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## Comment

## The MSDS Explosion and a Solution

Q. How do you put five gallons of paint in a one gallon can?
A. Very carefully!

Of course, there is no answer to the question; unless the laws of physics are suspended, there is no solution. And, there has been no solution to the explosion in the number of material safety data sheets and the capacity of any company to cope with the shear numbers involved and the 30 -year filing requirements issued by the government-until now!

In a perfect example of the FSCT philosophy, the Technical Committee of the Chicago Society examined this problem and saw a need to simplify the handling, filing, and accessing of MSDSs. Its investigation led to a possible solution - the CD-ROM (compact disk-read only memory).

This latest advance in communications technology offers vast information storage capacity, high accessibility, and durability. It is also very easy to use and is fully accepted by the U.S. Government for data storage. The committee envisioned a system in which all MSDSs used by the coatings industry would be electronically encoded onto a CD similar to audio CDs now on the market. The system would be available by subscription and updated quarterly.

Here the technology is identical: MSDSs are either electronically or optically scanned and the data stored on the CD is exactly as that presented on the original MSDS prepared by the raw material manufacturer. Since the data cannot be altered or changed in any way on the CD it becomes a permanent record. With search software also encoded on the CD, specific MSDSs can be found quickly and easily.

Just as important, frequently used MSDSs can be downloaded onto a company's computer for in-plant or customer distribution, a plant's unique raw material codes may be added, or a finished product MSDS can be compiled importing information directly from the original raw material MSDS.

In addition, the FSCT is currently discussing with the National Paint \& Coatings Association the possibility of including NPCA`s Raw Material Index on the CD-ROM, which would provide a wealth of information to the coatings manufacturer and formulator.

The FSCT is in the initial stages of production of the Coatings MSDS System on CDROM and is currently accepting raw material MSDSs from supplier companies. We request that FSCT manufacturing members urge their raw material suppliers to participate in this important project. Please contact FSCT Headquarters for more information.
Q. How can you put 60.000 MSDSs at your fingertips?
A. With the Coatings MSDS System on CD-ROM!


Robert F. Ziegler
Executive Vice President


#### Abstract

Development of a Predictive Model for the Changes in Roughness that Occur During the Painting Process-P-A. P. Ngo, G.D. Cheever, R.A. Ottaviani, and T. Malinski


JCT, 65, No. 821, 29 (June 1993)
A model involving surface and coating parameters was developed to relate their effects on the formation of the paint/air interface. In this investigation, the study included selective changes in coating material properties (molecular weight, percent solids, surface tension, and viscosity) in addition to the changes in substrate roughness (25.4, 50.8 , and $76.2 \mu \mathrm{~m}$ grooves) and film thickness. The change in roughness (DELTRT) that occurred with painting was used and is defined as the difference between the initial and the final peak-to-valley roughness, Rt. The change in the topcoat roughness was expressed as a function of initial roughness (RTB), film thickness (FILM), and paint properties. It was found that the initial roughness of the substrate was the main predictor followed by the film thickness. The viscosity (VISLOSHR) was found to be the only material property which influenced the topcoat. The model that best predicts the change in roughness is:
DELTRT $=-8.48+0.81$ RTB +1.87 FILM +0.001 VISLOSHR.

Changes in Hiding During Latex Film Formation Part V: Effect of Opaque Polymer-Cleveland Society for Coatings Technology

## JCT, 65, No. 821, 39 (June 1993)

In Part V of this continuing series, the Cleveland Society Technical Committee investigated how opaque polymer affects the changes in hiding of latex paints during the first hour of drying. Hiding was monitored during drying by measuring the reflectance (tristimulus Y) every 15 sec on paints drawn down over a black substrate. Addition of opaque polymer was found to have three main effects: (1) decreased titanium dioxide efficiency due to extender dilution effects; (2) increased dry hiding in paints above CPVC; and (3) increased hiding by the introduction of air voids which develop within the opaque polymer. Results suggest that void formation within the opaque polymer occurred rapidly; it reduced the initial loss in hiding due to film contraction, rather than contributing to the development of dry hiding in the later stages of drying.


#### Abstract

Développement d'un Modèle pour Prédire les Changements de Rugosté se Produisant Durant la Procédé de Mise en Peinture-P-A. P. Ngo, G.D. Cheever, R.A. Ottaviani, and T. Malinski


JCT, 65, No. 821, 29 (June 1993)
Un modèle impliquant des paramètres de surface de revêtement a été développé pour relier leurs effets sur la formation d'un interface peinture/air. Dans cette étude, les paramètres choisis incluent les changements sélectifs des propriétés d'un revêtement (poids moléculaire, pourcentage des matières solides, tension de surface et viscosité) en plus des changements de la rugosité du subjectile (rainures de 25.4,50.8 et $76.2 \mu \mathrm{~m}$ ) et l'épaisseur du feuil. Le changement de rugosité (DELTRT) se produisant avec le procédé de mise en peinture a été utilisé et est défini comme la différence entre la rugosité pic-vallée initiale et finale. Le changement de la rugosité de la couche de surface a été exprimé en fonction de la rugosité initale (RTB), épaisseur du feuil (FILM) et propriétés du revêtement. Les résultats obtenus démontrent que la rugosité initiale du subjectile est le paramètre le plus important, suivi de l'épaisseur du feuil. La viscosité (VISLOSHR) a été le seul paramètre qui a influencé la couche de surface. Le modèle prédisant le mieux le changement de rugosité est:
DELTRT $=-8.48+0.81$ RTB +1.87 FILM +0.001 VISLOSHR.

Changements d'Opacité Durant la Formation d'un Feuil de latex. 5ème Partie: Effet d'un Polymère Opaque-Cleveland Society for Coatings Technology

JCT, 65, No. 821, 39 (June 1993)
Dans la 5 ème partie de cette série, le comité technique de la Société de Cleveland a étudié les effets d'un polymère opaque sur l'opacité de peintures émulsion durant la première heure de séchage. L'opacité a été mesurée durant le séchage en mesurant la réflectance (tristimulus $Y$ ) chaque 15 secondes sur des peintures étalées sur un subjectile noir. L'addition d'un polymère opaque a provoqué trois effets principaux: (1) diminution de l'efficacité du bioxyde de titane dû à l'effet de dilution (2) augmentation de l'opacité pour des peintures audessus du CPVC et (3) augmentation de l'opacité par l'introduction de poches d'air

> Desarrollo de un Modelo Predictivo Para Los Cambios en la Rugosidad Que se Presenta Durante el Proceso de Pintado-P-A. P. Ngo, G.D. Cheever, R.A. Ottaviani, and T. Malinski

JCT, 65, No. 821, 29 (June 1993)

Se desarrolló un modelo que involucra parámetros de superficie y de recubrimientos para relacionar sus efectos en la formación de la interface pintura/aire. En esta investigación, el estudio incluyó cambios selectivos en las propiedades del material del recubrimiento (peso molecular, porciento de sólidos, tensión superficial y viscosidad) además de los cambios en la rugosidad del substrato (canales de 25.4, 50.8, y $76.2 \mu \mathrm{~m}$ ) y el espesor de la película. El cambio de rugosidad (DELTRT) que se presentó con el pintado, se usó y se definió como la diferencia entre la rugosidad picovalle inicial y final, Rt. El cambio en la rugosidad del recubrimiento se expresó como función de la rugosidad inicial (RTB), el espesor de la película (FILM) y las propiedades de la pintura. Se encontró que la rugosidad inicial del substrato fué el indicador de predicción principal, seguido del espesor de la película. Se encontró que la viscosidad (VISLOSHR) fué la única propiedad del material que influenció la superficie del recubrimiento. El modelo que mejor predice el cambio de rugosidad es:
DELTRT $=-8.48+0.81$ RTB +1.87 FILM +0.001 VISLOSHR.

Cambios en el Poder Cubriente Durante la Formacion de Una Pelicula de Latex, Parte V: Efecto del Polimero Opaco-Cleveland Society for Coatings Technology

JCT, 65, No. 821, 39 (June 1993)
En la parte V de la continuación de esta serie, el comité técnico de la sociedad de Cleveland investigó la manera en que un polímero opaco afecta los cambios en el poder cubríente de las pinturas de látex durante la primer bora de secado. El poder cubriente se monitoreó durante el secado midiendo la reflectancia (tristimulus y) cada 15 segundos en pinturas aplicadas sobre un substrato negro. Se encontró que la adición del polímero opaco ocasionó tres efectos principales: (1) disminución de la eficiencia del dióxido de titanio debido a los efectos de dilución de la partícula de pigmento, (2) aumento de de poder cubriente, en seco, en pinturas arriba de su

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Adsorption Layer Thickness of Poly(Methyl Methacrylate) on Titanium Dioxide and Silica-C.R. Hegedus and I.L. Kamel

JCT, 65, No. 821, 49 (June 1993)
The interface which results from filler par-ticle-polymer interactions in coatings and other particulate filled polymer composites was investigated through the measurement of the adsorbed polymer layer or adlayer thickness surrounding each particle. Centrifugation and viscosity measurements were used to calculate an effective diameter of the dispersed filler particles (titanium dioxide and silica) in a poly(methyl methacrylate) (PMMA) solution. The adlayer thickness was determined from the effective diameter due to the extension of the filler size with the adlayer formation. These adlayer thicknesses ranged from 9 to 100 nm . Adlayer thickness increased with particle size and PMMA-filler interaction, and values calculated from viscosity experiments were greater than those from centrifugal packing. These results led to a proposed model for the polymer adlayer state, consisting of an effectively bonded polymer shell surrounding the particle, with a loosely bonded region extending further into the bulk matrix.

> Use of Formic Acid in Controlling the Rate of the Michael Addition Reaction in Base Catalyzed, Thermally Cured Acetoacetylated Acrylic/ TMPTA Coatings-T. Li and J.C. Graham

JCT, 65, No. 821, 64 (June 1993)
Thermosetting coatings are formulated based on the Michael Addition reaction of acetoacetylated resins and acrylic crosslinkers catalyzed by 1,3-diaza-bicylo[5,4,0]undec-7-ene. The catalyst is blocked by an equivalent or larger amount of formic acid to extend the gel time from only two to three hours to over two months. The clear coatings and pigmented paints are cured upon baking for 40 min at $100^{\circ} \mathrm{C}$. This block technique brings no appreciable changes in the ultimate properties of coatings. By introducing reactive diluents and using powerful solvents such as methyl amyl ketone, we have been able to reduce the VOC to as low as $250 \mathrm{~g} / \mathrm{L}$.

## Formulating Printable Coatings via D-Optimality-K.W. Chau and W.R. Kelley

JCT, 65, No. 821, 71 (June 1993)
A general method which enables one to use D-optimal design to help formulate conventional printable coatings with a chosen set of ingredients is given. The D-optimality criterion is briefly reviewed and is applied to the formulation process. Using simple poly-
qui se développent à l'intérieur du polymère opaque. Les résultats suggèrent que la formation de poches d'air à l'intérieur du polymère opaque se produit rapidement; cela réduit la perte initiale d'opacité dû à la contraction du feuil, plutôt que de contribuer au développement de l'opacité durant les derniers stages de séchage.

> Epaisseur de la Couche d'Ad-sorption du Poly (méthyle méthacrylate) sur le Bioxide de Titane et la SiliceC.R. Hegedus and I.L. Kamel

## JCT, 65, No. 821, 49 (June 1993)

L'interface résultant des interactions particule-polymère présentes dans les revêtements a été étudié avec des mesures de la couche de polymère adsorbée entourant chaque particule. Des mesures de centrifugation et de viscosité ont été utilisées pour calculer le diamètre effectif des particules dispersées (bioxyde de titane et silice) dans une solution de poly (méthyle méthacrylate) (PMMA). L'épaisseur d'adsorption a été déterminée du diamètre effectif dû à l'extension de la grosseur de particule avec la formation de la couche d'adsorption. Ces couches d'adsorption étaient de 9 à 110 nm . La couche d'adsorption a augmenté avec la grosseur de particule et l'interaction PMMA-particule, et les valeurs calculées des mesures de viscosités étaient plus grandes que celles obtenues par centrifugation. Ces résultats ont mené à une proposition de modèle pour l'état de l'adsorption de polymère, consistant en un polymère lié tout autour de la particule, avec une région moins liée à mesure que l'on s'éloigne de la particule.

Utilisation de l'Acide Formique pour le Contrôle du Taux de Réaction d'Addition de Type Michael pour les Revêtements Acétoacétylés Acryliques/TMPTA Durcissant à la Chaleur et Catalysés Avec l'Aide d'une Base-T. Li and J.C. Graham

## JCT, 65, No. 821, 64 (June 1993)

Des revêtements thermodurcissables sont formulés basés sur la réaction d'addition de type Michael de résines acryliques acétoacétylées et d'agents réticulants acryliques catalysés par le 1,3-diazobicyclo [ $5,4,0$ ] undec-7-ene. Le catalyseur est bloqué par un équivalent ou plus d'acide formique pour étendre le temps de gélification de seulement deux à trois heures à plus de deux mois. Les revêtements clairs et pigmentés sont durcis suite à une cuisson de 40 minutes à $100^{\circ} \mathrm{C}$. Cette technique de blocage n'apporte pas de changements appréciables dans les propriétés des revêtements. En introduisant des diluants réactifs et utilisant des solvants puissants comme le méthyle amyl acétane, nous avons pu réduire le COV aussi bas que 250 g/L.

CPVC, y (3) aumento de poder cubriente con la introducción de burbujas de aire, las cuales se desarrollan en el interior del polímero opaco. Los resultados sugieren que la formación de burbujas dentro del polimero opaco occurre rápidamente, esto reduce la pérdida inicial del poder cubriente debido a la contracción de la pelicula, mas que estar contribuyendo al desarrollo del poder cubriente en seco en las etapas posteriores del secado.

Espesor de la Capa Adherida de Poli(metil metacrilato) Sobre Dioxido de Titanio y Silica-C.R. Hegedus and I.L. Kamel

## JCT, 65, No. 821, 49 (June 1993)

Se investigó la interface que resulta de las interacciones entre el polimero y la partícula de la carga, en un recubrimiento, mediante la medición del espesor de la capa de polímero adherido o del espesor de la capa que rodea a cada partícula. Se utilizaron mediciones de centrifugación y viscosidad para calcular el diámetro efectivo de las particulas de la carga dispersas (dióxido de titanio y silica) en una solución de poli(metil metacrilato) (PMMA). Se determinó el espesor de la capa adherida a partir del diámetro efectivo, el cual resulta del aumento del tamaño de partícula de la carga con la capa adherida. El espesor de esa capa osciló entre 9-100 nm, este espesor aumentó con el tamaño de la partícula y la interacción PMMA-partícula de la carga. Los valores calculados a partir de los experimentos de viscosidad fueron mas altos que los obtenidos por centrifugación. Estos resultados condujeron a un modelo propuesto para el estado de la capa adherida del polimero, la cual consiste de una capa de polímero que rodea la partícula de la carga con pérdida de una región unida la cual se extiende al interior de la matriz del material.

Uso de Acido Formico Para Controlar el Rendimiento de la Reaccion de Adicion de Michael en los Recubrimentos Acetoacetilados/ TMPTA Catalizados con Bases y Curados Termicamente-T. Li and J.C. Graham

## JCT, 65, No. 821, 64 (June 1993)

Los recubrimientos termofijos son formulados en base a la reacción de adición de Michael de las resinas acetoacetiladas acrílicas y los reticulantes acrílicos catalizados por el 1,3-diazabiciclo $(5,4,0)$ undec-7-eno. La catálisis se bloquea por una cantidad equivalente o mayor de ácido fórmico para extender el tiempo de gelación de solamente dos ó tres horas a casi 2 meses. Los recubrimientos claros y las pinturas pigmentadas se curan por horneo a $100^{\circ} \mathrm{C}$ durante 40 minutos. Esta técnica de bloqueo no trae cambios

nomials, one builds models to approximate coating properties. Viable models can help formulators in developing and manufacturing coatings. The formulation process of an actual coating is described in some detail to illustrate the procedure. Various merits and limitations of modeling with optimal designs are also discussed.

Influence of Particle Size Distribution of Zinc Dust in Water-Based, Inorganic, Zinc-Rich Coatings-E. Montes

JCT, 65, No. 821, 79 (June 1993)
New VOC regulations have brought renewed interest in water-based inorganic zinc silicate coatings. Selecting zinc dust solely from the various possible "average diameter" compositions may not always yield the desired results.

At the lower micron particle size range, surface area increases can have a tremendous influence on product application characteristics. Specific area becomes an important parameter. The fine fraction of any normal distribution of particle size is the predominant factor in the rheological properties of the mixed material.

Formulation de Revêtements pour Impression avec l'Aide d'un Design Optimum-D-K.W. Chau and W.R. Kelly

JCT, 65, No. 821, 71 (June 1993)
Une méthode gén"'rale est proposée pour l'utilisation d'une design optimum-D pour aider à la formulation de revêtements pour impression. Le critère du design est revu brièvement et est appliqué au procédé de formation. L'utilisation de polynômes permet de bâtir un modèle pour 'approximation des propriétés des revêtements. Des modèles viables peuvent aider les formulateurs à développer et fabriquer des revêtements. Le procéd" de formulation d'un revêtement est décrit en détail pour illustrer la procédure. Les mérites et limitations du design sont également présentés,

Influence de la Distribution de Taille de Particule de la Poussière de Zinc dans des Revêtements Aqueux-E. Montes

JCT, 65, No. 821, 79 (June 1993)
De nouvelles normes en matière de contenu en matières organiques volatiles a renouvelé l'intérêt pour les revêtements aqueux à base de silicate de zinc inorganique. Le choix de la poussière de zinc basé sur les compositions de "diamètre moyen" peut ne pas toujours donner les résultats escomptés.

Pour la gamme inférieure en microns de la taille de particule, la surface spécifique augmente et peut influencer de façon significative les caractéristiques d'application du produit. La surface spécifique devient un paramètre important. La fraction inférieure de la distribution de la taille de particule est le facteur prédominant pour les propriétés rhéologiques du matériel mélangé.
apreciables en las propiedades finales de los recubrimientos. Se ha podido reducir el VOC hasta valores de $250 \mathrm{~g} / \mathrm{lt}$, mediante la introducción de diluyentes reactivos y usando solventes fuertes como la metil amil cetona.

## Formulando Recubrimientos Para Impresion via Optimizacion-D-K.W. Chau and W.R. Kelly

JCT, 65, No. 821, 71 (June 1993)
Se properciona un método general el cual permite usar el dise'no de optimización-D como ayuda para la formulación de recubrimientos convencionales para impresión, con un conjunto dado de ingredientes. El criterio de optimización-D se revisa brevemente y se aplica al proceso de formulación.

Para estimar las propiedades de los recubrímientos se construyen modelos empleando polinomios simples. Los modelos viables pueden ayudar a los formuladores en el desarrollo y manufactura de los recubrimentos. Se describe, en detalle, el proceso de formulación de un recubrimiento actual para ilustrar el procedimiento. También se discuten algunas ventajas y limitaciones de modelar con diseños de optimización.

Influencia de la Distribucion de Tamaños de Particula del Polvo de Zinc, en Recubrimientos Base Agua, Inorganicos y Ricos en Zinc-E. Montes

JCT, 65, No. 821, 79 (June 1993)
Las nuevas regulaciones de VOC han renovado el interés en los recubrimientos inorgánicos de silicatos de zinc base agua. Seleccionando sólamente al zinc en polvo, dentro de las diferentes composiciones posibles de diámetros promedio, puede que no siempre produzca los resultados deseados.

En el rango inferior, en micras, de tamaños de partícula, los aumentos del área superficial pueden toner una influencia tremenda en las características de aplicación del producto. El área específica se convierte en un parámetro muy importante. La fracción fina de cualquier distribución normal de tamaños de partícula, es el factor predominante en las propiedades reológicas del material mezclado.

# FSCT Annual Meeting Focuses on Environmental Theme; Oceanographer Jean-Michel Cousteau to Give Keynote Address 

In keeping with the environmentally-focused theme of its Annual Meeting program, "Today's Competitive Coatings: Lean, Mean, and Green," the Federation of Societies for Coatings Technology has announced the selection of its Keynote Speaker-Jean-Michel Cousteau, Founding Director of the Cousteau Society and son of ocean explorer/ environmentalist Jacques Cousteau. The Keynote Address will be presented at Wednesday's Opening Session of the FSCT's 71st Annual Meeting in Atlanta, GA, on October 27-29.

Jean-Michel Cousteau, born in Toulon, France in 1938, has spent his life exploring the ocean aboard the research vessel Calypso. In the mid-1960's, he began organizing logistics for the televised film series, "The Undersea World of Jacques Cousteau."

Cousteau is a spokesman for the marine environment, and he communicates directly with the public through his lectures and an innovative educational field study program called "Project Ocean Search." Since 1973, the program has offered to people of all ages the opportunity to explore pristine marine environments and to participate firsthand in a Cousteau experience in marine studies.

He concentrates his efforts on public education in order to inspire in others a strong desire to protect and preserve the environment. Cousteau was elected to serve as Executive Vice President of The Cousteau Society in 1979.

A graduate of the Paris School of Architecture, Cousteau is a member of the Ordre National des Architectes, the French counterpart of the American Institute of Architects. Prominent among the design and architectural projects on which he has collaborated are artificial floating islands, six schools, a residential and recreational complex in Madagascar, and the headquarters of an advanced marine studies center in Marseille.

Instrumental in creating the plans for the development of a tropical island in the Bismarck Sea, he was selected by the Malagasy
government to participate in a national survey for the environmental protection and development of Madagascar. In 1969, he headed a team which converted a 100,000
sq. ft. section of the former ocean liner, The Queen Mary, into the Living Sea Museum in Long Beach, California.

Cousteau was a member of the selection committee for the National N A S A / A I A Space Station design competition in 1972. He is a Founding Member and Vice President of Foundation Cousteau, The Cousteau Society's sister company in France, created in 1981. He holds an honorary doctor's degree in Humane Letters from Pepperdine University in recognition of his contributions to education.

A prominent and active speaker, Cousteau has lectured to as many as 100,000 students in one year. In addition to his administrative responsibilities with The Cousteau Society, he is directing the design and development of Cousteau Ocean Centers, worldwide public attractions with the ocean as a central theme. He served as Executive Producer for the film entitled "Jacques Cousteau: The First 75 Years," for the Cousteau/Amazon film series, and for the Emmy Award-winning film, "Cousteau/Mississippi." He is currently Executive Producer and Producer of the television series, "Cousteau's Rediscovery of the World," which includes 35 hour-long television specials in addition to periodic onehour, "Special Reports" focusing on specific, timely environmental topics, such as "Outrage at Valdiz."

## Annual MeetingProgram Highlights

The basis for this year's Annual Meeting technical program theme is the understanding that success in the coatings industry, both now and in the future, belongs to those who take the lead in blending long-

## With 275 Exhibitors, FSCT's Paint Industries' Show Boasts World's Largest Coatings Exhibition

The place to be this October 27-29 is with your coatings industry colleagues in Atlanta, Georgia. More specifically, at the Georgia World Congress Center for the 58th FSCT Paint Industries' Show. With more than 8,000 attendees expected to attend from over 60 countries, this three-day event is the largest to take place worldwide.

To date, 275 exhibiting companies have reserved $98 \%$ of the available space for their displays. All the latest information on raw materials, manufacturing equipment, instrumentation, containers and filling equipment, laboratory apparatus, testing devices and services in the coatings industry will be shown in over $88,000 \mathrm{sq}$. ft. of space.

Of the current exhibitors, 16 are firstyear participants: Adhesion International; Cives Recycling; Color Communications

Inc.; CYDEC, Inc.; Georgia Pacific Resins; LaQue Center for Corrosion Technology; Ming-Zu Chemical Industries, Inc.; Rohm Tech, Inc.; Schuller Filtration; Steeltin Can Company; Coatings Laboratory, Inc.; Laidlaw Environmental Services, Inc.; Micromet Instruments, Inc.; Praxair, Inc.; Ronnigen-Petter; and U.S. Sack Company.

This internationally acclaimed show will be held concurrently with the FSCT's 71 st Annual Meeting, which will feature programming geared to the theme, "Today's Competitive Coatings: Lean, Mean, and Green."

Anyone involved in the coatings field, from raw materials and equipment suppliers, to the end users, will find something of interest as the FSCT Paint Industries' Show comes to Atlanta!
term profitability, coatings performance, and environmental protection. The theme recognizes these goals in the terms:

LEAN: as in cost effective; process efficient; and waste free;

MEAN: by being consistent; tough; durable; and resistant; and

GREEN: through being environmentally friendly; renewable; recyclable; and safe.

The following program session themes are being developed:

- Advanced Topics in Coatings Research
- Latex Technology
- Environmental Affairs Lean, Mean, Green and CLEANInnovative Equipment Cleaning Techniques
- Environmentally Compatible Corrosion Inhibitive Coatings
- Radiation Curing
- Characterization of Physical Properties of Coatings
- Roon Competition Papers
- International Papers
- APJ/Voss Award (FSCT Constituent Society) Competition Papers
Papers presented at the event will cover the previously mentioned topics and also include the following: powder coatings, adhesion, organic pigments, UV-curable coatings, low VOC coatings, formulating, highsolids coatings, and additives.


## 1993 FSCT Annual Meeting to Feature Poster Session

The 1993 FSCT Annual Meeting and Paint Industries' Show will feature a Poster Session as part of the technical programming. The announcement was made by Cliff Schoff, Chairman of the 1993 Annual Meeting Program Committee. The session will be held on Thursday, October 28, in a specially designated area on the main exhibit floor.

The poster session is designed to give individuals who are actively involved in coatings research a forum. It will allow each participant to display posters of the work and make brief presentations on the project. The purpose of the session is to provide a non-commercial arena for new ideas, new techniques, preliminary results, work that is significant but not ready for full publication, results or ideas that do not fit normal publication criteria, etc.

The session will again offer cash awards for the best poster displays. The amounts for 1993 are:

First Prize-\$300; Second Prize - $\$ 200$; Third Prize - $\$ 100$.

The projects will be judged on the following: originality/novelty, scientific content, and quality of display. Participation in the Poster Session is at the discretion of the Annual Meeting Program Committee.

Posters will be displayed on Thursday, October 28, from 9:00 am to 5:00 pm and authors are scheduled to be present from 9:00 am to 11:00 am and from 3:00 pm until 5:00 pm for judging. Each participant will be provided with a display board for the session.

The deadline for entry into the competition is July 31, 1993 and all interested parties should contact Ronda Miles, Chair of the Poster Session Subcommittee, Union Carbide Corp., UES Division, 2326 Lonnecker Dr., Garland, TX 75041, (214) 864-6011.

In addition, the Annual Meeting again will feature a Poster Session, scheduled to be displayed on Thursday, October 28, from 9:00 am to $5: 00 \mathrm{pm}$. (See related article above.)

## FSCT Annual Meeting Guest Activities

Guest activities begin on Wednesday, October 27, with a Welcome Social at the Marriott Marquis.

On Thursday, following a continental breakfast in the Marriott Marquis, registered guests will depart on deluxe motor coaches for a visit to Stone Mountain Park which features the world's largest mass of exposed granite. There, guests will stop at Memorial Hall for a view of the Confederate Memorial-a carving in the granite of Robert E . Lee, Stonewall Jackson, and Jefferson Davis. The carving, even bigger than Mount Rushmore, is the largest work of sculptured art in existence. Guests will have the opportunity to tour the park's authentic antebellum plantation featuring 20 structures dating between 1780 and 1880 .

From Stone Mountain, guests will board the mo-
tor coaches for the Georgia Freight Depot, a historical building in Atlanta featured in the scenes from the movie "Gone with the Wind." There, a delicious lunch will be served.

After lunch, guests will visit Underground Atlanta, a unique underground shopping district boasting retail shops and restaurants.

Highlighting the technical program will be the Mattiello Memorial Lecture scheduled for Friday morning.

## Hotel Reservations

Eight hotels have reserved blocks of rooms for this event. The Atlanta Marriott Marquis, located in the city's Peachtree Center, will serve as the headquarters hotel. Other hotels include the Hyatt Regency Atlanta, the Westin Peachtree Plaza, Atlanta Hilton and Towers, the Omni Hotel at CNN Center, the Radisson Hotel Atlanta, the RitzCarlton Atlanta and the Comfort Inn. All reservations will be processed through the FSCT Housing Bureau of the Atlanta Convention and Visitors Bureau, using the FSCT Reservation Form. Brochures containing these forms and information regarding hotel accommodations have been mailed to all members, and are included in this issue.

## Airline Information

The Federation's Travel Desk has negotiated reduced rates on Delta and Continental Air Lines. Continental is also offering convention discounts on international flights. To make your transportation arrangements to the Paint Show, you may use the FSCT Official Travel Agency or contact the airline directly.

FSCT Travel Desk: 1-800-448-FSCT
Delta: 1-800-241-6760
(reference file \# U0235)
Continental: 1-800-468-7022
(reference file \#ZJA35).
Please note that for each airline, certain restrictions apply.

# Latest in CD-ROM Technology to Assist Coatings Industry, as FSCT and NPCA Introduce Coatings MSDS System 


#### Abstract

The FSCT and the Technical Committee of the Chicago Society, in cooperation with the National Paint \& Coatings Association, are developing the Coatings MSDS System for paint and coatings manufacturers. The Coatings MSDS System uses the latest in compact disc technology (CD-ROM) to compile an ever-expanding data base of the MSDSs used by the Coatings Industry.


## The Coatings MSDS System

- Fills the need for a simple, durable, and accessible storage system using the latest in CD-ROM technology.
- Is fully accepted by the U.S. Government for data storage-MSDSs are input, optically or electronically, onto the CD-ROM (Compact Disc-Read Only Memory) which cannot be altered in any way.

The FSCT is in the initial stages of production of the Coatings MSDS System on CD-ROM and is now accumulating MSDS from raw material suppliers. The System is anticipated to be available at the FSCTAnnual Meeting and Paint Industries' Show, to be held in Atlanta, GA, on October 27-29.

In addition, the FSCT is currently discussing with the National Paint \& Coatings Association the possibility of including NPCA's Raw Material Index on the CDROM, which should provide an additional value to the industry.

## Raw Materials Supplier Participation

Material Safety Data Sheets for all of the raw materials used by the coatings industry should be submitted. These submissions should be in electronic format that will conform to one of the following standards:

- ASCII format. (The majority of programs, e.g., Wordperfect and Microsoft Word, have the capability to save files in ASCII format.)
- The media for submission must be either a high density 3.5 diskette or Sony P6 120 MP 8 mm Video ANSI labeled tape cartridge.
- Each diskette or tape should have the following information:
- Company
- A directory printout of each diskette
- A software package used to generate the file.
A hard copy of each MSDS sheet is required. Computer file name should be located on the MSDS hard copy.

OR
Paper format is acceptable if electronic format is not feasible.

Submissions should be sent to Michele Wollheim, Operations Manager, Accu-Mem Systems, Inc., 3105 N. Wilke Rd., Suite D, Arlington Heights, IL 60004.

## CD-ROM-The Latest Advance in Computer Technology

This new technology for storing and retrieving large amounts of information is designed for use with personal computers. The sheer volume of printed information that can be stored on a CD-ROM is astounding. It would take over 1.500 standard floppy discs to match the capacity of a single CD-ROM. That's as much information as is contained on 250,000 pages of typewritten text, or a stack of paper over 20 feet high!

## New and Revised MSDSs Updated Quarterly

Available by annual subscription, updated CD-ROMs will be forwarded quarterly. The updated versions will contain all of the original MSDSs plus all new and revised MSDSs. Superseded MSDSs, while remaining on the file (as required by law), will be flagged to alert the user that they have been replaced by a more recent version.

## Organized for Easy Access

All of the information on the MSDSs comes fully indexed, making it possible to find specific items in a matter of seconds. It's this accessibility, combined with the volume of information, that makes the Coatings MSDS System so attractive. Window and menu-driven software, together with a particularly simple yet powerful search software program called Personal Librarian, included with the CD-ROM, permits the user to search for specific items or general cat-
egories. By using key words, combinations of words. or CAS number, the user can quickly and easily compile a listing of all pertinent MSDSs.

With the Coatings MSDS System, you can use the stored information directly on your computer screen, or produce a "hard copy" off your regular printer.

## Create Your Own MSDSs

You can create your own MSDSs by directly incorporating information from the MSDSs stored on the CD-ROM. Besides saving time, this means that your MSDSs will contain the identical data shown on the original MSDS.

Frequently used MSDSs may be offloaded and filed into your own PC, assuring that an up-to-date listing is maintained for each department's use.

In addition, software will include a customization feature which will allow each subscriber to code and identify MSDSs of raw materials used at their location.

## Designed for Personal Computers

The Coatings MSDS System requires an inexpensive CD-ROM drive and may be used on both IBM compatible (PC/AT 386 or greater with MS.DOS 3.3 or later, with Microsoft Windows 3.0 or later, and 2 MB of RAM) or Apple Macintosh SE/30 or Macintosh II family with 2 MB of RAM. Host adapters and SCSI interface cables are also required.

If you have any questions concerning the Coatings MSDS System, please contact Michele Wollheim at Accu-Mem (708) 6707030, or FSCT Headquarters, at (215) 9400777. For additional information, circle No. 217 on the Reader Service Card.

To see a demonstration of the Coatings MSDS System on CD-ROM, be sure to visit the FSCT Booth at the Annual Meeting \& Paint Industries' Show, October 27-29, in Atlanta!

## An Infrared Spectroscopy Atlas for the Coatings Industry



## Two Volumes-1024 Pages, Over 2500 Spectra

This revised and expanded two-volume. fourth edition contains a compilation of more than 2,500 spectra, fully indexed, of materials commonly used in the coatings industry. All spectra have been generated on high resolution Fourier Transform spectrophotometers with recorded spectral ranges covering the region between 4,000 and $400 \mathrm{~cm}^{-1}$.

Authored by experts in the field of coatings infrared analysis, the 1024-page text consists of eight fundamental and comprehensive chapters, including theory, instrumentation, IR instrumentation accessories, sample preparation, and qualitative and quantitative analysis.

A fully indexed literature survey represents the most complete bibliography published in
this type of text. It is organized into sections such as theory, general information, reviews, instrumentation, experimental techniques, compilation of spectra, quantitative analysis, coatings, polymers applications and pigment applications. Each section is in chronological order.

This handsome set is packaged in a sturdy slip case for easy shelf storage.

Also, a computerized database of all the spectra featured in the Atlas has been developed by the Nicolet Instrument Corp., in cooperation with the Federation. The Nicolet Coatings Technology Database is available at additional cost from Nicolet to assist in computer searching during quantitative infrared analysis.

# Regulatory UPDATE 

This digest of current regulatory activity pertinent to the coatings industry is published to inform readers of actions which could affect them and their firms, and is designed to provide sufficient data to enable those interested to seek additional information. Material is supplied by National Paint and Coatings Association. Washington, D.C. and edited by members of the FSCT Environmental Affairs Committee.

## Department of Labor <br> Occupational Safety and Health Administration <br> 58 FR 26590-May 4, 1993 Lead Exposure in Construction <br> Action: Interim final rule

The Occupational Safety and Health Administration (OSHA) has issued an interim final rule amending standards for occupational health and environmental controls by adding a new section containing employee protection requirements for construction workers exposed to lead ( 29 CFR part 1926).

Employers must initiate certain compliance activities if the exposure to lead is at or above the action level of 30 micrograms per cubic meter of air as an eight-hour TWA, such as biological monitoring. Additional medical examinations are required for those with elevated blood-lead levels, and upon development of signs of lead intoxication. Exposures at or above the action level also require implementation of exposure monitoring and training. If employers can show that the exposure limit is less than the action level, most requirements of the interim final rule will not apply. The rule is effective June 3, 1993.

For further information, contact James Foster, OSHA, Office of Public Affairs at (202) 219-8151.

## Department of Transportation <br> Research and Special Programs Administration 58 FR 26040-April 29, 1993 Hazardous Materials Transportation; Registration and Fee Assessment Program Action: Notice of filing requirements

All persons who offer for transportation or transport certain hazardous materials are required to file an annual registration statement and pay a fee to the Department of Transportation by July 1, 1993.

Those subject to the registration requirement include anyone who offers or transports in commerce any of the following materials:
-Any highway route-controlled quantity of a Class 7 (radioactive) material;
-More than 25 kilograms ( 55 pounds) of a Division 1.1, 1.2 , or 1.3 (explosive) material in a motor vehicle, rail car, or freight container;
-More than one liter (1.06 quarts) per package of a material extremely toxic by inhalation (Division 2.3 Hazard Zone A, or Division 6.1, Packaging Group I, Hazard Zone A);
-A hazardous material in a bulk packaging having a capacity equal to or greater than 13,248 liters ( 3,500 gallons) for liquids or gases or more than 13.24 cubic meters ( 468 cubic feet) for solids; or
-A shipment, in other than a bulk packaging, of 2,268 kilograms ( 5,000 pounds) gross weight or more of a class of hazardous materials for which placarding of a vehicle, rail car, or freight container is required for that class.
Certain other materials will become subject to the Hazardous Materials Regulations (HMR) on October 1, 1993, as a result of being identified as a marine pollutant (Docket HM-211; 57 FR 52930, November 5, 1992), or meeting new hazard classification criteria adopted under Docket HM-181 (Performance Packaging Standards; 55 FR 52402, December 21, 1990).

The 1993-94 registration year begins July 1, 1993 and ends June 30, 1994. A person subject to the registration requirement must file a statement and pay a $\$ 300$ fee on or before July 1, 1993. RSPA strongly advises registering well in advance of July 1 , so as to ensure a timely receipt of a valid 1993-94 registration number to comply with recordkeeping requirements. A registration certificate is typically mailed within three weeks of RSPA's receipt of the registration statement.

For further information, contact David Donaldson, Office of Hazardous Materials Planning and Analysis, RSPA at (202) 366-4109.

Process Safety Management-According to terms of a settlement between OSHA and unions, both employers and the contractors they hire will be responsible for ensuring that subcontractors are aware of and comply with the federal process safety standard for the chemical and petrochemical industries.

The standard, which was published in February 1992, was challenged in court by several unions that maintained it did not go far enough to protect workers safety and health, particularly in provisions addressing safety training, em-

The Regulatory Update is made available as a service to FSCT members, to assist them in making independent inquiries about matters of particular interest to them. Although all reasonable steps have been taken to ensure the reliability of the Regulatory Update, the FSCT cannot guarantee its completeness or accuracy.
ployee involvement, and mandatory safety measures needed to prevent explosions and other hazards.

The settlement clarifies that it is the responsibility of both the primary employer and general contractors to inform subcontractors of potential hazards before work begins and to ensure compliance with the process safety standard.

To obtain a copy of the complete text of the clarifications, contact the Office of Information and Consumer Affairs, Occupational Safety and Health Administration, U.S. Department of Labor, Room N-3647, 200 Constitution Avenue, N.W., Washington, D.C. 20210, (202) 523-8151.

Aboveground Storage Tanks-Rep. James Moran (D-VA) has introduced legislation that will govern aboveground storage tanks used to store regulated substances.

The Safe Aboveground Storage Tank Act of 1993 (H.R. 1360) requires owners of aboveground storage tanks used to store regulated substances (as defined under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, including petroleum and excluding hazardous wastes regulated under the Solid Waste Disposal Act) to provide state or local authorities with all relevant particulars about such tanks, including age, size, type, location, and uses.

The legislation requires the administrator of the Environmental Protection Agency (EPA) to issue notification and performance standards for such tanks and requires states to inventory all tanks containing regulated substances. The bill also directs the administrator to issue release detection, prevention, and correction regulations, including requirements for leak detection systems, reporting, closure and upgrades, as well as evidence of financial responsibility.

While owners and operators of the tanks are liable for costs, the EPA administrator or a state official will be authorized to take corrective actions to "protect human health and the environment." There are also provisions for specific actions to be taken if an owner or operator has not complied with the regulations, or cannot meet financial responsibility requirements. Other provisions include a requirement that owners and operators furnish relevant government employees with all necessary information, including allowing their facilities to be inspected and monitored. The information submitted will be subject to confidentiality laws and criminal penalties imposed for prohibited disclosure.

The bill has been referred to the House Energy and Commerce Committee, but no action has been scheduled. A similar bill, S. 588-Robb (D-VA), has been introduced in the Senate.

EPA Cabinet Status-Legislation that would elevate the Environmental Protection Agency to cabinet level passed the Senate on May 4

The Department of the Environment Act of 1993, S. 171, sponsored by Sen. John Glenn (D-OH), redesignates the Environmental Protection Agency (EPA) as the Department of the Environment. The bill encourages the Secretary of the Environment to: 1) Assist the Secretary of State in participating in international environmental protection agreements and organizations; (2) Conduct research on and develop responses
to international environmental problems; and (3) Provide assistance to foreign countries and international bodies to improve the environment.

Other provisions include the abolishment of the Council on Environmental Quality and transfers the council's functions to the Secretary; the establishment of a Bureau of Environmental Statistics and an Advisory Council on Environmental Statistics; the authorization of grants to, and contracts with, state and local governments, universities, and other organizations to assist in data collection; conflict-ofinterest disclosure requirements for persons entering into arrangements for services with the Secretary; and a required public notice when the award of a contract may result in a conflict of interest.

The bill also establishes the Commission on Improving Environmental Protection to make recommendations on the implementation of federal environmental laws to protect human health and the environment.

The legislation has been sent to the House for concurrence, but significant opposition is expected.

Indoor Air Quality-Legislation directing the EPA administrator to establish a national research, development, and demonstration program to "assure the quality of indoor air," has been formally introduced by Sen. George Mitchell (D-ME).

The Indoor Air Quality Act of 1993 (S. 656) requires the administrator to report to the Congress on issues related to chemical sensitivity disorders, and to publish and biennially revise a list of contaminants known to occur in indoor air at levels expected to cause adverse health effects. The administrator would also be required to develop and publish a national indoor air quality response plan to reduce human exposure to listed indoor air pollutants and attain contaminant levels protective of human health. Additionally, the legislation mandates the creation of two new entities. An Office of Indoor Air Quality would be established to implement various agency responsibilities, and a Council on Indoor Air Quality to coordinate federal indoor air quality activities. The bill would also repeal Title IV of the Superfund Amendments and Reauthorization Act of 1986 concerning radon and indoor air quality research.

Under the bill, the Director of the National Institute of Occupational Safety and Health (NIOSH) would be required to develop a course to provide training in: (1) ventilation system operation and maintenance; (2) maintenance of records concerning indoor air quality; and (3) the identification of health threats posed by indoor air pollutants and options for reducing exposure to contaminants. NIOSH would also be responsible for implementing a Building Assessment Demonstration Program to support the development of methods for assessing indoor air contamination in non-residential, non-industrial buildings and to provide contamination reduction assistance and guidance to building owners and occupants.

A hearing before the Environment and Public Works Subcommittee on Clean Air and Nuclear Regulation is scheduled for May 25. Rep. Joseph Kennedy (D-MA) has introduced an indoor air quality bill (H.R. 1950) in the House.

## States Proposed Legislation and Regulations

## Alabama

Soybean Ink—AL S. 379 (Foshee), among other things, provides for the use of soybean based inks as an alternative to hazardous material based inks. The bill was reported with
substitute from the Senate Committee on Commerce, Transportation and Utilities on April 22.

Storm Water-AL S. 582 (Ellis) authorizes the governing bodies of counties and municipalities within the state to
establish intercooperative public corporations for efficient compliance with applicable federal and state laws and rules and regulations relating to the Federal Clean Air Act, which governs storm water discharge and the control of pollutants in storm water discharges; authorizes the counties and municipalities to levy and collect taxes and fees. The bill was reported favorably from the Senate Committee on Energy and Natural Resources.

## California

Lead (Litigation)—The California Paint Council (CPC) and the National Paint and Coatings Association (NPCA), and two paint manufacturing companies have filed a lawsuit in a California Superior Court challenging the legality of "fees" assessed on distributors of architectural coatings to pay for a lead screening program. Asserting, among other things, that the "fees" authorized by the childhood Lead Poisoning Prevention Act of 1991 are invalid because they are actually a tax passed in violation of the state's constitution and Proposition 13, the paint industry plaintiffs filed their suit on April 29, 1993 in an effort to obtain a temporary restraining order against further collecting of the "fees."

A hearing the next day in the case of California Paint Council v. State Department of Health Services (CPC v. $D H S$ ) resulted in the industry's request for a temporary restraining order being denied, although a hearing on a preliminary injunction, which could also temporarily prevent the collection of the "fees", was set for May 17, 1993. The temporary restraining order was denied by the court because, in spite of a showing of serious financial harm by many industry members, the court concluded that the harm would not be "irreparable," as is required in order to grant a temporary restraining order. A showing of irreparable harm will also be required to win a preliminary injunction at the May 17th hearing.

CPC and NPCA members inside and outside of California will be asked to help fund the legal action. Because the outcome of this litigation will influence future legislative and regulatory activities concerning lead, all members are strongly encouraged to respond to CPC's and NPCA's request for contributions. Non-members, suppliers, allied industries, and other interested parties will also be asked to contribute.

Additionally, while two paint manufacturers are currently named as plaintiffs in the suit, the CPC is hoping to attract additional parties as named plaintiffs. Companies that have experienced serious financial difficulty as a result of the "fees" are especially encouraged to consider participating as a named plaintiff. Companies interested in becoming plaintiffs should contact the California Paint Council as soon as possible. There are no additional costs associated with becoming named plaintiffs.

Now that the case has been filed, additional methods for bolstering the industry's chances for success are being explored. One option being considered is to have paint manufacturing companies and distributors request a refund for the full amount of the "fees" they have paid on the grounds that the "fees" were illegally assessed. When the claims are denied by the State Board of Equalization, the complaint in $C P C$ v. DHS could be amended to include an appeal of those denials. Because there are specific statutory requirements in connection with filing such claims, the CPC is in the process of preparing the model claim form to be used by industry members in making their claims for refund. It is important that the claim for refund filed by individual companies include the proper allegations, arguments, and citations to applicable code sections and case law, since the appeal of the denials will be based on these claims. Therefore, the Califor-
nia Paint Council and NPCA urges all members to contact CPC before submitting any claim for refund to the State Board of Equalization.

For additional information, please contact CPC's Matt Dustin at (916) 443-5095 or NPCA's David Lloyd at (202) 462-6272.

Graffiti-CA A. 169 (Horcher) provides that every person who maliciously sprays, scratches, writes on, or otherwise defaces any real or personal property with paint or any other liquid is punishable as a misdemeanor or felony depending on the amount of the defacement, damage, or destruction. Provides that in addition to the penalty that may be imposed for a misdemeanor violation, a person violating these offenses may be required to perform community service of at least 100 hours. The bill was heard in the Assembly Committee on Public Safety on May 4, with no further action.

CA A. 839 (Baca) authorizes the furnishing of aerosol containers of paint or related substances for use in schoolrelated activities that are part of the instructional program when used under controlled and supervised situations within the classroom or on the site of a supervised project. The bill was released from the Assembly Committee on Public Safety on May 4 and is in the Committee on Ways and Means.

CA A. 1530 (Caldera) provides in the case of a person who maliciously defaces with paint or any other liquid, damages or destroys any real or personal property not his or her own, that the burden of proof to raise a reasonable doubt that the property was that of the accused or that the act was done with the consent of the owner shall be upon the person charged with committing a violation of these premises. The bill was heard in the Assembly Committee on Public Safety on May 4, with no further action.

CA A. 1179 (Epple) makes it a misdemeanor or a felony for a person having been convicted of maliciously defacing, with paint or other liquid, damaging, or destroying any real or personal property not his or her own and having served a term therefore in any penal institution or having been imprisoned therein as a condition of probation for that offense, to be subsequently convicted of that offense. The bill, aimed at repeat offenders, was released from the Assembly Committee on Public Safety on May 4 and is in the Committee on Ways and Means.

CA A. 2297 (Umberg) creates the Graffiti Abatement and Apprehension Matching Fund for allocation on a matching basis by the Controller to Alameda, Orange, and Riverside Counties, and the bill appropriates a specified sum from the General Fund to that fund. States that there are unique circumstances requiring special legislation. On April 12, the bill was amended and re-referred to the Assembly Committee on Public Safety.

CA S. 375 (Hill) provides that every retailer selling or offering for sale, in this state, aerosol containers of paint capable of defacing property shall keep or display the containers in an area inaccessible to the consumer. Provides that the retailer, or his or her representative, shall make an aerosol container of paint accessible to consumer only upon request of the consumer. On April 22, the bill was amended and re-referred to the Senate Committee on Judiciary.

CA S. 527 (Presley) defines "maintain" and "maintenance," for purposes of the Landscaping and Lighting Act, to specifically include cleaning, sandblasting, and painting of improvements to remove or cover graffiti. Declares that it is to take effect immediately as an urgency statute. The bill passed the Senate on April 29 and was sent to the Assembly.

Hazardous Materials Transportation (Regulation)-The California Department of Toxic Substances Control has adopted rules establishing a fee structure for surface trans-
porters of hazardous materials (motor carriers and railroads), to provide revenue for the Railroad Accident Prevention and Immediate Deployment (RAPID) Force. For further information, contact Kathie Schievelbein at (916) 324-9933 or Ann Spivey at (916) 322-8676, at the Department of Toxic Substances Control, Sacramento, CA.

## Colorado

Hazardous Waste (Regulation)-The Colorado Department of Health, Division of Waste Management, Hazardous Waste Commission has proposed to amend its hazardous waste regulations concerning wood preserving and toxicity characteristics by incorporating federal regulations by reference. For further information, contact Karen Osthus, Hazardous Waste Commission, Department of Health at (303) 692-3321.

