1995 Mattiello Memorial Lecture
"Toward Solventless Liquid Coatings"
by Frank N. Jones

First-Place Roon Paper
"Latex Blends: An Approach
to Zero VOC Coatings"

Second-Place Roon Paper
"Film Formation Mechanism
of Two-Component Waterborne
Polyurethane Coatings"

SPECIAL ISSUE
Low VOC Coatings

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GENERAL

The JOURNAL OF COATINGS TECHNOLOGY is published monthly by the Federation of Societies for Coatings Technology for its membership of approximately 7,000 in 26 Constituent Societies in the United States, Canada, Great Britain, and Mexico. The JOURNAL is devoted to the advancement of knowledge in the science and technology of surface coatings, the materials comprising such coatings, and their use and performance.

The Editors invite submission of original research papers, review papers, and papers under the special headings *Open Forum* and *Back to Basics*, and *Letters to the Editor*. All manuscripts will be assumed to be previously unpublished writing of the authors, not under consideration for publication elsewhere. When review papers contain tables or graphs from copyrighted articles, the authors will be required to obtain permission for use from the copyright holders. When the organization with which the authors are affiliated requires clearance of publications, authors are expected to obtain such clearance before submission of the manuscript. Papers presented to associations other than the Federation must be released by written communication before they can be considered for publication in the JOURNAL OF COATINGS TECHNOLOGY. Authors are obligated to reveal any exceptions to these conditions at the time a manuscript is submitted.

The JOURNAL OF COATINGS TECHNOLOGY has first right to the publication of papers presented at the International Coatings Technology Conference of the Federation and at local regional meetings or symposia of the Constituent Societies.

Papers in which proprietary products or processes are promoted for commercial purposes are specifically nonacceptable for publication.

SUBMISSION OF MANUSCRIPTS...

...for the Journal

Four complete copies should be sent to the Editor, JOURNAL OF COATINGS TECHNOLOGY, 492 Norristown Rd., Blue Bell, PA 19422. The cover letter should address copyright, clearance, and release issues discussed above and should specify paper category: *Original Research, Reviews, Open Forum*, or *Back to Basics*.

Letters to the Editor: The JOURNAL will consider for publication all correspondence relevant to the coatings industry and to the contents of the JOURNAL. When a letter concerns an article appearing in the JOURNAL, the original author is usually given an opportunity to reply.

...by Constituent Societies For International Coatings Technology Conference Presentation

Ten complete copies of the manuscript are required for committee review. The set of copies should be addressed to Mike Bell, Director of Educational Services, FSCT, 492 Norristown Rd., Blue Bell, PA 19422.

...for Roon Foundation Award Competition

Ten complete copies of the manuscript are required, and should be submitted to Mike Bell at the address previously listed.(For complete details, see "Roon Awards" section of the JOURNAL in the January 1995 issue.)

MANUSCRIPT PREPARATION

In general, authors are advised to use the "Handbook for Authors" published by the American Chemical Society as a guide to the preparation of manuscripts (ACS, 1155 Sixteenth St., Washington, D.C. 20036). Another excellent reference work is "How to Write and Publish a Scientific Paper," by Robert A. Day (ISI Press, 3501 Market St., University City Science Center, Philadelphia, PA 19104).

Authors are encouraged to consider submissions in several categories and to prepare their manuscripts accordingly. The categories are:

Original Research Papers: The main technical content of the JOURNAL OF COATINGS TECHNOLOGY will continue to be original research papers. Editors support the trend in scientific writing to a direct, less formal style that permits limited use of personal pronouns to avoid repititious or awkward use of passive voice.

Review Papers: Papers that organize and compare data from numerous sources to provide new insights and unified concepts are solicted. Reviews that show how advances from other fields can beneficially be applied to coatings are also desired. Reviews that consist mainly of computer searches with little attempt to integrate or critically evaluate are not solicited.

Open Forum: Topics for this category may be nontechnical in nature, dealing with any aspect of the coatings industry. The subject may be approached informally. Editors encourage submission of manuscripts that constructively address industry problems and their solutions.

Back to Basics: Papers that provide useful guides to Federation members in carrying out their work are solicited. Topics in this category are technical but focus on the "how to" of coatings technology. Useful calculations for coatings formulation and procedures that make a paint test more reproducible are examples of suitable topics. Process and production topics, i.e., paint manufacture, will also be reviewed in the *Back to Basics* category.

If a submitted paper consists of the text of a presentation made previously to a monthly or special meeting of a Society for Coatings Technology, or to another technical group, the name of the organization and the date of the presentation should be given. If someone other than the author of the paper made the presentation, this information, too, should be noted. Papers originally composed for oral presentation will have to be revised or rewritten by the author to conform to the style described in this guide.

Manuscripts should be typed with double spacing on one side of 8 1/2 x 11 inch (22 x 28 cm) paper, with at least one-inch (2.5 cm) margins on all four sides. All paragraphs should be indented five spaces, and all pages should be numbered at the top center, or upper right corner.

Title

The title should be as brief and informative as possible. Selection of titles that are key word-indexable is a helpful and recommended practice.

Authors' Biographies and Photographs

Give complete names, company or institutional affiliations, and brief biographical sketches of all authors. If available, submit a 5 x 7 inch (13 x 18 cm) black-and-white photograph with glossy or smooth high sheen surface, for each author. See later section on photographs for further details.

Abstracts

A 75-100 word abstract must be part of the manuscript, and should be a concise description of the key findings or teachings of the work described in the paper. The abstract should not repeat the title or include reference numbers, nor should it duplicate the Conclusion or Summary.

Text

Main headings and sub-headings should be used to improve readability, and to break up typographical monotony. The text should *not* be presented as an alphanumeric outline.

The main headings usually should be INTRODUCTION, EXPERIMENTAL, RESULTS AND DISCUSSION, and SUMMARY or CONCLUSIONS. Sub-headings will be specific to the subject.

Only as much review as is necessary should be given to provide an introduction to the subject; the main burden for extensive background should be placed on the list of references.

Standard scientific and technical terminology should be used to convey clear and unambiguous meaning, but the use of technical jargon or slang should be avoided. Authors should bear in mind that the JOURNAL has an international audience, for many of whom English is a second, not native, language. Use of regional idioms or colloquialisms should be avoided. The use of obscure abbreviations is also discouraged. When appropriate, abbreviations should be made in parenthesis immediately following first mention of the term in the text, and then used alone whenever necessary.

Recent issues of the JOURNAL should be consulted for desired style and technical level.

Metric System

Metric system units should be used wherever applicable with the equivalent English units shown afterwords in parentheses. The ASTM Metric Practice Guide, E 380-72 (American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103) is a convenient reference.

Tables, Graphs, and Drawings

Tables, rather than descriptive text, should be used only when they are genuinely helpful. They should be proportioned in accordance with the height and width limitations of the JOURNAL'S pages. Each table should be typed on a separate sheet, rather than included in the text, and appended to the manuscript. Each table should be numbered and have a descriptive caption. Tables should be referenced in the text (e.g., "See *Table* 1").

In numerical data in tables, numbers less than one should have a zero before the decimal point.

Graphs should be on good quality white or nonphotographic blue-lined $8^{1}/_{2}$ x 11 inch paper. Each graph should be drawn on a separate sheet, numbered, and the captions listed on a *copy* of the original graph. Graph captions and legends should also be typed on a separate sheet from original for typesetting.

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Photographs

All photographs should be sharp, clear, black-and-white prints no larger than 8 x 10 inches in size. Photos should be clearly labeled on the reverse side, taking care not to mar the image.

Color prints and slides are unacceptable.

When illustrations are secured from an outside source, the source must be identified and the Editor assured that permission to reprint has been granted.

Nomenclature

Whenever possible, generic names should be used in preference to trade names. When trade names must be used to avoid ambiguity, and the name is a registered trademark, the symbol R, in a circle or parentheses, should be given immediately following, and the manufacturer listed as a footnote. In general, trade names should be used only in footnotes or in an appendix, rather than in the text.

If special nomenclature is used, include a nomenclature table giving definitions and dimensions for all terms.

Nomenclature of chemical compounds should conform to the style of *Chemical Abstracts* and the IUPAC rules. For oligomeric or polymeric materials, characteristics such as molecular weight, polydispersity, functional group content, etc. should be provided.

Equations

Equations must be typed, or written clearly, with equations numbered sequentially in parentheses to the right. If Greek letters are used, write out their names in the manuscript margin at the first point of use. Place superscripts^{a} and subscripts$_{b}$ accurately. Avoid the use of superscripts in a manner that can lead to their interpretation as exponents.

Summary

The paper should be concluded with a summary which is intelligible without reference to the main text. The summary may be more complete than the abstract, listing conclusions drawn from the text. A well written summary can serve to inspire the busy reader to turn back to the paper, to read it thoroughly.

Acknowledgment

If used, it should follow the summary.

References

These should be listed in the numerical order in which they are cited in the text, and should be placed at the end of the manuscript. Names of authors may or may not be shown in the text with reference numbers. If possible, include titles of articles referenced in the literature. The following are examples of acceptable reference citations for periodicals, [1,2,3] books, [4] and patents.[5]

(1) Pascal, R.H. and Reig, F.L., "Pigment Colors and Surfactant Selection," *Official* DIGEST, 36, No. 475 (Part 1), 839 (1964).
(2) Davidson, H.R., "Use and Misuse of Computers in Color Control," JOURNAL OF COATINGS TECHNOLOGY, 54, No. 691, 55 (1982).
(3) Stephen, H.G., "Hydrogen Bonding—Key to Dispersion?," *J. Oil & Colour Chemists' Assoc.*, 65, No. 5, 191 (1982).
(4) Patton, T. (Ed.), *Pigment Handbook*, Vol. 1, John Wiley & Sons, Inc., New York, 1973.
(5) Henderson, W.A. Jr. and Singh, B. (to American Cyanamid Co.), U.S. Patent 4,361,518 (Nov. 30, 1982).

OTHER INFORMATION

Galley proofs will be sent to the author for checking about six weeks prior to publication.

Offprints may be purchased in quantities of 100 or more. Authors will receive price quotations. Each author will receive a complimentary copy of the JOURNAL issue in which his or her paper was published.

* * * *

COMMENT

Looking into the Crystal Ball . . .

Who will win the 1996 Presidential race? How high will the stock markets rise? What team will triumph at the Super Bowl? How many inches of snow will fall in Philadelphia this year?

Fortunes can rise and fall with the accurate forecasting of these and other future events and trends.

Luckily, you don't have to be a Las Vegas oddsmaker to predict some of the directions the coatings industry will take in 1996. Increased pressure in the environmental regulations arena will continue to drive research and development efforts in the direction of more environmentally friendly products. Alternate approaches such as higher-solids, powder coatings and solventless emulsion technology will play a heavy role in the future. At the same time, coatings technologists must answer the demands for improved protective and decorative properties with whatever technology is chosen.

To help readers gain a fuller understanding of recent developments and ongoing research in this area, the JOURNAL OF COATINGS TECHNOLOGY offers this special issue on "Low VOC Coatings." Featured are six excellent articles which focus on different aspects of developing low to zero VOC coatings. Leading the issue is the 1995 Mattiello Lecture which was presented at the FSCT Annual Meeting & Paint Industries' Show in St. Louis. Mattiello Lecturer Dr. Frank N. Jones offers a progress report on a project that attempts to answer the question, "Is it feasible to entirely eliminate organic solvents from liquid decorative coatings formulations?"

Also featured are two award-winning papers from the 1995 Roon Awards Competition. First-place winners Dr. Mitchell A. Winnik and Jianrong Feng present a strategy for zero VOC coatings which involves blends of hard and soft latex particles. In their work on "Film Formation Mechanism of Two-Component Waterborne Poyurethane Coatings," second-place winners Charles R. Hegedus, Andrew G. Gilicinski, and Robert J. Haney explore the film formation mechanism of a coating system which has the potential to provide properties comparable to that of solvent-borne counterparts, with the benefit of low VOC levels.

All six papers presented in this issue provide insight into ongoing technical work which may assist in attaining lower VOC concentrations. Through work such as this, readers may take a step closer towards a future which attains the reduced VOC goals mandated by government regulations.

Now, as for predicting the answers to other questions regarding the future, the only consensus among prognosticators on a recent New Year's television special was that the Super Bowl would be won by the San Francisco 49ers. So much for their crystal balls . . .

Patricia D. Viola
Editor

Technical Abstracts

Toward Solventless Liquid Coatings—F.N. Jones

Results of an exploratory study of solventless (100% reactive) liquid polyester/melamine resin and polyester/polyisocyanate coatings are described. An investigation of how the chemical structure and the molecular shape of oligomeric polyester resins affects their viscosities found that slender molecules have very low viscosities. "Linear" oligoester diols composed entirely of diacids and diols of the structures HOOC$(CH_2)_n$COOH and HO$(CH_2)_m$OH with M_n of 700 or below have viscosities below 800 mPa·s at 25°C, low enough for potential use in solventless coatings. Physical properties of oligoester diols were studied, and quantitative relationships among viscosity (h), temperature (T), molar mass (M_n), glass transition temperature (T_g), and melting point (T_m) were demonstrated.

The next step was to formulate solventless coatings with linear oligoester diols. An arbitrary goal was to keep viscosity below 800 mPa·s at 25°C without adding organic solvents. A two-package solventless coating made from a "linear" oligoester diol and a low viscosity polyisocyanate crosslinker had a viscosity of 560 mPa·s at 25°C and excellent film properties; its VOC was 8 g/L. Polyester/melamine resin coatings with similar viscosities can be formulated, but their coating films tend to be soft and to have poor adhesion to metal. Film properties can be improved by adding hardeners to the formulations, but viscosity increases.

Viscosity of these solventless formulations can be further reduced by adding modest amounts of water (3 to 20 wt%). This expedient makes it possible to formulate one-package "water-thinnable solventless" coatings with reasonably good film properties from combinations of linear oligoester diols, hardeners, and melamine resins. Two-package coatings containing polyisocyanate crosslinkers can also be thinned with water with little effect on pot life.

Hacia Recubrimientos Líquidos Sin Solventes—F.N. Jones

Son descritos los resultados de un estudio exploratorio de resina de poliéster/melamina líquida (100% reactiva) sin solvente y de recubrimientos de poliéster/poliisocianato. Una investigación de como la estructura química y el contorno molecular de resinas de poliéster oligomérico afectan sus viscosidades y encuentran que las moléculas de poco diámetro tienen may bajas viscosidades. Los dioles de oligoester "lineales" compuestos totalmente de diácidos y dioles de las estructuras HOOC$(CH_2)_n$ COOH y HO$(CH_2)_m$ OH con Mn de 700 o por debajo tienen viscosidades menores a 800 m Pa·s a 25°C, bajos para el uso potencial en recubrimientos sin solventes. Fueron estudiadas las propiedades físicas de dioles de oligoester, también fueron demonstradas la viscosidad cuantitativa de mezclado (n) la temperatura (T), la masa molar (Mn), la temperatura de transición vítrea (T_g) y el punto de fusión (T_m).

El siguiente paso fue formular recubrimientos sin solvente con dioles de oligoester "ineales. Una meta arbitrario fue mantener la viscosidad por debajo de los 800 mPa·s a 25°C sin adicionar solventes orgánicos. Un recubrimiento sin solvente de dos paquetes fue hecho a partir de un diol de oligoester lineal y entrecruzador de poliisocianto de baja viscosidad tuvo una viscosidad de 560 mPa·s a 25°C y excelentes propiedades de película y su COV fue de 89/L.

Recubrimiento de resina de poliester/melamina con viscosidades similares pueden ser formuladas, pero sus películas de recubrimiento tienen a ser suaves y a tener una pobre adhesión sobre el metal. Las propiedades de la película pueden ser mejoradas por adición de endurecedores para las formulaciones, pero se incremento la viscosidad.

La viscosidad de estas formulaciones sin solvente pueden ser reducidas por el adicionamiento de modestas cantidades de agua (3 a 20% en peso). Este expediente hace esto posible para formular un paquete de recubrimientos "sin solvente adelgazable con auga" con propiedades de película razonablemente buenas a partir de combinaciones de dioles oligoester lineales, endurecedores y resinas de melamina.

Recubrimientos de dos paquetes conteniendo entrecruzadores de poliisocianato pueden también ser adelgazables con agua teniendo un pequeño efecto sobre el tiempo de uso.

Latex Blends: An Approach to Zero VOC Coatings—M.A. Winnik and J.Feng

An attractive strategy for zero VOC coatings involves blends of hard and soft latex particles. A dispersion of a latex with a low minimum film-forming temperature will form a transparent film upon evaporation, even when blended with a substantial amount of high T_g latex. The low T_g latex deforms to fill space as the dispersion dries, and the high T_g component imparts good block resistance and mechanical properties to the final film. Transparency requires that the hard latex be sufficiently small and well dispersed in the final film. In addition, the two components must have similar refractive indices. Two of our most surprising observations are that dispersions of soft latex particles dry more slowly than those of high T_g latex, and that mixtures of the two particles dry even more slowly. Consideration of these results leads to a new model for the drying mechanism of latex dispersions that takes into account the propagating drying front. Dynamic mechanical analysis indicates that the hard particles in blends improve significantly the mechanical properties for the films.

Mezclas de Látex Una Aproximación a Recubrimientos sin COV's—M.A. Winnik y J. Feng

Una atractiva estrategia para recubrimientos sin COV's involucra mezclas de partícula de látex suaves y duras. Una dispersión de un látex con una baja temperatura de formación de película mínima formará una película transparente por encima de la evaporación, aún cuando se mezcle con una cantidad sustancial de látex de alta T_g.

El látex de baja T_g deforma para llenar espacio como los secadores de dispersión y el componente grande de T_g confiere buena resistencia de bloque y buenas propiedades mecánicas para la película final. La transparencia requiere que el látex duro sea suficientemente pequeño y bien dispersado en la película final. En consecuencia, los dos componentes deben tener índices de refracción similares. Dos de nuestras observaciones más sorprendentes son que las dispersiones de partículas de látex suave secan más lentamente que aquellas de látex de alta T_g y aquellas mezclas de dos partículas secan aún más lentamente. La consideración de estos resultados mos lleva a un nuevo modelo para el mecanismo de secado de las dispersiones de látex que toma de manera exacta el frente de propagación de secado. El análisis mecánico-dinámico indica que las partículas duras de mezclas mejoran significativamente las propiedades mecánicas para las películas.

Film Formation Mechanism of Two-Component Waterborne Polyurethane Coatings—C.R. Hegedus, A.G. Gilicinski, and R.J. Haney

Two-component (2K) waterborne polyurethane coatings are a new technology which has been demonstrated in a number of heavy duty applications. They exhibit performance properties equivalent to 2K solvent-borne polyurethanes, with the advantage of reduced volatile organic compounds (VOCs). Although the use of these systems has been demonstrated successfully, the details of their film formation mechanism have not been established. With a better understanding of these factors, the chemistry and formulation of these systems can be adapted to increase the latitude of their applications while minimizing the potential for defects caused by poor film formation.

The objective of this work was to propose and confirm the film formation mechanism of these systems. A dynamic series of interrelated events which occur during the process was identified using a number of analytical techniques to study two isocyanate/hydroxyl functional dispersion systems. The mechanism is presented in terms of an "event timeline" that chronicles the critical events which occur prior to and after application of the coating. These events include particle coalescence and isocyanate chemistry both in the admixed state and after coating application. Evaporation of volatiles after application leads to a critical solids concentration within the film such that particle to particle contact is made throughout the applied coating. This allows complete coalescence and favors the isocyanate-hydroxyl reaction. Critical time points for all of the events occurring during film formation were identified.

Film property development after application also was evaluated and these results were analyzed in terms of the proposed film formation mechanism. In completing this work, it has been demonstrated that all of the events responsible for film formation interact to generate the film chemistry and development of mechanical

Mecanismos de Formación de Película de Recubrimientos de Poliuretano Base Agua de Dos Componentes—C.R. Hegedus, A.G. Gilicinski y R.J. Haney

Recubrimientos de poliuretano base agua de dos componentes son una nueva tecnología que ha sido demostrada en muchas aplicaciones de trabajo continuo. Muestran propiedades de comportamiento equivalentes a poliuretanos a poliuretanos base solvente 2K, con la ventaja de reducir los compuestos orgánicos volátiles (COV's). Aunque el uso de estos sistemas ha sido demostrado exitosamente, los detalles de su mecanismo de formación de película no han sido establecidos. Con un mejor entendimiento de estos factores, la química y la formulación de estos sistemas pueden ser adoptados para incrementar la latitud de sus aplicaciones mientras minimizan el potencial por defectos causados por una pobre formación de película.

El objetivo de este trabajo fue proponer y confirmar el mecanismo de formación de película de estos sistemas. Series dinámicas de eventos interrelacionados la cuales ocurren durante el proceso fueron identificados usando número de técnicas analíticas para estudiar dos sistemas de dispersión funcional hidroxil/isocianato. El mecanismo es presentado en términos de un "tiempo lineal del evento" que registra los eventos críticos los cuales ocurren antes y después de la aplicación de el recubrimiento. Estos eventos incluyen tanto la coalescencia de partícula como química de isocianato en el estado de mezclado y después de la aplicación del recubrimiento. La evaporación de volátiles después de la aplicación lleva a una concentración crítica de sólidos dentro de la película en la cual ese contacto de partícula a partícula es hecho a lo largo de todo el recubrimiento aplicado. Esto permite completar la coalescencia y favorece la reacción hidroxilo/isocianato. Fueron identificados los puntos de tiempo crítico para todos los eventos que ocurren durante la formación de película.

Además fue evaluado el desarrollo de la película después de la aplicación y estos resultados fueron analizados en término de el mecanismo de formación de película propuesto.

En resumen, este trabajo ha presentado todos los factores que interactúan en la formación de la película y en la generación de la estructura química de la misma, así como el desarrollo de el mecanismo durante el proceso de formación de película.

Low and No-VOC Architectural Coatings Containing Ambient Curing Functional Groups—Z. Wang and S.F. Thames

With increasing environmental pressures and resulting government regulations, the coatings industry is undergoing a rapid shift in technology in an effort to reduce volatile organic content (VOC) levels. Thus, we have successfully synthesized novel, solvent free, ambient cure, vinyl acrylic, and acrylic latexes with dimethyl meta-isopropenyl benzyl isocyanate (TMI) as the curing agent. The emulsion polymers were formulated into solventless coatings and their properties contrasted to commercial latexes that require coalescing agents.

Recubrimientos Arquitectónicos de Bajo Contenido de COV's y Sin COV's Conteniendo Grupos Funcionales Curados al Ambiente—Z. Wang y S. Thames

Con el incremento de las presiones ambientales y el resultado de las regulaciones gubernamentales, la industria de recubrimientos esta sufriendo un cambio rápido en tecnolgía en un esfuerzo para reducir los niveles de compuestos orgánicos volátiles. De este modo exitosamente hemos sintetizado látex acrílico y vinil acrílico con dimetil meta-isopropenil bencil isocianato (TMI) como el agente de curado. Los polímeros de emulsión fueron formulados a partir de recubrimientos insolubles y sus propiedades contrastadas con respecto a látex comerciales que requieren agentes coalescentes.

FSCT Publishes *Coatings Encyclopedic Dictionary;* Over 6000 Terms Defined for Interfacing Industries

The Federation of Societies for Coatings Technology is pleased to announce the publication of its much anticipated *Coatings Encyclopedic Dictionary*. Edited by Stanley LeSota, formerly of Rohm and Haas Co. and a Past-President of the Philadelphia Society, the *Dictionary* defines the terms of the coatings industry and its interfacing technologies.

The *Coatings Encyclopedic Dictionary* is an updated and expanded edition of the FSCT's very successful *Paint/Coatings Dictionary*, first published in 1978. The current *Dictionary* reflects the many changes experienced by the paint and coatings industry over the past 17 years and is based, in part, on the definitions contained in the previous edition.

Over 6000 definitions, including state-of-technologies and regulatory terminology, are presented in the 392-page publication. Encyclopedic discussions supplement the definitions for many of the terms provided. These succinct paragraphs relay significant information that the reader should know about the term defined. In many cases, ASTM Test Method references are provided, further enhancing the usefulness of the *Dictionary*.

The philosophy governing the *Coatings Encyclopedic Dictionary* was one of achieving consensus within the industry. Consensus dictated the choice of terms and their definitions. Close liaison was maintained with groups such as the definitions subcommittee of the ASTM Committee D-1 on Paints and Related Coatings, the National Coil Coaters Association, the National Association of Corrosion Engineers, and the FSCT's Inter-Society Color Council Committee. Most definitions were reviewed and approved by knowledgeable people in the industry.

The broad scope of terms included reveals the usefulness of this volume to a wide audience, from chemists to managers, students to technicians. Those involved in allied fields, such as art, architecture, decorating, furniture finishing, metal preparation, as well as the manufacture of shellacs, printing inks, waxes and polishes, can benefit from the publication.

A unique feature is the classification of all terms into one or more of 80 categories (such as color, pigments, additives, methods of applications, etc.) This categorical listing of terms serves as a check list for key words which assist in the preparation of research papers and literature searches. In addition there is a considerable amount of cross-referencing that refers the reader to other similar significant terms that may help in the understanding of definitions.

Included in this publication are the definitions for over 400 color terms detailing color difference equations, optical phenomena, gloss, hiding, color instrumentation, etc. Pigment terms are classified by the Colour Index Number which follows each common name of the defined pigment.

Complementing the text, the Appendix of the *Dictionary* contains a listing of industry-related associations and organizations, standard abbreviations, metric conversions charts, SI Units, a temperature conversion chart and the Periodic Table of the Elements.

The *Coatings Encyclopedic Dictionary* is available in a casebound version (member cost—$105, list price—$135); or in soft cover (member cost—$80 and list price—$105).

For ordering information, contact Meryl Simon, FSCT, 492 Norristown Rd., Blue Bell, PA 19422. Phone (610) 940-0777; FAX: (610) 940-0292.

Coatings Encyclopedic Dictionary

SAMPLE DEFINITIONS:

checking that phenomenon manifested in paint films by slight breaks in the film that do not penetrate to the underlying surface.[42,56,154] (ASTM) See COLD-CHECKING, and CHECKING RESISTANCE.[56,72]

The break should be called a crack if the underlying surface is visible. Where precision is necessary in evaluating a paint film, checking may be described as visible (as seen with the naked eye) or as microscopic (as observed under a magnification of 10 diameters).

checking resistance the ability of a coating to resist slight breaks in its film that do not penetrate to the underlying surface.[56,72] cf. CHECKING;[56,42,154]

The breaks should be called cracks if penetration extends through the underlying surface. See CRACKING RESISTANCE.[56,72] Where precision is necessary in evaluating a coating film, checking may be described as visible (as seen by the naked eye) or as microscopic (as observed under minimum magnification of 10 diameters). The FSCT Pictorial Standards of Coating Defects contains photographic standards for the degree of checking of exterior paints.
ASTM Test Method D660 has a different set of illustrated reference standards.

chelating agent (1) a sequestering or complexing agent that, in aqueous solution, renders a metallic ion inactive through the formation of an inner ring structure with the ion.[83] (2) ORGANIC COMPOUND that can remove many of the heavy metal cations from solution by forming soluble chelate compounds. Ethylenediamine tetraacetic acid (EDTA) is typical.[83] Syn: sequestering agent, chelate
Chelating agents are also used to treat metal poisoning.

- vocabulary entry
- source of definition
- cross-reference to another entry
- encyclopedic discussion
- cross-reference to another entry for comparison
- indicates word or phrase is also defined in this volume
- indicates classification category, refers to listing in second part of *Dictionary*
- synonyms

Coatings Societies International to Present Medallion Honoring Technical Achievement at Member Organization Events

Coatings Societies International has announced the sponsorship of an award honoring outstanding technical achievement in the presentation of technical papers presented at selected annual congresses of CSI-member organizations.

The award, a polished bronze medallion, inscribed with the CSI logo, will be presented initially at the "Coatings for Africa" Symposium sponsored by the Oil & Colour Chemists' Association, which will be held in Cape Town, in South Africa, March 25-29, 1996.

Future presentations are as scheduled to be made at the following CSI Member events:

FATIPEC—XXIII Congress, June 10-14, 1996, Brussels, Belgium;

SURFACE COATINGS ASSOCIATION AUSTRALIA—38th Conference (Golden Jubilee), August 14-17, 1996, Sydney, Australia;

SCANDINAVIAN PAINTMAKERS FEDERATION—Congress, May 29-June 1, 1997, Lillehammer, Norway;

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY—75th Anniversary Annual Meeting, November 3-5, 1997, Atlanta;

JAPAN SOCIETY OF COLOUR MATERIAL—70th Anniversary International Conference, October 22-24, 1997, Tokyo, Japan;

SURFACE COATINGS ASSOCIATION NEW ZEALAND—2nd Trans-Tasman Conference, July 1998, Auckland, New Zealand.

Judging will be made by the sponsoring member organization with the following criteria:

(1) Presentations must be prepared and submitted in advance of the meeting.

(2) Selection will be based on 80% content and 20% on the presentation.

Interested parties may contact CSI-member organizations directly concerning the specified event, or the CSI General Secretariat at the Federation of Societies for Coatings Technology, 492 Norristown Rd., Blue Bell, PA 19422 U.S.A.

Student Papers Invited for 1996 A.L. Hendry Awards Competition

Student authors are encouraged to submit entries in the 1996 Southern Society for Coatings Technology Alfred L. Hendry Award Competition.

This year's award features cash prizes to both the student author (or authors) and the author's sponsoring lab. The student receives a $1000 cash award and expenses covering attendance at the FSCT International Coatings Expo and Technology Conference in Chicago, IL, October 23-25, 1996 to receive the honor and a suitably inscribed certificate for the best paper submitted for the competition.

The competition is administered by the FSCT Educational Coordinating Committee and several committee members will judge the entries. In addition, the laboratory of the sponsoring school will also receive a grant of $500.

Submitted papers must describe the results of original research on a subject related to coatings technology, or present a significantly insightful, comprehensive review of a field of coatings technology. Work done on coatings related topics as part of an undergraduate research project or as a senior thesis is appropriate for submission.

Those wishing to enter the competition must send a letter of intent, along with the title of the proposed paper and a brief abstract, by March 15, 1996 to: Hendry Awards Committee, c/o FSCT, 492 Norristown Rd., Blue Bell, PA 19422-2350. The deadline for receipt of manuscripts is July 3, 1996.

The A.L. Hendry Award is sponsored by the Southern Society for Coatings Technology and commemorates the industry contributions of the late Alfred L. Hendry, president of A.L. Hendry Co. in Tampa, FL. He was a Past-President of the Southern Society and an active participant in many of FSCT's educational activities.

1996 Roon Awards Competition Underway
Entries Invited; Awards Total Up to $4,000

FSCT Roon Awards Committee Chairman Clifford Schoff of PPG Industries, Inc., Allison Park, PA, has announced a Call for Papers for the 1996 competition. Prospective authors have the opportunity to earn up to $4,000 in cash prizes for outstanding papers.

The annual awards are sponsored by the Coatings Industry Education Foundation (CIEF) and were established to honor the late Leo Roon, founder of Nuodex Products Co., with support funds coming from the Roon Foundation. The awards will be presented at the FSCT International Coatings Technology Conference, on October 23-25, 1996 in Chicago, IL.

To submit a paper for the competition, the following rules must be observed: (1) The paper must describe original work not previously published or presented; (2) The information must be directly related to the protective coatings industry; (3) It must be of such a caliber that it reflects a step forward in real scientific contribution to the coatings industry; and (4) It must be accom-panied by a clearance for publication. The paper must also be prepared by someone associated with the organic coatings industry, including raw material suppliers and educators.

All of those interested in entering the competition must send a letter of intent, along with the title of the proposed paper and a brief abstract by March 1, 1996 to: Roon Awards Competition, c/o FSCT, Attention: Michael G. Bell, Director of Educational Services, 492 Norristown Rd., Blue Bell, PA 19422.

Entries that arrive after March 1 will be considered for the 1997 competition.

1995 Roon Award Winners

FIRST PLACE—"Latex Blends: An Approach to Zero VOC Coatings,"—Mitchell A. Winnik and Jianrong Feng, of University of Toronto

SECOND PLACE—"Film Formation Mechanism of Two-Component Waterborne Polyurethane Coatings"—Charles R. Hegedus, Andrew G. Gilicinski, and Robert J. Haney, of Air Products and Chemicals, Inc.

THIRD PLACE—"Coalescence and Film Formation from Latexes"—Kenneth L. Hoy, of Applied Science Consulting Services.

Principles Governing the Roon Awards

These awards, established in 1957 by the late Leo Roon, founder of Nuodex Products Co., and supported by funds provided through the Roon Foundation, are for the best technical papers (other than those by a Constituent Society of the Federation) submitted for presentation at a Federation's International Coatings Technology Conference.

Papers to be considered for the competition will be those by individuals associated with the organic coatings industry, including raw material suppliers and educational institutions.

The principles governing the awards are as follows:

(1) The papers will be of such caliber that they will reflect a step forward in real scientific contribution to the coatings industries. The papers shall describe original work which has not been previously published or presented.

(2) Papers must be directly related to the protective coatings industry.

(3) None of the work shall originate from, be guided by, or be any part of, a Coatings Technology Society. These awards shall in no way detract from the cooperative efforts of Societies' Technical Committees and their convention papers.

(4) An Awards Committee, appointed by the President of the Federation, will judge the entries.

(5) The Committee is not obligated to award prizes if in its opinion none of the submitted papers are of a caliber to be worthy of such recognition.

(6) The submitted papers may be presented at the Conference with the consent of the President of the Federation and the Chairman of the Program Committee. Although it is the intent of the Roon Awards that winning papers will be presented at the Conference, papers accepted for presentation and papers awarded prizes are separate and distinct. An invitation from the Program Committee to present his/her paper should not be construed by any author as an indication that the Roon Committee has awarded the paper a prize.

(7) Winning papers will be published in the JOURNAL OF COATINGS TECHNOLOGY, which has prior rights to publication of all submitted papers.

(8) The papers shall be concise and informative discussions of up to approximately 6,000 words. Papers greatly exceeding this length should be divided into more than one paper. Multiple entries in the competition from a single author are acceptable. It is requested that manuscripts be prepared in accordance with JOURNAL OF COATINGS TECHNOLOGY style, as outlined in the Guide for Authors.

(9) A 150 to 200 word abstract shall accompany the paper.

(10) Papers will be rated with emphasis on: (a) Originality – 40%; (b) Scientific Importance – 20%; (c) Practical Value – 20%; and (d) Quality of Composition – 20%.

(11) The Awards will be open to anyone involved in study or engaged in work related to the protective coatings industries, including paint, varnish and lacquer manufacturers, raw material suppliers, research laboratories and universities. (The Committee, however, will not accept papers which involve raw material sales promotion or are self-serving in regard to exploiting a proprietary product.)

