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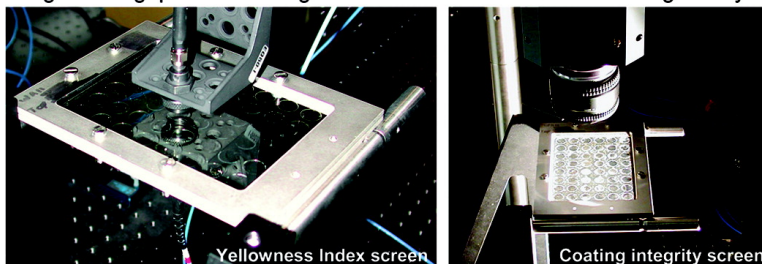
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High-Throughput Weathering Evaluation of Combinatorial Coatings Arrays

Yellowness Index screen

Coating integrity screen

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

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Combinatorial screening of materials formulations followed by the scale-up of combinatorial leads has been applied for the development of high-performance coating materials for automotive applications. We replaced labor-intensive coating formulation, testing, and measurement with a "combinatorial factory" that includes robotic formulation of coatings, their deposition as 48 coatings on a 9×12-cm plastic substrate, accelerated performance testing, and automated spectroscopic and image analysis of resulting performance. This high-throughput (HT) performance testing and measurement of the resulting properties provided a powerful set of tools for the 10-fold accelerated discovery of these coating materials. Performance of coatings is evaluated with respect to their weathering, because this parameter is one of the primary considerations in end-use automotive applications. Our HT screening strategy provides previously unavailable capabilities of (1) high speed and reproducibility of testing by using robotic automation and (2) improved quantification by using optical spectroscopic analysis of discoloration of coating-substrate structure and automatic imaging of the integrity loss of coatings. Upon testing, the coatings undergo changes that are impossible to quantitatively predict using existing knowledge. Using our HT methodology, we have developed several cost-competitive coatings leads that match the performance of more costly coatings. These HT screening results for the best coating compositions have been validated on the traditional scales of coating formulation and weathering testing. These validation results have confirmed the improved weathering performance of combinatorially developed coatings over conventional coatings on the traditional scale.

Introduction

Combinatorial and high-throughput (HT) methods are becoming common tools for discovery and optimization of difficult-to-predict entities, such as catalysts, and are gaining widespread acceptance in other areas of materials research.[1,2] The multidimensional nature of the interactions between the composition, process parameters, and end-use conditions of functional formulated materials, such as polymer-based sensor films,[3−5] organic coatings,[6−15] cured resin blends,[16] etc. also provides dramatic opportunities for combinatorial and HT research. In these materials, the formulation components may be highly interactive, resulting in complex, nonlinear structure−property relationships. Thus, performance testing is becoming critical for combinatorial experimentation with such advanced materials. We have recently demonstrated the effectiveness of HT multilevel performance testing for analyte-response properties of polymeric sensor materials,[5,17,18] wear abrasion,[10] adhesion of coating arrays,[13] and weathering of polymer blend compositions.[19,20] In addition, HT performance testing has been demonstrated in impact testing of polymers[21] and flammability and ignition testing of flame-retardant materials.[22] 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.[13] Importantly, combinatorially developed materials should be scalable, as was recently demonstrated with the scaling up of combinatorial coatings with respect to their adhesion.[13,23]

In this study, we report the development and implementation of a high-throughput screening factory for evaluation of weathering of organic protective coatings for automotive applications, followed by the scale-up of the best (lead) coating formulations. The primary considerations in the durable applications of such coatings are their resistance to wear abrasion,[10] adhesion to a plastic (polycarbonate) substrate,[13] and weathering performance. The environmental parameters affecting weathering of coatings are summarized in Figure 1 along with the important measured parameters of the weathered substrate and coating. The determining factors in the end-use outdoor weathering lifetime of organic coatings are the UV radiation dose received by a sample and atmospheric moisture.[24,25] Reliable quantification of weathering-induced coating degradation is performed using

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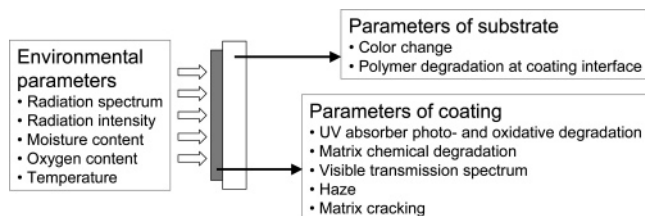
Figure 1. Environmental parameters that affect weathering of coatings and substrate.

yellowness index (YI), haze or gloss, and loss of coating integrity.[25−29]

Although outdoor weathering data are the most useful for the direct evaluation of material stability, a fundamental limitation is the need for multiyear exposure times. Thus, alternative weathering approaches are used to more rapidly qualify materials for particular applications in an effort to judge acceptable performance as well as to screen additives for efficacy. Accelerated outdoor weathering studies usually are performed at test sites in Florida or in Arizona for several years.[30] Further reduction of the testing time is achieved by using a xenon arc exposure test in which the equivalent of one year of Florida exposure can be reached in ~1100 h.[31]