Air Quality (Regulation)-The Colorado Department of Health, Air Quality Control Commission has proposed to adopt by reference and incorporation in the regulations on emissions of volatile organic compounds, the following federal documents: "Recordkeeping Guidance Document for Surface Coating Operations and the Graphic Arts Industry; Procedure for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings; Control of Perchloroethylene Dry Cleaning Systems; A Guideline for Graphic Arts Calculations; and Control of Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems. There will be a hearing on the proposal on June 24, 1993, and the comment deadline is July 2, 1993. For further information, contact Joseph Palomba, Jr., Technical Secretary, Air Quality Control Commission at (303) 6923180.

Storm Water (Regulation)-The Colorado Department of Health has proposed amendments to the water quality program to meet federal storm water permit requirements. For further information, contact the Water Quality Division at (303) 692-3520.

## Connecticut

Lead-CT H. 6816 (Committee on Public Health) concerns financial assistance for lead abatement activities in residential structures. The bill was reported with a substitute from the Joint Committee on Public Health on April 15 and was referred to the Joint Committee on Judiciary.

## Florida

Hazardous Waste (Regulation)-The Florida Department of Revenue has proposed regulations that would provide definitions of terms used in the advance disposal fee program; impose an advance disposal fee on the retail sale of certain containers beginning July 7, 1993; and provide guidelines to dealers, recycling centers, and consumers regarding the imposition of the advance disposal fee program. For further information, contact Charles B. Strausser, Bureau of Technical Assistance and Training, Department of Revenue, Tallahassee, FL.

Air Quality (Regulation)-The Department of Environmental Regulation has proposed to include in the Florida air quality program a number of federal "new source performance standards" (NSPS), some of which may affect emission controls for paint manufacturing facilities when they are built or modified. Additionally, the state proposed to adopt a number of EPA's air quality testing procedures. For further information, contact the Division of Air Resource Management at (904) 488-1344.

## Illinois

Lead-IL H. 1060 (Turner) provides that Housing Authority may make loans for lead hazard abatement. The bill passed the House with amendments on April 28 and was sent to the Senate.

Lead (Regulation)-The Illinois Department of Public Aid has adopted rules that comply with the Lead Poisoning Prevention Act; provide for the diagnostic procedure and blood lead screening for children between six months and six years of age, at intervals prescribed by the American Academy of Pediatric Guidelines. For further information, contact Joanne Jones, Bureau of Rules and Regulations, Department of Public Aid, Springfield, IL.

The Illinois Department of Public Health has proposed rules that specify criteria to be used by physicians and health care providers in screening children for lead poisoning. For further information, contact Gail DeVito, Division of Governmental Affairs, Department of Public Health, Springfield, IL.

Automotive Paint-IL H. 2065 (Morrow) amends the EPA Act; provides that no person may buy any toxic auto paint unless they have a hazardous waste generator identification number and present evidence of that to the seller. The bill passed the House on April 27 and was sent to the Senate.

Note-As passed, the legislation was heavily amended resulting in a "shell" bill, i.e., it has no specific provisions. The Illinois Paint Council has worked on this bill.

## Indiana

Hazardous Materials Transportation-IN S. 295 (Weatherwax) adds the safety and maintenance requirements for containers used to transport hazardous materials to the list of Federal Regulations enforced in Indiana. The bill was signed by the Governor on April 27.

## Iowa

Lead-IA S. 333 (Committee on Environment and Energy Utilities) relates to lead abatement by establishing a lead inspection and abatement program, and provides a penalty. The bill is in the Senate Committee on Environmental and Energy Utilities. sources.

Toxics-in-Packaging (Regulation)_The Iowa Environmental Protection Commission has proposed rules to implement state law that calls for the reduction of toxics in packaging waste by eliminating the additions of heavy metals such as lead, cadmium, mercury, and hexavalent chromium in packaging and packaging components. For further information, contact Reza Khosravi, Waste Management Assistance Division, Department of Natural Resources, Des Moines, IA.

## Louisiana

Lead-1993 LA H. 1978 (Carter) relates to lead abatement; creates the Louisiana Abatement Commission within the Department of Health and Hospitals; provides for its membership; sets forth its duties and responsibilities; provides with respect to certification, training, and licensing of persons engaged in environmental lead reduction; provides penalties for violations of rules or statutes relevant to environmental lead; provides for related matters. The bill was introduced on April 12 and referred to the House Committee on Health and Welfare.

LA S. 427 (Cravins) relates to environmental health; provides for lead abatement; provides for lead hazard reduction; provides for technician licensure and certification; pro-
vides for the promulgation of rules and regulations no less stringent than federal law; provides for funding. The bill passed the Senate on April 28 and was referred to the House Committee on Health and Welfare.

## Maine

Environmental Marketing (Regulation)-The Maine Waste Management Agency has proposed standards for the voluntary use of a recycling emblem and the terms, "reusable," "recyclable," "recycled," and "recycled content." For further information, contact Denise Lord, Waste Management Agency at (207) 287-5300.

## Maryland

Air Quality (Regulation)-The Department of Environment has issued in final form regulations that meet the new source review requirements of the Federal Clean Air Act Amendments of 1990 and that extend throughout the state "reasonably available control technology" requirements, including those that involve surface coating processes. For further information, contact Dorothy Guy, Air Management Administration at (410) 631-3240.

## Massachusetts

Hazardous Materials Transportation (Regulation)-The Massachusetts Board of Fire Prevention Regulations has adopted regulations concerning the transportation of flammable liquids, tanks, and containers. For further information, contact the Board of Fire Prevention Regulations, Boston, MA.

Lead (Regulation)-The Massachusetts Department of Public Health has proposed regulations that would establish a framework to allow the use of a new technology, encapsulation, for lead paint abatement. For further information, contact Roy Petre, Childhood Lead Poisoning Prevention Program, Jamaica Plain, MA at (617) 522-3700.

## Michigan

Aboveground Storage Tanks (Regulation)-The Michigan Department of Natural Resources has proposed rules listing the definitions and standards of compliance for aboveground tanks and containers; includes contingency plans and defines hazardous waste. For further information, contact the Department of Natural Resources, Waste Management Division, Lansing, MI.

Air Quality (Regulation)-The Michigan Air Pollution Control Commission has proposed several amendments to the Michigan air quality program, including those that would allow nitrogen oxide emissions reductions to serve as offsets for new construction of facilities emitting volatile organic compounds. Also proposed are exemptions from the new source review program for certain changes to surface coating operations. For further information, contact the Air Quality Division at (517) 373-7023.

## Minnesota

Lead-MN H. 1569 (Clark) specifies allowable disposal of residential lead paint waste, as defined to exclude waste removed with chemical strippers or waste mixed with water and containing free liquid, allows disposal in a variety of land disposal facilities meeting state requirements; makes persons whose activities produce such wastes responsible for them; requires non-residents who produce such waste to remove them and retain responsibility. The bill is in the House Committee on Health and Human Services.

Air Quality (Regulation)-The Minnesota Pollution Control Agency has proposed regulations that incorporate federal standards pertaining to pretest and reporting requirements as they relate to conducting air quality tests. For further information, contact the Division of Air Quality at (612) 296-7331.

## Missouri

Toxics-in-Packaging-MO S. 100 (Goode) prohibits the selling of packages, packing material, or components containing specified concentrations of lead, cadmium, mercury, or hexavalent chromium. The bill passed the Senate in March and is currently in the House Committee on Budget.

## New Hampshire

Lead-NH S. 231 (Shaheen) relates to lead poisoning and control and continually appropriates a fund to the Director of Public Health Services; concerns lead paint laws. The bill passed the Senate on April 15. It was reported from the House Committee on Executive Departments and Administration on May 7.

## New Jersey

Hazardous Materials Transportation (Regulation)-The New Jersey Department of Transportation is proposing to revise and update the regulations implementing the Hazardous Materials Transportation Uniform Safety Act of 1990 in the areas of shipping, packaging, marking, labeling, placarding, handling, and transportation of hazardous materials. For further information, contact Charles Meyers, Bureau of Policy and Legislative Analysis, Department of Transportation, Trenton, NJ.

Community Right-to-Know (Regulation)-The New Jersey Department of Environmental Protection (DEP) has proposed substantial amendments to the Worker and Community Right-to-Know program. The proposed amendments, among other things, would place the burden of proof on employers to demonstrate their eligibility for exemptions, revise the program's list of hazardous substances, and in some cases, exempt from the reporting requirements facilities with less than 500 pounds of certain hazardous substances. Comments are due June 19, 1993. For further information, contact Janis Hoagland, DEP at (609) 292-0716.

## New York

Lead-NY A. 278 (Clark) increases the penalty for the failure to comply with a notice and demand for the continuance of a paint condition conducive to lead poisoning from $\$ 2,500$ to $\$ 5,000$, and mandates such penalty. The bill was released from the Assembly Committee on Codes on May 4 and was referred to the Committee on Rules.

NY A. 3357 (Silver) enacts the Public Works Environmental Lead Abatement Act; provides for regulation of activities relating to the removal of lead-based paint from public works facilities. The bill was released from the Assembly Committee on Codes on May 4 and was referred to the Committee on Ways and Means.

NY A. 5974 (Eve) makes various provisions regarding lead inspection and abatement including licensing and certification requirements; makes lead testing requirements; requires coverage for screening and diagnosis for lead by certain insurers and imposes a special 25 cent per gallon surcharge on the sale of paint. The bill was released from the Assembly Committee on Codes on May 4 and was referred to the Committee on Ways and Means.

Household Hazardous Products-NY A. 4518 (Tokasz) regulates the sale at retail of household hazardous products and provides for management and disposal of such products. The bill was released from the Assembly Committee on Codes on May 4 and is in the Committee on Ways and Means.

## Ohio

Air Quality (Regulation) -The Ohio Environmental Protection Agency has issued in final form amendments to the Ohio Air Quality Program, some of which address surface coatings process requirements. For further information, contact the Air Pollution and Solid Waste Division at (614) 6442782.

## Oregon

Lead (Regulation)-The Department of Human Resources is proposing to revise federal lead screening guidelines for children ages six months through 72 months; develops lead screening risk questionnaire to determine if a child is low or high risk for lead poisoning; questionnaire used as basis for blood lead testing. Kathy Mickenham, Office of Medical Assistance Programs, Department of Human Resources at (503) 945-6507.

## Pennsylvania

Air Quality (Regulation)-The Pennsylvania Department of Environmental Resources (DER) is seeking comments concerning proposed "reasonably available control technologies" for facilities for which EPA has not issued a "control technique guideline." For further information, contact Wick Havens, DER at (717) 787-4310.

## Rhode Island

Lead-RI S. 756 (Izzo) provides a tax credit for homeowners for residential lead removal or abatement. The bill passed the Senate on April 23 and is in the House Committee on Finance.

## Texas

Lead-TX S. 1278 (Truan) relates to the regulation of lead-related activities. The bill passed the Senate on May 3 and was sent to the House.

Solid Waste (Regulation)—The Texas Water Commission has proposed rules that relate to operational standards for solid waste land disposal sites; includes pre-operation notice; record-keeping requirements; site operating plan; fire protection; unloading of waste; access control; easements and buffer zones; landfill markers and benchmark; materials along route to site; waste in enclosed containers or enclosed vehicles accepted at Type IV landfills; disposal of special wastes; screening of deposited waste; and contaminated water discharge. For further information, contact Nancy Frank Overesch, Ground Water Protection Section, Municipal Solid Waste Division, Water Commission at (512) 463-8069.

## Utah

Hazardous Materials Transportation-The Utah Department of Transportation is proposing regulations relating to safety regulations for motor carriers transporting hazardous materials and/or hazardous wastes; updates and clarifies existing rule; incorporates changes by reference from amendments made current through February 1, 1993; includes haz-
ardous materials description; flammable liquid; elevated temperature materials; training requirements; bulk packaging for certain elevated temperature materials and certain flammable elevated temperature materials; and driver training. For further information, contact Shirleen Hancock, Department of Transportation at (801) 965-4781.

## Vermont

Lead—VT S. 30 (Ready) proposes to establish a program for training and certification of lead hazard abatement workers, to make blood lead screening and testing of children available upon request of parents; provides for inspection and testing of child care facilities; ensures that lead-based paint hazards are disclosed in the sale or lease of pre-1978 housing. The bill was sent to the Governor for signature on April 27.

## Virginia

Hazardous Waste (Regulation)-The Virginia Department of Waste Management has adopted rules that simplify and reduce the volume of Hazardous Waste Materials Regulations; enhances safety through better classification and packaging; promotes flexibility and technological innovation in packaging and reduces the need for exemption from the Hazardous Waste Materials Regulations; and facilitates international commerce. For further information, contact C . Ronald Smith, Hazardous Waste Enforcement Chief, Department of Waste Management at (804) 225-4761.

## Washington

Lead (Regulation)-The Washington Department of Health is proposing regulations that would make blood lead a reportable condition; require that the results of all blood lead tests performed in Washington be submitted to the Department of Health; establish a special lead registry; allow the department to track the extent of the lead poisoning problem; allow the Department of Labor and Industries to intervene in cases of industrial exposure of workers to lead. The rule would affect organizations testing blood samples for lead in Washington or those organizations sending samples out-of-state to be tested. Each organization would be permitted to create its own reporting format for the Department of Health's approval. For further information, contact Ann Foster, Rules Coordinator, Washington Department of Health, Olympia, WA.

## Wisconsin

Hazardous Waste (Regulation)—The Wisconsin Department of Natural Resources is proposing regulations concerning the investigation and remediation of environmental contamination at sites or facilities subject to the Environmental Repair Statute, or regulated by the Hazardous Substance Spill Statute or the Abandoned Container Statute; the rules would establish standards and procedures for responding to environmental contamination situations including the discovery and reporting of the problem, site investigation, interim action, and the design of a remedy; includes leaking underground storage tank rules (LUST), definitions of highpriority sites, and federal funding of response actions; involves solid waste, hazardous waste, and wastewater facilities. For further information, contact Darsi Foss, Bureau of Solid and Hazardous Waste Management, Department of Natural Resources, Madison, WI.

Federation of Societies for Coatings Technology

## 1993 Annual Meeting \& Paint Industries' Show

Hotel Information/Reservation Application -Advance Registration Form .


Georgia World Congress Center Wednesday, Thursday, Friday • October 27-28-29, 1993

Atlanta, Georgia

## From the President:

> The combined Annual Meeting and Paint Industries' Show, to be held at the Georgia World Congress Center, is a major educational activity of the Federation of Societies for Coatings Technology. This international coatings manufacturing industry event consists of three days of technical program sessions and exhibits, running concurrently. Registration is required for admission.

The whole world is coming to Atlanta! We expect that representatives from 60 countries will be in attendance at the Federation's 71 st Annual Meeting \& 58th Paint Industries' Show. It is recognized internationally as the coatings industry's premier showcase for both Raw Material and Equipment Suppliers and the end users. In addition, the technical sessions are unrivaled in quality and variety. And if that isn't enough, Atlanta's mild climate, ambiance and southern hospitality will delight younot to mention its wonderful array of restaurants and stores.

Together, the combination is unbeatable! Take a few minutes to review this outstanding program and make your reservations early.
Looking forward to seeing y'all in Atlanta!


Colin D. Penny
President, FSCT

## "Today's Competitive Coatings: Lean, Mean and Green"

The basis for this year's Annual Meeting Technical Program theme is the understanding that success in the coatings industry both now and in the future belongs to those who take the lead in blending long-term profitability, coatings performance and environmental protection.
The theme recognizes these goals in the terms:
LEAN, as in cost effective; process efficient; and waste free
MEAN, by being consistent; tough; durable; and resistant; and
GREEN, through being environmentally friendly; renewable; recyclable; and safe.
The following program session themes are being developed:

- Advanced Topics in Coatings Research
- Environmental Affairs
- Latex Technology
- Lean, Mean, Green and CLEAN Innovative Equipment Cleaning Techniques
- Environmentally Compatible Corrosion Inhibitive Coatings
- Radiation Curing
- Characterization of Physical Properties of Coatings
- Roon Award Competition Papers
- International Papers
- APJ/Voss Award (Society) Competition Papers

Papers presented at the event will cover the previously mentioned topics and also include the following:

- Powder Coatings
- Adhesion
- Organic Pigments
- UV-Curable Coatings
- Low VOC Coatings
- Formulating
- High-Solids Coatings
- Additives

The Keynote Address will be delivered on Wednesday morning to kick off the event. Highlighting the technical program will be the Mattiello Memorial Lecture, scheduled for Friday morning.
A Poster Session, featuring non-commercial work covering new ideas and techniques in coatings research, will be held all day Thursday.

## World's Premier Paint Show to Feature Products of Over 267 Companies

The largest coatings-related exhibition in the worldthe FSCT Paint Industries' Show-will be held in conjunction with the Annual Meeting at the Georgia World Congress Center. Over 267 supplier companies to the coatings manufacturing industry will be present to discuss their newest products and services. In over $90,000 \mathrm{sq}$. ft. of exhibits will be displayed a wide variety of raw materials, production equipment, containers and filling equipment, laboratory apparatus, and testing devices for the paint and coatings producer.

Key personnel from the top technical and sales staff of supplier companies will be on-hand to provide attendees with an opportunity to learn of the latest developments in their products and services.

Exhibit hours will be:
Wednesday, October 27 ...............12:00 Noon-5:00 p.m.
Thursday, October 28 ......................9:00 a.m.-5:00 p.m.
Friday, October 29 ................................9:00 a.m.-12:00 Noon

## Hotel Reservation Instructions

Whether you wish the value of a moderately priced hotel or the luxury of an upscale property, the choice is yours. The FSCT has arranged for convention rates at eight official Paint Show hotels. To obtain these rates, requests for accommodations must be placed through the FSCT Housing Bureau of the Atlanta Convention and Visitors Bureau, using the FSCT Housing Form. The reservation cut-off date is September 24. Send your form to the FSCT Housing Bureau for processing. Be sure to include a phone number and keep a copy of the form for your records. Phone calls and faxes will not be accepted. The Housing Bureau will mail an acknowledgment of the reservation and the hotel assigned will then forward a confirmation. Allow two weeks for receipt of acknowledgment.
All hotels require a room deposit or credit card guarantee. If a credit card number has been given, a deposit is not required. Otherwise, please send the deposit amount indicated on the hotel confirmation directly to the hotel within two weeks of receipt of confirmation.
International attendees only may fax their request on the official housing form to (404) 521-6392.
All changes/cancellations must be placed in writing to the Housing Bureau. After September 24, changes and cancellations must be made directly with the hotel.

## Participating Hotels

## Atlanta Marriott Marquis (FSCT Headquarters)

The Marriott Marquis, located in the city's Peachtree Center, features a 50 -story interior atrium and glassenclosed bubble elevators as well as an abundance of greenery and artwork. The guest rooms offer climate control, AM/FM radios, color TVs with in-room movies and sports, in-room video check-out, and a separate desk area. Concierge level guest rooms are also available. The hotel operates ten restaurants and lounges, an indoor/outdoor pool, a health club, a sauna and a shopping level.
(404) 521-0000
(Requests for rooms limited to 10 per company.)

## Hyatt Regency Atlanta

This 23-story atrium hotel includes luxury guest rooms and suites, a landscaped outdoor pool, a whirlpool, and a fully equipped health and fitness center. The Hyatt is located in Peachtree Center, just across the street from the FSCT headquarters hotel. Available are three restaurants, including Polaris,


The Marriott Marquis-FSCT Headquarters Hotel
a 327 -foot high revolving rooftop restaurant accessible by a glass elevator.
(404) 577-1234

## Westin Peachtree Plaza

The Westin Peachtree Plaza is America's tallest hotel, boasting 73 stories, three restaurants, four lounges, an indoor/outdoor pool, 24-hour room service and a fullyequipped health club.
(404) 659-1400

## Atlanta Hilton and Towers

Eight restaurants and lounges, including the four-star "Nikolai's Roof," are housed by this hotel, which also provides a fully equipped health club, tennis courts, and jogging trail. (NPCA headquarters)
(404) 659-2000

## The Omni Hotel at CNN Center

The Omni is located in downtown Atlanta, adjacent to the Omni Coliseum, the Georgia World Congress Center and the Georgia Dome. The rooms and suites feature in-room movies, complimentary HBO, hair dryers, irons and ironing boards. Eighteen-hour room service is available, Bugatti for fine Northern Italian dining, and The Cafe for traditional American fare. The Take Two Lobby Lounge offers entertainment. Health Club facilities are also available.
(404) 659-0000
(Requests for rooms limited to 10 per company.)

## The Radisson Hotel Atlanta

Guest services at this hotel include dry cleaning and laundry services, a hair salon, and gift shop. The garden setting pool, surrounded by trees, flowers, and a fountain, is covered by a sun roof. A restaurant, lounge, and fitness club are also available in the hotel.
(404) 659-6500

## Ritz-Carlton Atlanta

The only four-star, four-diamond downtown property features a small, intimate club-like atmosphere. Award-winning cuisine is served in four restaurants and lounges. A health club facility is available.
(404) 659-0400

## The Comfort Inn

The convenient location of the Comfort Inn places guests two blocks from the Georgia World Congress Center, Peachtree Center, the CNN Center, and the MARTA Rapid Transit System. The hotel offers spacious guest rooms and suites, a restaurant and lounge, and a courtyard/pool reception area.
(404) 524-5555

| Hotel Room and Suite Rates |  |  |  |
| :---: | :---: | :---: | :---: |
| Property Single | Double | 1 BR Suite | 2 BR Suite |
| Marriott Marquis* ...................................................... Concierge Level | $\begin{aligned} & \$ 146 \\ & \$ 175 \end{aligned}$ | \$450-900 | \$550-1050 |
| Hyatt Regency .............................. $\$ 128$ | \$143 | \$325-800 | \$400-875 |
| Westin Peachtree ........................... $\$ 120$ | \$135 | \$350-1150 | \$500-1350 |
| Atlanta Hilton \& Towers ................ $\$ 122$ | \$135 |  |  |
| Omni Hotel at CNN Center* .......... $\$ 139$ | \$154 | \$650-800 | \$800-950 |
| Radisson Hotel .............................. $\$ 99$ | \$115 | \$260-480 | \$365-585 |
| Ritz-Carlton ................................. $\$ 140$ | \$155 | \$385-985 | \$580-1165 |
| Comfort Inn................................... 89 | \$99 |  |  |

- A limit of 10 rooms per company will be placed at the Marriott and also at the Omni Hotel. A parlor counts as one room.


## Shuttle Service

Shuttle Bus service will be provided between the cooperating hotels and the Georgia World Congress Center.

| Route 1 |  |
| :---: | :---: |
|  | ................. Courtland Street Entrance |
| Atlanta Hilton $\qquad$ Courtland Street @ Marquis |  |
| Comfort Inn .............................................International Blvd. |  |
|  | Route 2 |
| Westin Peachtree ...........Spring Street - Motor Lobby Entrance Hyatt Regency ...............Harris Street - Clock of Five Entrance |  |
|  |  |
| Route 3 |  |
| Ritz-Carlton | Ellis Street |
| Radisson ..... | nternational Blvd. - Ballroom Entrance |

## Hours of Operation

Tuesday, October 268:00 a.m. - 6:00 p.m.
Wednesday, October 27 7:30 a.m. - 6:00 p.m.
Thursday, October 287:30 a.m. - 6:00 p.m.
Friday, October 297:30 a.m. - 3:00 p.m.


1993 fSCT Annual Meeting and Paint Industries' Show
Georgia World Congress Center, Atlanta, Georgia Wednesday, Thursday, and Friday, October 27-29, 1993

HOTEL RESERVATION FORM


Georgia World Congress Center Atlanta, GA
October 27-28-29, 1993

Housing Bureau
233 Peachtree Street, NE
Suite 2000
Atlanta, GA 30303

## HOTEL PREFERENCE

List the three hotels of your preference. First choice will be assigned if available. List other preferences to avoid delay. Requests for the Atlanta Marriott Marquis and the Omni Hotel will be limited to 10 rooms per company. The deadline is September 24.

> (1)
(2)
(3) $\qquad$

RESERVATION REQUEST

| Names of Occupants | Room Type |  | Rate | Arrival |
| :--- | :--- | :--- | :--- | :--- |
| Departure |  |  |  |  |
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For additional reservations, feel free to copy this form.

## ROOM GUARANTEE

All hotels require a room deposit or credit card guarantee. List your credit card below or send a check directly to the hotel after you receive the hotel's confirmation.

CREDIT CARD (circle type): American Express, MasterCard, or VISA

(Number)

(Expiration Date)
(Signature)

## MAIL ALL CONFIRMATIONS TO:

| Name: |  |
| :--- | :--- |
| Company: | Telephone: |
| Address: | FAX: $\quad$ |
| City/State (Province): |  |
| Country (if other than U.S.): | Zip Code (Mailing Code): |


$\qquad$ has special needs: $\qquad$

## Registration Information

The Advance Registration fees include three days of admission to the Paint Industries' Show and the Opening Session, and all concurrent program sessions of the Annual Meeting. To register, simply complete the Advance Registration Form and forward it with payment to FSCT. The Advance Registration prices will be available until October 1. The form with accompanying payment must be received at FSCT by October 1. Registration options are listed below:

| Full Time | Advance | On-Site |
| :--- | :---: | :---: |
| Member........................ $\$ 75$ | $\$ 90$ |  |
| Non-member .............. $\$ 100$ | $\$ 125$ |  |
| Guest ....................... $\$ 60$ | $\$ 70$ |  |

## Method of Payment

Acceptable types of payments include checks in U.S. funds made payable to FSCT, as well as credit cards: VISA, MasterCard, and American Express. Payment is due with registration form. Forms received without payment will not be processed. Please note: if payment is made with a credit card, the form may be faxed to FSCT Headquarters Office. If faxing, please do not mail original form.
The Registration Services Area will be located at the Georgia World Congress Center and will be open over the following days and times for you to pick up your badge and registration materials.

| Day | Tim |
| :---: | :---: |
| Tues., Oct. 26 ...................... 8:00 a.m. - 5:00 p.m.Wed.-Thurs., Oct. 27-28 ......7:30 a.m. - 5:00 p.m.Fri., Oct. 29 ......................7:30 a.m. - 12 Noon |  |
|  |  |
|  |  |

On-site registration will also be available during the times noted above.

## Cancellation and Refund Policy

All cancellations must be submitted in writing to the FSCT Headquarters Office. Cancellations received by October 15 will be subject to a $\$ 10$ handling charge. A $\$ 25$ charge will apply after that date. All cash refunds will be processed after November 1. Credit card cancellations received after October 1 will not be processed until after November 1.

## Airport and City Transportation*

From Hartsfield Atlanta International Airport:
Airport Shuttle (service to downtown hotels, provided by Atlanta Airport Shuttle) is $\$ 8.00$ one way, $\$ 14.00$ round trip. The trip takes approximately 30 minutes.
Taxi Service from the airport to downtown hotels is $\$ 15.00$ for one person, $\$ 8.00$ per person with two passengers, and $\$ 6.00$ per person with three passengers in the taxi.
Public Transportation from the airport to the downtown area nearby the official hotels is available via MARTA (rapid transit). The fee is $\$ 1.00$ and the ride takes approximately 35 minutes.

[^0]
## Airline Information

Convention discounts of up to $10 \%$ on domestic flights are available from Delta and Continental Air Lines.* Continental is also offering convention discounts on international flights. To make your transportation arrangements to the Paint Show, you may use the Federation's Official Travel Agency or contact the airlines directly.

FSCT Travel Desk .....................1-800-448-FSCT
Delta. $\qquad$ . 1-800-241-6760 (ref. file \# U0235)
Continental .... 1-800-468-7022 (ref. file \# ZJA35)
*For each airline, certain restrictions apply.

## Guest Program

Guest Activities begin on Wednesday, October 27, with a Welcome Social at the Marriott Marquis.
On Thursday, following a continental breakfast in the Marriott Marquis, registered guests will depart on deluxe motorcoaches for a visit to Stone Mountain Park which features the world's largest mass of exposed granite. There, guests will stop at Memorial Hall for a view of the Confederate Memorial-a carving in the granite of Robert E. Lee, Stonewall Jackson, and Jefferson Davis. The carving, even bigger than Mount Rushmore's, is the largest work of sculptured art in existence.Guests also will have the opportunity to tour the park's authentic antebellum plantation featuring 20 structures dating between 1780 and 1880 .
From Stone Mountain, guests will board the motorcoaches for the Georgia Freight Depot, a historical building in Atlanta featured in scenes from the movie "Gone with the Wind." There, a delicious lunch will be served.
After lunch, guests will visit Underground Atlanta, a unique underground shopping district boasting retail shops and restaurants.

## Making Your Arrangements

(1) To place airline reservations, call the FSCT Travel Desk at 1-800-448-FSCT or (215) 628-2549 and mention Paint Show'93. To contact the carriers directly, call the following numbers and reference the file numbers provided:

Delta 1-800-241-6760 (ref. file \# U0235)
Continental 1-800-468-7022 (ref. file \# ZJA35)
(2) To make hotel reservations, mail your Hotel Reservations Form to the FSCT Housing Bureau. The cut-off date for reservations is September 24.
(3) Register in advance for the Annual Meeting and Paint Industries' Show by filling out the Registration Form and forwarding it to FSCT with payment. The deadline for Advance Registration is October 1.
(4) To register a spouse or guest, fill out the Guest portion of the Registration Form and provide the proper payment.
(5) Dates to keep in mind:

October 25-27-NPCA Annual Meeting, Hilton Hotel and Towers, Atlanta.
October 26-FSCT Board of Directors Meeting, 9:00 a.m., Marriott Marquis Hotel.
October 27-29-FSCT Annual Meeting \&
Paint Industries' Show, Georgia World
Congress Center.

## 1993 Advance Registration

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY ANNUAL MEETING \& PAINT INDUSTRIES' SHOW ATLANTA, GA - OCTOBER 27-29, 1993


YOUR POSITION (CHECK ONE ONLY)
KK $\square$ Management/Adm.
LL ᄀ Mfg. \& Engineering
MM $ᄀ$ Quality Control
NN ᄀ Research \& Development
PP $\square$ Technical Sales Service
QQ $\sqcap$ Sales \& Marketing
RR $ᄀ$ Consultant
SS ᄀ Educator/Student/Librarian
TT 7 Other

| C | Office Use Only |
| :---: | :---: |
|  | Auth. Code |
| U | Date Received |
|  | Amount \$ |
| V | Check No. |

Please name the Federation Society in which you are a paid-up member:

## Registration Fees:

| A FSCT Member | \$75.00 |
| :---: | :---: |
| B $\square$ Non-Member | \$100.00 |
| D - Guest | \$60.00 |
| Ga Special Fee for Retired Members | \$25.00 |
| H- Special Fee for Spouse of Retired Members | \$25.00 |

## Luncheon Tickets:

- NUMBER REQUIRED: $\qquad$ \$25.00 EACH.


## Method of Payment:

Payment is due with registration form.
Total Amount Due \$ $\qquad$
Please Check One:

- Enclosed is Check \# payable in U.S. Funds to FSCT
$\square$ Charge to the following card:
__MC
__VISA
AMEX

Card No.

Expiration Date: $\quad-\mathrm{Mo} \quad-._{\mathrm{Yr}_{r}}$

Signature (Credit card registrations only)
Please print cardholder's name

DEADLINE DATE FOR ADVANCE REGISTRATION IS OCTOBER 1. NONE WILL BE ACCEPTED AFTER THAT DATE. If paying by check, please fill out form and mail with a check in the correct amount (made payable to the FSCT) to the Federation address shown below. All checks must be payable in U.S. Funds. Any that are not will be returned. We are pleased to accept faxes on credit card charges only. A $\$ 10.00$ charge will be made for cancellations received prior to October 15. A $\$ 25.00$ charge will be made for cancellations received after that date.

492 Norristown Rd., Blue Bell, PA 19422-2350
Phone: 215-940-0777 • FAX: 215-940-0292

## 1993 PAINT INDUSTRIES' SHOW

## Current List of Exhibitors

Aceto Corp.
Adhesion International
Advanced Coating Technologies
Advanced Software Designs
Air Products \& Chemicals, Inc.
Alar Engineering Corp.
Alcan-Toyo America, Inc.
Alcoa Industrial Chemicals
Allied Signal Corp.
Alt-Chem International
American Felt \& Filter Co.
American Paint Journal Co.
Amoco Chemical Co.
ANGUS Chemical Co.
Anker Labelers USA, Inc.
Aqualon Co.
Arco Chemical Co
A.R. Arena Products, Inc.

Atlas Electric Devices Co.
Ashland Chemical Co., IC\&S Div.
Automated Filling Spec. Corp.
Aztec Catalyst Co.
B.A.G. Corp.

BASF Corp.
Blackmer Pump
Bohlin Instruments, Inc.
Brinkmann Instruments, Inc Brookfield Engineering Labs, Inc.
Brookhaven Instruments Corp.
Buckman Laboratories
Buhler Inc.
Bulk Lift International
Burgess Pigment Co
BYK-Chemie USA
BYK-Gardner, Inc
C\&E News/ACS
Cabot Corp., Cab-O-Sil \& Special Blacks Div.
Caframo Ltd.
Calgon Corp.
Cappelle Inc.
The Carborundum Co., Fibers Div. Cardolite Corp.
Cargill, Inc.
Carri-Med Americas, Inc
Carroll Scientific, Inc.
CB Mills, Div. Chicago Boiler Co.
CCP Polymers
Celite Corp.
Chemical Marketing Reporter
Chemical Week Associates
CIBA-GEIGY Corp.
Cives Recycling
The Coatings Laboratory Inc.
Coatings Magazine
Color Communications, Inc.
Color Corp. of America
Colorgen, Inc.
Colortec Associates Inc
Columbian Chemicals Co
Compliance Services, Inc.
Consolidated Research, Inc.
Cookson Pigments Inc.
Coulter Corp.
CPI Purchasing Magazine
CPS Chemical Co., Inc.
CR Minerals Corp.
Cray Valley Products
Crosfield Co.
Cuno, Inc., Process Filtration Prods. CYDEC, Inc.
CYTEC Industries

## D/L Laboratories

Daniel Products Co., Inc.
Datacolor International

Day-Glo Color Corp.
DeFelsko Corp.
Degussa Corp.
University of Detroit-Mercy
Distil-Kleen, Inc
Dominion Colour Corp.
Dow Chemical
Dow Corning Corp
Draiswerke, Inc.
Drew Industrial
Dry Branch Kaolin Co.
DSA Consulting, Inc.
Eagle Zinc Co.
Eastern Michigan University
Eastman Chemical Co.
Ebonex Corp.
ECC International
Eiger Machinery, Inc.
Elektro-Physik USA, Inc.
Elf Atochem
Elmar Worldwide
EM Industries, Inc.
Engelhard Corp.
Epworth Mfg. Co., Inc.
Etna Products, Inc., Specialty
Chemical Div.
European Coatings Journal
Exxon Chemical Co.
Fawcett Co., Inc.
Federation of Societies for Coatings Technology
Filter Specialists, Inc.
Fischer Technology Inc.
Fluid Management
FMC Div., Pharm. \& Bio. Div.
FMJ International Publications Ltd. H.B. Fuller Co.

Paul N. Gardner Co., Inc.
The BFGoodrich Co., Specialty
Polymers \& Chemicals Div.
The Goodyear Tire \& Rubber Co., Chemical Div.
Grace Davison (W.R. Grace \& Co) Guertin Polymers

## Haake Inc.

Halox Pigments
Harcros Pigments, Inc.
R.E. Hart Labs Inc

Henkel Corp., Coatings \& Inks Div. Heraeus DSET Laboratories, Inc.
Heucotech Ltd
Hilton Davis Co
Hockmeyer Equipment Co
Hoechst Celanese Corp., Pigments
Hoechst Celanese Corp., Waxes,
Lubricants \& Polymers
Horiba Instruments Inc.
J.M. Huber Corp.

Hüls America Inc.
Hunter Associates Laboratory, Inc.
Ideal Manufacturing \& Sales Corp. Industrial Finishing Magazine International Compliance Center International Resources, Inc. International Specialty Products ISP Filters, Inc.
ITT Marlow/ITT A-C Pump
SC Johnson Polymer
Journal of Coatings Technology

K-T Feldspar Corp.
Kenrich Petrochemicals, Inc
Kinetic Dispersion Corp.
Kemira, Inc.
King Industries, Inc.
KRONOS, Inc.
KTA-Tator, Inc.
Labsphere, Inc.
Laidlaw Environ. Services, Inc.
LaQue Center for Corrosion Tech.
Lawter International
Leeds \& Northrup/Microtrac Div.
Liquid Controls Corp.
The Lubrizol Corp.
Luzenac America
3M, Industrial Chemicals Prod. Div. $3 \mathrm{M} /$ Zeelan Industries, Inc.
Macbeth, Div. of Kollmorgen, Corp.
Magnesium Elektron Inc.
Malvern Instruments, Inc.
Malvern Minerals Co.
McWhorter, Inc.
The Mearl Corp.
Michelman, Inc.
Micro Powders, Inc.
Micromeritics Corp.
Micromet Instruments, Inc.
Mid-States Eng. \& Mfg.
Millipore Corp.
Mineral Pigments
Ming-Zu Chemical Ind., Ltd.
Minifibers, Inc.
Minolta Corp.
Mississippi Lime Co.
University of Missouri-Rolla
Modern Paint \& Coatings
Morehouse-Cowles Inc.
Morton International, Inc.,
Universal Color Dispersions
Mountain Minerals Co., Ltd.
Myers Engineering
Nacan Products Ltd.
National Chemical Co., Inc.
National Paint \& Coatings Assn.
Netzsch Inc.
Neupak, Inc.
New Way Packaging Machinery Inc.
Norman International
North Dakota State University
NYCO Minerals, Inc.
Obron Atlantic Corp.
Ohio Polychemical Co.
Olin Chemicals
Opticolor, Inc.
Ortech International
Pacific Micro Software Engineering
Paint \& Coatings Industry Mag.
Pen Kem Inc.
Peninsula Polymers
Perkin-Elmer
Physica USA
Pioneer Packaging Machinery, Inc.
Plastican, Inc.
Polar Minerals
Poly-Resyn, Inc.
PPG Industries, Inc., Silica Prods. PPG Industries, Inc., Spec. Chems. PQ Corp.
Praxair, Inc.
Premier Mill Corp.
Progressive Recovery, Inc.

Purity Zinc Metals Co., Ltd.
Pyosa, S.A de C.V.
Q-Panel Co.
Raabe Corp
RadTech Intl. North America
Ranbar Technology, Inc.
Reichhold Chemicals Inc.
RHEOX, Inc.
Rhone-Poulenc Inc.
Rohm and Haas Co.
Rohm Tech Inc.
Ronningen-Petter
Rosedale Products, Inc.
Charles Ross \& Son Co.
Russell Finex Inc.
Sandoz Chemicals Corp
Sanncor Industries, Inc.
Sartomer Co.
Schenectady International
Schold Machine Corp.
Schuller Filtration
SCM Chemicals
Scott Bader, Inc.
Semi-Bulk Systems, Inc
Serac, Inc.
Shamrock Technologies, Inc.
Sheen Instruments Ltd.
Shell Chemical Co.
Sherwin-Williams Co.
Shimadzu Scientific Inst., Inc. Silberline Manufacturing Co., Inc. Sino-American Pigment Systems Software 2000
Sonoco Products Co.
South Florida Test Service
Southern Clay Products, Inc.
University of Southern Mississippi Spartan Color Corp.
Specialty Minerals Inc
Startex Chemical, Inc.
Steel Structures Painting Council Steeltin Can Corp.
Sub-Tropical Testing Service
Sullivan Chemical
Sun Chemical Corp.
Systech Environmental Corp.
Taber Industries
Tego Chemie Service USA
Texaco Chemical Co.
Thiele Engineering
Troy Corp.
U.S. Silica Co.
U.S. Sack Corp

Union Carbide Corp.
Union Process Inc.
United Catalysts, Inc.
United Mineral \& Chemical Corp. United States Testing Co.

Van Waters \& Rogers Inc.
R.T. Vanderbilt Co., Inc.

Velsicol Chemical Corp.
Versa-Matic Pump Co.
Vorti-Siv Div., of M\&M Ind., Inc.
Wacker Silicones Corp.
Warren Rupp, Inc., a Unit of Idex
Wilden Pump \& Engineering Co.
Witco Corp.
X-Rite, Inc
ZENECA Biocides, Zeneca Inc.
ZENECA Resins

# David Broder and Warren Rudman to Be Speakers At NPCA Annual Meeting, in Atlanta, on Oct. 25-27 

Journalist David Broder, a syndicated newspaper columnist, national political correspondent, and Pulitzer prize-winner, is scheduled to be the Keynote Speaker at the Opening Session of the National Paint and Coatings Association's (NPCA) 106th Annual Meeting, on October 25-27, 1993, at the Atlanta Hilton \& Towers, in Atlanta, GA.

Mr. Broder's newspaper column, which has been syndicated by the Washington Post, appears in 300 newspapers across the country. He began his career as a reporter at The Daily Pantograph, in Bloomington, IL, then moved on to cover national politics at the Congressional Quarterly, The Washington Star, and The New York Times.

Mr. Broder has covered every national and major state political campaign and convention since 1960. In addition, he has written four books, including: Behind the Front Page: A Candid Look at How the News is Made; Changing of the Guard: Power and Leadership in America; The Party's Over: The Failure of Politics in America; and The Republican Establishment: The Present and Future of the G.O.P., of which he is co-author.

Mr. Broder is a native of Illinois, and earned the B.A. and M.A. Degrees from the University of Chicago.

Former Senator Warren Rudman will address the Breakfast Session during NPCA's Annual Meeting, on Wednesday October 27.

Mr. Rudman began his career in 1970, when he was appointed Attorney General of New Hampshire, and in 1975 he was elected President of the National Association of Attorney Generals. Mr. Rudman was elected to the U.S. Senate in 1980, where he served for 12 years.

During his career as a Senator, Mr. Rudman served on numerous committees and subcommittees, including Vice Chairman of the Senate Select Committee investigating the Iran-Contra affair, Chairman and Vice Chairman of the Ethics Committee, and co-author of the Gramm-RudmanHollings deficit reduction law.

He is now a partner in the international law firm Paul, Weiss, Rifkind, Wharton and Garrison. Also, Mr. Rudman is co-founder of the Concord Coalition, along with former Senator Paul Tsongas and former Commerce Secretary Peter Peterson. The coalition is a nonprofit grassroots organization aimed at
awakening the American public to the country's fiscal crisis.

Mr. Rudman is a lifelong resident of New Hampshire, and received the B.S. De-
gree from Syracuse University, and the L.L.B. Degree from Boston College Law School. In addition, he served in the U.S. Army during the Korean War.

## DuPont Mining Titanium Ore at New Deposit in Florida; New TiO 2 Technical Center Opened in Mexico

DuPont Company, Wilmington, DE, has begun mining operations at its multimillion dollar heavy minerals deposit in northeastern Florida.

The 7,200 -acre Maxville site will yield titanium ore, zircon, and staurolite. The Maxville location is on the northern extension of the Trail Ridge mining deposit where DuPont has conducted mining operations at two sections for more than 30 years. The Maxville site is expected to extend the deposit's mining operations to about 2015.

In other news, DuPont has announced the opening of a $\$ 1.3$ million Technical

Service Center in Mexico to support its TiPure titanium dioxide operation.

The center is located in Tlalnepantla, on a 500 -square meter site. The new facility is designed to serve the needs of over 200 Ti Pure customers from different industries throughout Mexico.

Heading up the service center will be Director of Operations for $\mathrm{TiO}_{2}$ Henri Irrthum.

In addition, DuPont has announced that a new titanium dioxide plant is under construction in Taiwan and is scheduled for start-up in October of this year.

## Ohio Paint Council Meets Twice; Wide Array of Issues Discussed

The National Paint and Coatings Association (NPCA), Washington, D.C., has announced that the Ohio Paint Council recently has conducted two meetings in Columbus, OH , in an effort to become a presence to members of the paint and coatings industry and representatives of Ohio legislature.

The first meeting was held on February 23 , and included discussions on the following issues: lead abatement, workers compensation statue-of-limitations extension, increased fines for solid and hazardous waste violations, and citizens' suits. Gary C. Suhadolnik, Chairman of the Senate Committee on Energy, Natural Resources and Environment was a featured guest at the group's initial meeting.

The Ohio Paint Council's second meeting was on April 20. Reports were
presented by four working subcommittees on upcoming annual legislative day, communications, and publicity. Special guests included several representatives from the Ohio Department of Health, aides to two sponsors of omnibus lead abatement legislation in the Senate and House, and Steve Sides, NPCA's Director of Health, Safety and Environment.

Serving as Chairman of the Ohio Paint Council is Mike Quinn, General Manager of Akzo Coatings, Inc.

The Ohio Paint Council is sponsored by NPCA in cooperation with the Cincinnati, Cleveland, and Toledo Paint and Coatings Associations, and the CDIC and Cleveland Societies for Coatings Technology. All members of the participating organizations are invited to attend the meetings and become active members of the Council.

## Witco Corporation Announces Major Restructuring Following Acquisition of Two Divisions from Schering AG Berlin

The Witco Corporation, New York, NY, has announced an organizational restructuring due to its recent acquisition of two divisions of Schering AG Berlin.

The changes involved both the Witco's established lines of polyurethane aqueous dispersions, surfactants, oleochemicals, and sulfonate raw materials, and the new epoxy

## Mergers \& Acquisitions...

## Bio-Lab Purchases Grow Group's AquaChem Division

Grow Group, Inc., New York, NY, has completed the previously-announced sale of certain assets and liabilities of its AquaChem Division to Bio-Lab, Inc., a subsidiary of Great Lakes Chemical Corporation.

Cash received from Bio-Lab and from certain assets retained by the Grow Group will be in excess of $\$ 20$ million. In addition, Grow is entitled to receive future payments based on a percentage of certain net revenues generated by AquaChem for an additional period

## Akzo and Harcros Chemicals Combine in Joint Additives Venture

The proposed pvc additives and related business joint venture between Akzo, in The Netherlands, and Harcros Chemicals, has been approved by the European Commission, in Brussels. The new company will be known as Akcros.

The agreement involves 12 different production sites in Europe and North America, employing approximately 1,100 people. Currently, the venture is awaiting the advice of a number of Works Councils in The Netherlands. The Akcros $50 / 50$ joint venture will begin operations as soon as advice is received and details finalized.

Akzo sites involved include Dahlem and Dueren, in Germany; Deventer and Bergen op Zoom, in The Netherlands; and a facility in New Brunswick, NJ.

## Ferro Corporation Purchases Powder Coatings Business; Agrees in Principle to Buy Italian Ceramic Operation

The ICI powder coatings business in North America and Europe has been purchased by Ferro Corporation, Cleveland, OH.

The straight cash transaction amounted to approximately $\$ 51$ million. Annual sales of the business are roughly $\$ 75$ million.

In conjunction with the acquisition, there is a one-time charge of approximately $\$ 3$ million on a pre-tax basis associated with the closing of some of Ferro's existing facilities.

In addition, Ferro has announced an agreement to purchase the Italian ceramic frit and color business from Bayer S.p.A., Milan. The deal is subject to finalization and signing of a definitive purchase agreement.

The sale includes a state-of-the-art manufacturing operation in Cannara, Italy, research laboratories in Spezzano, Italy, and a marketing and customer support facility in Fiorano, Italy.

## Shell Chemical Acquires Resins Businesses

Shell Chemical Company, Houston, TX, has completed the purchase of selective assets of Hi-Tek Inc.'s Specialty Resins Business, which produces specialty epoxy resins and curing agents.

Hi-Tek is a wholly-owned subsidiary of Rhône-Poulenc, Inc.
In other news, Shell Chemical also has completed the purchase of the epoxy curing agents and polyamide resins business of Schering Berlin Polymers Inc.

The transaction includes a manufacturing facility in Lakeland, FL.
and polyamide resin products and facility capabilities that come from its recent deal with Schering AG.

As part of the company-wide realignment, Witco has formed new business groups for its chemical and petroleum operations that reshape its domestic organization.

New groups serving the paint and coatings industry within the chemical segment are International/Europe Group, under the direction of Vice President Gerald Katz; and Oleochemicals/Surfactants Group, headed by Vice President Seymour Cohen. The Specialties Group, managed by Vice President Newton Brightwell, supplies products to the field.

A polyurethane products business unit has been established within the newly formed International/Europe Group to serve the protective coatings markets for aqueous polyurethane dispersions. This group is directed by Vice President Peter Loewrigkeit, and is supported by plants in Chicago, IL; Perth Amboy, NJ; Elbeuf, France; and Droitwich, England.

Oleochemicals and surfactants technology for the paint and coatings field has been brought together through a new markets business unit established within the Oleochemicals/Surfactants Group. Managing this unit is Vice President Michael Heath. The group's plants are located in Houston, TX; Memphis, TN; and newly acquired facilities in Germany, Spain, and the United Kingdom.

The Petroleum Specialties Group produces a line of products for making highperformance, rust-preventive coatings. This unit is managed by Vice President Thomas Pensak. The group's plants are located in Trainer and Petrolia, PA; Gretna, LA; and Scarborough, Ontario, Canada.

## Zeneca Resins Dedicates Pilot and Wastewater Plants

Zeneca Resins (formerly ICI Resins US) opened a new pilot plant and new wastewater pretreatment facility at its U.S. headquarters in Wilmington, MA.

The new pilot plant will allow Zeneca to increase small-scale production capacity.