(12) The Committee may award any number of prizes, the total of which is not to exceed $4,000.

(13) All papers must be accompanied by company or educational institutional clearance for publication.

(14) Those planning to submit a paper in 1996 must advise the Chairman through FSCT Headquarters (contact Michael G. Bell, Director of Educational Services, Federation of Societies for Coatings Technology, 492 Norristown Rd., Blue Bell, PA 19422) by March 1. FSCT must receive 10 publication manuscripts by May 15.

(15) The 1996 Awards and accompanying engraved plaques will be presented during the International Coatings Technology Conference, October 23-25, 1996, in Chicago, IL.

The Paint Stone

Route to:

FSCT Strategic Plan Moves Forward With International Coatings Technology Conference

The Federation's view toward the future detailed in its strategic plan reviewed at the Fall Meeting of the Board of Directors in St. Louis, moves ahead with the 1996 International Coatings Technology Conference, scheduled for October 23-25, in Chicago. The new conference program format aligns itself with the strategic plan objectives of expanding Federation technological offerings to a wider variety of coatings technologies, and the pursuit of international opportunities.

The Conference, a "stand-alone" program that will be held in conjunction with the FSCT's Annual Meeting and the International Coatings Expo (formerly Paint Industries' Show) is designed to offer a variety of "tracked" educational programs on specific topics. Presentations will be geared to fit learning objectives and guidelines targeted for a variety of factors, including

an individual's knowledge level, experience, and job functions.

The FSCT Program Committee is currently meeting to develop the full program. The goal of the Conference Program is to provide targeted information to meet the specific technical needs of the individual,

FSCT Speakers Program Gets High Marks from Societies

In December of 1994, the *Paint Stone* reported on the "Society Speakers Program," introduced by the FSCT Educational Coordinating Committee. This program was designed to help local Societies boost attendance and improve technical content of monthly meetings by scheduling relevant, interesting, and entertaining presentations by recognized industry leaders.

"The purpose of this program is to provide the Societies with a top-notch speaker who's going to bring people out," says Mike Bell, Director of Educational Services of the FSCT. The program debuted this past year and, to date, two Societies have benefited.

For its March meeting, featuring one of the speakers involved in the Society Speakers Program, the Pittsburgh Society reported

a 40% increase in attendance. The Louisville Society, which sponsored one of these presentations at its September meeting, found that while their numbers were about the same, the attendees at that

meeting were people who normally do not attend.

The FSCT has compiled a list of well-known and respected speakers who provide dynamic presentations on topics of interest to

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Inside This Issue

❖ *FSCT Strategic Plan Moves Forward with International Coatings Technology Conference*

❖ *FSCT Speakers Program Gets High Marks from Societies*

❖ *TechTips*

❖ *FSCT Emphasizes Educational Services in Current Promotional Campaign*

❖ *Calendar of Events*

The Northwestern Society for Coatings Technology will hold its 25th Annual Technical Symposium on March 5, 1996 at the Minneapolis Airport Marriott. The theme is "Waterborne Coatings: Formulating for the Future."

Cost of the symposium and dinner is $50 per person, pre-registered.

For additional information, contact Kristin Halverson at (612) 469-1500 or David Anson at (612) 522-6621.

Send Us Your "TechTips"

A popular feature of *The Paint Stone* has been the Tech Tips column which provides helpful hints to assist in all aspects of the coatings arena.

Please send any contributions c/o Editor, The Paint Stone, 492 Norristown Rd., Blue Bell, PA 19422. Unless requested otherwise, all contributions will be credited in the column.

Society Speakers Program

the coatings community *(for a listing of current topics and speakers, see sidebar)*. The Societies can select a topic they think will interest their membership and contact the FSCT about featuring that speaker at one of their upcoming meetings.

The Societies are not charged for the speaker, and the FSCT provides travel expenses. A biography and abstract are given to the Society for distribution to aid them in promotion of the event. The FSCT, who is responsible for the actual scheduling of the speakers, will only schedule two or three presentations a year for each speaker.

The positive responses from the Louisville and the Pittsburgh Societies demonstrate that the program has the potential to succeed in both of its goals—to step up attendance numbers at meetings and attract members who do not frequently attend the meetings.

"These good topics and marquee speakers will inspire people to make

attending that meeting a high priority," Mike comments. "People will take more of an interest than before."

The program is now completely in place and ready for Society involvement. If your group has been looking for a banner speaker to help your attendance, here is a great way to achieve that goal!

For more information, contact Mike Bell at FSCT Headquarters.

Society Speakers Program List

Dr. Kenneth Hoy
Applied Science Consulting
St. Albans, WV
"Decompression Atomization: A New Spray Technique."

Dr. John L. Massingill, Jr.
Eastern Michigan University
Ypsilanti, MI
"Development of Low Cost Reactive Diluents for Alkyd Coatings."

Mr. Sam Morell
S.P. Morell & Co.
Tarrytown, NY
"The Role of Acetylenic Glycols in Waterborne Coatings."

Dr. Richard R. Eley
The Glidden Co.
Strongsville, OH
"Characterization and Analysis of Coatings Rheology and Coatings Flows."

7ech 7ips...

Intercoat adhesion between coatings such as topcoat to primer, or primer to seal coat, can be difficult to evaluate. It is always desirable to isolate and then stress the interface of interest. One test which lends itself to this type of evaluation is a scrape adhesion test (ASTM D 2197). Specimens for the test are prepared by masking an area and then overcoating the specimen. For example, in testing the adhesion of a primer to a

substrate, a portion of the bare (uncoated) specimen is masked and then the primer is applied. In the case of evaluating the adhesion of a topcoat to a primer, the primer is applied to the entire substrate. After the primer has dried enough to apply and remove tape without substantial damage, an area is masked and the specimen is overcoated with the topcoat. After curing, the masking tape is removed, uncovering a portion of the specimen with primer. This also creates and exposes a lip at the primer-topcoat inter-

face.

The scrape adhesion test is performed by guiding a weighted stylus at a 45° angle to the specimen along the exposed substrate (or undercoat) into the coating system. In the case of a primer-topcoat, this would be the "lip" or edge that has been created at the primer—topcoat interface. The amount of weight on the stylus is increased until the coating is scraped from its interface. Good values for industrial type coatings are 3 kg or greater. If a scrape adhesion tester is not available, various hardness

pencils may be used. As with all adhesion tests, other mechanical properties of the system (besides the adhesive strength) affect the results. For example, a very soft coating may fail due to marring from the surface; a brittle coating may crack due to the compressive forces. However, the test does allow for the isolation and stressing of an interface between two coats.

—Submitted by
Charles Hegedus,
Air Products & Chemicals

FSCT Emphasizes Educational Services in Current Promotional Campaign

In recent strategic planning discussions among FSCT leadership, it was recognized that corporate consolidations and acquisitions have driven a rise in competitiveness that has placed greater demands on employees. As the need for technical information and expertise is accelerating, coatings technologists are seeking sources to improve their knowledge base and increase their value to employers.

Although the FSCT serves as a powerful educational resource for the coatings industry, some are not aware of the many ways in which membership in this organization can benefit them and their companies. To remedy this, the FSCT will be directing efforts to more actively promote its products and services, emphasizing the educational and professional development opportunities available.

To emphasize this focus, the FSCT has developed a promotional "identity ad"which utilizes the advice of Ben Franklin, "Tell me, and I forget. Teach me, and I may remember. Involve me, and I learn." As the FSCT Director of Marketing, Lyn Pollock, states, "Involve-

ment is the key. The FSCT has been fulfilling many of the professional development needs of our members through its publications, seminars and symposia, and trade show. Participation in FSCT activities has helped to improve many of the skills needed to succeed in today's competitive climate. Now it's time we let the entire industry know about this 'secret weapon'."

This message will be the focus of promotional pieces planned for the coming year. In addition, copies are available for Societies to use as part of a welcome "kit," for membership drives or for distribution at Society-sponsored symposiums, meetings, seminars or conventions.

Contact Lyn Pollock, Director of Marketing, at FSCT Headquarters, for additional details.

International Technology Conference

Continued from Page 1

while appealing to a wider base than in the past.

Traditional presentations, such as the Mattiello Lecture, Technical Focus Speaker, Society presentations, and international papers will be presented as part of the Annual Meeting Technical Program.

Michael Wolfe, Ben Carlozzo, Sharie Moskaluk, and Skip Glover (left to right) root for their favorite team at the Cleveland Society's October meeting

Past-Presidents of the Pacific Northwest Society (pictured below), Yvon Poitras, John Berghuis, and Otto Schmidt, recently organized the annual golf tournament of the Vancouver Section
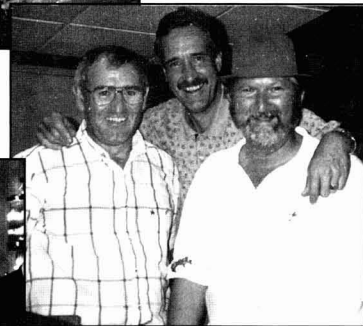
Frank Peters and Evans Angelos celebrate at the Joint Holiday Party of the Chicago Society and Chicago Paint & Coatings Association

Calendar of Events

February

- **14-16** 23rd Annual International Waterborne, High-Solids, and Powder Coatings Symposium, Sponsored by Southern Society and Univ. of Southern Mississippi, New Orleans, LA.

March

- **5** 25th Annual Technical Symposium of Northwestern Society. Minneapolis, MN.

- **20-22** Southwestern Paint Convention. Sponsored by Houston and Dallas Societies, Del Lago Resort, Conroe, TX.

April

- **16** FOCUS '96, Sponsored by Detroit Society. Troy, MI.

- **24-25** Cleveland Society Joint Manufacturing/Educational Conference, John S. Knight Center, Akron, OH.

May

- **3-4** 49th Annual Spring Symposium of Pacific Northwest Society, Seattle, WA.

- **3-5** FSCT Spring Week, held in conjunction with Pacific Northwest Society Spring Symposium, Seattle, WA.

- **8-9** Eastern Training Conference and Show. Sponsored by Philadelphia Society, Valley Forge, PA.

- **8-10** Southern Society Annual Meeting. Tampa, FL.

Hotel Fire in St. Louis Doesn't Dampen President's Reception

During the traditional reception honoring the 1995 FSCT President Joseph P. Walton and his wife, Kathy, held in St. Louis during the FSCT Annual Meeting, the hosts and their guests were treated to some unexpected excitement as flames from a fire in the hotel's laundry two floors below rose past the reception's windows. Joe assumed his leadership role and moved his guests to safer quarters. The fire company responded quickly and within 30 minutes the reception resumed. The photo was taken by Francis Borel, Secretary-General of FATIPEC, to whom we are indebted.

Kline & Co. Forecasts Four Percent Growth Rate in Specialty Silicas Market by the Year 2000

A recent study by Kline & Co., Inc., Fairfield, NJ, predicts that through the year 2000, the global market for specialty silicas is expected to grow at a rate of over four percent a year (in real terms, excluding inflation), reaching $2 billion in that year. In 1994 the global market for specialty silicas, which include precipitated silica, silica gel, fumed silica, and colloidal silica, was estimated at 700,000 ton, valued at almost $1.7 billion.

In anticipation of the increase in global capacity, several specialty silicas suppliers have announced capacity expansions. Ac-

cording to Kline & Co., Inc., demand in Asia/Pacific exceeded that in North America for the first time during 1994. With this forecasted growth rate, suppliers will continue to expand.

The report stated that precipitated silica, with a global market of roughly $600 million, will experience an increase in demand of five percent a year through the year 2000.

Another area with growth potential is silica gel. With a global market of roughly $350 million, it is expected to grow three percent a year.

Fumed silica, with a global market of $550 million, is heavily dependent on silicone rubber compounding, and has an expected growth rate of four percent per year.

Colloidal silica represents the smallest product, with sales in 1994 estimated at $200

million. In addition, colloidal silica has the slowest forecast growth rate at 2.5% per year.

There are dozens of end uses for specialty silicas. But, because it represents a significant market for precipitated and fumed silica, rubber applications dominate in use of specialty silicas, exceeding $500 million in 1994. Food and healthcare rank second, primarily for toothpaste thickener applications where precipitated silica and silica gel find widespread use. In coatings, silicas are primarily used as thixatropes. Here silica gel, precipitated silica, and fumed silica all find use. Plastics applications include flow aids and antiblocks for film. Fumed silica is the major product consumed, but precipitated silica, silica gel, and colloidal silica also find use.

For more information on the Kline & Co., Inc., report, contact Carl Eckert, Kline & Co., 165 Passaic Ave., Fairfield, NJ 07004.

Degussa IPDA Plant Inaugurated in Belgium

Degussa Antwerp NV, Frankfurt Am Main, Germany, recently inaugurated a new plant for the production of Degamin IPDA® (isophorone diamine).

The IPDA plant has been erected on a new site but utilizes the existing infrastructure. A sum of around 750 million BEF has been invested in this project. With an annual capacity of 10,000 tons per year, Degussa is now producing isophorone diamine in Antwerp according to new two-stage process developed by Degussa's Research Division. This process involves the addition of hydrocyanic acid to isophorone, followed by low-pressure hydrogenation.

U.S. Filter Acquires Jet Tech and Continental Water

U.S. Filter Corp., Palm Desert, CA, has signed a definitive agreement to acquire Jet Tech, Inc., Edwardsville, KS, for approximately $12 million in cash and stock. Jet Tech is expected to realize revenues of approximately $16 million for the 1995 calendar year.

Jet Tech designs and manufactures sequencing batch reactors and autothermal

thermophilic aerobic digesters with high efficiency air diffusion and mixing to enhance the biological destruction of organic wastes.

In addition, U.S. Filter announced the acquisition of Continental Water Systems Northwest, Auburn, WA. Continental Northwest had been a U.S. Filter franchised dealer for several years. Terms were not disclosed. Continental Northwest sells and services high-purity water products from its facilities in Auburn and Vancouver, WA, and owns and operates a resin regeneration facility in Vancouver, which serves, among others, the electronics industry in Portland, OR.

Electrotechnology Applications Center Provides Cost Solutions to Small and Mid-Size Companies

In response to environmental compliance mandated by the United States Environmental Protection Agency, the Pennsylvania Power and Light Co. and the Northampton Community College have formed The Electrotechnology Applications Center (ETAC), located in Bethlehem, PA.

Engelhard Expands Capacity at Louisville Pigments Facility

Engelhard Corp., Iselin, NJ, has increased the manufacturing capacity for organic color pigments by 35% at its Louisville, KY, facility.

This expansion will enable Engelhard to increase the supply of organic color pigments for the paint and coatings, plastics and ink industries, expand technical support to customers, and grow its portfolio of colors. Investment in the expansion is in excess of $2 million.

ETAC provides manufacturers with an opportunity to test electrotechnological curing and drying processes for the reduction of harmful volatile organic compound emissions before committing to the purchase of expensive equipment. In so doing, the 9,100 square foot facility provides infrared and ultraviolet technology alternatives for paper, printing, textile, appliance, automobile, furniture, and fabrication manufacturers.

Serving the entire Mid-Atlantic region, ETAC's equipment represents a conveyorized process line that is typically found in many manufacturing plants that have coating or drying operations. The facility houses an electric infrared oven; a three-dimensional ultraviolet curing chamber, electric convection oven, and a dry powder and wet spray booth.

For more information contact, ETAC, 3835 Green Pond Rd., Bethlehem, PA 18017; (610) 861-5081.

ASTM Relocates Headquarters to West Conshohocken, PA

The American Society for Testing and Materials' international headquarters has moved to West Conshohocken, PA, a suburb of Philadelphia. The new, four-floor office building encompasses 82,000 square feet.

Highlights of the new headquarters building include accessibility, expanded meeting areas, enhanced information transfer capabilities, new order-servicing techniques, and a modern, state-of-the-art office environment.

ASTM may be reached at the following: ASTM, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959; (610) 832-9500; Fax: (610) 832-9555.

OCCA's South African Division to Host "Coatings for Africa" in Cape Town

The Oil & Colour Chemists' Association's (OCCA) South African Division in conjunction with SURFEX Ltd., OCCA's exhibition and conference organization company will conduct "Coatings for Africa," on March 25-29, 1996, in Cape Town, South Africa.

The Congress will cover all aspects of the surface coatings industry, and will enable attendees to expand their knowledge and their horizons, and to develop profitable business relationships. This event is divided into the following four components:

OCCA Symposium—The 16th National symposium of the South African Division of OCCA;

SURFEX—an exhibition of raw materials, equipment, services, and products relating to all aspects of the surface coatings industry;

Advances in Paint and Ink Technology— a technical conference organized by the Paint Research Association (PRA);

Understanding corrosion a one day entry level course to be run by the Corrosion Institute of Southern Africa.

In addition to the previously mentioned components, the following papers are scheduled to be presented:

"New Amine Technology for High-Solids and Waterborne Epoxies"—P.A. Lucas, of Air Products Ltd.;

"Color Fastness and Durability of Waterborne Decorative Coatings"—S. Attwood, of Plascon Paints;

"Combined Corrosion and Weathering Exposure"—P.J. Brennan, of Q-Panel Co.;

"Application of Standards in the Paint Industry with Emphasis on Application of Coatings"—G. Munro, of SA Bureau of Standards;

"Polysulphide Modified Epoxies"—T. Rees, of Morton International;

"Formulating with Nontoxic Corrosion Inhibitors"—P. Peterson, of Halox Pigments;

"New Aluminum Pigments"—D. King, of Silberline;

"New Developments in Masonry Coatings"—D. Sykes, of Rohm and Haas;

"Computer Aided Coatings Selection"— R. Draper, of Draper, Duligal, Penhall and Associates;

"PIA, TMA, and TA—Versatile Monomers for Low VOC Polyesters and Alkyds"— T. Greenwood, of Amoco Chemicals;

"High Molecular Weight Dispersing Agents"—M. Jorna, of Efka Chemicals;

"Bimodal Dispersions in Coatings Applications"—R. Arnoldus, of Zeneca Resins;

"Use of Electrochemical Impedance Spectroscopy to Develop Paint Coatings for Aluminum"—J. Leitch, of Hulett Aluminum;

"Innovative Two-Stage Alkyd Resins"— G. McAuliffe, of Croda Resins; and

"Complex Inorganic Pigments—Candidates for Aggressive Environments"—G.T. Peake, of Shepherd Color Co.

For additional information on "Coatings for Africa," contact Christopher Pacey-Day, SURFEX Ltd., Priory House, 967 Harrow Rd., Wembley HA0 2SF, England.

Philadelphia Society Plans Coatings Course for Industry Newcomers on May 8-10, 1996

The Philadelphia Society for Coatings Technology will host the first annual "Eastern Training Conference and Show" on May 8-10, 1996 at the Valley Forge Convention Center, Valley Forge, PA. This two-day training course will introduce coatings technology to technical and nontechnical newcomers to the industry.

A series of 11 lectures will cover the basic principles of coatings technology. The topics to be discussed include:

DuPont Releases Schedule for Upcoming DOE Seminars

DuPont's Quality Management and Technology Center, Wilmington, DE, has announced the schedule for the upcoming public seminars on the design of experiments.

"Strategy of Experimentation" will be held on the following dates: Feb. 20-22— Orlando, FL; Mar. 19-21—Wilmington, and Houston, TX; Apr. 16-18—San Francisco, CA; May 14-16—Washington, D.C. and Wilmington; and June 18-20—Philadelphia, PA.

The schedule for "Strategy of Formulations Development" is as follows: Mar. 26-28—Wilmington, and May 21-23—Washington, D.C.

For additional registration information, contact DuPont Quality Management & Technology, 1007 Market St., Nemours Bldg. 6498, Wilmington, DE 19898.

- A history of coatings technology
- Resins and solvents used in architectural, industrial maintenance, and OEM coatings applications
- Water soluble and emulsion resins used in industrial and architectural applications
- Pigments, applications, and uses
- Additives for industrial and architectural coatings
- Paint testing methods
- Paint calculations
- Application of paint in industrial and architectural coatings.

The fee for the two-day course is $125 and includes the course, lecture notes, and lunch. Registration is limited to 150 attendees.

In conjunction with the course, a "Show" will feature exhibits of suppliers to the paint and coatings industry. This event will be open to the industrial community and admission is free.

For more information on the training course, contact Wayne Kraus, Hercules Incorporated, Research Center, 500 Hercules Rd., Wilmington, DE 19808; (302) 995-3435. For exhibiting information contact, Sam Firestone, S.E. Firestone Associates, Inc., 101 Surrey Rd., Melrose Park, PA 19027; (215) 635-1366.

Eastern Training Conference and Show

May 8-10, 1996

Valley Forge Convention Plaza
King of Prussia, PA

Purpose and Overview

An introductory course aimed at an increased understanding of coatings for both technical and nontechnical personnel. The course will cover the essentials of coatings technology, and chart the course the industry is taking in its accelerated evolution towards an exact science. Attendees will learn the language of the industry and further their understanding of how raw materials function in both architectural and industrial finishes. Topics will range from simple calculation and basic formulations all the way to the driving forces that influence coating compositions.

Who Should Attend?

Anyone in the industry who wishes to gain a comprehensive understanding of its products and trends. Not only will lab technicians and formulators find it useful, but purchasing agents, sales, production, and manufacturing personnel will also benefit. The informal style of presentation encourages full class participation. No chemistry background is required but is always helpful. Attendees will benefit from the opportunity to network with others in the industry with whom they can share problems and solutions in class and for years to come.

Registration

Registration fee for the Eastern Training Conference and Show is $125.00 per person.

$ 125.00 X_____   Total Enclosed = _____
                Registrations

Registration is limited to 150 on a first come, first served basis.

Registration fee includes two luncheons. Complimentary materials consist of a compilation of notes on the subject matter presented.

The Show will take place in a nearby hall with tabletop displays. Attendees of the Conference will be provided adequate time to visit the exhibition and become familiar with the latest in raw materials, equipment, and service suppliers.

Registration Application

Please Print

Name_____

Company_____

Address_____

City_____ State _____ ZipCode_____

Phone Number _____ Fax:_____

Make Checks Payable to: **Eastern Training Conference and Show**

Mail registration and check to: Mr. Sam Firestone, S.E. Firestone Associates, 101 Surrey Rd., Melrose Park, PA 19027-2931.

For additional information, contact: Wayne A. Kraus, Hercules Incorporated, (302) 995-3435.
For registration and exhibit rental information, contact: Sam Firestone, S.E. Firestone Associates, (215) 635-1366.

Frank N. Jones

A Professor at Eastern Michigan University, Dr. Frank N. Jones also serves as Director of the National Science Foundation Industry/University Cooperative Research Center in Coatings at Eastern Michigan University, Michigan Molecular Institute, and North Dakota State University.

He moved to EMU in 1990 after seven years as Professor and Chair of the Department of Polymers and Coatings at North Dakota State University. Previously he held research and management posts with Du Pont, Celanese, and Cargill, working mainly in the fields of synthetic polymer chemistry, polymeric materials, and coatings. He received an A.B. in Chemistry from Oberlin College and a Ph.D. in Organic Chemistry from Duke University.

Dr. Jones is author of over 100 papers and has been awarded about 15 U.S. patents, most in the areas of synthetic polymer chemistry and coatings. He is co-author, with Zeno Wicks and Peter Pappas, of a two-volume test and reference book, *Organic Coatings: Science and Technology*, published by John Wiley & Sons in 1992 and 1994. Current research interests include polymer synthesis and crosslinking, properties of industrial coatings, and methods to eliminate solvent from liquid coatings.

Dr. Jones is a frequent contributor to the JOURNAL OF COATINGS TECHNOLOGY and has been the recipient of three Roon Foundation Awards from the FSCT. He is a member of the Detroit Society.

Active in the American Chemical Society Division of Polymeric Materials: Science and Engineering, Dr. Jones currently serves as Vice-Chair. He has been an organizer and chair of symposia at American Chemical Society National Meetings.

Dr. Jones serves as a reviewer for the *JCT*, the *Journal of Applied Polymer Science*, *Journal of Polymer Science*, *Polymer Chemistry*, and the *Journal of Physical Chemistry*.

❋ 1995 Mattiello Memorial Lecture ❋

Toward Solventless Liquid Coatings

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Results of an exploratory study of solventless (100% reactive) liquid polyester/melamine resin and polyester/polyisocyanate coatings are described. An investigation of how the chemical structure and the molecular shape of oligomeric polyester resins affects their viscosities found that slender molecules have very low viscosities. "Linear" oligoester diols composed entirely of diacids and diols of the structures $HOOC(CH_2)_nCOOH$ and $HO(CH_2)_mOH$ with M_n of 700 or below have viscosities below 800 mPa·s at 25°C, low enough for potential use in solventless coatings. Physical properties of oligoester diols were studied, and quantitative relationships among viscosity (η), temperature (T), molar mass (M_n), glass transition temperature (T_g), and melting point (T_m) were demonstrated.

The next step was to formulate solventless coatings with linear oligoester diols. An arbitrary goal was to keep viscosity below 800 mPa·s at 25°C without adding organic solvents. A two-package solventless coating made from a linear oligoester diol and a low viscosity polyisocyanate crosslinker had a viscosity of 560 mPa·s at 25°C and excellent film properties; its VOC was 8 g/L. Polyester/melamine resin coatings with similar viscosities can be formulated, but their coating films tend to be soft and to have poor adhesion to metal. Film properties can be improved by adding hardeners to the formulations, but viscosity increases.

Viscosity of these solventless formulations can be further reduced by adding modest amounts of water (3 to 20 wt%). This expedient makes it possible to formulate one-package "water-thinnable solventless" coatings with reasonably good film properties from combinations of linear oligoester diols, hardeners, and melamine resins. Two-package coatings containing polyisocyanate crosslinkers can also be thinned with water with little effect on pot life.

INTRODUCTION

Is it feasible to entirely eliminate organic solvents from liquid decorative coating formulations? My co-workers and I have been exploring this question for several years. Here we offer a progress report on a project that is still ongoing. The results presented will leave loose ends and unanswered questions. It will be concluded that solventless liquid coatings may be feasible for many applications, although much further development will be needed. The subject is broad, and it is impractical to provide complete experimental details here; more detailed publications are planned.[1-4]

Of course, solventless liquid paints are nothing new. Cave persons painted their walls with pigments dispersed in vegetable oils 30,000 years ago. Howard Gerhart[5] quoted a charming recipe from an 11th Century monk, Theophilus, for making a solventless linseed oil varnish. Theophilus claims his varnish is "beautiful and durable forever." Today, thick-film solventless liquid coatings are common. Examples include epoxy floor coatings and polyurethane mastics.

Our interest is in a more challenging problem: thin-film industrial coatings for metal, wood, and plastics. Our ultimate goal is solventless coatings that equal the quality of modern thin-film (15-60 μm) solvent-borne decorative coatings and that can be applied at ambient or slightly elevated temperature by spray, roll coat, etc. and cured thermally. The upper limit of viscosity for sprayable coatings with contemporary

equipment can be considered to be in the range of 300 to 1200 mPa·s, depending on the equipment and the application. Heating to 35 or 40°C to reduce viscosity is often feasible. We arbitrarily set a goal of making good formulated coatings with viscosities below 800 mPa·s at 25°C and preferably below 500 mPa·s. It is expected that coatings with viscosities in this range could be applied with a wide variety of equipment, especially in cases where mild heating is feasible.

Others have worked on solventless coatings. A 1974 patent by Henshaw and Leary[6] disclosed solventless coatings. Resin suppliers offer a variety of low viscosity polyester resins and reactive diluents for very high solids formulations, some of which might be useful in solventless coatings as well. Solventless, low-viscosity melamine resin and polyisocyanate crosslinkers are also available. Since 1993, a "solventless high-solids heat cured" polyester coating has been marketed in the U.S.[7] Its viscosity is said to be about 10,000 mPa·s at room temperature and about 1,250 mPa·s at 54°C (130°F); thus, considerable heating would be required to spray it with most, if not all, commercial equipment.

A traditional approach to the challenging problem of eliminating solvents has been to incrementally remove solvent from high-solids coatings. Typically formulators find that the task becomes exponentially more difficult as more solvent is removed. As regulations become increasingly more restrictive, many have concluded that very high-solids and solventless coatings are less practical than waterborne or powder coatings, and have shifted efforts in those directions.

We took a different approach. Rather than incrementally removing solvent, we eliminated solvent entirely and then tried to find out what is necessary to make good coatings. We set ground rules that allow us to do anything we can think of except adding organic solvent. In recent months we relaxed our self-imposed ground rules to allow addition of small amounts of acetone, since acetone is now considered non-photochemically reactive and is exempt from VOC regulations in the U.S.

We concentrated on two types of formulations—polyester/melamine resin and polyester/polyisocyanate coatings. In current high-solids formulations, the polyester contributes most of the viscosity, so we focused on polyesters.

Figure 1—Viscosity of a terephthalate oligoester.
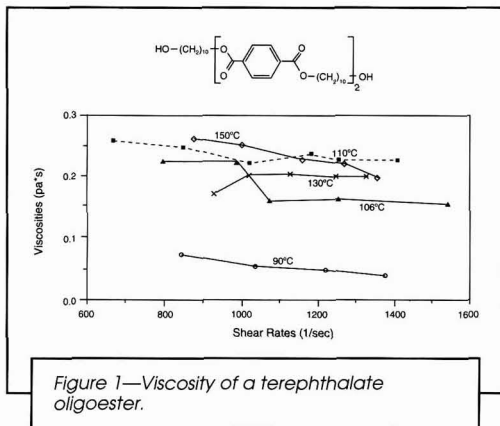
LOW-VISCOSITY POLYESTER RESINS

Background

What would it take to make a polyester with a viscosity low enough to make a solventless liquid coating? It is well known that it should be an oligomer with a low glass transition temperature (T_g), a low number average molar mass (M_n), and the narrowest possible dispersity of molar masses (M_w/M_n and/or M_z/M_n).[8] It will also be desirable to minimize associative effects, especially hydrogen bonding.[8] However, there have been few reports of how chemical structure and molecular shape influence the viscosities of the oligomeric polyesters. Our initial goal was to learn more about how the chemical structure and the molecular shape of oligomers affect their viscosity.

The published literature on high polymer melts furnished considerable background. The effects of chemical structure and molecular shape on the melt viscosity of high polymers have been studied extensively.[9,10]

Oligomers Based on Terephthalic Acid and Diols of Structure HO(CH₂)ₙOH

We started with terephthalate oligomers of the general formula (1).

$$HO-(CH_2)_n \left[\begin{array}{c} O \\ \parallel \\ O \end{array} - - \begin{array}{c} O \\ \parallel \\ O \end{array} - (CH_2)_n \right]_m OH \qquad (1)$$

n = 4, 6, 10, 15   m = 2-5
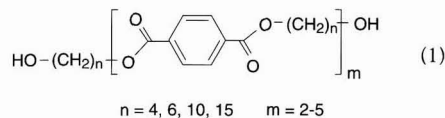
As we previously reported,[11-13] these oligomers are very interesting in several ways. They can be crosslinked with melamine resins and with polyisocyanates to make coatings with excellent film properties. The problem is that they are all crystalline solids at ambient temperature. Most of them melt at 70 to 120°C, and the high melting point causes severe application problems. We tried to overcome the problem by dissolving or dispersing the terephthalate oligomers in liquid coating components[12] or by chemically modifying them;[13] these expedients gave good coatings, but required solvent.

Another interesting feature of these oligomers has not yet been reported. Their rheological behavior is odd. An example is shown in Figure 1, for structure 1 where m = 10 and n = 2. This particular oligomer melts at about 85°C. At 90°C its melt viscosity is very low, about 60 to 80 mPa·s. Surprisingly, as the melt is heated, the viscosity increases until it is about 250 mPa·s at 150°C. There are two or more possible explanations for this unusual phenomenon: perhaps only the low molar mass, low viscosity fraction of the oligomer melts at 90°C, and as temperature increases higher molar mass fractions melt and raise viscosity; or, perhaps the material is displaying nematic characteristics at 90-130°C. Whatever the reasons, this kind of behavior should be very attractive for solventless coatings since it should help minimize oven sagging, one of the most serious problems anticipated.

The viscosity of solventless blends of these oligomers with crosslinkers is low enough for solventless application at 90°C. However, the engineering problems of applying them appear formidable, especially since the oligomers begin to separate

rapidly if the formulations are allowed to cool at any time during storage and application. Being chemists, not engineers, we set out to look for different structures that might have similar behavior with lower melting points.

Linear Oligomers Based on Dicarboxylic Acids of Structure HOOC(CH₂)mCOOH and Diols of Structure HO(CH₂)ₙOH

The trail led, in a roundabout way, to oligomers of the general structure (2).

$$HO-(CH_2)_n \left[\begin{array}{c} O \\ \parallel \\ C \end{array} (CH_2)_m \begin{array}{c} O \\ \parallel \\ C \end{array} O-(CH_2)_n \right]_x OH \quad (2)$$
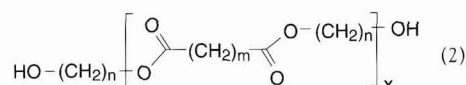
We call these "linear" oligomers because of the absence of branching, even by a methyl group. Note that this use of the word linear, while convenient, is unconventional. In the polymer field it is conventional to call polymers with methyl, phenyl, etc. branches from the side chain linear as long as the branches derive from a single monomer unit.

Oligomers of formula 2 are also crystalline solids at 25°C, but they have lower melting points than terephthalate oligomers (1). They also have low viscosities at temperatures just above their melting points. However, formulation and application still present practical problems because oligomers of structure 2 *separate quickly whenever solventless formulations cool below 30 to 50°C*.

This problem was overcome by replacing the single dicarboxylic acids in formula 2 with mixtures of dicarboxylic acids. It was found that a mixture of glutarate, adipate, and azelaate esters in a 1:1:1 mol ratio would suppress the melting point of the oligoesters below room temperature. The composition represented by formula 3 proved satisfactory.

$$HO-(CH_2)_4 \left[\begin{array}{c} O \\ \parallel \\ C \end{array} X \begin{array}{c} O \\ \parallel \\ C \end{array} O-(CH_2)_4 \right]_x OH \quad (3)$$
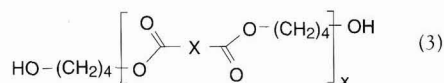
where X = –(CH₂)₃–, –(CH₂)₄–, and –(CH₂)₇– in a 1:1:1 (mol ratio) mixture

With one exception, this mixture of three diacids was used in all studies reported in the following; the exception is noted.