The commonly used approach of weathering evaluation of coatings has several shortcomings that make this approach inapplicable for HT screening of combinatorial libraries. These drawbacks include multiple manual steps of measurement of color (YI) and coating integrity; the need to have a relatively large coating area for testing and measurements; difficulties in rapid measurements of multiple samples; and difficulties in measurement automation. To address these limitations of conventional test and measurement methods of weathering, we have developed HT testing, measurement, and data analysis methodology for the quantitative determination of weathering of combinatorial arrays of coatings. The approach included fabrication, weathering, automatic spectroscopic determination of the resulting YI, and automatic imaging of the integrity of coatings arrays, followed by the decision-making step. Our combinatorial chemistry methodology, array fabrication conditions, performance testing methods, and measurement techniques provided results that correlated well with the more conventional test and measurement methods. Combinatorial methods are useful in development of cost-effective coating formulations that match the performance of more costly coatings. Several cost-competitive coatings leads developed using HT tools were successfully scaled up and demonstrated excellent performance, as compared with conventional coatings.

HT Concept for Weatherability Testing of Coatings Formulations

Two main parameters in the weathering of coatings are the increase in yellowness index (YI) and mechanical degradation of coating material. To differentiate coatings on the basis of these parameters, weathering must accumulate at least 2000 kJ/m^2 at 340 nm of UV exposure dose and include water spray, elevated humidity and temperature phases in the weathering cycle. Because of the need for

evaluation of both YI and coating integrity, separate measurements are manually performed on different types of equipment.

We developed a measurement method and an associated automated system for rapid determination of YI and degradation of weatherable coatings in multiple samples, such as those created as combinatorial libraries. Our new method eliminates the complexity of the known methods for separate evaluation of YI and integrity of each coating upon weathering. These measurement capabilities are combined in a single automated modular system that automatically determines the physical condition of a coating and measures its YI. In particular, degradation condition and degradation products of coatings and the substrate are analyzed using electronic absorption spectroscopy and reflected light imaging. Characterization of the weatherability of combinatorial libraries of coatings is performed in a fraction of the time required for such analysis using known test and analysis approaches. These time savings originate from parallel weathering of multiple coatings in an array format and more rapid analysis of properties after weathering.

Our HT weathering testing methodology adapts the principles of the well-accepted accelerated weathering method based on xenon-arc exposure,[19] yet it provides previously unavailable capabilities of fabricating coatings with high speed and reproducibility through robotic automation and improved quantitation through high signal-to-noise automatic spectroscopic analysis and reflected light imaging. In the manual method, weathering is performed on relatively large areas of coatings (25 cm^2 or more) followed by manual measurement of YI and coating integrity. Ranking of coating weathering is done by the smallest YI and least degradation of coating. This approach has a large historical database for weathering determinations, so it was adapted for the HT coatings evaluation.

One of the requirements for HT determination of coating weathering was the capability to operate with a coating sample size of only 10 mm in diameter when 48 coatings are produced as an 8 × 6 array. This layout of coating libraries was jointly developed with Avery Research[32] for determination of wear abrasion, adhesion loss, and barrier properties.[10,13,14] Another requirement was improved quantification of degradation of the coating integrity, because the standard method involved manual visual determination of the coating condition. In the HT system, this improved quantification was achieved through the high signal-to-noise automatic imaging of the coating regions and determination of different types of coating degradation.

A schematic of our HT weathering testing methodology is shown in Figure 2. The approach included fabrication, weathering, automatic spectroscopic determination of the resulting YI, and automatic imaging of the integrity of coatings arrays, followed by the decision-making step. Quantitative macroscopic visualization of organic coatings using digital imaging was introduced by NIST to the organic coatings industry in the early 1990s to provide robust and quantitative analysis capabilities.[33] In weathering studies, measurements of coatings appearance and the kinetics of the appearance changes can often provide insight into the
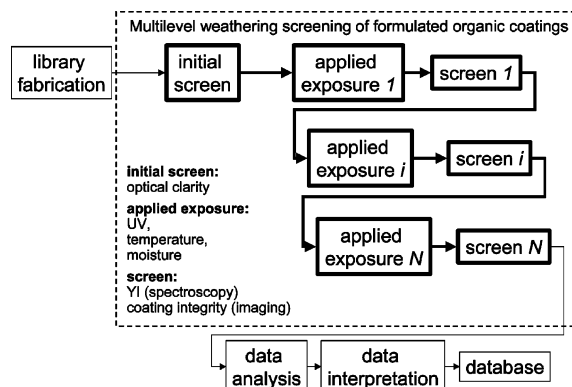
Figure 2. A schematic of the approach for the high-throughput weathering screening of formulated libraries of organic coatings.

