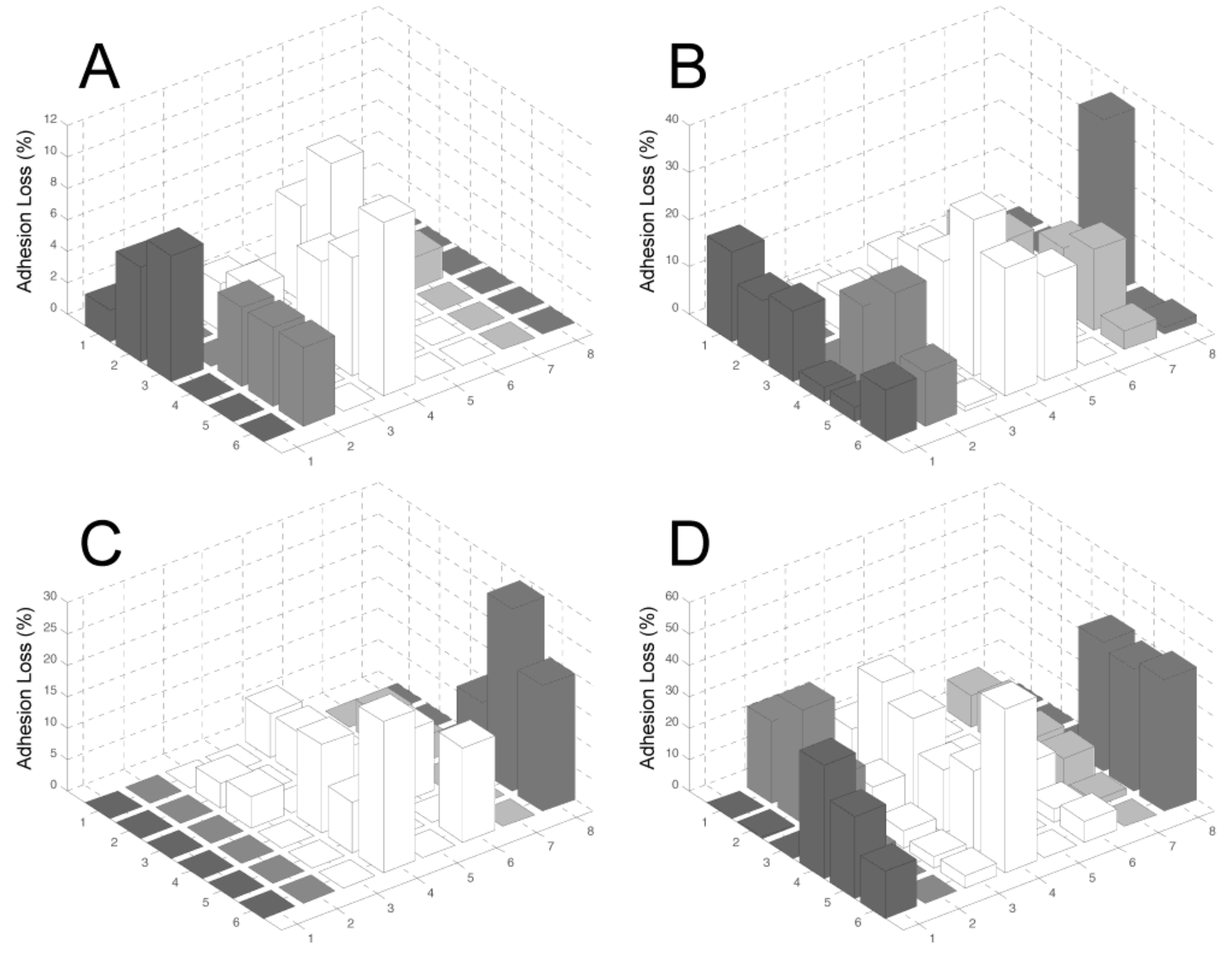

Figure 8. Typical results of adhesion analysis of several types of 48-element coating arrays during a routine combinatorial screening operation. Each array contains the same $2^4 = 16$ formulations in triplicate. A, B, C, and D are a $2^{3-1} = 4$ design in UV dosage, UV intensity, and preheat temperature. A, high UV dosage, low UV intensity, and low preheat temperature; B, high UV dosage, high UV intensity, and high preheat temperature; C, low UV dosage, low UV intensity, and high preheat temperature; D, low UV dosage, high UV intensity, and low preheat temperature. The *z* axis is percentage of coating loss.

adhesion testing was completed in two steps. First, coated panels were placed in a humidity chamber for one heat, freeze, and heat cycle (85 °C, 95% humidity, 8 h; −20 °C, 0% humidity, 2 h; and 85 °C, 45% humidity, 4 h). Next, these coated panels were placed in boiling water and tested for tape pull adhesion at various intervals.

The results of the scale-up tests are summarized in Figure 9. The coatings identified using the combinatorial process showed an excellent improvement in adhesion over the standard material. The coating performance was ranked by the standard ASTM method[31,32] by five levels of coating performance from 5 (best) to 0 (worst). The laboratory-scale formulations 1 and 2 were based on two different materials discovered using the combinatorial process. The variation in these formulations was induced by changing the ratio of the formulation components.

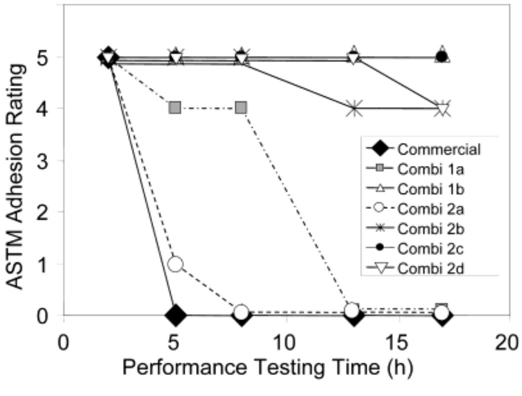

Figure 9. Results of scaling up of combinatorially developed coatings with high adhesion performance. Performance test, boiling water. Adhesion varies from 5 (best) to 0 (worst). Combi 1a−b and 2a−d are laboratory scale formulations based on two different formulations discovered using the combinatorial process.

Conclusions

Combinatorial methodologies in materials science provide important time savings in materials development in the initial discovery and optimization phase. The scalability of these materials to the industrial-scale levels is the most important aspect for the acceptance of the combinatorial and HT methodologies in industry.

Although the HT methodologies were reborn in 1995 with the pioneering work of Xiang and co-workers,[10] little or no results have been published to date describing the scaling-up of combinatorial materials leads. The only reported successes are in the area of catalysis where UOP,[36] Dupont,[37] and Symyx reported scale-up of the combinatorially discovered catalysts. With our report, we demonstrate that the combinatorial developments progress from the small scale into traditional scale for other types of materials, such as high-performance organic coatings for automotive applications.

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Supporting Information Available. Video files are available in Microsoft Video format: a video *GE-Built Crosshatch Robot* illustrates operation of a robot for automatic crosshatching of 6 × 4 arrays of organic coatings, a video *Auto Adhesion Screening* demonstrates operation of an automated imaging system for evaluation of adhesion loss of individual coatings in the 6 × 4 array after an adhesion test, and a video *Fluorescence Images of Adhesion Loss* presents a sequence of fluorescence images of individual coatings in the 6 × 4 array after the adhesion test. This material is available free of charge via the Internet at http://pubs.acs.org.

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