Synthesis of Linear Oligomers

These oligomers can be synthesized a number of ways. The synthetic route we found most useful for oligomers made from 1,4-butanediol is represented in *Chart* 1. It involves two steps, *performed in a single reactor:* (1) catalyzed transesterification of a mixture of dimethyl esters of the three dicarboxylic acids with excess diol with removal of methanol followed by (2) catalyzed transesterification of the product with removal of diol until the desired molar mass is attained. The products are colorless liquids. For oligomers destined to be crosslinked with melamine resins, the reactions proceed readily with 0.1 to 0.2 wt% of zinc acetate dihydrate catalyst. For oligomers intended to be crosslinked with polyisocyanates, only low levels of Zn(OAc)₂·2H₂O (more typically 0.01 wt%) can be tolerated. Alternative catalysts such as p-toluene sulfonic acid or methane sulfonic acid can be used, although acid catalysts impart a yellowish or reddish color.

Good Synthetic Route

$$H_3COOC(CH_2)_mCOOCH_3 + 2\ HO(CH_2)_4OH$$

Zn(OAc)₂·2H₂O
150-210°C
[Distill CH₃OH]

$$HO-(CH_2)_4-O \begin{array}{c} O \\ \parallel \\ C \end{array} (CH_2)_m \begin{array}{c} O \\ \parallel \\ C \end{array} O-(CH_2)_4-OH$$

Zn(OAc)₂·2H₂O
210-240°C
[Distill HO(CH₂)₄OH]

$$HO-(CH_2)_4 \left[O \begin{array}{c} O \\ \parallel \\ C \end{array} (CH_2)_m \begin{array}{c} O \\ \parallel \\ C \end{array} O-(CH_2)_4 \right]_x OH$$

Chart 1—Synthesis of linear oligoester diols
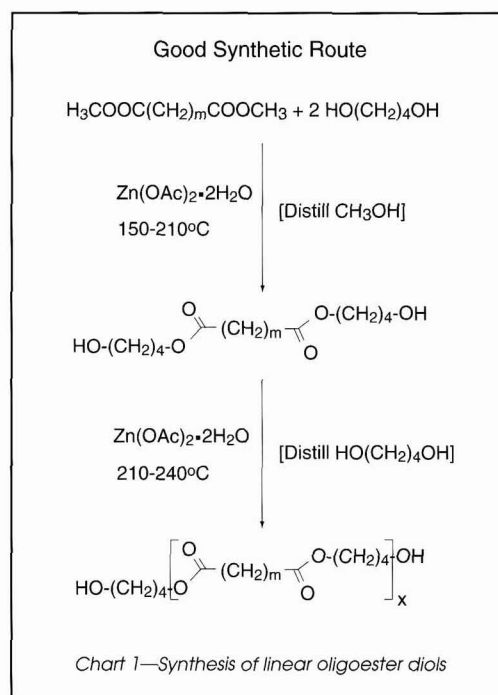
The transesterification process has several advantages. It can be controlled to successfully target any M_n from 300 up to at least 15,000. A series of oligomers with different M_ns can be conveniently made by withdrawing portions of the product at intervals during step two of the process. The process can yield oligoester diols that are virtually free of methyl ester ends and, thus, are capable of crosslinking fully. (Levels of methyl ester residues can be conveniently assessed by ^{13}C NMR; distortionless enhancement by polarization transfer (DEPT) NMR is especially useful because it readily distinguishes between –CH₂– and –CH₃ groups.) Starting materials are all available in large quantities, although it is desirable to re-distill commercial grade dimethyl azelaate. Excess 1,4-butanediol and by-product methanol could presumably be recycled.

The same process was used to prepare oligoester diols from the standard mixture of dicarboxylic acid diesters and different diols: 1,3-butanediol (1,3-BD), diethylene glycol (DEG), and neopentyl glycol (NPG). However, as the volatility of the diol decreases (DEG and NPG) and with solid diols (NPG) the process becomes less convenient and produces yellowish-tan products. We call the oligomers made from 1,3-BD and from NPG "non-linear" because of the methyl branches.

M_n of all oligomers is conveniently measured by ^{1}H NMR. Comparison of the peak areas at 4.0 ppm [–C(=O)OCH₂–] and 3.6 ppm [–CH₂OH] provided M_n data which closely agreed with M_n data obtained by end group analysis (hydroxyl number measurement). Gel permeation chromatography (GPC) with the columns and calibration standards available gave unreliable (high) values of M_n.

Table 1—Characteristics of Oligoester Diols

$$HO(CH_2)_4\left[OOC-A-COO(CH_2)_4\right]_x OH$$

A = –(CH₂)₃–, –(CH₂)₄–, and –(CH₂)₇– (1:1:1)

A = $-(CH_2)_3-$, $-(CH_2)_4-$, and $-(CH_2)_7-$ (1:1:1)

M_n	x	T_m, °C	Viscosity, mPa·s @ 25°C	T_g, °C
310	1.0	–9	270	–98
520	2.1	1	590	–83
670	2.8	2	760	–79
840	3.6	7	1440	–76
1420	6.4	9	3300	–71
2900	13	13	19000	–66
14800	70	15	—	–64

Table 2—Viscosity and T_g of Oligoesters Made from Different Diols

$$HOB\left[OOC-A-COOB\right]_x OH$$

A = $-(CH_2)_3-$, $-(CH_2)_4-$, and $-(CH_2)_7-$ (1:1:1)
B = diol residue

Diol	M_n	η, mPa·s, 25°C	T_g, °C
1,4-BD	520	590	–83
1,4-BD	670	760	–79
DEG	540	550	–68
DEG	630	710	–65
1,3-BD	560	1060	–64
1,3-BD	690	1450	–61
NPG	560	1430	–64

Diols		CH₃ groups
1,4-BD	= 1,4-butanediol	0
DEG	= diethylene glycol	0
1,3-BD	= 1,3-butanediol	1
NPG	= neopentyl glycol	2

Table 3—Influence of M_n of Activation Energy for Flow (E)

Mixed Diacid Oligoester Diols					
1,4-Butanediol		Diethylene Glycol		1,3-Butanediol	
M_n	E, kJ/mol	M_n	E, kJ/mol	M_n	E, kJ/mol
300	35.5	310	37.8	350	45.9
520	39.4	540	43.9	455	42.0
735	40.4	630	43.0	560	43.5
840	41.4	750	43.8	690	45.7
1000	42.9	800	44.7	930	48.1
1600	42.9				

Table 4—Activation Energy for Flow (E) of High Polymers

Polymer	E, kJ/mol
Polyethylene, linear	25
Polypropylene	44
Poly(methyl methacrylate)	65
Poly(butyl methacrylate)	72
Poly(decamethylene adipate)	29
Poly(decamethylene sebacate)	30

N.G. Kumar, J. Polymer Sci.: Macromol. Rev., 15, 255-325 (1980).

Physical Properties of Linear and Non-Linear Oligoester Diols

Having a convenient way to synthesize series of oligomers with different molar masses presented an opportunity to learn more about their physical properties. Characteristics of the 1,4-butanediol oligoesters at selected molar masses are shown in *Table* 1. Those in the M_n range 300-700 [degree of polymerization = 1-2.5] have viscosities below about 800 mPa·s at 25°C. Heating them to 40°C cuts their viscosities sharply. Thus, these oligoesters are candidates for use in solventless coatings that could meet our viscosity goals. Melting points (T_m) are comfortably below room temperature. Glass transition temperatures (T_g) are very low.

Viscosities were measured at 25 to 60°C with a Brookfield Thermo-Cell viscometer. They were Newtonian in the shear rate range 0.5 to 20 sec⁻¹. Viscosities of several oligomers were also measured at the same temperatures with a Bohlin research grade viscometer. The results agreed closely. In the ensuing discussion of viscosity it is assumed that the M_w/M_n of the different series of oligomers are similar.

DEPENDENCE OF VISCOSITY ON STRUCTURE—The viscosities of oligomers made from different diols, but of similar M_n, are compared in *Table* 2. It is evident that the linear diols have the lowest viscosity. A single methyl branch on each diol unit (1,3-BD) almost doubles the viscosity, and two methyl branches (NPG) almost triple it. We obtained similar results in comparing melts of oligomers of structure 2 with comparable oligomers based on NPG. Thus, we are confident that the relatively low viscosity of linear diols shown in *Table* 2 is characteristic of this class of oligomers.

There is no discernable correlation of viscosity with T_g. Glass transition temperature was measured by DSC.

DEPENDENCE OF VISCOSITY ON TEMPERATURE—It is common practice to use an equation of the form (4) to relate viscosity to temperature of high polymers[10] and oligomers.[14]

$$\ln \eta = \ln A + \frac{E}{RT} \qquad (4)$$

Here η = viscosity, T is temperature in Kelvin, and A and E are constants. This equation was proposed by Gay-Lussac and popularized by Arrhenius for chemical reaction kinetics.[15] It was adapted by Andrade for studies of polymer flow and was popularized by Eyring. In this context the constant E is termed the "activation energy for flow."

Figures 2-4 are plots of ln η versus 1/T for oligomers of several molar masses derived from each of three different diols. If equation (4) is valid, the data should fit straight lines. Computer curve fitting suggests that they do, calculating a regression coefficient (R) of 1.00 for a linear fit. However, on inspection, one can see that the best fit may not really be a straight line, but rather is biased toward a shallow dish shape. In fact, fitting the same data to an exponential equation also gives R-1.00. Examples of such exponentially fitted data are shown in *Figure* 5 for the 1,4-butanediol oligoester; exponential plots for the other oligomers were similar.

Deviation from linearity of the data in *Figures* 2-4 is no surprise. Equation (4) is widely used, but it is acknowledged to be approximate. Hill and Wicks[8] cited several examples of similar deviations in the literature, and Wicks et al.[16] observed very similar deviations from equation (4) in studies of acrylic oligomer solutions.
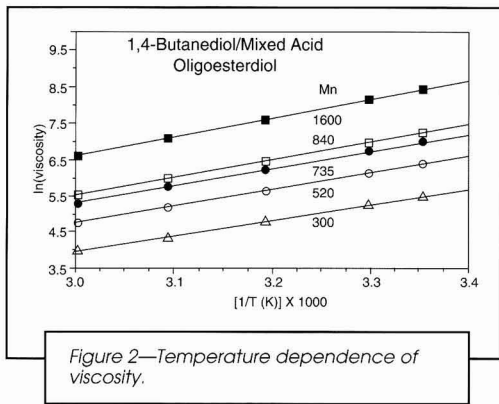
Figure 2—Temperature dependence of viscosity.

Despite its limitations, equation (4) has been used by many other workers to analyze flow of polymers and oligomers.[9] The common experience is that equation (4) is valid in a narrow range of temperatures. Following this precedent we calculated E values for the different oligomers. They are shown in *Table 3* and are plotted as a function of $1/M_n$ in *Figure 6*. While the correlation factors are not perfect, this plot gives some notion of how E might relate to structure. With further work it might prove useful to correlate oligomer structure with E values and to use such plots as a way of comparing oligomers.

The data in *Figure 6* suggest that linear oligomers may have lower E values than non-linear ones. If true, this would be consistent with literature E values for high polymers, where a wealth of data is available.[9] Examples are shown in *Table* 4. Linear polyethylene has the lowest E values, and E generally increases as the bulk of side chain branches increases. Branches, even methyl groups, on high polymers increase the resistance to flow and the E value. Our results for oligomers fit this pattern. Thus, it can be postulated that linear oligomers will have lower viscosities than any other kind of oligomers, other factors being equal.

This hypothesis makes intuitive sense on a physical basis. It seems plausible that slender oligomers should be able to "swim" past one another more readily than bulky ones. If they become partly aligned in a shear stress field, linear oligomers would present a smaller cross-section transverse to the stress than non-linear oligomers and might be expected to offer less resistance to flow. They could flow into smaller "holes" between molecules in the liquid. Analogous explanations have been postulated to explain observations that n-alkane solvents evaporate faster from polymer films than isomeric branched alkanes, even though the branched alkanes evaporate faster by themselves.[17] Oligomer flow and solvent diffusion through polymers are related phenomena. A difficulty with this hypothesis is that it implies that there should be a correlation between T_g and viscosity, but no such correlation was observed. Further study of the relationships among viscosity, T_g, and molecular shape is needed to clarify this situation.

The Williams-Landel-Ferry (WLF) equation correlates the dependence of viscosity on temperature for a wide variety of high polymer melts.[9] It can, with several assumptions described by Hill et al.,[18] be simplified to equation (5).

$$\log \eta = 13 - \frac{A(T - T_g)}{B + (T - T_g)} \qquad (5)$$

Where η = viscosity at the measurement temperature
T = measurement temperature
T_g = glass transition temperature
A and B = constants
13 = log of viscosity in poise at T_g (approximate)

Since values of A and B are similar for many high polymer melts, Nielsen[19] assigned approximate "universal" values A = 17.44 (when base 10 logarithms are used) and B = 51.6. A limitation is that the WLF equation is considered valid only in the temperature range between T_g and about T_g + 100 K.

Wicks et al.[16] showed that the WLF equation (5) "provides a better model of viscosity as function of temperature than an Arrhenius type expression" (4) for acrylic oligomer solutions and "for a wide range of other oligomers and other oligomer solutions." However, they observed that A and B are not universal constants, but vary with the system and with the concentration of solutions of a given oligomer. Others have made similar observations.

We measured the viscosity of oligoesters based on 1,4-BD at temperatures of 298-333 K (25-60°C). Representative T_gs are shown in *Table 1*, where it can be seen that our data were
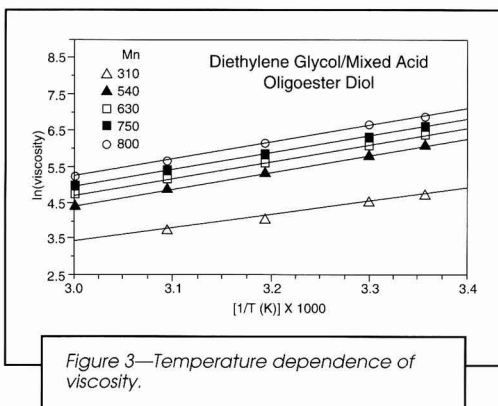
Figure 3—Temperature dependence of viscosity.
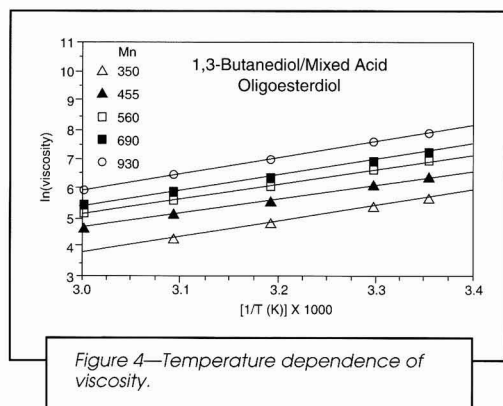
Figure 4—Temperature dependence of viscosity.

Figure 5—Temperature dependence of viscosity.
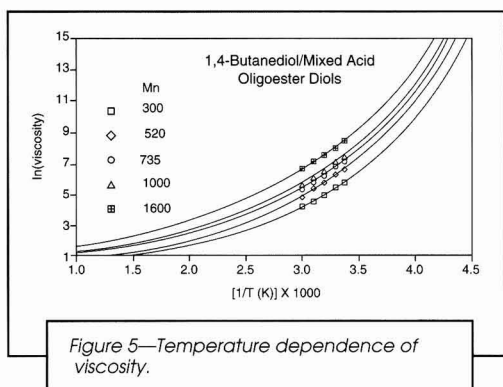
obtained in the range $T_g + 91$ K to $T_g + 158$ K, largely outside the range at which the WLF equation is considered valid. Nonetheless, WLF plots of these oligomers (*Figure* 7) gave straight lines. However, the values of the purported constants, A and B, differed substantially from the universal values and generally decreased with increasing M_n. Representative values for 1,4-BD oligoester diols were:

$\underline{M_n}$	$\underline{A}$	$\underline{B}$
300	16.2	35.1
520	15.8	32.1
735	15.5	30.8
1600	14.9	29.7

WLF plots for oligoesters based on DEG and 1,3-BD gave similar results.

Thus, the WLF equation may provide a useful model at temperatures ranging up to $T_g + 150$ K or higher, but the constants A and B can be expected to vary for each oligomer.

DEPENDENCE OF VISCOSITY ON M_n—As shown in *Figure* 8, the relationship of viscosity to M_n for oligoesters of 1,4-BD can be modeled by equation (6).

$$\ln \eta = B + C(\ln M_n) \tag{6}$$

Figure 6—Influence of M_n on Arrhenius flow activation energy, E, of various mixed acid/oligoesterdiols.
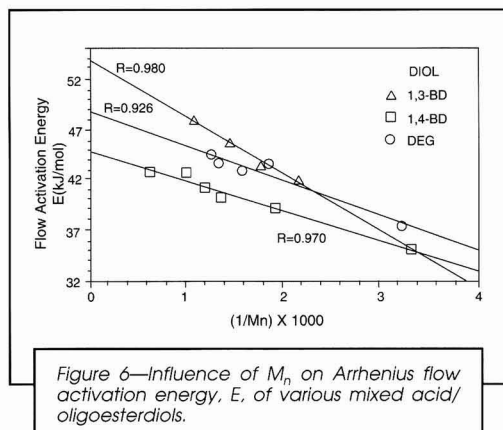
Here η is the viscosity (which must be Newtonian) and B and C are constants. Plots similar to *Figure* 8 were obtained for oligoesters based on 1,3-BD and DEG. All these oligoesters were essentially Newtonian in the range of shear rates from 0.5 to 20 sec^{-1}.

Holda[20] proposed equation (6) in 1972. He found it to be widely applicable, although not completely general. It works well for polyester powder coating resin melts. Fox and Losheak[21] proposed a similar equation for high polymer melts where viscosity is extrapolated to zero shear rate and M_w rather than M_n is used.

DEPENDENCE OF GLASS TRANSITION TEMPERATURE ON M_n—For all oligoester diols studied, T_g (measured by DSC) was related to M_n by equation (7).

$$T_g = T_{g\infty} - \frac{K}{M_n} \tag{7}$$

A plot of T_g vs $1/M_n$ for the oligomers made from 1,4-BD is shown in *Figure* 9. The other oligomers gave similar patterns. Note that the intercept is T_g at infinite M_n, 210 K in this case. This result is no surprise. Equation (7) is theoretically well founded and describes the behavior of many other oligomers and polymers.[22]

DEPENDENCE OF MELTING POINT ON M_n—As shown in *Figure* 10, these parameters are approximately related by equation (8), similar in form to equation (7). T_m was measured by DSC.

$$T_m = T_{m\infty} - \frac{K}{M_n} \tag{8}$$

FORMULATING WITH LINEAR OLIGOESTER DIOLS

Solventless Coatings

BACKGROUND—We have been trying to learn how to formulate good coatings with linear oligoester diols without using solvent. The program is still underway, and further progress is anticipated. Here we will outline what we have learned so far and will give a few exemplary formulas.

As shown in *Table* 1, linear diols with M_n less than 700 have viscosities below 800 mPa·s at 25°C. If combined with crosslinkers of similar viscosity they should make solventless liquid formulations that meet our arbitrary viscosity goal, <800 mPa·s. Both melamine resin and polyisocyanate crosslinkers with viscosities in the desired range are available.

POLYISOCYANATE CROSSLINKERS—Simple clearcoat formulations with aliphatic polyisocyanate crosslinkers gave low VOCs and excellent film properties. An example is shown in *Table* 5. This formulation employs a low-viscosity polyisocyanate derived from hexamethylene diisocyanate using technology described by Wojcik.[23] Viscosity is 560 mPa·s. Because there are no volatile crosslinking reaction by-products, the VOC is very low, 8 g/L. This formulation is a two-package system with a pot life of about three hours. (Pot life is taken as the time at 25°C after mixing the two components before the viscosity doubles.) Three-hour pot life is possible only if oligoester diols made with very low levels (0.01 wt%) of zinc
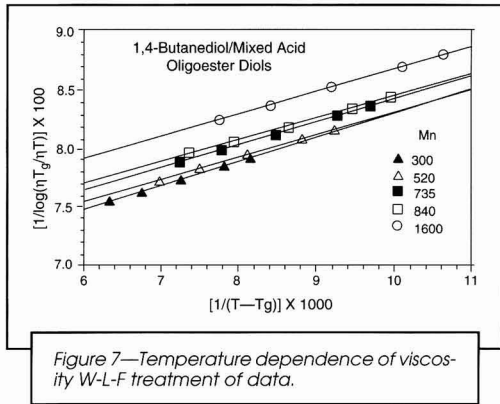
Figure 7—Temperature dependence of viscosity W-L-F treatment of data.

Table 5—A Solventless Two-Package Polyurethane

Component	Weight %
Diol, M_n = 315	39
Di/triisocyanate[a]	61
BYK-077[b]	0.4
Total	100.4
Viscosity, 25°C, mPa·s	560
NVW, wt%, 110°C	99.1
VOC, g/L	8
Bake 120°C for 30 min	
Hardness, pencil	4H
Impact resistance, D/R, in-lb	160/160
Adhesion, X-hatch	5B
Solvent resistance, MEK double rubs	>200

(a) Luxate XHD-0700 (Olin).
(b) BYK-Chemie.

acetate dihydrate catalyst are used. The presence of 0.1-0.2 wt% of $Zn(OAc)_2 \cdot H_2O$ residues in the oligomer drastically shortens pot life. Oligoester diols made with non-metal catalysts, such as 0.01 wt% of methane sulfonic acid, are also usable and give pot lives of several hours.

Besides being a two-package system, the formulation in *Table 5* has the drawbacks of requiring careful handling to minimize worker exposure to the polyisocyanate and of requiring a very high proportion of isocyanate, which would increase cost. The proportion of isocyanate can, of course, be reduced by increasing the M_n of the diol, but this results in higher, though perhaps still acceptable, viscosity and softer, though still useful, films.

MELAMINE RESIN CROSSLINKERS—More economical, one-package coatings can be formulated with melamine resin crosslinkers, but it is much more challenging to get good film properties. Simple formulations of linear diols with methylolated hexamethoxy methyl melamine resins with high monomer content (such as Cymel 300 or Resimene 2612) or with low-viscosity mixed ether melamine resins (such as Cymel 1135 or Resimene 755) can give viscosities in the range of 400 to 700 mPa·s at 25°C. For example, an acid catalyzed formulation using an oligoester diol of M_n = 735 and a mixed ether melamine resin in a 70/30 wt ratio had a viscosity of 520 mPa·s. It cured sufficiently to have excellent solvent resistance when baked at 150°C for 30 min, but the coating film was too soft (pencil hardness F) for most applications. The softness was not unexpected in view of the very low T_g (−78°C) of the oligomer and its difunctionality, which is expected to result in lower crosslink density than conventional polyester resins having similar M_n but higher functionality. What was surprising is that the films also had poor (0B) adhesion to pretreated (Q-phos) steel panels. Adhesion to primers was much better. While such formulations are solventless, it should be noted that they typically have VOCs on the order of 100 g/L and sometimes higher. The VOCs are composed primarily of alcohols evolved during the crosslinking reaction and of a small fraction of the oligoester diols volatilized during bake.

Ways to overcome the film property deficiencies of simple melamine/oligoester formulations were sought. Simply adjusting the oligoester M_n, the melamine resin type, the proportions, and the cure conditions shifted the balance of film

Figure 8—Influence of M_n on viscosity.

Table 6—Water-Thinnable Solventless Polyurethane

Component	Weight %
Oligoester diol[a]	60.6
Triisocyanate[b]	36.5
Water	2.9
Total	100

(a) Prepared with 0.01 wt% methane sulfonic acid catalyst; M_n = 300
(b) HDI biuret, Desmodur N-3200, Bayer.
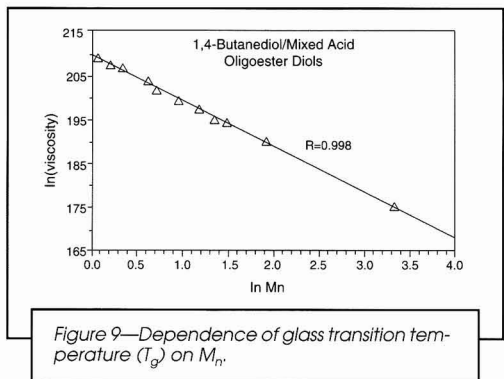
Figure 9—Dependence of glass transition temperature (T_g) on M_n.

Figure 10—Dependence of melting point (T_m) on M_n.

Figure 11—Viscosity reduction by water addition.

Figure 12—Viscosity reduction by water addition to 70/30 oligoesterdiol/HMMM solution.
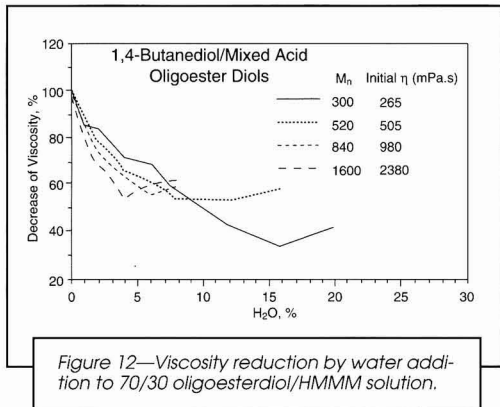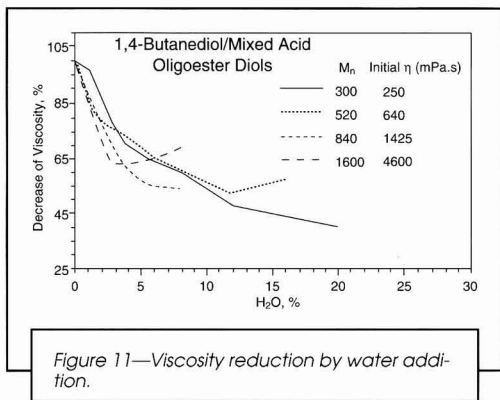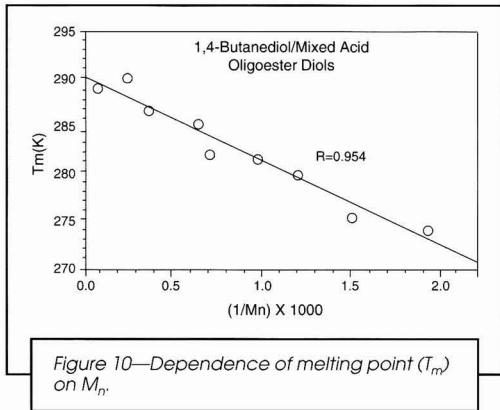
properties but fell short of our ultimate goal of film properties equal to the best contemporary coatings for demanding applications. Harder films can be obtained by using oligomers with lower M_n to increase crosslink density. However, because we usually formulate these coatings with about a 50% stoichiometric excess of melamine resin, oligomers with low M_n require very high proportions of melamine resin and give off considerable VOC during cure.

"Hardeners," other ingredients that could be added to the simple formulations to improve hardness and adhesion, were then studied. Examples of substances that showed promise among the many tested are:
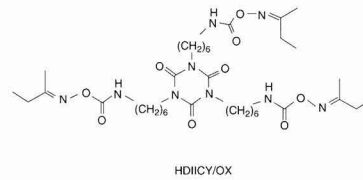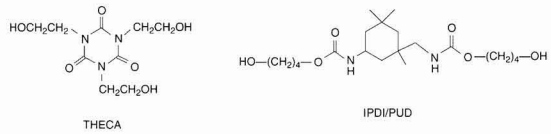
These three substances are commercially available or can be made in one step from commercially available materials. A variety of blocked isocyanates can be used: HDIICY/OX is only one example. Similarly, IPDI/PUD is just one example of a polyurethane diol; others can be used.

These and similar hardeners were tested in a variety of formulations. In general it can be said that all make films substantially harder, and most improve adhesion to metal. Hardeners that leave residual urethane groups (HDIICY/OX and IPDI/PUD) are especially effective adhesion promoters.

A drawback of these hardeners is that they increase viscosity of the formulations. In certain cases, notably with TH-ECA, there are also miscibility limitations. It is possible to stay within our viscosity goals only if modest amounts of the hardeners are used. Low viscosity formulations with limited hardener content have film properties that might be satisfactory for some industrial coating applications, but not for the majority.

PIGMENTED SOLVENTLESS COATINGS—Pigmented solventless coatings can be formulated by conventional means. The volume of pigment that can be used without increasing viscosity above 800 mPa·s is, of course, limited. It is possible to disperse 12 to 15 vol% of TiO_2 pigments without substantially increasing viscosity providing pigment dispersion stabilizers are used to obtain a deflocculated dispersion. Commercial stabilizers designed for use in solvent-borne coatings are satisfactory. Such pigmented solventless coatings can have good gloss and hiding at film thicknesses of 25 μm. The pigment often has a modest hardening effect on the films obtained from such formulations, giving properties that might be satisfactory for some applications.

Incremental improvements could no doubt be made by further formulating refinements. However, our attention turned

to another expedient that might make it possible to use higher levels of hardeners and still meet the viscosity goal of <800 mPa·s at 25°C. This expedient is adding water.

Water-Thinnable Solventless Coatings

BACKGROUND—We observed that solventless formulations can dissolve limited amounts of water (up to 20 wt% depending on the formulation) and that adding water, usually 5 to 15 wt%, reduces viscosity by 40 to 60%. There is little or no effect on coating film properties.

We call such formulations "water-thinnable solventless coatings" to differentiate them from the commonly used "water-reducible" coatings. The latter formulations contain coupling solvents and volatile amine, both sources of air pollution. Water-thinnable formulations contain no solvents or amines. However, water-thinnable formulations can dissolve only limited amounts of water, so it is desirable to start with a low viscosity formulation before thinning.

Addition of small amounts of water to solvent-borne coatings to reduce viscosity is an old formulation trick, especially in epoxy coatings. Water thinnable solvent-borne polyester/ melamine resin coatings have been described.[25] In this case we propose to thin solventless decorative coatings with water.

We are in the middle of a program to learn to formulate water-thinnable solventless coatings. While the program is incomplete, preliminary results are summarized here.

UNPIGMENTED WATER-THINNABLE SOLVENTLESS COATINGS—The effect on viscosity of adding water to linear oligoester diols made from 1,4-BD is shown in *Figure* 11. In this figure, the percentage reduction of viscosity is plotted as a function of the amount of water added. Of course, the starting viscosity varies with M_n of the oligomers, as indicated. Adding a few percent of water to each oligomer sharply reduces viscosity; the mixtures are transparent at this stage and appear to be true solutions of water in diol. Presumably the sharp viscosity reduction results from disruption of hydrogen bonding among the diol molecules by water. As more and more water is added, viscosity reduction continues, but the curve is less steep. Still more water causes the curve to level off, and the solution becomes turbid. Finally, with more water, macro phase separation occurs. Typical curves research their lowest levels at about the point where turbidity is first observed. The amount of water that can be added without turbidity decreases as M_n of the oligoester diol increases; the oligomer of M_n 300 can dissolve 20% of its weight of water, while the one having M_n of 1600 becomes turbid after only 4 wt% is added. The percentage effect of adding small amounts of water (1-3 wt%) is greatest with high M_n oligoesters and decreases as M_n decreases. Oligoester diols in the M_n range 300-900, the range of greatest interest for water-thinnable coatings, can dissolve enough water at 25°C to reduce viscosity by 40 to 55%.

What about oligoester diol/crosslinker solutions? As shown in *Figure* 12, the effect of adding water to 70/30 oligoester diol/melamine resin solutions is very similar to the effect of adding it to the diol alone. In this case a nearly monomeric methylolated melamine resin (HMMM, "Resimene 2612") was used. With the oligomer of $M_n = 300$, viscosity can be reduced by as much as two-thirds. While they are not entirely water soluble, HMMM resins are soluble in water/solvent blends, and it is not surprising that their solutions in oligoester diols are partially miscible with water.
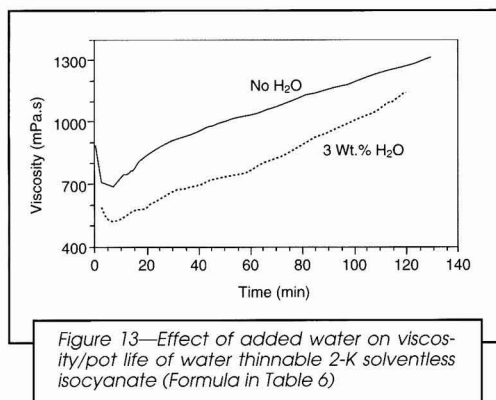
Figure 13—Effect of added water on viscosity/pot life of water thinnable 2-K solventless isocyanate (Formula in Table 6)

Freshly prepared solutions of diols with isocyanate crosslinkers can also dissolve water. Water has little effect on pot life. As with melamine resins, small amounts sharply reduce viscosity. An example is the simple oligoester diol/ triisocyanate formulation shown in *Table* 6. The effect of adding 3 wt% of water to this formulation is shown in *Figure* 13. Viscosity is reduced from 700 to 500 mPa·s, and then gradually doubles in about two hours. Not shown in *Figure* 6 is the fact that both solutions gel in about five hours. It should also be noted that such formulations are sometimes hazy when initially mixed with or without water; they clear up in an hour or two. The rate of viscosity increase is similar with or without water. In this case the oligoester diol was synthesized using 0.01 wt% of p-toluenesulfonic acid as the transesterification catalyst. Oligoester diols synthesized with 0.01 wt% of $Zn(OAc)_2 \cdot 2H_2O$ catalyst give similar results. While adding water had little effect on pot life, it did affect film properties in

Table 7—A Water-Thinnable Solventless Coating

Component	Weight %
Diol, $M_n = 313$	24.8
PUD[a] (88% in water)	24.8
HDIICY/OX[b]	19.3
HMMM[c]	19.1
Surface tension modifier[d]	0.3
DNNDSA[e]	0.5
Water (to a total of 13.6%)	10.6
Total	100

Viscosity, mPa·s, 25°C, 2 sec^{-1} 450

Bake at 140°C for 30 min:

Film Properties

Film thickness, μm	20
Hardness, pencil	2H
Impact resistance, D/R, in-lb	160/100
Adhesion, X-hatch	4B
Solvent resistance, MEK double rubs	>200
NVW, wt%, 110°C	80

(a) UD-320W (King Industries); 88% solids in water.
(b) Isocyanurate derived from hexamethylene diisocyanate (Desmodur N-3300, Bayer) blocked with 2-butanone oxime.
(c) Resimene HM-2612 melamine resin (Monsanto).
(d) BYK-301 (BYK).
(e) Dinonylnaphthalene disulfonic acid catalyst (King Industries).