Table 1. Compositions of Coating Formulations

coating	acrylates, wt %						photo-initiator	UV absorber
formulation	A	B	C	D	E	F	wt %	wt %
1	35.5	35.5				20	3	6
2	35.5			35.5		20	3	6
3			35.5	35.5		20	3	6
4			35.5		35.5	20	3	6
5	71					20	3	6
6	71					20	3	6
7	35.5	35.5				20	3	6
8	35.5			35.5		20	3	6
9			35.5	35.5		20	3	6
10			35.5		35.5	20	3	6
11	71					20	3	6
12	71					20	3	6

underlying factors, such as chemical or mechanical degradation of performance.[33-35] Depending on the coatings nature, weathering-induced degradation modes of organic coatings include blistering, delamination, cracking, haze, chalking, and some others which are determined from the image analysis data.[25,36-39]

Experimental Section

Materials. Compositions of coating blend formulations are presented in Table 1. Formulation components A−E were acrylated aliphatic urethane oligomers of variable functionality Ebecryl 1290, Ebecryl 140, Ebecryl 8301, SR355, and SR399 purchased from UCB Chemical Corp., North Augusta, SC, and Sartomer Co., West Chester, PA. Formulation component F was an acrylated coating formulation containing acrylate-functionalized colloidal silica particles (formulation FCS 100 available from GE Silicones, Waterford, NY). Details of formulations A−F are provided in Table 2. A photoinitiator Darocur 4265 was purchased from Ciba Chemicals. A photoabsorber was a reactive benzophenone-based UV absorber manufactured at GE.

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. Each coating element was 10 mm in diameter and 2−5 μm thick. Coating formulations were cured upon exposure to UV

radiation using a curing system containing two Hg Arc lamps (Fusion UV Systems, Inc.). Further details of the library preparation are reported elsewhere.[9,13,32] For demonstration of the operation of the automated weathering-evaluation system described in this article, coating arrays were fabricated that contained acrylate-based coating blend formulations in each array, as shown in Table 1, with four replicates each.

Weathering. For weathering testing, coating arrays were loaded into holders and positioned in the weatherometer. Weathering was performed in a weatherometer equipped with a Xenon lamp (Atlas Electric Devices Co., Chicago, IL, model Ci35A, 0.77 W/m^2 irradiance at 340 nm) with inner and outer filters of the lamp made of borosilicate glass. The weathering cycle for coating arrays was 160 min of light (air temperature 45 °C, black panel temperature 70 °C, 50% relative humidity) followed by 5 min dark and 15 min of dark and water spray (air temperature 20 °C, 100% relative humidity). The samples accumulated 59.04 kJ/(m^2 nm) at 340 nm of radiation in a 24-h period, which is an approximate 8-fold acceleration over Miami, FL.

HT Spectroscopy and Imaging. A schematic of the automated modular measurement system for spectroscopic (YI) and mechanical integrity analysis of coatings arrays is presented in Figure 3. General views of the system are depicted in Figure 4. For YI measurements, the system operated with a deuterium−halogen light source (Ocean Optics, Inc., Dunedin, FL), an assembled transmission probe, and a portable spectrometer (Ocean Optics, model S2000). Each coating element deposited onto the substrate was automatically measured in the transmission mode over the spectral range from ∼250 to 800 nm. Absorbance values in the range from 400 to 500 nm were further used to calculate YI values.

For determination of the integrity of each coating in the array, the system operated with a halogen 60-W lamp to uniformly illuminate the coating array for imaging with a detector (ICCD camera, Andor Technologies). Images of individual coating elements for determination of the integrity of coatings were collected in sequence. The 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 were used for development of image analysis algorithms.

For spectroscopic and image analysis, the array of coatings was positioned onto a computer-controlled $X-Y$ translation stage. The stage was operated in concert with either the portable spectrometer or the CCD camera.

Results and Discussion

Evaluation of Weathering Reproducibility. To understand the sources of variation in the weathering, in our initial experiments, we evaluated the reproducibility of weathering of uncoated substrates. Results of these evaluations are presented in Figure 5. These data demonstrate the reproducibility of measurements of YI for two control substrates. One substrate was an unweathered polycarbonate sheet. The second substrate was a polycarbonate sheet exposed to weathering conditions identical to those of the weathering

Table 2. Details of Coating Formulations

acrylate	coating formulation name	description
A	Ebecryl 1290 acrylated urethane	acrylated aliphatic urethane oligomer hexa-functional
B	Ebecryl 140 acrylate ester	tetraacrylate monomer
C	Ebecryl 8301 acrylated urethane	acrylated aliphatic urethane oligomer
D	SR355	ditrimethylolpropane tetraacrylate
E	SR399	dipentaerythritol pentaacrylate
F	FCS 100	functionalized colloidal silica suspended in a liquid diacrylate
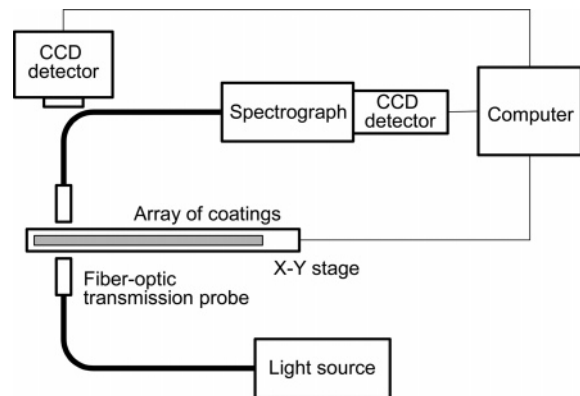
Figure 3. Schematic of an automatic measurement system for determination of YI and integrity of each coating in the combinatorial library.

conditions of arrays of coatings. Each substrate was measured in 48 locations, the same locations as for measurements of 48-element coating libraries. Further, four measurements were combined into a single representation (similar to four replicate coatings in the libraries). Thus, the data shown in Figure 5 present 12 means of such measurements on both types of controls.