The fully-automated wastewater pretreatment plant is a state-of-the-art facility that uses clean biotechnology to break down organic wastes with no harmful by-products generated, adjusts the pH of the effluent, and reduces emissions to below required levels.

This facility has been in full operation for 12 months, has enabled Zeneca to exceed the requirements of the Massachusetts Water Resources Authority.

# Development of a Predictive Model for the Changes in Roughness that Occurs During the Painting Process 

Phuong-Anh P. Ngo, G. Dale Cheever, and Robert A. Ottaviani<br>General Motors Corporation<br>NAO Research and Development Center*

Tadeusz Malinski<br>Oakland University ${ }^{\dagger}$


#### Abstract

A model involving surface and coating parameters was developed to relate their effects on the formation of the paint/air interface. In this investigation, the study included selective changes in coating material properties (molecular weight, percent solids, surface tension, and viscosity) in addition to the changes in substrate roughness ( $25.4,50.8$, and $76.2 \mu \mathrm{~m}$ grooves) and film thickness. The change in roughness (DELTRT) that occurred with painting was used and is defined as the difference between the initial and the final peak-tovalley roughness, Rt. The change in the topcoat roughness was expressed as a function of initial roughness (RTB), film thickness (FILM), and paint properties. It was found that the initial roughness of the substrate was the main predictor followed by the film thickness. The viscosity (VISLOSHR) was found to be the only material property which influenced the topcoat. The model that best predicts the change in roughness is:


DELTRT $=-8.48+0.81$ RTB +1.87 FILM +0.001
VISLOSHR

## INTRODUCTION

Previous research covered the physical effects of the substrate, primers, and topcoat layers on the appearance of the finished product. The roughness of the initial substrate-phosphate layer and the clearcoat thickness were found to be the most important factors influencing the final roughness and

[^1]appearance of the topcoat. It was found that subjective appearance (forced ranking: good, fair, and poor) was a function of the paint thickness and the initial substrate roughness. It was found that the $30^{\circ}$ gloss and distinction of image (DOI) optical methods gave better correlation with subjective rankings than the currently used $20^{\circ}$ gloss method. In addition, the final roughness of the paint layer was found to be a good indicator of the appearance as measured by ranking or $30^{\circ}$ gloss/DOI. ${ }^{1}$ The peak-to-valley roughness, Rt, was selected as a better predictor of appearance than the currently specified average roughness, Ra. ${ }^{1-4}$ If the initial substrate-phosphate layer has a smooth surface, the potential exists to generate a paint finish having good appearance using up to $100 \mu \mathrm{~m}$ ( 4 mils ) of primer and basecoat/clearcoat ( $\mathrm{BC} / \mathrm{CC}$ ) enamel. If the surface is coarse, good appearance

## Table 1-Percent Solids of the Coating Materials Used in the Studies

Percent Solid
High solids enamel ..... 71
High solids melamine ..... 62
p-TSA-4040 catalyst .....  41
High solids resin
(enamel + melamine + catalyst) ..... 74
Low solids enamel ..... 64
Low solids melamine ..... 53
Low solids resin (enamel + melamine) ..... 57
3M Fluorocarbon (Fluorad ${ }^{\text {® }}$ ) ..... 73

## P-A. P. NGO et al.

Table 2-Resin Viscosity With and Without Surfactant

| Substance | High Shear Rates ( $\mathrm{sec}^{-1}$ ) | Viscosity (mPa•S) |
| :---: | :---: | :---: |
| High solids without surfactant ${ }^{\text {a }}$ | .. 40-80 | 2410 |
| High solids with surfactant | ......40-80 | 2346 |
| Low solids without surfactant | .....40-80 | 1787 |
| Low solids with surfactant ..... | .....40-80 | 1495 |
| Substance | Low Shear Rates ( $\mathrm{sec}^{-1}$ ) | Viscosity (mPa.S) |
| High solids without surfactant | .......6-8 | 3207 |
| High solids with surfactant ..... | .......6-8 | 2920 |
| Low solids without surfactant | .........6-8 | 1955 |
| Low solids with surfactant .... | ........6-8 | 2731 |
| (a) 3M Fluorocarbon (Fluorad). |  |  |

cannot be generated with a normal film thickness of paint. The characteristics of the paint materials and the application process can also affect the appearance of the topcoat. Paints have a tendency to replicate the geometric patterns of the substrate. Consequently, in this investigation, the study was expanded to include selective changes in coating material properties in addition to the changes in substrate roughness. The coatings were applied in an identical manner (doctor
blade) so as to emphasize substrate and material parameters rather than application effects.

## EXPERIMENTATION

## Photo Etching

Copper substrates, $12.7 \times 38.1 \mathrm{~cm}(5 \times 15 \mathrm{in}$.), were photo-etched with ferric chloride. First, the panels were buffed to remove surface tarnish and small surface scratches and then hand abraded for a smoother finish. They were laminated with Kodak dry film photoresist, Riston ${ }^{\circledR}$, and then etched in ferric chloride at $43^{\circ} \mathrm{C}\left(109.4^{\circ} \mathrm{F}\right)$. The panels were processed for different periods of time to obtain the respective depths of 1,2 , and 3 mils $(25.4,50.8$, and $76.2 \mu \mathrm{~m}) .{ }^{5}$ Side views of the panels are shown in Figure 1.

## Percent Solids Determination

A weight determination method was used to determine the percent solids. The weight of each resin before and after baking was measured using an analytical balance. Resins were baked until they reached a constant weight. This required four hours at $135^{\circ} \mathrm{C}\left(275^{\circ} \mathrm{F}\right)$ for the low-solids resin and overnight at $173^{\circ} \mathrm{C}\left(343.3^{\circ} \mathrm{F}\right)$ for the high-solids resin. The percent solids of each resin is given in Table 1.

PHUONG-ANH P. NGO is a Project Scientist in the Polymers Department of the General Motors Corporation NAO R \& D Center. At present, she is concerned with the effects of processing, equipment, and materials on the spray process. Mrs. Ngo received the B.S. Degree from Wayne State University in 1982 and the M.S. Degree from Oakland University in 1990.
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Figure 1-Schematic representation of the different depths and widths of grooves, and their corresponding roughness values

## Viscosity Determinations

The viscosity of the resins was determined with Haake model M500 (high shear rate) and CV100 (low shear rate) viscometers. ${ }^{6}$ The viscosity at high and low shear rates was measured using spindles MVI and ZB30, respectively. Four samples, high solids and low solids with and without a 3 M fluorocarbon surfactant (Fluorad), were run at $28^{\circ} \mathrm{C}\left(82.4^{\circ} \mathrm{F}\right)$. Table 2 gives the viscosity of the resins.

## Surface Tension Measurements

The surface tension of the resins was measured using the duNuoy ring method. ${ }^{7.8}$ The surface tension, in dynes $/ \mathrm{cm}$, of the high- and low-solids acrylic enamel resins with and without the addition of the fluorocarbon surfactant are given in Table 3.

## Molecular Weight Determinations

The molecular weights of the resins were determined by gel permeation chromatography (GPC). Samples were run in THF at $35^{\circ} \mathrm{C}\left(95^{\circ} \mathrm{F}\right)$. The column set was calibrated with polystyrene standards. Table 4 summarizes the molecular weights of the resins. Figure 2 shows the GPC chromatograms of the resins.

## Resin Preparations

A total of $35 \%$ by weight of a melamine crosslinking agent was added to each of the acrylic enamel resins. A total of four samples were prepared for the study. Two samples, high and low molecular weight, were treated with $0.1 \%$ by weight of surfactant (Fluorad). The fluorocarbon surfactant altered the surface tension ${ }^{9.10}$ and viscosity of the resin.

## Coating of Substrates

The original copper sheets were cut into smaller panels, $10.2 \times 10.2 \mathrm{~cm}(4 \times 4 \mathrm{in}$.). The copper substrates were cleaned with VM\&P naptha and isopropyl alcohol and then blown dry. Panels were doctor bladed with 50.8, 76.2, and $177.8 \mu \mathrm{~m}(2,4$, and 7 mils $)$ of wet resins and then flashed overnight in the oven at $28^{\circ} \mathrm{C}\left(82.4^{\circ} \mathrm{F}\right)$. The coatings were applied in an identical manner so as to emphasize substrate

Table 3-Surface Tension of Each Acrylic Enamel Resins Using the duNuoy Ring Method

| Substance | Surface Tension (dynes/cm) |
| :---: | :---: |
| High solids without surfactant ${ }^{\text {a }}$ | .......... $31.5 \pm 0.3$ |
| High solids with surfactant .. | ............ $30.7 \pm 0.2$ |
| Low solids without surfactant. | ............. $30.8 \pm 0.3$ |
| Low solids with surfactant .... | ..............29.1 $\pm 0.8$ |
| (a) 3M Fluorocarbon (Fluorad). |  |


a.

b.

Figure 2-GPC chromatograms of: a-acrylic enamel; and bmelamine crosslinking agent

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| Table 4-Molecular Weight of Coating Materials |  |  |  |
| :---: | :---: | :---: | :---: |
| Sample $\mathbf{M N a}^{\mathbf{a}}$ | MW ${ }^{\text {b }}$ | M ${ }^{\text {c }}$ | MP ${ }^{\text {d }}$ |
| High solids melamine ........ 300 | 430 | 630 | 300 |
| High solids enamel .......... 2000 | 6000 | 12100 | 4100 |
| Low solids melamine ......... 830 | 7600 | 27000 | - ${ }^{\text {c }}$ |
| Low solids enamel ........... 3800 | 14300 | 32900 | 8700 |
| (a) $\mathrm{MN}=$ Number average molecular weight. <br> (b) $\mathrm{MW}=$ Weight average molecular weight. <br> (c) $\mathrm{MZ}=\mathrm{Z}$ average molecular weight. <br> (d) MP $=$ Peak molecular weight. <br> (e) See Figure 2. |  |  |  |

and material parameters rather than application effects. In order to prevent popping, a graduated bake was used. The substrates were baked at $51^{\circ} \mathrm{C}\left(123.8^{\circ} \mathrm{F}\right)$, and then the temperature was raised to $66^{\circ} \mathrm{C}\left(150.8^{\circ} \mathrm{F}\right)$ and finally to $121^{\circ} \mathrm{C}$ $\left(249.8^{\circ} \mathrm{F}\right)$. All substrates were baked horizontally for 30 min . The panel identification number (ID), the system used, and the film build (FILM) in micrometers ( $\mu \mathrm{m}$ ) are given in Table 5.

## Sample Preparations for Scanning Electron Microscope (SEM)

Copper samples were first cut on a table saw and then manually polished on edge with Microcut ${ }^{88} 600$-grit sand paper. The samples were cleaned thoroughly with isopropyl alcohol in an ultrasonic bath for 15 min to remove polishing debris and then blown dry with compressed air. An ISI Model DS 130 SEM was used to examine the polished samples.

## Surface Roughness Measurements

The initial and final roughnesses of the substrate were measured with a Gould 1201 Surfanalyzer. Figures $3-5$ show the surface profiles of the uncoated substrates (25.4, 50.8, and $76.2 \mu \mathrm{~m}$ deep) and the corresponding surface profiles of the same substrates after coating with $76.2 \mu \mathrm{~m}$ of resin. The surface roughness values of each panel were measured at a minimum of two areas on the panels and reported separately (Table 5).

Table 5-Panel Identification Number, the System Used, the Film Build ( $\mu \mathrm{m}$ ), Individual Initial, and Final Substrate Roughness Values ( $\mu \mathrm{m}$ ) of 36 Photoetched Copper Panels

| Panel | System | Film | Initial RT (RTB) | Final RT (RTA) | Panel | System | Film | Initial RT (RTB) | Final RT (RTA) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P1 | $\mathrm{b}^{\text {a }}$ | 78.23 | 58.47 | 10.58 | P19 | d | 36.44 | 52.61 | 11.24 |
| P1 | b | 78.23 | 59.10 | 10.42 | P19 | d | 36.44 | 51.57 | 11.91 |
| P2 | b | 64.51 | 76.80 | 13.83 | P20 | $c^{\text {d }}$ | 85.54 | 77.36 | 11.07 |
| P2 | b | 64.51 | 76.35 | 13.33 | P20 | c | 85.54 | 72.54 | 10.80 |
| P3 | $\mathrm{a}^{\text {b }}$ | 40.64 | 64.49 | 21.30 | P21 | c | 62.33 | 49.86 | 8.66 |
| P3 | a | 40.64 | 66.57 | 22.81 | P21 | c | 62.33 | 51.26 | 8.51 |
| P4 | b | 33.78 | 32.03 | 5.46 | P22 | d | 89.94 | 34.32 | 4.60 |
| P4 | b | 33.78 | 32.16 | 6.32 | P22 | d | 89.94 | 32.78 | 4.26 |
| P5 | a | 56.39 | 35.16 | 6.40 | P23 | d | 82.85 | 32.40 | 5.30 |
| P5 | a | 56.39 | 32.60 | 6.03 | P23 | d | 82.85 | 32.33 | 4.66 |
| P6 | b | 33.27 | 28.70 | 5.73 | P24 | d | 33.42 | 48.20 | 10.00 |
| P6 | b | 33.27 | 29.19 | 6.27 | P24 | d | 33.42 | 47.80 | 9.77 |
| P7 | a | 58.42 | 27.92 | 5.64 | P25 | c | 87.32 | 84.40 | 12.76 |
| P7 | a | 58.42 | 27.88 | 5.19 | P25 | c | 87.32 | 81.83 | 11.07 |
| P8 | b | 81.28 | 61.99 | 10.51 | P26 | c | 57.22 | 50.13 | 9.32 |
| P8 | b | 81.28 | 60.48 | 10.80 | P26 | c | 57.22 | 50.02 | 9.19 |
| P9 | b | 60.20 | 67.62 | 11.76 | P27 | d | 51.40 | 26.52 | 6.11 |
| P9 | b | 60.20 | 69.30 | 11.91 | P27 | d | 51.40 | 26.55 | 5.63 |
| P10 | a | 37.84 | 70.73 | 19.31 | P28 | c | 35.59 | 26.78 | 6.00 |
| P10 | a | 37.84 | 74.06 | 18.10 | P28 | c | 35.59 | 28.10 | 5.98 |
| P11 | a | 66.80 | 33.68 | 4.93 | P29 | d | 33.04 | 70.93 | 14.18 |
| P11 | a | 66.80 | 31.52 | 5.56 | P29 | d | 33.04 | 72.43 | 14.37 |
| P12 | b | 79.76 | 79.08 | 12.14 | P30 | c | 81.20 | 61.32 | 10.97 |
| P12 | b | 79.76 | 75.52 | 11.84 | P30 | c | 81.20 | 61.79 | 10.16 |
| P13 | b | 57.40 | 52.02 | 9.31 | P31 | c | 60.14 | 72.40 | 11.93 |
| P13 | b | 57.40 | 52.90 | 9.36 | P31 | c | 60.14 | 78.09 | 11.76 |
| P14 | a | 36.32 | 48.47 | 11.20 | P32 | d | 36.58 | 72.59 | 14.98 |
| P14 | a | 36.32 | 48.51 | 10.53 | P32 | d | 36.58 | 73.13 | 14.50 |
| P15 | b | 86.87 | 88.88 | 11.13 | P33 | c | 83.16 | 61.34 | 9.67 |
| P15 | b | 86.87 | 78.70 | 10.68 | P33 | c | 83.16 | 64.69 | 9.30 |
| P16 | b | 61.98 | 49.79 | 8.82 | P34 | c | 62.89 | 64.99 | 11.56 |
| P16 | b | 61.98 | 48.66 | 8.60 | P34 | c | 62.89 | 66.37 | 11.70 |
| P17 | a | 33.52 | 49.69 | 14.22 | P35 | d | 40.87 | 33.87 | 6.57 |
| P17 | a | 33.52 | 49.29 | 13.63 | P35 | d | 40.87 | 34.29 | 7.22 |
| P18 | a | 72.67 | 34.96 | 5.48 | P36 | c | 38.86 | 29.40 | 6.49 |
| P18 | a | 72.67 | 33.38 | 5.42 | P36 | c | 38.86 | 28.12 | 5.84 |
| (a) $\mathrm{b}=$ Low molecular weight resin with surfactant. <br> (b) $a=$ Low molecular weight resin without surfactant. <br> (c) $\mathrm{d}=$ High molecular weight resin with surfactant. <br> (d) $\mathrm{c}=$ High molecular weight resin without surfactant. |  |  |  |  |  |  |  |  |  |


a.

gure 3-Surface profile of uncoated and coated copper substrate with $25.4 \mu \mathrm{~m}$ deep grooves. a-uncoated substrate, RT = $32.82 \mu \mathrm{~m}$; and b-substrate with $76.2 \mu \mathrm{~m}$ of resin, RT $=5.01 \mu \mathrm{~m}$

Figure 4-Surface profile of uncoated and coated copper substrates with $50.8 \mu \mathrm{~m}$ deep grooves. a-uncoated substrate, RT $=61.93 \mu \mathrm{~m}$; and b -substrate coated with $76.2 \mu \mathrm{~m}$ of resin, RT $=9.38 \mu \mathrm{~m}$

a.

b.

a.

b.

Figure 5-Surface profile of uncoated and coated copper substrates with $76.2 \mu \mathrm{~m}$ deep grooves. a-uncoated substrate, RT $=83.92 \mu \mathrm{~m}$; and b -substrate coated with $76.2 \mu \mathrm{~m}$ of resin, RT $=10.48 \mu \mathrm{~m}$

Figure 6-SEM micrographs of uncoated substrates. a- $25.4 \mu \mathrm{~m}$ deep; b-50.8 $\mu \mathrm{m}$ deep; and c-76.2 $\mu \mathrm{m}$ deep



Figure 7-SEM micrographs of copper substrates coated with $76.2 \mu \mathrm{~m}$ resin. a-25.4 $\mu \mathrm{m}$ deep; $\mathrm{b}-50.8 \mu \mathrm{~m}$ deep; and $\mathrm{c}-76.2 \mu \mathrm{~m}$ deep

Figure 8-SEM micrographs of cross sections of uncoated substrates. a- $25.4 \mu \mathrm{~m}$ deep; b- $50.8 \mu \mathrm{~m}$ deep; and $\mathrm{c}-76.2 \mu \mathrm{~m}$ deep


## RESULTS AND DISCUSSION

In an earlier paper, ${ }^{1}$ peak-to-valley roughness, Rt, was found to be the best predictor of appearance. In this investigation, we examined the change in roughness (DELTRT), defined as the difference between the initial and the final Rt roughness, that occurred with painting. It was stated earlier that the goal of this work was to establish the principal paint properties which affect the appearance of the topcoat. This study includes selective changes in the molecular weight, the
percent solids, the surface tension, and the viscosity of the resin in addition to changes in substrate roughness and film thickness (FILM). It is desirable to develop a predictive model which expresses the change in roughness (DELTRT) as a function of these principal paint properties.

To reach this goal, we used regression analyses. Regression analyses are the most commonly used tools for mathematical model building. The resulting model, called the regression equation, takes the form

$$
Y=\beta_{0}=\beta_{1} X_{1}+\beta_{2} X_{2}+\ldots+\beta_{n} X_{n}+\varepsilon
$$



Figure 9-SEM micrographs of cross sections of copper substrates coated with 76.2 $\mu \mathrm{m}$ of high percent solids resin. a-25.4 $\mu \mathrm{m}$ deep; $b-50.8 \mu \mathrm{~m}$ deep; and $\mathrm{c}-76.2 \mu \mathrm{~m}$ deep

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Figure 10-SEM micrographs of cross sections of copper substrates coated with 76.2 $\mu \mathrm{m}$ of low percent solids resin. a- $25.4 \mu \mathrm{~m}$ deep; $\mathrm{b}-50.8 \mu \mathrm{~m}$ deep; and $\mathrm{c}-76.2 \mu \mathrm{~m}$ deep
where Y is the dependent variable (DELTRT). The Xs are the independent variables, they can be linear terms: initial roughness, film thickness, and the paint properties: molecular weight, percent solid, surface tension, and viscosity. The variables can also be square (RTB2) or interaction (F2RES, FLMRES) terms. $\beta$ are the estimated parameter or coefficient. When a successful regression has been generated, the error or residual term, $\varepsilon$, can be omitted from the equation.

The Stepwise regression was used to determine the main predictors of the best independent variables as a function of the change in roughness DELTRT. In a stepping manner, Stepwise procedure ${ }^{11}$ begins by finding the variable that produces the largest R-square. In our study, RTB was selected with R-square of 0.9872 . In the second step, the procedure finds that variable which, when added to the already chosen variable, results in the largest reduction in the residual sum of squares (or increase in R-square), RTB and FILM were the best linear predictors $(0.9940)$. And if a 3predictor model was used, RTB, FILM, and VISLOSHR (low shear viscosity) were the best linear predictors ( 0.9953 ).

Two criteria are available for defining the best regression: maximum R-Square and minimum $C(p)$ which is the measure of the total square error. For the Stepwise predictor selection criteria, R-Square should be as large as possible and $\mathrm{C}(\mathrm{p})$ should be as small as possible and still be close to $p$, the number of predictors. ${ }^{12}$ In the case under study, the combined variable predictors ( 0.996 ) gave no significant improvements in fitting the experimental data than the linear predictors $(0.995)$ alone. Also, the $\mathrm{C}(\mathrm{p})$ value (7.2) of the regression with linear terms is 6.30 times smaller than the $\mathrm{C}(\mathrm{p})(45.6)$ of the linear combined with interaction variables. Thus, the regression equation with linear independent variables is preferred over the regression with combined variables, squares, and pairwise interactions of the independent
variables. At $0.1 \%$ level of surfactant additive used in this study, the results showed it had no significant influence on the change in roughness of the topcoat.

The regression analysis for the difference between the initial and final roughnesses using linear terms consists of the initial roughness, the film thickness, and the viscosity. The predictive equation that best predicts the change in roughness is

DELTRT $=-8.48+0.81$ RTB +1.87 FILM +0.001 VISLOSHR
To demonstrate the applicability of the model, cross validation was tested. ${ }^{13}$ To cross validate, the same model was tested with missing values using multiple regression analysis. This cross-validation test was done 12 times, where six observations were removed in generating the predicting model and then used for the prediction of the six missing observations previously mentioned. It was found that the predicted values for the 36 copper substrates with all data points used for developing the model and the predicted values using the cross validation test agreed well with the observed DELTRT. Thus, the model is acceptable.

## Scanning Electron Microscopy

Figures 6-10 are SEM micrographs of the substrates, coated and uncoated. Figure 6 (a-c) shows the initial substrates with groove depths of $25.4,50.8$, and $76.2 \mu \mathrm{~m}$. Figure 7 (a-c) shows the same substrates coated with $76.2 \mu \mathrm{~m}$ resin. The replication of the grooves with $76.2 \mu \mathrm{~m}$ of resin is better defined as the depth of the grooves increases. Figure 8 (a-c) presents cross-sectional samples of the uncoated samples, and Figures 9 and $10(\mathrm{a}-\mathrm{c})$ are SEM micrographs of the coated samples with high and low percent solid resins, respectively. The separation of the resins from the substrates, which is seen in Figures 9 and 10, is believed to be caused

## DEVELOPMENT OF A PREDICTIVE MODEL

by the cutting and polishing techniques. The SEM micrographs show that the resin filled the grooves; however, the geometric patterns of the substrate are replicated in the surface of the topcoat, and the distance between the crests (width) at the top of the grooves is wider as the depth of the grooves increases. The mechanisms of these two effects are not known and would have to be established by further work.

## CONCLUSIONS

A model involving surface and coating parameters was developed to determine the formation of air/paint interfaces on substrates having grooves of $25.4,50.8$, and $76.2 \mu \mathrm{~m}$ deep. The initial roughness, film thickness, and viscosity of the resin have the most influence on the roughness of the topcoat. The results showed that the addition of $0.1 \%$ fluorocarbon surfactant did not influence the change in roughness. The resins are capable of filling the grooves; however, the geometric patterns of the substrates are replicated in the surface of the topcoat.

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Changes in Hiding During Latex Film Formation Part V: Effect of Opaque Polymer
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\begin{abstract}
In Part V of this continuing series, the Cleveland Society for Coatings Technology Technical Committee investigated how opaque polymer affects the changes in hiding of latex paints during the first hour of drying. Hiding was monitored during drying by measuring the reflectance (tristimulus Y ) every 15 sec on paints drawn down over a black substrate. Addition of opaque polymer was found to have three main effects: (1) decreased titanium dioxide efficiency due to extender dilution effects; (2) increased dry hiding in paints above critical pigment volume concentration; and (3) increased hiding by the introduction of air voids which develop within the opaque polymer. Results suggest that void formation within the opaque polymer occurred rapidly; it reduced the initial loss in hiding due to film contraction, rather than contributing to the development of dry hiding in the later stages of drying.
\end{abstract}

\section*{INTRODUCTION AND REVIEW}

In previous work, a method was developed to monitor changes in hiding during latex film formation. \({ }^{1}\) Briefly, the method consisted of making a drawdown of the test paint over a contrast ratio chart (Leneta Form 5C) with a 7-mil clearance blade (Dow Film Caster). The wet drawdown over the black portion of the chart was placed against a spacer affixed to the viewport of a computer-interfaced spectrophotometer (Spectro-Sensor II, Datacolor International). By selecting the "Long Term Drift" option, the reflectance \({ }^{2}(\mathrm{Y})\) of the
*Coatings Research Group. Inc.. 2340 Hamilton Ave., Cleveland, OH 44114.
drawdown was measured every 15 sec for 60 min . To compensate for differences in calibration associated with placement of the spacer, changes in reflectance ( \(\Delta \mathrm{Y}=\mathrm{Y}-\mathrm{Y}_{\mathrm{i}}\) ) relative to the initial reading \(\left(\mathrm{Y}_{\mathrm{i}}\right)\) were plotted as a function of dry time. Because white paints were applied to a black substrate, changes in reflectance were assumed to represent changes in hiding.

During the initial stages of drying, the coating loses hiding due to:
(1) A decrease in the difference of refractive index between pigment and surrounding medium. As the paint dries, pigment-water interfaces are replaced by pigment-polymer interfaces. Because pigment-water has a greater difference in refractive index than pigment-polymer, light scattering and, therefore, hiding decreases.
(2) An increase in optimum titanium dioxide \(\left(\mathrm{TiO}_{2}\right)\) particle size. Optimum pigment particle size for light scattering


Figure 1-The three types of drying behavior
\begin{tabular}{|c|}
\hline \multirow[t]{14}{*}{Cleveland Society 1991 Technical Committee} \\
\hline \\
\hline \\
\hline \\
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\hline \\
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\hline
\end{tabular}
is inversely proportional to the difference in refractive index between the pigment and surrounding medium. Optimum particle size of \(\mathrm{TiO}_{2}\) in water is \(0.25 \mu \mathrm{~m}\); in polymer, 0.29 \(\mu \mathrm{m}\). Because typical paint grades of \(\mathrm{TiO}_{2}\) have a mean particle size of \(0.25 \mu \mathrm{~m}\), a decrease in hiding would be expected.
(3) An increase in \(\mathrm{TiO}_{2}\) concentration. \({ }^{3.7}\) In the wet coating, \(\mathrm{TiO}_{2}\) particles are separated by a greater distance than in the dry film. Because \(\mathrm{TiO}_{2}\) hiding power decreases with increasing concentration, hiding decreases as the coating contracts during drying.


Figure 2- \(\Delta \mathbf{Y}_{\mathrm{f}}-\Delta \mathbf{Y}_{\mathrm{m}}\) as a function of PVC for three extenders
(4) Loss of hiding from the latex. As the coating dries, polymer-water interfaces are lost and hiding decreases.

As drying progresses, three distinct types of behavior are observed. If the coating is below the critical pigment volume concentration (CPVC), \({ }^{8}\) (Case I), hiding continues to decrease to a final value which is the minimum value \(\left(0>\Delta Y_{f}\right.\) \(=\Delta \mathrm{Y}_{\mathrm{m}}\) ). If the coating is slightly above CPVC (Case II), hiding will start to increase slightly after it reaches a minimum value, but the wet paint still hides better than the dry film \(\left(0>\Delta Y_{f}>\Delta Y_{m}\right)\). This increase in hiding is due to air void formation. For coatings well above CPVC (Case III),

Table 1-Test Formulas
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline \multirow[t]{2}{*}{} & \multicolumn{2}{|c|}{15\% PVC} & \multicolumn{2}{|c|}{35\% PVC} & \multicolumn{2}{|c|}{55\% PVC} \\
\hline & Pounds & Gallons & Pounds & Gallons & Pounds & Gallons \\
\hline Water & 300.00 & 35.96 & 300.00 & 35.96 & 300.00 & 35.96 \\
\hline Hydroxyethyl cellulose \({ }^{\text {a }}\)...... & ... 7.00 & 0.61 & 7.00 & 0.61 & 7.00 & 0.61 \\
\hline Dispersant, 25\% \({ }^{\text {b }}\)............... & ... 3.00 & 0.33 & 5.63 & 0.61 & 18.25 & 0.90 \\
\hline 2-Amino-2-methyl-1-propanol \({ }^{\text {c }}\). & ... 2.00 & 0.26 & 2.00 & 0.26 & 2.00 & 0.26 \\
\hline Package preservative \({ }^{\text {d }}\)........... & .. 2.00 & 0.21 & 2.00 & 0.21 & 2.00 & 0.21 \\
\hline Defoamer \({ }^{\text {c }}\) & 2.00 & 0.27 & 2.00 & 0.27 & 2.00 & 0.27 \\
\hline \(\mathrm{TiO}_{2}\), Type \(\mathrm{II}^{\mathrm{f}} . .\). & . 149.85 & 4.50 & 149.85 & 4.50 & 149.85 & 4.50 \\
\hline Calcined clay: & ...- & - & 131.40 & 6.00 & 262.80 & 12.00 \\
\hline Nonionic surfactant \({ }^{\text {h }}\). & ... 2.00 & 0.23 & 2.00 & 0.23 & 2.00 & 0.23 \\
\hline Defoamer \({ }^{\text {e }}\) & ... 2.00 & 0.27 & 2.00 & 0.27 & 2.00 & 0.27 \\
\hline Coalescent \({ }^{\text {i }}\)... & ... 14.82 & 1.88 & 11.33 & 1.43 & 7.84 & 0.99 \\
\hline PVA latex, \(55 \%\).. & . 448.96 & 49.60 & 343.32 & 37.94 & 237.68 & 26.26 \\
\hline Water ................................. & ...49.05 & 5.88 & 97.66 & 11.71 & 146.28 & 17.54 \\
\hline & 982.68 & 100.00 & 1056.19 & 100.00 & 1129.71 & 100.00 \\
\hline
\end{tabular}

Disperse first eight items at high speed. Let down with remaining items in order listed.
\begin{tabular}{lccccc} 
& \begin{tabular}{c} 
By \\
Weight
\end{tabular} & \begin{tabular}{c} 
By \\
Volume
\end{tabular} & \begin{tabular}{c} 
By \\
Weight
\end{tabular} & \begin{tabular}{c} 
By \\
volume
\end{tabular} & \begin{tabular}{c} 
By \\
Weight
\end{tabular} \\
Volume
\end{tabular}

\footnotetext{
(a) Cellosize ER-15000. Union Carbide.
(b) Tamol 731. Rohm and Haas.
(c) AMP-95. ANGUS.
(d) Nuosept 95 . Hüls.
}
(f) Ti-Pure R-900, Du Pont.
(g) Satintone No. 5. Engelhard.
(h) lepal CTA-639. Rhône-Poulenc.
(i) Texanol. Eastman.
(j) UCAR 367, Union Carbide.
\begin{tabular}{lccc}
\hline \multicolumn{4}{c}{ Table 2-Opaque Polymer Properties \({ }^{\text {a }}\)} \\
& & \\
& Opaque polymer
\end{tabular}
hiding also increases after reaching a minimum value; however, the dry film hides better than the wet paint \(\left(\Delta \mathrm{Y}_{\mathrm{f}}>0>\right.\) \(\Delta \mathrm{Y}_{\mathrm{m}}\) ). These three types of behavior are illustrated in Figure 1.

An alternative way of viewing these results is to plot \(\Delta Y_{f}\) \(-\Delta Y_{m}\), or the increase in reflectance from minimum to final value, as a function of pigment volume concentration (PVC). For paints below CPVC, \(\Delta \mathrm{Y}_{\mathrm{f}}-\Delta \mathrm{Y}_{\mathrm{m}}\) is equal to zero; for paints above CPVC, it is greater than zero and increases with increasing PVC. This type of plot appears in Figure 2 for three different oil absorption extenders.

Results can also be explained in terms of the KubelkaMunk Two-Constant theory. \({ }^{9}\) By assuming that the absorption coefficient ( K ) does not change during drying, the change in scattering coefficient ( S ) was calculated as a function of time. Thus, the quantities \(\mathrm{S}_{\mathrm{i}}, \mathrm{S}_{\mathrm{m}}\), and \(\mathrm{S}_{\mathrm{f}}\) correspond to the scattering coefficients at the initial \(\left(\mathrm{Y}_{\mathrm{i}}\right)\), minimum \(\left(\mathrm{Y}_{\mathrm{m}}\right)\), and final \(\left(Y_{f}\right)\) reflectances, respectively.

Using these quantities, a model was developed that described how the scattering coefficient changed as a function of dry time: \({ }^{10}\)
\[
\begin{equation*}
\mathrm{S}(\mathrm{t})=\mathrm{S}_{\mathrm{TiO}_{2}}+\mathrm{A}(\mathrm{t}) \mathrm{S}_{\text {space }}+\mathrm{B}(\mathrm{t}) \mathrm{S}_{\mathrm{dry}} \tag{1}
\end{equation*}
\]
where:
\(S(t)=\) scattering coefficient at time \(t\)
\(\mathrm{S}_{\mathrm{TiO}_{2}}=\) scattering coefficient of \(\mathrm{TiO}_{2}\) in the dry film
\(\mathrm{S}_{\text {space }}=\) additional scattering mainly due to the improved efficiency of \(\mathrm{TiO}_{2}\) in the wet film
\(\mathrm{S}_{\mathrm{dry}}=\) scattering due to dry hiding
The constants \(\mathrm{A}(\mathrm{t})\) and \(\mathrm{B}(\mathrm{t})\) are functions of time which describe how scattering is lost during film contraction and gained during air void formation. Initially, \(\mathrm{A}=1\) and \(\mathrm{B}=0\), reducing equation (1) to:
\[
\begin{equation*}
\mathrm{S}_{\mathrm{i}}=\mathrm{S}_{\mathrm{TiO}_{2}}+\mathrm{S}_{\text {space }} \tag{2}
\end{equation*}
\]

After the film is completely dry, \(\mathrm{A}=0, \mathrm{~B}=1\) and equation (1) becomes:
\[
\begin{equation*}
\mathrm{S}_{\mathrm{f}}=\mathrm{S}_{\mathrm{TiO}_{2}}+\mathrm{S}_{\mathrm{dry}} \tag{3}
\end{equation*}
\]

By determining \(\mathrm{A}(\mathrm{m})\) and \(\mathrm{B}(\mathrm{m})\), the value of the constants at minimum scattering, it was concluded that film contraction and air void formation do not occur during two distinct phases of drying. Rather, these processes overlap to a large extent, indicating that air void formation appears before film


Figure 3-Relation of \(\mathrm{S}_{\text {TiO }}, \mathrm{S}_{\text {space }}\) and \(\mathrm{S}_{\text {dry }}\) to change in scattering coefficient during latex film formation

Table 3-Pigment Properties \({ }^{\text {a }}\)
\begin{tabular}{|c|c|c|}
\hline Property & Type II
\(\mathrm{TiO}_{2}{ }^{\mathrm{b}}\) & Calcined clay \({ }^{\text {c }}\) \\
\hline Density, Ib/gal .............. & 33.3 & 21.9 \\
\hline Refractive index ................ & .... 2.73 & 1.62 \\
\hline Oil absorption \({ }^{\text {d }}\) & ... 16 & 85-95 \\
\hline Mean particle size, microns & ..... 0.25 & 0.8 \\
\hline G.E. brightness ............. & ... 96 & 90-92 \\
\hline
\end{tabular}
(a) As reported by manufacturer.
(b) Ti-Pure R-900, Du Pont.
(c) Satintone No. 5. Engelhard.
(d) Spatula rub-out. ASTM D 281-84.


Table 4-Dry Film Properties
\begin{tabular}{lcccccc}
\begin{tabular}{c} 
PVC \\
Extender
\end{tabular} & OP
\end{tabular}
(a) Opaque polymer.
(b) Reflectance over scaled white chart.
(b) Reflectance over c
(c) ASTM D 2805-88.
(d) ASTM D \(3258-80\).
(d) ASTM D \(3258-80\). (f) ASTM D 523-80.


Figure 4a-Contrast ratio as a function of opaque polymer PVC


Figure 4b-Decrease in reflectance after staining with K\&N Ink as a function of opaque polymer PVC
contraction is complete. These concepts are illustrated in Figure 3.

By using this model, changes in scattering coefficient during drying were related to changes in hiding for Case I, II, and III type coatings. Generally:
\[
\begin{align*}
& \text { Case I: } \quad \Delta Y_{\mathrm{f}}<0 ; \Delta \mathrm{Y}_{\mathrm{f}}=\Delta \mathrm{Y}_{\mathrm{m}}  \tag{4}\\
& \Delta Y_{f}-\Delta Y_{m}=0  \tag{5}\\
& S_{d r y}=0  \tag{6}\\
& S_{m}=S_{\mathrm{f}}  \tag{7}\\
& \text { Case II: } \quad 0>\Delta Y_{f}>\Delta Y_{m}  \tag{8}\\
& \Delta Y_{f}-\Delta Y_{m}>0  \tag{9}\\
& \mathrm{~S}_{\text {space }}>\mathrm{S}_{\text {dry }}  \tag{10}\\
& S_{\mathrm{i}}>\mathrm{S}_{\mathrm{f}}  \tag{11}\\
& \text { Case III: } \quad \Delta \mathrm{Y}_{\mathrm{f}}>0>\Delta \mathrm{Y}_{\mathrm{m}} \tag{12}
\end{align*}
\]

The Technical Committee of the Cleveland Society for Coatings Technology undertook several projects to determine what factors influence the changes in hiding during latex film formation. Part I of this series \({ }^{1}\) discussed PVC, extender pigment oil absorption, and glycol type and level; Part \(\mathrm{II}^{11}\) addressed pigment packing effects; Part III \({ }^{12}\) highlighted the effects of coalescent level, latex polymer glass transition temperature \({ }^{13}\left(\mathrm{~T}_{\mathrm{g}}\right)\), and latex particle size; and Part IV discussed the effect of film thickness, \(\mathrm{TiO}_{2}\) level, and toning. \({ }^{10}\) In Part I of this series, it was hypothesized that microvoidcontaining pigments may interfere with the developed method.' Opaque polymer is an emulsion of hollow polymer "beads" filled with water which is displaced with air upon drying. \({ }^{14}\) In effect, it imparts dry hiding to coatings even if they are below CPVC. However, this dry hiding is irreversible and should not be lost when the film is rewet. \({ }^{15}\) In this study, effects of opaque polymer level and void volume in conjunction with extender (calcined clay) PVC are investigated.

\section*{TEST PAINTS}

The starting formulations were \(30 \%\) nonvolatile by volume (NVV) interior latex flats based on a \(55 \%\) nonvolatile by weight (NVW) PVA latex and contained \(15 \%\) PVC ( 149.85 \(\mathrm{lb} / 100\) gal) ASTM D 476-84 Type II rutile \(\mathrm{TiO}_{2}\). The extender pigment levels (calcined clay) were \(0,20(131.40 \mathrm{lb})\), or \(40 \%\) PVC ( \(262.80 \mathrm{lb} / 100 \mathrm{gal}\) ) for the three formulas producing total PVCs of 15,35 , and \(55 \%\), respectively. Starting formulations appear in Table 1; properties of the \(\mathrm{TiO}_{2}\) and calcined clay pigments appear in Table 2.

For each formula, additional versions were made by adding 10,20 , or \(30 \%\) PVC of OP-0, OP-15, or OP-30. OP-0, OP-15, and OP-30 are opaque polymer emulsions of equal particle size containing approximately 0,15 , and \(30 \%\) voids-by-volume in the dry polymer. The opaque polymer emulsions were supplied by Rohm and Haas Company and reported properties appear in Table 3. In all paints, dispersant level was maintained at \(0.5 \%\) active based on total pigment weight \(\left(\mathrm{TiO}_{2}\right.\) and calcined clay) and coalescent level at \(6.0 \%\) based on latex and opaque polymer solids.


Figure 4c-Decrease in reflectance upon rewet with mineral oil as a function of opaque polymer PVC

In effect, this series represents a full factorial experimental design of three variables each at three levels: (1) extender PVCs of 0,20 , and \(40 \%\); (2) opaque polymer PVCs of 10 , 20 , and \(30 \%\); and (3) opaque polymer void volumes of 0,15 , and \(30 \%\). This produced a total of 27 paints and three nonopaque polymer-containing controls for testing.

\section*{PROCEDURE}

To characterize the paints, several common tests were performed:
(1) Contrast Ratio (ASTM D 2805-88) and Reflectance: Each paint was drawn down over a sealed black and white chart (Leneta Form 5C). The reflectance of the dry film over the black substrate is reported as a percentage of the reflectance of the film over the white substrate. Contrast ratio is a measure of film hiding. Reflectance of the film over the white substrate is also reported as a measure of overall film brightness.
(2) Change in Reflectance with Staining Medium (ASTM D 3258-80): Each paint was drawn down over a sealed white chart (Leneta Form WB) and the decrease in reflectance after the application of staining medium ( \(\mathrm{K} \& N \mathrm{~N}\) Ink) is reported. This is a measure of film porosity.


Figure 4d- \(85^{*}\) Sheen as a function of opaque polymer PVC
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline \multicolumn{7}{|c|}{Table 5-Changes in Hiding During Latex Film Formation} \\
\hline \begin{tabular}{c} 
PVC \\
\hline Extender OPa \(^{\text {a }}\)
\end{tabular} & OP type \({ }^{\text {a }}\) & Film thickness, mils & \(Y_{i}{ }^{\text {b }}\) & \(\Delta \boldsymbol{Y}_{m}{ }^{\text {c }}\) & \(\Delta \mathbf{Y}_{\text {d }}^{\text {d }}\) & \(\Delta \mathbf{Y}_{\mathbf{f}}-\Delta \mathbf{Y}_{\mathbf{m}}\) \\
\hline 0 ....................... 0 & - & 1.9 & 85.65 & -6.50 & -6.50 & 0.00 \\
\hline 0 ..................... 10 & OP-0 & 1.9 & 85.96 & -6.97 & -6.97 & 0.00 \\
\hline 0 ..................... 20 & OP-0 & 1.9 & 85.84 & -7.61 & -7.61 & 0.00 \\
\hline 0 ..................... 30 & OP-0 & 1.9 & 85.36 & -8.35 & -8.35 & 0.00 \\
\hline 0 ..................... 10 & OP-15 & 1.9 & 85.52 & -6.29 & -6.29 & 0.00 \\
\hline 0 ..................... 20 & OP-15 & 1.8 & 85.00 & -6.19 & -6.19 & 0.00 \\
\hline 0 ..................... 30 & OP-15 & 1.8 & 85.15 & -5.99 & -5.99 & 0.00 \\
\hline 0 ..................... 10 & OP-30 & 1.9 & 85.87 & -5.57 & -5.57 & 0.00 \\
\hline 0 ..................... 20 & OP-30 & 1.9 & 85.85 & -4.53 & -4.53 & 0.00 \\
\hline 0 ..................... 30 & OP-30 & 1.8 & 85.36 & -3.92 & -3.92 & 0.00 \\
\hline 20 ..................... 0 & - & 1.9 & 85.55 & -8.73 & -8.73 & 0.00 \\
\hline 20 ................... 10 & OP-0 & 1.9 & 84.54 & -8.46 & -8.36 & 0.10 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 20 ~\) & OP-0 & 1.8 & 83.97 & -5.86 & -3.37 & 2.49 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 30 ~\) & OP-0 & 1.9 & 84.69 & -4.51 & 0.04 & 4.55 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 10 ~\) & OP-15 & 1.9 & 84.99 & -7.54 & -7.44 & 0.10 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 20 ~\) & OP-15 & 1.9 & 84.43 & -5.59 & -2.31 & 3.28 \\
\hline 20 .................... 30 & OP-15 & 1.9 & 84.59 & -4.20 & 1.17 & 5.37 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 10 ~\) & OP-30 & 1.8 & 84.54 & -7.06 & -6.94 & 0.12 \\
\hline \(20 . . . . . . . . . . . . . . . . . . . ~ 20 ~\) & OP-30 & 1.9 & 84.55 & -5.51 & -1.46 & 4.05 \\
\hline 20 ................... 30 & OP-30 & 1.9 & 84.17 & -4.05 & 2.17 & 6.22 \\
\hline 40 ..................... 0 & - & 1.9 & 85.58 & -2.82 & 3.58 & 6.40 \\
\hline 40 ................... 10 & OP-0 & 1.9 & 84.93 & -2.72 & 4.67 & 7.39 \\
\hline \(40 . . . . . . . . . . . . . . . . . . . ~ 20 ~\) & OP-0 & 1.9 & 85.38 & -2.79 & 5.26 & 8.05 \\
\hline 40 .................... 30 & OP-0 & 1.9 & 85.27 & -2.75 & 5.95 & 8.70 \\
\hline 40 ................... 10 & OP-15 & 1.8 & 85.08 & -2.75 & 4.76 & 7.51 \\
\hline 40 .................... 20 & OP-15 & 1.8 & 85.33 & -2.74 & 5.56 & 8.30 \\
\hline 40 ................... 30 & OP-15 & 1.8 & 85.13 & -2.65 & 6.22 & 8.87 \\
\hline 40 ................... 10 & OP-30 & 1.9 & 85.44 & -2.96 & 4.78 & 7.74 \\
\hline 40 .................... 20 & OP-30 & 1.8 & 85.20 & -2.54 & 5.86 & 8.40 \\
\hline 40 .................... 30 & OP-30 & 1.8 & 84.78 & -2.29 & 6.66 & 8.95 \\
\hline \multicolumn{7}{|l|}{\begin{tabular}{l}
(a) Opaque polymer. \\
(b) Reflectance 60 sec after draw down. \\
(c) Reflectance at relative minimum minus \(Y\), \\
(d) Reflectance at 60 min after drawdown minus \(Y\)
\end{tabular}} \\
\hline
\end{tabular}
(3) Change in Reflectance upon Rewet with Mineral Oil: Each paint was drawn down over a sealed black chart (Leneta Form 5C) and the decrease in reflectance after application of mineral oil is reported. This is a measure of dry hiding.
(4) \(85^{\circ}\) Sheen (ASTM D 523-80): Each paint was drawn down over a sealed white chart (Leneta Form WB) and \(85^{\circ}\) sheen measured. This is a measure of overall surface roughness and is affected by, among other things, PVC and pigment particle size and oil absorption.

For each test, films were cast using a 7 -mil clearance blade (Dow Film Caster) and allowed to dry at ambient conditions for one week. Results appear in Table 4 and are graphed in Figures 4a-4d.

Changes in hiding during latex film formation were monitored for each test paint by a previously developed method \({ }^{1}\) as modified in later work to allow for the calculation of scattering coefficients. \({ }^{9}\) Briefly, a film was cast over a black substrate (Leneta Form 5C) using a 1.5 mil clearance Bird Film Applicator. A 7 -mil clearance blade was not used because this technique shows greater sensitivity at low film thickness. \({ }^{10}\) The wet drawdown was weighed so that wet film thickness could be calculated from the drawdown's area and the paint's density. All wet film thicknesses were maintained at 1.75-1.94 mils. The drawdown was positioned in the viewport of a CS-5 Chroma-Sensor spectrophotometer (Data-
color International) and, after 60 sec , changes in spectral included reflectance were measured every 15 sec for 1 hr . Initial reflectance \(\left(\mathrm{Y}_{\mathrm{i}}\right)\), change in reflectance to the minimum value \(\left(\Delta Y_{m}\right)\), change in reflectance to the final value \(\left(\Delta Y_{f}\right)\), change in reflectance from minimum to final ( \(\Delta \mathrm{Y}_{\mathrm{f}}-\Delta \mathrm{Y}_{\mathrm{m}}\) ), and wet film thickness data appear in Table 5 and are plotted as a function of opaque polymer PVC in Figures 5a-5c.

A Kubelka-Munk analysis was carried out by determining scattering and absorption coefficients on dry films rewet with mineral oil ( \(\mathrm{S}_{\text {rewet }}\) and K ). Absorption coefficients were averaged for the paints containing 0,20 , or \(40 \%\) PVC calcined clay; it was assumed that calcined clay was the major source of film toning. Using the average absorption coefficients, the initial ( \(\mathrm{S}_{\mathrm{i}}\) ), minimum ( \(\mathrm{S}_{\mathrm{m}}\) ), and final \(\left(\mathrm{S}_{\mathrm{f}}\right)\) scattering coefficients during drying were calculated for each paint.
\(\mathrm{S}_{\mathrm{i}}, \mathrm{S}_{\mathrm{m}}, \mathrm{S}_{\mathrm{f}}\), and \(\mathrm{S}_{\text {rewet }}\) were then separated into quantities defined in previous work. \({ }^{10}\) Scattering coefficients due to \(\mathrm{TiO}_{2}\) in the dry films ( \(\mathrm{S}_{\mathrm{TiO}_{2}}\) ) were assumed to be equal for paints of a given extender and opaque polymer PVC. The scattering coefficients of films containing OP-0 rewet with mineral oil were used because rewetting the films does not fill the air voids formed in OP-15 and OP-30 during drying (compare \(\mathrm{S}_{\text {rewet }}\) and \(\mathrm{S}_{\mathrm{TiO}_{2}}\) in Table 6). Scattering coefficients due to the improved spacing of \(\mathrm{TiO}_{2}\) in the wet paint ( \(\mathrm{S}_{\text {space }}\) ) were calculated using equation (2); scattering coefficients due to dry hiding ( \(\mathrm{S}_{\text {dry }}\) ) were calculated using equation (3).