Table 8—A Pigmented Water-Thinnable Solventless Coating

Component	Weight %
Oligoester diol, M_n = 313	14.84
PUD[a] (88% in water)	14.84
HDIICY/OX[b]	11.36
HMMM[c]	11.29
BYK-302 (BYK)	0.17
FC 430 (3M)	0.08
DNNDSA	0.26
Dispersion stabilizer[d]	3.39
TiO$_2$[e]	32.44
Disperse by HSD.	
Stir in "free water"	11.33[f]
Total	100
Viscosity, mPa·s, 25°C, 2 sec^{-1}	1200
10,000 sec^{-1}	560
Bake, 30 min, °C	140
Film thickness, μm	22-25
Hardness, pencil	3H
Impact resistance, D/R, in-lb	160/100
Adhesion, X-hatch	4B
Solvent resistance, MEK double rubs	>200

(a) UD-320W (King Industries); 88% solids in water.
(b) Desmodur N-3300 (Bayer) blocked with 2-butanone oxime.
(c) Resimene HM 2612 (Monsanto).
(d) Joncryl-60 (SC Johnson); 34% in water.
(e) R-900 (DuPont).
(f) Total water content: 15.35 wt%. Sources of water: PUD, 1.78 wt%; Joncryl 60, 2.24 wt%; and "Free" water, 11.33 wt%.

some circumstances. When the formulations similar to the ones in *Figure* 13 were cured at ambient temperature, the one without water gave better film properties than the one with water. However, when the two formulations were quickly baked at 110°C after application, both gave excellent and similar film properties.

The package stability of the water thinned triisocyanate/ diol solutions may seem surprising in view of the reactivity of isocyanates with water. However, in recent years it has been recognized that reaction with water is slow enough to permit formulation of two-component, water-reducible polyurethane coatings. Jacobs and Yu[25] gave examples of such polyurethanes and showed that a solution of an aliphatic isocyanate and water react only to the extent of five percent in four hours at 25°C.

The compatibility of solventless formulations with water greatly expands formulating latitude. The expanded latitude is especially useful with melamine crosslinked formulations, because it becomes possible to use larger amounts of hardeners and, by thinning with water, still achieve our arbitrary target viscosity of <800 mPa·s at 25°C.

Hardeners vary in their effect on the formulation's ability to dissolve water. IPDI/PUD seems to increase the amount of water a formulation can tolerate, while HDIICY/OX reduces it. THECA was not studied. Other polyurethane diols (PUDs) behave similarly to IPDI/PUD. A low molecular weight PUD is available commercially and seems well suited as a component of water-thinnable solventless formulations. It is presumably the PUD described by Blank.[26]

An example of an unpigmented water-thinnable solventless formulation that gives good film properties is shown in *Table* 7. It employs two binder components with a high

affinity for water (an oligoester diol of low M_n and the commercial PUD described), a third which is neutral toward water (HMMM resin), and a fourth which is relatively hydrophobic but is beneficial to film properties (HDIICY/OX). This formulation remains transparent and stable even with the addition of as much as 13.6 wt% water. This amount of water gives a viscosity of 450 mPa·s at 25°C. The measured NVW is 80 wt%, but this is somewhat misleading because the ASTM standard measurement temperature, 110°C, is lower than the bake temperature required for good cure.

PIGMENTED WATER-THINNABLE SOLVENTLESS COATINGS— Formulation of pigmented water-thinnable solventless coatings poses an unusual challenge. These coatings are in "no man's land" between solvent-borne and waterborne coatings. Additives intended specifically for one type of coating or the other sometimes do not work very well in water-thinnable formulations. Pigment dispersion stabilizers are an example.

Various pigment dispersion stabilizers were screened in pigmented solventless formulations based on the binder combination in *Table* 7. Generally, stabilizers that give deflocculated dispersions before thinning with water cause severe flocculation after thinning. Stabilizers designed for waterborne coatings tend to have the inverse problem. The most useful stabilizer identified so far is "Joncryl-60," said to be an acrylic acid copolymer. A formulation employing this stabilizer is shown in *Table* 8. The pigment is dispersed using a high-speed disperser before free water is added, although it should be noted that the dispersant and the PUD bring about four percent water into the formulation at the grind stage. The result is a pasty, highly flocculated dispersion. Its shear thinning characteristics allow satisfactory deagglomeration during grinding. Incremental addition of free water at first has little effect, but when enough water is added to bring the total water content to about 15 wt%, the dispersion deflocculates. The result is a fluid, slightly shear thinning liquid with a viscosity of 1200 mPa·s at a shear rate of 2 sec^{-1} and 530 mPa·s

Table 9—A Water- and Acetone-Thinnable Exempt Solvent Coating

Component	Weight %
Diol[a], M_n = 329	27.9
Polyurethane diol[b]	28.0
HDIICY/OX[c]	21.7
HMMM[d]	21.5
BYK-301 (BYK)	0.3
DNNDSA[e]	0.6
Total	100
Let stand 14 hr to release air.	
Measure Initial viscosity, then add	
Acetone	6 phr
Measure viscosity A6, then add	
Water	6 phr
Measure viscosity A6+W6, then add	
Water	6 phr
Measure viscosity A6+W12, then add	
Water	6 phr
Measure viscosity A6+W18.	

(a) Oligoester diol made from 1,4-BD and a 50/50 (mol) mixture of glutaric and adipic acids.
(b) UD-320W (King Industries); 88% solids in water.
(c) Isocyanurate derived from hexamethylene diisocyanate (Desmodur N-3300, Bayer) blocked with 2-butanone oxime.
(d) Resimene HM-2612 melamine resin (Monsanto).
(e) Dinonylnaphthalene disulfonic acid. (Not added until viscosity studies were completed).

when measured on the ICI viscometer (estimated shear rate: 10,000 sec⁻¹). Such formulations can be applied with a conventional suction spray gun at 25°C to give glossy coatings. Very good film properties are attainable, as exemplified in *Table 8.*

It was hoped that these rheological characteristics would help control sagging after spray and during bake. Perhaps as water evaporates, low shear viscosity would rise and sag resistance would be imparted. This hope is not yet fully realized. Some sag resistance may have been imparted, but sagging was still evident when panels were sprayed in a vertical position.

Some pigmented formulations appear to have a higher capacity to dissolve water than their unpigmented counterparts. With pigment present it is difficult to judge the physical condition of the water; perhaps part of the water dissolved and part is emulsified by the pigment dispersion stabilizers and/or associated with the pigment surface. For example, the formulation shown in *Table 7* can accept 13.6 wt% of water but not much more. The pigmented formulation of *Table 8*, with a similar binder system, can accept 22.7 wt% of water calculated on the weight of the binder. The formulation in *Table 8* seems stable for at least a month at 25°C, but in other cases we have observed that water-thinned formulations that initially appear uniform may stratify within a few days. Stability usually decreases as the amount of water in excess of the capacity of the binder increases.

SOLVENTLESS COATINGS THINNED WITH WATER AND ACETONE—Acetone was recently exempted from VOC control regulations by the U.S. Environmental Protection Agency. This change prompted a brief study of the possibility of using modest amounts of acetone in addition to water to thin solventless coatings. A typical formulation and thinning procedure are shown in *Table 9.* In this formulation a linear oligoester diol made from 1,4-butanediol and a 1/1 mol ratio mixture of dimethyl glutarate and dimethyl adipate was used; otherwise the formula was very similar to the water-thinnable formulation given in *Table 7*, and it gives similar film properties.

Acetone by itself proved to be an efficient viscosity reducer, and it has the additional advantage of increasing the capacity of coatings to dissolve water. The combination makes very substantial viscosity reductions possible. As shown in *Table 10*, the viscosity of the formulation in *Table 9* at 2 sec⁻¹ and 25°C is reduced from 2450 to 780 mPa·s by thinning with 6 phr (parts per hundred) of acetone. The resulting acetone-thinned coating can dissolve more than 20 parts per hundred of water, with additional sharp viscosity reduction, as shown in *Table 10*. Catalyst was excluded from this formulation until the viscosity measurements were complete to assure that crosslinking reactions do not begin to increase viscosity prematurely. It should be noted that such formulations typically display moderately shear thinning rheology in the shear rate range 1 to 20 sec⁻¹, as illustrated in *Table 10*. The solutions appear transparent. The reasons for the apparent small degree of shear thinning indicated in *Table 10* are not known; an instrument artifact is suspected.

CONCLUSION

It was demonstrated that linear oligoester diols have lower viscosities than oligoester diols with comparable M_n made

Table 10—Effect of Acetone and Water on Viscosity of an Exempt Solvent Coating (Formula: *Table 9*)

Shear Rate, sec⁻¹	Viscosity, mPa·s, 25°C				
	Initial	A6	A6+W6	A6+W12	A6+W18
1	2700	830	480	330	240
2	2450	780	460	300	220
4	2300	720	440	290	220
10	—	660	390	270	200

from diol monomers with methyl side groups. Linear diols of M_n less than 700 have viscosities less than 800 mPa·s and are, therefore, candidates for formulation into solventless coatings. Several quantitative relationships relating viscosity to M_n and temperature were demonstrated.

Linear oligoester diols can be formulated with low-viscosity polyisocyanates to make two-package solventless coatings with excellent film properties and very low VOC. Formulation of one-package coatings with melamine resins is more difficult. Addition of hardeners improves film properties, but increases viscosity. Formulation latitude is constrained by the need to keep viscosity low for application.

Formulation latitude can be greatly increased by thinning the formulations with water. This expedient reduces viscosity by about 50% and sometimes more. This makes it possible to use substantial amounts of hardeners and attain good film properties while keeping viscosity below 800 mPa·s. Formulating latitude can be further broadened by adding a combination of acetone and water. Two-package polyisocyanate crosslinked coatings can also be thinned with water with little adverse effect on pot-life.

ACKNOWLEDGMENTS

References

(1) Fu, S., Hua, J., Zhang, S., Jing, W., Yan, Q., Subrayan, R., and Jones, F.N., "Low-Viscosity Oligoester Diols. I. Oligomers of 1,4-Butanediol with Mixed Dicarboxylic Acids, HOOC(CH₂)ₙCOOH," in manuscript.

(2) Zhang, S., Fu, S., Jing, W., Yan, Q., Subrayan, R., and Jones, F.N., "Low-Viscosity Oligoester Diols. II. Oligomers of 1,3-Butanediol, Diethylene Glycol, and Neopentyl Glycol with Mixed Dicarboxylic Acids, HOOC(CH₂)ₙCOOH," in manuscript.

(3) Subrayan, R., Fu, S., Hua, J., Zhang, S., Jing, W., Yan, Q., Yuan, X., and Jones, F.N., "Solventless Coatings Based on Low-Viscosity Oligoester Diols," in preparation.

(4) Fu, S., Jing, W., Subrayan, R., Zhang, S., Yan, Q., and Jones, F.N., "Water-Thinnable Solventless Coatings Based on Low-Viscosity Oligoester Diols," in preparation.

(5) Gerhart, H.L., in Craver, J.K. and Tess, R.W., (Eds.), "Applied Polymer Science," Organic Coatings and Plastics Chemistry Division of the American Chemical Society, p. 11, 1975.

(6) Henshaw, B.C. and Leary, B., "Thermosetting Coating Compositions," U.S. Patent 3,857,817 (1974). To Dulux Australia, 994,851 (1976).

(7) Schrantz, J., *Mod. Paint Coat.*, 74-77, September 1994.

(8) Hill, L.W. and Wicks, Z.W. Jr., "Design Considerations for High-Solids Coatings," *Prog. Org. Coat.*, 10, 55 (1982).

(9) Kumar, N.G., "Viscosity-Molecular Weight-Temperature-Shear Rate Relationships of Polymer Melts; A Literature Review," *J. Polymer Sci.: Macromol. Rev.*, 15, 255-325 (1980).

(10) Ober, C.K. and Weiss, R.A., "Current Topics in Liquid-Crystalline Polymers," in Weiss, R.A. and Ober, C.K., (Eds.), *Liquid-Crystalline Polymers*, ACS Symp. Ser. 435, American Chemical Society, p. 9-10, Washington, 1990.

(11) Teng, G., Du, C., Wang, D-Z, Dimian, A.F., and Jones, F.N., "Liquid Crystalline Oligoesters Containing Single-Ring Aromatic Units Separated by Aliphatic Spacers," *Polymer Mater. Sci. Eng.*, 65, 33 (1991).

(12) Teng, G. and Jones, F.N., "High Solids Non-Aqueous Dispersion Coatings Based on Crystalline Oligoesters," JOURNAL OF COATINGS TECHNOLOGY, 66, No. 829, 31 (1994).

(13) Teng, G. and Jones, F.N., "End-Grafting of Oligoesters Based on Terephthalic Acid and Linear Diols for High Solids Coatings," *J. Appl. Polymer Sci.*, in press.

(14) Patton, T.C., "Paint Flow and Pigment Dispersion," 2nd Ed., Wiley-Interscience, p 93, 103, New York, 1979.

(15) Brock, W.H., "History of Chemistry," Norton, London, 1992.

(16) Wicks, Z.W. Jr., Jacobs, G.F., Lin, I-C., Urruti, E.H., and Fitzgerald, L., "Viscosity of Oligomer Solutions," JOURNAL OF COATINGS TECHNOLOGY, 57, No. 725, 51 (1985).

(17) Ellis, W.H., "Comparative Solvent Evaporation Mechanisms for Conventional and High Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, 55, No. 696, 63 (1983).

(18) Hill, L.W., Kozlowski, K., and Sholes, R.L., "Theory and Practice of Viscosity Reduction in High Solids Systems," JOURNAL OF COATINGS TECHNOLOGY, 54, No. 692, 67 (1982).

(19) Nielsen, L.E., *Polymer Rheology*, Marcel Dekker, New York, 1977.

(20) Holda, E.M., JOURNAL OF PAINT TECHNOLOGY, 44, No. 570, 75 (1972).

(21) Fox, T.G. and Losheak, S., in "Rheology IV," Eirich, F.R. (Ed.), Academic Press, New York.

(22) Fox, T.G. and Losheak, S., *J. Polymer Sci.*, 15, 371 (1955).

(23) Wojcik, R.T., "Low Viscosity Polyisocyanates for Higher Solids Coatings," *Polymer Mater. Sci. Eng.*, 70, 116 (1994).

(24) Olson, M.R., Larson, J.M., and Jones, F.N., "Water-Extendible High-Solids Enamels," JOURNAL OF COATINGS TECHNOLOGY, 55, No. 699, 45 (1983).

(25) Jacobs, P.B. and Yu, P.C., "Two-Component Waterborne Polyurethane Coatings," JOURNAL OF COATINGS TECHNOLOGY, 65, No. 822, 45 (1993).

(26) Blank, W.J., "Polyurethane Oligomers for Waterborne and High-Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, 60, No. 764, 43 (1988).

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Regulatory Update January 1996

Department of Labor
Occupational Safety and Health Administration
November 7, 1995 - 60 FR 56127
Respiratory Protection
Action: Reopening the record for comments

On November 15, 1994, the Occupational Safety and Health Administration (OSHA) published proposed revisions to the Respiratory Protection Standard. Following an extended comment period and public hearings, OSHA contracted with Dr. Mark Nicas to prepare recommendations for evaluating protection factor studies and combining information across studies for use in setting assigned protection factors (APFs). OSHA is considering using the recommendations included in that report as an aid in establishing APFs for the final Respiratory Protection Standard.

Therefore, OSHA is reopening the record for the Respiratory Protection Standard for the purpose of receiving public comments on the Nicas report. Comments should address the appropriateness and completeness of the issues identified, the statistical methodology, and the solutions offered for other issues. They may also include any additional opinions or information concerning statistical methodologies and evaluation criteria for APF studies.

Written comments must be postmarked on or before January 8, 1996. They should be submitted in quadruplicate or 1 original hardcopy and 1 disk (5 1/4 or 3 1/2 inch) in WordPerfect or ASCII. Any information not contained on a disk must be submitted in quadruplicate. Address comments to: Docket Office, Docket H-049, U.S. Department of Labor, Occupational Safety and Health Administration, Room N-2625, 200 Constitution Ave., N.W., Washington D.C. 20210, (202) 219-7894. Comments that are less than ten pages may be faxed to (202) 219-5046, provided that the original and three copies are submitted thereafter.

For additional information, contact Anne Cyr, OSHA, (202) 219-8148. To receive a copy of the Nicas Report, contact John Steelnack, (202) 219-7151. Electronic copies are available through the Labor News Bulletin Board, (202) 219-4748 or through OSHA's WebPage, http://www.osha.gov/.

Environmental Protection Agency
December 7, 1995— 60 FR 62930
National Emission Standards for Hazardous Air Pollutants; Final Standards for Hazardous Air Pollutant Emissions from Wood Furniture Manufacturing Operations
Action: Final rule and test method

This final rule promulgates standards that limit the emissions of hazardous air pollutants (HAPs) from new and existing wood furniture manufacturing operations located at major sources, as required by Section 112(b) of the Clean Air Act. Under the regulation, major sources must control emissions to the level attainable by implementing the maximum achievable control technology (MACT), taking into consideration the cost of achieving such emission reductions, air quality-related health and environmental impacts, and energy requirements. The regulation was developed through a regulatory negotiation in cooperation with industry.

The EPA is also finalizing Method 311 with the standards which will be used to assist in demonstrating compliance with the emissions limitations.

A background information document (BID) for the promulgated NESHAP may be obtained from the EPA Air and Radiation Docket and Information Center, (202) 260-7548; or from the U.S. EPA Library, (919) 541-2777. Electronic versions of the BID and of the final rule are available from the EPA Technology Transfer Network bulletin board at (919) 541-5742.

For additional information, contact Paul Almodovar, Coatings and Consumer Products Group, EPA, (919) 541-0283.

Department of Health & Human Services National Institute for Occupational Safety and Health
November 6, 1995 - 60 FR 56060
National Occupational Research Agenda
Action: Notice

The National Institute for Occupational Safety and Health (NIOSH) is developing a national agenda for occupational safety and health research for the next decade. The program, called the National Occupational Research Agenda (NORA), is designed to help organizations in the private and public sectors to coordinate research activities and to target the highest scientific priorities for preventing work injuries and illnesses.

As part of the process of gathering information and input from the public, NIOSH is scheduling a series of meetings in which the public is invited to participate. The first meeting was held on November 6. The final agenda is scheduled to be issued in April, 1996.

NIOSH encourages both oral comments at meetings, as well as the submission of written comments, which must be received by March 6, 1996. Address comments to Diane Manning, NIOSH, Robert A. Taft Laboratories, M/S C34, 4676 Columbia Parkway, Cincinnati, OH

45226. For further information on NORA, contact Sandy Lange, NIOSH, (202) 401-0721.

Environmental Protection Agency—On November 28, the U.S. Environmental Protection Agency published its semi-annual regulatory agenda, highlighting the agency's future goals concerning proposed rulemakings, final regulations, and notices.

Hazardous Waste—EPA plans to issue several proposals designed to help streamline requirements for the management of hazardous waste under RCRA. Two rules which would exempt specific low-risk hazardous waste from RCRA Subtitle C requirements will be published within the next few months. EPA also plans to finalize a land disposal restriction rule focusing on whether de-characterized wastewater falls under RCRA treatment standards.

Air Quality—According to the agenda, the agency will propose a number of regulations dealing with air pollution control. Included are rules which will amend the operating permit program and the new source review program for stationary sources. These regulations are expected to be published in March and September 1996, respectively. EPA is also planning to amend its compliance assurance monitoring program to make it more flexible, concentrating on pollution prevention techniques. In addition, the EPA hopes to finalize a rule concerning the establishment of

a model open-market trading program for ozone precursors by June 1996.

Toxic Substances—In 1996, EPA plans to publish a proposed rule that will expand the number of sources required to report toxic chemicals to the Toxics Release Inventory (TRI). It is also in the process of developing a proposal for collecting uniform facility identification information under one regulation in order to reduce the regulatory burden.

Lead—Within the next several months, a final rule will be issued which will establish standards for determining hazards associated with lead-based paint and lead-contaminated soil.

Superfund Markup Postponed until 1996—Because Superfund taxes were extended through an amendment in the current budget-reconciliation bill, the House Commerce Committee reportedly has decided to postpone marking up stand-alone Superfund legislation until next year. However, if the President and Congress cannot agree on the budget bill before December 31, the Superfund taxes will formally expire. A renewal of the taxes will require a two-thirds vote under House rules.

Water Quality—EPA plans revisions to the national pollutant discharge elimination system permits program by reducing monitoring and reporting requirements and making permit applications and modifications easier.

House Subcommittee Approves Land Disposal Legislation—The Land Disposal Program Flexibility Act of 1995 (HR 2036), which is sponsored by Representative Oxley (R-OH), was approved by the House Subcommittee on Commerce, Trade, and Hazardous Materials on November 30 for action by the full House Commerce Committee.

Under this bill, characteristic solid waste that is no longer considered to be hazardous and will be disposed of in a surface impoundment or underground injection well is not subject to hazardous waste treatment and disposal regulation under the Resource Conservation and Recovery Act (RCRA). It is part of the administration's "rifle-shot" reform legislation package, designed to amend sections of RCRA that are costly but result in few environmental benefits.

Notice—A rash of deliberately set fires in the stairwells of New York City public housing units has caused the Housing Authority to examine the paint that is being used on the walls, in the stairwells, and in the units themselves. City officials, including the fire chief and some members of the City Council, believe that the many layers of oil-based paint on the walls may have played some role in intensifying the arsonist's fires. As a result, the New York City Housing Authority has issued a "stop work order" on painting with oil-based paint in the public housing units. For more information, call Heidi McAuliffe or Kevin Sall, NPCA, (202) 462-6272.

States Proposed Legislation and Regulations

ALABAMA

Air Quality (Regulation)—The Alabama Department of Environmental Management (DEM) adopted a final rule which revises the definition of "volatile organic compounds" (VOCs) to be consistent with the federal Environmental Protection Agency (EPA) definition and incorporates by reference federal national emission standards for hazardous air pollutants. The rule became effective November 23, 1995. Contact Office of the General Counsel, DEM, (205) 270-5606.

Hazardous Waste (Proposed Regulation)—A proposed rule of the Alabama DEM would revise regulations to incorporate changes to federal EPA hazardous waste standards. Contact Office of General Counsel, DEM, (334) 270-5606.

ARKANSAS

Air Quality (Proposed Regulation)—The Arkansas Department of Pollution Control and Ecology (DPCE) has issued a proposal which would amend regulations in order to separate state and federal requirements for air pollution control, including modifications for permitting of sources that have emissions between 10 to 50 and 50 to 100 tons-per-year. Contact Mike Porta, DPCE, (501) 682-0780.

CALIFORNIA

Hazardous Waste (Regulation)—The California Department of Toxic Substances Control (DTSC) announced the readoption of an emergency rule which revises regulations in reference to the use of tank systems for the transfer, storage,

or treatment of hazardous waste. The rule became effective on October 16, 1995 and extends to January 1, 1998. Contact Joan Ferber, DTSC, (916) 322-6409.

The readoption of an emergency rule, announced by the California DTSC, amends land disposal restrictions and revises standards for permit requirements for hazardous waste. The rule became effective on October 16, 1995. Contact Joan Ferber, DTSC, (916) 324-9933.

Toxic Substances (Proposed Regulation)—The California Environmental Protection Agency (Cal EPA) has issued a notice which announces the consideration of 13 new chemicals which may meet the standard for listing as carcinogens under Proposition 65. Contact Kelli Okuma, Cal EPA, (916) 445-6900.

37A

COLORADO

Air Quality (Regulation)—An emergency rule of the Colorado Department of Public Health and Environment (DPHE), effective September 21, 1995, clarifies federal standards, incorporated by reference, for the control of hazardous air pollutants. Contact Air Quality Control Commission, DPHE, (303) 692-3100.

The Colorado Air Quality Control Commission (AQCC) adopted a rule which adds federal maximum achievable control technology (MACT) monitoring and reporting requirements to current standards, affecting halogenated solvent degreasers and epoxy resin producers. The rule became effective on December 10, 1995. Contact Technical Secretary, AQCC, (303) 692-2000.

Water Quality (Proposed Regulation)—The Colorado DPHE has proposed amendments to regulations which would clarify that a Colorado Discharge Permit System (CDPS) permit is necessary for any non-stormwater discharge of pollutants from any industrial, commercial, or sanitary system into the stormwater. Stormwater discharges are not impacted by this regulation. A hearing on this proposal will be held on February 12, 1996. Contact DPHE, (303) 692-3520.

DELAWARE

Hazardous Waste (Proposed Regulation)—A proposed rule of the Delaware Department of Natural Resources and Environmental Control (DNREC) would revise the management of extremely hazardous substances by revising permit standards, adopting a fee schedule, and changing the registration process to every three years. Contact Bob Barrish, DNREC, (302) 739-4791.

FLORIDA

Air Quality (Proposed Regulation)—The Florida Department of Environmental Protection (DEP) has proposed a rule which would define certain terms related to stationary sources and clarify that public notice of renewal of a federally enforceable state operation permit is required only when the renewal involves a material change. The regulation would also prescribe new exemptions for surface coating operations.

The Florida DEP has adopted a final rule which amends regulations concerning the processing of permit applications and clarifies Title V air general permits and nonTitle V general permit rule language. The rule was effective October 16, 1995. Contact Michael Hewett, DEP, (904) 488-0114.

*Proposed rules of the Florida DEP would amend stationary source emissions regulations by (1) revising the definition of VOCs to incorporate federal EPA changes and clarifying the definition of "affected pollutant"; (2) clarifying permit renewal provisions and adding exemptions for certain sources; (3) specifying exemptions from annual compliance tests; and (4) adding sampling requirements to VOC capture efficiency test procedures. Contact Michael Hewett, DEP, (904) 488-0114.

GEORGIA

Hazardous Waste (Regulation)—The Georgia Department of Natural Resources (DNR) announced a correction to the effective date of a final rule which clarifies the payment of hazardous waste fees and establishes requirements for the payment of hazardous substance reporting fees. The rule became effective on March 20, 1995. Contact Tim Cash, DNR, (404) 657-8600.

A final regulation of the Georgia DNR, complying with federal Resource Conservation and Recovery Act (RCRA) requirements, updates standards for (1) hazardous waste generators, transporters and facilities; (2) permit requirements; and (3) land disposal restrictions. Contact Bill Mundy, DNR, (404) 656-7802.

Water Quality (Regulation)—A final rule of the Georgia DNR adopts regulations which update provisions regarding general permit requirements and permit requirements for water treatment, pretreatment, land disposal, sewage sludge and publicly owned treatment works pretreatment programs. The rule was effective September 19, 1995. Contact Jeffrey Larson, DNR, (404) 362-2680.

IDAHO

Environmental Audits (Regulation)—The Idaho Health and Welfare Board (HWB) approved regulations on November 17 which provide immunity to companies who voluntarily disclose results of environmental audits and attempt to correct the problems. Companies have 60 days to begin to remedy the problems the audit uncovers. Contact Orville Green, HWB, (208) 334-5898.

A proposed rule of the Idaho Department of Health and Welfare (DHW) would update hazardous waste standards to remain consistent with federal EPA regulations. Contact John Brueck, DHW, (208) 373-0298.

Water Quality (Proposed Regulation)—The Idaho DHW intends to propose a regulation to modify water quality standards and wastewater treatment requirements pursuant to federal Clean Air Act requirements. Contact Mark Shumar, DHW, (208) 373-0260.

ILLINOIS

Air Quality (Regulation)—The Illinois Pollution Control Board (PCB) adopted a final regulation which updates the definition of volatile organic material (VOM) to conform to the federal definition of VOCs and revises the definitions of "organic material" and "organic solvent." Additionally, acetone and its alternative names have been exempted from the definition of VOM and the regulation for the control of ozone precursors. Contact Michael McCambridge, PCB, (312) 814-6924.

Hazardous Waste (Regulation)—An announcement by the Illinois PCB delays the adoption of regulations to incorporate federal RCRA standards. The standards address hazardous waste testing and monitoring, cement kiln dust, universal waste and air emissions. Contact Pollution Control Board, (312) 814-3620.

INDIANA

Air Quality (Proposed Regulation)—The Indiana Department of Environmental Management (DEM) has announced its intention to amend regulations to limit potential air emissions and eliminate the need for Title V permits by developing new source-specific operating agreements. Contact Mike Brooks, DEM, (317) 233-5686.

Automotive Refinishing (Regulation)—A final regulation of the Indiana DEM adopts new limits for VOCs which are emitted by coatings used in automotive refinishing operations in certain counties. The rule became effective on November 2, 1995. Contact Patricia Troth, DEM, (317) 233-5681.

Water Quality (Proposed Regulation)—A proposed rule has been recalled by the Indiana Department of Environmental Management (DEM) that would have repealed specific

pretreatment regulations and adopted regulations defining pretreatment requirements for industrial pollutant dischargers to publicly owned treatment works (POTWs). Contact Phil Preston, DEM, (317) 232-8728.

IOWA

Air Quality (Proposed Regulation)— The Iowa Environmental Protection Commission (EPC) proposed a rule which would require Title V operating permits to be paid at the beginning of the fiscal year and change the date for Title V sources to submit emissions inventories to March 31. Contact Catharine Fitzsimmons, EPC, (515) 281-8941.

KENTUCKY

Hazardous Materials Transportation (Proposed Regulation)—A proposed regulation of the Kentucky Transportation Cabinet (TC) would incorporate by reference federal hazardous transportation standards. Contact Sandra Sullen, TC, (502) 564-4890.

A final rule of the Kentucky Department of Environmental Protection (DEP) institutes standards governing site characterization, risk assessment, and remedial options. The rule was effective October 11, 1995. Contact James Hale, DEP, (502) 564-2225.

Final rules of the Kentucky DEP adopt and amend regulations regarding underground storage tank systems. Among other things, the regulations define underground storage tank terminology, revise procedures for documentation and extensions, and clarify fee schedules and registration requirements for owners of underground storage tank systems. The rules became effective November 14, 1995. Contact James Hale, DEP (502) 564-2225.

MAINE

Lead (Proposed Regulation)—The Maine Department of Human Services (DHS) has issued a proposal which removes the basic education requirement, discontinues the experience requirement for environmental lead inspectors, and decreases the number of annual training hours from 15 to 8. This regulation would apply to any person who conducts environmental lead inspections, lead abatement, or to person(s) located in other states who offer lead-related services to residents of Maine. Contact Edna Jones, DHS, (207) 287-4311.

MARYLAND

Water Quality (Proposed Regulation)—A proposed rule of the Maryland DOE would amend discharge limitations and permits. The regulation would recognize new detection methods for chlorine in addition to many other things. Contact Deanna Miles-Brown, DOE, (410) 631-3173.

MINNESOTA

Air Quality (Proposed Regulation)— The Minnesota Pollution Control Agency (PCA) announced its intention to amend regulations establishing a new air quality continuous monitoring system. Certification of monitoring systems and pretest standards for accuracy tests would be addressed. The proposal would also monitor installation and operation, quality assurance and quality control requirements, recordkeeping and reporting requirements, and sample frequency. Contact Steve Sommer, PCA, (612) 282-5851.

A notice issued by the Minnesota PCA announces its plan to adopt regulations which would regulate national emission standards for hazardous air pollutants (NESHAPs) source categories. Federal standards would be incorporated into state law to help the enforcement of the NESHAPs source categories. Contact Sherryl Livingston, PCA, (612) 296-3107.

The Minnesota PCA announced their tentative decision to issue a general permit for stationary general manufacturing sources. The permit includes conditions to limit the potential-to-emit (PTE) of VOCs, identifies criteria to consider sources ineligible for the proposed permit, and supplies a summary of the highest allowable PTE rates for the stationary sources listed in the permit. Contact Amrill Okonkwo, PCA, (612) 282-2603.

MISSISSIPPI

Air Quality (Proposed Regulation)— The Mississippi Department of Environmental Quality (DEQ) has proposed amendments to Section VI, "Permit Fees," "Air Emissions Operating Permit Regulations for the Purposes of Title V of the Federal Clean Air Act," to revise the due date for the air operating permit fee in accordance with state law. Contact Dwight Wylie, DEQ, (601) 961-5171.

MISSOURI

Air Quality (Proposed Regulation)—A proposed rule of the Missouri Department of Natural Resources (DNR) would amend regulations by incorporating federal regulations concerning new source performance regulations and hazardous air pollutants. Contact Air Pollution Control Program, DNR, (314) 751-7840.

MONTANA

Air Quality (Regulation)—A final regulation of the Montana Board of Environmental Review (BER) revises the definition of VOCs in order to be consistent with federal standards. The rule went into effect on November 10, 1995. Contact Yolanda Fitzsimmons, DEQ, (406) 444-2544.

The Montana BER adopted a final rule to increase air quality operation and permit application fees, and to clarify that fees must be collected from all permitted air contaminant sources. Contact Yolanda Fitzsimmons, DEQ, (406) 444-2544.

Highway Transportation (Proposed Regulation)—A proposed rule of the Montana Department of Justice (DOJ) would make motor carrier safety consistent with federal standards for motor carrier safety and hazardous materials transportation. Contact Curt Rissman, Montana Highway Patrol, (406) 444-3780.

Water Quality (Proposed Regulation)—The Montana Department of Environmental Quality (DEQ) has proposed a rule which would amend regulations in reference to surface and ground water quality zones, and nondegradation of water quality. Contact Yolanda Fitzsimmons, DEQ, (406) 444-2544.

NEBRASKA

Air Quality (Proposed Regulation)—The Nebraska Department of Environmental Quality (DEQ) has proposed a rule which would exempt four chemicals from the definition of VOCs, adopt federal hazardous pollutant standards, define "solid waste," and provide the appropriate situations to combine pollutant emissions in emissions reporting. The four chemicals that would be exempted from the definition of VOCs are acetone, perchloroethylene (perc), volatile methyl siloxanes, and parachlorobenzotrifluoride. However, perc is still considered a hazardous air

pollutant. Contact Susan Fields, DEQ, (402) 471-2186.

Hazardous Waste (Regulation)—A final regulation of the Nebraska DEQ revises hazardous waste management provisions. The rule updates public notice requirements for emergency permits and changes the method for the calculation of treatment of disposal fees to allow a per pound fee and a volumetric fee. The rule became effective on September 20, 1995. Contact Joe Francis, DEQ, (402) 471-2186.

NEVADA

Air Quality (Regulation)—A final rule has been issued by the Nevada State Environmental Commission (SEC) in reference to air pollution which clarifies the reporting of excess emissions, and the billing of service and maintenance fees. The rule was effective on October 30, 1995. Contact David Cowperthwaite, SEC, (702) 687-4670.

Hazardous Waste (Proposed Regulation)—A proposed rule of the Nevada SEC would provide regulatory relief to tank owners and operators by adding the use of risk-based evaluations and making remedial activity requirements cost-effective. Contact David Cowperthwaite, SEC, (702) 687-4670.