The increase in the YI of the weathered control indicates the capabilities of the weathering test and YI measurement system, as shown in Figures 3 and 4. The instrument precision was better than 2% RSD, as determined from the spread in YI determinations of the unweathered control substrate. The test precision was 4% RSD, as determined from the spread in YI determinations of the weathered control substrate at the highest exposure. It was observed that the test precision degraded with the exposure. Overall, it was determined that the accelerated weathering process which included UV exposure, water spray, and temperature cycles, provided only a slight increase in the variability of measurements.

Initial Evaluation of YI and Mechanical Degradation of Coatings. Measurements of YI were performed in the automatic mode on weathered coating arrays. Typical results are presented in Figure 6, which highlight the performance of an unprotected substrate upon weathering, measurements of a control nonweathered unprotected substrate, and two best types of acrylate coatings (A + F and C + E + F). The largest increase in the YI as a function of exposure dose was observed for an uncoated substrate. This could be expected because the coatings are clear formulations that do not contain any colored species (see Table 1), and their purpose is to reduce the discoloration of the polycarbonate substrate.

Two types of acrylate coating materials, A + F and C + E + F, have demonstrated the smallest increase in YI over

almost 1400 kJ/m² of exposure. Acrylates A, C, and E are all aliphatic and of relatively high molecular weight. Since they are aliphatic, they do not absorb much UV light. In addition, the relatively high molecular weight of these materials results in a lower content of acrylate groups per unit volume of material. Thus, the small number of residual acrylate groups present after curing was in part responsible for better chemical stability. The error bars represent one standard deviation from the mean of four measurements of YI. The somewhat larger error bars of the coatings as compared to the bare substrate materials are due to the slight variation in coating thickness across four replicate coating elements of each of coatings compositions.

Several coating formulations demonstrated significant mechanical degradation with different types of degradation mechanisms. It is known that depending on the coatings nature, weathering-induced degradation modes of organic coatings determined from image analysis include blistering, delamination, cracking, haze, chalking, and some others.[25,36−39] Typical modes of degradation of coatings are summarized in Figures 7 and 8, obtained with the automated imaging system and an optical microscope, respectively. The degradation modes included crack and void formation (observed after a 1395 kJ/m² exposure) and delamination of coatings from a substrate (observed after a 1738 kJ/m² exposure). Crack and void formation was observed in formulations C + D + F and A + B + F. Delamination of coatings was observed in formulations A + D + F. Coating formulations A + F and C + E + F showed no degradation of the matrix material upon this exposure dose.

Factory-Mode Operation. In the factory mode, we have screened a large variety of formulations. The nature of these formulations has been outlined in our earlier reports.[10,11] Four different formulations were deposited in groups of four in three different locations on a substrate. Weathering was performed with a maximum exposure of 4215 kJ/m². As a control, a separate array was fabricated with control coatings (48 replicates). Data analysis was performed by averaging measured YI for each group of four coating formulations and plotting three averages and respective standard deviations for each formulation. Screening results for the YI of weathered coating formulations identified from the primary screen are summarized in Figure 9. These data identify two lead coating formulations (nos. 4 and 2) as the ones with the smallest YI.