Until this work, the quantity \(\mathrm{S}_{\text {dry }}\) was considered to result mainly from air void formation associated with a coating above CPVC. However, the presence of opaque polymer can contribute to this term. This effect can be calculated by defining:
\[
\begin{equation*}
\mathrm{S}_{\mathrm{OP}}=\mathrm{S}_{\mathrm{dry}}-\mathrm{S}_{\mathrm{dry}}, 0 \mathrm{OP}-0 \tag{16}
\end{equation*}
\]
where \(S_{O P}\) is the scattering coefficient due to air voids in the opaque polymer and \(\mathrm{S}_{\text {dry } . O p-0}\) is equal to \(\mathrm{S}_{\text {dry }}\) of the same paint containing voidless opaque polymer. Results of these calculations appear in Table 6; \(\mathrm{S}_{\mathrm{TiO}_{2}}\) and \(\mathrm{S}_{\text {dry }}\) are plotted as a function of opaque polymer PVC in Figures 6a and 6b, respectively.

\section*{DISCUSSION}

To ascertain the effect of extender pigment, the paints containing \(0 \%\) PVC opaque polymer should be compared. Increasing extender PVC from 0 to \(20 \%\) showed a slight decrease in contrast ratio because of extender dilution effects which decreased \(\mathrm{TiO}_{2}\) efficiency. \({ }^{16}\) A further increase to \(40 \%\) PVC of extender increased contrast ratio because of dry hiding. As expected, increasing extender PVC increased film porosity as measured by \(K \& N\) Ink and rewetting with mineral oil. Because sheen is a minimum at CPVC, \({ }^{17}\) the paint with \(20 \%\) PVC extender has the lowest sheen (it is nearest CPVC).

Changes in contrast ratio with the addition of opaque polymer can be explained by three effects:
(1) Decreased \(\mathrm{TiO}_{2}\) efficiency due to extender dilution effects;
(2) Increased dry hiding in paints above CPVC; and
(3) Increased hiding from the addition of air voids which are contained in the opaque polymer.

In the paints containing \(0 \% \mathrm{PVC}\) extender, the first effect is responsible for the decrease in contrast ratio when OP-0 is added (Figure 4a). These paints are below CPVC and dry hiding is not observed; also, OP-0 does not contain microvoids. When OP-15 is added, the increase in hiding due to introducing microvoids just balances the loss in \(\mathrm{TiO}_{2}\) efficiency. Adding OP-30 results in a net increase in hiding because of the greater hiding imparted by the larger microvoids.

In the paints containing 20 and \(40 \%\) extender, the main effect of opaque polymer addition was increased dry hiding due to a PVC increase. This was much more easily observed in the paints with \(20 \%\) PVC extender than the paints with \(40 \%\) PVC extender because the latter are much closer to complete hiding (contrast ratio is greater than \(99 \%\) ).

Addition of opaque polymer increased film porosity as measured by reflectance loss after application of K\&N Ink (Figure 4b) or mineral oil (Figure 4c). This is mainly a consequence of a PVC increase rather than an inherent property of opaque polymer. In the paint containing \(40 \%\) PVC extender, porosity appeared to decrease with the addition of \(30 \%\) PVC opaque polymer. This probably resulted from poorer film integrity; when the excess K\&N Ink or mineral oil was removed, some of the film was probably abraded away. Differences observed between OP-0, OP-15, and OP30 were minimal and probably due to differences in the relative hiding of the paints.


Figure \(5 \mathrm{a}-\Delta \mathrm{Y}_{\mathrm{m}}\) as a function of opaque polymer PVC


Figure \(5 b-\Delta \mathbf{Y}_{+}\)as a function of opaque polymer PVC


Figure \(5 c-\Delta Y_{t}-\Delta \mathbf{Y}_{m}\) as a function of opaque polymer PVC

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Again, sheen is a minimum at CPVC; any PVC change away from CPVC should increase sheen. Thus, in Figure 4d, increasing opaque polymer PVC in the paints with \(0 \%\) PVC extender decreased sheen (PVC was increasing towards CPVC) while in the paints with 20 or \(40 \%\) PVC extender, sheen increased (PVC was increasing beyond CPVC). In all cases, OP-0, OP-15, and OP-30 had a nearly identical effect on sheen, indicating that all three opaque polymers had similar oil absorptions and particle size distributions.

As with contrast ratio, OP- 0 decreased \(\Delta \mathrm{Y}_{\mathrm{m}}\) and \(\Delta \mathrm{Y}_{\mathrm{f}},{ }^{18}\) OP-15 maintained these quantities and OP-30 increased them in the paints containing \(0 \%\) PVC extender (Figures 5a and \(5 b)\). In the paints with 20 and \(40 \%\) extender, \(\Delta \mathrm{Y}_{\mathrm{m}}\) and \(\Delta \mathrm{Y}_{\mathrm{f}}\) were increased by all opaque polymer versions. Again, this results from a balance of reduced \(\mathrm{TiO}_{2}\) efficiency, the hiding imparted by air voids within the opaque polymer and, if above CPVC, between the pigment particles.

The reduction in \(\mathrm{TiO}_{2}\) efficiency in the paints containing \(0 \% \mathrm{PVC}\) extender can be seen in a plot of \(\mathrm{S}_{\mathrm{TiO}_{2}}\) (Figure 6a). In the paints containing 20 or \(40 \%\) extender, \(\mathrm{TiO}_{2}\) efficiency is reduced mainly by extender; addition of opaque polymer had little effect. The paints containing \(40 \%\) PVC extender showed greater \(\mathrm{TiO}_{2}\) efficiency than those containing \(20 \%\), probably because the calcined clay imparted some hiding.

Total dry hiding is depicted in a plot of \(\mathrm{S}_{\mathrm{dry}}\) (Figure 6b). Increasing opaque polymer level and void volume increased \(\mathrm{S}_{\text {dry }}\) in the paint with \(0 \%\) PVC extender because of the introduction of voids from the opaque polymer; in the 20 and \(40 \%\) PVC paints, it was due to air voids from the opaque polymer and an increase in total PVC.

As expected, increasing level or void volume of opaque polymer increased \(\Delta Y_{f}-\Delta Y_{m}\) because this is a direct measure of hiding due to air void formation (Figure 5c). This is also seen in the quantity \(\mathrm{S}_{\mathrm{OP}}\) (Table 6). Because the introduction of OP-15 or OP-30 did not produce a positive value for \(\Delta \mathrm{Y}_{\mathrm{f}}-\Delta \mathrm{Y}_{\mathrm{m}}\) in the paints containing \(0 \%\) PVC extender, water loss from the opaque polymer void must occur rapidly, mostly during the early, rather than the later, stage of drying. Therefore, hiding due to air void formation within the opaque polymer diminishes the loss in hiding due to film contraction rather than occurring after contraction is complete.

These concepts complement the newer idea that CPVC is a point of phase inversion rather than the onset of air void formation. \({ }^{19}\) Classically, CPVC is the PVC at which just enough binder is present to satisfy the adsorbed polymer layer on the pigment particles and to just fill the voids between the pigment particles in their closest random packing arrangement. Any subsequent removal of binder results

Table 6-Kubelka-Munk Constants \({ }^{\text {a }}\)
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline PVC & \multirow[b]{2}{*}{OP Type \({ }^{\text {b }}\)} & \multirow[b]{2}{*}{K} & \multirow[b]{2}{*}{\(\mathrm{S}_{\text {Rewet }}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{1}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{\mathrm{m}}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{4}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{\mathrm{f}}-\mathrm{S}_{\mathrm{m}}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{\mathrm{TiO}_{2}}\)} & \multirow[b]{2}{*}{\[
S_{\text {space }}
\]} & \multirow[b]{2}{*}{\(\mathbf{S}_{\text {dry }}\)} & \multirow[b]{2}{*}{\(\mathrm{S}_{\mathrm{OP}}\)} \\
\hline Extender OPb & & & & & & & & & & & \\
\hline 0 ................ 0 & - & 0.0011 & 1.99 & 3.14 & 1.99 & 1.99 & 0.00 & 1.99 & 1.15 & 0.00 & - \\
\hline \(0 \ldots \ldots \ldots \ldots \ldots . .10\) & OP-0 & 0.0006 & 1.83 & 3.32 & 2.04 & 2.04 & 0.00 & 1.83 & 1.49 & 0.21 & - \\
\hline 0 .............. 20 & OP-0 & 0.0008 & 1.78 & 3.28 & 1.94 & 1.94 & 0.00 & 1.78 & 1.50 & 0.16 & - \\
\hline 0 .............. 30 & OP-0 & 0.0001 & 1.74 & 3.08 & 1.76 & 1.76 & 0.00 & 1.74 & 1.34 & 0.02 & - \\
\hline 0 .............. 10 & OP-15 & 0.0010 & 1.97 & 3.20 & 2.07 & 2.07 & 0.00 & 1.83 & 1.37 & 0.24 & 0.03 \\
\hline 0 ............... 20 & OP-15 & 0.0012 & 2.00 & 3.14 & 2.04 & 2.04 & 0.00 & 1.78 & 1.36 & 0.26 & 0.10 \\
\hline 0 .............. 30 & OP-15 & 0.0007 & 2.04 & 3.28 & 2.17 & 2.17 & 0.00 & 1.74 & 1.54 & 0.43 & 0.41 \\
\hline 0.............. 10 & OP-30 & 0.0014 & 2.06 & 3.22 & 2.16 & 2.16 & 0.00 & 1.83 & 1.39 & 0.33 & 0.11 \\
\hline 0 .............. 20 & OP-30 & 0.0008 & 2.16 & 3.25 & 2.32 & 2.32 & 0.00 & 1.78 & 1.47 & 0.54 & 0.38 \\
\hline \multirow[t]{2}{*}{\(0 . . . . . . . . . . . . .30\)} & OP-30 & 0.0004 & 2.24 & 3.34 & 2.51 & 2.51 & 0.00 & 1.74 & 1.60 & 0.77 & 0.75 \\
\hline & Average: & 0.0008 & & & & & & & & & \\
\hline \(20 . . . \ldots \ldots \ldots \ldots .0\) & - & 0.0035 & 1.71 & 3.13 & 1.75 & 1.75 & 0.00 & 1.71 & 1.42 & 0.04 & - \\
\hline \(20 . . . . . . . . . . .10\) & OP-0 & 0.0033 & 1.69 & 3.01 & 1.73 & 1.74 & 0.01 & 1.69 & 1.32 & 0.05 & - \\
\hline \(20 . . . \ldots \ldots \ldots . .120\) & OP-0 & 0.0030 & 1.72 & 2.93 & 1.99 & 2.32 & 0.33 & 1.72 & 1.21 & 0.60 & - \\
\hline \(20 . . . \ldots \ldots \ldots . .30\) & OP-0 & 0.0028 & 1.69 & 3.03 & 2.20 & 3.04 & 0.84 & 1.69 & 1.34 & 1.35 & - \\
\hline \(20 . . . \ldots \ldots \ldots . .10\) & OP-15 & 0.0022 & 1.77 & 3.02 & 1.82 & 1.83 & 0.01 & 1.69 & 1.33 & 0.14 & 0.09 \\
\hline \(20 . . . \ldots \ldots \ldots . . .20\) & OP-15 & 0.0035 & 1.86 & 3.01 & 2.05 & 2.54 & 0.49 & 1.72 & 1.29 & 0.82 & 0.22 \\
\hline \(20 . . . \ldots \ldots \ldots . . .30\) & OP-15 & 0.0032 & 1.87 & 3.01 & 2.23 & 3.30 & 1.07 & 1.69 & 1.32 & 1.61 & 0.26 \\
\hline \(20 \ldots \ldots \ldots \ldots . .10\) & OP-30 & 0.0030 & 1.81 & 3.10 & 1.94 & 1.95 & 0.01 & 1.69 & 1.41 & 0.26 & 0.21 \\
\hline \(20 . . . \ldots \ldots \ldots . . .20\) & OP-30 & 0.0028 & 1.93 & 2.97 & 2.03 & 2.66 & 0.63 & 1.72 & 1.25 & 0.94 & 0.34 \\
\hline \multirow[t]{2}{*}{\(20 . . . . . . . . . . .30\)} & OP-30 & 0.0040 & 2.13 & 2.91 & 2.19 & 3.47 & 1.28 & 1.69 & 1.22 & 1.78 & 0.43 \\
\hline & Average: & 0.0031 & & & & & & & & & \\
\hline \(40 . . . \ldots \ldots \ldots \ldots . .10\) & - & 0.0065 & 1.89 & 3.29 & 2.64 & 4.66 & 2.02 & 1.89 & 1.40 & 2.77 & - \\
\hline \(40 . . . . . . . . . . .10\) & OP-0 & 0.0061 & 1.90 & 3.33 & 2.71 & 5.21 & 2.50 & 1.90 & 1.43 & 3.31 & - \\
\hline \(40 \ldots \ldots \ldots \ldots \ldots . .20\) & OP-0 & 0.0060 & 1.91 & 3.29 & 2.65 & 5.62 & 2.97 & 1.91 & 1.38 & 3.71 & - \\
\hline 40 ............ 30 & OP-0 & 0.0060 & 1.90 & 3.28 & 2.65 & 6.11 & 3.46 & 1.90 & 1.38 & 4.21 & - \\
\hline \(40 \ldots \ldots \ldots \ldots \ldots .10\) & OP-15 & 0.0059 & 1.92 & 3.27 & 2.65 & 5.20 & 2.55 & 1.90 & 1.37 & 3.30 & 0.01 \\
\hline \(40 . . . . . . . . . . .20\) & OP-15 & 0.0062 & 2.03 & 3.34 & 2.70 & 5.92 & 3.22 & 1.91 & 1.43 & 4.01 & 0.30 \\
\hline \(40 . . . \ldots \ldots \ldots . . .30\) & OP-15 & 0.0069 & 2.09 & 3.44 & 2.81 & 6.58 & 3.77 & 1.90 & 1.54 & 4.68 & 0.47 \\
\hline 40 ............ 10 & OP-30 & 0.0062 & 2.02 & 3.31 & 2.63 & 5.35 & 2.72 & 1.90 & 1.41 & 3.45 & 0.14 \\
\hline \(40 . . . \ldots \ldots . . . . .20\) & OP-30 & 0.0059 & 2.13 & 3.33 & 2.73 & 6.10 & 3.37 & 1.91 & 1.42 & 4.19 & 0.48 \\
\hline \multirow[t]{2}{*}{40 ............ 30} & OP-30 & 0.0065 & 2.30 & 3.32 & 2.79 & 6.61 & 3.82 & 1.90 & 1.42 & 4.71 & 0.50 \\
\hline & Average: & 0.0062 & & & & & & & & & \\
\hline
\end{tabular}


Figure \(6 \mathrm{a}-\mathrm{S}_{\mathrm{TiO}_{2}}\) as a function of opaque polymer PVC
in air void formation between the pigment particles. In the phase inversion model, air voids form at even 0\% PVC due to packing imperfections of latex particles. As pigment is introduced in the film, the packing imperfections become more prevalent, producing more air voids. \({ }^{20}\) The PVC at which the air void phase dominates over the polymer phase is CPVC.

Why does the quantity \(\Delta Y_{f}-\Delta Y_{m}\) remain zero below CPVC? If air void formation occurs below CPVC, dry hiding is present and hiding should increase during the later stages of drying. Apparently, formation of discrete air voids from packing imperfections, just as with discrete opaque polymer voids, diminishes the loss in hiding due to film contraction rather than producing a gain in hiding after contraction is complete.

\section*{CONCLUSION}

Addition of opaque polymer to paints can have differing effects on changes in hiding during latex film formation depending on opaque polymer properties and formulation constants. Generally, opaque polymer:
(1) Decreases \(\mathrm{TiO}_{2}\) efficiency due to extender dilution effects;
(2) Increases dry hiding in paints above CPVC; and
(3) Increases hiding from the addition of air voids which develop within the opaque polymer.

Only when solid opaque polymer ( \(0 \%\) void volume) was added to paints below CPVC was the first effect prevalent. In all other cases, the hiding increase due to the introduction of air voids from the opaque polymer and/or increasing PVC was greater than the decrease in \(\mathrm{TiO}_{2}\) efficiency. This effect was greater with increasing opaque polymer void volume and/or level. In actual practice, because opaque polymer is often substituted for an extender, rather than added to the total formula, extender dilution effects that reduce \(\mathrm{TiO}_{2}\) efficiency should be minimal.

From previous work:
\[
\begin{equation*}
\text { If } \Delta \mathrm{Y}_{\mathrm{f}}-\Delta \mathrm{Y}_{\mathrm{m}}>0 \text {, then } \mathrm{PVC}>\mathrm{CPVC} \tag{17}
\end{equation*}
\]

Although opaque polymer introduces air voids into films, it


Figure \(\mathbf{6 b}-\mathrm{S}_{\text {dry }}\) as a function of opaque polymer PVC
was not found to be an interference for determining CPVC by equation (17).

Even in paints below CPVC containing up to \(30 \%\) PVC opaque polymer, \(\Delta \mathrm{Y}_{\mathrm{f}}-\Delta \mathrm{Y}_{\mathrm{m}}\) remained zero. This indicates that water loss from the opaque polymer void occurs rapidly and reduces the initial loss in hiding due to film contraction, rather than occurring in the later stages of drying when coalescence occurs.

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\title{
Adsorption Layer Thickness of Poly(methyl methacrylate) on Titanium Dioxide and Silica
}

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}

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}

\begin{abstract}
The interface which results from filler particle-polymer interactions in coatings and other particulate filled polymer composites was investigated through the measurement of the adsorbed polymer layer or adlayer thickness surrounding each particle. Centrifugation and viscosity measurements were used to calculate an effective diameter of the dispersed filler particles (titanium dioxide and silica) in a poly(methyl methacrylate) (PMMA) solution. The adlayer thickness was determined from the effective diameter due to the extension
\end{abstract}
of the filler size with the adlayer formation. These adlayer thicknesses ranged from 9 to 110 nm . Adlayer thickness increased with particle size and PMMA-filler interaction, and values calculated from viscosity experiments were greater than those from centrifugal packing. These results led to a proposed model for the polymer adlayer state, consisting of an effectively bonded polymer shell surrounding the particle, with a loosely bonded region extending further into the bulk matrix.

\section*{INTRODUCTION}

A number of researchers have investigated the mechanism of attraction between polymers and inorganic solid surfaces. Fowkes and co-workers have led the argument that this attraction is due to both nonpolar dispersion forces and acidbase interactions between chemical groups on the solid surface and within the polymer chain. \({ }^{1-5}\) One example of this adsorption process is the dispersion and wetting of discrete filler particles in a polymer matrix as in the case of pigmented coatings. There is evidence which indicates that this adsorption process results in a layer or "shell" of polymer surrounding the particles and that this adlayer has significant effects on composite properties.

The physical evidence confirming the existence of an adlayer on filler particles in a polymer matrix has been the observation of changes in glass transition temperature \(\left(\mathrm{T}_{2}\right)^{6-12}\) permeability, \({ }^{13.14}\) viscoelastic behavior, \({ }^{15.16}\) and actual measurements of the adlayer thickness. \({ }^{16,17}\) A number of reports

\footnotetext{
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}
have been published on the increase in \(\mathrm{T}_{\mathrm{g}}\) of polymer systems upon the addition of filler particles. For example, Kamel \(^{6}\) found that silica particles with hydroxyl surface groups increased the \(\mathrm{T}_{\mathrm{g}}\) of poly(acrylic acid) by \(10^{\circ} \mathrm{C}\), while the same filler with surface methyl groups and less opportunity for polar interactions only increased the \(\mathrm{T}_{\mathrm{g}}\) by \(3^{\circ} \mathrm{C}\). An explanation for this phenomenon is the adsorption of polymer chains onto the solid surface, causing increased morphological order and tighter chain packing. Even though these effects have been observed in amorphous systems, an analogy with transcrystallinity can be made where neighboring chains adsorb onto the solid surface and form a tighter molecular structure. In this case, the effect is extensive enough to raise the observed \(\mathrm{T}_{\mathrm{g}}\) of the polymer system.

When a filler phase is introduced into a polymer matrix, the permeability of the polymer is expected to decrease for two reasons. The first is a decreased concentration of the polymer phase available for the permeating species, and the second is an increased path length for the absorbing molecules to travel. With a knowledge of the filler volume concentration and the filler and polymer diffusion properties, mass transfer calculations can be used to predict the perme-

Table 1-Summary of Adlayer Thickness Measurements
\begin{tabular}{|c|c|c|c|}
\hline System Method & Thickness (Nanometers) & Reference & \(\Delta r / R^{\text {a }}\) \\
\hline Polyurethane/glass .............................. Energy dissipation-viscosity & 2500 & 16 & 0.14 \\
\hline PS \& PMMA/glass \& mica ................... Energy dissipation-DMA & 60-1400 & 20 & 0.04 \\
\hline  & 1-20 & 18 & .01-0.2 \\
\hline PVC \& PVA/Fe \(\mathrm{O}_{2} / \mathrm{O}_{3} / \mathrm{TiO}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots . . . . . . . . . .\). Energy dissipation-DMA & 30-110 & 19 & . \(20-35\) \\
\hline PVA/PS particles ............................... Ultracentrifuge & 3-25 & 23 & .08-0.7 \\
\hline \[
\begin{aligned}
& \text { PVA/PS particles .................................... Ultracentrifuge } \\
& \text { Slow-speed centrifuge intensity } \\
& \text { fluctuation electrophoreses }
\end{aligned}
\] & 3-40 & 17 & .08-1.1 \\
\hline SBR/carbon black \(\qquad\) Dilatometry-thermal expansion/free volume & 3 & 8 & - \\
\hline  & 2-40 & 15 & .02-0.4 \\
\hline Linseed oil/carbon black ...................... Oil absorption & 2.5 & 24 & 1.0 \\
\hline SBR/carbon black ...............................DMA & 2 & 25 & - \\
\hline Sulphonic acid calcium carbonate .......... Neutron scattering & 2 & 20 & 0.3-1.0 \\
\hline Elastomer/carbon black ........................ Bound (unextractable) rubber & 2.2-5.5 & 21 & .06-. 14 \\
\hline
\end{tabular}
(a) \(\Delta r=\) increase in adsorption layer thickness; \(R=\) filler particle radius.


Figure 1-Suspected relationship between Young's modulus of a polymer matrix and distance from filler particle surface as proposed by Ziegel \({ }^{16}\)
ability of the composite. However, in some filled systems, permeability values are significantly lower than predicted from these calculations. This phenomenon is attributed to the dense adlayer formed around filler particles. It has been argued that the adlayer has lower permeability than the bulk matrix due to the morphological differences described previously. Therefore, the composite is observed as having a higher effective loading level due to the increased volume contributed by the adlayer.

Possibly the most conclusive evidence for the existence of a polymer adlayer surrounding filler particles is the determination of the adlayer thickness from experimental data. A number of approaches have been taken to directly and indirectly determine this thickness, including viscosity, \({ }^{15.16}\) dynamic mechanical analysis (DMA), \({ }^{18-20}\) thermal expansion, \({ }^{8}\) glass transition, \({ }^{21}\) small angle neutron scattering, \({ }^{22}\) centrifugation, \({ }^{17,23}\) and electrophoresis. \({ }^{17}\) The results of these studies are summarized in Table 1. One observation from this data is the discrepancy in the magnitude of the adlayer thickness. Values from several nanometers up to several microns have been reported for different systems. These authors believe the large variation in reported values is due to the size and concentration of the filler particles and to the variation in the interpretation of the adlayer and where it ends in relation to the bulk polymer phase. Another issue which remains is a definitive explanation of this adlayer's effect on coating properties. Therefore, the objectives of this effort were to:
(1) Measure the thickness of the interphase region caused by polymer adsorbed onto dispersed pigment particles.
(2) Obtain an indication of the physical and morphological state of the polymer chains in this adsorbed layer.
(3) Ascertain the effects of this adlayer on coating properties.

Prior to presenting experimental details associated with this study, a review of literature concerning the measurement of adlayer thickness will be provided.

\section*{A REVIEW OF ADLAYER THICKNESS: THEORY AND MEASUREMENT}

\section*{Energy Dissipation Caused by Adlayer Formation}

Ziegel \({ }^{16}\) approached the study of filler volume and interfacial effects via energy loss aspects of particulate-filled composites. A prerequisite of this model is the assumption that filler particles are discrete and inextensible within the polymer matrix. This assumption is valid for common inorganic fillers such as metal oxides and salts which are rigid. A lack of interaction between filler and matrix causes a clear distinction between the filler particle surface and the matrix [Figure 1 (A)]. However, an interacting system causes a change in properties stemming from the interface into the bulk matrix [Figure 1 (B)].

For a homogeneous polymer, energy dissipated, W, at a particular vibrational frequency has been shown to be \({ }^{26}\) :
\[
\begin{equation*}
\mathrm{W}=\pi \mathrm{E}^{\prime \prime} \mathrm{e}^{2} \tag{1}
\end{equation*}
\]
where \(\mathrm{E}^{\prime \prime}\) is the loss modulus and e is the extensional strain on the material. By dispersing rigid filler particles, unable to dissipate vibrational energy, into the polymer, the volume fraction of loss matrix is reduced. In this case, the loss modulus of the composite equals that of the polymer, while the extensional strain of the composite equals that of the composite. Therefore, equation (1) can be modified for the resulting composite:
\[
\begin{equation*}
\mathrm{W}_{\mathrm{c}}=\pi \mathrm{E}_{\mathrm{p}} \mathrm{e}_{\mathrm{c}}^{2}\left(1-\mathrm{v}_{\mathrm{f}}\right) \tag{2}
\end{equation*}
\]
where \(v_{f}\) is a compositional filler volume fraction and the subscripts \(c, p\), and \(f\) refer to the composite, polymer, and filler, respectively. The ratio of energy dissipation of composite material to the homogeneous polymer is:
\[
\begin{equation*}
\frac{W_{c}}{W_{p}}=\frac{e_{c}^{2}}{e_{p}^{2}}\left(1-v_{f}\right) \tag{3}
\end{equation*}
\]

The assumption that the loss modulus of the polymer matrix controls the mechanical dissipation of energy must be noted. This is not exact since Figure 1 (B) portrays a gradual change in properties from the filler surface to the bulk matrix. However, at low filler loading levels (low pigment volume concentrations), the volume of adlayer is small, and the adlayer effect does not dominate; this assumption is valid.

Consider the elongation of two materials, one being a pure polymer, the other having a dispersed particle phase. If the samples have the same original dimensions and are stressed to the same elongation (length \(=\mathrm{L}\) ), the strain placed on the polymer in the filled material will be greater than that on the unfilled polymer due to reduced volume fraction of the extensible phase. This is illustrated in Figure 2. The ratio of elongations of polymer in these two samples is:


Figure 2 - Volume element of a filled composite with an elastic matrix and a rigid filler. The dispersed phase is concentrated at the left end of the model- \(L_{1} \times L_{1} \times L_{2}\)
\[
\begin{equation*}
\frac{e_{c}}{e_{p}}=\frac{L / L_{o}^{\prime}}{L / L_{o}}=\frac{L_{o}}{L_{o}^{\prime}} \tag{4}
\end{equation*}
\]
where \(L_{o}\) is the initial sample length and \(L_{o}^{\prime}\) is the effective dimension of the composite matrix material due to the reduction in matrix material volume. As illustrated in Figure 2, the total volume of the composite, \(v_{c}\), is the product of ( \(\mathrm{L}_{\mathrm{o}} \times \mathrm{L}_{1} \times\) \(\mathrm{L}_{2}\) ) and the volume of the polymer, \(\mathrm{v}_{\mathrm{p}}\), in the composite is ( \(\mathrm{L}_{0} \times \mathrm{L}_{1} \times \mathrm{L}_{2}\) ). Note that the volume of filler in the composite is \(\left(V_{c}-V_{p}\right)\). Solving these relationships for \(L_{o}\) and \(L_{o}{ }^{\prime}\) respectively and substitution into equation (4) yields:
\[
\begin{equation*}
\frac{e_{c}}{e_{p}}=\frac{v_{c}}{V_{p}} \tag{5}
\end{equation*}
\]

Considering the volume fraction of polymer in the composite can be expressed as:
\[
\begin{equation*}
v_{p}=\left(1-v_{\mathrm{f}}\right)=\mathrm{V}_{\mathrm{p}} / \mathrm{V}_{\mathrm{c}} \tag{6}
\end{equation*}
\]
equation (5) can be represented as:
\[
\begin{equation*}
\frac{e_{c}}{e_{p}}=\frac{1}{\left(1-v_{f}\right)} \tag{7}
\end{equation*}
\]

Now, as described previously, when a pigment is dispersed into a polymer matrix, the resulting interactions may cause the formation of an immobilized layer on the pigment

Table 2-Summary of Adlayer Thickness and Heats of Adsorption, \(\Delta \mathrm{H}\), of PMMA and PS on Glass and Mica \({ }^{20}\)
\begin{tabular}{|c|c|c|}
\hline System B & \[
\begin{gathered}
\Delta r \\
(\mu \mathrm{~m})
\end{gathered}
\] & \[
\begin{gathered}
\Delta H^{\mathrm{a}} \\
(\mathrm{kcal} / \mathrm{mol})
\end{gathered}
\] \\
\hline PMMA-glass ...................... 1.23 & 1.4 & 1.7 \\
\hline PMMA-mica ...................... 1.51 & 0.11 & 2.3 \\
\hline PS-glass ............................. 1.16 & 1.0 & 0.64 \\
\hline PS-mica ............................. 1.31 & 0.06 & 0.98 \\
\hline
\end{tabular}


Figure 3- \(\eta_{\text {sp }} / \mathbf{v}_{\mathrm{t}}\) vs reciprocal shear rate for dispersions of glass beads in various polymer melts \({ }^{16}\)
surface. This layer increases the effective particle radius to \((R+\Delta r)\) where \(R\) is the filler radius and \(\Delta r\) is the adlayer thickness. The increase in effective particle radius causes an increase in fraction of effective filler volume, \(\mathrm{v}_{\mathrm{e}}\) :
\[
\begin{equation*}
v_{e}=v_{\mathrm{f}}+v_{\mathrm{i}} \tag{8}
\end{equation*}
\]
where \(v_{i}\) is the composite volume fraction composed of the immobilized polymer adsorbed layer. The fractional increase in filler volume, B, leading to the effective filler volume is:
\[
\begin{equation*}
B=\frac{4 / 3 \pi(R+\Delta r)^{3}}{4 / 3 \pi\left(R^{3}\right)}=(1+(\Delta r / R))^{3} \tag{9}
\end{equation*}
\]
and
\[
\begin{equation*}
v_{e}=v_{f}(1+\Delta r / R)^{3}=v_{\mathrm{f}} B \tag{10}
\end{equation*}
\]

B is also called the correction parameter since it corrects for the adsorption of an immobilized layer thickness. It follows from equations (3) and (8)-(10) that:
\[
\begin{equation*}
\frac{W_{c}}{w_{p}}=\left(1-v_{f} B\right) \tag{11}
\end{equation*}
\]

Several researchers \({ }^{16.17 .19,20}\) have used this concept to determine adlayer thickness of various polymers onto filler surfaces. In each case, however, different forms of energy dissipation have been utilized. Ziegel \({ }^{16}\) used the Einstein equation for specific viscosity, \(\eta_{\mathrm{sp}}\), of a dispersion of noninteracting spheres in a fluid medium:
\[
\begin{equation*}
\frac{\eta-\eta_{o}}{\eta_{o}}=\eta_{\mathrm{sp}}=(5 / 2) \mathrm{v}_{\mathrm{f}} \tag{12}
\end{equation*}
\]
where \(\eta_{0}\) is the viscosity of the fluid medium and \(\eta\) is the observed viscosity of the dispersion. For systems with no interaction between matrix and filler [Figure \(1(\mathrm{~A})\) ], the viscosity is independent of shear rate and \(\eta_{\mathrm{sp}} / \mathrm{v}_{\mathrm{f}}=5 / 2\). However, if there is interaction [Figure 1 (B)], \(\eta_{\text {sp }}>5 / 2\). Furthermore, if the adlayer is deformable, a shear thinning effect is expected. Ziegel suggested that if there is an immobilized layer with a distinct thickness, \(v_{f}\) in equation (12) can be substituted with \(v_{e}\), the effective volume as a result of the observed increase in particle diameter and volume. Assuming that the
immobilized layer remains intact even at an infinite shear gradient, equations (10) and (12) can be combined to determine the adlayer thickness, \(\Delta \mathrm{r}\) :
\[
\begin{equation*}
\frac{\Delta r}{\mathrm{R}}=\left[\frac{2 \eta_{\mathrm{sp}}}{5 \mathrm{v}_{\mathrm{f}}}\right]^{1 / 3}-1 \tag{13}
\end{equation*}
\]

Ziegel \({ }^{16}\) dispersed \(18 \mu \mathrm{~m}\) diameter glass beads into polychloroprene, polybutene, poly(propylene glycol), and polyurethane melts, respectively, at concentrations up to eight percent by volume and subsequently measured specific viscosity as a function of shear rate (Figure 3). At low shear rates, all four dispersions exhibited non-Newtonian behavior. However, at infinite shear rate, all of the dispersions except polyurethane result in \(\left(\eta_{\text {sp }} / v_{\mathrm{f}}=5 / 2\right)\). For the three polyurethane dispersions \(\left(\mathrm{v}_{\mathrm{f}}=0.0225,0.0415,0.0842\right), \eta_{\mathrm{sp}} /\) \(\mathrm{v}_{\mathrm{f}}=5.25\) at infinite shear rate. Substitution into equation (13) indicates an adlayer thickness of \(2.5 \mu \mathrm{~m}\). Although this is orders of magnitude higher than molecular dimensions and values reported for other systems (Table 1), Ziegel attributes this to interchain association due to entanglements and selfassociation of the adsorbing polymer. It should also be noted that the relative increase in radius, \(\Delta r / R\), is only 0.14 which is comparable to other results listed in Table 1. Ziegel provided no explanation for the different results from polymer to polymer.

Iisaka and Shibayama \({ }^{20}\) also used the dissipated energy concept and equation (11) to determine adlayer thicknesses. However, instead of using specific viscosity as an indication of energy dissipation, loss modulus, \(\mathrm{E}^{\prime \prime}\), as determined by DMA was used. Thus:
\[
\begin{equation*}
E_{p}{ }^{\prime \prime} / E_{c}{ }^{\prime \prime}=\left(1-v_{f} B\right) \tag{14}
\end{equation*}
\]

The resulting \(B\) and \(\Delta r\) values for glass beads and mica flakes in poly(methyl methacrylate) (PMMA) and polystyrene (PS) are presented in Table 2 along with heats of adsorption of the respective monomers on the filler surface. A partial explana-


Figure 4-Graphical model of matrix immobilization as a function of distance from filler particle surface \({ }^{20}\)
tion for the higher heats of adsorption of PMMA is the higher polarity of PMMA relative to PS. This explanation is reasonable since the dipole moment of PMMA is greater than five times that of PS. However, no explanation is provided for measured adlayers on glass being an order of magnitude greater than that on mica. This result may be due to differences in surface chemistry and/or particle geometry. Iisaka postulates that the thickness and immobilization of the adlayer is a direct function of the interaction strength as illustrated in Figure 4. Comparing the data in Table 2, this can only be partially true, otherwise the adlayer of PMMA on mica would be larger than the others analyzed.

Boluk and Schreiber \({ }^{18}\) applied DMA \(\tan \delta\) data to equation (11) to obtain adlayer thicknesses of various titanium dioxide samples on chlorinated polyethylene (CPE):
\[
\begin{equation*}
\frac{\tan \delta_{\mathrm{c}}}{\tan \delta_{\mathrm{p}}}=\left(1-\mathrm{B} \mathrm{v}_{\mathrm{f}}\right) \tag{15}
\end{equation*}
\]

Results are presented in Table 3 along with an acid-base interaction parameter, \(\Omega\), obtained from inverse gas chromatography. [References (27)-(29) provide a review of IGC theory and additional experimental results, respectively.] Adlayer thickness values range from 1 to 20 nm , more consistent with molecular dimensions and results from other researchers.

Schrieber's interaction parameter reflects Lewis acidbase characteristics: \(\Omega<0\), acidic; \(\Omega=0\), neutral; and \(\Omega>0\), basic. CPE has an \(\Omega\) of -1.71 and therefore it is a Lewis acid and will interact with bases. Figure 5 illustrates the relationship between the pigment interaction parameter and adlayer thickness for the \(\mathrm{TiO}_{2}\)-CPE system. It illustrates that as \(\Omega\) increases (higher basicity pigment), the adlayer thickness also increases up to a maximum value. This result appears to be in agreement with the physical phenomenon. If a polymer chain strongly adsorbs onto a surface, it may extend out into the bulk phase and its mobility may be restricted by the conformation of surrounding chains in the same adsorbed state. However, since the "unattached" chain end is essentially mixed with chains in the bulk state which have greater mobility, the thickness of this immobilized adlayer formed by adsorbed chains must be on the order of molecular dimensions. Pigments which only weakly attract the polymer phase will not form a strong, stable adlayer, and the effect will not be as significant. Therefore, having a large interaction between the filler surface and polymer chains only allows for the possibility of a tightly bound and larger adlayer, it does not guarantee that this effect will occur. The thickness must also depend on the conformation of the adsorbed polymer relative to the adsorbate surface. It should be noted that if the polymer had been basic, acidic pigments would have had stronger reactions and theoretically, thicker adlayers.

Isobe et al. \({ }^{19}\) utilized equation (14) with loss modulus, \(\mathrm{E}^{\prime \prime}\), to calculate adlayer thicknesses of poly(vinyl chloride) on titanium dioxide and iron oxide. However, to calculate the correction parameter, B, they used an approach presented by Sato \({ }^{30}\) :
\[
\begin{equation*}
\mathrm{B}=1+\left(\rho_{\mathrm{f}} \mathrm{~S} \Delta \mathrm{r}\right) \tag{16}
\end{equation*}
\]
where \(S\) and \(\rho_{\mathrm{f}}\) are the filler specific surface area and density, respectively. Thus the product ( \(\rho_{\mathrm{f}} \times \mathrm{S} \times \Delta \mathrm{r}\) ) is a dimensionless quantity indicative of the increase in the effective filler
\begin{tabular}{|c|c|c|}
\hline \multicolumn{3}{|l|}{Table 3-Summary of Adlayer Thickness of Chlorinated Polyethylene on Titanium Dioxide Samples and Interaction Parameters \({ }^{18}\)} \\
\hline System Designation [in reference (18)] & (nanometers) & \(\Omega^{\text {a }}\) \\
\hline  & 1.0 & 0.02 \\
\hline \(\mathrm{TiO}_{2}-2\)............................ 1.27 & 7.0 & 0.06 \\
\hline \(\mathrm{TiO}_{2}-3\)............................ 1.74 & 19.5 & 1.69 \\
\hline \(\mathrm{TiO}_{2}-4\)............................ 1.84 & 19.0 & 5.25 \\
\hline \(\mathrm{TiO}_{2}-5\)............................ 1.70 & 17.0 & 1.27 \\
\hline  & 20.0 & 5.05 \\
\hline  & 9.0 & -0.02 \\
\hline \(\mathrm{TiO}_{2}-8\)........................... 1.23 & 6.0 & -0.42 \\
\hline  & 6.0 & \(-0.50\) \\
\hline (a) Calculated from inverse gas chroma & data. & \\
\hline
\end{tabular}
volume. Using this approach, variations in adlayer thickness versus filler volume were determined. Figure 6 illustrates that as the pigment concentration increases, the adlayer decreases. This result confirms that adlayer thickness is not solely dependent upon strength of interaction. If this were true, the correlation in Figure 6 would be linear, indicating constant adlayer thicknesses independent of pigment concentration.

In order to compare \(B\) and \(\Delta r\) values determined from Ziegel's approach [equation (9)] with those from Sato's approach [equation (16)], data provided in references (17) and (19) were applied to both equations respectively. The resulting \(\Delta r\) values were typically within five percent of each other.

\section*{Accelerated Sedimentation Studies}

Garvey et al. have presented adlayer thickness results of poly(vinyl alcohol) (PVA) on polystyrene (PS) latex particles based on ultracentrifugation ( \(50,000 \mathrm{RPM})^{23}\) and slowspeed centrifugation ( 1000 RPM ). \({ }^{17}\) The former is based on the sedimentation coefficient, \(\mathrm{s}_{0}\), which is a measured rate of particle sedimentation. \({ }^{31}\) The sedimentation coefficient of a particle in a noninteracting medium is determined by \({ }^{23}\) :
\[
\begin{equation*}
\mathrm{s}_{\mathrm{o}}=\frac{4 / 3 \pi \mathrm{R}^{3}\left(\rho_{\mathrm{f}}-\rho_{\mathrm{p}}\right)}{6 \pi \eta_{\mathrm{o}} \mathrm{R}}=\frac{2 \mathrm{R}^{2}\left(\rho_{\mathrm{f}}-\rho_{\mathrm{p}}\right)}{9 \eta_{\mathrm{o}}} \tag{17}
\end{equation*}
\]


Figure 5-Chlorinated polyethylene adlayer thickness as a function of titanium dioxide acid-base parameter \({ }^{18}\)


Figure 6-Poly(vinyl chloride) adlayer thickness on various fillers as a function of filler volume concentration \({ }^{19}\)

Table 4-Summary of Adsorbed Layer Thickness (in Nanometers) of Poly(Vinyl Alcohol) on Polystyrene Latex Particles \({ }^{17}\)



Figure 7-Proposed model for the effect of adsorption of a polymer matrix on a filler particle surface
where \(\eta_{0}\) is the viscosity of the fluid medium, in this case the polymer solution or monomer. However, if the particle interacts with the surrounding fluid, creating an immobilized adlayer, the adlayer thickness can be introduced into equation (17):
\[
\begin{equation*}
\mathrm{s}_{\mathrm{o}}=\frac{2 \pi \mathrm{R}^{3}\left(\rho_{\mathrm{f}}-\rho_{\mathrm{p}}\right)+2 \pi\left[(\mathrm{R}+\Delta \mathrm{r})^{3}-\mathrm{R}^{3}\right]\left(\rho_{\mathrm{f}}-\rho_{\mathrm{p}}\right)}{9 \pi \eta_{\mathrm{o}}(\mathrm{R}+\Delta \mathrm{r})} \tag{18}
\end{equation*}
\]

By measuring the sedimentation coefficient (rate) and applying the results to equation (18), adlayer values can be calculated. Using this approach, the adlayer thickness of PVA on PS latex particles ranged from 3.3 to 25.5 nm , depending on the molecular weight of the PVA (Table 4). Increased molecular weight yielded thicker adlayers which would appear reasonable if the chains extend from the surface of the particle into the bulk matrix phase.

In a follow-up study, \({ }^{17}\) Garvey et al. compared the adlayer thickness obtained by ultracentrifugation, slow-speed centrifugation, diffusion using intensity fluctuation spectroscopy, and electrophoresis. Reference (17) provides a description of the theory and experimental methods for the latter two approaches. The slow-speed centrifugation method is simply based on the volume of packed particles due to forced sedimentation. Applying a centrifugal force to a dispersion of particles of higher density than their dispersing medium causes the particles to form a tightly packed sediment with surface-to-surface contact. From a knowledge of the amount of filler present and the resulting packing arrangement, the effective particle radius, \(R_{e}\), can be calculated. This distance is equal to the true particle radius plus the adlayer thickness:
\[
\begin{equation*}
\mathrm{R}_{\mathrm{c}}=\mathrm{R}+\Delta \mathrm{r}=\frac{\left(\phi \mathrm{V} \rho_{\mathrm{f}}\right)^{1 / 3}}{\mathrm{~W}} \tag{19}
\end{equation*}
\]
where \(\phi\) is the packing factor of the pigment particles in the sediment, V is the bulk sediment volume, and W is the weight of particles. Since R and all of the terms on the right hand side of equation (19) are known or measurable, \(\Delta \mathrm{r}\) can be calculated.

A summary of adlayer thickness values from reference (17) are presented in Table 4. With the exception of the electrophoretic method, the various techniques resulted in comparable adlayer thicknesses. Several reflections on the implications of this work must be presented. First, the PS latex particles studied had densities not much greater than the dispersing PVA medium, causing sedimentation to be slow and less compact. Pigment particles, having densities of greater than \(2 \mathrm{~g} / \mathrm{mL}\) and up to \(5 \mathrm{~g} / \mathrm{mL}\), will compact relatively quickly and firmly since there is a greater gravitational force applied and the difference in density between phases is much greater. Therefore, the ultracentrifugation is not practical for use with pigment dispersions. However, high pigment density is advantageous for performing slow-speed centrifugation since it assists settling and compaction. Finally, it should be recognized that compaction of particles under these conditions is far from the conditions of low concentration required by the energy dissipation approach presented previously, but rather more similar to the condition at the critical pigment volume concentration.

These results and observations have led these authors to propose a model for the physical state of the polymer adlayer
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline \multicolumn{7}{|c|}{Table 5-Polymer Sample Designations, Suppliers, Molecular Weight, and Glass Transition Temperature} \\
\hline Polymer Designation & Supplier & \(M_{w}\) & M \({ }_{\text {n }}\) & \(M_{2}\) & \(M_{w} / M_{z}\) & \(\mathrm{T}_{9}\left({ }^{\circ} \mathrm{C}\right)\) \\
\hline PMMA-1 ... & Aldrich & 10,700 & 6.610 & 15,900 & 1.62 & 96 \\
\hline PMMA-2 ... & Polysciences & 25.500 & 13,800 & 38,500 & 1.84 & 116 \\
\hline PMMA-3 ..... & Rohm and Haas & 41,900 & 19,000 & 19,000 & 2.21 & 70 \\
\hline PMMA-4 ..... & Aldrich & 55,000 & 26,400 & 86,300 & 2.08 & 109 \\
\hline PMMA-5 ..... & Polysciences & 50,100 & 25,800 & 76,200 & 1.94 & 94 \\
\hline
\end{tabular}
surrounding a filler particle. Consider the following scenario. The inner region of the adlayer, in close proximity to the pigment surface, mainly consists of polymer chains which are bound at one or more sites to the filler surface, causing them to be immobile and fairly rigid. At relatively low filler concentrations (far below the critical pigment volume concentration), the polymer in the outer regions of the adlayer, further from the particle surface, are held in the adlayer by entanglements and association with bound chains, allowing them to be more mobile. As the pigment concentration is increased, the forced compaction of filler particles displaces this outer region of the adlayer and allows chains to become bound to two adjacent particles. As this occurs, bound chains in the rigid "shell" remain but the loosely bound region is displaced. Figure 7 is a graphical presentation of this model. It varies from the Guggenheim \({ }^{32}\) and Fowkes \({ }^{33}\) models which illustrate a distinct boundary between two phases. It varies from the Ziegel model (Figure 1) by predicting a rigid shell of adsorbed polymer near the filler surface. These authors propose that the slow-speed centrifugation method results in determination of the rigid shell illustrated in Figure 7 region A , while the further extending adlayer region can be determined by the energy dissipation methods with low filler concentrations (Figure 7 - regions A and B). Experimental results will be presented to support this model.

\section*{EXPERIMENTAL}

\section*{Materials}

The titanium dioxide and silica pigments used in this study have been extensively characterized and described previously. \({ }^{28,29}\) Particle size and size distributions were required to determine pigment particle packing factors during the centrifugation experiments. As described in detail in reference (29), particle sizes were obtained using scanning electron microscopy at \(20,000 \mathrm{X}\). The titanium dioxide samples had varying degrees of silica and/or alumina surface treatments. The silica was an untreated pyrogenic silica (Aerosil A130, Degussa Corp.). These fillers have been designated TIO-1, TIO-2, TIO-3, and SIO-1, respectively. Reference (34) reviews the use of rutile titanium dioxide in polymer systems; references (35)-(39) discuss pyrogenic silica and its use in coatings and other polymer systems. Five commercially available poly(methyl methacrylate) samples were obtained and designated PMMA-1 through 5. Table 5 lists their molecular weights and \(\mathrm{T}_{\mathrm{g}} \mathrm{s}\).

The preparation of the dispersions for the centrifugation experiments is described in the Procedures section. The viscosity dispersions were prepared in the following manner.

The respective PMMA samples were prepared in a solution of methyl ethyl ketone and propylene glycol monomethyl ether (PM) acetate as described in Table 6. The resulting solutions were mixed with the respective titanium dioxide and silica pigments in one liter glass jars half filled with glass shot 5 mm in diameter. The titanium dioxide dispersions were \(6.4 \%\) by volume of the entire solution while the silica dispersions were \(2.1 \%\). The silica could not be added at the higher concentration due to its extremely large surface area and its extensive interaction with the polymer. These mixtures were milled on a paint shaker for 30 min to allow thorough wetting of the pigment with the resin solution. The Hegman fineness-of-grind rating (ASTM D 1210) of the resulting dispersions was greater than seven which indicates a fine dispersion. At this point, the mixtures were ready for viscosity measurements.