Water Quality (Regulation)—The Nevada SEC has issued a final rule amending discharge permit provisions to be consistent with federal water pollution control regulations. Among other things, the rule deletes the requirement that effluent limitations be expressed by weight in the permits. The rule is effective upon filing with the secretary of state. Contact David Cowperthwaite, SEC, (702) 687-4670.

NEW HAMPSHIRE

Lead (Regulation)—The New Hampshire Department of Health and Human Services (DHHS) has adopted a final rule which amends regulations to clarify, simplify, and reorder childhood lead poisoning prevention standards. Among other things, the rule specifies when "interim controls" can be used as an alternative to lead abatement and the types of activities that will result in administrative fines. The rule became effective October 15, 1995 and expires on October 15, 2003. Contact Jean Bergman, DHHS, (603) 271-4501.

NEW JERSEY

Air Quality (Regulation)—A final rule of the New Jersey Department of Environmental Protection (DEP) adopts regulations for the control and prohibition of VOCs in non-paint consumer and commercial products manufactured after April 30, 1996. The rule establishes VOC content standards and test methods, and specifies penalties for failure to comply. The rule went into effect on November 6, 1995. Contact Janis Hoagland, DEP, (609) 292-0716.

Spray Paint Restrictions—NJ A. 3266 (Garcia), identical to S. 2283, prohibits the sale, transportation, and possession of certain spray paints and indelible markers. The legislation was introduced on December 4 and referred to the Assembly Committee on Judiciary, Law. and Public Safety.

NEW MEXICO

Hazardous Waste (Regulation)—A final rule of the New Mexico Environmental Improvement Board (EIB) incorporates by reference federal hazardous waste standards. The rule became effective on November 1, 1995. Contact Coby Muckelroy, EIB, (505) 827-4308.

NEW YORK

Air Quality (Proposed Regulation)—A notice of the New York Department of Environmental Conservation (DEC) announces a hearing on January 16, 1996 to discuss a proposed state implementation plan (SIP) in reference to national ambient air quality standards for inhalable particulate matter. Comments for this proposal are due on February 2, 1996. Contact David Park, DEC, (518) 457-2823.

NORTH CAROLINA

Air Quality (Proposed Regulation)—The North Carolina Department of Environment, Health, and Natural Resources (DEHNR) has proposed a rule which would clarify and amend permit processing and permit fee provisions. The regulation would also incorporate new federal source performance and maximum achievable control standards. Comments are due on January 19, 1996. Contact Thomas Allen, DEHNR, (919) 733-1489.

NORTH DAKOTA

Highway Transportation (Proposed Regulation)—A proposed regulation of the North Dakota Public Service Commission (PSC) would repeal existing standards for motor carriers to comply with a 1995 law passed by the legislature which deregulated the motor carrier industry. Comments are due January 13, 1996. Contact Jon Mielke, PSC, (701) 328-2400.

OHIO

Community Right-to-Know (Regulation)—The Ohio State Emergency Response Commission has issued a final rule amending regulations concerning local emergency planning committees. The rule includes application procedures for a variance from specific provisions, defines the criteria for granting a variance, and establishes decision-making procedures. Contact Jeff Beatie, Ohio EPA, (614) 644-2260.

Highway Transportation (Regulation)—A final regulation of the Ohio Public Utilities Commission (PUC) updates provisions for annual registration and tax receipts of motor carriers, permit applications, and registration of hazardous wastes. The rule went into effect on September 21, 1995. Contact Division of Motor Carriers, PUC, (614) 466-3682.

PENNSYLVANIA

Air Quality—PA H.R. 255 (George) orders the review of the historical development and current status and implementation of regulations pursuant to the Clean Air Act Amendments. The resolution was introduced on November 20 and referred to the House Committee on Rules.

SOUTH CAROLINA

Air Quality (Proposed Regulation)—The South Carolina Department of Health and Environmental Control (DHEC) has proposed a regulation which would revise the definition of VOCs by exempting such compounds as acetone and volatile methyl siloxanes. A hearing is scheduled for January 11, 1996. Contact Mohamed Abdelsalam, DHEC, (803) 734-4463.

Water Quality (Proposed Regulation)—A proposed rule of the South Carolina DHEC would amend NPDES permit requirements by incorporating the most recent federal standards and general pretreatment regulations. Additionally, the proposed rule would include the adoption of provisions for use and disposal of sewage sludge. Contact

Russell Sherer, DHEC, (803) 734-5300.

TENNESSEE

Air Quality (Regulation)—The Tennessee Department of Environment and Conservation (DEC) has issued a notice which announces a correction to the effective date of a final rule that adopted standards for wood furniture coating lines in several counties. The rule is now effective August 15, 1995. Contact Malcolm Butler, DEC, (615) 532-0600.

A notice of the Tennessee DEC announces further correction to the effective date of a final rule which establishes standards for VOC emissions from certain facilities in counties that have the aggregate potential to emit 50 tons or more per year of VOCs on or after November 15, 1996. In addition, the regulation specifies recordkeeping and reporting requirements, and exempted facilities. The rule is now effective as of October 15, 1995. Contact Malcolm Butler, DEC, (615) 532-0600.

Water Quality (Regulation)—A final rule of the Tennessee DEC amended regulations for water pollution control permits and for licensing requirements incorporating federal provisions. The rule went into effect on December 10, 1995. Contact Division of Water Pollution Control, DEC, (615) 532-0625.

Texas

Air Quality (Proposed Regulation)—The Texas Natural Resource Conservation Commission (TNRCC) has proposed a rule which affects permits for new construction or modification. Among other things, the rule would set forth criteria for permit amendments that must be followed by qualified facilities. Contact Thomas Ortiz, TNRCC, (512) 239-1054.

A final rule of the Texas TNRCC, adopted November 16, prohibits the agency from imposing permit renewal requirements that are more stringent than those in the original permit. The agency can only impose tougher standards if there is a possibility of air pollution or to meet compliance with federal and state air quality requirements. Contact Sam Wells, TNRCC, (512) 239-1441.

Hazardous Waste (Proposed Regulation)—The Texas TNRCC has proposed regulations which would amend regulations governing industrial solid waste and municipal hazardous waste, incorporating federal hazardous waste standards by reference. Contact Ray Austin, TNRCC, (512) 239-6814.

A final regulation of the Texas TNRCC, effective November 8, 1995, incorporates risk-based corrective action for the treatment of leaking storage tank sites. Contact Jackie Hardee, TNRCC, (512) 239-2160.

Waste Management (Proposed Regulation)—A proposed regulation of the Texas TNRCC would clarify the definition of solid waste and expand and clarify the exemptions from the definition of solid waste. The proposal would also expand the range of some variances from classification as solid waste. Contact Hygie Reynolds, TNRCC, (512) 239-6825.

UTAH

Air Quality (Regulation)—A final rule of the Utah Department of Environmental Quality (DEQ) revises the definition of VOCs to correspond to the federal definition. The rule became effective on October 12, 1995. Contact Jan Miller, DEQ, (801) 536-4042.

A proposed regulation of the Utah DEQ would amend control of installations by defining the requisite sources to submit an annual emission inventory. The due date for submittal of all annual emission inventories would be April 15. Contact Jan Miller, DEQ, (801) 536-4042.

The Utah Department of Environmental Quality (DEM) adopted a final rule which incorporates revisions to the state implementation program for ozone control measures for area and point sources. Contact Jan Miller, DEQ, (801) 536-4042.

Hazardous Materials Transportation (Proposed Regulation)—Proposed rules of the Utah Department of Transportation (DOT) would amend safety requirements for motor carriers transporting hazardous materials and or waste, incorporating by reference federal amendments. Contact Shirleen Hancock, DOT, (801) 965-4781.

The Utah DEQ has proposed a rule which would amend regulations adding air emission control requirements for generators in RCRA permit-exempt tanks and containers accumulating waste-on-site. Contact Susan Toronto, DEQ, (801) 538-6776.

A proposed regulation issued by the Utah DEQ would amend hazardous waste definitions and references, and incorporate federal amendments. Contact Susan Toronto, DEQ, (801) 538-6776.

VERMONT

Community Right-to-Know (Regulation)—A final regulation of the Vermont Department of Public Safety (DPS) revises fees for reporting information on reportable quantities in reference to the emergency planning and community right-to-know program. The rule became effective on October 9, 1995. Contact Kelman Craige, DPS, (802) 244-8721.

VIRGINIA

Air Quality (Regulation)—An emergency rule of the Virginia Air Pollution Control Board (APCB) requires operating permits for stationary sources pursuant to Title V of the federal Clean Air Act. Among other things, the rule references federal requirements for source applicability and changes the stationary source permit fee to $25. Contact Nancy Saylor, APCB, (804) 786-1249.

Lead (Regulation)—The Virginia Department of Professional and Occupational Regulations (DPOR) issued an emergency rule establishing the procedures and requirements for lead-based paint activities. These requirements include accreditation of programs, certification of individuals and firms, and standards for performing such activities. The rule was effective October 1, 1995. Contact Board for Asbestos Licensing and Lead Certification, DPOR, (804) 367-8589.

WASHINGTON

Permits (Proposed Regulation)—A proposed regulation of the Washington Department of Ecology (DOE) would establish a single permit process rule. Among other things, the regulation would establish application information requirements for designating a coordinating permit agency. Contact John Aden, DOH (360) 664-0441.

Latex Blends: An Approach to Zero VOC Coatings

Mitchell A. Winnik and Jianrong Feng—University of Toronto*

INTRODUCTION

Concern for the environment is leading to changes in coatings technology. In the U.S. and around the world, agencies are in the process of implementing increasing limitations on the emission of volatile organic compounds (VOCs). These emissions are believed to be the primary cause of photochemical smog and ozone pollution. A significant portion of the VOCs currently released into the atmosphere derive from industrial and architectural paints and coatings. The coatings industry has responded to this challenge by trying to replace solvent-based coatings either with waterborne or high-solids systems.[1,2]

Even within water-based systems, volatile organics are used to promote coalescence. These film-forming aids lower the modulus of the latex polymer to promote particle deformation during drying, and they act as plasticizers to promote polymer diffusion in the newly formed film.[1,3] In this way they enhance the development of good film properties. If they remained within the resin, the film would be soft and have poor mechanical properties and poor block resistance. In this technology, good film properties are achieved when the solvent evaporates from the film into the atmosphere.

A number of strategies are currently being tested which will lead to film formation from aqueous latex dispersions without the need for volatile additives. One of the most attractive of these involves blends of hard and soft latex.[4,5] A dispersion of a latex with a glass transition temperature (T_g) below room temperature (a low T_g latex) will form a continuous film upon evaporation at room temperature, even when blended with a substantial amount of high T_g latex. The low T_g polymer deforms to fill space as the dispersion dries, and the high T_g component imparts good block resistance to the final film. Under some circumstances one can obtain transparent films. As we shall see in the following, this result requires that the hard latex be sufficiently small and well dispersed within the matrix of the soft polymer and that the refractive indices of the two latex polymers be similar.

Although the topic of latex blends is actively being investigated in the industry, there have been few publications which examine the formation and properties of latex blend films. These blends provide a number of surprises, which are

An attractive strategy for zero VOC coatings involves blends of hard and soft latex particles. A dispersion of a latex with a low minimum film-forming temperature will form a transparent film upon evaporation, even when blended with a substantial amount of high T_g latex. The low T_g latex deforms to fill space as the dispersion dries, and the high T_g component imparts good block resistance and mechanical properties to the final film. Transparency requires that the hard latex be sufficiently small and well dispersed in the final film. In addition, the two components must have similar refractive indices. Two of our most surprising observations are that dispersions of soft latex particles dry more slowly than those of high T_g latex, and that mixtures of the two particles dry even more slowly. Consideration of these results leads to a new model for the drying mechanism of latex dispersions that takes into account the propagating drying front. Dynamic mechanical analysis indicates that the hard particles in blends improve significantly the mechanical properties for the films.

important from both a scientific and technological point of view. One of the most interesting concerns is how these blended dispersions dry.

The body of this paper is divided into five parts which follow a short Experimental Section. The first presents the idea of a transparency phase diagram, and examines the surface and bulk morphology of blend films. As the fraction of low T_g latex in the dispersion is increased, there is a sharp transition from turbid to transparent films. The subsequent

Table 1—PMMA Latex Characteristics

Sample	PMMA Latex				
Diameter (nm) ...	44	110	167	230	400
Polydispersity	0.005	0.005	0.005	0.005	0.005
Mw (x10⁻⁵)	4.6	2.1	—	—	—
Mw/Mn	2.0	2.3	—	—	—

three sections, which are the main contributions of this paper, examine in detail the drying behavior of single-component and blended dispersions. We emphasize an important feature that latex dispersions dry with a drying front, which separates a dry film part from a wet dispersion region and propagates directionally as the drying proceeds. We report and explore the finding that blends of hard and soft latex dry more slowly than either individual dispersion. This kind of rate difference can only occur if the drying rate is not controlled by the wet region, but by the boundary between the wet and dry regions of the film. From these observations, we develop a new model of the drying process. Finally we look briefly at how the high T_g latex affects the mechanical properties of the blend films.

Some experiments involve blends of poly(methyl methacrylate) [PMMA] as the hard latex with various butyl methacrylate-butyl acrylate copolymer [P(BMA-co-BA)] latex as the low T_g component. Other experiments involve two samples of poly(methyl methacrylate-co-butyl acrylate) [P(MMA-co-BA)] with slightly different compositions, one with T_g = 48°C, the other with T_g = 17°C.

EXPERIMENTAL

The latex samples employed here have been described previously.[4,6] The characteristics of these samples are collected in *Tables* 1-3. To prepare films, latex dispersions were placed on a flat glass substrate or quartz plate and air dried. For some samples, an inverted petri dish was used to cover the drying dispersions to slow the process of film formation. Other samples were dried directly in the open air. The films formed had a thickness of ~ 50 μm.

Measuring Water Loss During Drying

All dispersions were adjusted to an initial solids content of 5 wt%. For each set of samples to be compared, the initial quantities of dispersion (e.g., 0.300 g) were weighed as identically as possible (± 0.3%). The dispersions were spread on individual glass plates to produce wet films with similar surface areas (e.g., 5.0 ± 0.2 cm²). With practice we could achieve this reproducibility. Films were dried at ambient temperature (22 ± 1°C) and humidity in an area of the laboratory free from drafts. The humidity changed from 45 to 65% relative humidity day to day, but it was fairly constant (with a small deviation < ± 2% relative humidity) during the measurement time of each set of samples. The samples were weighed at regular time intervals using an analytical balance: each half hour at early stages, and each 10-15 min at later stages, of drying. The changes in solids content with time were calculated from the water loss data. In our experiments, the latex drying occurs as a moving front, showing a decrease in surface area of the wet part of the film. A ruler was placed over the film surface after each time interval to measure the dimensions of the wet region.

Film Characterization

Film transparency was monitored with a Hewlitt-Packard model 8452A diode array UV-VIS spectrophotometer (400 to 700 nm). The percent transmittance was recorded at 550 nm. Freeze-fracture transmission electron micrographs (FFTEM) were taken in the laboratory of Professor R.S. Shivers at the University of Western Ontario. Details are given in references 4 and 7. Scanning electron micrographs (SEM) were taken in Toronto using a Hitachi S-570 system under low voltage to prevent the melting of the soft component. Atomic force microscopy (AFM) measurements were carried out in Toronto in the laboratory of Professor J. Vancso using the Nanoscope III in the TappingMode™. Dynamic mechanical analysis (DMA) measurements were performed with a Perkin-Elmer DMA-7 system. Thick films (.025-0.50 mm) were prepared by air drying the dispersions in a Teflon mold and then cutting the films into rectangular pieces (10 mm × 4 mm). Measurements were made in the extension mode to obtain E´, E˝, and tan δ.

TRANSPARENCY AND MORPHOLOGY OF BLEND FILMS

Transparency

There are several requirements for transparency in a latex blend film. First, the number of voids in the film that can scatter light must be negligible.[1] This requires complete coalescence of particles for the latex system. In our binary latex system, the hard particles are not able to deform; therefore it is essential that the soft particles deform to fill space, as well as serving as a binder for the hard particles. In addition, the refractive indices of the two polymers must be similar,[8] or, if they differ, the dispersed domain sizes must be small.[9] In the blends described here, the latex particles are rather small. Their refractive indices are unlikely to be very different, based upon the values of the corresponding homopolymers, 1.490 for PMMA, 1.483 for PBMA, and 1.474 for PBA.[10]

Table 2—P(BMA-co-BA) Latex Characteristics

Sample	P(BMA-co-BA) Latex			
Diameter (nm)	43	32	38	49
Polydispersity	0.008	0.026	0.017	0.077
T_gᵃ (°C)	–33.0	–6.9	4.1	9.9
Mw (x10⁻⁵)	8.4	6.7	3.5	1.1
Mw/Mn	1.7	1.9	2.4	6.9

(a) Only one T_g was observed by DSC for each copolymer sample.

Table 3—P(MMA-co-BA) Latex Characteristics

Sample	High T_g Latex	Low T_g Latex
D_n (nm)	111	103
D_w/D_n	1.11	1.10
Mw (x10⁻⁵)	2.3	2.5
Mw/Mn	2.9	3.1

Figure 1—Plots of percent transmittance at 550 nm as a function of blend composition: (a) blends of 110 nm PMMA latex with 38 nm P(BMA-co-BA) latex of $T_g = 4.1°C$; (b) blends of P(MMA-co-BA) latex of $T_g = 48°C$ with that of $T_g = 17°C$, both samples of $d \sim 110$ nm. The dashed line represents our definition of the critical volume fraction of the soft component for film transparency.
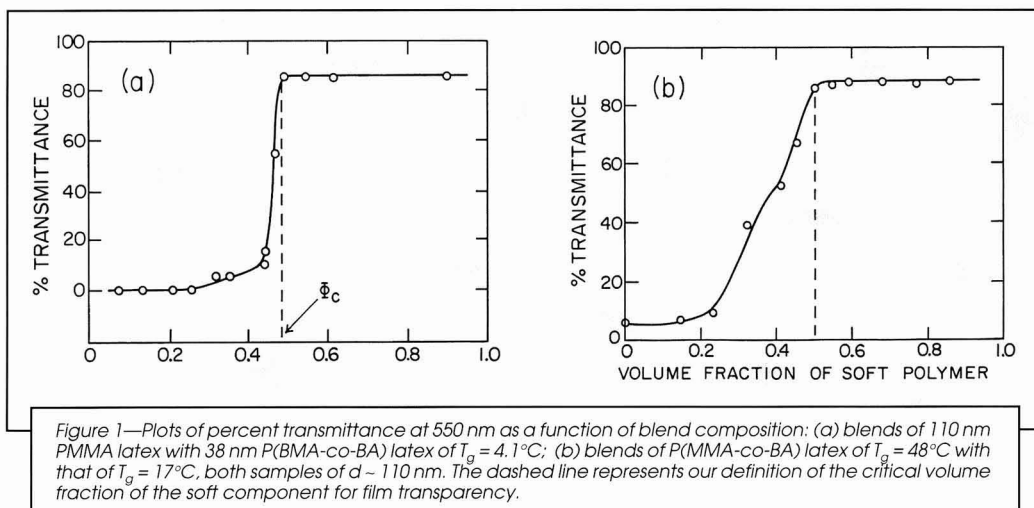
We obtained films which are transparent to the eye in blends rich in the soft component. UV-VIS measurements indicate that the transmittance of these samples is on the order of 85 to 95% over the entire visible wavelength range. Turbid samples were obtained from blends rich in hard latex. Here the transmittance is only 5-20%.[4] In all the cases, we found that there is a value of the volume fraction of soft polymer at which we could obtain a clear film, and below which we only could get a turbid film with cracks or, in the extreme, a white powder. We define this as the critical volume fraction of soft polymer, Φ_c, in these composite films.

Figure 1 shows two examples of transparency phase diagrams, i.e., plots of light transmission versus blend composition. The plot in *Figure* 1a describes blends of 110 nm PMMA latex with 38 nm P(BMA-co-BA) latex of $T_g = 4.1°C$. The transition between turbid and transparent films is extremely sharp. The two components of this blend differ in refractive index by about 0.01, which can be sufficient to scatter light if the hard particles are not well separated in the blend. *Figure* 1b is for blends of P(MMA-co-BA) latex of $T_g = 48°C$ with that of $T_g = 17°C$, both having a diameter of 110 nm. Here we observe cracks at a soft fraction between 0.3 and 0.5. Since the two components differ in refractive index by only about 0.001, the turbidity seen at lower fractions of soft component likely arises from void scattering.

One might expect that the volume fraction of soft polymer necessary to give transparent films would correspond to that necessary to fill the void volume of close-packed hard spheres. This volume fraction Φ_{soft} would be equal to 0.26 or 0.34 depending upon whether the close packing was face-centered cubic or random. Φ_c values found in our experiments are always above these values and close to 0.5. This implies that the soft polymer forms a continuous phase in transparent films, with the hard particles dispersed in it.

Morphology

Film surface morphologies were examined by scanning electron microscopy (SEM), and in some instances, by atomic force microscopy (AFM). In blends of PMMA and P(BMA-co-BA) particles, SEM images show that transparent films are characterized by a uniform distribution of hard particles in the low T_g matrix. When the hard particles are too large (e.g., 230 or 400 nm), they tend to aggregate during the drying process. It is very difficult to obtain transparent films from these blends. Even when the PMMA latex particles are appropriately small (e.g., 110 nm), if they aggregate during film formation, the resultant films are turbid.

A number of these film samples were examined by FFTEM. This technique provides a rich view of the fracture surface of
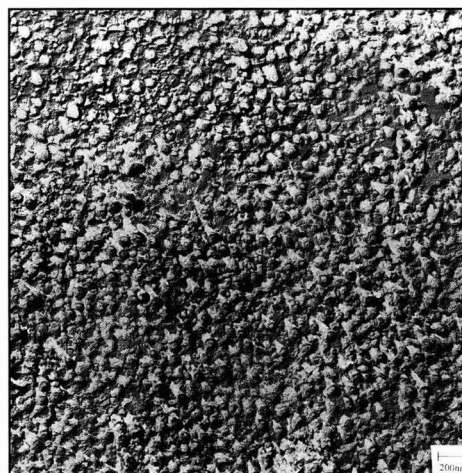
Figure 2—FFTEM image of a latex blend film containing a 1:1 mixture of 110 nm PMMA particles and P(BMA-co-BA) particles of d = 32 nm and T_g of −6.9°C. The film was fractured at −170°C, and shadowed with platinum-carbon.

Figure 3—AFM images (three-dimensional, 1 μm × 1 μm × 400 nm) of the surface of blends of high T_g and low T_g P(MMA-co-BA) samples (both d ~ 110 nm) with compositions of Φ_{soft} = (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8, respectively.
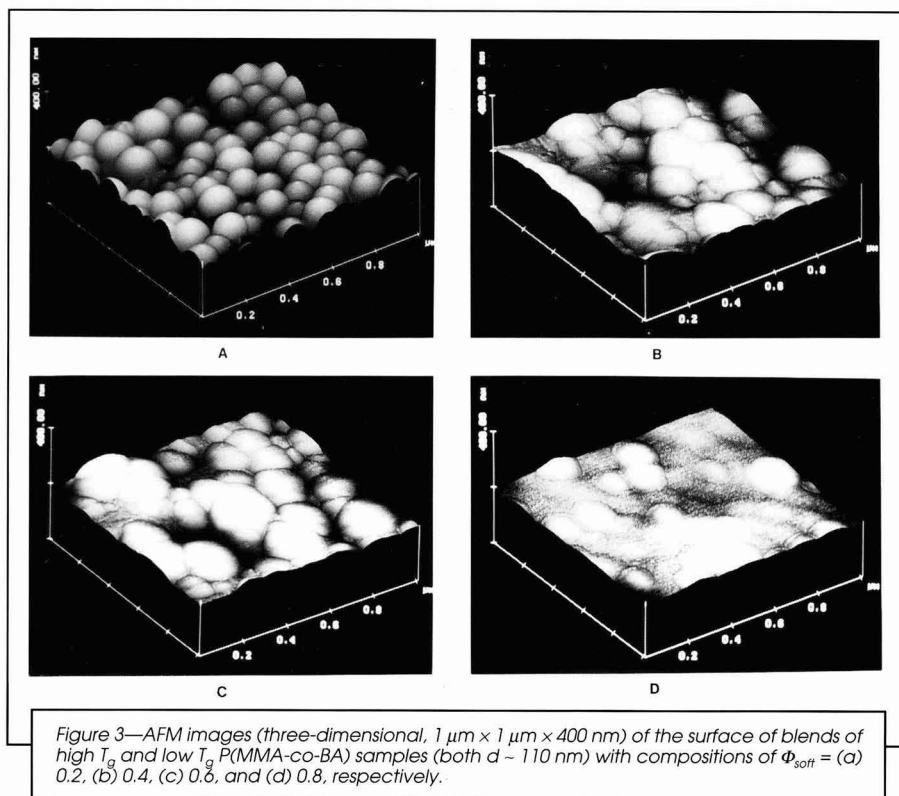
the film interior with high resolution and with minimal distortion. In *Figure 2*, we present an FFTEM image of a transparent film comprised of a 1:1 mixture of 110 nm PMMA particles and small soft P(BMA-co-BA) latex. One can see that the hard (PMMA) particles preserve their size and spherical shape. The soft particles have deformed and result in a void-free internal structure. The hard particles are uniformly distributed in the soft polymer matrix. These results support the idea that film transparency is dependent on the distribution of hard particles in the soft polymer matrix.

Figure 3 shows AFM images of P(MMA-co-BA) latex blend films of different compositions. In these blends, the hard particles (T_g = 48°C) and soft particles (T_g = 17°C) are of similar size (d = 110 nm). At a soft particle volume fraction of 0.2, the hard particles are still apparent as undeformed spheres, held together by a "glue" of deformed soft particles, as seen in *Figure* 3a. At Φ_{soft} = 0.4 (*Figure* 3b) and 0.6 (*Figure* 3c), further soft particle coalescence can be seen. The most striking feature of these images is the presence of bumps which appear larger than the size of either of the individual hard or soft particles. This may be due to particle clustering. Because the bumps are quite smooth and resemble boulders more than spheres, it is reasonable to suppose that they are formed by coalescence of soft particles over the underlying hard particles. This idea is supported by the observation that as the hard particle volume fraction is decreased, the number of

bumps also decreases, as seen in the image for a Φ_{soft} = 0.8 film (*Figure* 3d).

The AFM surface images correlate with the phase diagram shown in *Figure* 1b. In the sample of Φ_{soft} = 0.2 film, void spaces between hard particles are apparent, suggesting the presence of extensive voids within. The phase diagram indicates a transition to void-free films at Φ_{soft} = ca. 0.5. In the AFM images of the Φ_{soft} = 0.4 and Φ_{soft} = 0.6 films, possible voids between particles are much harder to discern. The film surfaces are not very smooth, although the roughness is on the order of a particle diameter. If there is clustering of the higher T_g latex in the sample of Φ_{soft} = 0.6, this would be unlikely to lead to turbidity because of the very small difference of refractive indices between the two polymers. In the sample with Φ_{soft} = 0.8, the soft polymer forms the matrix. There are no voids, and the hard particles are well dispersed.

KINETICS OF DRYING

Most coatings formulations contain latex dispersions at relatively high solids, i.e., > 40 wt%. As a consequence, most previous studies of the drying process began with dispersions at high concentrations. Since we wished to look carefully at the early stages of drying, we chose to dilute all dispersions including blends to 5.0 wt% solids. Some dispersions con-

tained an anionic surfactant (sodium dodecyl sulfate or SDS, 2-6 wt% solids), whereas other dispersions were cleaned carefully to remove all salts and surfactant. In the following paragraphs, we compare the rates of water loss from samples of soft latex, hard latex, and their blends. When examining a given variable, we compare samples prepared to have equal area, mass, and wet film thickness and whose water-loss rates were measured simultaneously. The reproducibility between identical samples examined in this way was excellent, and the data quality can be judged by reference to the figures presented in the following.

Water Evaporation Rate at Low Solids

An example of a water evaporation experiment is shown in *Figure* 4, where we compare mass loss as a function of time from three liquid films: pure water, a soft latex dispersion [P(BMA-co-BA), d = 43 nm, T_g = –33°C], and a hard latex dispersion (PMMA, d = 110 nm). The two dispersions were cleaned to remove surfactant. The first feature that one notices is that water loss over 2/3 of the drying is linear in time. In addition, the water loss curves of pure water and the dispersions overlap in this linear region, indicating an identical drying rate, with a water evaporation rate of 3.5 ± 0.1 × 10^{-4} g min^{-1} cm^{-2}. This value is not very different from those reported in the literature. Vanderhoff[11] reported in his early paper that latex dispersions dried at a similar rate to thin films of water. Croll[12] found that latex dispersions and various pigment dispersions dried initially at a constant rate which was about 85% of that of pure water. Numerical simulations by Vanderhoff and coworkers using heat and mass transfer equations also gave a similar factor of about 85%.[13] We find a negligible difference in initial drying rates between water and latex dispersions. Note that our latex drying experiments begin at a much lower solids content (5 wt%) than those of Vanderhoff and Croll (ca. 50 wt%).

Drying Front

Published models of latex drying assume that water evaporation occurs uniformly over the entire film surface. In all of our experiments, the films dried as a propagating front. When the dispersions were placed in a small circular dish with a vertical wall, a concave meniscus was formed with a thicker edge near the wall and a thin central region. Here drying takes place first at the center where the liquid is thinnest and moves outward towards the thick edge. Concurrently, drying from the top of the liquid at the wall surface also occurred, progressing downward to the bottom of the dish. The film formed at the bottom of the dish had a much thicker edge (e.g., 200 μm) and a very thin center (e.g., 10 μm).

When the dispersions were spread onto a flat glass surface, a flat liquid drop with a slightly convex surface formed spontaneously. Here the liquid center is relatively thick with a thinner edge. Drying occurs initially at the outermost region, and the dry region grows inward toward the center. We observe this process for both surfactant-containing and surfactant-free dispersions. Films formed on a flat glass surface often have a relatively thicker edge (e.g., 60 μm) surrounding a large flat portion (e.g., 45 μm thick) in the center. With surfactant and salts removed, the ridge at the edge is barely discernible. This kind of drying behavior characterized by a propagating drying front in latex dispersions has been men-
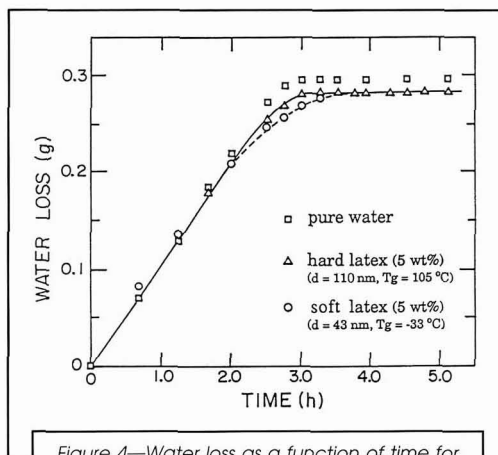
Figure 4—Water loss as a function of time for water (squares), a dispersion of soft latex (circles), and of hard latex (triangles). In the soft latex: d = 43 nm, T_g = –33°C and in the hard latex: d = 110 nm. The latex samples are surfactant-free, initially at a concentration of 5 wt%.

tioned previously,[14,15] but we wish to emphasize that models of the drying process have not taken the drying front into account.

Figure 5 illustrates the drying process of our latex dispersions spread on a flat glass surface. A dry region forms at the edge of the film. There is a thin transition region which represents the drying front that separates the dry region from the inner wet dispersion. With time, the drying front moves inward, accompanied by a decrease in surface area of the wet center.

Comparison of Hard and Soft Latex Dispersions

In our experiments, we monitored both water loss and the area of the wet center as a function of time. We are thus able to relate the loss of water and the growth in percent solids to
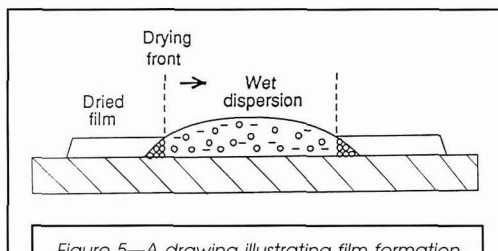
Figure 5—A drawing illustrating film formation on a flat substrate during drying. A transparent film at the edge is separated from an inner wet dispersion by a boundary referred to as the drying front. The drying process is characterized by movement of the drying front towards the center until the wet dispersion fades, and the film is entirely dry.
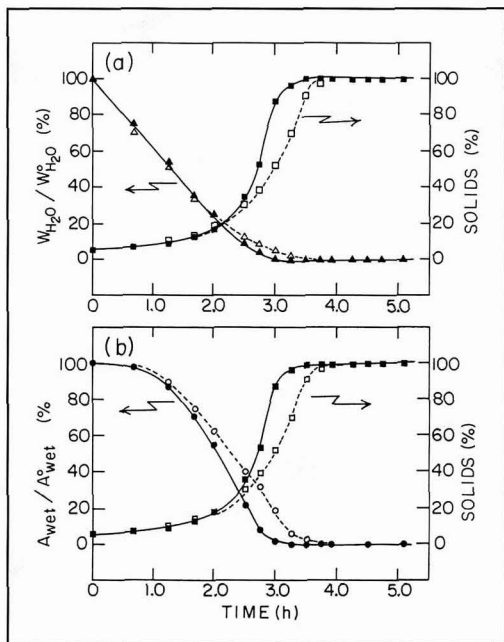
(a)

(b)

Over the first 2.5 hr, the weight fraction of water remaining in the dispersion decreases linearly with time. The linearity of water loss persists even when the measured wet area has decreased by a significant extent (e.g., by 60% of its initial value). This implies that water evaporation occurs not only in the wet dispersion part, where water loss rate (g min^{-1}) is proportional to the surface area, but also in other regions of the film, which must be near the wet-dry boundary. We will discuss this important issue in the following. After 2.5 hr, when the solids content has reached 30 wt%, the wet area has already decreased to 30% of its initial value. At this point, the rate of water loss for both dispersions begins to decrease, characterized by non-linearity in the water loss curves. Further water loss corresponds to a large, rapid increase in solids content. Above 60 to 80% solids, there is a marked slowing of the water evaporation rate. The wet drop is very much reduced in size and disappears during this stage of the drying process. The solids content eventually reaches its equilibrium value (typically 97-99%).