Upon reaching the 4215 kJ/m² exposure, the coatings on the control array were mostly delaminated, and the remaining coatings were hazy. The screening results for matrix stability of weathered coating formulations with the exposure dose of 4215 kJ/m² are presented in Figure 10. In these studies, matrix stability was considered at three broad levels, includ-
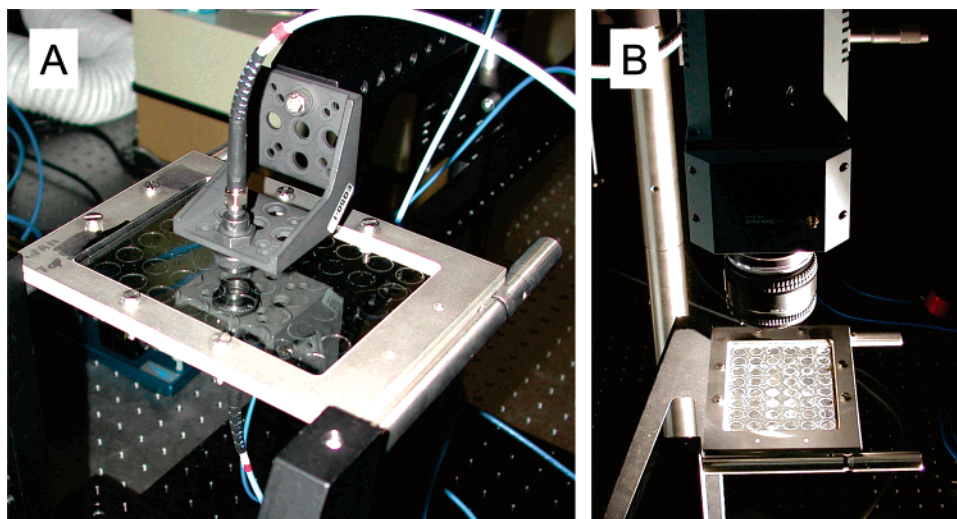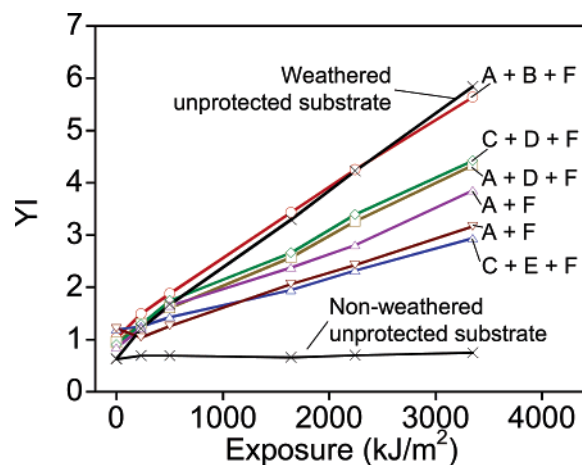
Figure 4. Sections of the automatic measurement system for (A) spectroscopic determination of YI and (B) imaging of integrity of each coating in the combinatorial library.
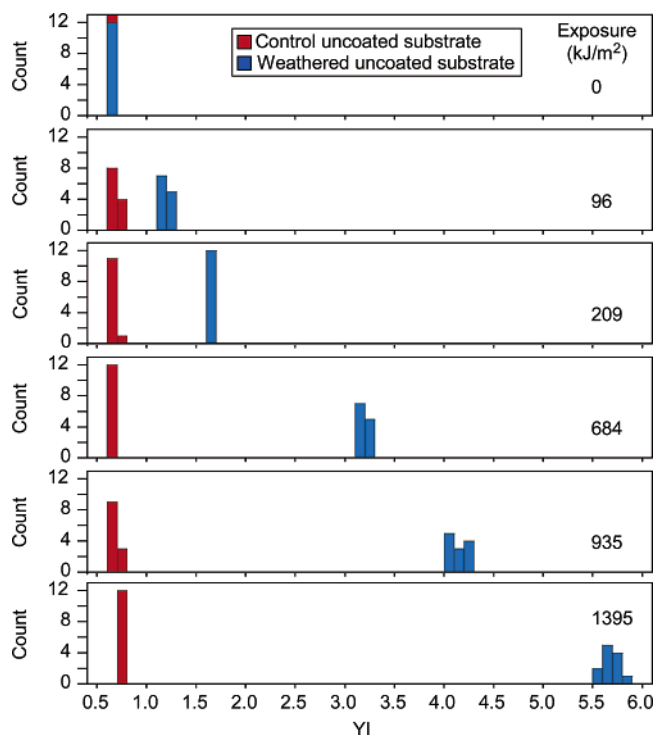
Figure 5. Results of the evaluation of performance capabilities of the system for automated measurement of YI.


Figure 6. Results of measurements of YI performed in the automatic mode on a weathered coating array and two control materials. Controls: an unweathered polycarbonate sheet and weathered polycarbonate sheet exposed to weathering conditions identical to those of the weathering conditions of arrays of coatings.

ing severe coating delamination, formation of hazy regions of the coating, and no detectable coating changes. Such matrix stability levels are common in evaluation of organic coatings.[33] For comparison, this Figure also illustrates the matrix stability of weathered control array of coatings with 48 replicates. Lead coating formulations in regard to matrix stability were identified from the weathering screen as those that have the smallest matrix degradation. The lead coating formulations for matrix stability were nos. 4, 1, and 2.

Scale-Up of HT Lead Coatings. As a result of the combinatorial studies that utilized test and measurement steps described above, three lead coating formulations were identified as potential lower-cost alternatives to replace the current commercial material. These lead formulations were scaled up and evaluated with xenon-accelerated weathering tests. Two measurement parameters included $\Delta\%$ haze and ΔYI.

The first set of scale-up results is summarized in Figure 11, which compares the $\Delta\%$ haze of one combinatorial lead formulation with a commercial control formulation. The combinatorial lead formulation performed well during the test with respect to $\Delta\%$ haze. Both formulations had similar induction periods, but combinatorial lead demonstrated slightly better performance over the control: ~30% relative improvement in $\Delta\%$ haze at the longest xenon exposure of 3000 h.