\section*{Equipment}

The slow-speed centrifugation studies were performed with a floor model centrifuge (International Centrifuge Inc., Boston, MA) using 100 mL Goetz centrifuge tubes. These tubes are pear-shaped with a 0.2 mL protrusion at the bottom which is graduated in 0.01 mL increments, thereby allowing accurate measurement of the pigment sediment volume. With these tubes in place, the centrifuge has a moment arm of approximately 0.2 m with rotational speeds up to 7000 RPM.

The viscosity studies were performed using a WellsBrookfield cone and plate viscometer (model DV-1, Brookfield Viscosity Instruments Inc., Stoughton, MA) with a \#40 cone spindle (cone angle \(=0.8^{\circ}\), radius \(=2.4 \mathrm{~cm}\) ). The advantage of this viscometer is that it imparts a uniform shear rate throughout the fluid sample, allowing accurate


Figure 8-Ln \(\tau\) vs \(\operatorname{Ln} \dot{\gamma}\) for unfilled PMMA solutions
\begin{tabular}{|c|c|}
\hline Component & Percent by Weight \\
\hline Poly(methyl methacrylate) ............................. & ............ 20 \\
\hline Methyl ethyl ketone (MEK) ........................... & ............ 30 \\
\hline Propylene glycol monomethyl ether (PM) acetate . & .............. 50 \\
\hline
\end{tabular}
analysis of viscosity data. A discussion of the theory and operation of the cone and plate viscometer is provided in reference (40). The viscometer allowed adjustable rotational speeds from 0.5 to 100 rotations per minute which imparted shear rates of 750 to \(3.75 \mathrm{sec}^{-1}\), respectively. A Brookfield EX100 constant temperature bath was attached to the cone and plate chamber to maintain sample temperatures within \(\pm\) \(0.05^{\circ} \mathrm{C}\).

\section*{Procedures}

The centrifuge dispersions were prepared in a Goetz tube by adding \(0.13 \pm 0.01\) grams of \(\mathrm{TiO}_{2}\left(0.013 \pm 0.005\right.\) for \(\left.\mathrm{SiO}_{2}\right)\) to 25 mL of the PMMA solution of interest (Table 6). Particular care was taken to prevent the pigment sample from entering the protrusion at the bottom of the tube prior to centrifugation. A magnetic stirring bar was added with the tube lying horizontally on a stirring plate. In this position, the dispersions were vigorously stirred for 24 hr . After this time, the stirring bar was removed and the tube was placed into the centrifuge. A chemically resistant stopper was used to seal the tube during stirring and centrifugation.

The centrifuge samples were initially spun at 500 RPM for a minimum of 20 hr . At that time, the sediment volume of the pigment sample was recorded and spinning at this speed was resumed until the volume level remained constant. The rotational speed was then increased to 1000 RPM until the sediment level stabilized, which typically occurred after 20 hr . Finally, the speed was increased to 1500 RPM and maintained there until once again the pigment sediment level stabilized. Increasing the centrifuge speed above this level had no further consequences. At this time, the final pigment sediment volume was recorded and applied to equation (19) to determine the adlayer thickness. Pigment densities were determined from a pycnometer technique (ASTM D 153). Pigment packing factors required for equation (19) were determined by measuring particle size distributions with a scanning electron microscope and applying them to Lee's algorithm. \({ }^{41}\) It must be noted that in using this approach to estimate the packing factor, it was assumed that the particles undergo dense random packing with the strongly adsorbed PMMA remaining intact on the surface of the particles. This would appear to be a reasonable assumption based on previous studies. \({ }^{42-44}\)

The viscosity measurements were obtained by adding approximately 0.5 mL of the dispersions described in the previous section to the test chamber in the cone and plate viscometer. The temperature of this chamber was maintained at \(24.95 \pm 0.05^{\circ} \mathrm{C}\). The viscosity readings were obtained by starting the spindle/cone at the lowest rotational speed and proceeding through to the highest speed. Readings were made at each shear rate as soon as they stabilized on the

Table 7-Viscosity (Centipoise) of Unfilled and Filled PMMA Solutions. Titanium Dioxide Dispersions at \(6.4 \mathrm{v} / \mathrm{o}\), Silica Dispersions at \(2.1 \mathrm{v} / \mathrm{o}\)
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline & \multicolumn{6}{|c|}{Viscosity (cps)} \\
\hline & \multicolumn{6}{|c|}{Shear Rate ( \(\mathrm{sec}^{-1}\) )} \\
\hline Polymer Pigment & 18.75 & 37.5 & 75 & 150 & 375 & 750 \\
\hline PMMA-1 ................................... & 1.05 & 1.05 & 1.05 & 1.05 & 1.10 & 1.10 \\
\hline PMMA-2 .................................. & 3.14 & 3.14 & 3.41 & 3.28 & 3.30 & 3.30 \\
\hline PMMA-3 & 9.43 & 9.43 & 8.91 & 9.04 & 9.12 & 9.17 \\
\hline PMMA-4 ................................... & 11.53 & 11.53 & 11.27 & 11.53 & 11.69 & 11.71 \\
\hline PMMA-5 ................................... & 6.29 & 6.29 & 6.55 & 6.68 & 6.65 & 6.65 \\
\hline PMMA-1 ...................................TIO-1 & 1.05 & 1.57 & 1.83 & 1.83 & 1.83 & 1.81 \\
\hline PMMA-2 .................................. TIO-1 & 8.34 & 7.86 & 7.07 & 6.81 & 6.45 & 6.16 \\
\hline PMMA-3 ...................................TIO-1 & 14.67 & 14.67 & 14.15 & 14.15 & 13.99 & 13.81 \\
\hline PMMA-4 ...................................TIO-1 & 26.20 & 23.06 & 20.96 & 19.13 & 17.13 & 16.43 \\
\hline PMMA-5 ...................................TIO-1 & 22.01 & 17.82 & 14.93 & 13.36 & 12.05 & 11.50 \\
\hline PMMA-1 ...................................TIO-2 & 2.10 & 2.62 & 2.36 & 2.10 & 1.99 & 1.97 \\
\hline PMMA-2 ...................................TIO-2 & 8.38 & 7.86 & 7.34 & 6.94 & 6.45 & 6.21 \\
\hline PMMA-3 .................................. TIO-2 & 23.06 & 20.44 & 19.91 & 18.34 & 16.72 & 16.09 \\
\hline PMMA-4 ...................................TIO-2 & 44.02 & 33.54 & 27.25 & 23.19 & 19.91 & 18.42 \\
\hline PMMA-5 ...................................TIO-2 & 26.20 & 20.96 & 17.55 & 15.20 & 13.26 & 12.45 \\
\hline PMMA-1 ...................................TIO-3 & 5.24 & 3.67 & 3.14 & 2.62 & 2.36 & 2.20 \\
\hline PMMA-2 ...................................TIO-3 & 10.48 & 8.91 & 7.86 & 7.21 & 6.65 & 6.29 \\
\hline PMMA-3 ................................... TIO-3 & 15.72 & 16.24 & 15.46 & 15.46 & 15.41 & 15.43 \\
\hline PMMA-4 ...................................TIO-3 & 48.21 & 36.16 & 28.82 & 24.10 & 20.49 & 18.76 \\
\hline PMMA-5 ...................................TIO-3 & 35.63 & 26.72 & 21.22 & 17.82 & 14.99 & 13.76 \\
\hline PMMA-1 ...................................SIO-1 & 8.38 & 6.81 & 5.24 & 4.32 & 3.67 & 3.35 \\
\hline PMMA-2 ..................................SIO-1 & 57.64 & 41.92 & 29.08 & 20.57 & 14.41 & 11.79 \\
\hline PMMA-3 ..................................SIO-1 & 59.74 & 45.59 & 31.70 & 31.05 & 26.72 & 24.60 \\
\hline PMMA-4 ...................................SIO-1 & 306.0 & 177.1 & 108.7 & 73.36 & - & - \\
\hline PMMA-5 ...................................SIO-1 & 327.0 & 185.5 & 109.0 & 60.78 & 37.62 & - \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline \multicolumn{5}{|l|}{Table 8-Flow Index Values, n, and Equation Correlation Coefficients for PMMA Solutions and Dispersions. Correlation Coefficients are in Parentheses} \\
\hline System PMMA-1 & PMMA-2 & PMMA-3 & PMMA-4 & PMMA-5 \\
\hline 1.02
Unfilled ...................................................... 99.99\()\) & \[
\begin{gathered}
1.01 \\
(99.98)
\end{gathered}
\] & \[
\begin{gathered}
0.99 \\
(99.99)
\end{gathered}
\] & \[
\begin{gathered}
1.01 \\
(100.00)
\end{gathered}
\] & \[
\begin{gathered}
1.02 \\
(99.99)
\end{gathered}
\] \\
\hline  & \[
\begin{gathered}
0.92 \\
(99.99)
\end{gathered}
\] & \[
\begin{gathered}
0.98 \\
(100.00)
\end{gathered}
\] & \[
\begin{gathered}
0.87 \\
(99.98)
\end{gathered}
\] & \[
\begin{gathered}
0.83 \\
(99.84)
\end{gathered}
\] \\
\hline  & \[
\begin{gathered}
0.92 \\
(100.00)
\end{gathered}
\] & \[
\begin{gathered}
0.91 \\
(99.99)
\end{gathered}
\] & \[
\begin{gathered}
0.77 \\
(99.80)
\end{gathered}
\] & \[
\begin{gathered}
0.80 \\
(99.88)
\end{gathered}
\] \\
\hline  & \[
\begin{gathered}
0.87 \\
(99.94)
\end{gathered}
\] & \[
\begin{gathered}
0.99 \\
(99.99)
\end{gathered}
\] & \[
\begin{gathered}
0.75 \\
(99.77)
\end{gathered}
\] & \[
\begin{gathered}
0.74 \\
(99.76)
\end{gathered}
\] \\
\hline  & \[
\begin{gathered}
0.56 \\
(99.75) \\
\hline
\end{gathered}
\] & \[
\begin{gathered}
0.89 \\
(95.53) \\
\hline
\end{gathered}
\] & \[
\begin{gathered}
0.31 \\
(98.65) \\
\hline
\end{gathered}
\] & \[
\begin{gathered}
0.27 \\
(97.24) \\
\hline
\end{gathered}
\] \\
\hline
\end{tabular}
display, which was typically within 10 sec . The spindle torque spring, which is used to determine viscosity, was calibrated prior to each run and glycerine was used as a control to ensure day-to-day consistency.

\section*{RESULTS AND DISCUSSION}

The PMMA solution and dispersion viscosities are presented as a function of shear rate, \(\dot{\gamma}\), in Table 7. From this data, it is immediately apparent that dispersion viscosities are higher than those of their parent PMMA solutions. In addition, dispersion viscosities typically decrease with increasing shear rate (i.e., shear thinning). This initial evidence suggests that the PMMA is interacting with the filler particles to some extent.

Viscosity, \(\eta\), is defined as:
\[
\begin{equation*}
\eta \equiv \frac{\tau}{\dot{\gamma}} \tag{20}
\end{equation*}
\]
where \(\dot{\gamma}\) is the applied shear stress. Furthermore, shear stress and shear rate have been related by:
\[
\begin{equation*}
\mathrm{t}=\mathrm{K} \dot{\gamma}^{\mathrm{n}} \text { or } \operatorname{Ln} \tau=\operatorname{Ln} \mathrm{K}+\mathrm{n} \operatorname{Ln} \dot{\gamma} \tag{21}
\end{equation*}
\]
where n is called the flow behavior index and K is the consistency index. For Newtonian fluids, there is a direct linear relationship between shear stress and shear rate, causing n in equation (21) to be one. However, non-Newtonian fluids deviate from this linear relationship with \(n\) typically less than one and its magnitude being a measure of the deviation from Newtonian behavior.

Using equations (20) and (21), the data in Table 7 were converted to \([\operatorname{Ln} \tau]\) versus \([\operatorname{Ln} \gamma]\) and plotted. Figure 8 illustrates the response for the unfilled polymer solutions. Figure 9 illustrates the data for the TIO-3 filled solutions and it is representative of the other dispersions. As equation (21) indicates, n is observed to be the slope of these graphs. These n values were determined by applying the data to a least squares regression analysis to obtain a linear equation for the graphs. Table 8 provides the resulting n values and the equation correlation coefficients. These results illustrate that the unfilled PMMA solutions display Newtonian behavior. However, as filler is added to the solutions, the dispersions tend to
deviate to non-Newtonian behavior. This is especially true for the higher PMMA molecular weight materials (PMMA-4 and 5), and the trend is most significant for dispersions with TIO-3 and SIO-1. The first observation is expected since increasing molecular weight increases chain entanglements which cause non-Newtonian behavior. In addition, interactions between filler materials and polymer chains complicate flow properties and lead to non-Newtonian behavior. This is suggested by the Einstein theory [equation (12)] and Ziegel's results. \({ }^{16}\)

Applying the viscosity data in Table 7 to the Einstein model, it is clear that equation (12) is not strictly valid for the dispersions studied. In all cases, \(\eta_{\text {sp }} / v_{\mathrm{f}}\) values are greater than 2.5 , indicating that all of these fillers interact to some extent with the PMMA solutions. To evaluate further the extent of this interaction and the resulting effective filler volume ( \(\mathrm{v}_{\mathrm{e}}\) ) due to the adsorbed layer \((\Delta r), \eta_{s p} / \mathrm{v}_{\mathrm{f}}\) was plotted as a function of reciprocal shear rate. Figure 10 illustrates the response for the TIO-3 systems. As in Ziegel's approach described earlier, these values were extrapolated to infinite shear rate \((1 / \gamma \longrightarrow 0)\). The resulting values were applied to equation (13) to obtain \(\Delta r\), the thickness of the adlayer "shell." It should be noted that the theoretical basis for these calculations (as described previously) requires that the particles be noninteracting. Although this is not usually the case


Figure 9-Ln \(\tau\) vs \(\operatorname{Ln} \dot{\gamma}\) for PMMA solutions filled with 6.4 v/o TIO-3 titanium dioxide


Figure \(10-\eta_{\text {sp }} / v_{1}\) vs reciprocal shear rate for PMMA solutions filled with 6.4 v/o TIO-3 titanium dioxide


Figure 11-Adlayer thickness of PMMA-1 on filler particles


Figure 12—Adlayer thickness of PMMA-2 on filler particles


Figure 13-Adlayer thickness of PMMA-3 on filler particles


Figure 14-Adlayer thickness of PMMA-4 on filler particles


Figure 15-Adlayer thickness of PMMA-5 on filler particles
\begin{tabular}{|c|c|}
\hline Filler & Effective Filler Volume Concentration (\%) \\
\hline TIO-1 & ... 25.6 \\
\hline TIO-2 & ...... 27.4 \\
\hline TIO-3 & ........ 26.4 \\
\hline SIO-1 & .............. 84.0 \\
\hline
\end{tabular}
for filler particles in paints, it would appear to be a valid assumption at the extremely high shear rates experienced during the viscosity measurements.

Figures 11-15 compare the adlayer thickness values generated from this analysis of viscosity characteristics with those determined directly from centrifugation. The values range from 9 to 110 nanometers, and they did vary with filler and the experimental method. The effective filler volume levels resulting from these radial increases are presented in Table 9. These results are evidence that PMMA adsorbs onto the filler surface, thereby creating a shell of polymer which remains attached to the filler particles even at high shear rates.

In all cases, \(\Delta \mathrm{r}\) values determined from centrifugation are lower than those from viscosity. In order to explain this observation, centrifuge and viscosity experimental conditions are compared. Centrifugation compacts the particles into a high concentration with maximum dense random packing within the sediment. This forces unbound polymer chains in solution away from the surface. The ease with which this fluid separates from the solid is inversely proportional to the degree of filler-resin interaction. It may be suggested that this condition of high pigment concentration and high compaction forces allows only firmly adsorbed molecules to remain at the filler surface, thereby forming a rigid polymer shell. In contrast, calculations based on the Einstein model and viscosity data dictate that pigment concentration be low for the analysis to be valid. Furthermore, viscosity measurements, which start at low shear, are sensitive to chains that may have little direct interaction with the solid surface, but are attached to the adlayer through entanglements and secondary bonding. In this case, an extended adlayer exists. This explanation is consistent with results presented by Isobe \({ }^{19}\) and described earlier in this paper that adlayer thicknesses decrease to a minimum value with increasing pigment concentration. The results in the current study and the coinciding explanation support the rigid shell-extended adlayer model proposed earlier in this
paper, and explain the consistently higher estimates of adlayer thickness from viscosity data in comparison with centrifugation.

Concerning adlayer variations between particles, it is interesting to note that the PMMA adlayer thicknesses on the filler particles generally follow the trend of TIO-1 > TIO-2 > TIO-3 > SIO-1. This follows the trend of their reactivity with PMMA and methyl methacrylate monomer as determined from \(\mathrm{IGC}^{28}\) and flow calorimetry, \({ }^{45}\) providing support for the theory that increased filler-polymer interaction leads to thicker adlayers. Furthermore, there is a general trend that adlayer thickness increases with increasing particle size, but the relative increase in adlayer thickness, \(\Delta r / R\), decreases with increasing particle size (Table 10). This is especially true for SIO-1. Several researchers \({ }^{17.23}\) also have reported the former observation of increased adlayer with increasing particle size.

One explanation for this observation is that polymer molecules adsorbing from a melt or high concentration solution onto a surface will usually orient in a "tail and loop" configuration (Figure 16) as described by Silberberg \({ }^{46}\) and Scheutjens. \({ }^{47.48}\) In the case of a flat or large curvature surface (large radius), full surface coverage and reduced surface curvature excludes some molecular segments from multiple adsorption on the surface due to volume restrictions. Consequently, a lower number of segments are attached to the surface but the extension of the polymer chains away from the surface will be greater, causing a thicker adlayer. In effect, the chains are forming fewer but longer tails and loops. However, smaller particles allow greater access to their surface due to increased curvature, further allowing higher adsorption densities (i.e., individual chains have more adsorption sites with shorter tails and loops).

Another observation from Figures 11-15 is that the lower molecular weight PMMA (PMMA-1) has higher adlayer thicknesses than the other PMMA samples in nearly all of the centrifuge results. One explanation may be that lower molecular weight species are more prone to orient in the tail configuration with just one end of the molecule attached to the surface (i.e., no or few loops).

It should be noted that an increase in particle radius imparts a cubic increase in the volume occupied by that particle:
\[
\begin{equation*}
\frac{V_{f}}{V_{i}}=\frac{(R+\Delta r)^{3}}{R^{3}} \tag{22}
\end{equation*}
\]
where \(V_{i}\) is the volume occupied by a particle of radius \(R\) prior to adsorption and \(\mathrm{V}_{\mathrm{f}}\) is the volume occupied by that particle after formation of the adlayer, \(\Delta \mathrm{r}\). (Note that this

Table 10-Normalized Adlayer Thickness Values ( \(\Delta r / R\) ) for Titanium Dioxide and Silica in PMMA-3. Adlayer Thickness Values Determined from Viscosity Measurements
\begin{tabular}{|c|c|c|c|}
\hline Filler \(\quad\)\begin{tabular}{c} 
Particle Radius \\
\((R\) in \(n m)\)
\end{tabular} & Adlayer Thickness ( \(\Delta \mathrm{r}\) in nm ) & Relative Radial Increase ( \(\Delta r / R\) ) & Relative Volume Increase \(\left(\mathbf{v}_{i} / V_{t}\right)\) \\
\hline TIO-1 ................................................. 150 & 70 & 0.47 & 3.97 \\
\hline TIO-2 ................................................... 96 & 65 & 0.67 & 4.28 \\
\hline TIO-3 ................................................... 73 & 51 & 0.63 & 4.13 \\
\hline SIO-1 ..................................................... 8 & 17 & 2.18 & 40.00 \\
\hline
\end{tabular}


Figure 16-Train, tail, and loop model for adsorption of a polymer chain onto a solid particle
relationship is also equal to \(\mathrm{v}_{\mathrm{e}} / \mathrm{v}_{\mathrm{f}}\).) Due to this relationship, an equivalent increase in adlayer thickness will have a greater effect with smaller particles. Table 10 compares relative increases in particle radius and volume, \(\Delta r / R\) and \(V_{t} / V_{i}\), for the composites tested. It is clear that adlayer formation on SIO-1 has by far the most significant effect on relative radial and volumetric increases. However, even the \(\mathrm{TiO}_{2}\) fillers have relative increases greater than those of previously analyzed systems (Table 1). This is probably due to the high reactivity of \(\mathrm{TiO}_{2}\) and \(\mathrm{SiO}_{2}\) surface, especially \(\mathrm{SiO}_{2}\). The effect on composite properties should be similar to that of increasing pigment loading level, such as increased modulus with decreased toughness and permeability.

\section*{CONCLUSIONS}

Centrifugation and viscosity measurements were used to calculate an effective diameter of the dispersed filler particles in a polymer solution. The effective diameter is based on the extension of the filler particle size due to a polymer adsorbed layer (adlayer) firmly adhered to the surface of filler particles. These adlayer thicknesses ranged from 9 to 110 nm for silica and titanium dioxide fillers in PMMA, varying with filler type and polymer molecular weight. Adlayer thickness increased with increasing particle size. However, relative increase in adlayer thickness ( \(\Delta r / R\) ) and the associated increase in effective filler volume was more significant with small particles. This effect was attributed to geometric limitations causing polymer chain conformation restrictions. Furthermore, lower molecular weight PMMA ( \(\mathrm{M}_{\mathrm{w}}=11,000\) ) formed thicker adlayers. It was proposed that the lower molecular weight species adsorb mostly in tail configurations, while higher molecular weight species form both tails and loops which do not extend as far from the particle surface. An analogy with transcrystallinity was made, where lower molecular weight species form thicker crystalline domains.

The adlayer thicknesses calculated from viscosity experiments were typically greater than those from the centrifugal packing. These results led to propose a model for the polymer adlayer state, consisting of an effectively bonded shell surrounding the particle surface, with a loosely bonded region extending further into the bulk matrix.

All of the viscosity measurements on dispersed filler systems indicated a shear thinning effect (i.e., decreased viscosity with increased shear rate). This effect is usually attributed to loosely entangled polymer chains being freed as shear increased. The effect was much more significant with the nanometer-size silica filler SIO-1, and was attributed to its small particle size which caused a larger effective filler volume.

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\title{
Use of Formic Acid in Controlling the Rate Of the Michael Addition Reaction in Base Catalyzed, Thermally Cured Acetoacetylated Acrylic/TMPTA Coatings
}

\author{
T. Li* and J.C. Graham \\ Eastern Michigan University \({ }^{\dagger}\)
}

\begin{abstract}
Thermosetting coatings are formulated based on the Michael Addition reaction of acetoacetylated acrylic resins and acrylic crosslinkers catalyzed by 1,8 -diazabicyclo[5,4,0]undec-7-ene. The catalyst is blocked by equivalent or larger amount of formic acid to extend the gel time from only two to three hours to over two months. The clear coatings and pigmented paints are
\end{abstract}
cured upon baking for 40 min at \(100^{\circ} \mathrm{C}\). This block technique brings no appreciable changes in the ultimate properties of the coatings. By introducing reactive diluents and powerful solvents such as methyl amyl ketone, we have been able to reduce the volatile organic content to as low as \(240 \mathrm{~g} / \mathrm{L}\).

\section*{INTRODUCTION}

In searching for new approaches to replace isocyanate/alcohol and melamine/alcohol based two-package coatings, \({ }^{1.2}\) several studies have examined the Michael Addition reaction of the acetoacetyl group with acrylate double bond. \({ }^{3-5}\) This reaction proceeds rapidly at room temperature in the presence of basic catalysts such as 1,8 -diazabicyclo[5,4,0]undec7 -ene (DBU), producing a mixture of mono-(I) and bisadducts(II), as illustrated in the following:


\footnotetext{
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}

Literature also shows that high polymers are prepared based on this reaction. \({ }^{6}\)

The acetoacetyl group is typically incorporated into acrylic resins by conventional radical copolymerization of acrylic monomers such as methyl methacrylate (MMA) and acetoacetoxyethyl methacrylate (AAEM). Trimethylolpropane triacrylate (TMPTA), a commercial trifunctional acrylate, is usually used as the crosslinker.

This reaction provides three advantages to the coating formulation: (1) both resins and crosslinkers are acrylics in nature, which generates good weathering stability; (2) the acetoacetyl monomer units lower the viscosity of the resins with a reduction in volatile organic content (VOC); and (3) the coating can be cured rapidly at room temperature.

On the other hand, problems exist with these coatings in that their short pot life limits the application of this technology. To prolong the pot life with a balance of good cure speed and good coating properties, we have developed a technique to block the base catalyst with formic acid (FA). The coating is cured at elevated temperatures as the acid releases. Similar concepts have been found in other systems such as blocked sulfonic acid in polyester/melamine coatings. \({ }^{7}\) The coatings are stable at room temperature and cure

by baking when the acid catalyst is released. Another example is the neutralization of acid groups with volatile amines in water-soluble acrylic coatings. \({ }^{8.9}\) These acid groups are regenerated for crosslinking as the amines evaporate from the film surface, particularly at high temperature. DBU, the catalyst most commonly used in the Michael Addition reaction, is a fairly strong base ( \(\mathrm{pKb} 12.5^{4}\) ) and forms salts with acids. In a recent European patent, \({ }^{10}\) carboxylic acids including FA were employed to block the amidine catalyst in reactions of activated unsaturated group and activated CH group to form long pot life coatings. In some samples, the gel time was extended to as long as four weeks at \(50^{\circ} \mathrm{C}\).

\section*{EXPERIMENTAL}

\section*{Materials}

MMA, ethyl acrylate (EA), butyl acrylate (BA), xylenes, methyl amyl ketone (MAK), 2-mercaptoethanol, DBU, ethyl acetoacetate (EAA), TMPTA, triethylamine (TEA), triethanolamine (TEOA), FA, acetic acid (AA), and ptoluenesulfonic acid monohydrate (p-TSA) were purchased from Aldrich. Acetoacetoxy-ethyl methacrylate and t-butyl
\begin{tabular}{|c|c|c|c|}
\hline \multicolumn{4}{|l|}{Table 2-Resin Properties and Their Cure Performance \({ }^{\text {a }}\)} \\
\hline Acrylic Resin No. 6 & Acrylic Resin No. 3 & Acrylic Resin No. 7 & Acrylic Resin No. 8 \\
\hline \begin{tabular}{l}
MMA/BA/AAEM \\
(mol) ................... 58/32/10
\end{tabular} & 50/25/25 & 42/18/40 & 35/10/55 \\
\hline T, \(\left({ }^{\circ} \mathrm{C}\right)\) (calculated) ..... 16 & 16 & 16 & 16 \\
\hline Nonvolatile \% ........... 59.2 & 60.1 & 60.8 & 61.2 \\
\hline \begin{tabular}{l}
Viscosity \\
Brookfield (cps) ....... 208
\end{tabular} & 158 & 142 & 110 \\
\hline Molecular weight
\[
\left(M_{n}, \text { GPC }\right) \ldots \ldots \ldots \ldots . . .2,200
\] & 2,300 & 2,700 & 2,300 \\
\hline \(\mathrm{M}_{\mathrm{u}} / \mathrm{M}_{n}\).................... 1.69 & 1.57 & 1.48 & 1.84 \\
\hline Acetocetyl group/ molecular chain \(\qquad\) & 4.2 & 7.2 & 7.7 \\
\hline Gel time (hours) .......... 8.0 & 3.5 & 2.5 & 1.5 \\
\hline Acetone rub ............... 10 & 200 & 200 & 200 \\
\hline Pencil hardness \({ }^{\text {b }}\)......... \(<5 \mathrm{~B}\) & 5 H & 5 H & 5 H \\
\hline Impact resistance ..... 160/160 & 60/70 & 40/60 & 20/5 \\
\hline \multicolumn{4}{|l|}{(a) TMPTA/AAEM \(=0.75\). \(\mathrm{DBU}=2.0 \%\), room temperature curing. (b) Values of direct/reverse. The same in the following tables.} \\
\hline
\end{tabular}
acetoacetate ( \(\mathrm{t}-\mathrm{BAA}\) ) were obtained from the Eastman Company. 2.2'-Azobis (2-methylbutyronitrile) (AIBN) and titanium dioxide \(\left(\mathrm{TiO}_{2}\right)\) were obtained from the Du Pont Company. Tetraethyleneglycol diacrylate (TTEGDA) and anti-Terra-U were obtained from Sartomer and BYK-Chemie, respectively. All chemicals were used as received.

\section*{Synthesis of Acrylic Copolymers}

The acrylic (MMA/BA/AAEM) copolymers were synthesized by conventional radical polymerization under a monomer starved condition at \(95^{\circ} \mathrm{C}\) in xylenes or in MAK, using AIBN ( \(1.0 \%\) by wt.) as an initiator and 2 mercaptoethanol ( \(3.0 \%\) by wt.) as a chain transfer agent. The reactions were carried out for nine hours until \(100 \%\) conversion was reached as confirmed by IR and solids determination. The polymer solutions were used in coating formulations without precipitation. The composition and properties of the acrylic resins are shown in Tables 1 and 2.

\section*{Molecular Weight Determination}

Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC). The instrument included a Waters Model 510 pump, a Waters Model R410 differential refractometer detector, and four columns: one Phenogel \(500 \AA\) and three \(100 \AA\) columns. Tetrahydrofuran was used as the eluant and polystyrene was used as the standard.

\section*{Model Reactions}

Model reactions of EAA/EA/DBU system in the presence or in the absence of FA were monitored by gas chromatography (GC) using a Hewlett-Packard 3393A integrator and a Superox ( 30 m length, 0.25 mm diameter) capillary column. EAA ( \(2.6 \mathrm{~g}, 20 \mathrm{~m} \mathrm{~mol}\) ) and EA ( \(2.0 \mathrm{~g}, 2.0 \mathrm{~m} \mathrm{~mol}\) ) were mixed in a 10 mol vial and the solvent xylene was added to a total volume of 9 mL . DBU ( \(0.1 \mathrm{~g}, 0.066 \mathrm{~m} \mathrm{~mol}\) ), and FA \((0.03 \mathrm{~g}, 0.066 \mathrm{~m} \mathrm{~mol})\) were then introduced. After shaking, the solution was kept at room temperature. Samples were taken for GC analysis at various time intervals. Before injection, the reaction mixture was quenched by HCl solution in ether. No further attempts were made to control the reaction temperature.

\section*{Clear and Pigmented Coating Formulations}

The clear coatings based on acetoacetylated acrylic resin, TMPTA and DBU (and FA in some formulations), were drawn on phosphated steel panels (R-36-P, Q-Panel Company) using a \#36 wire-wound draw bar. The films were kept at room temperature for five days before measuring the properties. No property changes were observed thereafter. Film thickness was 1.4 mil as measured by Mikrotest III Thickness Gauge.

To formulate a paint, acrylic resin (two-thirds of the total amount), DBU, dispersing agent Anti-Terra-U (1.5\% of pigment loading) were dispersed for 30 min , with \(\mathrm{TiO}_{2}\) added slowly. Then, the remaining acrylic was introduced and the mixture was dispersed for another 20 min . The paint samples were stabilized for 24 hr before xylene, TMPTA, and FA were added. The pigment/binder ratio was \(0.9 / 1.0\). The paint films were drawn as for clear coatings and cured in an airforced oven at \(100^{\circ} \mathrm{C}\) for 40 min and then stored at room temperature for five days for property measurement. The film thickness was 1.0 mil .

\section*{Gel Time Tests}

Gel time tests were carried out in sealed tubes at room temperature. Acrylic copolymer (containing DBU catalyst) and TMPTA were introduced into the tube and the mixture was shaken by hand. The time at which the system stopped flowing was defined as get time.

\section*{Other Measurements}

Nonvolatile content, Brookfield viscosity, Sward hardness, and adhesion were measured using ASTM D 2369-87, D 2196-86, D 2134-66, and D 3359-97 procedures, respectively. VOC was determined according to ASTM D 3960-87. Zahn cup viscosity was measured according to ASTM D 3794-79 using a \#2 cup. Gloss was measured by ASTM D 523-85. Solvent rub resistance was measured by double rubbing with acetone saturated nonwoven paper (Kim-Wipe). Pencil hardness was measured by ASTM D 3363-74, and impact resistance tests were carried out using a Gardner Impact tester with a maximum impact of \(160 \mathrm{in} .-\mathrm{lb}\).

\section*{RESULTS AND DISCUSSION}

\section*{Curing Performance of Acetoacetylated Acrylic/ TMPTA/DBU Systems at Room Temperature}

To investigate the general cure performance of acetoacetylated acrylics/TMPTA coatings in the presence of DBU, a series of terpolymers of MMA/BA/AAEM was synthesized as coating resins. The MMA/BA molar ratios varied from \(1 / 0\) to \(0 / 1\) while the AAEM level was kept at \(25 \%\). See Table 1 for the composition and selected properties.

The effect of MMA/BA ratio of the copolymer on the curing was investigated at room temperature. The coatings were formulated with the copolymer containing 1 mol AAEM unit, 0.66 mol TMPTA (equivalent ratio of TMPTA/AAEM \(=1)\) and 0.02 mol DBU. Table 1 shows that with increasing the BA/MMA ratio, the gel time becomes longer and the solvent resistance and pencil hardness of the coatings dete-
\begin{tabular}{ccccc}
\hline \multicolumn{5}{c}{ Table 3-Effect of TMPTA/AAEM on the Cure Performance \({ }^{\mathrm{a}}\)} \\
TMPTA/AAEM \({ }^{\mathrm{b}}\) & \begin{tabular}{c} 
Gel Time \\
(Hours)
\end{tabular} & \begin{tabular}{c} 
Acetone \\
Resistance
\end{tabular} & \begin{tabular}{c} 
Pencil \\
Hardness
\end{tabular} & \begin{tabular}{c} 
Impact \\
Resistance
\end{tabular} \\
\hline 0.25 & 9.0 & 10 & F & \(160 / 160\) \\
0.50 & 4.2 & 47 & 5 H & \(100 / 80\) \\
0.75 & 3.3 & 200 & 5 H & \(20 / 20\) \\
1.00 & 2.4 & 200 & 5 H & \(10 / 5\) \\
1.25 & 2.2 & 200 & 5 H & \(30 / 20\) \\
2.00 & 1.8 & 54 & 5 H & \(160 / 160\)
\end{tabular}
(a) Resin No. \(2(\mathrm{MMA} / \mathrm{BA} / \mathrm{AAEM}=60 / 15 / 25), \mathrm{DBU}=2,0 \%\), room temperature curing.
(b) The equivalent ratio of TMPTA to AAEM unit of the acrylic resins.
riorate. The impact resistance is substantially improved which might, however, reflect an incomplete cure. Apparently, more flexible molecular chains (higher BA/MMA) of the copolymer did not respond as well to the Michael Addition crosslinking reaction as might be expected. The slower reaction can be attributed to steric hindrance of the n-butyl groups. Increasing the BA/MMA ratio would increase this hindrance.

It seems that good coatings are formulated with resins containing at least 50\% MMA. A small amount of BA units can reduce the resin viscosity (see Table 1), which leads to reduced VOC, and improves the impact resistance of the coating.

The equivalent ratio of TMPTA to AAEM units (TMPTA/ AAEM) affects the cure performance significantly. As shown in Table 3 a TMPTA/AAEM ratio between 0.75 and 1.25 generates good film properties. Below or above this level, the coating formulations are not able to produce satisfactory solvent resistance because of low crosslinking density. In these cases, the effective functionality of either the acetoacetyl group or TMPTA was actually reduced.

Resins with \(60 / 15 / 25\) and 50/25/25 of MMA/BA/AAEM seem to form promising coatings at the TMPTA/AAEM ratio from 0.75 to 1.25 . However, the gel times of about two to three hours are too short to be useful in most coating applications.

The effect of the functionality of the copolymer on the cure performance is shown in Table 2. Samples No. 6, 3, 7, and 8 have increased AAEM unit amounts from 10 to \(55 \%\). A constant glass transition temperature \(\left(\mathrm{T}_{\mathrm{g}}\right)\left(16^{\circ} \mathrm{C}\right)\) was obtained by varying MMA/BA ratio so that the additional effect of chain flexibility was ruled out.

Table 4-Cure Performance of Acrylic/TMPTA Coatings in the Presence of Formic Acid \({ }^{\text {a }}\)
\begin{tabular}{lcccc} 
FA/DBU & \begin{tabular}{c} 
Gel Time \\
(Hours)
\end{tabular} & \begin{tabular}{c} 
Acetone \\
Resistance
\end{tabular} & \begin{tabular}{c} 
Pencil \\
Hardness
\end{tabular} & \begin{tabular}{c} 
Impact \\
Resistance
\end{tabular} \\
\hline 0 & 1.5 & 200 & 5 H & \(10 / 10\) \\
0.5 & 2.5 & 200 & 5 H & \(40 / 5\) \\
0.8 & 10.0 & 200 & 4 H & \(60 / 10\) \\
1.0 & \(>2\) months & 160 & 5 H & \(60 / 10\) \\
2.0 & \(>2\) months & 160 & 5 H & \(50 / 10\) \\
4.0 & \(>2\) months & 140 & 5 H & \(120 / 120\) \\
\(1.0(\mathrm{DBU}=\) & & & & \\
\(6.0 \%)\) & \(>2\) months & 200 & 5 H & \(60 / 10\)
\end{tabular}
(a) Resin No. 2 (MMA/BA/AAEM \(=60 / 15 / 25\) ). TMPTA/AAEM \(=1.0, \mathrm{DBU}=4.0 \%\), baked at \(100^{\circ} \mathrm{C}\) for 40 min .

Table 5-Effect of Storage Time of Coatings on Film Properties \({ }^{\text {a }}\)
\begin{tabular}{lcccc} 
DBU Amount & \begin{tabular}{c} 
Storage \\
Time (Day)
\end{tabular} & \begin{tabular}{c} 
Acetone \\
Resistance
\end{tabular} & \begin{tabular}{c} 
Pencil \\
Hardness
\end{tabular} & \begin{tabular}{c} 
Impact \\
Resistance
\end{tabular} \\
\hline \(4.0 \%\) & 0 & 160 & 5 H & \(60 / 10\) \\
& 1 & 155 & 5 H & \(70 / 20\) \\
& 4 & 150 & 5 H & \(80 / 40\) \\
\(6.0 \%\) & 10 & 150 & 5 H & \(50 / 10\) \\
& 0 & 200 & 5 H & \(30 / 10\) \\
& 1 & 200 & 5 H & \(50 / 10\) \\
& 4 & 200 & 5 H & \(50 / 10\) \\
& 10 & 200 & 5 H & \(20 / 20\) \\
(a) FA/DBU \(=2.0\). other conditions are the same as in Table 4. & \\
\hline
\end{tabular}
\(\mathrm{T}_{\mathrm{g}} \mathrm{s}\) of these copolymers are calculated with the following equation: \({ }^{11}\)
\[
100 / \mathrm{T}_{\mathrm{g}}=\mathrm{a} / \mathrm{T}_{\mathrm{g} 1}+\mathrm{b} / \mathrm{T}_{\mathrm{g} 2}+\mathrm{c} / \mathrm{T}_{\mathrm{g} 3}
\]
where \(\mathrm{T}_{\mathrm{g} 1}, \mathrm{~T}_{\mathrm{g} 2}\) and \(\mathrm{T}_{\mathrm{g} 3}\) refer to the glass transition temperatures of homopolymers of MMA, BA, and AAEM, respectively, and \(\mathrm{a}, \mathrm{b}\), and c the molar percentages of the monomer units in the copolymer. The \(T_{g}\) on the left hand of the equation represents the glass transition temperature of the copolymer. Since the molecular weights of the resins are low, this equation can only provide a rough estimate of the \(\mathrm{T}_{\mathrm{g}}\).

At a high AAEM content (No. 8, 55\% by mol), embrittlement was the result of a high crosslink density, as shown from the impact data. The gel time was short ( 1.5 hr ). On the other hand, resin No. 6 had a low AAEM content ( \(10 \%\) ) and thus a low average functionality per chain (less than two). Although it provided a fairly long pot life (gel time of eight hours), no applicable properties could be obtained because of the incomplete curing. Compromising the coating properties and pot life, and considering that AAEM


Figure 1-Consumption of EAA and EA with time in Michael Addition in the absence and in the presence of formic acid. ( \([E A A]=[E A]=2.2 \mathrm{M},[\mathrm{DBU}]=6.6 \times 10^{-2}\), in xylene). (1) EAA ([FA] \(=0)\); (2) EA ([FA] = 0); (3) EAA ([FA] \(\left.=6.6 \times 10^{-2} \mathrm{M}\right)\); and (4) EA
([FA] \(=6.6 \times 10^{-2} \mathrm{M}\) )
is a relatively expensive monomer, a level of \(25 \%\) AAEM would be an optimum composition.

\section*{Inhibition Effect of Formic Acid in Model Reaction}

The previously mentioned results indicate that clear coatings based on acetoacetylated acrylic/TMPTA/DBU can be cured at room temperature; however, they have generally short pot life. Although some approaches, such as increasing BA/MMA ratio and lowering AAEM unit content in the acrylic composition, could prolong the gel time, the coating properties would suffer. Using a volatile acid to "block" the basic catalyst was then considered and FA was chosen because of its low boiling point \(\left(100^{\circ} \mathrm{C}\right)\).

The model reaction of EAA and ethyl acrylate (EA) catalyzed by DBU was investigated. Compared to the rapid reaction in the absence of FA, in which EA was nearly consumed completely within three hours, the addition of an equimolar amount (to DBU) of FA suppressed the reaction dramatically. Only \(5 \%\) of the available amount of EA was reacted after 7.5 hr (Figure 1) and the appearance of monoand bis-adducts also was very slow (Figure 2).

Apparently, salt formation leads to deactivation of the DBU catalyst as shown in the following:
\[
\mathrm{DBU}+\mathrm{HCOOH}^{\rightleftarrows} \longrightarrow \mathrm{DBUH}^{+} \mathrm{HCOO}^{-}
\]

This reaction can reasonably by considered in an equilibrium with a small amount of free FA and DBU existing in solution. Unfortunately, the free acid and base were not detectable with GC analysis; these two compounds have very low GC responses. However, when FA was replaced with AA, a small amount of free acid (less than \(1 \%\) ) was detected from the chloroform solution of DBU/AA salt.

As expected, at higher temperatures, decomposition of the \(\mathrm{DBUH}^{+} \mathrm{COO}^{-}\)salt releases volatile FA , regenerating free DBU which then is available for catalyzing the Michael Addition reaction:


Figure 2-Production of mono-and bis-adducts with time in Michael Addition in the absence and in the presence of formic acid. \(\left([E A A]=[E A]=2.2 \mathrm{M},[D B U]=6.6 \times 10^{-2} \mathrm{M}\right.\), in xylene). (1) mono-adduct ( \([F A]=0\) ); (2) bis-adduct ( \([F A]=0\) ); (3) monoadduct ([FA] \(=6.6 \times 10^{-2} \mathrm{M}\) ); and (4) bis-adduct \(\left([F A]=6.6 \times 10^{-2} \mathrm{M}\right.\) )
\[
\mathrm{DBUH}^{+} \mathrm{COO} \xrightarrow{\Delta} \mathrm{DBU}+\mathrm{HCOO} \uparrow
\]

Such a reaction was indeed observed for DBU/AA salt. The salt was heated at \(90^{\circ} \mathrm{C}\) with the help of vacuum evaporation for two hours and the remaining AA was analyzed by GC. About \(20 \%\) of this acid was lost. In this procedure, the salt, before and after heating, was dissolved in chloroform and reacted with excess of strong acid \(\mathrm{HC1}\). The acetic acid was replaced quantitatively and was determined by GC. A faster evaporation might be expected when the acid is well dispersed in the coating mixture and when a thin film is applied, especially for the more volatile FA.

\section*{Clear Coatings with Blocked Catalyst and Baked at Elevated Temperature}

Clear coatings were formulated based on acetoacetylated acrylic resin, TMPTA, and DBU with AAEM/TMPTA \(=1\), using FA to retard the reaction, and then baked at \(100^{\circ} \mathrm{C}\) for 40 min . The results are shown in Table 4.

While the gel time was only slightly extended at the ratio FA/DBU \(<1\) (by mol), it was prolonged dramatically when FA/DBU \(>1\). The samples could be stored for at least two months without gelling. After baking for 40 min , a tack-free film was immediately obtained although the ultimate, stable properties were finally achieved after five days at room temperature. DBU was introduced ( \(4.0 \%\) ) to produce fairly good properties and \(6.0 \%\) DBU produced coatings with desirable properties equal to those coatings containing \(2 \%\) DBU without using FA (compare to Tables 1 and 3). It might be because the DBU/FA salt was only partially decomposed upon baking. Changing the acid amount from 1.0 to 4.0 did not show appreciable effect on the cure performance.

The film properties are little affected by the storage time of the coatings prior to baking, as shown in Table 5. After 10 days, coatings with FA blocked DBU still produced the same properties as the freshly prepared samples. This advantage allows storage of the formulated coatings for a fairly long period of time before use.

\section*{Room Temperature Curing}

The previously mentioned formulations can also be used to form ambient temperature curable coatings, although the reaction is much slower than under baking conditions (Table 6). For example, a coating based on resin No. 2 (MMA/BA/ AAEM \(=60 / 15 / 25\) ) and TMPTA produced a film after five days of room temperature curing, although the solvent resistance was poorer than those obtained under baking conditions. Crosslinking continually developed over a longer time period and eventually (after one month or longer) reached the properties very close to baked coatings. It appears that FA can be released gradually from the salt and evaporates out of the film surface even at room temperature. Nevertheless, the rather long tack-free time (eight hours to two days, depending on the DBU amount and FA/DBU ratio) may limit this technique to only some special applications.

\section*{Comparison with Other Catalyst Systems}

A few other acids were also examined, both at ambient condition and baking condition (Table 7). HC1 and p-TSA,

Table 6-Room Temperature Curing of Acrylic/TMPTA Coatings in the Presence of Formic Acid \({ }^{\text {a }}\)
\begin{tabular}{lcccc} 
DBU & FA/DBU & \begin{tabular}{c} 
Acetone \\
Resistance
\end{tabular} & \begin{tabular}{c} 
Pencil \\
Hardness
\end{tabular} & \begin{tabular}{c} 
Impact \\
Resistance
\end{tabular} \\
\hline \(4.0 \%\) & 1.0 & 80 & 4 H & \(160 / 140\) \\
& 2.0 & 80 & 4 H & \(160 / 160\) \\
\(6.0 \%\) & 1.0 & 150 & 5 H & \(100 / 100\) \\
& 2.0 & 150 & 5 H & \(120 / 100\) \\
\begin{tabular}{l} 
(a) Resin No. 2 (MMA/BA/AAEM \(=60 / 15 / 25)\).
\end{tabular} \\
\begin{tabular}{l} 
measured after five days.
\end{tabular}
\end{tabular}


\begin{tabular}{|c|c|c|c|}
\hline \multicolumn{4}{|l|}{Table 9-Paint Formulation and Properties} \\
\hline Paint No. 1 & Paint No. 2 & \begin{tabular}{l}
Paint \\
No. 3
\end{tabular} & Paint No. 4 \\
\hline Resin ........................ 100 & 100 & 100 & 100 \\
\hline t-BAA .......................- & - & - & 8.37 \\
\hline TMPTA .................. 25.48 & 11.91 & 25.48 & 35.49 \\
\hline TTEGDA ...................- & 9.59 & - & - \\
\hline DBU (4.0\%) ............... 0.78 & 0.78 & 0.78 & 1.01 \\
\hline FA ............................ 0.94 & 0.94 & 0.21 & 1.34 \\
\hline FA/DBU ..................... 4 & 4 & 0.9 & 4 \\
\hline \(\mathrm{TiO}_{2}\)....................... 85.93 & 88.97 & 85.93 & 102.89 \\
\hline Anti-Terra-U ............... 1.29 & 1.33 & 1.29 & 1.54 \\
\hline MAK ....................... 22.5 & 22.5 & 22.5 & 21.5 \\
\hline Solid \% .................... 79.40 & 78.95 & 80.85 & 82.82 \\
\hline lb/gal ....................... 11.54 & 11.63 & 11.58 & 11.85 \\
\hline VOC (lb/gal) ............... 2.38 & 2.45 & 2.22 & 2.02 \\
\hline FA (lb/gal) ................. 0.056 & 0.054 & 0.012 & 0.068 \\
\hline PVC (\%) .................. 20.4 & 20.4 & 20.4 & 20.1 \\
\hline Pot life ................ \(>2 \mathrm{wk} / 50^{\circ} \mathrm{C}\) & \(>2 \mathrm{wk} / 50^{\circ} \mathrm{C}\) & \(8 \mathrm{hr} / \mathrm{r} . \mathrm{t}\). & 10 days \(/ 50^{\circ} \mathrm{C}\) \\
\hline \multicolumn{4}{|l|}{Viscosity} \\
\hline Zahn Cup (\#2) ........ 74.3 & 66.1 & 75.0 & 86.7 \\
\hline Ford (\#4) ................ 45.7 & 42.7 & 46.0 & 49.8 \\
\hline Brookfield (cps) ....... 488 & 460 & 480 & 600 \\
\hline
\end{tabular}
two strong acids, form stable salts with DBU that do not decompose at our baking temperatures. Consequently, no DBU was regenerated and no crosslinking occurred upon heating. However, if the ratio was slightly less than one, as in the case of p-TSA/DBU \(=0.9\), partial crosslinking was obtained because of the presence of a small amount of free DBU. The behavior of AA was quite similar to FA except for a little less solvent resistance of the resulting coatings probably because AA evaporates less rapidly than FA.