Once these latex films become transparent or apparently dry to the eye, no further weight decrease is detected during further aging in air. The residual water content, measured by the weight lost during heating the films under vacuum, is small (< 3 wt%). This result differs from that reported by

the propagation of the drying front during the entire process from a dilute dispersion to a solid film. An example of one of our experiments is given in *Figure 6*, where we show drying curves for two latex samples, one hard and one soft. We plot in *Figure 6*a the solids content (in weight percent) and the fraction of water remaining (W_{H2O}/W_{H2O}^0, in %) in the latex samples as a function of time. In *Figure 6*b, for the same samples, we compare the area of the wet region relative to its initial value (A_{wet}/A_{wet}^0, in %) as a function of time. The plots of solids content versus time are sigmoidal, with a slow upward curvature, and a sharp break as the lines approach 100% solids. Initially, the solids content changes slightly with time. This is a consequence of starting the experiment at a low solids concentration: when half the water has evaporated, the solids content has only increased from 5 to 10 wt%. In the very beginning, the wet area does not change very much, but after about 40 min, a dry edge appears, and the drying front starts to move inward.

(a)

(b)

Vanderhoff,[11] who observed significant water loss (~ 10 wt%) over a prolonged aging period.

An interesting observation is that the drying front moves at different rates during the experiment. At very early times, there is only a wet dispersion. After a certain period (here, 40 min), the dry edge appears. The propagation of the drying front is initially slow, but becomes rapid at the transition region where most of the water has evaporated, and the polymer changes from the minor to the major component. Near the end of the drying process, the propagation rate diminishes. Finally the liquid dispersion fades, and the wet area approaches zero. One can see that the rapid rate of decrease in the area of the wet drop (t = 1.5 to 3 hr in *Figure* 6b) precedes the rapid rate of increase of latex solids (t = 2.5 to 3.5 hr) in the system.

The most interesting result in *Figure* 6 is that the dispersion of PMMA particles dries significantly faster than that of the P(BMA-co-BA) latex with a T_g below room temperature. This difference may be a matter of particle size, or, as we show in the following, a fundamental difference in behavior between dispersions of hard and soft latex particles. In the cases we have examined, dispersions of latex with T_g well above room temperature often dry more rapidly than dispersions of low T_g latex.

DRYING OF LATEX BLENDS

Latex blends were prepared by mixing dispersions of a hard latex with those of a soft latex. *Figure* 7 shows drying curves for a set of surfactant-free dispersions, in which percent solids is plotted versus time in *Figure* 7a, and the relative wet area is plotted versus time in *Figure* 7b.

The first feature one notices in the drying curves is that latex blends dry differently from the dispersions of soft and the hard latex alone. As seen in *Figure* 6, the hard latex dispersion dries faster than the dispersion of soft latex. One might imagine that blending these samples would lead to intermediate drying rates. What one observes is that for most of the compositions studied, the blends dry much slower than the dispersions of either pure component. As the weight fraction of hard component increases from 0 to 0.56, the time taken for the dispersions to reach high solids increases systematically, implying a decrease in drying rates. One also observes that the drying front propagates more slowly for blend samples with Φ_{hard} below ~0.5 than that for either the soft or hard latex dispersion (cf. Φ_{hard} = 0.33 in *Figure* 7b). It is only when the blends become non-film forming (e.g., Φ_{hard} = 0.78), that they exhibit rapid drying.

We also observed a decrease in the drying rate in blends in which the hard latex was replaced by samples of d_{hard} = 167 or 44 nm, and when the soft latex was replaced with a sample of d_{soft} = 49 nm and T_g = 9.9°C.

Figure 8—Comparison of drying rates for latex blend dispersions as a function of composition: (a) instantaneous water evaporation rates (g.min⁻¹) at 50, 75, and 90 wt% solids; (b) the time taken (in hr) during drying for each dispersion to reach 50, 75, and 90 wt% solids. The data are derived from Figure 7.

Figure 9—Comparison of drying rates for SDS-containing latex blends as a function of composition: the time taken (in hr) during drying for each dispersion to reach 50, 75, and 90 wt% solids. The samples are identical to those in Figures 7 and 8 except that 6 wt% SDS, based upon latex solids, has been added to the initial dispersion.

M.A. Winnik and J. Feng
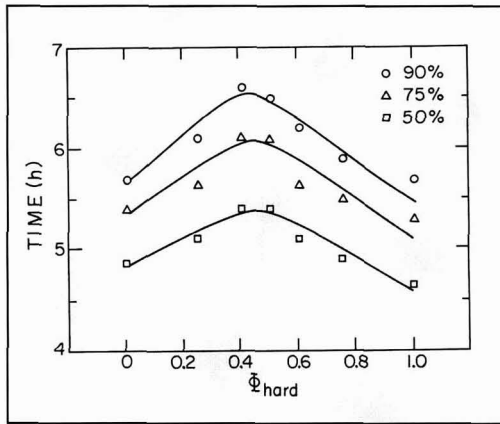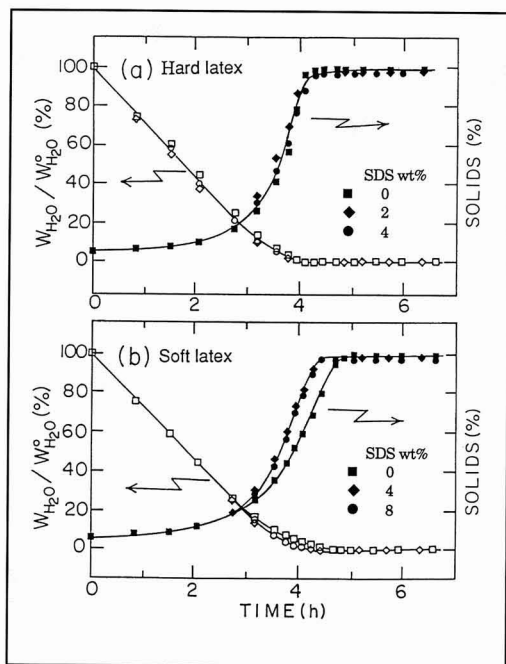
Figure 10—Comparison of the drying process, with and without SDS, for soft and hard latex dispersions: (a) drying curves for a surfactant-free PMMA latex (d = 110 nm, squares) and samples with post-added SDS: 2 wt% (diamonds), 4 wt% (circles); (b) drying curves for soft latex (d = 43 nm, T_g = –33°C) dispersions containing 0 wt% (squares), 4 wt% (diamonds), and 8 wt% (circles) SDS. The amount of surfactant is calculated based upon latex solids.

shrinks more slowly in the later stages than for the samples of Φ_{hard} = 0.33 (or 0.47), as seen in *Figure* 7b. Because we were surprised, we repeated these experiments several times and this behavior is reproducible.

Surfactant Effects on the Drying Rate

Figure 9 shows corresponding data for surfactant-containing dispersions. These are the same samples shown in *Figures* 7 and 8 but with 6 wt% SDS present, based upon latex solids. The drying behavior observed is similar to that seen in *Figure* 8: with increasing Φ_{hard} the drying rate passes through a minimum. These dispersions show a narrower range of drying rates than those without surfactant. This points to a surfactant effect on the drying rate itself, which is described in more detail in the following.

Figure 10 presents comparisons between latex dispersions with and without surfactant (SDS). Both series were dried at the same time and under identical conditions. In the case of hard latex (d = 110 nm), there is no significant difference between the SDS-free sample and those with post-added 2 and 4 wt% SDS, respectively. For soft latex (d = 43 nm, T_g = –33°C), addition of 4 wt% SDS to the surfactant-free dispersion leads to an increase in the drying rate. Further increases in SDS content up to 8 wt% has no additional effect on the drying rate.

There are two ways to appreciate the effect of composition on the drying rate. First, the drying process can be characterized by the instantaneous water evaporation rate, i.e. the slope at each point in the water loss curve. For a series of different blends, these water-loss rates can be compared among samples of identical solids content. In *Figure* 8a, we plot the water-loss rate vs Φ_{hard}, comparing samples at 50, 75, and 90 wt% solids. A second measure of the drying rate is the time needed to reach a given solids content. This comparison is shown in *Figure* 8b.

We note that there is a distinct composition at which the drying occurs at the slowest rate. At 50 wt% solids, samples of Φ_{hard} = 0.47 and 0.56 have a decreased water evaporation rate. Only the two non-film forming samples (Φ_{hard} = 0.78 and 1) exhibit a significantly faster evaporation rate than that measured for samples of Φ_{hard} less than or equal to ~0.55. More pronounced effects are seen at the later stages of drying. At both 75 and 90 wt% solids, the water evaporation rates exhibit a clear minimum at Φ_{hard} close to 0.5.

The same trend is seen in *Figure* 8b. There is a peak in each plot of the global drying time versus Φ_{hard} at various solids contents, representing the slowest rate of drying. There is also a small shift in the peak position, from $\Phi_{hard} \cong 0.5$ in *Figure* 8a to $\Phi_{hard} \cong 0.55$ in *Figure* 8b. What is particularly curious about this system is that the blend with Φ_{hard} = 0.56 dries very differently from those of lower values of Φ_{hard}. For example, in *Figure* 7a one finds that water evaporation of this sample occurs very slowly at early times (t < 2.5 hr) and after 2.5 hr, it dries more rapidly. The overall drying time for this sample is the longest, but the instantaneous drying rate at 50, 75, and 90 wt%, respectively, is not the slowest. In contrast, the dry edge is fast to develop at early times and the wet center
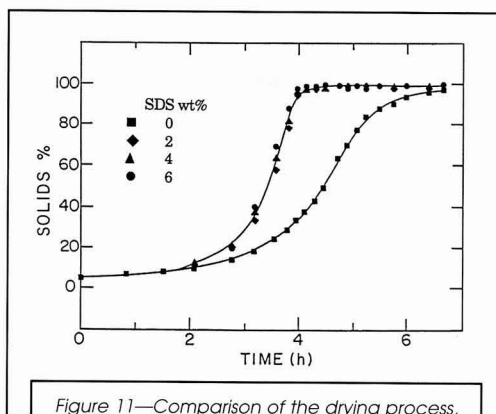
Figure 11—Comparison of the drying process, with and without SDS, for latex blend dispersions containing 0 wt% (squares), 2 wt% (diamonds), 4 wt% (triangles), and 6 wt% (circles) SDS. The blends contain a 1:1 weight ratio of soft latex (d = 43 nm and T_g = –33°C) and PMMA (d = 110 nm).

The previously mentioned results indicate that the drying rate of soft latex dispersions is sensitive to the presence of SDS, but, above a certain amount, is insensitive to the amount present. Another interesting point is that for surfactant-free samples, the hard latex dispersion dries significantly faster than that of the soft latex (4 hr for the hard latex, and 4.75 hr for the soft latex dispersion to reach 97 wt% solids), whereas in the presence of SDS their drying rates become very similar.

We emphasize this point in *Figure* 11, where we show the drying curves for blends of Φ_{hard} = 0.5 with different amounts of SDS. The surfactant-free sample dries much slower than the surfactant-containing samples. When 2, 4, and 6 wt% SDS were added into the latex, the drying becomes much faster, but is again independent of the SDS amount. Isaacs[16] also reported that surfactant accelerates water evaporation during the late stages of film formation. What is curious here is that the amount of surfactant needed to promote the drying rate is less than that needed for monolayer coverage of the latex. Coverage can be estimated by assuming that the area per SDS molecule at saturation is 0.8 nm² on a PMMA surface and 0.6 nm² on PBMA or PBA.[17] For monolayer coverage, one needs 2.7 wt% SDS for 110 nm PMMA latex particles, and 11 wt% for 43 nm P(BMA-co-BA) latex particles. In *Figures* 10 and 11, we see that 2-4 wt% SDS is enough to increase the drying rate for the dispersion of tiny P(BMA-co-BA) latex particles.

MODELS FOR THE DRYING PROCESS

The previous results indicate that there is a distinct composition in latex blends at which the dispersion dries at a slowest rate. For the dispersions examined, this composition corresponds to a Φ_{hard} value close to 0.5. We have some evidence that for very small PMMA particles (44 nm), the minimum is shifted to a lower value of Φ_{hard}. This retardation in drying rate represents a fundamental feature of film formation which must be accommodated into realistic models of the drying process.

Classic Models of Drying

The classic model for the drying process for latex dispersions was proposed by Vanderhoff.[11] He discerned three regions in the plot of cumulative water loss versus drying time. In stage 1, in which the particles remain separated, water evaporates at its normal rate from the surface of the dispersion. Stage 2 commences as the particles come into close contact. The water evaporation rate slows as the particles deform, and the surface area of the water pool decreases. Eventually, coalescence leads to closing of the surface. In stage 3, the loss of the last traces of water is very slow because the water now must diffuse through the continuous polymer phase.

Other models have been put forward for the drying process, for example by Croll,[12] and more recently by Rudin.[18] The Croll model also treats the drying process as occurring uniformly across the surface, with a flocculated phase separating the wet dispersion from the air. Rudin modified the Croll model to include skin formation across the surface of the dispersion during drying.

The Vanderhoff model is often cited and has an appealing simplicity and generality. It and the Croll model, however,

overlook important aspects of the drying process. These models presume, for example, that drying is uniform and neglects the propagating drying front. The Vanderhoff model suggests that water evaporates at the same rate from the dispersion as from a liquid water surface, and continues to evaporate at this rate until the meniscus of the water approaches the tops of the particles in the film. This view is problematic because the area of the wet portion of the film contracts during drying.

Recent Views of the Drying Process

It is important to mention here two sets of experiments described in the recent literature. First, a group at Rhône-Poulenc examined the role of polar material at the surface of latex particles in the film formation process.[14] This material forms an interconnected membrane in newly formed films. If the membrane phase is sufficiently robust, or if the film is examined shortly after drying, the membrane can be rehydrated. Neutron scattering experiments on films rehydrated with D_2O give diffraction peaks corresponding to the size of the original latex particles, implying that a continuous network of membranes persists throughout the film. Note the implication that the latex particles deform before they come into contact, a result which receives strong support from recent experiments reported by Crowley et al.[19] We believe that the structure of this kind of interconnected membrane

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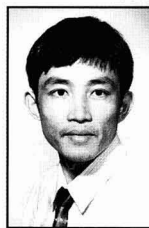
must be important for determining the drying rates during film formation.

The second set of experiments come from a Japan-Bulgaria collaboration investigating the forces which cause spherical particles in dispersion to form ordered monolayers upon drying. Denkov et al.[15] monitored the drying of micron-sized polystyrene latex dispersions by optical microscopy. They observed a convective flux of the particles tending to form a close-packed particle phase, and the direction of particle motion depended on whether the liquid droplet was concave or convex in shape. On a flat glass surface where the liquid film was convex, particle accumulation occurred first at the edge. The particle arrays built up at the periphery as a result of a particle flux from the droplet toward the boundary. When a concave liquid was formed inside a Teflon ring, the formation of close-particle-packing started from the central part of the dispersion. This group argued that once the particles came in contact with the substrate so that they protruded from the water surface, the high surface area would lead to enhanced evaporation from this region, with capillary forces supplying water from the droplet. This in turn sets up a flux of water from the droplet to the drying edge, transporting latex from the bulk to the edge. When the drying rate is sufficiently slow, the forces involved are enough to lift particles above the dried particle layer at the edge, making the final particle layers thicker at the edge than in the center.

(A) Water flux at the drying boundary

(B) Obstacle effect of hard particles in blends

Figure 12—A pictorial view of the drying mechanism. In (a) we show that there is convective flow of water towards the drying boundary and fast evaporation of water in this region due to its high surface area. In (b) we show that as a film forms from soft latex, water is transported through the hydrophilic membrane between the particles. In the blends, hard particles form obstacles and act as a barrier to capillary transport.

This description of the drying mechanism accommodates two key features of the process which other models cannot explain. First, it explains the origin of the drying front and the direction of its propagation. Second, it explains the observation that films formed on flat glass substrates are often thicker at the edges than in the center, especially at slow evaporation rates.

Our View of the Drying Process

From the previously mentioned point of view, the reason that dispersions of hard latex dry faster than those of similar-sized soft latex is related to the magnitude of the capillary transport of water at the wet-dry interface. High T_g latex do not deform during drying. The pore structure that remains can conduct water from the wet domain into this high surface area region of the film. Deformation of the soft latex will lead to smaller capillaries and reduced flow of water. When surfactant is present, it would form a hydrophilic membrane, and this would have a larger effect on the capillary of the soft latex than on the larger pores formed when the hard latex dispersions dry.

In latex blends, the soft latex can deform to fill the spaces between the hard particles. At low values of Φ_{hard}, the hard particles act as obstacles to the diffusion of water through the capillaries of the soft latex matrix. Obstacles decrease the diffusion or capillary flow rate by increasing the tortuosity of the path.[20] At high values of Φ_{hard}, the soft latex polymer plugs the pores between the hard latex. This also produces obstacles to water flow, and the drying rate is slower than for the hard particle dispersion itself.

A somewhat similar observation was reported many years ago by Sullivan[21] on evaporation of organic solvents from the newly dried pigmented latex films. He found that organic solvents (e.g., ethylene glycol) evaporated slowest from the nearly dried films when the pigment volume concentration (PVC) was ~50%. In these pigmented latex systems, the major components are the hard, large pigment particles and the soft binder latex. There is also a critical volume concentration (CPVC) of the pigment particles at which the polymer phase changes from continuous to discontinuous, which is also close to 50%.[22,23] Sullivan explained that large pigment particles gave rise to circuitous pathways and more resistance for organic solvent transport when PVC < CPVC, while the fast evaporation observed when PVC > CPVC was also attributed to the presence of large voids.

To summarize, as water evaporates from a latex dispersion, a dry edge forms at the thinnest portion of the wet film. Drying occurs as a propagating front because water evaporates more rapidly from the high surface area region at the wet-dry boundary than from the wet surface of the droplet itself. Water is constantly wicked through the pore structure to this dry region, and this in turn creates a flux of water and particles from the droplet to the dry edge. In Figure 12a we present a pictorial view of the flux of water and particles toward the drying boundary where fast evaporation occurs. This view may be modified for the case in which salts and surfactant have been removed from the system. Here there can be strong long-range forces between the latex particles in the liquid droplet. These can slow down the flux of particles toward the edge, and if a colloidal crystalline phase is formed, particle transport may be suppressed. In Figure 12b we show that as a film forms from soft latex, water is transported through the

Figure 13—Dynamic mechanical analysis of latex films composed of 110 nm PMMA particles and P(BMA-co-BA) soft polymer: (a) Log plots of E', E", and tan δ versus T under controlled-strain conditions (strain 0.04%, frequency 1 Hz) for a latex blend film of Φ_{hard} = 0.5; (b) Log plots of the dynamic storage modulus (E') versus temperature (strain 0.025%; frequency 1 Hz) for films consisting of different amounts of hard component. Curves 1, 2, and 3 refer to Φ_{hard} = 0, 0.25, and 0.5, respectively.

hydrophilic membrane between the particles, and in blends, hard particles act as a barrier to the water transport and hence reduce the evaporation rate at low Φ_{hard}.

From the systems examined in *Figures* 7-9, we see that dispersions with a composition near Φ_{hard} = 0.5 dry at the minimum rate. Note that this composition lies in the same range as the critical composition (close to 0.5) at which the films formed from dispersions change from continuous, transparent to turbid (see *Figure* 1). We suspect that there is a connection between more rapid water loss for larger values of Φ_{hard} and the onset of turbidity in the films. Turbidity indicates the presence of voids which the soft latex is unable to fill completely. These voids can act as conduits for water transport during the later stages of drying and water evaporation occurs fast as Φ_{hard} increases from ~0.5 to higher values.

MECHANICAL PROPERTIES

One of the reasons that latex blend films represent a useful strategy for zero VOC coatings is that the films have enhanced mechanical properties. There appears to be a strong interaction between the hard latex and the soft matrix, which gives useful mechanical coupling between them. In this section, we examine briefly the nature of this interaction.

Blend films of PMMA and P(BMA-co-BA) were investigated by dynamic mechanical analysis (DMA). *Figure* 13a shows a typical result for a blend film sample with Φ_{hard} = 0.5. We show changes in the storage modulus E', the loss modulus E", and loss tangent (tan δ) versus T (°C). The first transition, characterized by the sharp decrease of E', and peaks for E" and tan δ at about –10°C, reflects the glass transition of the soft component. The second transition occurs at T > 110°C, where the PMMA hard particles begin to soften, and the composite starts to flow. The most interesting information comes from comparing samples from different blend compositions. For this purpose, in *Figure* 13b we plot the storage modulus versus temperature for film samples with Φ_{hard} = 0, 0.25, and 0.50, respectively.

There are several noteworthy features in *Figure* 13. First, we see that the overall film modulus is significantly increased when the soft polymer is blended with the hard latex. Second,

the high modulus region of the DMA spectrum extends to a much higher temperature when the hard component is present. In addition, the glass transition of the soft component becomes broader and shifts to higher temperature when the amount of hard particles increases, indicating that the physical properties of the soft polymer itself have been modified due to the interaction with the hard particles. These results are of particular importance for the use of latex blends in coatings. These dispersions form films at room temperature without the need for any coalescing aid, yet the films that form have a much higher modulus at room 22°C (E' on the order of 10^8 Pa) than the low T_g latex polymer.

The dynamic mechanical properties of these latex blend films resemble those of polymers compounded with inorganic filler. Physical models[24,25] of polymer/filler systems invoke the idea that a layer of soft polymer adjacent to a hard surface becomes stiffer. NMR studies[26,27] reveal that there is a reduction of molecular mobility of the soft polymer adjacent to the filler particles that causes the shift of glass transition position and the increase of the modulus of the matrix. When the volume fraction of hard particles increases, the fraction of soft component that is influenced by the hard particles increases, and the effect of reinforcement becomes more pronounced.

The PMMA particles in the soft polymer matrix act as reinforcing filler in our blend films. They increase the modulus, the hardness and the block resistance of these films. This effect is rather remarkable, considering that there is no obvious source of chemical interaction between the components, as one would have between an acrylate polymer and a silica or TiO_2 surface. These are dissimilar polymers, and if one had only van der Waals interactions at the surface, one might imagine that the adhesion forces would be rather weak.

CONCLUSIONS

Latex blend films were prepared from dispersions containing a mixture of hard and soft latex particles. For films spread on a flat glass surface, the drying process exhibits a drying front which propagates from the edge towards the center. Dispersions of soft latex dry more slowly than those of a corresponding latex with a T_g above room temperature. Blends of these

M.A. Winnik and J. Feng

dispersions take longer to dry, and there exists a distinct composition which dries at the slowest rate. The presence of surfactant facilitates the water evaporation rate. We propose a model to explain the drying mechanism.

Transparent films are obtained when sufficient soft component is present. This corresponds to the concentration at which it becomes the continuous phase. The surface and bulk morphologies, studied by atomic force microscopy, scanning electron microscopy, and freeze-fracture transmission electron microscopy, reveal that transparency of the films corresponds to a random distribution of hard spheres in the soft matrix. An intimate contact is achieved between the two polymer phases. In these blend films, the hard particles act as a reinforcement filler and provide a remarkable improvement in the mechanical properties of the films formed.

ACKNOWLEDGMENTS

References

(1) Karsa, D.R., *Additives for Water-Based Coatings*, Royal Society of Chemistry, London, 1991.
(2) Broek, A.D., *Prog. Org. Coat.*, 22, 55 (1993).
(3) Winnik, M.A., Wang, Y., and Haley, F., "Latex Film Formation at the Molecular Level: The Effect of Coalescing Aids on Polymer Diffusion," JOURNAL OF COATINGS TECHNOLOGY, 64, No. 811, 51 (1992).
(4) Feng, J., Winnik, M.A., Shivers, R., and Clubb, B., *Macromolecules*, 28, 7671 (1995).
(5) (a) Friel, J., European Patent Application, 0466 409 A1 (1992); (b) Snyder, B.S., U.S. Patent 5308890 (1994).
(6) Patel, A., Feng, J., Winnik, M.A., Vancso, J., and McBain, C., *Polymer*, 1995, in press.
(7) Wang, Y., Kats, A., Juhué, D., Winnik, M.A., Shivers, R., and Dinsdale, C., *Langmuir*, 8, 1435 (1992).
(8) Bohn, L., in *Polymer Handbook, 2nd Edition*, Brandrup, J. and Immergut, E.H. (Eds.), , Wiley-Interscience, NY, p. 111-211, 1975.
(9) Rosen, S.L., *Polymer Eng. Sci.*, 7 (2), 115 (1967).
(10) Mark, H.F., Bikales, N.M., Overberger, C.G., and Menges, G., *Encyclopedia of Polymer Science and Engineering*, Vol. 1, John Wiley and Sons, New York, p. 257, 1985.
(11) Vanderhoff, J.W., Bradford, E.B., and Carrington, W.K., *J. Polymer Sci.: Symposium No. 41*, 155 (1973).
(12) Croll, S.G., "Drying of Latex Paint," JOURNAL OF COATINGS TECHNOLOGY, 58, No. 734, 41 (1986).
(13) Pramojaney, N., Poehlein, G.W., and Vanderhoff, J.W., *Drying'80, Vol. 2*, p. 93-100, 1980.
(14) Chevalier, Y., Pichot, C., Graillat, C., Joanicot, M., Wong, K., Lindner, P., and Cabane, B., *Colloid Polymer Science*, 270, 806 (1992).
(15) Denkov, N.D., Velev, O.D., Kralchevsky, P.A., Ivanov, I.B., Yoshimura, H., and Nagayama, K., *Langmuir*, 8, 3183 (1992).
(16) Isaacs, P.K., *J. Macromol. Chem.*, 1, 163 (1966).
(17) Vijayendran, B.R., *J. Appl. Polymer Sci.*, 23, 733 (1979).
(18) Eckersley, S.T. and Rudin, A., *Prog. Org. Coat.*, 23, 387 (1994).
(19) Crowley, T., Sanderson, A., Morrison, J., Barry, M., Morton-Jones, A.J., and Rennie, A.R., *Langmuir*, 8, 2110 (1992).
(20) Mackie, J.S. and Meares, P., *Proc. R. Soc. London*, A 1955, 232, 498.
(21) Sullivan, D.A., "Water and Solvent Evaporation from Latex and Latex Paint Films," JOURNAL OF PAINT TECHNOLOGY, 47, No. 610, 60 (1975).
(22) Stieg, F.B., *Prog. Org. Coat.*, 1, 351 (1973); Stieg, F.B., "Particle Size as a Formulating Parameter," JOURNAL OF PAINT TECHNOLOGY, 39, No. 515, 701 (1967).
(23) Schaller, E., "Critical Pigment Volume Concentration of Emulsion Based Paints," JOURNAL OF PAINT TECHNOLOGY, 40, No. 525, 433 (1968).
(24) Mations, V.A., *Polymer Eng. and Sci.*, 9, 90 (1969).
(25) Vollenberg, P.H.T. and Heikens, D., *Polymer*, 30 (9), 1656 (1989).
(26) Douglass, D.C. and McBrierty, V.J., *Polymer Eng. and Sci.*, 19, 1054 (1979).
(27) Mahoney, D. and Meerwall, E.V., *J. Polymer Sci. Polymer Phys.*, 31, 1029 (1993).

Film Formation Mechanism of Two-Component Waterborne Polyurethane Coatings

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Air Products and Chemicals, Inc.*

INTRODUCTION

Two-component (2K) waterborne polyurethane coatings are a relatively new technology which has been demonstrated in automotive, aerospace, industrial maintenance, wood, and plastic coating applications.[1-6] They consist of a water dispersible, multi-functional isocyanate which is mixed with a dispersion of hydroxy-functional polymer. The popularity and importance of these coatings is growing significantly due to their potential for providing excellent properties, equivalent to those of their solvent-borne counterparts, combined with a low concentration of volatile organic compounds (VOCs). Current waterborne formulations have VOCs of less than 250 grams per liter of paint and this evolving technology has the potential for eliminating VOCs entirely.

Although researchers have been successful in developing these coatings into practical systems, one important aspect that is not well understood is their film formation mechanism. This is due to their relatively recent development, as well as the complexity of their drying/curing process. As with all coatings, proper film formation is essential for optimum coating performance. Film formation of 2K waterborne polyurethanes is especially critical due to their use in heavy duty applications where long-term performance (e.g., adhesion, durability, substrate protection) is paramount. Their film formation process is unusually complex and consists of a dynamic series of events which are interrelated. The order of and extent to which these events occur has a major impact on the quality and performance of the applied coating. The film formation process includes the traditional difficulties of water-based systems, namely evaporation of water and organic volatiles with concomitant coalescence of polymer particles. It is complicated further by the need for thorough coalescence of dissimilar species (polyisocyanate and polyol) and competing reactions between hydroxyl groups and water with the isocyanate (*Figure* 1). Furthermore, the reaction of isocyanate with water ultimately produces carbon dioxide which must leave the system in such a way as to avoid film defects. Although these critical issues have been recognized, until now no detailed film formation mechanism for these systems has been proposed and substantiated.

Two-component (2K) waterborne polyurethane coatings are a new technology which has been demonstrated in a number of heavy duty applications. They exhibit performance properties equivalent to 2K solvent-borne polyurethanes, with the advantage of reduced volatile organic compounds (VOCs). Although the use of these systems has been demonstrated successfully, the details of their film formation mechanism have not been established.

The objective of this work was to propose and confirm the film formation mechanism of these systems. A dynamic series of interrelated events which occur during the process was identified using a number of analytical techniques to study two isocyanate/hydroxyl functional dispersion systems. The mechanism is presented in terms of an "event timeline" that chronicles the critical events which occur prior to and after application of the coating.

Film property development after application also was evaluated and these results were analyzed in terms of the proposed film formation mechanism.

The objective of this work was to propose and confirm the film formation mechanism of 2K waterborne polyurethane coatings. The approach was to isolate each of the events which occur along the timeline of this process, identify the critical issues influencing these events, and determine the extent to which film formation and coating properties are affected by these events. With a better understanding of these factors, the chemistry and formulation of these systems can be adapted to increase the latitude of their applications while minimizing the potential for defects caused by poor film formation. In this paper we present the following:

R—NCO + R'—OH → R—NH—COOR'
Urethane Formation

- -

R—NCO + H₂O → [R—NH—COOH]
Carbamic Acid

[R—NH—COOH] → R—NH₂ + CO₂

R—NCO + R'—NH₂ → R—NH—C—NH—R'
Urea Formation

Figure 1—Reactions of isocyanate with hydroxyl and water.
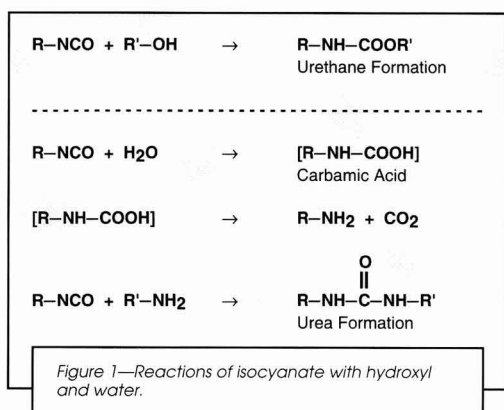
(1) A brief review of film formation mechanisms, concentrating mainly on those issues pertinent to 2K waterborne polyurethanes.

(2) A proposed mechanism for these systems which describes the timeline of events and their respective interactions.

(3) A description of the experimental details.

(4) Empirical results which confirm the proposed mechanism and identify the critical issues affecting coating properties.

BACKGROUND ON FILM FORMATION

As mentioned previously, proper film formation is critical to coating performance and much research has been performed to determine film formation mechanisms for various types of coatings. In general terms, it is convenient to classify these as:

(1) Thermoplastic polymers from solution.

(2) Thermoplastic polymers from dispersion.

(3) Thermosetting polymers from solution.

Clearly, film formation of thermosetting polymers from dispersion and, more specifically, that of 2K waterborne polyurethane coatings is not covered under these traditional categories. It would seem, however, that some principles associated with film formation of thermoplastics from dispersion and thermosetting polymers from solution would be related to those of 2K waterborne polyurethanes. Certainly the requirements of particle coalescence (associated with dispersions of thermoplastics) and crosslinking reactions (associated with thermoset systems) must exist with 2K waterborne polyurethanes. A more detailed look at the mechanisms of the former systems will provide insight concerning that of the latter.

Traditional waterborne coatings are prepared from an aqueous dispersion of polymer particles, commonly referred to as a latex. *Figure* 2 is a schematic that depicts their basic film formation process. Upon application of the latex, water and other volatile components begin to evaporate, forcing the polymer particles closer together. As this evaporation process continues, the concentration of polymer particles increases until eventually the particles come into contact. At this point they have formed a close-packed arrangement with volatiles

in the interstitial regions. As the remaining volatiles evaporate from within the polymer particles and the interstitial regions, forces begin to compress and coalesce the particles. Numerous models and mechanisms have been proposed on the origin and extent of these forces[7-11] but all agree that complete film formation of these systems requires diffusion of polymer molecules across particle boundaries. As this occurs, individual particles cease to exist. Cohesive strength of the film is enhanced significantly by increased chain entanglements and secondary bonding. The end result is the formation of a solid, cohesive film on the substrate.

A critical factor in this film formation process is the diffusion of polymer molecules required for coalescence. This is associated with large-scale motion of molecular chains, such that polymers at temperatures above their glass transition temperature, (T_g) will form films more easily than those below their T_g. Unfortunately, polymers with lower T_g normally produce coatings with lower strength, durability, abrasion, and chemical resistance. To overcome these performance deficiencies, higher T_g and higher molecular weight polymers are used. In order to properly film form, such dispersions require either additional solvent to swell the polymer particles (thereby reducing T_g), or higher drying temperature, which increases the mobility of the polymer chains. Of course these modifications cause higher VOCs or baking requirements which are undesirable for many applications.

Film formation of thermosetting polymers from solution occurs via a completely different mechanism from that described previously. In this case, the system is a solution of reactive species in organic solvents. The solvents are selected to keep the coating in a liquid state until application, at which time they begin to evaporate. The reaction, which is designed to build molecular weight and crosslinking of the polymer, normally can proceed prior to and/or after application of the coating. In the case of two-component coatings (e.g., 2K epoxies and polyurethanes), the reaction kinetics occur quickly enough that the reactants must be mixed just prior to application or else the systems will gel prematurely. Two-component polyurethanes normally are formed from the reaction of a multi-functional isocyanate with a hydroxy-

Coating applied, polymer spheres dispersed in water
⇩
Initial bulk water evaporation and particle packing
⇩
Close-packed particles with water-filled interstices
⇩
Continuing evaporation of volatiles, initial particle compaction
⇩
Initial film formation with compacted particles
⇩
Inter-particle diffusion of polymer molecules
⇩
Isotropic polymer film
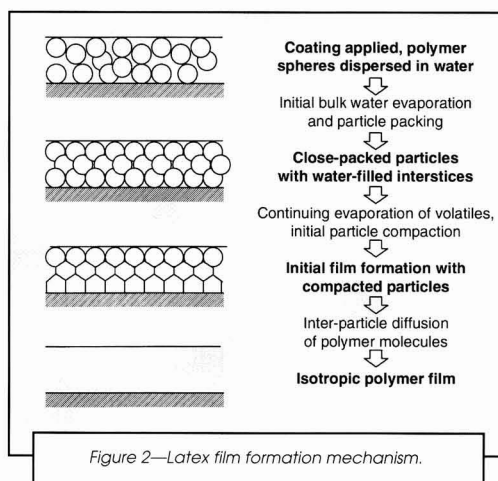
Figure 2—Latex film formation mechanism.

functional polyester or acrylic. In this case, the kinetics normally follow a second order relationship.[12] (Note: The gel time of these 2K solvent-borne polyurethane coatings ranges from several minutes up to eight hours depending on the specific reactants, catalyst(s), and application/cure temperature.)