The second set of scale-up results is summarized in Figure 12, which compares the YI of the combinatorial lead formulation with the commercial control formulation. Again, the combinatorial lead formulation performed well during the test with respect to ΔYI. The control had a negligibly less YI than the combinatorial lead, with the maximum difference of only ~0.3 YI units at the longest exposure time of 3000 h. However, the absolute values of ΔYI for both
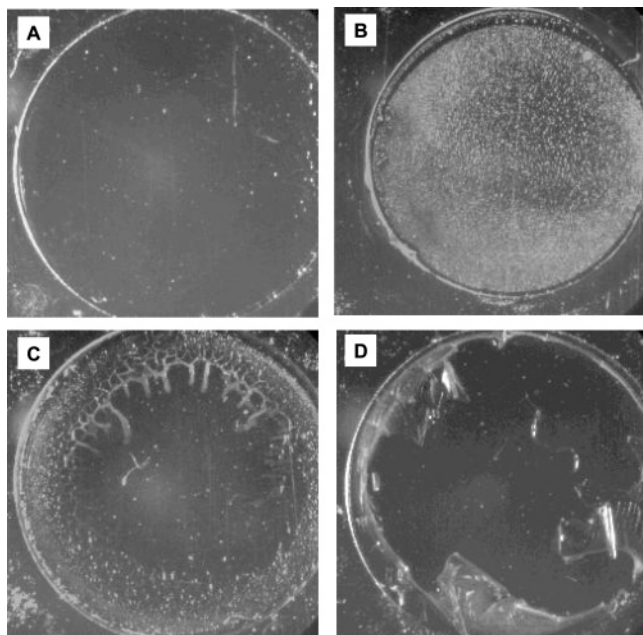
Figure 7. Typical modes of degradation of coatings as analyzed by an automated imaging reflected light system shown in Figure 4B. Degradation modes of coating materials in the weathered array of coatings: (A) good condition of coating, (B) crack formation, (C) void formation, and (D) delamination observed after a 1738 kJ/m^2 exposure.
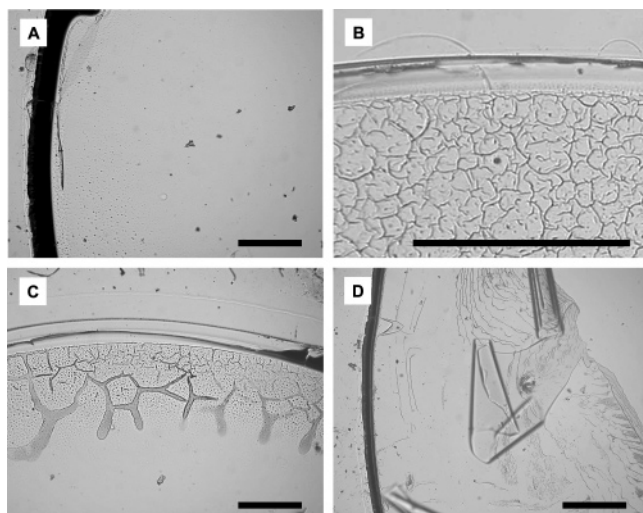

Figure 8. Typical modes of degradation of coatings as analyzed by optical (transmitted light) microscopy in the weathered array of coatings: (A) good condition coating, (B) crack formation, (C) void formation, and (D) delamination. A, B, and C observed after a 1395 kJ/m^2 exposure; D observed after a 1738 kJ/m^2 exposure. Curved regions on each image are the edges of coatings. Scale bar, 500 μm.

formulations are quite low (YI < 4), which indicates that both formulations are acceptable with respect to YI. Therefore, at this point in the testing, this small difference is not of a critical concern, although continued weathering testing is being completed.

Conclusions

Combinatorial methodologies in materials science provide important time savings in materials development in the initial discovery and optimization phases. This report demonstrates
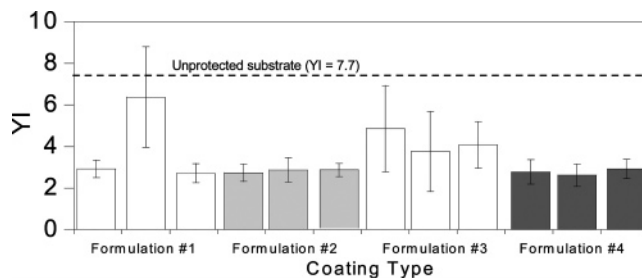

Figure 9. Screening results for YI of weathered coating formulations, exposure dose of 4215 kJ/m^2. Error bars, one SD from four coatings. Lead coating formulations in regard to YI identified from the weathering screen are shown as gray and dark gray bars.
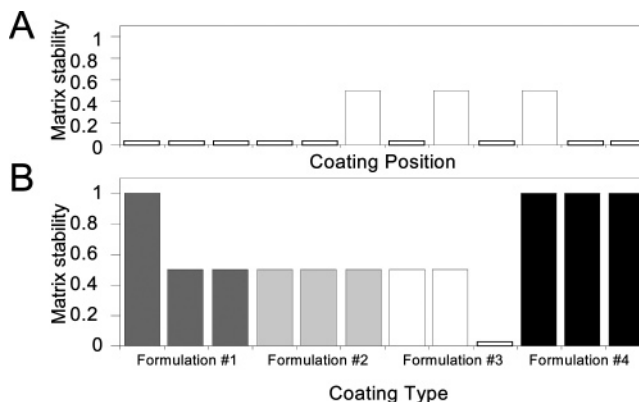
Figure 10. Screening results for matrix stability of weathered coating formulations, exposure dose of 4215 kJ/m^2. Averages of four samples are shown. (A) Control array of coatings with 48 replicates. (B) Coatings with four new formulations identified from primary screen. Lead coating formulations are shown as gray, dark gray, and black bars. Key: 0, severe delamination; 0.5, small to medium haze; 1, excellent stability.
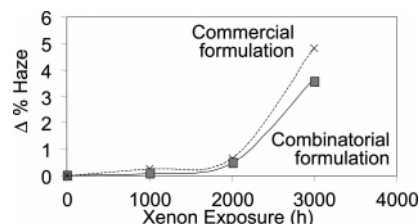
Figure 11. Comparison of Δ% haze weathering performance of combinatorial lead and commercial control formulations.
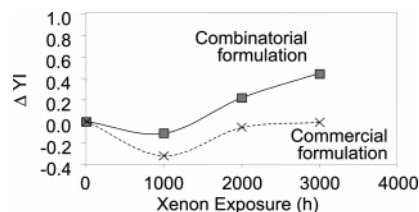
Figure 12. Comparison of ΔYI weathering performance of combinatorial lead and commercial control formulations.