Although triethylamine (TEA) and triethanolamine (TEOA) catalyzed the EAA/EA reaction at elevated temperature slowly, they did not lead to a practical coating. The film was still not dry after five days.

\section*{Paint Formulations}

Based on the previously mentioned investigation, several pigmented paints were formulated. The xylene-based resins provided an applicable paint viscosity and good film properties; however, the lowest VOC we reached was \(310 \mathrm{~g} / \mathrm{L}(2.6\) \(\mathrm{lb} / \mathrm{gal})\), a little higher than our target \((300 \mathrm{~g} / \mathrm{L})\). The resin was then synthesized in a more powerful solvent MAK. Table 8 shows its composition and properties and Table 9 presents the paint formulation and properties.

Paint No. I was formulated from acetoacetylated acrylic resin (MMA/BA/AAEM \(=50 / 25 / 25)\), TMPTA, and DBU ( \(4 \%\) ). FA ( 4 mol to 1 mol DBU ) was added to block the catalyst. At a \#4 Ford viscosity of 45.7 sec , this paint is suitable for brush application. The VOC was determined as low as \(290 \mathrm{~g} / \mathrm{L}(2.4 \mathrm{lb} / \mathrm{gal})\) and the FA released upon baking was calculated to be no more than \(7.0 \mathrm{~g} / \mathrm{L}(0.056 \mathrm{lb} / \mathrm{gal})\) assuming all the FA evaporates out during the curing. After baking at \(100^{\circ} \mathrm{C}\) for 40 min , a tack-free film was obtained and was continually cured at room temperature. The solvent resistance, hardness, impact, and adhesion of the film were fairly good (Table 10) and the gloss data before and after QUV are also included in this table. The viscosity of the paint did not change much after immersion in a water bath at \(50^{\circ} \mathrm{C}\) for two weeks (Figure 3), and the properties of the film cured from such "aged" paint showed only a slight difference from those freshly prepared (expressed as "fresh" in the


Figure 3-Viscosity change of the paints with time \(\left(50^{\circ} \mathrm{C}\right)\). (1) Paint No. 1; (2) Paint No. 2; and (4) Paint No. 4
\begin{tabular}{|c|c|c|c|}
\hline \multicolumn{4}{|l|}{Table 10-Physical Properties of the Paint Films} \\
\hline Paint No. 1 & Paint No. 2 & \begin{tabular}{l}
Paint \\
No. 3
\end{tabular} & Paint No. 4 \\
\hline Curing temp. ............ \(100^{\circ} \mathrm{C}\) & \(100^{\circ} \mathrm{C}\) & r.t. & \(100^{\circ} \mathrm{C}\) \\
\hline \begin{tabular}{l}
Acetone rub \\
(fresh/aged)
\[
.200 / 150
\]
\end{tabular} & 170/1450 & 200\% & 200/160 \\
\hline \begin{tabular}{l}
Pencil hardness \\
(fresh/aged) \(\qquad\) \(4 \mathrm{H} / 4 \mathrm{H}\)
\end{tabular} & 4H/4H & \(4 \mathrm{H} /{ }^{p}\) & 4H/4H \\
\hline Impact
fresh ......................... 80/60
aged .................. 160/160 & \[
\begin{aligned}
& 160 / 160 \\
& 160 / 160
\end{aligned}
\] & \[
\begin{gathered}
10 / 5 \\
\square
\end{gathered}
\] & \[
\begin{aligned}
& 20 / 20 \\
& 60 / 60
\end{aligned}
\] \\
\hline Sward hardness fresh \(\qquad\) 17 & 11 & 23 & 22 \\
\hline Adhesion (fresh) .......... 3B & 4B & 1 B & 4B \\
\hline Gloss (fresh) & & & \\
\hline \(20^{\circ}\)........................ 48.4 & 48.4 & 51.5 & 20.2 \\
\hline \(60^{\circ} \ldots . . . . . . . . . . . . . . . . . . . . ~ 82.3 ~\) & 83.3 & 82.9 & 68.0 \\
\hline \(85^{\circ}\)........................ 88.2 & 90.3 & 88.3 & 82.3 \\
\hline Gloss (after 9 days QUV) & & & \\
\hline \(20^{\circ}\)........................ 20.5 & 14.1 & 8.4 & 6.5 \\
\hline \(60^{\circ}\)........................ 56.0 & 48.2 & 45.5 & 42.2 \\
\hline \(85^{\circ} \ldots \ldots . . . . . . . . . . . . . . . . . . ~ 59.8 ~\) & 69.7 & 64.8 & 58.3 \\
\hline
\end{tabular}
(a) Fresh = film was drawn and cured immediately after the paint was formulated: aged = film was drawn and cured after the paint wan aged at \(50^{\circ} \mathrm{C}\) for two weeks (for Paint No. 4, five days). (b) Paint was gelled after eight hours.
table). A paint prepared with the same formulation, except with no FA, increased its viscosity (cps) rapidly, twice of its initial value after 20 min , and was gelled within one hour.

Paint No. 1 indicates that a balance of low VOC, low viscosity, long pot life, and good cure performance can be reached by this acid blocking technique.

Paint No. 2 was formulated to evaluate the effect of added TTEGDA, a flexible difunctional acrylate, on film properties. It appears that the impact resistance was improved by introducing this reactive diluent, while the solvent resistance and hardness were only slightly affected.

The formulation of Paint No. 3 was exactly the same as Paint No. 1 except for a lower FA/DBU ratio (0.9). This paint had a much shorter pot life, gelling in eight hours at room temperature. However, the film from this paint could be cured at room temperature (tack-free time was four hours) and showed appreciable properties.

In Paint No. 4, a reactive diluent tBAA was introduced, resulting in a decrease in the VOC to \(240 \mathrm{~g} / \mathrm{L}(2.0 \mathrm{lb} / \mathrm{gal})\). The only problem with this formulation was the shorter pot life (determined at \(50^{\circ} \mathrm{C}\) ) than that observed in Paint Nos. 1 and 2 although we did not see a significant increase in viscosity (i.e., less than twice of the initial value) at room temperature after one month. The film was somewhat brittle, otherwise the properties were good.

These formulations do not necessarily represent optimum formulations.

\section*{CONCLUSIONS}

Acetoacetylated acrylic/TMPTA systems have the potential to replace two-package isocyanate/alcohol based coatings. However, the Michael Addition reaction is too rapid at room temperature, leading to a short pot life for the coatings based on this reaction. Several approaches might be used to extend the pot life, such as increasing the BA/MMA ratio
and decreasing AAEM content in the resin, or using a lower crosslinker/resin ratio; however, they invariably lead to a serious deterioration in film properties.

By using four molar equivalents of formic acid to block the basic catalyst DBU, coatings can be developed which are stable at \(50^{\circ} \mathrm{C}\) for more than two weeks and the cure at \(100^{\circ} \mathrm{C}\) generates coating films. This technique shows several advantages: (1) it extends the pot life dramatically; (2) fast cure is balanced upon baking; (3) the introduction of FA has no or little effect on the ultimate properties of the coating; (4) the storage time does not significantly affect the coating properties; and (5) FA is used in very small amounts which does not cause a VOC problem.

Several paints were formulated, and by introducing a reactive diluent, or by using MAK as solvent, we achieved VOCs as low as \(240 \mathrm{~g} / \mathrm{L}(2.0 \mathrm{lb} / \mathrm{gal})\).

\section*{ACKNOWLEDGMENT}

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\title{
Formulating Printable Coatings via D-Optimality
}

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Kin W. Chau and Wayne R. Kelley \\ W.H. Brady Company*
}

\begin{abstract}
A general method which enables one to use D-optimal design to help formulate conventional printable coatings with a chosen set of ingredients is given. The D-optimality criterion is briefly reviewed and is applied to the formulation process. Using simple polynomials, one builds models to approximate coating properties. Viable models can help formulators in developing and manufacturing coatings. The formulation process of an actual coating is described in some detail to illustrate the procedure. Various merits and limitations of modeling with optimal designs are also discussed.
\end{abstract}

\section*{INTRODUCTION}

A coating generally serves to cover, hide, protect, or modify its substrate (the surface to which the coating is applied). A printable coating, in addition to fulfilling one or more of these functions, must also absorb inks sufficiently well so that it can be printed on and that the printed image remains on the coating permanently.

Such a coating is often needed on industrial identification labels and tags. It typically consists of one or more finely ground pigments evenly dispersed in one or more polymeric binders. Examples of pigments commonly used in printable coatings are alumina trihydrate, barium sulfate, calcium carbonate, calcium sulfate, carbon black, kaolin, mica, silica, titanium dioxide, and talc.

The binders, usually synthetic polymers, hold the pigments such that the resulting coating forms a continuous film. The commonly used polymeric binders are usually impervious to liquids and do not absorb an adequate amount of ink. They are therefore not printable. The

\footnotetext{
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}
ground pigments, without any binder, on the other hand, absorb a large amount of ink. However, they themselves cannot form a coherent film or adhere firmly to any substrate. A proper mixture of binder(s) and pigment(s) can form a printable coating which adheres to a substrate. Therefore, both binder(s) and pigment(s) are essential ingredients in a conventional printable coating.

The procedure of formulating a printable coating may be divided into two steps:

STEP 1-Specific ingredients (i.e., pigments and binders) are selected if the formulator believes their mixture will produce a coating which meets certain set criteria.

Step 2-The formulator determines which ratios of selected ingredients and which processing conditions (e.g., coating thickness, drying temperature) if any, yield a coating satisfying all the set criteria. Those ingredient ratios and processing conditions which yield a satisfactory coating constitute acceptable formulations.
When the formulator arrives at mixtures which meet the set criteria in Step 2, he succeeds. If he fails to do so after considering all promising domains, he returns to Step 1, selects another set of ingredients and repeats the process.

Although Step 1 may be a non-trivial process of interest to many, it is not the subject of this discussion. Rather, our attention is restricted to Step 2 for which we propose a general method that can be followed in the search for acceptable formulations.

\section*{Performance Criteria and Coating Formulation}

Consideration of a printable coating's functions discussed in the previous section leads us to conclude that, in order for a printable coating to be acceptable, it must satisfy all of the following criteria: (1) adhere sufficiently well to intended substrate; (2) exhibit adequate cohesive strength to withstand abrasion; (3) must be sufficiently opaque to hide substrate; and (4) absorb ink adequately such that the printed image is permanent.


Figure 1-If the solid curve represents the true behavior of a coating property, the broken straight line constitutes a rather poor approximation in the pigment concentration interval \(\left[X_{a}, X_{d}\right]\). However, within the narrower domain [ \(X_{b}, X_{c}\) ], the straight line agrees much better with the true behavior. If one is interested in modeling the coating property only within the narrower domain and can ignore its behavior elsewhere, the straight line may suffice

In addition, a coating destined for the surfaces of industrial identification labels must be die-cut with reasonable ease. In particular, it must not be too hard or so tenacious that it cannot be cut consistently with the usual cutting tools. Neither should it be so brittle or so thick that it chips or crumbles along the cut edges. The formulator's goal is to obtain a coating which meets all these requirements.

One notes that, for coatings constructed from the same ingredients, some of the above mentioned criteria are mutually antagonistic in the sense that a change in composition (i.e., ratios of the selected ingredients) which improves certain properties of the coating inevitably harms others. For example, a coating with a lower pigment/binder ratio generally exhibits superior cohesive and adhesive strengths than one with a higher pigment/ binder ratio. On the other hand, its ink absorbency (and hence its printability) is generally inferior to that of the latter. It is also true that while a thicker coating is more opaque and therefore offers more hiding power, it is more liable to chip along the cut edges during die cutting. The formulator must seek the appropriate compositions and processing conditions such that the resulting coating exhibits well-balanced properties while meeting cost targets.
It is a fact that coating properties such as cohesive and adhesive strengths and opacity depend on the mixture variables (i.e., ratios of the ingredients) and its thickness, a process variable. These coating properties may therefore be treated as mathematical functions of such variables which span the formulation space (the space of all possible formulations). The task of formulating a satisfactory coating is thus equivalent to conducting a search, in a multi-dimensional formulation space, for a region in which all the performance criteria are satisfied. Furthermore, in order that a coating can be manufactured consistently, the said region must be sufficiently large and, within that region, the crucial coating properties must be
reasonably insensitive to slight variations in composition and processing conditions. A region in which all such requirements are met, if it exists, is often termed a "sweet spot" by the optimist because it yields balanced coating properties. A pessimist, on the other hand, may view it as a "refuge" because it is located at safe distances from the danger zones in the formulation space where the coating fails one or more of the performance criteria. While personal philosophies differ, choices for final formulation inevitably concur.

We believe that coating properties are governed by its composition according to some natural laws. Knowledge of these laws is equivalent to complete determination of the coating's behavior and, therefore, all information concerning the sweet spot. Unfortunately, these laws are almost always unknown. We resort to approximating them with models constructed from simple mathematical expressions containing parameters which are chosen such that the models' predictions agree with the observed coating behavior. In what follows, we describe one scheme with which one can construct some viable models.

\section*{D-Optimality for Linear Regression Designs}

A given property of a coating (e.g., its opacity or cohesive strength) may be treated as an observable random variable R whose distribution depends on:
(1) The set of \(q\) mixture and process variables (i.e., ratios of the selected ingredients and coating thickness) which can be listed as a \(q\)-tuple of real numbers
\[
\mathbf{u}=\left(X_{1}, X_{2}, \ldots, X_{\mathbf{4}}\right)^{t}
\]
denoting a point in formulation space; superscript \(t\) denotes transpose of a matrix, and
(2) a set of p parameters which can also be listed as a p-tuple
\[
\mathbf{b}=\left(b_{1}, b_{2}, \ldots, b_{p}\right)^{t}
\]

The p parameters are unknown to the formulator but are of primary interest because, as shown in the following, if these parameters are found, the proposed model of \(R\) is determined. The task of formulating a coating is, indeed, equivalent to determining the behavior of R for each of the crucial coating properties. One proceeds by assuming a linear regression model
\[
\begin{equation*}
R_{i}=\mathbf{f}^{\prime}\left(\mathbf{u}_{i}\right) \mathbf{b}+E_{i}, i=1,2, \ldots, n \tag{1}
\end{equation*}
\]
where \(\mathbf{f}\) is an ordered set of \(p\) functions whose form is believed to describe R well. \(\mathrm{E}_{\mathrm{i}}\) is the error or noise for the \(i^{\text {th }}\) observation, i.e., the difference between the value predicted by \(\mathbf{f}\) and the result obtained from observation at point \(\mathbf{u}_{i}\). In matrix notation, equation (1) can be expressed as
\[
\begin{equation*}
\mathbf{R}=\mathbf{F b}+\mathbf{E} \tag{2}
\end{equation*}
\]
where \(\mathbf{R}\) is an n-tuple of observed values, \(\mathbf{F}\) is an \(\mathrm{n} \times \mathrm{p}\) matrix of which the \(i^{\text {th }}\) row is \(\mathbf{f}^{t}\left(\mathbf{u}_{i}\right)\), and \(\mathbf{E}\) is an n-tuple of errors.

The formulator's task is to estimate the set of parameters \(\mathbf{b}\) such that the errors in \(\mathbf{E}\) are minimized. The least squares estimates of \(\mathbf{b}\) are given by
\[
\begin{equation*}
\hat{\mathrm{b}}=\left(\mathbf{F}^{\prime} \mathbf{F}\right)^{-1} \mathbf{F}^{\prime} \mathbf{R} \tag{3}
\end{equation*}
\]

If the errors are independently and identically distributed random variables with mean zero and a constant variance \(S^{2}\), the variance-covariance matrix of the least squares estimator \(\hat{\mathbf{b}}\) is
\[
\begin{equation*}
\operatorname{var}(\hat{\mathbf{b}})=\mathrm{S}^{2}\left(\mathbf{F}^{\prime} \mathbf{F}\right)^{\prime} \tag{4}
\end{equation*}
\]

The predicted response at the point \(\mathbf{u}\) is
\[
\begin{equation*}
\hat{\mathbf{R}}(\mathbf{u})=\mathbf{f}^{\prime}(\mathbf{u}) \hat{\mathbf{b}} \tag{5}
\end{equation*}
\]

An indicator commonly used to determine the quality of inference is the variance of the predicted response at \(\mathbf{u}\), which is
\[
\begin{equation*}
\mathrm{d}(\hat{\mathbf{R}}(\mathbf{u}))=\mathrm{S}^{2} \mathbf{f}^{\prime}(\mathbf{u})\left(\mathbf{F}^{t} \mathbf{F}\right)^{-1} \mathbf{f}(\mathbf{u}) \tag{6}
\end{equation*}
\]

Both quantities in equations (4) and (6) depend on the experimental design (i.e., the choice of set of points \(\mathbf{u}_{i}\) at which observations are made) only through the \(p \times p\) matrix \(\left(\mathbf{F}^{t} \mathbf{F}\right)^{-1}\) and suggest that a desirable design will be one which, in some given sense, minimizes the "size", of this matrix. Since there is no universally agreed-on size-ordering of \(p \times p\) matrices, various criteria have been proposed as measures of smallness. The D-optimality criterion proposes minimizing \(\operatorname{det}\left(\mathbf{F}^{t} \mathbf{F}\right)^{-1}\). The design points \(\mathbf{u}_{\mathrm{i}}\) in our observations are selected according to this criterion. A more detailed discussion of D-optimal design is found in the review by St. John and Draper. ' Other optimality criteria are discussed by Silvey \(^{2}\) as well as Steinberg and Hunter. \({ }^{3}\)

One consistent experimentation scheme can thus proceed as follows. We guess a mathematical function which describes the behavior of a coating property and use it to construct \(\mathbf{f}\). We make observations at the set of \(\mathbf{u}_{i}\) 's which is chosen with the D-optimality criterion. The least squares estimates of the set of parameters \(\mathbf{b}\) are obtained from equation (3), using values of \(\mathrm{R}_{\mathrm{i}}\) from observations. Once the estimates of the parameters \(\mathbf{b}\) are obtained, one can generate a response function \(\mathbf{R}\) via linear regression using the model in equation (2).

Wynn \({ }^{4}\) proposed and proved the convergence of an algorithm to compute experimental designs suitable for model-building. We use a commercially available computer program ECHIP \({ }^{5}\) which generates designs with the Wynn algorithm and conducts regression and statistical analyses.

\section*{Example}

We illustrate how D-optimality and subsequent regression can be exploited in the formulation process by describing a simple but actual coating. It contains three ingredients: two pigments which will be referred to as Pigment 1 and Pigment 2, and one polymeric binder. Relevant properties of the two pigments are listed in Table 1.

Both pigments are essential. Pigment 1 is required to impart sufficient hiding power. This may be attributed to the pigment's high refractive index of 2.7. On the other hand, its oil absorption value is relatively low (16-17). It is so hard (6.5-7.0 Mohs) that a coating filled only with Pigment 1 to the concentration at which it absorbs ink satisfactorily is too hard to cut with the usual tools.

Pigment 2 is considerably softer (3.0 Mohs), such that a coating filled only with this pigment to any usable
concentration can be cut with ease. Its higher oil absorption value (52-62) reflects the fact that it is effective in imparting ink absorbency. However, its relatively low refractive index of 1.6 prevents a coating filled only with Pigment 2 from acquiring the needed opacity at desired coating thicknesses.

Crucial coating properties are found to depend on four variables:


The above definitions of weight fractions dictate that the three mixture variables satisfy the constraint
\[
\begin{equation*}
x_{1}+x_{2}+X_{3}=1 \tag{7}
\end{equation*}
\]

\section*{Selection of Observation Domain Q}

As a scheme for building models for any coating property, optimal design requires observed values of that property [see equations (2) and (3)]. A region of the formulation space where one makes observations is an observation domain.

We note that because not all possible formulations yield functional coatings, not the entire formulation space is of interest. Obvious examples of regions which are not functional are those in the immediate neighborhoods of the three points \(X_{1}=1.0, X_{2}=1.0\), and \(X_{3}=1.0\). Formulations which fall within the first two inevitably yield coatings with unacceptably low cohesive and adhesive strengths, regardless of their thickness. Those which fall within the third one yield coatings which do not absorb ink adequately and are hardly printable. In fact, only a small subspace of the entire formulation space represents usable formulations. The observation domain Q must contain such a subspace. This domain must be selected such that no part of it represents formulations which are too far from acceptable standards. One would be wasting effort studying fruitless formulations otherwise.

Since our aim is to model coating behavior with a simple mathematical expression, of yet greater concern is the fact that coatings of widely differing pigment/binder ratios behave very differently. This is well illustrated by the many examples found in Patton's treatise. \({ }^{6}\) These examples show many coating properties, any one of which when expressed as a function of pigment concentration, exhibits contrasting behaviors in the region below
\begin{tabular}{|c|c|c|}
\hline \multicolumn{3}{|l|}{Table 1-Relevant Properties of the Two Pigments} \\
\hline Pigment/Property & Pigment 1 & Pigment 2 \\
\hline \begin{tabular}{l}
Oil absorption \\
(ASTM D281)
\end{tabular} & 16-17 & 52-62 \\
\hline \begin{tabular}{l}
Hardness \\
(Mohs)
\end{tabular} & 6.5-7.0 & 3.0 \\
\hline Refractive index . . . . . . . . . . . & 2.7 & 1.6 \\
\hline
\end{tabular}


Figure 2a-Pictorial representation of the fifteen distinct design points generated by D-optimality criterion and the Wynn algorithm. The infinitely tall prism represents the entire formulation space. The shaded region represents the observation domain \(Q\), the boundaries of which are defined by the inequalities (8)
the critical pigment volume concentration (CPVC) and in the region above it. It may not be possible to accommodate a coating's behavior throughout its entire pigment concentration range with one simple mathematical expression. Our intended regression of a simple polynomial on observed data is likely to yield more satisfactory results if the undertaking is restricted to a narrower domain located at either a region well below or well above the CPVC. In particular, if its area is sufficiently small, even a region of a curved surface may be approximated with a plane-an object which requires simpler description.


Figure 2b-Pictorial representation of the same object in Figure 2a when viewed from directly above. The \(X_{4}\) axis is now perpendicular to this page. The entire triangle represents all possible mixtures which can be obtained from the three components \(X_{1}, X_{2}\), and \(X_{3}\). The shaded parallelogram represents the projection of the observation domain \(Q\)

This idea is illustrated in Figure 1. It is obviously advantageous if one can avoid an elaborate model which contains a large number of parameters and therefore requires a large number of observations in its construction, and instead adopt a simpler one which contains fewer parameters, therefore requiring fewer observations and less labor.

Experience with our particular coating reveals that its pigment concentration must be well above the CPVC to ensure adequate ink absorption. The region at and below the CPVC is therefore of little interest and may be ignored. We thus select our observation domain \(\mathbf{Q}\) with such considerations in mind, taking care that it is not chosen to be larger than is necessary.

Having said that, we must hasten to add that, on the other hand, the observation domain must not be chosen to be too narrow either, lest one will likely miss some area which contains usable formulations. Ideally, one seeks a region \(\mathbf{Q}\) which comfortably encloses the sweet spot. However, the size and location of the sweet spot is unknown to the formulator at this stage. The formulator must rely on judgment and intuitive feel, which come only after sufficient experience with the chosen ingredients has been acquired.

We discovered, through trial and error, the following facts concerning the ingredients chosen for this coating:
(1) \(X_{1}\) (weight fraction of Pigment 1) must be \(\geq 0.13\) in order that the coating be of sufficiently high opacity. \(\mathrm{X}_{1}\) must be \(\leq 0.45\) or else the coating will be too hard to cut with the usual cutting tools.
(2) \(X_{2}\) (weight fraction of Pigment 2) must be \(\geq 0.21\) in order that the coating absorbs ink adequately. \(\mathrm{X}_{2}\) must be \(\leq 0.67\) or else the coating's cohesive and adhesive strengths will be unacceptably low.
(3) The above mentioned empirically determined boundaries, together with the constraint in equation (7), necessarily restrict \(\mathrm{X}_{3}\) (weight fraction of binder) to the interval [0.20, 0.34].
(4) \(X_{4}\) (coating thickness) must be \(\geq 10 \mu \mathrm{~m}\) in order that the coating be of sufficient hiding power. \(\mathrm{X}_{4}\) must be


Figure 3-Contour map representation of predicted opacity for \(10 \mu \mathrm{~m}\) thick coating

Table 2-Design Points, Replicates, Checkpoints, and Corresponding Observation at Each Point
Points 1 through 15 are design points calculated with D-optimality criterion. Observations for points 1 through 8 are replicated. Points 16 through 26 are checkpoints where observations are made to check the validity of the model.
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline Point & X \({ }_{1}\) & \(\mathrm{X}_{2}\) & \(\mathrm{X}_{3}\) & \(\mathrm{X}_{4}\) & Observed Opacity & Point & X & \(\mathrm{X}_{2}\) & \(\mathrm{X}_{3}\) & \(\mathrm{X}_{4}\) & Observed Opacity \\
\hline 1... & 0.13 & 0.67 & 0.20 & 10 & 0.710 & 1... & 0.13 & 0.67 & 0.20 & 10 & 0.680 \\
\hline 2. & 0.13 & 0.67 & 0.20 & 28 & 0.908 & 2. & 0.13 & 0.67 & 0.20 & 28 & 0.901 \\
\hline 3... & 0.45 & 0.21 & 0.34 & 10 & 0.823 & 3... & 0.45 & 0.21 & 0.34 & 10 & 0.798 \\
\hline 4. & 0.45 & 0.35 & 0.20 & 28 & 0.976 & & 0.45 & 0.35 & 0.20 & 28 & 0.940 \\
\hline 5... & 0.13 & 0.67 & 0.20 & 19 & 0.780 & 5... & 0.13 & 0.67 & 0.20 & 19 & 0.791 \\
\hline 6. & 0.13 & 0.53 & 0.34 & 28 & 0.912 & 6... & 0.13 & 0.53 & 0.34 & 28 & 0.930 \\
\hline 7... & 0.13 & 0.53 & 0.34 & 10 & 0.698 & 7... & 0.13 & 0.53 & 0.34 & 10 & 0.711 \\
\hline 8... & 0.45 & 0.35 & 0.20 & 10 & 0.802 & 8... & 0.45 & 0.35 & 0.20 & 10 & 0.822 \\
\hline 9... & 0.29 & 0.37 & 0.34 & 10 & 0.772 & 16... & 0.13 & 0.67 & 0.20 & 11 & 0.706 \\
\hline 10... & 0.29 & 0.44 & 0.27 & 19 & 0.861 & 17... & 0.13 & 0.67 & 0.20 & 21 & 0.820 \\
\hline 11. & 0.45 & 0.21 & 0.34 & 28 & 0.992 & 18... & 0.45 & 0.35 & 0.20 & 19 & 0.871 \\
\hline 12.. & 0.13 & 0.60 & 0.27 & 10 & 0.700 & 19... & 0.13 & 0.53 & 0.34 & 20 & 0.796 \\
\hline 13.. & 0.13 & 0.53 & 0.34 & 19 & 0.782 & 20... & 0.45 & 0.35 & 0.20 & 13 & 0.794 \\
\hline 14.. & 0.29 & 0.51 & 0.20 & 10 & 0.772 & 21... & 0.29 & 0.37 & 0.34 & 11 & 0.750 \\
\hline 15. . & 0.45 & 0.28 & 0.27 & 10 & 0.818 & 22... & 0.29 & 0.44 & 0.27 & 11 & 0.818 \\
\hline & & & & & & & 0.45 & 0.21 & 0.34 & 19 & 0.874 \\
\hline & & & & & & & 0.13 & 0.60 & 0.27 & 14 & 0.717 \\
\hline & & & & & & & \[
0.45
\] & 0.21 & 0.34 & 12 & 0.838 \\
\hline & & & & & & & 0.29 & 0.44 & 0.27 & 18 & 0.840 \\
\hline
\end{tabular}
\(\leq 28 \mu \mathrm{~m}\) lest the coating is likely to chip along the cut edges.

These requirements led us to select for our observation domain \(\mathbf{Q}\), the parallelepiped defined by the following boundaries:
\[
\begin{array}{ll}
0.13 \leq X_{1} \leq 0.45 & , \quad 0.21 \leq X_{2} \leq 0.67 \\
0.20 \leq X_{3} \leq 0.34, & 10 \mu \mathrm{~m} \leq X_{4} \leq 28 \mu \mathrm{~m} \tag{8}
\end{array}
\]

\section*{Experimental Design and Observation}

The treatment thus far is applicable to modeling any coating property. Since we must limit our discussion to a reasonable length, we will, from here onward, describe only the modeling of opacity. It should suffice to illustrate the procedure. Other coating properties can be modeled in a similar manner.

Our experience shows that, within the domain \(\mathbf{Q}\), opacity may be described by a smooth function of the \(\mathrm{X}_{\mathrm{j}}\) 's \((j=1,2,3,4)\). Such a function is differentiable and may therefore be represented by an infinite series (e.g., Taylor series) in the \(X_{j}\) 's. Since we can only make a finite number of experimental observations, we attempt to approximate the opacity with a truncated series, i.e., a polynomial. Specifically, for our model in equation (1), we choose
\[
\begin{equation*}
\mathbf{f}^{t}=\left(1, x_{1}, x_{2}, x_{3}, x_{4}, x_{1}^{2}, x_{2}^{2}, x_{3}^{2}, x_{4}^{2}, x_{1} x_{2}, x_{1} x_{3}, x_{1} x_{4}, x_{2} x_{3}, x_{2} x_{4}, x_{3} x_{4}\right) \tag{9}
\end{equation*}
\]

The set of parameters to be estimated is
\[
\begin{equation*}
\mathbf{b}=\left(b_{0}, b_{1}, \ldots, b_{14}\right)^{t} \tag{10}
\end{equation*}
\]

Thus, this model predicts, at any given point \(\mathbf{u}_{\mathrm{i}}\) in the formulation space, a response (which, is the opacity)
\[
\begin{aligned}
R_{1}= & b_{0}+b_{1} x_{1}+b_{2} x_{2}+b_{3} x_{3}+b_{4} x_{4}+b_{5} x_{1}{ }^{2}+b_{6} x_{2}{ }^{2}+b_{7} x_{3}{ }^{2}+b_{8} x_{4}{ }^{2} \\
& +b_{9} x_{1} x_{2}+b_{10} x_{1} x_{3}+b_{11} x_{1} x_{4}+b_{12} x_{2} x_{3}+b_{13} x_{2} x_{4}+b_{14} x_{3} x_{4}
\end{aligned}
\]

A D-optimal experimental design was generated with the computer program ECHIP which uses the Wynn computation algorithm. The design consists of fifteen distinct points (numbered 1 through 15) chosen from within the
observation domain \(\mathbf{Q}\). The first eight of these fifteen observations were replicated and additional observations were made at eleven checkpoints (numbered 16 through 26). Results from these points are needed to assess the validity of the model obtained from regression. These design points, replicates, and checkpoints are listed in Table 2. These points may be represented pictorially. The fifteen distinct design points are shown in Figures 2a and 2b.

Coating mixtures with compositions listed in Table 2 were prepared. Coating opacity was observed as follows:
(1) The coating was applied onto one side of the intended substrate (a transparent film) to the desired thickness.
(2) The coated film was placed on the white background of a standard panel so that the uncoated side of the film was in contact with the panel. The colorimetric density Dy (to be defined in the following) was measured


Figure 4-Contour map representation of predicted opacity for \(19 \mu \mathrm{~m}\) thick coating


Figure 5-Contour map representation of predicted opacity for \(23.5 \mu \mathrm{~m}\) thick coating
with a Minolta CR-200 tristimulus color analyzer whose light source is a Xenon arc lamp.
(3) The same coated film was transported onto the black backing of the standard panel and the colorimetric density of the same spot on the coated film was recorded.
(4) Opacity was computed from the relation

Dy (on white background) \(\div D y\) (on black background)
The standard black and white panel previously mentioned was purchased from the Leneta Co., of Mahwah, NJ, which designates it "Form 5C-Opacity."

Colorimetric density is defined with the common logarithm
\[
\mathrm{Dy}=-\log \left(\mathrm{y} / \mathrm{y}_{\mathrm{o}}\right)
\]
where \(y=\) the lightness factor of the 1931 Commission Internationale de l'Eclairage tristimulus values, expressed as a percentage based on the perfect reflectance of \(100 \%\).
\(y_{0}=\) the lightness factor of the tristimulus values of the light source used; it is set to 93.50 with the reflectance from a standard white calibration plate (CR-A43) supplied by Minolta.
Coating thickness was measured with a Mitutoyo Digimatic micrometer to within \(\pm 1 \mu \mathrm{~m}\).

The order in which the thirty-four observations were made was, of course, randomized. The results (observed opacities) are listed in the last column in Table 2.

\section*{Assessment of Model Validity}

Using equation (3) and the observed data at the fifteen distinct design points and eight replicates listed in Table 2 , one generates the least squares estimates of the set of parameters \(\mathbf{b}\). It is a fact that repeated observations, even at the same point, almost always yield a range of values. This inherent variation in observed data is referred to as experimental noise or error \(\left[\mathrm{E}_{\mathrm{i}}\right.\) in equation (1)]. The estimate for each parameter \(b_{k}(k=0,1, \ldots, 14)\) inherits this uncertainty and therefore assumes a range of values
instead of one number with unlimited precision. The opacity model was generated with equation (11), using a mean value for each \(\mathrm{b}_{\mathrm{k}}\). The model's prediction at a given point is only the expectation of the values which may be observed at that point. The actual observed data may not exactly equal the model's prediction but are likely to fluctuate around it.

The model's predictions may be represented pictorially. Predicted opacities for coatings of various thicknesses are shown as contour maps in Figures 3 through 6a. The triangle in these diagrams represents only a portion of the triangle in Figure 2b. The contour map in Figure 6a is reproduced in Figure 6 b in the form of a three-dimensional drawing to help the reader maintain a sense of perspective. Opacity is represented as a surface (for this reason, it is often called a response surface) in a multi-dimensional formulation space. To be prudent, we only use predictions within the observation domain \(\mathbf{Q}\) and make no extrapolation to regions beyond.

In order for a model to be meaningful, its predictions must at least qualitatively agree with experimentally observed behavior. If they contradict observed results, the model is questionable and ought to be discarded. In particular, the opacity was observed to show the following trends:
(1) For coatings with the same composition, a thicker coating exhibits higher opacity.
(2) For coatings of the same thickness, the one containing a higher concentration of Pigment 1 exhibits higher opacity.
(3) For a coating of a given thickness, its opacity increases steeply with an increase in Pigment 1 content when the concentration of Pigment 1 is relatively low. When Pigment 1 concentration is relatively high, an increase in Pigment 1 content produces a far smaller increase in opacity.

Table 3-Summary of the Effect and Confidence Level of Each Term in Opacity Model
\begin{tabular}{|c|c|c|}
\hline Term in Opacity Model [(Equation (11)] & Effect & Sigres \\
\hline \(\mathrm{b}_{0}\). & 0.9234 & - \\
\hline \(\mathrm{b}_{1} \mathrm{X}_{1}\) & 0.0718 & 0.1550 \\
\hline \(\mathrm{b}_{2} \mathrm{X}_{2}\) & . -0.0866 & * \\
\hline \(\mathrm{b}_{3} \mathrm{X}_{3}\) & 0.0138 & 0.0789 \\
\hline \(\mathrm{b}_{4} \mathrm{X}_{4}\) & 0.1883 & *** \\
\hline \(\mathrm{b}_{5} \mathrm{X}_{1}{ }^{2}\) & -0.1163 & * \\
\hline \(\mathrm{b}_{6} \mathrm{X}_{2}{ }^{2}\). & -0.0534 & 0.1694 \\
\hline \(\mathrm{b}_{7} \mathrm{X}_{3}{ }^{2}\). & -0.0746 & 0.2746 \\
\hline \(\mathrm{b}_{8} \mathrm{X}_{4}{ }^{2}\) & 0.0180 & * \\
\hline \(\mathrm{b}_{9} \mathrm{X}_{1} \mathrm{X}_{2}\) & 0.0005 & 0.0489 ! \\
\hline \(\mathrm{b}_{10} \mathrm{X}_{1} \mathrm{X}_{3}\) & 0.0780 & 0.2127 \\
\hline \(\mathrm{b}_{11} \mathrm{X}_{1} \mathrm{X}_{4}\) & . - 0.0692 & *** \\
\hline \(\mathrm{b}_{12} \mathrm{X}_{2} \mathrm{X}_{3}\) & 0.0242 & 0.1313 \\
\hline \(\mathrm{b}_{13} \mathrm{X}_{2} \mathrm{X}_{4}\) & 0.0057 & 0.0370 \\
\hline \(\mathrm{b}_{14} \mathrm{X}_{3} \mathrm{X}_{4}\) & 0.0519 & 0.1085 \\
\hline Residuals standard deviation & \(=0.0134\) & \\
\hline Replicates standard deviation & \(=0.0156\) & \\
\hline Raw standard deviation & \(=0.0922\) & \\
\hline Checkpoints root mean squared & \(=0.0189\) & \\
\hline Influence & \(=0.0827\) & \\
\hline Degrees of freedom for error & \(=13\) & \\
\hline
\end{tabular}
(4) When pigment/binder ratio is relatively low, an increase in pigment concentration increases opacity.

We are pleased to note that the model's predictions, shown pictorially in Figures 3 through 6b, are in agreement.

Our next step is to carry out a quantitative assessment. The results are summarized in Table 3. We begin by considering the average of the differences or residuals between the observed opacities and the model's predictions at the fifteen distinct design points. A common indicator which measures this is the standard deviation which was found to be 0.0134 . If one repeats the same calculation for the differences at the eight replicates, a standard deviation of 0.0156 is obtained. The fact that these two numbers are sufficiently small and are comparable to each other indicates the model fits the observed data well at those fifteen points.

As a further evaluation of the model's validity, observations were made at eleven checkpoints (points 16 through 26 listed in Table 2) chosen within the domain \(\mathbf{Q}\). The discrepancies between the observed data and the model's predictions were recorded and their root mean squared value was found to be 0.0189 . This is sufficiently low and can be ignored in our manufacturing process. This shows that the model provides adequate precision in \(\mathbf{Q}\).

The opacity model in equation (11) consists of fifteen terms. The effect of each term listed in Table 3 is the change in the predicted opacity caused by that term if the variables \(\mathrm{X}_{1}, \mathrm{X}_{2}, \mathrm{X}_{3}\), and \(\mathrm{X}_{4}\) were allowed to vary through their full ranges in the observation domain \(\mathbf{Q}\). For example, the term \(b_{1} x_{1}\) causes a net increase of 0.0718 , while the term \(b_{2} x_{2}\) causes a net decrease of 0.0866 in the predicted opacity if \(X_{1}\) were to increase from 0.13 to 0.45 and \(X_{2}\) from 0.21 to 0.67 . Clearly, the effect of each term is directly determined by the estimated value for each \(b_{k}\). Since each \(b_{k}\) was estimated with observed data, it carries uncertainty. We must face the question: Could it be possible that the true effect of each term is zero (i.e., no effect on opacity), and what is obtained in Table 3 is the mere result of noise (i.e., fluctuation) inherent in our observations?

We estimate the probability or likelihood of seeing each term achieve its listed effect through pure chance by treating each \(b_{k}\) as a random variable obeying the \(t\) distribution. If this likelihood is sufficiently low (specifically, \(\leq 0.05\) ), we can be confident that the given term truly contributes the listed effect to the model's prediction. In Table 3, the terms which can, by chance, assume their listed effects with a likelihood of \(\leq 0.05\) are marked with one asterisk under the Sigres column. Terms which can, by chance, assume their listed effects with a likelihood of \(\leq 0.001\) are marked with three asterisks under the Sigres column.
We cannot be as confident with the effects estimated for the remaining terms in Table 3. The effects shown for these terms can occur just by chance with likelihoods of well above 0.05 . These terms are marked with numbers under the Sigres column. Each number is the minimum effect the indicated term must achieve before one can consider it a true contribution, i.e., when the likelihood of its occurring by pure chance decreases to \(\leq 0.05\). Such cases occur frequently in modeling. Their confidence


Figure 6a-Contour map representation of predicted opacity for \(28 \mu \mathrm{~m}\) thick coating
levels usually increase if more observations are made. The term \(b_{9} X_{1} X_{2}\) is marked with an exclamation under the Sigres column because its effect is so low that it can hardly be distinguished from that of mere noise. One might consider eliminating it from the model.

Since the term \(b_{0}\) does not change with coating composition, its contribution towards the model remains constant throughout \(\mathbf{Q}\). The confidence level of this term was not evaluated.

\section*{DISCUSSION}

Using the previously mentioned procedure, one can build models for other coating properties deemed important to one's applications. Guided by these models, one


Figure 6b-Same opacity model as in Figure 6a, but drawn in three dimensions. The shaded parallelogram represents the projection of the observation domain \(Q\)
can select a region which offers balanced properties. Such a region, if it exists, is the sweet spot-the object of the search.
Valid models of crucial coating properties offer a number of benefits:
(1) They reveal regions in formulation space which yield coatings with desirable properties, and where such properties are reasonably stable with respect to slight variations in coating composition and processing conditions. They offer prescriptions for dependable manufacturing. For example, formulations which fall within the neighborhood of design point 10 in Table 2 fulfill such requirements and have been prescribed for actual products.
(2) They constitute satisfactory pictures of coating behavior and enable more useful information to be transferred from one generation of formulating personnel to the next. Manufacturers who build such models are rewarded with savings and efficiency in their operations.
(3) In the event new coating performance criteria arise, one refers to these models to determine if the same set of ingredients can possibly yield a coating which fulfills the new requirements. At the very least, the models can help eliminate costly and futile reformulation exercises.

While it may offer such advantages, modeling via optimal design and regression is by no means omnipotent. Indeed, it suffers from limitations which sometimes prove to be fatal. First, one must be aware of the fact that the models are beneficial only when they make reasonably accurate predictions. Often, one's livelihood depends on certain peculiar coating properties for which available methods of observation are unsatisfactory; either they do not offer adequate precision or the variance of repeated observations at the same point is unacceptably large. Modeling such properties is hardly feasible. This situation is rather common and constitutes an almost insurmountable barrier to model-building which would be in much wider use otherwise. Second, we recall the very reason which forces one to resort to modeling: the natural laws governing the coating's behavior are unknown. However, unlike methods such as simplex-lattice designs, \({ }^{7}\) optimal design can proceed only after the form of the model underlying data to be collected is guessed [see equation (1)]. The resulting design is often highly sensitive to the chosen model [see equations (4) and (6)]. This usually constitutes a drawback unless the approximate form of the true law which governs the coating property is known a priori. It is in this respect that the scheme of optimal design presents some awkwardness in its concept if not in practice. One can only rely on experience with the chosen ingredients when selecting a model for equation (1). In general, satisfactory results cannot be guaranteed.

We chose a model represented by equations (9) and (11), and estimated the set of parameters \(\mathbf{b}\) to fit the observed data. Although the model obtained proves to be satisfactory, we suspect that the true law which governs the opacity is of a considerably different form. The model we built represents only an approximation and claims validity only within the domain \(\mathbf{Q}\).

The process of selecting a suitable observation domain is another aspect which cannot be overemphasized. Mathematics offers little guidance in this area. It is chosen with the help of the formulator's knowledge of the selected ingredients. Indeed, the formulator's experience and intuitive feel are indispensable. Only when they are fully exploited can optimal designs be effective in building models. Optimal designs can by no means replace the experienced coating formulator. Rather, they serve as useful tools which can enhance the latter's practice.

\section*{SUMMARY}

A general method which uses D-optimal design and regression to help formulate conventional printable coatings from a chosen set of ingredients has been proposed. The application of this method to the formulation of an actual coating has been described in some detail as an illustration. It is emphasized that, in order for the technique to be effective, it must be guided with the formulator's experience and intuitive feel. Despite some noted limitations, the proposed method proves to be a useful tool under appropriate circumstances and offers many benefits.

\section*{ACKNOWLEDGMENT}

We are grateful to Janice Wensing, who prepared the manuscript, and to Robert Doepke, who drew some of the diagrams. Their skills and expertise were indispensable.

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\title{
Influence of Particle Size Distribution of Zinc Dust in Water-Based, Inorganic, Zinc-Rich Coatings
}

\author{
Ernesto Montes \\ Ameron Protective Coatings Division*
}

\begin{abstract}
New VOC regulations have brought renewed interest in water-based inorganic zinc silicate coatings. Selecting zinc dust solely from the various possible "average diameter" compositions may not always yield the desired results.

At the lower micron particle size range, surface area increases can have a tremendous influence on product application characteristics. Specific area becomes an important parameter. The fine fraction of any normal distribution of particle size is the predominant factor in the rheological properties of the mixed material.
\end{abstract}

\section*{INTRODUCTION}

Using water in inorganic zinc silicates coatings offers several advantages, such as no volatile organic compounds (VOC), nonflammability, nontoxicity (relative to solvents), and lack of odor. High market demand for the low emissions of organic solvents and the nonflammable properties of water makes water-based zinc silicate a preferable choice for the industry.

However, water has the following limitations: relatively poor wetting, poor flow, sensitivity to high humidity, and slow rate of evaporation.

The poor wetting of water-based silicate binders requires careful selection of zinc dust in order to achieve proper flow application characteristics. The drying and cure rates after application are dependent on environment, temperature, and relative humidity.

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26-28. 1992. New Orleans. LA.
*201 N. Berry St.. Brea. CA 92622-1020

Table 1-Liquid Potassium Silicate
\begin{tabular}{|c|c|c|c|}
\hline \[
\begin{aligned}
& \text { \%K2 }{ }_{2} \\
& \text { Wt } \%
\end{aligned}
\] & \[
\% \mathrm{SiO}_{2}
\]
Wt \% & \[
\begin{gathered}
\mathrm{SiO}_{2} / \mathrm{K}_{2} \mathrm{O} \\
\mathrm{Wt} \%
\end{gathered}
\] & Viscosity \\
\hline 8.30 & 20.8 & 2.50 & 40 cps \\
\hline 9.05 & 19.9 & 2.20 & 7 cps \\
\hline 12.50 & 26.3 & 2.10 & 1060 cps \\
\hline
\end{tabular}

\section*{Binders Used in Water-Based Inorganic Zinc Silicate}

There are two types of silicate binders used in these coatings: those that are in solution and those that are colloidal dispersions. The state of these binders and/or combination of them will affect the application properties and zinc dust selection. While potassium and sodium silicate are the most common solution binders, both silica and lithium are available as colloidal dispersions.

Tables 1 and 2 show the potassium and sodium silicate most commonly used. Typical colloidal silica are shown in Table 3.

Alkali/silica ratios define certain characteristics of the binders, including: stability, viscosity, and insolubility.