A critical issue associated with this mechanism is the relative rate of solvent evaporation versus that of the curing reaction. Rapid curing reaction and the associated molecular weight increase can cause a number of potential problems. Solvents may become trapped and eventually form small blisters or "solvent pops" within the film. In addition, if molecular weight builds too quickly during the early stages of curing, diffusion of reactive groups can become hindered. This prevents complete reaction and leaves unreacted lower molecular weight species within the film. These unreacted molecules usually have detrimental effects on mechanical and chemical resistance properties. Finally, quick reactions will shorten pot life and may cause immobility of the molecular system. This latter effect may result in internal stresses within the coating which are potential sites for mechanical failure. On the other hand, slow reactions can cause slow drying and property development which also is undesirable.

From the description of 2K waterborne polyurethane coatings provided in the Introduction Section, one would imagine that some facets of their film formation mechanism would be related to a combination of those described. It would appear that the following steps must take place in some overlapping order:

- Evaporation of volatiles;
- Coalescence of polyol and polyisocyanate particles; and
- Reaction between polyol and polyisocyanate.

This process is complicated by the fact that when the components of the coating are combined the reactive species are not immediately in the same phase within the dispersion but ultimately must be so to react. It is further complicated by the competing reactions of isocyanate with both hydroxyl groups and water (Figure 1). While the former reaction yields the preferred polyurethane, the latter reaction produces urea and CO_2. The CO_2 must leave the coating before the completion of film formation to avoid defects within the bulk or the surface of the cured coating.

Some researchers have provided limited evidence as to the order and extent of events during film formation of these systems. It has been suggested that as the two components are mixed, the polyol dispersion emulsifies the isocyanate by encapsulating it.[3,4,6,13] Kubitza[13] reported polyisocyanate particle size of 0.1 to 0.5 microns (depending on agitation severity) shortly after mixing with a hydroxy-functional acrylic dispersion. After one hour, particle diameters of up to 10 microns were measured. Jacobs and Yu[4] utilized a hydroxy-functional polyurethane dispersion with a particle size of less than 25 nm but reported the dispersed polyisocyanate particle size was approximately two microns. In fact, scanning electron micrographs of applied polyisocyanate from a five percent aqueous dispersion illustrated isolated particles 1 to 10 microns in diameter. Bock and Petzoldt[6] also reported that they observed an isocyanate-enriched phase with larger particles than the initial dispersion.

Mixing of the polyisocyanate and polyol dispersion prior to application will initiate the isocyanate-hydroxyl and isocyan-

Figure 3—Proposed film formation mechanism "event timeline" for 2K waterborne polyurethane coatings.
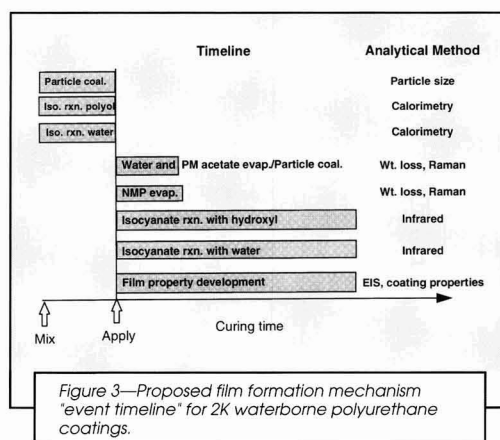
ate-water reactions. If coalescence of polyisocyanate and hydroxy-functional particles occurs at this time, it will facilitate the preferred isocyanate-hydroxyl reaction. This effect is enhanced even further if the polyol "encapsulates" the polyisocyanate. Hare[14] has stated that this encapsulation does occur and the reaction initiates at hydrophilic centers at the polyisocyanate-polyol interface. The reaction of typical polyisocyanates with hydroxyl appears to be faster than that with water.[4,15,16] However, some reaction with water is inevitable. Bock[6] has reported detection of CO_2 approximately 30 min after mixing. To ensure complete reaction of hydroxyls, it has become common to use excess polyisocyanates at NCO/OH ratios of 1.5 to 3.

The coating must be applied before the curing reaction(s) proceed to any substantial extent. Otherwise, molecular weight and crosslinking would occur to such an extent that particle coalescence after application would be difficult due to diffusion limitations. Upon application of the coating, volatiles (water and solvents) begin to evaporate. It has been stated that most of the water has evaporated in 20 to 60 min after application.[4,14] This forces the particles together, allowing for more thorough diffusion and reaction. Ultimately, a crosslinked polymer coating is formed. Jacobs and Yu[4] reported that maximum levels of solvent resistance, impact resistance, and hardness were reached in two days, and ultimate tensile strength was fully developed in four to five days. They related these results to dynamic mechanical analysis results which showed that storage modulus stabilization occurred after two days but it took three days for stabilization of tan δ curves. Kubitza[13] found T_g values from DSC data increased until day 12.

PROPOSED FILM FORMATION MECHANISM FOR 2K WATERBORNE POLYURETHANE COATINGS

The mechanism is presented in terms of an "event timeline" that identifies the following interrelated processes that occur during film formation: particle coalescence, reactions of isocyanate with hydroxyl groups and water, water evaporation, and solvent evaporation. These are schematically depicted in Figure 3. All these events interact to establish the film chem-

C.R. Hegedus, A.G. Gilicinski, and R.J. Haney

Table 1—Materials and Suppliers

Product	Description	Manufacturer
Hybridur® 710EXP (ACPU-1)	Hydroxy-functional acrylic-polyurethane	Air Products and Chemicals, Inc.
Bayhydrol® XP-7044 (PUD-1)	Hydroxy-functional polyurethane	Miles, Inc. (now Bayer)
Bayhydur® XP-7063	HDI based polyisocyanate	Miles, Inc. (now Bayer)
Dabco® T1402	Dibutyltin Bis(1-thioglycerol)	Air Products and Chemicals, Inc.
BYK® 345	Polyether modified polydimethylsiloxane	BYK-Chemie, Inc.

istry and development of mechanical integrity during cure. The event timeline starts after mixture of the two components, at which point particle coalescence and isocyanate chemistry are the key processes that affect the coating system. After coating application, these continue to affect the system, however, water and solvent evaporation now become key processes as well.

To verify this mechanism and generate an understanding of the time frame in which these events dominate, a number of analytical characterization tools were utilized with two isocyanate/hydroxy-functional dispersion systems (as listed in *Figure* 3 and described in the Experimental Section). Particle coalescence was measured by particle size as a function of induction time (i.e., the time elapsed after mixing the two reactive components). The reaction chemistry and rates during this time were monitored using isothermal calorimetry which was correlated with viscosity effects. After application of the coating, particle packing factor calculations coupled with weight loss data were used to study the initial phase of coalescence as water evaporated and particle close-packing was achieved. Water and solvent evaporation were monitored by weight loss studies and infrared (IR) spectroscopy. Film formation was also studied using electrochemical impedance spectroscopy (EIS) and Raman spectroscopy. Isocyanate reaction chemistry of applied films was monitored by infrared, and EIS studies. The surface chemistry after cure was examined using X-ray photoelectron spectroscopy (XPS).

In addition to the analytical approach described previously, the development of film properties was characterized. This was completed by performing standard chemical and

Table 2—Properties of Dispersions and Isocyanate Used

Property	PUD-1	ACPU-1	Isocyanate
Solids, wt%	40	43	100
Water, wt%	47	50	0
N-methylpyrrolidinone (NMP), wt%.	11	7	0
Equivalent wt.	2200	1810	243
Density, g/ml	1.06	1.04	1.16

Table 3—Typical Hydroxy-Functional Acrylic-Polyurethane Based Formulation Evaluated

	Percent by Weight
ACPU-1	70.27
BYK 345	0.28
Dabco T1402	0.02
XP-7063	19.20
PM acetate	10.23

mechanical evaluation techniques on coatings as a function of time after application. EIS was also performed as part of this evaluation.

EXPERIMENTAL

Materials and Coating Preparation

The materials used in this study and their manufacturer are listed in *Table* 1. These systems are representative of available 2K waterborne polyurethane technology. Two hydroxy-functional dispersions were utilized, a polyurethane (PUD-1) and an acrylic-polyurethane hybrid (ACPU-1). These dispersions were crosslinked with a hexamethylene diisocyanate (HDI) trimer which was modified to improve water dispersibility. *Table* 2 lists properties of these materials. Further material descriptions are provided in references (17) and (18).

Coatings were prepared by adding surfactant and catalyst to the hydroxy-functional dispersion while mixing under mild agitation. The surfactant was added at a concentration of 0.4% by weight of the dispersion. Catalyst concentration was 0.04% by weight based on total polymer solids of the final coating. A 65% solution of the isocyanate in propylene glycol methyl ether (PM) acetate was prepared. When combined with the aqueous dispersions, a coating VOC (minus water) of approximately 250 grams per liter was formed. The admixed coating was prepared prior to application by adding the isocyanate solution to the dispersion while under mild agitation. The components were combined to obtain an NCO/OH ratio of 2.0. *Table* 3 provides an example of the ACPU-1 formulation evaluated. The standard induction time prior to application of the admixed coating was 15 min; however, the effects of induction time on heat of reaction and dispersion particle size were studied. Unless otherwise specified, the coatings were applied to a dry film thickness of 50±5 microns (2±0.2 mils) using conventional air spray. Coatings were applied to cold rolled 1020 steel with a zinc phosphate treatment (Bonderite® 952) and a chromate sealer (Parcoolene® 60). Unless otherwise noted, the coating drying and storage conditions were 21°C, 50% relative humidity.

Equipment and Procedures

Table 4 lists the ASTM methods used to evaluate admixed and applied coating properties. Weight loss of applied coatings after application was obtained by applying a film with a 152 micron (6 mil) drawdown bar and weighing the sample at specified time intervals after application. The property development assessment was done by preparing the specimens described earlier and performing specified tests at predetermined times after application.

Table 4—Procedures Used to Evaluate Admixed and Applied Coatings

Property	ASTM Method
Viscosity (Zahn 2)	D4212
Adhesion	
Tape adhesion	D3359A
Scrape adhesion	D2197A
Persoz hardness	D4366
Solvent resistance	D4752

Particle size distributions of dispersions were obtained using capillary hydrodynamic fractionation (CHDF).[19] Samples were prepared by mixing the isocyanate solution (XP-7063/PM acetate) into the desired hydroxy-functional dispersion to obtain an NCO/OH ratio of 2.0. After combining the two materials, the dispersions were shaken vigorously for 1-2 min. A sample of XP-7063/PM acetate solution was also mixed into water. Particle size measurements were periodically obtained for these samples over their pot life. Just prior to particle size analysis, a sample of each dispersion was diluted to one percent solids using distilled water and injected into the CHDF. The particles flow within a capillary tube. The laminar flow profile within the tube causes the particles to separate according to size with the larger particles leading the flow and exiting the capillary first, followed by smaller particles. The particles are detected via turbidity using a UV detector. The chromatograms were deconvoluted to generate number and weight average particle size diameters and distributions.

Heat flow profiles for the reaction of isocyanate with hydroxy-functional dispersion and water were obtained with a Setaram C80D (differential heat flux) calorimeter. Identical test cells are placed into sample and reference chambers within the temperature control block. Thermopiles are used to monitor the heat flow into or out of each chamber. The difference between the sample and reference signals is used to eliminate heat flux associated with temperature control of the calorimeter. For the present work, the calorimeter was used isothermally at 21°C. Prior to mixing, the isocyanate solution and aqueous dispersion components were placed into the lower and upper chambers of the stainless steel membrane mixing cell, respectively. The chambers were separated by a Teflon membrane. The upper chamber of the reference cell was filled with the same amount of dispersion as in the sample cell, but the lower chamber was left empty. After insertion of the cells into the calorimeter, and equilibration to a stable heat flux baseline, the membranes of the sample and reference cells were punctured simultaneously, and the cells were mixed using manual impellers for one minute. Following that process, the cells were not disturbed as the heat flux was monitored over a 24-hr period.

IR spectroscopy was done using an attenuated total reflectance (ATR) system which allowed the coating to be measured during cure.[20] A CIC Photonics Fresnel ATR held the crystal horizontally inside the IR (Nicolet 510 interferometer) sample compartment. A 45° incident angle AMTIR-1 crystal (2 cm diameter sampling area) was used. A film was spread onto the crystal with a 127 micron (5 mil) draw-down bar. The infrared spectrum was obtained by co-adding 64 scans at 4.0 cm^{-1} resolution, and spectra were obtained and saved at 15-min intervals for 24 hr and then daily for three weeks.

Electrochemical impedance spectroscopy (EIS) was performed using a commercial coatings cell (EG&G Instruments) with a 1 cm diameter gasket defining the working electrode in a three electrode cell. Measurements were controlled by a commercial software package (EG&G 398) with a potentiostat (EG&G 273A) and lock-in amplifier (EG&G 5210) at individual frequencies for 5 Hz to 100 kHz. Low frequency data were obtained in a multi-sine wave experiment. The data were combined into one EIS spectrum for analysis. Modeling was done using Equivcrt,[21] and a simple coating model (pore resistance and coating capacitance) was used to evaluate the coatings.

EIS was used in two ways in this work. To probe effects of water evaporation and film formation over time, coatings were drawn onto the substrate and pieces were cut with tin shears at specified time intervals and analyzed. EIS spectra were obtained after 15 min of equilibration in 3% NaCl solution to minimize the effect of contact with electrolyte on the curing film. A comparison with fully cured coatings was made in EIS experiments done after 15 min and after 24 hr exposure to NaCl solution. These studies were done at three locations on the coating.

The surface composition of cured coatings was determined with XPS using a PHI (Physical Electronics) 5000LS surface spectrometer, equipped with a hemispherical analyzer (SCA), an Omni Focus III lens system, and a multi-channel detector (MCD). Maximum sampling depth was about 10 nm. High resolution multiplex spectra were collected, for each elemental species detected in the survey scan, at 23.50 eV Pass Energy, 0.100 eV per step, and 100 ms per step. The high resolution regions were used to calculate the surface composition by measuring the area under each peak envelope and
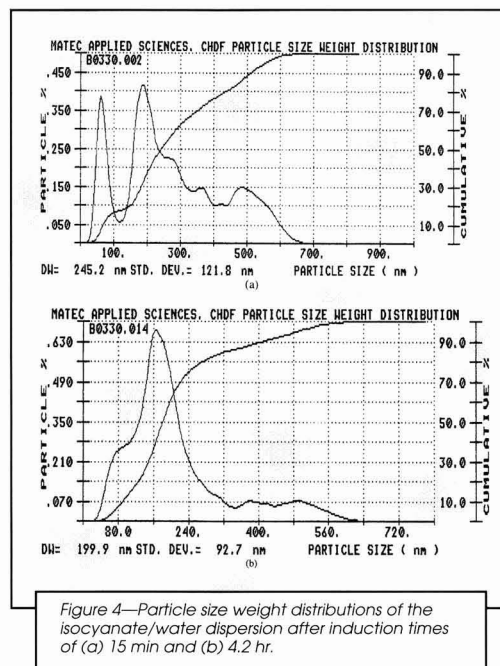

Figure 4—Particle size weight distributions of the isocyanate/water dispersion after induction times of (a) 15 min and (b) 4.2 hr.

C.R. Hegedus, A.G. Gilicinski, and R.J. Haney

Table 5—Particle Size (nm) of Dispersions

Induction Time (hr)	Isocyanate in water			Isocyanate in ACPU-1			Isocyanate in PUD-1		
	D_n	D_w	D_w/D_n	D_n	D_w	D_w/D_n	D_n	D_w	D_w/D_n
0.0	76	245	3.2	66	206	3.1	62	323	5.2
0.5	—	—	—	70	213	3.0	56	310	5.5
1.0	79	263	3.3	—	—	—	—	—	—
1.5	—	—	—	—	—	—	—	—	—
2.0	82	245	3.0	74	142	1.9	62	276	4.5
3.25	—	—	—	79	172	2.2	58	271	4.7
4.25	102	200	2.0	79	140	1.8	62	252	4.1
5.5	114	223	2.0	81	148	1.8	59	261	4.4
7.0	96	210	2.2	66	75	1.1	—	—	—

applying area sensitivity factors (ASF) in the analysis software.

RESULTS AND DISCUSSION

Results from the range of analytical tests are described in the context of the timeline of events which we propose occurs during the entire film formation sequence as outlined in *Figure* 3. Film property development after application was evaluated using EIS and other standard coating characterization methods. These results were analyzed in terms of the proposed film formation mechanism.

Particle Coalescence in the Admixed State

After mixing but prior to application (referred to as the induction time), the events which may potentially occur relative to film formation are coalescence of isocyanate particles with the hydroxy-functional dispersion particles, and reactions of the isocyanate with both hydroxyl groups and water (*Figure* 1). Particle coalescence during this stage of film formation was analyzed using in-situ particle size measurements. Prior to mixing with the isocyanate, ACPU-1 had a number average particle size (Dn) of 66 nm, a weight average particle size (Dw) of 75 nm, and Dw/Dn = 1.1. The particle size distribution curves for ACPU-1 had a classic Gaussian shape. PUD-1 has a particle size of ~25 nm.[4] Particle size data over the induction time are listed in *Table 5*.

The dispersion of isocyanate in water had an initial average particle size of Dw = 245 nm and Dn = 76 nm. Dw decreased slightly over the seven-hour induction time down to 210 nm. Similar studies were obtained with both mild and vigorous agitation. In addition, the graph of particle size weight distribution went from the initial multi-peak distribution to a single peak distribution at 4.25 hr (*Figure* 4). The graphs suggest that smaller particles (D ~60 nm) are growing in size but large particles (D ~200 nm) do not seem to be changing. Particle size increase of small particles would be more evident and this change may be due to coalescence or flocculation of the particles, and/or reaction of water with isocyanate which produces urea.

Dn of the water/isocyanate system increased slightly over the first two hours of induction time and then more significantly between two and six hours . The number distribution curve initially had a narrow single peak at ~60 nm, which is indicative of the main particle population at induction times of less than two hours. At two hours, most of this population

remains but a smaller population at ~200 nm became evident. By four hours, the two populations had begun to merge as evidenced by a significant broadening of the higher portion of the curve up to 240 nm. At the four-hour time, it was also noticed that the temperature of the vial containing the admixed coating had increased significantly, indicating that the exothermic isocyanate-water reaction was proceeding significantly. This was examined further in calorimetry work as discussed in the following.

The PUD-1/isocyanate dispersion had a bimodal distribution with the main particle population at 60 nm and a much smaller population between 200 and 600 nm. This is consistent with results reported by Kubitza[13] but considerably smaller than that reported by Jacobs and Yu.[4] The smaller particles may be from the PUD-1 dispersion; however, our results with PUD-1 and previous reports[4] indicate this dispersion has a particle size much smaller than 60 nm. Based on the particle size results reported, these smaller particles most likely are from the isocyanate dispersion. The larger particles (200-600 nm) in the PUD-1/isocyanate dispersion are certainly isocyanate. Contrary to previous reports,[4,13] the distribution did not change much over the five-hour induction period. Dn did not change and Dw decreased only slightly from 323 to 261 nm. From these data, it does not appear that coalescence is occurring to a major extent.

The ACPU-1/isocyanate dispersion had a slightly different particle size distribution than the water/isocyanate and the PUD-1/isocyanate dispersions. There was a large population between 50 and 80 nm which is indicative of the ACPU-1 particles and probably some isocyanate particles. A second, much smaller population existed in the 100 to 200 nm range, also from isocyanate. Over the five-hour induction period, Dn increased only slightly from 66 to 81, and Dw decreased from 206 to 148 nm. Initially, Dw/Dn was 3.1 but by two hours it had decreased to approximately two, after which it was constant over the remaining induction period. In comparing the ACPU-1 results with those of the PUD-1, both had a main distribution in the 60 to 80 nm range which remained relatively constant over the five-hour induction time. Both dispersions with the isocyanate had a smaller population at larger diameters; however, this population was in the 100 to 200 nm range with ACPU-1 and 200 to 600 with PUD-1. For both systems, the smaller particles remain relatively constant over the induction time while the larger particles appear to decrease slightly in size.

The particle size results illustrate that there is a significant difference in isocyanate particle size depending on the component in which it is dispersed. It appears that the ACPU-1

emulsifies the isocyanate into smaller particles than in the other systems evaluated. This would tend to improve film formation since smaller particles coalesce more completely. In addition, the results show that particle size of the isocyanate/polymer dispersions does not change significantly over time in the admixed state during typical induction times. This suggests that particle coalescence or flocculation does not occur to a significant extent.

Isocyanate Reaction in the Admixed State

Isothermal (21°C) calorimetry experiments as a function of induction time were performed on reaction mixtures to identify timescales for the reaction chemistry in the system. *Figure* 5 illustrates the response for three systems: (a) water/isocyanate; (b) ACPU-1/isocyanate; and (c) PUD-1/isocyanate. In all three, the point of mixing is observed as an initial sharp exothermic rise in heat flow. This is almost certainly caused by a heat of mixing which lasts over the first 15 to 20 min of induction time.

The water/isocyanate system displays several exotherms which follow the heat of mixing. The first occurs approximately 2.6 hr after mixing, a second is at 4.8 hr, and a broad exotherm is observed between 8.2 and 11.8 hr. The exotherm at 4.8 hr correlates with the temperature rise observed during in-situ particle size measurements of this system. It is interesting to note that Dn for this system increased significantly between two and six hours, which coincides with the first two exotherms. During the reaction time urea formation is certainly occurring. Although it is not entirely clear what intermediate chemical reactions are responsible for each of the exotherms observed, various experimental results provide some evidence. As *Figure* 1 illustrates, the reaction of isocyanate with water to form urea consists of several steps. In the first step, carbamic acid is produced which subsequently decomposes into amine and carbon dioxide. The reaction sequence continues with amine and remaining isocyanate to form urea. During viscosity/pot life studies, a substantial increase in foaming was observed five to six hours after mixing the two components. This suggests that the first exotherm may be due to production of carbarmic acid, while the second exotherm is due to its decomposition which produces carbon dioxide. In addition to these reactions, isocyanates also can react with previously formed urethanes and ureas to form allophonates and biurets. It is believed that these play only a minor role in the film formation of 2K waterborne polyurethanes but they may be responsible for some of the latter exotherms in *Figure* 5a.

The ACPU-1 system (b) exhibits an exotherm which continues from the heat of mixing and reaches a maximum exothermic heat flow approximately five hours after mixing. After this time, the heat flow decreases and essentially returns to the baseline by ~8 hr. The PUD-1 exotherm reaches its peak approximately 2.2 hr after mixing. It is not as intense but it is broader (in time) than that with the ACPU-1.

It would seem highly desirable to apply these coatings between the time of mixing and not long after the maximum heat flow. If applied after this time, molecular weight and crosslinking buildup may prevent complete particle coalescence after application.

Concerning the relative rates of the curing reactions in these systems (i.e., hydroxyl-isocyanate and water-isocyan-

ate), the calorimetry data strongly suggest that the reaction of isocyanate with hydroxyl groups begins almost immediately, while that with water is delayed for more than two hours. This is in agreement with previous reports.[4,15,16] Pertaining to application and cure of these systems as coatings, it certainly is desirable for curing reactions to occur quickly for drying and establishment of properties. However, pot life is also a consideration, and if reactions occur too quickly, pot life may be undesirably short. This issue is addressed in the following.

Pot life of the ACPU-1 coating was evaluated by performing viscosity measurements (Zahn 2 cup) as a function of

Figure 5—Calorimetry results for (a) water/isocyanate, (b) ACPU-1/isocyanate, and (c) PUD-1/isocyanate.
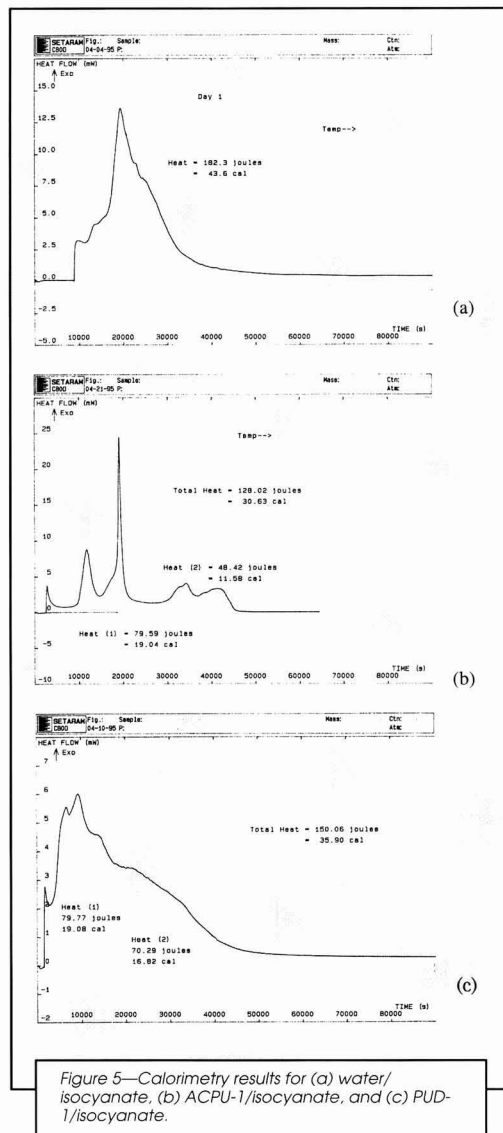
Table 6—Catalyst Level Effect on Zahn 2 Cup Viscosity (sec) versus Induction Time

Induction Time (hr)	Catalyst Level (%)							
	0	0.02	0.03	0.04	0.05	0.06	0.08	0.1
0.25	22.2	23.2	23.1	23.8	24.5	24.5	25.3	25.7
0.5	22.1	23.5	24	24.5	25.2	26.4	26.7	27.9
1	22.2	24.9	25.7	27	28.8	28.1	29.2	29.8
1.5	22.7	26.4	26.9	28.5	30	29.3	28.8[a]	26.5[a]
2	23.9	27	27	27.7[a]	26.9[a]	24.2[a]	24.4	25
3	25.2	27.3	27.1	26.6	25.5	26	28.1	29.8
4	25.3	25.7[a]	26.7[a]	25	28	—[b]	—[b]	—[b]
5	26	26	25	—[b]	—[b]			
7	26	—[b]						

(a) The admixed coating had become slightly foamy.
(b) The admixed coating had become extremely foamy.

induction time. In these experiments, catalyst level was varied from 0 to 0.10% based on polymer solids. These admixed coatings initially had a viscosity of ~35 sec. Approximately six percent deionized water was added to reduce the viscosity to the 22 to 26 sec range. As can be seen in *Table* 6, the viscosity of the coatings with catalyst increased slightly over the first one to two hours, after which viscosity decreased slightly. As the viscosity decrease occurred, the coatings appeared to become slightly foamy but application at this time still yielded coatings with good optical, chemical, and mechanical properties. It is suspected that the viscosity decrease

and observed foam is caused by generation of CO_2 from the isocyanate/water reaction. The amount of foam increased over time until the system was excessively foamy. Others have reported similar observations.[1,6] These results are quite different from those of traditional 2K solvent-based polyurethane systems which increase in viscosity as the molecular weight and crosslinking build until the system eventually gels. In the case of these 2K waterborne polyurethanes, the pot life appears to be limited not by viscosity/gelling effects, but by generation of carbon dioxide and the resulting foam. The use of optimum catalyst level, defoamers, and agitation rate may be used to control this effect and extend pot life considerably.

It is interesting to note with the 0.04% catalyst system (*Table* 6) that the initial observation of foam after two hours and excessive foam at five hours coincides with the reaction times observed from the calorimetry study with this system which reached a peak heat flow at approximately five hours.

Evaporation of Volatiles and Particle Coalescence after Application

After application, the volatiles within the coating begin to evaporate, causing the particles to come closer together until they come into contact with each other "throughout the film." This marks a critical solids concentration and point in time during the film formation process. When the particles come into contact, the potential for coalescence and reaction of isocyanate with hydroxyls increases dramatically. The solids content of the coating at this point (i.e., when particle to particle contact is first made throughout the coating) is equal to the packing factor of the dispersion particles. Many researchers have observed hexagonal close packing of dispersions with narrow particle size distributions.[9,22,23] In this case, the volume packing factor is 0.74. Others have observed a random close-packed arrangement[24] in which case the packing factor can be determined by applying the dispersion particle size distribution to an empirically derived algorithm.[25,26] Using this approach, the packing factors for the systems in this study are estimated as 0.68. This indicates that the critical solids volume concentration during drying, which causes particle to particle contact throughout the coating, is between 68 and 74%. With the density of the polymer and volatile constituents estimated at 1.15 and 1 g/ml, respectively, this critical concentration is 71 to 77% by weight.

During in-situ Raman and EIS analysis of applied coatings, distinct changes in the response spectra were observed be-

Figure 6—Plot of (a) disappearance of water, PM acetate, and NMP in curing coating; and (b) disappearance of isocyanate peak intensity with and without moisture during cure as monitored by IR as a function of time.

tween 15 and 30 min. Results indicated that the coatings appeared to change from a fluid state to a thinner, solid-like stat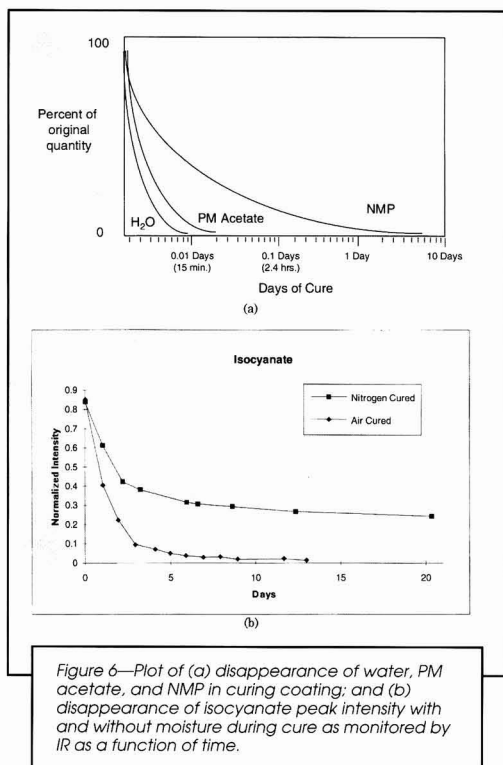e as would be expected during drying. Subsequent weight loss versus time data (*Table* 7 and *Figure* 6) indicated that by 15 min after application, the ACPU-1 coating was above this critical solids concentration. Other weight loss studies on this system were conducted with VOCs ranging from 150 to 350 g/L and catalyst concentrations up to 0.10% (which encompasses the typical range for these formulation parameters). All of these systems reached this critical solids concentration within 15 min as well. These results directly indicate that within this 15 min time frame after application, particle-to-particle contact is completed throughout the coating. As a consequence, particle coalescence within the film should be occurring relatively rapidly. However, it must be noted that if induction times were substantially extended hours into the pot life (i.e., well past exotherms), the urethane and urea forming reactions would build molecular weight and crosslinking to the extent that diffusion of the co-reactants may be limited and even close packing of the particles may not allow coalescence to occur.

IR spectroscopy was used to track the evaporation of water and organic solvent components of the coating system after application. Water was tracked by following the 3384 cm^{-1} band, propylene glycol methyl ether acetate was tracked using the 1236 cm^{-1} band, and N-methylpyrrolidone (NMP) was studied by following the 1296 cm^{-1} band over time. Decreases in concentrations (from peak intensity decreases versus initial values) are plotted for these three components of the curing coating in contact with laboratory atmosphere (*Figure* 6a). Water and PM acetate were decreased to trace levels within 15-30 min after application, while NMP dropped to trace levels within about six hours.

The rapid evaporation of water correlated well with weight loss results described, as was the relatively rapid evaporation of PM acetate. The vapor pressures of water and PM acetate are 18.65 and 3.8 torr (at 21 and 25°C, respectively). The vapor pressure of NMP is lower (0.29 torr at 20°C), and the evaporation time for NMP was much longer. However, it was in marked contrast to conventional expectation that NMP remains in the coating until much later in cure, and was much shorter than predicted by vapor pressure arguments. The effect of NMP on film formation and development of mechanical properties in the film must be considered. It should be noted that although these IR studies showed volatile loss within six hours, trace levels of water and solvents may remain in the film for days or possibly weeks.

Isocyanate Reaction after Application

The reaction of isocyanate with hydroxyl groups and water within the dispersion was monitored with IR-ATR spectroscopy. These experiments were done with specimens at ambient conditions as well as with a dry nitrogen purge. *Figure* 6b illustrates the isocyanate intensity loss over time after coating application. From this data it is obvious that the coating in ambient conditions is curing relatively rapidly, with over 75% of the isocyanate reacted within the first two days and over 90% after three days. This suggests that substantial crosslinking has occurred within this time frame, further suggesting that chemical resistance and mechanical integrity of the film is also improving. As will be further illustrated and discussed,

this agrees well with coating characterization results. By seven days after application, 97% of the isocyanate has reacted and it appears virtually complete by 13 days. Due to the high NCO/OH ratio some of this reaction is most certainly due to moisture cure of the isocyanate to form urea.

Figure 6b also illustrates a stark difference in the curing of the coating in ambient laboratory conditions versus a dry nitrogen atmosphere. It should be noted that these systems were formulated at an NCO/OH ratio of 2.0 in order to allow for reaction of isocyanate with water. Although the weight loss and Raman data presented indicates quick evaporation of the water, the IR results clearly indicate moisture curing of the systems still occurs with trace amounts of water remaining from the dispersion and/or moisture from the air. Furthermore, the ambient cured system is observed to cure at a much faster rate than that in dry nitrogen. Presumably, this would indicate quicker property development of the coating as well. After cure at ambient conditions, XPS results after one week showed only traces of isocyanate functional groups in the C(1s) spectra, indicating that complete reaction had occurred in ambient cured coatings. XPS composition also showed a relatively high nitrogen/carbon ratio which reflects a significant ratio of urea/urethane in the cured coating.