that combinatorial methods are useful in development of cost-effective coating formulations that match the performance of more costly coatings. 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 and academia. Only a limited number of reports exist on the scalability of combinatorial leads of materials. The most recent reports include adhesion performance of

scaled-up automotive protective coatings,[13,23] and catalyst scale-ups from combinatorial to laboratory and pilot plant sizes.[4,40] With our report, we demonstrate that the combinatorial developments and scale-up of the cost-competitive leads progress into such a difficult area of performance testing as weathering of high-performance organic coatings for automotive applications.

Supporting Information Available. Video files are available in *.avi format: AnalysisCoatingsYI.avi illustrates operation of an automated spectroscopic system for measurements of discoloration of individual coatings in the 8×6 array upon weathering; AnalysisCoatingsIntegrity.avi illustrates operation of an automated spectroscopic system for measurements of discoloration of individual coatings in the 8×6 array upon weathering.

References and Notes

(1) Potyrailo, R. A., Amis, E. J., Eds. *High Throughput Analysis: A Tool for Combinatorial Materials Science*; Kluwer Academic/Plenum Publishers: New York, 2003.

(2) Potyrailo, R. A., Karim, A., Wang, Q., Chikyow, T., Eds. *Combinatorial and Artificial Intelligence Methods in Materials Science II*; Materials Research Society: Warrendale, PA, 2004; Vol. 804.

(3) Matzger, A. J.; Lawrence, C. E.; Grubbs, R. H.; Lewis, N. S. *J. Comb. Chem.* **2000**, *2*, 301−304.

(4) Amis, E. J. *Nat. Mater.* **2004**, *3*, 83−85.

(5) Potyrailo, R. A. *Polymeric Materials Science and Engineering. Polymer Preprints* **2004**, *90*, 797−798.

(6) Schrof, W.; Lehmann, S.; Hadeler, J.; Oetter, G.; Dralle-Voss, G.; Beck, E.; Paulus, W.; Bentz, S. *Proc. 2001 Athens Conf. Coat. Sci. Technol.* **2001**, *27*, 283.

(7) Pilcher, G. R. *J. Coat. Technol.* **2001**, *73*, 135−143.

(8) Wicks, D. A.; Bach, H. *Proc. 29th Int. Waterborne, High-Solids, Powder Coat. Symp.* **2002**, *29*, 1−24.

(9) Chisholm, B. J.; Potyrailo, R. A.; Cawse, J. N.; Shaffer, R. E.; Brennan, M. J.; Moison, C.; Whisenhunt, D. W.; Flanagan, W. P.; Olson, D. R.; Akhave, J. R.; Saunders: D. L.; Mehrabi, A.; Licon, M. *Prog. Org. Coat.* **2002**, *45*, 313−321.

(10) Potyrailo, R. A.; Chisholm, B. J.; Olson, D. R.; Brennan, M. J.; Molaison, C. A. *Anal. Chem.* **2002**, *74*, 5105−5111.

(11) Chisholm, B. J.; Potyrailo, R. A.; Shaffer, R. E.; Cawse, J. N.; Brennan, M. J.; Molaison, C. A. *Prog. Org. Coat.* **2003**, *47*, 112−119.

(12) Chisholm, B. J.; Potyrailo, R. A.; Cawse, J. N.; Shaffer, R. E.; Brennan, M. J.; Molaison, C. A. *Prog. Org. Coat.* **2003**, *47*, 120−127.

(13) Potyrailo, R. A.; Chisholm, B. J.; Morris, W. G.; Cawse, J. N.; Flanagan, W. P.; Hassib, L.; Molaison, C. A.; Ezbiansky, K.; Medford, G.; Reitz, H. *J. Comb. Chem.* **2003**, *5*, 472−478.

(14) Grunlan, J. C.; Mehrabi, A. R.; Chavira, A. T.; Nugent, A. B.; Saunders: D. L. *J. Comb. Chem.* **2003**, *5*, 362−368.

(15) Saunders: D.; Grunlan, J.; Akhave, J.; Licon, M.; Murga, M.; Chavira, A.; Mehrabi, A. R. In *High Throughput Analysis: A Tool for Combinatorial Materials Science*; Potyrailo, R. A., Amis, E. J., Eds.; Kluwer Academic/Plenum Publishers: New York, 2003, Chapter 14.