Solubility of the binder is determined by the level of silica. The higher the ratio of silica/alkali, the less soluble the
\begin{tabular}{cccc}
\hline \multicolumn{4}{c}{ Table 2—Liquid Sodium Silicate } \\
\(\%_{N a} \mathbf{O}\) & \(\% \mathrm{SiO}_{2}\) & \(\mathrm{SiO}_{2} / \mathbf{N a}_{2} \mathrm{O}\) & \\
\(\mathrm{Wt} \%\) & \(\mathrm{Wt} \%\) & \(\mathrm{Wt} \%\) & Viscosity \\
\hline 6.7 & 25.3 & 3.75 & 220 cps \\
8.9 & 28.7 & 3.22 & 180 cps \\
9.1 & 29.5 & 3.22 & 400 cps \\
11.0 & 31.7 & 2.98 & 960 cps \\
13.8 & 33.2 & 2.40 & 2100 cps \\
\hline
\end{tabular}

\section*{E. MONTES}

Table 3-Typical Colloidal Silica
\begin{tabular}{|c|c|c|c|}
\hline \begin{tabular}{l}
Mean Particle \\
Size (microns)
\end{tabular} & Conc Wt \% & Specific Surface & Viscosity \\
\hline 4 .................. & 15.0 & \(750 \mathrm{~m}^{2} / \mathrm{g}\) & 18 cps \\
\hline 5 .................... & 14.5 & \(600 \mathrm{~m}^{2} / \mathrm{g}\) & 5 cps \\
\hline 13 ................ & 30.0 & \(230 \mathrm{~m}^{2} / \mathrm{g}\) & 4 cps \\
\hline 20 ................ & . 50.0 & \(150 \mathrm{~m}^{2} / \mathrm{g}\) & 40 cps \\
\hline 20 ................... & . 34.0 & \(150 \mathrm{~m}^{2} / \mathrm{g}\) & 10 cps \\
\hline
\end{tabular}


Figure 1-Particle size vs specific surface. Series 1: - . Different samples of zinc dust
\begin{tabular}{|c|c|}
\hline \multicolumn{2}{|c|}{Table 4-Average Molecular Weight Potassium Silicate at Different Ratio} \\
\hline \[
\begin{gathered}
\mathrm{SiO}_{2} / \mathrm{K}_{2} \mathrm{O} \\
\mathrm{Wt} \%
\end{gathered}
\] & Wt Average Molecular Wt in Solution \\
\hline 1.00 & ........ 56 \\
\hline 1.75 & ............ 115 \\
\hline 2.50 .. & ............. 295 \\
\hline 2.80 .. & .............. 304 \\
\hline 3.31 .... & ............... 495 \\
\hline 3.62 . & .............. 628 \\
\hline 3.97 .. & ............... 848 \\
\hline
\end{tabular}


Figure 2-Zinc dust sample No. 6. Supertine dust. Series 6: Median: \(4.6 \mu \mathrm{~m}\); specific surface: \(0.254 \mathrm{~m}^{2} / \mathrm{g}\)
\begin{tabular}{|c|c|c|}
\hline \multicolumn{3}{|l|}{Table 5-Typical Properties of Zinc Dust} \\
\hline Regular & Fine & Superfine \\
\hline Median diameter \(\mu \mathrm{m}\)................8.0 & 5.0 & 4.0 \\
\hline \% Smaller than \(10 \mu \mathrm{~m}\)........... 65.0 & 95.0 & 99.0 \\
\hline Surface area, \(\mathrm{m}^{2} / \mathrm{g}\)...................0.1 & 0.16 & 0.2 \\
\hline Apparent density \(\mathrm{g} / \mathrm{cm}^{3} \ldots \ldots . . . . . . . .3 .038\) & 2.398 & 2.196 \\
\hline \% Under \(44 \mu \mathrm{~m}\).....................98.0 & 99.0 & 100.0 \\
\hline
\end{tabular}

Table 6-Most Common Diameter
\(d=\) Diameter, mean class, micron; \(\boldsymbol{n}=\) Frequency
\[
\begin{aligned}
\text { Length mean } & =\frac{\sum n d^{2}}{\sum n d} \\
\text { Surface mean } & =\frac{\sum n d^{3}}{\sum n d^{2}} \\
\text { Volume, weight mean } & =\frac{\sum n d^{4}}{\sum n d^{3}} \\
\text { Surface diameter } & =\sqrt{\frac{\sum n d^{2}}{\sum \mathrm{n}}} \\
\text { Volume diameter } & =3 \sqrt{\frac{\sum n d^{3}}{\sum \mathrm{n}}}
\end{aligned}
\]

Table 7-Specific Surface of Zinc Dust at Different Surface Mean Diameter
\begin{tabular}{|c|c|c|c|}
\hline Zinc Dust & Diameter & Specific Surface
\(\mathrm{m}^{2} / \mathrm{g}\) & Type \\
\hline 1 .............. & ...... 6.24 & 0.1373 & STD \({ }^{\text {a }}\) \\
\hline 2 .............. & .....5.35 & 0.1601 & STD \\
\hline 3 ............ & ..... 5.31 & 0.1615 & STD \\
\hline 4 .............. & ...... 4.96 & 0.1720 & F \\
\hline 5 .............. & ..... 4.69 & 0.1839 & F \\
\hline 6 .............. & ..... 3.92 & 0.210 & SF \\
\hline 7 .............. & ..... 4.2 & 0.204 & SF \\
\hline 8 .............. & ..... 3.57 & 0.240 & SF \\
\hline
\end{tabular}

Table 8-Application Test
\begin{tabular}{|c|c|c|c|}
\hline Sample No. & Specific Surface & Viscosity CPS & Results \\
\hline 4 ............... & .......0.172 & 150 & Erratic flow, sagging \\
\hline 5 ............... & .........0.1839 & 160 & Sagging \\
\hline 6 ............... & .........0.219 & 270 & Good application \\
\hline 7 ............... & ......... 0.204 & 240 & Good, smooth surface \\
\hline
\end{tabular}

ERNESTO MONTES has been employed at Ameron Protective Coatings Division in Brea, CA for more than 18 years. He started in the inorganic area, in the development of inorganic zinc-rich coatings, and is currently acting as Product Evaluation Manager. He worked for three years at Rohm and Haas Company in Spain after leaving his native Cuba. Mr. Montes has a degree in Chemical Engineering.
silicate becomes. When the silica content of sodium silicate is increased above a certain level, the blend becomes unstable. As the silica level is increased, potassium silicate becomes viscous and more difficult to handle.

With the increased ratio of silica content, the average molecular weight of potassium silicate increases, as shown in Table 4.

The silica/alkali ratio can be increased by incorporating colloidal silicate into the solution. Silica in the colloidal state can be used in conjunction with alkali-silicate, thus bringing some special characteristics to the binder. Colloidal silica is translucent in appearance and has highly swollen particles. Alkali silicates are monomeric, while colloidal silicates are polymeric aggregates. The colloidal dispersion yields higher application solids.

\section*{Zinc Dust}

The commercial grade of zinc dust consists of particles under \(44 \mu \mathrm{~m}\). The median particle size diameter in microns is the industrial standard used to characterize zinc dust. Zinc dust is classified as standard, fine, very fine or superfine.

The typical properties of zinc dust are given in Table 5. However, selecting a zinc dust from these parameters is simply not enough when trying to obtain good spray application properties. Other factors, such as the fraction of fines, must be considered when selecting zinc dust.

\section*{Average Diameter}

The average diameter for any size distribution can be calculated. Many possible average diameters can be obtained, including number diameter, length diameter, etc. The most common are shown in Table 6.

For a selected mean diameter, a number of different size distributions can be applied. It then becomes possible to have different application properties for different samples with the same mean diameter.

\section*{EXPERIMENTAL}

As the particles become smaller, surface area increases, and this is particularly noticeable in the lower micron range. With the particle size distribution or percentage by weight, or the number of each different size fraction within a zinc dust sample, any mean value can be calculated. \({ }^{2}\) The type of mean value employed depends on which property of the whole mass is found to be of interest. For example, in different samples of zinc dust \({ }^{3}\) whose surface mean diameter were selected, the corresponding specific area was calculated by considering the particle to be spherical and its density to be \(7.1 \mathrm{~g} / \mathrm{cc}\), as shown in Table 7. When the particle diameter versus specific surface is plotted on log-log paper, a straight
\begin{tabular}{|c|c|c|c|}
\hline \multicolumn{4}{|r|}{Table 9-Surface Below and Above the Median (\%)} \\
\hline Sample No. & Median (Microns) & \begin{tabular}{l}
\% Surface \\
(< Median)
\end{tabular} & \begin{tabular}{l}
\% Surface \\
(> Median)
\end{tabular} \\
\hline 4 ................ & .... 5.8 & 75.7 & 24.8 \\
\hline 5 ................ & ...... 5.7 & 78.4 & 21.6 \\
\hline 6 ................ & ...... 4.6 & 86.7 & 13.3 \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|}
\hline \multirow[b]{2}{*}{\begin{tabular}{l}
Mean, Class \\
Size, d
\end{tabular}} & \multicolumn{3}{|l|}{Table 10-Particle Size Distribution and Data Sheet for SSD} \\
\hline & Frequency, n & \(\mathrm{d}^{2} \mathrm{n}\) & \(d^{3} n\) \\
\hline 2.00 & . 3129.00 & 12516.0 & 25032.0 \\
\hline 2.52 & . 3027.1 & 19223.3 & 48442.7 \\
\hline 3.17 ......... & ..... 2230.0 & 22409.1 & 71036.7 \\
\hline 4.00 ......... & ..... 1417.8 & 22684.8 & 90739.2 \\
\hline 5.04 ...... & ..... 567.6 & 14417.9 & 72666.5 \\
\hline 6.35 ...... & ....... 178.2 & 7185.5 & 45627.7 \\
\hline 8.00 ....... & ....... 34.3 & 2195.2 & 17561.6 \\
\hline 10.08 ........ & .......... 6.8 & 690.9 & 3687.1 \\
\hline 12.70 ........ & .......... 1.8 & 290.3 & 3687.1 \\
\hline 16.0 ....... & .......... 1.2 & 307.2 & 4915.2 \\
\hline 20.2 ........ & .......... 0.4 & 163.2 & 3296.9 \\
\hline 25.4 ........ & ..........0. 1 & 64.5 & 1638.7 \\
\hline 32.0 ........... & .......... 0.3 & 307.2 & 9830.4 \\
\hline Totals ......... & .. 10.594.5 & 102,455.2 & 401,439.3 \\
\hline
\end{tabular}
line is obtained \({ }^{4}\) (see Figure 1). This is a very useful correlation when considering zinc dust to be selected.

\section*{Influence of the Fraction of "Fines"}

Samples No. 4-7 in Table 7, which are classified as fine and superfine, were tested in a typical water-based product. \({ }^{3}\) The results of the application are shown in Table 8.

\section*{RESULTS AND DISCUSSION}

Zinc dust with a specific surface lower than \(0.2 \mathrm{~m}^{2} / \mathrm{g}\) is not acceptable. Those with specific surfaces greater than 0.2 \(\mathrm{m}^{2} / \mathrm{g}\) perform very well. The contribution of the fine portion can be seen by calculating the fraction of the total surface below and above the median particle size, as in Table 9.

The samples in which the higher percentage of the surface \((86.7 \%)\) is made up of particles less than the median size work very well. The fraction of fines in the dust is the most influential part of the rheological properties of the mix.

Certain applications require a limitation of the fine fraction in order to avoid increased viscosity. Limitation of the coarser parts will be necessary in certain cases where a higher viscosity is needed. A practical way to establish the required limits of zinc dust is through the use of ASTM Method D 1366. \({ }^{5}\) For example, from Table 10 and from the cumulative size distribution of sample No. 6 (Figure 2), the following parameters can be defined per ASTM D 1366-85.5

\section*{Specific Surface Diameter}
\[
S S D=\frac{d^{\prime} n}{d^{2} n}=3.92
\]
\[
D P=\frac{\begin{array}{l}
\text { Dispersion Parameter } \\
d \text { at } 75 \%-d \text { at } 25 \% \\
\operatorname{SSD}
\end{array} 100=66}{}
\]

Coarseness Parameter
\(C P=32\)
Where:
SSD \(=\) Diameter of the sphere having the specific surface characteristics of the zinc dust.
E. MONTES
\[
\begin{aligned}
\mathrm{DP}= & \text { The ratio of the micrometer size within which } \\
& 50 \% \text { of the pigment lies, to the specific surface } \\
& \text { diameter. }
\end{aligned}
\]
\(\mathrm{CP}=\) Diameter below which \(99.5 \%\) of the pigments fall.
\(\mathrm{d}=\) Mean class size in microns.
\(\mathrm{n}=\) Frequency.

\section*{SUMMARY}

By plotting on a log-log scale particle diameter versus specific surface, a very useful correlation for the appropriate selection of zinc dust is obtained.

Depending on the viscosity desired, certain applications require a limitation of the fine fraction; others require limitations on the coarse fraction of the dust.

A reliable way to characterize the zinc dust is through the use of ASTM D 1366-85.

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\section*{Circle the numbers of the items you would like more information on, and mail it-postage paid!}
\begin{tabular}{lllllllllllllll}
001 & 021 & 041 & 061 & 081 & 101 & 121 & 141 & 161 & 181 & 201 & 221 & 241 & 261 & 281 \\
002 & 022 & 042 & 062 & 082 & 102 & 122 & 142 & 162 & 182 & 202 & 222 & 242 & 262 & 282 \\
003 & 023 & 043 & 063 & 083 & 103 & 123 & 143 & 163 & 183 & 203 & 223 & 243 & 263 & 283 \\
004 & 024 & 044 & 064 & 084 & 104 & 124 & 144 & 164 & 184 & 204 & 224 & 244 & 264 & 284 \\
005 & 025 & 045 & 065 & 085 & 105 & 125 & 145 & 165 & 185 & 205 & 225 & 245 & 265 & 285 \\
006 & 026 & 046 & 066 & 086 & 106 & 126 & 146 & 166 & 186 & 206 & 226 & 246 & 266 & 286 \\
007 & 027 & 047 & 067 & 087 & 107 & 127 & 147 & 167 & 187 & 207 & 227 & 247 & 267 & 287 \\
008 & 028 & 048 & 068 & 088 & 108 & 128 & 148 & 168 & 188 & 208 & 228. & 248 & 268 & 288 \\
009 & 029 & 049 & 069 & 089 & 109 & 129 & 149 & 169 & 189 & 209 & 229 & 249 & 269 & 289 \\
010 & 030 & 050 & 070 & 090 & 110 & 130 & 150 & 170 & 190 & 210 & 230 & 250 & 270 & 290 \\
011 & 031 & 051 & 071 & 091 & 111 & 131 & 151 & 171 & 191 & 211 & 231 & 251 & 271 & 291 \\
012 & 032 & 052 & 072 & 092 & 112 & 132 & 152 & 172 & 192 & 212 & 232 & 252 & 272 & 292 \\
013 & 033 & 053 & 073 & 093 & 113 & 133 & 153 & 173 & 193 & 213 & 233 & 253 & 273 & 293 \\
014 & 034 & 054 & 074 & 094 & 114 & 134 & 154 & 174 & 194 & 214 & 234 & 254 & 274 & 294 \\
015 & 035 & 055 & 075 & 095 & 115 & 135 & 155 & 175 & 195 & 215 & 235 & 255 & 275 & 295 \\
016 & 036 & 056 & 076 & 096 & 116 & 136 & 156 & 176 & 196 & 216 & 236 & 256 & 276 & 296 \\
017 & 037 & 057 & 077 & 097 & 117 & 137 & 157 & 177 & 197 & 217 & 237 & 257 & 277 & 297 \\
018 & 038 & 058 & 078 & 098 & 118 & 138 & 158 & 178 & 198 & 218 & 238 & 258 & 278 & 298 \\
019 & 039 & 059 & 079 & 099 & 119 & 139 & 159 & 179 & 199 & 219 & 239 & 259 & 279 & 299 \\
020 & 040 & 060 & 080 & 100 & 120 & 140 & 160 & 180 & 200 & 220 & 240 & 260 & 280 & 300
\end{tabular}

Name
Company
Address \(\qquad\)
City \(\qquad\) State___Zip.

Phone \(\qquad\) FAX \(\qquad\)


\section*{Society Meetings}

CDIC.
..................................APR.

\section*{"Waterborne Resins"}

The Nominating Committee slate of nominees for Society officers positions for 1993-94 was disclosed as follows: Presi-dent-Paul R. Guevin Jr., of P.R. Guevin Associates; Vice President-Alan L. Machek, of Dow Corning Corporation; Secre-tary-John C. Avery, of Cintech Industrial Coatings, Inc., and Kenneth Pendleton, of K.A. Pendleton Company, Inc; and Trea-surer-Sherrill Henegar, of Reilly Industries, and William Jelf, of Akzo Coatings, Inc.

It was announced that Joseph Reckers, retired from Perry \& Derrick Company, Inc., had been elected to Society Honorary Membership.

Federation Honorary Member Lewis P. Larson introduced Paul E. Thalen, of Cintech Industrial Coatings, as the winner of the 1992-93 Lewis Larson scholarship. Mr. Thalen will use the scholarship to attend a mini-course at the University of MissouriRolla, in Rolla, MO.

The meeting's technical speaker was Rich Johnson, of Cargill, Inc. The Northwestern Society member discussed "New Developments in Waterborne Resins."

The speaker covered new developments in waterborne coatings, including: present government legislation, the driving force behind new developments, trends in the industry, waterborne resins for air-dry and baked coatings, waterborne dispersion resins, and thermoset acrylic waterborne resins.

Mr. Johnson pointed out that government legislation is either "toxilogical" or "ecological." It was stated that Title I is ecologically oriented, particularly with reference to VOC measurement. Title III contains a list of 189 hazardous air pollutants which the government would like to reduce. According to the speaker, only MEK, MIBK, toluene, and xylene pertain to the paint and coatings industry. In addition, Title V refers to chlorinated solvents.

Mr. Johnson said that waterborne resins are expected to increase by four percent over the next two years. He indicated that low-solids, solvent-borne coatings should decrease by three to four percent. However, growth is expected in high-solids, two-component, radiation cure, and powder coatings.

The survey determined that the obstacles which may have the largest impact on the industry are: lack of compliance with EPA; reluctance to change; how to change; and cost.

Mr. Johnson also discussed ways to improve low VOC formulations in order to overcome some of the drawbacks currently encountered.
Q. Do you have any reading on changes in the EPA guideline which will affect highsolids coatings?
A. The law is going to get tougher. VOC limits will get lower and lower. High-solids and waterborne products won't go away. NAD are being used on the West Coast. We offer \(340 \mathrm{~g} / \mathrm{L}\) chain-stopped alkyds. There's a lot of technology coming, but it will get tougher to meet requirements.
Q. How do you control hydrolysis?
A. Get rid of the ester linkages! I don't think you can. The worst thing is to have solvents with terminal hydroxyl groups. You have transesterification going on also. We have extended shelf life from 3-6 months to 12-18 months, but the clock is always ticking.

Paul R. Guevin Jr., Acting Secretary

\section*{CHICAGO APR.}
"Waterborne Industrial Coatings"
It was announced that the following members have been elected as Society officers for 1993-94: President-Gregory M. McWright, of ANGUS Chemical Company; Vice President-Natu C. Patel, of Ace Hardware Corporation, Paint Division; Sec-retary-C. David Stromberg, of Standard T Chemical; Treasurer-Marcella G. Nichols, of DSM-Desotech, Inc.; and Associate Representative-Alison Azar, of Seegott, Inc.

Evans Angelos, of Omya, Inc., will continue to serve as the Society Representative to the FSCT's Board of Directors.

Ronald K. Litton, of Eastman Chemical Company, presented a technical talk on "Coalescing Aid Selection for Waterborne Industrial Emulsion Coatings."

Mr. Litton said that air quality regulations are continuing to drive the paint industry towards more environmentally acceptable coatings. Mr. Litton explained that recently coatings formulators have focused on developing waterborne emulsion coatings for OEM/industrial applications. The emulsions designed for these markets have higher glass transition temperatures than emulsions used in architectural coatings. Thus, these emulsions with higher \(T_{g}\) require higher levels of coalescing aid to achieve good
film formation. What this entails is that the coalescing aid efficiency with a given emulsion system is very important, from both an ecological (lower VOC) and economic viewpoint.

In conclusion, Mr. Litton examined the key factors in choosing a coalescing aid for waterborne industrial, emulsion coatings. Clifford O. Schwahn, Publicity

\section*{CLEVELAND}

MAR.

\section*{"Formulating Colors"}

FSCT Secretary-Treasurer Joseph P. Walton, of Jamestown Paint Company, addressed the membership and spoke on many various topics regarding the Federation.

Mr . Walton discussed the importance of generating interest in the coatings industry among young people, which can be accomplished through local scholarships, career nights, and local science fairs.

He spoke about the FSCT seminar, "The Influence of Substrates and Application Methods/Techniques on Coatings Performance," scheduled for presentation during this year's Spring Week, and the theme of the 1993 Annual Meeting technical program, "Today's Competitive Coatings: Lean, Mean and Green."

Mr. Walton also reviewed the goals of the Coatings Industry Education Fund, and the Coatings Industry Honor and Remembrance Fund.

In conclusion, he stated that it is important for the industry to educate the people who develop legislation, because we will have to live with the laws for many years.


\section*{Constituent Society Meetings and Secretaries}

BALTIMORE (Third Thursday-Martins West, Baltimore, MD). Helene J. Ranfone, Duron, Inc., 10460 Tucker St., Beltsville, MD 20705.

BIRMINGHAM (First Thursday-Strathallan Hotel, Birmingham, England). D.C. Morris, PPG Industries (UK) Ltd., P.O. Box 359, Birmingham, B16 0AD, England.

CDIC (Second Monday-Location alternates between Columbus, Cincinnati, Dayton, and Indianapolis). Jeffery I. Buchman, Akzo Coatings, Inc, P.O. Box 147, Columbus, OH 43216-0147.

CHICAGO (First Monday-Sharko's Restaurant, Villa Park, IL). Natu C. Patel, Ace Hardware Corp., Paint Div., 21901 S. Central Ave., Matteson, IL 60443.

CLEVELAND (Third Tuesday-Brown Derby, Independence, OH in Nov., Mar., and Apr.; Cleveland Hilton, Cleveland, OH, in Feb.; Landerhaven, Mayfield Heights, OH, in May). Constance F. Williams, The Glidden Co., 801 Canterbury Rd., Westlake, OH 44145.

DALLAS (Thursday following second Wednesday-Holiday Inn Crowne Plaza, Dallas, TX). Benny Puckett, Kelly-Moore Paint Co., Inc., 301 W. Hurst Blvd., Hurst, TX 76053.

DETROIT (Second Tuesday-meeting sites vary). Jane Allen, Reichhold Chemicals, Inc., 814 Commerce Dr., Oakbrook, IL 60521.

GOLDEN GATE (Monday before third Wednesday-alternates between Francesco's in Oakland, CA, and Holiday Inn in S. San Franscisco). Richard Cooper, Synergistic Performance Corp., 5801 Christie Ave., \#590, Emeryville, CA 94608.

HOUSTON (Second Wednesday-Hobby Airport Hilton, Houston, TX). Tом Fitzgerald, Monarch Paint Co., P.O. Box 55604, Houston, TX 77255.

KANSAS CITY (Second Thursday-Cascone's Restaurant, Kansas City, MO). Lawrence J. Murphy, Tnemec Co. Inc., 123 W. 23rd Ave., N. Kansas City, MO 64116. LOS ANGELES (Second Wednesday-Steven's Steakhouse, Commerce, CA). John C. Kulnane, Ameritone Paint Corp., 18414 S. Santa Fe Ave., P.O. Box 190, Long Beach, CA 90801.

LOUISVILLE (Third Wednesday-Executive West Motor Hotel, Louisville, KY). William Leightner, C.L. McGuire \& Co., 8134 Newlagrange Rd., Louisville, KY 40222. MEXICO (Every fifteen days-Gabriel Mancera, Mexico City, Mexico). Sergio Rojas, Pinturas International, S.A. De C.V., Ganaderos 234, Col. Granjas Esmeralda, 09810 Mexico, D.F., Mexico.

MONTREAL (First Wednesday-Le Bifthèque Steakhouse, Ville St. Laurent, Quebec). Esther Rouleau McCarthy, Stochem Inc., 1455 32nd Ave., Lachine, Que. H8T 3J1, Canada.

NEW ENGLAND (Third Thursday-Sheraton Lexington Hotel, Lexington, MA, and other locations in Massachusetts and Rhode Island). Charles Shearer, ICI Resins US, 730 Main St., Wilmington, MA 01887.

NEW YORK (Second Tuesday-Landmark II, East Rutherford, NJ). George M. Amrich Jr., Benjamin Moore \& Co., 134 Lister Ave., Newark, NJ 07105.

NORTHWESTERN (Jax Cafe, Minneapolis, MN). Michael Grivna, Hirshfield's Paint Mfg., Inc., 4450 Lyndale Ave., N., Minneapolis, MN 55412.

Pacific northwest (Portland Section-Third Tuesday; Puget Sound Sec-tion-Third Wednesday; Vancouver Section-Third Thursday). John Westendorf, Lipscomb Chemical Northwest, 2627 NW Nicolai, Portland, OR 97210.

PHILADELPHIA (Second Thursday-Williamson's Restaurant, GSB Bldg., Bala Cynwyd, PA). Robert D. Thomas, M.A. Bruder \& Sons, Inc., 52nd \& Grays Ave., Philadelphia, PA 19143.

PIEDMONT (Third Wednesday-Ramada Inn Airport, Greensboro, NC). Dale BaKER, Kohl Marketing, Inc., 3859 Battleground Ave., Ste. 203, Greensboro, NC 27410.

PITTSBURGH (Second Monday-Montemurro's Restaurant, Sharpsburg, PA). Mark A. Harley Jr., PPG Industries, Inc., 4325 Rosanna Dr., P.O. Box 9, Allison Park, PA 15101.

ROCKY MOUNTAIN (Monday following first Wednesday-Zangs Brewery, Denver, CO). Christine LesCamela, Luzenac America, Inc., 8985 E. Nichols Ave., Englewood CO 80112.

ST. LOUIS (Third Tuesday-Salad Bowl Cafeteria, St. Louis, MO). Chuck Reitter, American Paint Journal Co., 2911 Washington Ave., St. Louis, MO 63103.

SOUTHERN (Gulf Coast Section-third Thursday; Central Florida Section-third Thursday after first Monday; Atlanta Section-third Thursday; Memphis Section-bimonthly on second Tuesday; and Miami Section-Tuesday prior to Central Florida Section). Jeff Shubert, Shubert Paints, Inc., 2157 Mountain Industrial Blvd., Tucker, GA 30084.

TORONTO (Second Monday-Cambridge Motor Hotel, Toronto). Bob C. Ng, Hoechst Canada Inc., 100 Tempo Ave., Willowdale, Ont. M2H 2N8, Canada.

WESTERN NEW YORK (Third Tuesday-meeting sites vary). Marko Markoff, 182 Farmingdale Rd., Cheektowaga, NY 14225.

The meeting's technical program focused on a talk by Baltimore Society member James M. Delaney, of CIBA-GEIGY Corporation. Mr. Delaney's topic was "Formulating Colors with Lead-Free Pigments."

The speaker provided an overview of the pigment options available to formulators of organic pigments. He stated that formulators have to look at replacing lead or heavy metal pigments as part of new technology. However, he said that replacing lead or a heavy metal pigment with an organic pigment can not be accomplished for the same price, opacity, or durability.

Mr. Delaney discussed the properties of chrome pigments, highlighting both the positive and negatives factors. Manufacturing problems also were reviewed.

The different categories of organic pigments, including some of the options and benefits, were explained.

In conclusion, Mr. Delaney stressed that formulators must work with the pigment supplier because it will take a lot of work testing the pigments in water-based and highsolids systems. He stated that formulators will help customers by switching to organic pigments, and also waste disposal and industrial hygiene.
Q.There are certain pigments that when mixed together do not appear compatible. Why does this happen?
A. The only pigments that this may occur with are the metallized azo pigments in water-based systems where the amino would attack the other metal salt.
Q. You stated there are cubical and spherical pigment structures that are preferred over the needle structure. Why?
A. Needles tend to clump together forming a fiber type network, and this fiber type rheology is not good if you want Newtonian structure. Needles tend to interact and block flow while the spheres will roll around like ball bearings.

Constance F. Williams, Secretary

\section*{LOS ANGELES}

APR.

\section*{Bosses' Night}

A moment of silence was observed in memory of Robert W. Waltman, of Cal Western Paints Corporation, who died recently. Mr. Waltman is credited with establishing Cal Western Paints.

Environmental Committee Chairman Dave Muggee, of E.T. Horn Company, reported on the latest news regarding the paint and coatings industry. Mr. Muggee discussed the Child Lead Poisoning Prevention Act of 1991. He said fees, billed by the state Board of Equalization, were due April 1. The fee was based on total 1991 gallonage of architectural coatings sold in the state of Califor-
nia. Presently, a difference of opinion exists as to what constitutes an architectural coating. Mr. Muggee said the Department of Health Services includes architectural coatings that contain lead or formerly contained lead, including traffic paint.

Also discussed was the proposed new fees for Air Toxic Hot Spots, from \(\$ 818\) to \(\$ 4,366\) per facility for plan and report. Risk assessment will cost from \(\$ 977\) to \(\$ 12,206\) per facility.

The final item on Mr. Muggee's report was the new OSHA-proposed glycol ether exposure limits

Technical Committee Chairman V.C. "Bud" Jenkins, consultant, announced that the second copy of the LASCT Graffiti Abatement and Prevention Handbook is available.

Horst Vlatvsky, of Tego Chemie, presented the meeting's technical talk. His topic was entitled, "The Foam Story."

The speaker characterized foam as the most common paint problem, and compared the theoretical difference between defoaming versus deaerating, and the test that can be conducted to test for air entrapment.

Mr. Vlatvsky discussed craters and pinholes, two problems associated with coatings. He explained how using defoamers or deaerators can help eliminate both microfoam and macrofoam.

The speaker reviewed several theories that have been developed to explain defoaming.

In conclusion, Mr. Vlatvsky stated that foam leads to craters in the film and entrapped air leads to pinholes. Also, the distinction between defoamer and deaerator is vital in solving the foaming problem.
Q. What types of defoamers are better, silicone or nonsilicone?
A. Silicone defoamers are expensive, but less is required and gloss development is better. However, if a lot is required, a nonsilicone defoamer is better.
Q. What is the most effective deaeration technique to ensure accurate filling weights?
A. There is no answer unless for low viscosity liquids.

John C. Kulnane, Secretary

\section*{LOUISVILLE}

JAN.

\section*{Past-Presidents' Night}

The Society Past-Presidents in attendance were recognized as follows: Joseph A. Bauer, retired (1968-69); James A. Hoeck, retired (1970-71); Herb Wilson, retired (1974-75); Paul M. Nilles, of Hy-Klas Paint Company (1975-76); John C. Ballard, of Burgess Pigment Company (1976-77); Nick Lanning, of Progress Paint Company (1977-78); Kirk Menefee, of Hy-Klas Paint
(1980-81); Joyce S. St. Clair, of Kentucky Partners (1985-86); Larry F. Pitchford, of Reynolds Metals Company (1988-89); and Kris J. Grauer, of Ashland Chemical Company (1991-92).

Mr. Hoeck, who had served as the Society Representative to the FSCT's Board of Directors, was recognized and presented a plaque for his long and distinguished service to the Society.

Educational Committee Chairman Paul R. Baukema, of Akzo Coatings, Inc., introduced Charles Adams, of United Catalysts, Inc., the winner of the the Society's 1992 Scholarship Award.

Mr. Adams gave a brief overview of the "Dispersion Technology" course he attended.

William Leightner, Secretary

\section*{NEW YORK}

MAR.

\section*{Mini Workshop}

A moment of silence was observed in memory of Society Honorary Member Elias Singer, who died on January 23. Mr. Singer was the founder of Troy Corporation.

Theodore Young, retired, was nominated for Society Honorary Member. Mr. Young has been a member since 1953, and is a Society Past-President.

The mini workshop featured a total of four technical talks, including: "ADHESION TO Chalky Substrates"-Tammy L. Maver, of Rohm and Haas Company; "Аnatomy of Coatings"-Society member Donald E. Brody, consultant: "Plant Safety"-Marvin Specht, of Hercules Incorporated; and "Waste Minimization"-Kevin Reed, of Ort \& Boss.

George M. Amrich Jr., Secretary

\section*{NORTHWESTERN}

MAR.

\section*{22nd Annual Symposium}

Four technical presentations were geared toward the theme of this year's symposium "Waterborne Coatings for the 90s."

The first speaker was Society member Rich Johnson, of Cargill, Inc., who discussed, "Resins for Waterborne Coatings."

The speaker reviewed some of the new developments in resins for waterborne coatings. He explained how environmental regulations are the driving force behind much of the new technology, specifically the Clean Air Act of 1990.

Mr. Johnson said Title I of the act is concerned with low ozone levels, and limits VOCs in architectural coatings. Title III focuses on toxic chemicals and contains a list of 190 Hazardous Air Pollutants. Accord-
ing to the speaker, this list will be finalized in 1994, with inforcement beginning in 1996 or 1997.

It was noted that some majors producers are participating in the EPA's \(33 / 50\) Project, a voluntary program whereby the usage of 17 chemicals is to be reduced \(33 \%\) by the end of 1993 , and \(50 \%\) by the end of 1996.

The speaker stated that the leading growth areas for compliant coatings includes high-solids and water-reducible systems.

In conclusion, Mr. Johnson said that most coatings manufacturers are preparing now for future legislation. He stated that waterborne technology is available today for compliance with future needs. Also, dispersions are being developed for the future.

Philadelphia Society member L. Joseph Junker, of ARCO Chemical Company, gave a talk on, "PnB/Cosolvents Applications in Waterborne Coatings."

Discussed were the issues leading toward the use of propylene-based glycol ethers, including: toxicity, environmental concerns, and the Clean Air Act of 1990.

The speaker said that propylene glycol ethers are not on the Clean Air Act Hazardous Air Pollutant list, or the Superfund (CERCLA), RCRA, or the California Safe Drinking Water Act lists.
"Formulating Waterborne Coatings, a Formulating Guide for the 90s," was presented by Chicago Society member Henry A. Solle, of Union Carbide Corporation.

Reviewed were the new requirements facing the formulator: toxicity, VOC reduction, higher scrub resistance, higher gloss, better flow and leveling, film build, and maintaining or lowering costs.

Mr. Solle discussed the tools which are available to the formulator for coping with the environmental demands, including: titanium dioxide; plastic pigments, extenders, biocides, and dispersants; associative thickeners; and new colorant lines.

In conclusion, the speaker stated that the general guidelines for formulation begin with "keep it simple."

The symposium concluded with a presentation by Steve Kish, of Graco, Inc. His talk was entitled, "Application/Equipment for Waterborne Coatings."

The speaker discussed the many equipment concerns since the change to waterborne coatings systems. Some areas of concern that the speaker reviewed included: corrosion susceptibility, viscosity, shear sensitivity, agglomeration, skinning, aeration, fluid velocity, and temperature control.

Michael Grivna Secretary
Circte the desimnated Reader Service Number for the latest product. equipment and worvec information availuble wo the paint and coatms in. dustry loday.

\section*{Elections}

\section*{CDIC}

Active
Montjoy, Tony L.-Yenkin-Majestic Paint Corp., Columbus, OH .

\section*{CHICAGO}

\section*{Active}

Ahluwalia, Diljit S.-Alfa Manufacturing Industries, Inc., Skokie, IL.
Baird.James Walter-USG Corp., Libertyville, IL.
Benson, Rohert L.-Stuart Industrial, Chicago, IL.
Foster, John C.-Nicoat Inc., Chicago.
Glanz. Matthew A.-lowa Paint Mfg. Co.. Des Moines, IA.
Harrington, Terry R.Seymour of Sycamore, Sycamore, IL.
Karavida. Michael S.-Premier Coatings, Elk Grove Village, IL.
Lawrence, James A.-Superior Graphite Co., Chicago.
Middlebrooks, Charles H.-Grundy Industries, Inc., Joliet, IL.
Patel, Ken-Blockson \& Co., Michigan City. IN.
Potter. Gary L.-H.B. Fuller Co., Tinley Park. IL.
Rasmussen. William A.-Morton International, Lansing, IL.
Rehel. Bill-Construction Tech. Lab., Inc., Skokie.
Seffrood, Paul J.-Finishes Unlimited, Sugar Grove, IL.
Slama. Francis I.-Finishes Unlimited, Sugar Grove.
Smith, Stephen M.-Seymour of Sycamore. Sycamore, IL.
Stapp. Stephen E.-Moline Paint Manufacturing Co., Moline, IL.
West, Gerald L.-Ace Hardware Paint Div., Matteson, IL.
Woodhouse, Brian M.-Morton International. Lansing.

\section*{Associate}

Beagle, John L.-Einhorn Associates, Milwaukee, WI.
Chidley, Roland H.-The Chidley \& Peto Co., Arlington Hts., IL.
Einhorn. Stephen-Einhorn Associates, Milwaukee.
Frankovich, John M.-Degussa Corp., Arlington Hts.

\section*{CLEVELAND}

Associate
Daugherty, Jon M.-Zinc Corp. of America, Copley, OH.

\section*{Educator/Student}

Kim, Yeong-An-Case Western Reserve University, Cleveland Heights, OH .

\section*{NEW YORK}

\section*{Active}

Sheerin, Robert J.-Benjamin Moore \& Co.. Newark, NJ .
Spencer, Rohert J.-R.J. Spencer Consultants, Inc., Maplewood, NJ.
White. David M.-Cardinal Color Inc., Paterson, NJ.

\section*{Associate}

Chung, Philip D.-Shamrock Technologies Inc., Newark, NJ.
Falco, John J.-E.W. Kaufmann, Clark, NJ.
Fischer, Robert E.-Verflex-MartinPicard, Wood Ridge, NJ.
Hussey, EdwinJ.-D.H. Litter Co., Inc., Elmsford, NY.
Konopka, Anthony P.-Polacryl, Stamford, CT.
Lehmbeck. Richard D.-Coating Technologies International, West Caldwell, NJ.
Ryan, Jane F.-Coating Technologies International, West Caldwell.
Strauss. MichaelJ.-Amber Inc., Tarrytown, NY.
Weise. Mark K.-Praxair Inc., Tarrytown.
Zezza. Charles A.-Rhone-Poulenc Inc., Cranbury, NJ.

\section*{Retired}

Jubanowsky, Louis J.-Hilton Head, SC.

\section*{NORTHWESTERN}

\section*{Active}

Johnston. Glenn R.-Louis O. Werneke Co.. Plymouth, MN.

\section*{Educator/Student}

Pu, Xinyu-North Dakota State University, Fargo, ND.
Yang. Hui-North Dakota State University, Fargo.

\section*{PACIFIC NORTHWEST}

\section*{Active}

Chinn, Robert A.-Imperial Paint Co., Portland, OR.
Yip, Winnie-Flecto Coatings Ltd., Richmond, B.C.

\section*{Associate}

Chlipala, Rohert F.-Clark Schwebel Distributors, Seattle, WA.
Geerstgens. William W.-The CP Hall Co., Vancouver, WA.

\section*{PHILADELPHIA}

\section*{Active}

Awadalla, Samir F.-Rohm and Haas Co, Philadelphia, PA.

Gillis, Teresa M.-Rohm and Haas Co.. Cherry Hill, NJ.
Lin. Tyau-Ieen-E.I. du Pont Co., Philadelphia.

\section*{Associate}

Fisher, James R.-Ibma, Inc., Princeton Jct., NJ. Moffat, David-Rohm and Haas Co., Cherry Hill, NJ.

\section*{SOUTHERN}

Active
Addison, Edward M.-Lilly Industries, Inc., Tampa, FL.
Albanese. Louis-Linear Dynamics, Inc., Canton, GA.
Baker. David-Lilly Industries, Inc., Tampa.
Bruner. George L.-Egyptian Lacquer Manfacturing Co., Franklin. TN.
Brunori, David.J.-Lilly Industries, Inc., Tampa.
George. Scott E.-Eastman Chemical Co.. Kingsport, TN.
Harpole. Troy L.-National Coatings Co., Jacksonville, AR.
Jones, Patricia D.-Kemira Inc., Savannah, GA.
Kight, Robert W.-Union Camp Corp., Savannah.
Lathrope, D. Bruce-Epifanes USA, Fort Lauderdale, FL.
Levy. Stanley S.-Consultant Chemist, Cocoa Beach, FL.
Mills. Gary L.-Rohm and Haas Co., Charlotte, NC.
Walsh, John C.-Crystal-Tech Ltd., Memphis, TN.
Ward, Michael E.-Stebbins \& Roberts, Little Rock, AR.

\section*{Associate}

Bennick, Barry K.-Rohm and Haas Co., Charlote, NC.
Bradfield. Suzzette-George Missbach \& Co., Atlanta, GA.
Goodhew, Alex P.-Deeks \& Co., Inc., Birmingham, AL.
Grant, Patrick F.-Harcros Pigments Inc.. Easton, PA.
Jenikovsky, Richard E.-Premier Mill Corp., Reading. PA.
Kraushaar, Douglas J.-Tioxide America Inc., Clayton, NJ.
Moore, Jerry N.—Azalea Color Co., Atlanta.
Rambo, George E.-Harcros Pigments Inc., Mooresville, NC.
Ritchic, Ed-Chemarco, Birmingham.
Sheppard, Mike-Armstrong Container, Atlanta.
Stobierski, William D.-Lawter International, Doraville, GA.
Wilson, James B.-Rohm and Haas Co., Atlanta.
Wise, Sanford-Milwhite Inc., Tallahassee, FL.

\section*{Educator/Student}

Gooch, Jan W.-Georgia Tech., Atlanta. GA.

\section*{People}

The appointment of J. Brian O'Connor to Account Manager in the Midwest was announced by McWhorter, Inc., Carpentersville, IL. His new territory will include Louisville, Cincinnati, Indianapolis, Chicago, and Western Michigan. Prior to joining McWhorter's resin facility in Philadelphia, where he most recently served as Plant Manager, Mr. O'Connor held several positions with the McCloskey Corp. He is a member of the Chicago Society.

J.B. O'Connor

United States Filter Corp., Palm Desert, CA, has selected G.G. Pique to spearhead their international sales effort. He will focus on building U.S. Filter's overseas base of business. Mr. Pique brings international management and consulting engineering experience to his new position.

Englehard Corp., Iselin, NJ, has announced the appointment of three directors for the company's Specialty Minerals and Colors Group. Craig J. Stoneback, has been appointed Business Director of Specialty Minerals. Mr. Stoneback will manage the marketing, technical services, and applications lab operations for the specialty minerals segment. Prior to his new position, he served as Marketing Director for Colors and Specialty Minerals, Product Manager for Specialty Kaolin Products and Technical Service Group Leader for Specialty Minerals. Mr. Stoneback is a member of the New York Society.

Carlton Johnson was named Business Director of Colors. Mr. Johnson will be responsible for the marketing of dry colors and dispersions and will focus on commercialization of new value-added products. Previously, Mr. Johnson served as the Business Manager of Color Pigments.

As Director of New Business Development, Subhash Lele will be responsible for new business programs, market and product development, and bridging minerals and colors technology. Mr. Lele served as the Group Leader of Technical Service for Minerals, and as Technical Service Director and Technical Service Manager for Colors and Minerals.

Edna Stern Finegold, Executive Vice President of Jolie Papier, and Howard Isenberg, CEO, Canada Wallcoverings Corp., have been elected to the Wallcoverings Association's Board of Directors.

The Packaging Products Division of The Dexter Corp., Waukegan, IL, has announced the promotion of Ted Wenzel to Product and Technical Service Manager for The Americas. Mr. Wenzel's new duties include responsibility for customer technical service needs among North, Central, and South American packaging sales and technical support. Prior to this promotion, he was a Technical Account Manager in the Beverage Group.

In addition, the newly created position of Director of Marketing for The Americas has been accepted by Chris John. He will assume strategic and marketing development responsibilities for food and beverage can coatings in North, Central, and South America. Previously, Mr. John served as Packaging Coatings Manager-Europe for Courtaulds Coatings (Holdings) Ltd. He will be relocating from the United Kingdom to the Chicago, IL, area.

Amoco Oil Co., Chicago, IL, has announced the appointment of Roxanne J. Decyk as Vice President of Polymers Marketing and Sales. In her new capacity, Ms. Decyk will be responsible for business direction and strategy of polypropylene and polystyrene, and polypropylene licensing activities. She replaces Steven K. Welch, who has been named Amoco Corp.'s Manager of Corporate Planning. Most recently, Ms. Decyk had been Amoco Oil Co.'s Vice President of Commercial and Industrial Sales.

C.V. Thompson

Carl V. Thompson has accepted a newly created position as Corporate Chemical Engineering Man-ager-Finishing for Superior Industries International, Inc., Van Nuys, CA. Mr. Thompson brings over 30 years of coatings related experience to this position. He is a past officer of the Golden Gate Society and a member of the Los Angeles.

The Canadian Decorating Products Association (CDPA) has named Paul Williams as Sales Manager. In his new position, Mr. Williams will be responsible for building sales in CDPA's Decorating Centre magazine and exhibitor booth space sales for CDPA's Decor Showcase exhibition. He previously worked in advertising sales for Moorshead Publications and Thomson Newspapers.

Douglas W. Huemme, Chairman, President and Chief Executive Officer of Lilly Industries, Inc., Indianapolis, IN, has been named Vice President of the National Paint and Coatings Association, Washington, D.C. Mr. Huemme will succeed J. Larry Jameson, who has resigned as President of BASF Corporation's Coatings and Colorants Div. in Clifton, NJ. Before joining Lilly Industries in 1990, Mr. Huemme was Vice President of the chemicals group of the Whittaker Corp. Currently a member of the NPCA Board of Directors and Executive Committee, he will be named President of the association at its 1993 annual meeting in October. Mr. Huemme also serves on the boards of directors of Lilly Industries, The Somerset Group, Inc., and the Coil Coaters Association.

\section*{CLASSIFIED ADVERTISING}

\section*{Professor/ChairmanDepartment of Polymers and Coatings}

North Dakota State University invites applications or nominations for the position of Professor/Chairman in the Department of Polymers and Coatings. Applicants are required to have a Doctorate Degree in Chemistry, Polymer Science, Material Science, or Chemical Engineering. Candidates should have an established research record, good communication skills, a commitment to undergraduate and graduate education, and proven ability to interact with industry. Preference will be given to applicants who have expertise in synthetic polymer and coatings chemistry, and experience in administration.

A curriculum vitae, a description of research interests and plans, and three letters of recommendation should be sent by June 15, 1993, or until position is filled to: Allan G. Fischer, Dean, College of Science and Mathematics, North Dakota State University, Fargo, ND 58105-5517; (701) 237-7411. North Dakota State University is an Equal Opportunity/Affirmative Action Employer.

KTA-Tator, Inc., Pittsburgh, PA, has announced that W. Stephen Parks Jr., will manage the New England Regional Operations for the company. Mr. Parks, formerly with the Glidden Co. and Ameron Protective Coatings Div., will provide coatings consulting and inspection services to the New England area.

Also, Rich Burgess was named Manager of the Gulf Coast Operations. Mr. Burgess will manage the coatings consulting, inspection, and other coatings services from the Humble, TX, office. He has been with KTA since 1991.

In other news, Alison Kaelin recently has joined KTA-Services, Inc.-KTA Environmental Div. She is a consultant for lead paint inspection and field services for both housing and industrial projects. She was formerly with the Bureau of Air Pollution Control.

Duane Smith has been appointed Manager of Operations by ICI Paints, Cleveland, OH. He will direct ICI Paints' plants in 12 countries in the Asia Pacific Region. Prior to his new position, Mr. Smith was the Site Manager and Plant Superintendent for the Glidden Co. plant in Reading, PA. He had been with Glidden since 1971.
J. Winn Darden has joined the staff of Hüls America Inc., Piscataway, NJ, as Western Regional Sales Representative for Coatings Raw Materials. He is responsible for the sales and marketing of the full line of coatings raw materials products for resins, coatings, sealants, adhesives and elastomers in his territory which covers 17 western states in the U.S. Mr. Darden most recently served as a Market Development Supervisor with Texaco Chemical Co.

Also, Richard Kowach has been appointed to the position of Sales Representative, Western Region, for the Colorants and Additives Division. Mr. Kowach will direct sales operations for architectural and industrial colorants and additives in Southern California, Arizona, and parts of Texas and New Mexico from the Hüls West Coast office in Newport Beach, CA.

In addition to these appointments, Hüls America has announced that the product marketing responsibilities within its Colorants and Additives Division have reorganized. Taking on new responsibilities and titles are the following: Donald P. Miller-Director of Marketing, Architectural and Industrial Colorants; Michael C. Spangler-Manager, Marketing, Architectural Machine Colorants and Color Systems; Lisa A. Westerfield-Manager, Marketing, In-Plant Colorants: and Martin FeldmanManager, Marketing, Industrial Colorants.

Dr. Feldman is a member of the New York Society.

David Wacker has been promoted to Sales Office Manager for Raabe Corp., Menomonee Falls, WI. He will be responsible for the management of the inside sales force, inside sales training and procedures, and the customer service department. Mr. Wacker has been with Raabe Corp. for seven years and most recently served as their Marketing Project Manager.

D. Wacker

The new Vice President of Manufacturing at Morehouse-COWLES, Inc., Fullerton, CA, is Albert G. Brutsche. Mr. Brutsche, who has a background in equipment manufacturing, is expected to decrease lead times on custom standard machines, and add to the services available to customers.

George Hughes has joined the staff of Johnson Matthey, Stoke-on-Trent, Staff., England, as General Sales Manager-Pigments and Dispersions. Mr. Hughes is to enhance the company's customer service and expand their global presence. He was previously employed as an Ink Industry Manager UK for CIBA-GEIGY.

SCM Chemicals, Baltimore, MD, has made recent appointments in its Americas Division. Brian D. Pickett has joined the sales staff as District Sales Manager-Central District and will be based in the Hudson, OH, District Office. Prior to his new position, Mr. Pickett was a Marketing Manager with Union Carbide.

Another addition to the sales staff is Paul A. Rodrigues. He will act as the Senior Sales Representative - Canada. His new responsibilities include the planning and execution of all sales for the Canadian market. Mr. Rodrigues held several sales and account management positions with Union Carbide before joining SCM.

Patrick C. Miller becomes the new Sales Representative-Midwestern District. His territory covers Ohio, Indiana, and Kentucky. Most recently, Mr. Miller was a Process Specialist with Betz PaperChem, Inc.

The new Sales Representative-Dallas is Charles L. Tramel, II. He is responsible for a region that includes Texas, Arkansas, Oklahoma, Kansas, and Colorado. Mr. Tramel has been with SCM for eight years, and most recently was a Materials Analyst.

Rick Spehn has joined Liquid Carbonic Noncryogenic Systems as National Sales and Marketing Manager. Liquid Carbonic Noncryogenic Systems is a business unit of Liquid Carbonic Industries Corp., Chicago, IL.

\section*{Obituary}

Anthony J. (Tony) Gomes, a member of the Dallas, Kansas City, and Houston Societies for Coatings Technology, died April 6, 1993, in Spring, TX.

Mr. Gomes was a Sales Representative in the South-Central region of the United States for Zeneca Resins, with whom he had been employed by for eight years. Prior to joining Zeneca, he worked for Witco Chemical Co. as National Sales Manager.

Mr. Gomes was a native of North Arlington, NJ, and a graduate of St. Peter's College in Jersey City, NJ. He resided in Spring, a Houston suburb, with his family.

Warren Bair, died on November 18, 1992. While Cleveland Society President during the years 1964-1965, Mr. Bair worked at Lacquer Products, Inc.

Robert W. Waltman, Owner and President of Cal Western Paints, Santa Fe Springs, CA, died recently. He was 64 years old.

Mr . Waltman was a 25 -year member of the Los Angeles Society for Coatings Technology. In addition, he was a Korean War veteran.

He is survived by his wife, Donna and four children.

Harold H. Goslen, Past-President of the Southern Society for Coatings Technology, and long-time employee of the Gilman Co., Chattanooga, TN, died on January 3, 1993.

A native of North Carolina and a World War II Navy veteran, Mr. Goslen was a 1945 Chemical Engineering graduate of North Carolina State University. A research grant with the Research Institute of the University of Chattanooga brought him to Tennessee in 1947. Two years later in 1949, he began his 37 years of distinguished service to the Gilman Co., which ended with his retirement in 1986. At various times throughout his Gilman career, Mr. Goslen managed the resin lab, the consumer products lab, and the industrial coatings lab.