(16) Hamerton, I.; Herman, H.; Mudhar, A. K.; Chaplin, A.; Shaw, S. J. *Polymer* **2002**, *43*, 3381−3386.

(17) Potyrailo, R. A.; Morris, W. G.; Wroczynski, R. J. In *High Throughput Analysis: A Tool for Combinatorial Materials Science*; Potyrailo, R. A., Amis, E. J., Eds.; Kluwer Academic/Plenum Publishers: New York, 2003, Chapter 11.

(18) Potyrailo, R. A. *Macromol. Rapid Commun.* **2004**, *25*, 77−94.

(19) Potyrailo, R. A.; Pickett, J. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 4230−4233.

(20) Potyrailo, R. A.; Wroczynski, R. J.; Pickett, J. E.; Rubinsztajn, M. *Macromol. Rapid Comm.* **2003**, *24*, 123−130.

(21) Meredith, C.; Sormana, J.-L.; Tona, A.; Elgendy, H.; Karim, A.; Amis, E. *Polymer Preprints* **2001**, *42*, 649−650.

(22) Gilman, J. W.; Davis, R.; Nyden, M.; Kashiwagi, T.; Shields, J.; Demory, W. In *High Throughput Analysis: A Tool for Combinatorial Materials Science*; Potyrailo, R. A., Amis, E. J., Eds.; Kluwer Academic/Plenum Publishers: New York, 2003, Chapter 19.

(23) Ezbiansky, K.; Medford, G.; Reitz, H.; Potyrailo, R. A.; Chisholm, B. J.; Morris, W. G.; Cawse, J. N.; Flanagan, W. P.; Hassib, L.; Molaison, C. A. In *Combinatorial and Artificial Intelligence Methods in Materials Science II, MRS Symposium Proceedings*; Potyrailo, R. A., Karim, A., Wang, Q., Chikyow, T., Eds.; Materials Research Society: Warrendale, PA, 2004; Vol. 804, pp 129−136.

(24) Pickett, J. E.; Webb, K. K. *Makromol. Chem.* **1997**, *252*, 217−236.

(25) Yang, X. F.; Tallman, D. E.; Bierwagen, G. P.; Croll, S. G.; Rohlik, S. *Polym. Degrad. Stab.* **2002**, *77*, 103−109.

(26) Wypych, G. *Handbook of Material Weathering*; ChemTec: Toronto, Canada, 1995.

(27) Shah, V. *Handbook of Plastics Testing Technology*; Wiley: New York, 1998.

(28) Zweifel, H., Ed. *Plastics Additives Handbook*; Hanser: Munich, Germany, 2001.

(29) van der Ven, L. G. J.; Leuverink, R.; Henderiks, H.; van Overbeek, R. *Prog. Org. Coat.* **2003**, *48*, 214−218.

(30) Sherbondy, V. D. In *Paint and Coating Testing Manual*; Koleske, J. V., Ed.; Americal Society for Testing and Materials: Philadelphia, PA, 1995; pp 643−653.

(31) Pickett, J. E.; Moore, J. E. *Makromol. Chem.* **1995**, *232*, 229−238.

(32) Saunders, D. L.; Akhave, J. R.; Potyrailo, R. A.; Olson, D. R.; Flanagan, W. P. *An improved combinatorial testing method and apparatus for coat material formulations and methods*; World Patent Application WO0132320, 2001.

(33) Lee, F.; Pourdeyhimi, B.; Adamsons, K. In *Service Life Prediction of Organic Coatings*; Malhotra, R., Ed.; American Chemical Society: Washington, DC, 1999; Vol. 722, pp 207−232.

(34) McKnight, M. E.; Martin, J. W. *Prog. Org. Coat.* **1998**, *34*, 152−159.

(35) Kramb, V. A.; Hoffmann, J. P.; Johnson, J. A. In *Review of Progress in Quantitative Nondestructive Evaluation, Volume 22B*; Thompson, D. O., Chimenti, D. E., Eds.; AIP Conference Proceedings, 2003; Vol. 657, pp 1111−1118.

(36) Oosterbroek, M.; Lammers, R. J.; Van der Ven, L. G. J.; Perera, D. Y. *J. Coat. Technol.* **1991**, *63*, 55−60.

(37) Hainsworth, S. V.; McGurk, M. R.; Page, T. F. *Surf. Coat. Technol.* **1998**, *102*, 97−107.

(38) Valet, A. *Prog. Org. Coat.* **1999**, *35*, 223−233.

(39) Nichols, M. E.; Gerlock, J. L.; Smith, C. A.; Darr, C. A. *Prog. Org. Coat.* **1999**, *35*, 153−159.

(40) Spivack, J. L.; Webb, J.; Flanagan, W. P.; Sabourin, C.; May, R. J.; Hassib, L. In *Combinatorial and Artificial Intelligence Methods in Materials Science II, MRS Symposium Proceedings*; Potyrailo, R. A., Karim, A., Wang, Q., Chikyow, T., Eds.; Materials Research Society: Warrendale, PA, 2004; Vol. 804, pp 199−204.