Mr. Goslen was President of the Southern Society for Coatings Technology during 1970-71. He was also active in the Chattanooga Chapter of the American Chemical Society. Mr. Goslen served as chairman in 1959, and received their Distinguished Service Award in 1972.

Mr. Goslen is survived by his wife, Shirley; two sons, Alan H. and Andrew Q., and two brothers.

\title{
19th International Conference on Organic Coatings Slated for July 12-16, 1993 in Athens, Greece
}

The 19th International Conference in Organic Coatings Science and Technology is planned for July 12-16, in Athens, Greece. The purpose of the conference is to bring together leading scientists, engineers, industrialists, and educators in an international forum to discuss all aspects of organic coatings science and technology, including inks.

The conference has been designed for chemists or other professionals who want to understand the principles involved in the science and technology of organic coat-ings-their manufacture, applications to surfaces, and properties. In addition, the latest developments in the field of organic coatings will be presented in a manner which will permit the scientist or engineer to integrate fundamental scientific principles with processing and application technology.

The following are papers scheduled to be delivered:

Keynote Speaker-Dr. John C. Padget, Senior Research Associate, ICI Resins"Polymers for Waterborne Coatings-A Systematic Overview"
"Metal Pigments for Non-Polluting Coat-ings"-Robert Besold, Eckart-Werke GmbH \& Co., Germany
"Progress in Product Development for Powder Coatings Technology"-Manfred Bock and H.U. Meier-Westhues, Bayer AG, Germany
"Fluorescence Cure Studies of AminoEpoxy Systems"-Robert Brady Jr., Dept. of Navy, USA and John M. Charlesworth, Materials Research Laboratory, Australia
"Gloss of Paint Films II: Effects of Pigment Size"-Juergen Braun, DuPont Chemicals, USA
"Synthesis, Structure and Properties of Hydrophobically Associating Polymers"F. Candau, J. Selb, and S. Biggs, Institute Charles Sadron, France
"Organic Coatings for Marginally Prepared Surfaces"-Giacomo Cerisola, University of Genova, Italy
"Rheology Control of Organic Coatings with New Hydrophobic Silicas"-Ulrich Christ and A. Bittner, Degussa AG, Germany
"Paint Reformulations and Photochemical Ozone Creations Potential"-I. Dobson, BP Chemicals, UK
"The Autoassociative Polymers in Wa-ter-Borne Paintings. Synthesis, Characterization of Model Polymers, Study of Their

Association in Water in the Absence and Presence of Surfactants"-Jeanne Francois, Institute Charles Sadron, France
"Ambient Cure Mechanism of Acrylosilane Coatings"-Hisao Furukawa, Yasushi Kato, and Naotami Ando, Kaneka Corporation, Japan
"New System for Electrodeposition Coatings Based on N-Methacryloylcarbamate"M. Furukawa, S. Urano, N. Tsuboniwa, S. Shirakawa, E. Yamanaka, and M. Yabuta, Nippon Paint Co., Ltd., Japan
"The Surface Embrittlement of a Ductile Blend Due to a Brittle Paint Layer"-J.L. Gacougnolle, CNRS, ENSMA; C. Verpy, Renault S.A.; A. Chestneau and F. Cozette, AKZO Coatings S.A., France
"Polymer Encapsulation of Inorganic Particles"-A.M. van Herk, R.Q.F. Janssen,
A.A.W.G. Jansen, and A.L. German, Eindhoven University of Technology
"New Developments in Weatherable Clear Coatings"-Loren Hill, H. Korzeniowski, and M. Ojunga-Andrew, Monsanto, USA
"Alkyd Emulsion"-M. Hulden, Institute for Surface Chemistry, Sweden
"Recent Studies of Self-Condensation and Co-condensation of Melamine Formaldehyde Resins: Cure at Low Tempera-tures"-Frank N. Jones and Guobei Chu, Eastern Michigan University, USA
"Restricted, Endangered, Extinct? Chemical in the Shadow of Environmental Constraints"-H. Jotischky, Paint Research Association, UK

Continued on next page.

\section*{CALL FOR PAPERS}

\section*{21st Annual Waterborne, Higher-Solids, and Powder Coatings Symposium \\ \\ Sponsored by \\ \\ Sponsored by Southern Society for Coatings Technology Southern Society for Coatings Technology and and University of Southern Mississippi} University of Southern Mississippi}

February 9-11, 1994 New Orleans, LA
All prospective authors are invited to submit papers for presentation at the 21st Annual Waterborne, Higher-Solids, and Powder Coatings Symposium on February 9-11, 1994, in New Orleans, LA.

Papers relating to the chemistry, formulation, and marketing of waterborne, higher solids, powder, and other advanced coatings systems are solicited. Papers relating to engineering aspects of coatings systems or solvent abatement are also solicited.

Titles, abstract, and author's names (speaker's name underlined) should be submitted by August 13, 1993, to Dr. Robson F. Storey or Dr. Shelby F. Thames, Co-Organizers, WBHS \& PC Symposium, Department of Polymer Science, The University of Southern Mississippi, Box 10076, Hattiesburg, MS 39406-0076.

The completed paper should be submitted by November 29, 1993. The preliminary program will be developed based on the submitted abstracts. Manuscripts will be required for inclusion in the Symposium Proceedings.

It is required that all papers be original and of scientific value.
For additional information call Drs. Storey or Thames at (601) 266-5193, 4879 , or -5618.

\section*{Organic Coatings Conference}

\author{
Continued from previous page.
}
"Reactive Acid Curing Waterborne Microparticles"-Kerstin Kjellqvist, Nobel Paint and Adhesives, Sweden
"Development of Water-Based Algae Resistant Wall Paint in Singapore"-Wah Sing Loh, Singapore Institute of Standards \& Industrial Research, Singapore
"New Developments in the Color Measurement of Mica-Colors"-Roman Maisch, Peter Gabel, and Werner R. Cramer, E. Merck AG, Germany
"Mechanistic Study of Alkyd Drying Using Ethyl Linoleate as a Model Com-pound"-W.J. Muizebelt, J.C. Hubert, and R.A.M. Venderbosch, AKZO Research Laboratories Arnhem, Netherlands
"Mechanical Stress in Automotive Electrocoat Primers: the Role of Temperature and Water Adsorption"-Steve Mazur, DuPont Corporate Research, USA
"Electropolymerization: A Straight Route from Monomers to Polymer Coatings"Marco Musiani and G. Mengoli, IPELP CNR, Italy
"Effect of Physical Aging on Stress Development in Powder Coatings"-D.Y. Perera and P. Schutyser, CORI, Belgium
"Characterization of Active Pigments in Damages of Organic Coatings on Steel by Means of Electrochemical Impedance Spec-
troscopy"-U. Rammelt and G. Reinhard, Technical University of Dresden, Germany
"A Comparative Study of the Available Electrochemical Methods for the Investigation of High-Tech Organic Coatings Dete-rioration"-Y.B. Miskovic-Stankovic, F. Deflorian, L. Fedrizzi, and P.L. Bonora, University of Trento, Italy
"Novel Analytical Techniques to Analyze the Emission Products from Epoxy Res-ins"-Paul Swaraj, PP Polymer AB, Sweden
"Unique Molecular Aggregation of Novel Naphthalocyanine"-Seiji Tai, Nobuyuki Hayashi, and Mitsuo Katayose, Hitachi Chemical Laboratory, Japan
"Self-Crosslinkable Graft Copolymers with Blocked Isocyanate and Other Functionalities: The Synthesis, Reactivity, and Application to Thermoset Coatings"Y. Yukawa, M. Yabuta, and A. Tominaga, Pansai Paint Co. Ltd., Japan

The registration fee for the conference is \(\$ 650\) which includes participation in the scientific sessions and the book of the published proceedings of the conference. Additional information may be obtained by writing Angelos V. Patsis, Institute of Materials Science, State University of New York, New Paltz, New York, 12561.

\section*{ACS/OSA to Jointly Sponsor Meeting on Organic Thin Films for Photonic Applications}

The POLY and PMSE Divisions of the American Chemical Society and the Optical Society of America are cosponsoring a meeting on "Organic Thin Films for Photonic Applications," at the Royal York Hotel in Toronto, Ontario, Canada, October 6-8, 1993. This meeting, the first in a series of ACS/OSA joint programming activities, will be held in conjunction with the Optical Society of America Annual Meeting. Subsequent joint programs will be co-located with future ACS and OSA meetings. This initial combined effort by the two societies will address the rapidly emerging field of organic thin film materials for photonic and optical applications. The meeting will serve as a common forum for chemical and optical scientists interested in the latest developments and advances in this field.

Possible topics to be considered at the meeting are: material synthesis and characterization, processing techniques, measurement techniques, theory of nonlinear optical materials, poled nonlinear optical polymers, Langmuir-Blodgett and self-assembled films, passive polymer waveguide device applications, and polymer optical fibers.

For more information on the "Organic Thin Films for Photonic Applications" meet-
ing, contact the Optical Society of America, 2010 Massachusetts Ave., NW, Washington, D.C. 20036-1023.

\section*{Short Course on Compliance with Air Quality Regulations Offered by UC Berkeley Extension}

The course "Getting into Compliance with Air Quality Regulations for Paints, Coatings, and Printing Facilities" will be sponsored by Continuing Education in Engineering, University Extension, University of California, Berkeley on June 8-11, 1993, in San Francisco, CA.

This three-and-a-half-day course will provide information about the consequences of the Clean Air Act and state and local regulations for paints, coatings, and printing facilities. Also, the course will include special sessions on the EPA's progress on permitting rules and CTGs.

To obtain more information on the course, write Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, CA 94720.

\title{
ACS Division of Polymeric Materials: Science and Engineering \\ \\ Sponsors Symposium on \\ \\ Sponsors Symposium on "High Solids Coatings"
} "High Solids Coatings"
}

\author{
March 13-18, 1994 \\ San Diego, CA
}

The Polymeric Materials: Science and Engineering (PMSE) Division of the American Chemical Society is inviting authors to submit papers for their symposium on "High Solids Coatings" to be held March 13-18, 1994, in San Diego.

The symposium will concern all scientific and technological aspects of liquid high solids coatings except for radiation curable coatings. Papers addressing both practical aspects of the subject and those addressing underlying scientific and engineering principles will be considered. Appropriate topics include, but are not limited to:
- Synthesis of oligomers and polymers
- Crosslinkers and crosslinking reactions
- Catalysis
- Advances with conventional binderspolyesters, acrylics, aminos, polyurethanes, and epoxies
- Newer types of coatings binders
- Solvents and reactive diluents
- Non-aqueous dispersions
- Pigments
- Additives
- Formulation
- Production of oligomers and polymers
- Properties of oligomers and polymers
- Production of coatings
- Pigment dispersion
- Solventless liquid coatings
- Rheology of high solids coatings-sag control
- Structure of films-network theory
- Film properties-adhesion, corrosion resistance, weatherability, acid resistance, etc.
- Application-electostatics; robotics
- High solids coatings for specific uses automotive, appliance, industrial, architectural, etc.
- Environmental, regulatory and safety issues
- Quality and statistical quality control

The deadline for receipt of preliminary titles is September 1. For more information, contact one of the following symposium organizers: Frank N. Jones, Coatings Research Institute, Eastern Michigan University, 430 W. Forest St., Ypsilanti, MI 48197; or George R. Pilcher, Akzo Coatings, Inc., P.O. Box 147, Columbus, OH 43216-0147.

\section*{Literature}

\section*{Refinery Gas Analyzer}

Two new application notes that describe refinery gas analyzers have been released. Both are designed to perform gas analysis of refinery-type gases and similar gaseous mixtures with separations of all light saturated and olefinic hydrocarbons, hydrogen, hydrogen sulfide, and the fixed gases. For a free copy of the Engineered Chromatography Products and Systems Application Note on the RGA Model 1001 (order number GCENG-1) or the RGA Model 1003 (order number GCENG-5), write The Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 068590012.

Circle No. 200 on Reader Service Card

\section*{Rheometer Hardware}

The availability of a speed and position hardware upgrade for controlled stress rheometers has been announced. The new specifications provide a top speed of \(320 \mathrm{rad} / \mathrm{sec}\) and a resolution of \(1.3 \times 10^{-6}\) radians. For additional information on the hardware upgrade for the CS 10 and CS 50 Bohlin Controlled Stress Rheometers, contact John Casola, Bohlin Instruments, Inc., 2540 Route 130, Cranbury, NJ 08512.

Circle No. 201 on Reader Service Card

\section*{Portable Spectrophotometer}

The introduction of a precision, portable spectrophotometer has been made through a product release. The spectrophotometer is designed to function as a stand-alone instrument for color QC applications and as a benchtop instrument in color formulation applications. For more information on Microflash 200d, contact Datacolor International, 5 Princess Rd., Lawrenceville, NJ 08648.

Circle No. 202 on Reader Service Card

\section*{Data Acquisition and Process Supervision Software}

Datavue \({ }^{\text {TM }}\) software, upgraded to work under Microsoft \({ }^{\circledR}\) Windows \({ }^{\text {¹4 }}\), is highlighted in a data sheet. The software options allow users to generate free-form reports, data logs, trends, and custom graphic displays for data analysis. Literature on Datavue for Windows is available from Leeds \& Northrup, P.O. Box 2000, North Wales, PA 19454.

Circle No. 203 on Reader Service Card

\section*{Coatings Additives}

An eight-page brochure describing the typical use levels, performance expectations, applications, and incorporation procedures for a broad range of coatings additives is now available. To obtain "Metal Soaps, Specialty Additives and Biocides for the Coatings Industries," technical data, and samples, contact Hüls America Inc., Colorants \& Additives Div., P.O. Box 456, Piscataway, NJ 08855-0456.

Circle No. 204 on Reader Service Card

\section*{Product Catalog}

A new product catalog detailing the company's products is now available. The publication includes full descriptions, instructions, specifications, and pricing on many new test instruments. To obtain a free copy of mini-catalog \#13, contact the Paul N. Gardner Co., Inc., P.O. Box 10688, Pompano Beach, FL 33061-6688.

Circle No. 205 on Reader Service Card

\section*{Storage Tank}

A new aboveground storage tank within a concrete vault is the focus of recently published literature. The new product, which is designed to provide added safety and full secondary containment for secure fuel storage, features an integral pump island and a built-in fill/spill trap. Further information on the Liqui-Vault AST is available from Clawson Tank Co., P.O. Box 350, 4545 Clawson Tank Dr., Clarkston, MI 483460350.

Circle No. 206 on Reader Service Card

\section*{OSHA Answer Book}

A new 300-page book designed to assist employers with their OSHA compliance responsibilities has been published. This book contains an explanation of OSHA inspections, standards, citations and penalties, and a state-by-state directory of experts who will provide employers with free on-site consultation and answer any OSHA question. Copies of The 1993 OSHA Answer Book, or further information can be obtained by contacting Moran Associates, 919 18th Street, N.W., Washington, D.C. 20006.

Circle No. 207 on Reader Service Card

\section*{Polyurethane Prepolymers}

Information on polyurethane prepolymers for coatings applications is now available in a literature kit. The packet provides information on a company's commercial and developmental prepolymer formulations, as well as two questionnaires. For a complimentary copy of "Polyurethane Specialty Products for Coatings" information kit, contact Air Products and Chemicals, Inc., Polyurethane Chemicals Div., 7201 Hamilton Blvd., Allentown, PA 18195-1501.

Circle No. 208 on Reader Service Card

\section*{Carton Printer}

A new high resolution carton printer is detailed in a brochure. This brochure highlights the print capabilities: high resolution (200 dots per inch) text, graphics, and inspec bar codes. To receive the new Iconotech \({ }^{\text {rW }}\) Digital Carton Printing System (DCP) brochure, contact Dave Loesche, Coding Systems Product Supervisor, Diagraph Corp., 3401 Rider Trail South, St. Louis/ Earth City, MO 63045-1110.

Circle No. 209 on Reader Service Card

\section*{SMC Reinforcement}

A fiber glass roving for sheet molding composite (SMC) has been introduced through literature. The new product is a medium-soluble, medium-hard reinforcement designed to have good molding performance during processing and virtually no fiber read-through in the painted part. The roving is available with inside payout, air-spliced for package-to-package transfer, and controlled yield. Information about Type 5530 SMC roving is available from PPG Industries, One PPG Place, 32 West, Pittsburgh, PA 15272.

Circle No. 210 on Reader Service Card

\section*{SITUATIONS WANTED}

A Chemical Engineer with 24 years of experience in trade sales seeks a senior management position in plant, technical and/ or quality assurance. Experience in formulation, process improvements, trouble shooting. Antoine Chaoui, 3481 Belcourd Rd., Longueuil, Quebec, J4M 2KG Canada.

\section*{Surfactants}

A new product guide describes a family of surfactants screened as agents to help coating formulators improve the performance of their systems or solve specific problems. The brochure provides a fold-out chart listing the structure, properties, and applications for the surfactants. A copy of the guide "Witflow \({ }^{\text {TM }}\) Surfactants for Paints and Coatings," may be obtained from Witco Corp., 3230 Brookfield St., Houston, TX 77045-5296.

Circle No. 211 on Reader Service Card

\section*{Rinse Additive}

Literature has been released on a rinse additive that has been specially formulated for application in the two-piece aluminum beverage container industry. This product was designed to reduce the friction between cans as they move through track work, increase water drainage when added to the final washer rinse, improve drying efficiency of can washer ovens, and reduce spoilage during the lithographic phase of production. For more information DR-1597 rinse additive, contact Man-Gill Chemical, 23000 St. Clair Ave., Cleveland, OH 44117.

Circle No. 212 on Reader Service Card

\section*{Tile-Clad High Solids}

A product release highlights a new twocomponent, VOC compliant, epoxy-polyamide coating for use in industrial maintenance and high performance architectural applications in moderate to severely corrosive environments. This product contains \(57 \%\) volume solids and 3.12 lb of solvent per gallon, and provides a tile-like surface which offers chemical and abrasion resistance. All inquiries for more information should be identified as Tile-Clad High Solids (SWS-3716), and sent to The SherwinWilliams Co., c/o HKM Direct, 5501 Cass Ave., Cleveland, OH 44102.

Circle No. 213 on Reader Service Card

\section*{Propylene Glycol}

Newly revised literature on propylene glycol, used in the formulation of unsaturated polyester resins, foods, pharmaceuticals, personal care, functional fluids, and paints and coatings, is now available. The information includes market conditions and end-use applications. More information is available from The Dow Chemical Co., Midland, MI 48674.

Circle No. 214 on Reader Service Card

\section*{Silica Glass and Fabricated Products}

A new four-color brochure discusses silica glass products that are supplied to the optics industry, the semiconductor fabrication industry, and the fiber optics industry. The brochure also includes a listing of the company's facilities throughout the U.S. and abroad. For a copy of "Your Global Resource: Heraeus Silica Glass and Fabricated Products," write Glenn Rush, Heraeus Amersil, Inc., 3473 Satellite BIvd., Duluth, GA 30136-5821.

Circle No. 215 on Reader Service Card

\section*{Engineered Polymer}

Information has been published on an engineered polymer that can be used in vanity top applications. This product reportedly provides cost reductions due to high productivity and low scrap, impact resistance, reduced brittleness, and mar-resistant appearance demanded in solid-surface products. For more information on Valox \({ }^{\circledR}\) engineered polymer, contact GE Plastics, Inquiry Handling Service-PR \#5-93, One Plastics Ave., Pittsfield, MA 01201.

Circle No. 216 on Reader Service Card

\title{
When you need a pigmentextender,
}

\begin{abstract}
CAMEL-WITE \({ }^{*}\) \& CAMEL-WITE SLURRY. \({ }^{*}\) The industry CAMEL-CARB. A quality extender that's economically standard. Exceptionally white, fine particle size, wet-ground priced. Produced from white Calcite. Provides uniform product produced from high-grade calcite limestone. low vehicle demand, good color, high brightness. CAMEL-TEX. . Fine ground general purpose grade of cal- CAMELCAL \({ }^{*}\) \&CAMEL-CALSLURRY. \({ }^{*}\) New from Genstar. cium carbonate produced from extremely white Calcite. Ultra-fineground calcite limestone with extender efficiency Low vehicle demand, rapid dispersibility. and hiding power of precipitated calcium carbonate.
\end{abstract}

\section*{CrossLinks}
by Earl Hill


Published in July Issue

No. 54

\section*{ACROSS}
1. \(37 \%\) aqueous solution of formaldehyde used as a starting material in the manufacture of ureaformaldehyde resins
4. An anti-skin chemical
7. A cutout overlay for designs or letters
8. Part of a production mixer (2 words)
11. Kind of agent, F \(\qquad\)
12. Calcium carbonate (Syn.)
15. What one does to a painted car
17. Water used in salt fog testing chambers
19. Slightly more exotic paint application process
20. Type of finishing
22. Having to do with bitumen
25. To slough off for thermal protection
27. Epoxy resin curative
30. To dot, as in painting art
31. A kind of store (PI.)
32. Sticken stuf

\section*{DOWN}
1. Fine short fibers
2. The type of 30 Across
3. To produce a very fine pigment
5. The science of the relationship between organisms and their environment
6. An exterior substrate
9. To make
10. Sandarac (Syn.)
13. Another part of 8 Across
14. Referring to paint in a can under pressure
15. Acidity or alkalinity, e.g.
16. Unit of measure (Abr.)
17. Heat unit
18. Chemical used in polymerization
21. Aluminum oxide (2 words)
23. Another name for a rubber gasket
24. To dilute; thin (2 words)
26. A framed sheet of glass
28. Yellow earth
29. Opposite of alkali

\title{
. . . More on "Service Life Prediction" (June 1992 JCT)
}

\section*{To the Editor:}

The challenge by Ray Dickie and the responses by Juergen Braun and the FSCT Corrosion Committee (see JCT . April 1993. pg. 77) encouraged me to contribute my own thoughts to this discussion. I have been involved in research on coatings for over 40 years, and during that time my perspective has grown and I hope, matured; certainly it has changed.

Coatings are extremely complex systems, and failure can take many forms. I agree fully with the previous letters that there is a need for some generally, and internationally agreed on definitions of what constitutes acceptable durability, and what constitutes premature failure. After all, we know that all coatings fail eventually, the problem is to define premature failure. These definitions may have to take into consideration the use (i.e., the exposure), the substrate, the application process, and also the expectations. The buyer who pays for a minimum paint and for the lowest possible film build must also understand that he cannot expect the same durability as one who applies several coats of a premium product. It will not be easy to reach such agreements, but that is to a large extent the realm of the ASTM and other standards organizations. The development of standard tests and their interpretation may be the most that we can hope for in the next decade or so.

However, my principal interest is the technical problem. Coatings, even the simplest of them, are systems. The substrate, the several layers, and the application processes are all involved. Premature failure can take many forms, and have innumerable causes, some of which may not be amenable to accelerated testing.

Basically, when one starts to discuss service life prediction one talks modeling. I am not sure that we have the necessary techniques or even all the relevant facts to start a modeling program. To begin with, all coatings on metal substrates are under substantial stress. Stress can originate in systems cured by heating during the cooling process, when the temperature falls through the glass transition temperature \(\left(\mathrm{T}_{\mathrm{g}}\right)\) of the coating, because the coefficient of thermal expansion of metals is an order of magnitude smaller than that of the organic polymer. Thus, at the temperature that equals the \(\mathrm{T}_{\mathrm{g}}\) of the coating the polymer can no longer contract as much as it wants to and the
result is that it is under two-dimensional tension. In air-dried systems, when the loss of solvent has reached the point where the combination of coating and remaining solvent has the \(\mathrm{T}_{\mathrm{g}}\) that equals the ambient temperature, or if the coatings crosslink when solvent is still present any further loss of solvent will also cause stress. In many systems stress has been shown to increase reactivity, for instance, the oxidation of stressed rubber.

The interaction of coating with the substrate is affected by adhesion, cleanliness, application conditions, solvent, and a myriad of influences. Trying to model a single coating on a single substrate, just varying some of the noted factors may take a major effort. Adding new variables, such as pigment volume, primer or tie coats, or film thickness simply compounds the difficulty.

The industry has used accelerated weathering techniques for decades, but the confidence (or lack of it) that these inspire is evidenced by the fact that generally the user wants to see some long-term exposure before accepting the accelerated exposure, and only minor changes are acceptable after that. We know that film degradation is caused by oxygen, water, light, various impurities in the air, as well as continuation of cure reactions that originally converted the liquid film former into a solid film. We do not know how these interact in many cases, and which of the various possible reactions are rate controlling; after all, there is no point in trying to accelerate a particular reaction if the precursor reaction is rate controlling, and it is not accelerated. While heat accelerates most reactions, it does not do this equally to them; the acceleration depends on the activation energy, and for example, the formation of free radicals by peroxide decomposition has a higher activation energy than their recombination, which often is 0 . In many films, the rate is not controlled by reaction rates but by diffusion rates. Again, these are affected by the size and mobility of the diffusing species. We can increase reaction temperature, but we do not know how to predict the effect of that. We cannot (or generally do not) increase oxygen concentration, and while we can apply water more often, we do not understand the consequences of that either. If time and light exposure are needed at certain points in the weathering cycle, we have no good way of predicting when these critical points are reached.

The criteria of failure depend on the end use, as pointed out by Braun. When we have determined the mechanism of action that is rate controlling for the critical failure we may have a shot of doing the kind of service life prediction. Dickie and his coworkers have gone a long way of doing this in the case of metal-primer interface failures; Braun and others have done beautiful work on the mechanisms of \(\mathrm{TiO}_{2}\) catalysis of film degradation and chalking; however, many of these results are applicable to a narrow range of materials and situations, and even then, how much would you risk on the correctness of the predications without real-life exposures?

The problem, as I see it, is that the industry deals with so many raw materials and combinations of materials and so many imponderables that service life prediction seems highly futuristic at this time. Consider, for instance, the effect of different pigment grinding processes on gloss and gloss retention of the same pigment and binder; or the effect of small quantities of additives; how would you include these in the predicting process? I am not advocating that the industry should stop fundamental research (because that is what is involved) and I agree with the proposals of the FSCT Corrosion Committee in a general way; I do however want to point out, that if we, as an industry, start down this road, we should be aware of how long and difficult and expensive it is likely to be, and how many different factors we may have to consider. Even if we are phenomenally successful, we would still have to limit our predictions to very specific situations, and we could never expect that anyone who mixes paints could apply some magic formula or computer program that will automatically give him/her an accurate service life prediction.

Submitted by
Werner S. Zimmt
Bala Cynwyd, PA

For Complete Details on the FSCT's 1993 Annual Meeting \& Paint Industries' Show, See page 19.

\section*{Coming Events}

\section*{FEDERATION MEETINGS}

For information on FSCT meetings, contact Federation of Societies for Coatings Technology, 492 Norristown Rd., Blue Bell, PA 19422 (215) 940-0777, FAX: (215) 940-0292.

\section*{1993}
(Oct. 27-29)—71st Annual Meeting and 58th Paint Industries' Show. World Congress Center, Atlanta, GA.

1994
(May 12-15)—Federation "Spring Week." Spring Seminar on the 12th and 13th; Incoming Society Officers Meeting on the 14th; Board of Directors Meeting on the 15th. Marriott City Center Hotel, Minneapolis, MN.
(Oct. 12-14)-72nd Annual Meeting and 59th Paint Industries' Show. New Orleans Convention Center, New Orleans, LA.

\section*{1995}
(Oct. 9-11)-73rd Annual Meeting and 60th Paint Industries' Show. Cervantes Convention Center, St. Louis, MO.

\section*{SPECIAL SOCIETY MEETINGS}

\section*{1993}
(June 4-5)-Joint Meeting of the Kansas City and St. Louis Societies. Holiday Inn, Lake of the Ozarks, MO.
(June 8-9)—New England Society. Coatings Tech Expo '93. "Com-pliance-Options for the 21st Century." Sheraton Tara Hotel \& Resort, Danvers, MA. \{Joanne Monique, Ashland Chemical, Inc., 400 Main St., Tewksbury, MA 01876; (800) 962-5388\}.
(June 14)-Golden Gate Society Manufacturing Committee Seminar. "Process and Compliance." Ramada Inn, S. San Francisco, CA. \{Ronald Hughes, Ashland Chemical, Inc., 8600 Enterprise Dr., Newark, CA 94560; (510) 796-9333\}.

\section*{1994}
(Feb. 9-11)-21st Annual Waterborne, Higher-Solids, and Powder Coatings Symposium. Sponsored by the Southern Society for Coatings Technology and The University of Southern Mississippi (USM). New Orleans, LA. (Robson F. Storey or Shelby Thames, Co-Organizers, WBHS\&PC Symposium, Dept. of Polymer Science, USM, P.O. Box 10076, Hattiesburg, MS 39406-0076).

\section*{OTHER ORGANIZATIONS}

\section*{1993}
(June 14-17)-"Coatings Science for Coatings Chemists." Short course sponsored by The University of Southern Mississippi (USM), Hattiesburg, MS. (Debbie Ballard or Shelby Thames, USM, Dept. of Polymer Science, Southern Station, P.O. Box 10076, Hattiesburg, MS 39406-0076).
(June 14-25)-"Coatings Science." Short course sponsored by North Dakota State University (NDSU), Fargo, ND. (Marek W. Urban, Program Director, or Debbie Shasky, Program Coordinator, Dunbar Hall, Rm. 54, NDSU, Fargo, ND 58105).
(June 15 and 17)-"Rheology" Seminar. Sponsored by Brookfield Engineering Laboratories, Inc. Chicago, IL on the 15th, and Lansing, MI on the 17th. (Barbara Cunningham, Marketing Dept., Brookfield Engineering Laboratories, 240 Cushing St., Stoughton, MA 02072).
(June 21-22)-"Thin Film Coatings: Topics in Coating and Drying Technology." Short course sponsored by the University of Minnesota, Minneapolis, MN. (Jackie O'Brien, Dept. of Chemical Engineering \& Materials Science, University of Minnesota, 421 Washington Ave. SE, Minneapolis, MN 55455).
(June 21-23)—International Colouristic Symposium. Sponsored by the Colouristic Section of the Hungarian Chemical Society, Balatonszéplak (by Lake Balaton), Hungary. (Hungarian Chemical Society, Colouristic Symposium Organizing Committee, H-1027 Budapest Fo u. 68, Hungary).
(June 22-24)-"Predictive Technology" Symposium and Exhibition. Sponsored by American Defense Preparedness Association Twin Towers Hotel and Convention Center, Orlando, FL. (Tracy Stuckrath, American Defense Preparedness Association, Two Colonial Place, 2101 Wilson Blvd., Ste. 400, Arlington, VA 22201-3061).
(June 23-25)-Tecnopinturas '93. First Argentine Congress on the Technology of Coatings, Resins, Varnishes, Printing Inks, and Related Products. Sponsored by the Argentine Chemical Association. Buenos Aires, Argentina. (TAL Organizaciones y Servicios, A.J. de Sucre 1552, 8vo. Piso "A" (1428) Buenos Aires, Argentina).
(June 23-25)-"Coating Process Fundamentals." Short course sponsored by University of Minnesota, Minneapolis, MN. (Jackie O'Brien, Dept. of Chemical Engineering \& Materials Science, University of Minnesota, 421 Washington Ave. SE, Minneapolis, MN 55455).
(June 27-July 2)—ORGABROM '93. 2nd International Symposium. Sponsored by the Dead Sea Bromine Group in cooperation with the Casali Institute of Applied Chemistry. The Hebrew University of Jerusalem. (Secretariat, P.O. Box 50006, Tel Aviv 61500, Israel).
(July 11-14)-Sixth International Symposium on "Polymer Analysis and Characterization." Crete, Greece. (Judith A. Sjoberg, Professional Association Management, 815 Don Gaspar, Santa Fe, NM 87501).
(July 12-16)-19th International Conference in Organic Coatings Science and Technology. Ledra Marriott Hotel, Athens, Greece. (Angelos Patsis, Institute of Materials Science, State University of New York at New Paltz, New Paltz, NY 12561).
(July 25-29)-Conference on "Lead in Paint, Soil, and Dust." Cosponsored by ASTM Committees D-22, E-6, D-1, and D-18. University of Colorado, Boulder, CO. (ASTM, 1916 Race St., Philadelphia, PA 19103).
(July 28-30)-"Basic Coatings for Sales and Marketing Personnel." Short course sponsored by University of Missouri-Rolla (UMR). St. Louis, MO. (Cynthia N. Campbell, UMR Coatings Institute, Dept. of Chemistry, 142 Schrenk Hall, Rolla, MO 65401).
(Aug. 2-6)-Gordon Research Conference on "Chemistry and Physics of Coatings and Films." Colby-Sawyer College, New London, NH. (A.K. St. Clair, Head, Advanced Aircraft Program Office, Materials Div., NASA, Langley Research Center, Hampton, VA 236810001).
(Aug. 3-5)-"Fundamentals of Corrosion and Its Control." Course sponsored by LaQue Center for Corrosion Technology. Blockade Runner Hotel, Wrightsville Beach, NC. (LaQue Center for Corrosion Technology, Inc., P.O. Box 656, Wrightsville Beach, NC 28480).
(Aug. 9-12)-"Coatings Science of Powder Coatings." Short course sponsored by The University of Southern Mississippi (USM), Hattiesburg, MS. (Debbie Ballard or Shelby Thames, USM, Dept. of Polymer Science, Southern Station, P.O. Box 10076, Hattiesburg, MS 39406-0076).
(Sept. 5-10)-3rd International Congress on Polymer Photochemistry. Sponsored by Manchester Metropolitan University and University of Milan. Genova, Italy. (Emmezeta SRL, Via C. Farini, 70, I-20159, Milano, Italy).
(Sept. 8-10)-3rd International Paint Congress and Exhibition on Paint Industry Suppliers. Sponsored by the Brazilian Association of

Paint Manufacturers. Palácio de Convenções do Anhembi, São Paulo, Brazil. (Especifica S/C Ltda, Rua Augusta, 2516-2nd, Cj 22, 01412100 São Paulo SP, Brazil).
(Sept. 8-11)-Conference on "Innovative Responses from an Industry under Siege." Sponsored by the Skandinaviska Lackteknikers Forbund (SLF) Congress. Copenhagen, Denmark. (Michael Symes, President, SLF, Strandboulevarden 38, DK-2100, Copenhagen, Denmark).
(Sept. 12-14)-"Back to Basics." 81st Annual Convention of the Canadian Paint and Coatings Association (CPCA). Queen's Landing Inn, Niagara-on-the-Lake, Ontario, Canada. (CPCA, 9900 Cavendish Blvd., Ste. 103, St.-Laurent, Quebec H4M 2V2, Canada).
(Sept. 13-17)-"Basic Composition of Coatings." Short course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (Cynthia N. Campbell, UMR Coatings Institute, Dept. of Chemistry, 142 Schrenk Hall, Rolla, MO 65401-0249).
(Sept. 14-17)-Eurocoat ' 93 and XXth Congress of the French Association of Technicians of Paints, Varnishes, Printing Inks, and Adhesives (AFTPV). Acropolis Palace, Nice, France. (Secretariat UATCM, c/o AFTPV, 5 rue Etex, F. 75018 Paris, France).
(Sept. 15)-"Developments in the Field of Water Paints for the Surface Improvement of Materials." Symposium sponsored by the Association de Recherches Scientifiques Paul Neumann in conjunction with the Association of Technicians of Paints, Varnishes, Printing Inks, and Adhesives. Nice, France. (Mme Pertuisot, Tour Roussel Hoechst, 92080, Paris/La Defense, France).
(Sept. 20-24)-"Introduction to Paint Formulation." Short course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (Cynthia N. Campbell, UMR Coatings Institute, Dept. of Chemistry, 142 Schrenk Hall, Rolla, MO 65401-0249).
(Sept. 23)-Detroit Colour Council Meeting. Michigan State Management Education Center, Troy, MI. (James Hall, General Motors Corp., 30009 Van Dyke, Warren, MI 48090).
(Sept. 29-30)-"Advanced Radiation (UV/EB) Curing Marketing/ Technology." Seminar sponsored by Armbruster Associaties, Inc. Marriott Hotel, Newark Airport, Newark, NJ. (David Armbruster, Ambruster Associates, Inc., 43 Stockton Rd., Summit, NJ 07901).
(Sept. 29-Oct. 1)-"Accelerated and Natural Weathering Techniques for Coatings and Polymers." Short course sponsored by Kent State University (KSU), Kent, OH. (Carl J. Knauss, Director, Cooperative \& Continuing Education-Chemistry, KSU, P.O. Box 5190, Kent, OH 44242-0001).
(Oct. 3-5)-"Crosslinked Polymers: Chemistry, Properties and Applications"; "Fundamentals of Adhesion: Theory, Practice and Applications"; and "Polymer Blends and Alloys: Phase Behavior, Characterization, Morphology, Alloying Technology." Conferences sponsored by State University of New York (SUNY) at New Paltz. New Orleans, LA. (Angelos Patsis, Institute of Materials Science, SUNY, New Paltz, NY 12561).
(Oct. 4-6)-"Polyethylene '93." Conference sponsored by Maack Business Services, Swissôtel Zürich, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804, AU/ZH, Switzerland).
(Oct. 5-8)-"Introduction to Coatings Technology." Short course sponsored by Kent State University (KSU), Kent, OH. (Carl J. Knauss, Director, Cooperative \& Continuing Education-Chemistry, KSU, P.O. Box 5190, Kent, OH 44242-0001).
(Oct. 6-8)-"Organic Thin Films for Photonic Applications." Topical meeting sponsored by American Chemical Society and Opitcal Society of America. Royal York Hotel, Toronto, Ont., Canada. (Optical Society of America, Meetings Dept., 2010 Massachusetts Ave., NW, Washington, D.C. 20036-1023).
(Oct. 10-12)-"Advances in Polymer Colloids/Emulsion Polymers"; and "Principles of Polymer Degradation and Stabilization." Conferences sponsored by State University of New York (SUNY) at New Paltz. Orlando, FL. (Angelos Patsis, Institute of Materials Science, SUNY, New Paltz, NY 12561).
(Oct. 12-14)-"Industrial Painting: Application Methods." Short course sponsored by Kent State University, Kent, OH. (Carl J. Knauss, Director, Cooperative \& Continuing Education-Chemistry, KSU, P.O. Box 5190, Kent, OH 44242-0001).
(Oct. 19-20) -"Aspects of Photoinitiation." Conference sponsored by Paint Research Association (PRA). Anugraha Conference Centre, Egham, England. (Richard Kennedy, Radcure Services Dept., PRA, 8 Waldegrave Rd., Teddington, Middlesex, TW11 8LD, England).
(Oct. 25-26)-"Polymer Coatings." Mini-course cosponsored by The University of Southern Mississippi (USM) and University of Missouri-Rolla. Atlanta Marriott Marquis, Atlanta, GA. (Shelby Thames or Debbie Ballard, USM, Dept. of Polymer Science, P.O. Box 10076, Hattiesburg, MS 39406-0076).
(Oct. 25-27)-106th National Meeting of the National Paint and Coatings Association (NPCA). Hilton Hotel and Towers, Atlanta, GA. (NPCA, 1500 Rhode Island Ave., NW, Washington, D.C. 20005).
(Oct. 25-27)-"Polypropylene '93." Conference sponsored by Maack Business Services, Swissôtel Zürich, Switzerland. (Maack

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Any exhibiting company in the 1993 Paint Industries' Show, sponsored by the Federation of Societies for Coatings Technology (FSCT), on October 27-29, at the Georgia World Congress Center, in Atlanta, GA, may take advantage of this offer.

This pocket-size publication is distributed at the show, and is the principal source of information during the convention.

Included in the Program Book are: a list of Paint Show exhibitors, including booth numbers; a brief description of each exhibit; floor plan of Show; and exhibitor listing by product/service classification.

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Business Services, Moosacherstrasse 14, CH-8804, AU/ZH, Switzerland).
(Oct. 25-29)-"Image Analysis and Measurement in Scanning Electron Microscopy"; "Scanning Electron Microscopy and X-Ray Microanalysis for Materials Science. An Introductory Course"; and "Scanning Electron Microscopy for Polymeric Science. An Introductory Course." Conferences sponsored by State University of New York (SUNY) at New Paltz. Nevele Resort Hotel, Ellenville, NY. (Angelos Patsis, Institute of Materials Science, SUNY, New Paltz, NY 12561).
(Nov. 1-4)-12th Biennial Symposium on Managing Corrosion with Plastics. Sponsored by National Association of Corrosion Engineers (NACE), American Society for Testing Materials, Materials Technology Institute of the Chemical Process Industries, Inc., SPI Composites Institute, and Technical Association of the Pulp and Paper Industry. Baltimore, MD. (NACE, P.O. Box 218340, Houston, TX 77218-8340).
(Nov. 2-4)-"Fundamentals of Corrosion and Its Control." Training course sponsored by LaQue Center for Corrosion Technology. Holiday Inn, Wrightsville Beach, NC. (LaQue Center for Corrosion Technology, Inc., P.O. Box 656, Wrightsville Beach, NC 28480).
(Nov. 3-5)-"Polymer Surface Modification: Relevance to Adhesion." Symposium sponsored by IBM. Las Vegas, NV. (K.L. Mittal, Organizer, Skill Dynamics, an IBM Co., 500 Columbus Ave., Thornwood, NY 10594).
(Nov. 8-10)-"Polymerization/Deposition: Fundamental and Applied Aspects." Symposium sponsored by IBM. Las Vegas, NV. (K.L. Mittal, Organizer, Skill Dynamics, an IBM Co., 500 Columbus Ave., Thornwood, NY 10594).
(Nov. 9-11)-9th Annual Advanced Composites Conference and Exposition and 3rd Annual Advanced Coatings Technology Conference and Exposition. Sponsored by The Engineering Society. Hyatt Regency, Dearborn, MI. (Clare B. Ellis, The Engineering Society, 2350 Green Rd., Ste. 190, Ann Arbor, MI 48105).
(Nov. 10-12)-Electroless Nickel '93. Conference sponsored by Products Finishing. Orlando Airport Marriott, Orlando, FL. (Cindy Goodridge, Gardner Management Services, 6600 Clough Pike, Cincinnati, OH 45244).
(Nov. 15-16)-"Fundamentals of HPLC." Short course sponsored by Kent State University (KSU), Kent, OH. (Carl J. Knauss, Director, Cooperative \& Continuing Education-Chemistry, KSU, P.O. Box 5190, Kent, OH 44242-0001).
(Nov. 15-17)-"Powder Coatings." Paint Research Association's (PRA) 13th International Conference. Brussels. (Conference Secretary, PRA, 8 Waldegrave Rd., Teddington, Middlesex TW11 8LD, United Kingdom).
(Nov. 19-21) - 46th Annual National Decorating Products Show. Sponsored by National Decorating Products Association (NDPA). Indiana Convention Center, Indianapolis, IN. (Ruth Wilms, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).
(Nov. 23-25)-Conchem '93. International Exhibition and Conference sponsored by Reed Exhibition Companies. KKA Congress and Exhibition Centre, Karlsruhe, Germany. (Diane R. Tiberio, Reed Exhibition Companies, 999 Summer St., P.O. Box 3833, Stamford, CT 06905-0833).
(Dec. 6-8)-"Styrenics '93." Conference sponsored by Maack Business Services, Swissôtel Zürich, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804 AU/ZH, Switzerland).

\section*{1994}
(Feb. 11-13)-37th Annual Southern Decorating Products Show. Sponsored by National Decorating Products Association (NDPA). Georgia International Convention \& Trade Center, College Park (Atlanta), GA. (Ruth Wilms, NPDA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).
(Mar. 5-6)-38th Annual Canadian Decorating Products Show. Sponsored by National Decorating Products Assoication (NDPA). International Centre, Toronto, Ontario, Canada. (Ruth Wilms, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).
(Mar. 13-18)-"High Solids Coatings" Symposium. Sponored by American Chemical Society Division of Polymeric Materials: Science and Engineering. San Diego, CA. (Frank N. Jones, Coatings Research Institute, Eastern Michigan University, 430 W. Forest St., Ypsilanti, MI 48197 or George R. Pilcher, Akzo Coatings, Inc., P.O. Box 147, Columbus, OH 43216-0147).
(Mar. 14-18)-"Recycle '94." Forum and Exposition. Sponsored by Maack Business Services. Congress Centre, Davos, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804 AU/ZH, Switzerland).
(Mar. 23-25)—Electrocoat '94. Sponsored by Products Finishing Magazine. Hyatt Orlando, Orlando, FL. (Cindy Goodridge, Gardner Management Services, 6600 Clough Pike, Cincinnati, OH 45244).
(Apr. 14-16)—Paint Show '94. Sponsored by Japan Paint Manufacturers Association, Japan Paint Commerce Association, Japan Painting Contractors Association, and Nippon Toryo (Paint) Club. Nippon Convention Center, Tokyo, Japan. (Paint Show '94 Executive Committee, Overseas Operation,c/o Space Media Japan Co., Ltd., Asahi Bldg. 4F, 2-31-3 Taito, Taito-ku, Tokyo 110 Japan).
(Apr. 17-19)-"Volatile Organic Compounds (VOCs) in the Environment" Symposium. Sponsored by ASTM Committee E-47. Montreal, Que., Canada. (Wuncheng Wang, Symposium Chairman, U.S. Geological Survey, WRD, P.O. Box 1230, lowa City, IA 52244).
(Apr. 23-24)—Eastern Decorating Products Show. Sponsored by National Decorating Products Association (NDPA). Garden State Convention \& Exhibit Center, Somerset, NJ. (Ruth Wilms, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).
(May 1-5)-RadTech '94 North America. Conference sponsored by RadTech International North America. Walt Disney World Dolphin Hotel, Orlando, FL. (Chris Dionne, RadTech International North America, 60 Revere Dr., Suite 500, Northbrook, IL 60062).
(June 5-9) -XXIInd FATIPEC Congress and Exhibition. Budapest Convention Centre, Budapest, Hungary.
(July 11-15)—MACROAKRON '94 International Symposium. Sponsored by the International Union of Pure and Applied Chemistry. University of Akron, Akron, OH. (Dr. Joseph P. Kennedy, Chairman of the Organizing Committee, or Cathy Manus-Gray, Symposium Coordinator, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 44325-0604).
(Nov. 6-10)—International Adhesion Symposium. Sponsored by The Adhesion Society of Japan. Tokyo, Japan. (Hiroshi Mizumachi, Professor, Chemistry of Polymeric Materials, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ko, Tokyo 113, Japan).

\section*{Advertisers Index}

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NOTE: The Advertisers' index is published for the convenience of our readers and as an additional service to our advertisers. The publisher assumes no liability for errors or omissions.

\section*{'SCumbug' from SCillman}

Saul Spindel came up with this ad found in, of all places, the Florida Network on Disabilities (must be a story there):

Wanted: Parent!-Job description: On call 24 hours, no pay, no days off, must be willing to travel, must be warm, gentle and loving at all times.

Must possess knowledge of mechanics, cooking, education, medicine, pets, weather, history, and all related subjects. Must have answers to all questions.

I promised you more from Dr. Bob Brady's storage of nonsense. Sometimes I keep my promises, like now:

\section*{Ultra Modern Math's Metric Units}


Fax expert, Frank Borrelle, favored me with "A Guide to Safe Fax" he found in the Birmingham (England) Paint, Varnish and Lacquer Club Newsletter. At my age, I guess the advice could be somewhat superfluous but it does answer questions like "Do I have to be married to have safe fax?" and "How old do you think someone should be before they can have fax?" A valuable source of information for those interested in the communication, field!

Old timers, please note the nostalgic name of the organization!

Some time ago, reliable correspondent Dave Platt contributed these observations. The time has come to share them:
-Previous appointment: A device used to get rid of a pain in the neck.
—Why are they called the "Golden Years?" Because nobody can afford them.
-Hypochondriac: A person who loves sham pain.
-If your sick of backseat drivers, there's one solu-tion-get a job driving a hearse.
-A government that robs Peter to pay Paut can always count on the support of Paul.
-Even today two can live as cheaply as one. But today, the two must both be working.
-If Mother Nature doesn't make mistakes, why do cakes, pies, ice cream, and candy taste better than broccoli, kale, and spinach?
-Whoever thought up, "It's only a game" probably just lost one.
-A perfect example of minority rule is having a baby in the house.
-Teaching pre-school has been compared to trying to keep 30 corks under water at the same time.
-Trying to teach his small son table manners, the father reprimanded, "Junior, one more bite like that and you'll be leaving the dinner table."
"One more bite like that," answered the youngster, "and l'll be through."
-Inflation: A condition that allows you to live in a more expensive neighborhood without ever moving.
-The man noticed that he had no spoon for his coffee. "Waiter," he said, "this coffee is too hot to stir with my finger."

The waiter soon returned with another cup of coffee. "Here, try this one. It's not as hot."
-Teenage driver to mechanic: "Can you fix this fender so my dad will never know I bent it?"

Mechanic: "I doubt it, sonny. But I can fix it so you can ask him how he bent it."
-A man walked into a psychiatrist's office with a chicken on his head.
"You need help!" declared the doctor.
"You bet I do," the chicken replied. Get this guy out from under me."
-The Lion

Dear Internal Revenue Service: I dislike everything about your service. Therefore, this is to inform you that I wish to cancel all further services.

By the time the meek inherit the earth, I often wonder what it will be worth.
-1978 Farmer's Almanac```


[^0]:    * Prices are subject to change.

[^1]:    *Polymers Department. Warren. M1 48090-9055.
    *Chemistry Dept.. Rochester. MI 48309.