Development of Film Integrity

A probe for the initial development of film integrity was EIS measurements made as a function of cure time. EIS spectra showed essentially gel behavior at early times (~15 min), however, by three hours after application, the spectra took on a film-like character. Equivalent circuit modeling of the three-hour point showed that pore resistance of the coating had climbed to 1 megaohm after 15 min immersion in electrolyte. This reflects the development of significant barrier properties in the curing coating, which are reflected in the increasing barrier to ionic penetration of the polymer system. After six hours, the coating barrier properties had achieved a maximum film character in the 15 min immersion experiments, stabilizing at a pore resistance of over 1 gigaohm. For example, after full cure, these coatings had a pore resistance of over 1 gigaohm after 15 min equilibration in electrolyte, and about 30 megaohms after 24 hr in electrolyte solution. EIS results showed that film formation had occurred to a significant extent by three hours after application, and that between

Table 7—ACPU-1/Isocyanate Coating Weight Loss and Solids Content After Application

Time After Application, hr	Coating Remaining, %[a]	Solids Content, %[b]
0	100	50
0.25	58	86
0.5	56	89
1	54	91
2	53	93
3	52	96
4	51	97
5	51	98
6	50	99
24	50	99
48	50	100

(a) Weight percent of coating remaining compared to weight at application.
(b) Weight percent of remaining coating present as solids.
Note: Theoretical solids content of the admixed coating is approximately 49.7% by weight.

Table 8—ACPU-1/Isocyanate Property Development

Day	Persoz Hardness (sec)	Solvent Resistance	Scrape Adhesion (kg)	Dry Tape (5A- No Removal)	Water Immersion
1	16	Fair	8	5A	No effect
2	32	Fair	8	5A	
3	50	Good	10	5A	No effect
5	55	Good	10	5A	No effect
7	59	Good	10	5A	
10	55	Good	10	5A	No effect
17	70	Good	10	5A	No effect

three and six hours after application, the film rapidly developed further barrier properties.

The development of coating mechanical properties and chemical resistance was monitored by evaluating adhesion, hardness, water, and solvent resistance up to 17 days after application (*Table* 8). The results indicate that water resistance and dry tape adhesion developed rapidly, as evidenced by acceptable performance 24 hr after application. The coating hardness developed at a slightly slower rate. The Persoz (pendulum) hardness improved quickly over the first three days and then gradually increased to a maximum at about 17 days. (Films which have cured for several months have values of approximately 70 sec.) Hardness development over the first three days is also evidenced by the scrape adhesion results in which the mode of failure at days one and two was indicative of a marring of the coating. Finally, solvent resistance tests were performed by double rubs of methyl ethyl ketone (MEK), toluene, and isopropanol, respectively. The coating response to these solvents during days one and two was marring of the surface and softening of the film. After that time, the coating

Figure 7—Timeline of events in film formation mechanism of 2K waterborne polyurethane coatings.

resisted in excess of 200 double rubs with no effect. These results correlate well with the results from IR spectroscopy. By the third day, over 90% of the isocyanate has reacted (under ambient conditions). This indicates quite substantial crosslinking which would result in improved solvent resistance. In order to further substantiate these results, dynamic mechanical analysis of films during cure is currently being undertaken. These data will provide a direct indication of the rate of crosslinking within the polyurethane system after application.

Property development of the PUD-1 system was reported by Jacobs and Yu.[4] They reported maximum solvent resistance, impact and hardness after two days, ultimate tensile strength after four to five days, storage modulus stabilization after two days, and tan delta stabilization after three days. These results would seem to be in general agreement with our findings for the ACPU system.

SUMMARY

In this work, a model for the mechanism of film formation for 2K polyurethane coating systems was proposed in terms of a timeline of interrelated events. A range of analytical methods were used to probe the relative times for the mechanistic events, and an overall framework for film formation was described. The specific events and their timeframes are shown schematically in *Figure* 7. The dispersion of isocyanate in the aqueous system appears to occur immediately upon addition and mixing. Particle coalescence during the admixed state was found to be minimal by particle size experiments. Isocyanate reaction with hydroxyl groups occurred within two to five hours, as evidenced by the maximum exotherm from calorimetry data. Reaction with water occurred at a much slower rate, as shown in calorimetry work on a water/isocyanate system. These results correlated well with pot life studies and CO_2 generation from the isocyanate/water reaction.

After application, evaporation of volatiles occurred within 30 min. During this time, a critical solids content of the coating was reached, such that particle-to-particle contact was completed throughout the film. When this occurs, diffusion of polymer molecules across particle boundaries leads to particle coalescence. This also favors the isocyanate/hydroxyl group reaction. Isocyanate reactions after application are 80% complete within three days, suggesting substantial crosslinking by this time. To account for isocyanate/water reaction and ensure complete hydroxyl reaction, NCO/OH ratios were 2.0. Studies on film property development illustrated that barrier properties began to be established within three hours, and chemical resistance developed within three days.

This study was completed with a limited set of formulation and application parameters. It did not fully evaluate the effects of level of agitation, solvent concentration, catalyst concentration, induction time, temperature, and humidity on resulting film formation. Further work to probe these variables and their effects on cure and coatings properties is in progress. This is the first detailed examination of film formation for this class of polyurethane coatings and provides a framework for further study and for improved understanding of this growing coating technology.
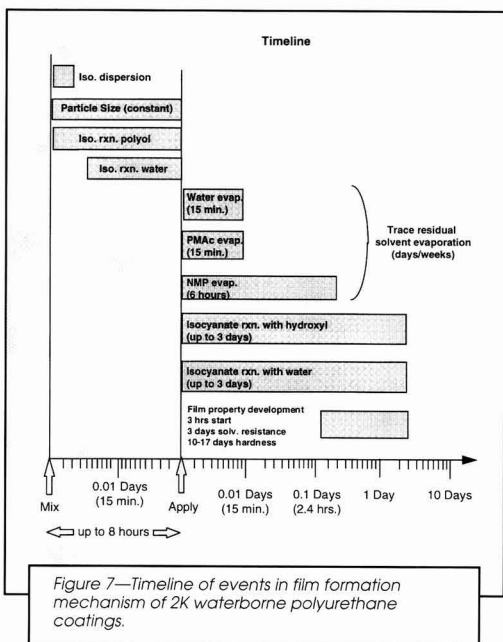
References

(1) Kahl, L. and Bock, M., "Waterborne Two-Component PU Clear Coats for Automotive Coatings: Development of Raw Materials and Mixing Technology," *Proc. Third Nurnburg Congress*, Nurnburg, Germany, March 13-15, 1995.
(2) Jacobs, P.B. and McClurg, D.C., "Water-Reducible Polyurethane Coatings for Aerospace Applications," *Proc. Low and No VOC Coating EPA Conference*, San Diego, CA, May 25-27, 1993.
(3) Bittner, A. and Ziegler, P., "Waterborne Two-Pack Polyurethane Coatings for Industrial Applications," *Proc. Third Nurnburg Congress*, Nurnburg, Germany, March 13-15, 1995.
(4) Jacobs, P.B. and Yu, P.C., "Two-Component Waterborne Polyurethane Coatings," JOURNAL OF COATINGS TECHNOLOGY, 65, No. 822, 45 (1993).
(5) Renk, C.A. and Swartz, A.J., "Fast Drying, Ultra Low VOC, Two-Component Waterborne Polyurethane Coatings for the Wood Industry," *Proc. 22nd Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, February 22-24, 1995.
(6) Bock, M. and Petzoldt, J., "Aqueous Polyurethane Coatings Systems for Plastics," *Proc. 22nd Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, February 22-24, 1995.
(7) Dillon, W.E., Matheson, D.A., and Bradford, E.B., *J. Colloid Sci.*, 6, 109 (1951).
(8) Brown, F.L., *J. Polymer Sci.*, 22, 423 (1956).
(9) Vanderhoff, J.W., *Br. Polymer J.*, 2, 161 (1970).
(10) Sheetz, D.P., *J. Appl. Polymer Sci.*, 9, 3759 (1965).
(11) Voyutskii, S.S. and Usinova, Z.M., *J. Adhesion*, 9, 39 (1977).
(12) Oertel, G., *Polyurethane Handbook*, Hanser Publishers, New York, pp. 90-96, 1985.
(13) Kubitza, W., *Surface Coatings International* (JOCCA), 75, No. 9, 340 (1992).
(14) Hare, C.H., *Protective Coatings: Fundamentals of Chemistry and Composition*, Technology Publishing Co., Pittsburgh, PA, p. 263.
(15) Seneker, S.D. and Potter, T.A., "Solvent and Catalyst Effects in the Reaction of Dicyclohexyl-Methane Diisocyanate with Alcohols and Water," JOURNAL OF COATINGS TECHNOLOGY, 63, No. 793, 19 (1991).
(16) Ihms, D., Stoffer, J.O., Schneider, D.F., and McClain, C., "The Effect of Catalysts on Kinetics and Mechanism of Urethane Film Formation," *Proc. 10th Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, February 16-18, 1983.
(17) Kubitza, W., Gruber, H., and Probst (to Bayer), U.S. Patent 5,075,370 (Dec. 24, 1991).
(18) Laas, J.J., Hassel, T., Kubitza, W., and Noll, K. (to Bayer), U.S. Patent 5,252,696 (Oct. 12, 1993).
(19) DosRamos, J.D. and Silebi, C., in *Particle Size Distribution and Assessment*, Provder, T. (Ed.), ACS Sympsoium Series #472, American Chemical Society, Washington, D.C., p. 292-307, 1991.
(20) Wilks, P.A. Jr., "Internal Reflection Methods in Infrared Spectroscopy," *Amer. Lab.*, 4 (11), p. 42 (1972).
(21) Boukamp, B.A., "A Microcomputer Based System for Frequency Dependent Impedance/Admittance Measurements," *Solid State Ionics*, 20, p. 31 (1986).
(22) Juhue, D. and Lang, J., *Langmuir*, 9, 792 (1993).
(23) Verge, C. and Sarrazin, L., *Double Liaison*, 463, 11 (1994).
(24) Butt, H.J., Kuropka, R., and Cristensen, B., *Colloid & Polymer Sci.*, 272, 1218 (1994).
(25) Lee, D.I., "Packing of Spheres and Its Effect on the Viscosity of Suspensions," JOURNAL OF PAINT TECHNOLOGY, 42, No. 550, 579 (1970).
(26) Hegedus, C.R. and Eng, A.T., "Coating Formulation Development Using CPVC Prediction and Statistical Design," JOURNAL OF COATINGS TECHNOLOGY, 60, No. 767, 77 (1988).

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Low and No-VOC Architectural Coatings Containing Ambient Curing Functional Groups

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and
Shelby F. Thames—The University of Southern Mississippi†

INTRODUCTION

I n the industrial countries, concerns over VOCs require that the coatings industry consider alternatives to much of the current technology.[1] Thus, powder coatings and solventless emulsion technology are two approaches that hold much interest. This concept is given much impetus by governmental regulations addressing environmental issues, health and safety issues, and the consumer's desire for reduced odor product.[2]

Traditionally, latex coatings have required the use of coalescing agents or VOCs in substantial quantities in order to achieve optimum film properties. Coalescing agents and high glass transition (T_g) latexes produce low minimum film formation temperatures (MFT) that provide properties required of high performance latexes. Thus, future technologies must substantially omit VOCs and allow the separation of MFT and T_g without volatile coalescing agents.

Several approaches to reduce VOCs have been reported. For instance, flexibilizing ethylene moieties have been incorporated into the polymer chain to increase flexibility, therefore, lowering the MFT of the coatings.[3] An alternative approach is to effectively separate the MFT of the latex and the T_g of the resulting cured product. This has been affected by combining ambient cure crosslinking agents into the thermoplastic latex systems and examples include drying oil moieties,[4] or acetoacetate functional groups.[5,6]

It is well known that the isocyanate moiety can, under appropriate use conditions, result in high performance coatings. However, their high reactivity with aqueous media has made this technological approach difficult.[7-9] The use of a sterically hindered isocyanate monomer, dimethyl meta-isopropenyl benzyl isocyanate (TMI), has recently been reported in the synthesis of acrylic[10] or styrene modified acrylic latexes.[11] In this investigation, we have extended the application of TMI in emulsion polymerizations to include all acrylic and vinyl acrylic emulsions with low surfactant levels, and have formulated the latexes into solventless coatings. The

With increasing environmental pressures and resulting government regulations, the coatings industry is undergoing a rapid shift in technology in an effort to reduce volatile organic content (VOC) levels. Thus, we have successfully synthesized novel, solvent free, ambient cure, vinyl acrylic, and acrylic latexes with dimethyl meta-isopropenyl benzyl isocyanate (TMI) as the curing agent. The emulsion polymers were formulated into solventless coatings and their properties contrasted to coatings of commercial latexes that require coalescing agents.

film properties of these coatings have been compared with films derived from commercial latexes with coalescing aids.

EXPERIMENTAL DETAILS

Chemicals

All ingredients were used without further purification. Methyl methacrylate (MMA, 99%, inhibited with 10 ppm MEHQ), vinyl acetate (VA, 99+%, inhibited with 3-5 ppm HQ), dimethyl meta-isopropenyl benzyl isocyanate (TMI, 96%), and ammonium persulfate (98+%) were purchased from Aldrich. Sodium formaldehyde sulfoxylate (SFS, 35%) was obtained from Royce, and sodium bicarbonate (A.C.S. grade) from Fisher Scientific. Rhodacal DS-10 (98% solids and sodium dodecylbenzene sulfonate) was obtained from Rhône-Poulenc.

Latex Synthesis

Starve-fed emulsion copolymerizations were affected in a 1 L reactor fitted with a paddle stirrer to allow the stirrer blades to be adjusted from time to time to ensure that the

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Z. Wang and S.F. Thames

Table 1—Recipes for Starve-Fed Vinyl Acrylic and Acrylic Latexes

Latex Code	USM VAC (Vinyl-Acrylic)	USM AC (Acrylic)
Deionized water (g)	300	240
DS-10 (g)	1.4	3.0
Sodium bicarbonate (g)	0.4	0.4
Ammonium persulfate (g)	1.0	1.0
SFS° 35% (g)	1.2	1.2
$FeSO_4 \cdot 7H_2O$ (g)	0.01	0.01
Vinyl acetate (g)	146	0
Methyl methacrylate (g)	0	82
Butyl acrylate (g)	50	114
TMI (g)	4	4

(a) Sodium formaldehyde sulfoxylate.

Table 3—Mill Base Preparation[a]

Ingredients	Parts by weight (g)	Suppliers
Tronox CR-800	1200	Kerr-McGee
Kathon LX 1.5%	2	Rohm & Haas
KTPP[b]	5	Pfaltz & Bauer
BYK 034[c]	9	BYK
Tamol 731 25%	30	Rohm & Haas
Surfynol 465[d]	4	Air Products
Deionized water	500	—
Total	1750	

(a) Ingredients added at 800 rpm, then mixed at 3500 rpm for 20 min.
(b) Potassium tripolyphosphate, 94%.
(c) VOC content < 2%.
(d) VOC content <0.01%.

fresh monomer feed was always introduced into the body of the reaction mixture. The stirrer speed was maintained at 200 rpm during the feeding, and reduced to 150 rpm for post-reaction. The remaining two outlets of the reactor were used for a water-cooled condenser and a nitrogen inlet. Nitrogen was bubbled throughout the reactor before the addition of the monomer to purge oxygen from the system and subsequently to provide a continuous nitrogen head during the reaction. The reactor was maintained at 40°C by immersion in a thermostatted water bath. The polymerization recipes for latexes are shown in *Table 1*.

In each of the acrylic latexes synthesis, 150 g of water, 2.5 g of DS-10, 0.2 g of ammonium persulfate, and 0.01 g of iron (II) sulfate heptahydrate was added to the reactor. The reactor contents were pre-heated in a water bath at 40°C for 30 min, and concomitantly purged with nitrogen. Ten percent of pre-emulsion (including all monomers, 50 g of water, 0.5 g of DS-10, 0.8 g of ammonium persulfate, and 0.4 g of sodium bicarbonate) and half the SFS solution (1.2 g of 35% SFS and 30 g of water) was added to the reactor. After stirring for 10 min, the remaining pre-emulsion was fed to the reactor over a four- to five-hour period to ensure starve-fed conditions. After monomer feed, the remaining SFS solution was fed over one and half hour followed by heating at 40°C for one hour to complete the polymerization.

The vinyl acrylic emulsion polymerizations were conducted in a similar manner with the exception that ammonium persulfate was fed separately, and the reaction time was extended to 10 hr.

Latex Characterization

The latex properties have been measured and tabulated in *Table 2*, together with two high performance commercial

Table 2—General Properties of Latexes Used in Paint Formulation

Latex Code	USM VAC	USM AC	Latex A	Latex B
Solids content (%)	40	45.2	55[a]	50[a]
pH	3.8	4.0	5	9
Dn (nm)	161	102	265	242
T_g^{exp} (°C)	33.8	21.3	14.5	12.8
T_g^a (°C)	—	—	12	16
MFT[exp] (°C)	2	0	5.5	5
MFT[a] (°C)	—	—	8	9

(a) Technical data obtained from manufacturing specifications.

latexes, A and B. Latex A is a vinyl acrylic, while latex B is all acrylic. The solids contents were determined gravimetrically, while the particle sizes were measured by a Coulter N4 MD sub-micron particle analyzer. A Mettler DSC-30 measuring cell was used to determine the T_g of the latex films (mid-point value). The conditions for analysis were: progress rate of 10°C/min, temperature range of –50 to 150°C, and nitrogen purging speed of 20 ml/min. Minimum film forming temperatures of latexes were determined by an MFFT Bar 90.

Paint Formulations

The mill bases shown in *Tables 4* and *5* were the products obtained from the same batch in order to reduce performance variables. The mill base was prepared from the recipe of *Table 3*. For convenience, the defoamer (BYK 034) and microbicide (Kathon LX) were included in the mill base. The formulation recipes for the vinyl acrylic paints at 20 and 60% PVC using latexes USM VAC and latex A are recorded in *Table 4*, while the formulation recipes for acrylic paints at 20 and 45% PVC from latexes USM AC and latex B are listed in *Table 5*.

Coating Characterization

Tensile strength and percent elongation of the films were determined using an 810 material test system. The test samples were prepared to a width of 13 mm, a thickness of 0.06-0.12 mm and a gauge length of 15 mm. Drying times of paint films were determined on 7-mil wet films by a Gardner circular drying time recorder. Coating film pencil hardness was measured according to ASTM standard D 3363, while the conical mandrel flexibility was examined following ASTM standard D 522. The scrub resistance test was conducted to obtain the number of cycles to initial break or film failure with 10-mil brass shim, as required by ASTM standard D 2486. Specular gloss at 20, 60, and 85° was determined using a BYK-Gardner Micro Triglossmeter.

RESULTS AND DISCUSSION

The synthesis of the vinyl acrylic and all acrylic latexes with TMI (*Table 1*) was performed in triplicate, with consistent results. Butyl acrylate was helpful in lowering MFT of the copolymer emulsion. The recipes were designed to achieve a calculated T_g (using Fox equation[12]) near 0°C for vinyl acrylic and –5°C for the all acrylic polymers. The functional mono-

Table 4—Formulations of Vinyl Acrylic Paints

Paint Code[a]	USM VAC-20	A-20	USM VAC-60	A-60	Suppliers
Mill base[b] (g)	80	80	193	193	This work
Natrosol Plus[c](3.5%) (g)	32	0	38.6	0	Aqualon
QR-708[d] (7%) (g)	0	53	0	42.4	Rohm & Haas
Deionized water (g)	25	35.8	2.7	9.6	—
Na_2CO_3 (10%) (g)	2.5	1.5	0	0	Fisher
Surfynol 465[e] (g)	1.3	1.3	1	1	Air Products
Triton X-100 (g)	1.3	1.3	1.1	1.1	Rohm & Haas
USM VAC (40%) (g)	158.5	0	64	0	This work
Latex A (55%) (g)	0	115.4	0	46.5	
Butyl carbitol (g)	0	2.9	0	1.2	Aldrich
Propylene glycol (g)	0	8.8	0	3.7	Aldrich
Total	301	300	300.3	298.6	—
Paint Properties					
PVC (%)	20	20	60	60	
Volume solids (%)	27	27	27.7	27.7	
Weight solids (%)	39.3	39.5	52.6	52.9	
Stormer viscosity (KU)	85	85	70	85	
ICI (poise)	1.8	2.6	1.0	2.2	
pH, initial	8.8	8.4	8.2	8.3	
VOC (g/L)	<0.2	238	<0.4	152	

(a) Latex name–PVC value; for latex name USM VAC, see *Table 1*.
(b) See *Table 3*.
(c) Pre-mixed at 500 rpm to obtain 3.5% Natrosol Plus (grade 330) water solution.
(d) 140 g of QR-708 (35%) was diluted in 560 g of water and pre-mixed, containing 7.8% of propylene glycol.
(e) VOC content <0.01%.

Table 5—Formulations of Acrylic Paints

Paint Code[a]	USM AC-20	B-20	USM AC-45	B-45	Suppliers
Mill base[b] (g)	92.2	92.2	171	171	This work
Natrosol Plus[c](3.5%) (g)	25.8	0	34.0	0	Aqualon
QR-708[d] (7%) (g)	0	37.0	0	47.0	Rohm & Haas
Deionized water (g)	14.8	13.0	0	0	
Na_2CO_3 (10%) (g)	0.9	0	0	0	Fisher
Surfynol 465[e] (g)	1.5	1.5	1.0	1.0	Air Products
Triton X-100 (g)	1.5	1.5	1.0	1.0	Rohm & Haas
USM AC (45%) (g)	163.3	0	92.5	0	This work
Latex B (50%) (g)	0	147.0	0	83.2	
Butyl carbitol (g)	0	1.9	0	1.1	Aldrich
Propylene glycol (g)	0	5.6	0	3.2	Aldrich
Total	300	299.7	299.5	307.5	
Paint Properties					
PVC (%)	20	20	45	45	
Volume Solids (%)	32.2	32.2	31.1	30.6	
Weight solids (%)	45.6	45.6	53.1	51.7	
Stormer viscosity (KU)	112	83	91	93	
ICI (poise)	1.9	1.9	1.2	3.1	
pH, initial	8.8	8.4	8.2	8.3	
VOC (g/L)	<0.2	133	<0.3	125	

(a) Latex name–PVC value; for latex name USM AC, see *Table 1*.
(b) See *Table 3*.
(c) See footnote (c) of *Table 4*.
(d) See footnote (d) of *Table 4*.
(e) VOC content <0.01%.

Figure 1—DSC thermogram for clear vinyl acrylic latex (USM VAC) film air-dried for 10 days, T_g is 33.8°C.

Figure 2—DSC thermogram for clear acrylic latex (USM AC) film air-dried for 10 days, T_g is 21.3°C.
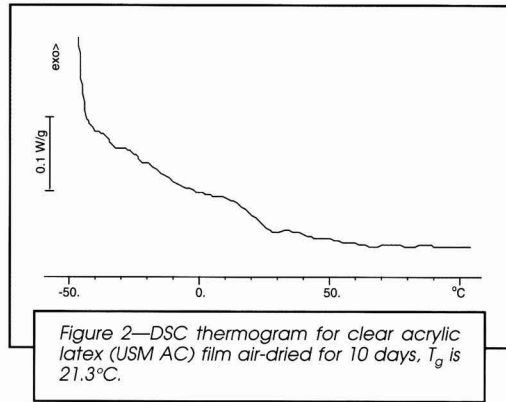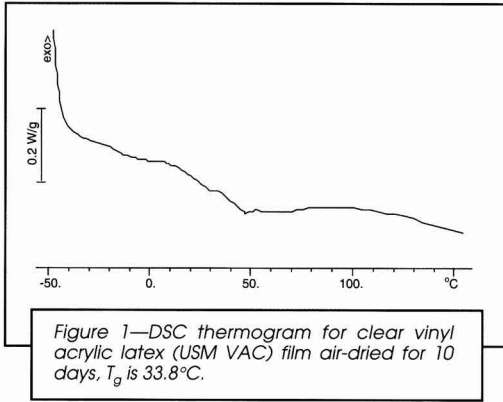
Table 6—Vinyl Acrylic Coating Film Properties[a]

Paint Code	USM VAC-20	A-20	USM VAC-60	A-60	ASTM Method
Tensile strength (psi)	987	456	553	340	D 2370
Elongation at break (%)	277	686	10.2	6.5	D 2370
Wet thickness (mil)	7	7	7	7	
Volume solids (%)	27	27	27.7	27.7	
Drying time (min)	80	110	40	50	D 1640
Pencil hardness[b]	HB	2B	F	B	D 3363
Conical mandrel (1/8")	pass	pass	pass	pass	D 522
Scrub					
Initial break	1800	1800	200	190	D 2486
Film failure	2200	2300	240	230	D 2486
85° gloss	64.8	76.3	75.7	67.0	D 523
60° gloss	31.9	54.9	17.0	12.7	D 523
20° gloss	4.8	19.5	1.8	1.9	D 523
Contrast ratio	95.6	93.0	98.6	97.8	D 3022

(a) For coating films with wet thickness of 7 mil and air-dried at room temperature for 7 days, except tensile and elongation tests (16-mil wet drawdown, same ambient drying conditions).
(b) Scratch hardness.

Figure 3—Scrub resistance for vinyl acrylic coatings.

Figure 4—Scrub resistance for all acrylic coatings.

Table 7—Acrylic Coating Film Properties[a]

Paint Code	USM AC-20	B-20	USM AC-45	B-45	ASTM Method
Tensile strength (psi)	702	567	780	529	D 2370
Elongation at break (%)	274.4	700.4	70.4	18.0	D 2370
Wet thickness (mil)	7	7	7	7	
Volume solids (%)	32.2	32.2	31.1	30.6	
Drying time (min)	50	60	50	60	D 1640
Pencil hardness[b]	HB	B	HB	B	D 3363
Conical mandrel (1/8")	pass	pass	pass	pass	D 522
Scrub					
Initial break	>3000	340	1200	120	D 2486
Film failure	—	400	1600	150	D 2486
85° gloss	89.4	88.2	73.8	64.9	D 523
60° gloss	78.4	56.4	39.3	6.5	D 523
20° gloss	36.3	10.8	4.7	1.8	D 523
Contrast ratio	96.6	95.3	97.3	96.8	D 3022

(a) For coating films with wet thickness of 7 mil and air-dried at room temperature for 7 days, except tensile and elongation tests (16-mil wet drawdown, same ambient drying conditions).
(b) Scratch hardness.

mer, TMI, was incorporated at 2% of total monomer weight as recommended.[10,11] Surfactant was incorporated at 0.7%-1.5% based on monomer weight or 0.3%-0.7% based on latex weight. The latexes are stable at room temperature and can be obtained at solids content as high as 50%.

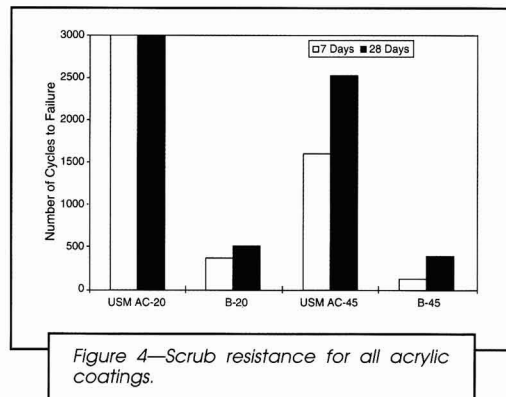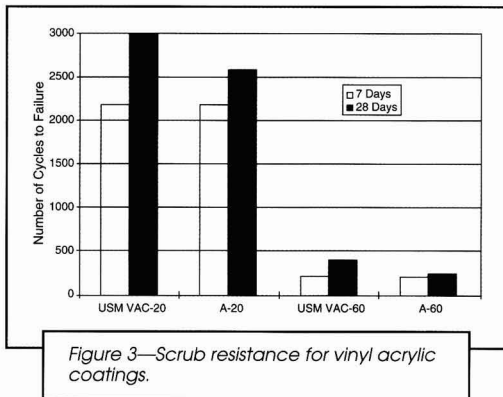When acrylic or methacrylic acids were incorporated (Table 1), vinyl acrylic or acrylic latexes were prepared at a solids content between 40 to 50%. However, extensive coagulation resulted within one week. This is in contrast with an earlier report[11] although their work reported higher surfactant levels and the latex was a styrene modified acrylic.

The measured T_g (Table 2) and the reported values of the commercial latexes varied by 2.5°C and 3.2°C for latexes A and B, respectively, while variations in measured MFT and the technical data is 2.5°C and 4°C for latexes A and B, respectively. Moreover, separation of MFT and the T_g of the commercial latexes, A and B, is less than 10°C, i.e., 9°C for the former and 7.8°C for the latter. However, this work has produced latexes with a wider temperature window separating MFT and T_g at 30°C for the vinyl acrylic polymer (USM VAC) and 20°C for the all acrylic polymer (USM AC).

The T_g values for latexes USM VAC and USM AC (Table 2) were taken from their clear films that had air-dried for 10 days. The differential scanning calorimetry (DSC) thermograms are shown in Figures 1 and 2. Figure 1 suggests the presence of two phases in the dried USM VAC film.

The vinyl acrylic latexes, commercial and those generated in these laboratories, were formulated into paints at 20 and 60% PVC, according to the formulations of Table 4. Similarly, the acrylic latexes were formulated into paints at 20 and 45% PVC, according to the formulations of Table 5. In the case of the solventless paints, USM VAC-20, USM VAC-60, USM AC-20, and USM AC-45, no coalescing aids were included and the amount of organic compounds introduced from defoamer addition (BYK-034) was at a negligible level. VOC calculated values for paints USM VAC-20, USM VAC-60, USM AC-20, and USM AC-45 are all less than 0.4 g/L. Alternatively, conventional paints from latexes A and B contained coalescing aids at an upper limit level as suggested by the latex manufacturer (Tables 4 and 5). Water-based thickeners (Natrosol Plus, grade 330) would not effectively thicken

paints A-20, A-60, B-20, and B-45, and thus the rheology modifier QR-708 (containing 7.8% of propylene glycol) was added.

Free films of the formulated paints (Tables 4 and 5) were prepared by application onto polyethylene panels and dried for seven days at ambient, before removal from the panels and physical property testing (Tables 6 and 7).

Film formation or coalescence process is crucial to property development and thus film formation efficacy was monitored by tensile property evaluation. The paint films were removed from the polyethylene panels immediately before testing. All the films prepared from solventless paint formulations were much stronger than their counterpart, i.e., films derived from conventional latexes.

The drying times of the solventless paints were less than the conventionally formulated coatings. In addition, the solventless coatings dried to harder films.

Wet adhesion is instructive in predicting the performance of waterborne coatings, especially in alkaline and/or wet conditions. A quantitative measure of wet adhesion is (1) an indication of the hydrophobicity of the latex paint and (2) is predictive of blister resistance and water absorption. Thus, scrub resistance tests were performed (Table 6) with the result that the solventless vinyl acrylic latex paints were comparable to the commercially available products under test. The CPVC for the USM VAC-60 paint is approximately 45-50%, but it was formulated at 60% PVC in an effort to evaluate its performance in a binder limited matrix. Surprisingly, the scrub resistance of all acrylic, solventless paints approached 10 times of that of their counterparts (Table 7), as films prepared with USM AC-20 remained unbroken even after 3,000 scrub cycles.

It has been suggested that the analytical methods for testing solventless coatings should be reviewed since no- and low-VOC coatings are new technology.[2,3] Thus, scrub resistance of the coatings was evaluated at 28-day dry time as well, consistent with the DIN 53.778 standard scrub test used in Germany.[3] The results are compared with those for seven day dry time in Figures 3 and 4. As expected, extending drying time can improve polymer coalescence which is confirmed by all improved scrub resistance data. However, the greatest

Z. Wang and S.F. Thames

improvement in scrub resistance was developed for the solventless coatings USM VAC-20, USM VAC-60, USM AC-20, and USM AC-45 by simply extending the drying time from 7 to 28 days.

Gloss measurements (*Tables* 6 and 7) are instructive in determining coalescence efficacy. The gloss values demonstrate that the solventless coatings are certainly comparable in gloss development with coatings that contain coalescing aids.

CONCLUSION

Solventless vinyl acrylic and all acrylic, room temperature curing latexes have been synthesized and evaluated for film performance. Since the MFT of the latexes are near the freezing point of water, no-VOC architectural coatings have been successfully formulated and applied at ambient. Their properties, as evaluated, are comparable with those of conventional coatings formulated with coalescing aids. Although these low surfactant level, acid free emulsion polymers remained stable at room temperature, more work needs to be done in paint formulations in order to extend the paint shelf life. We can state with confidence at least that the freshly formulated paints described in this work will offer extremely superior film properties.

ACKNOWLEDGMENTS

References

(1) Klein, R.J., "Formulating Low-Odor, Low-VOC Interior Paints," *Mod. Paint Coat.*, 83, 3, 37 (1993).
(2) Leman, A., "Solvent-Free Architectural Coatings," 47th Annual Spring Symposium, Pacific Northwest Society for Coatings Technology, Victoria, Canada, April 28-30, 1994.
(3) Currie, B., "EVA Maintains Paint Properties, Lowers VOC," *Mod. Paint Coat.*, 83, 9, 34 (1993).
(4) Grawe, J.R. and Bufkin, B.G., "Survey of the Applications, Properties, and Technology of Crosslinking Emulsions," JOURNAL OF COATINGS TECHNOLOGY, 50, No. 643, 67 (1978).
(5) Arthur, D.B., Charles, L.A., and David, E.W., EP 0 492 847 A2, 1992.
(6) Say, T.E., U.S. Patent 4,906,684, (1990).
(7) Fujimoto, M., Yamashita, T., and Matsumoto, T., JP 6 213 425, 1987.
(8) Chao, Y.Y.H., U.S. Patent 4,636,546, 1987.
(9) Terasawa, H., Fujii, Y., Okada, A., and Tanaka, M., JP 63 118 377, 1986.
(10) CYTEC Industries Inc., Urethane Chemicals, Technical Information, West Paterson, NJ, 1994.
(11) Inaba, Y., Daniels, E.S., and El-Aasser, M.S., "Film Formation from Conventional and Miniemulsion Latex Systems Containing Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI)—A Functional Monomer/Crosslinking Agent," JOURNAL OF COATINGS TECHNOLOGY, 66, No. 832, 63 (1994).
(12) Rudin, A., *The Elements of Polymer Science and Engineering*, Academic Press, Orlando, FL, p. 402, 1982.

Volatile Methylsiloxanes as Exempt Solvents in Protective Coatings

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To minimize ozone and smog generation, the protective coatings industry is being forced to reduce volatile organic compounds (VOCs). At the same time, upper atmospheric ozone depleting substances such as chlorofluorocarbons and halogenated hydrocarbons will have to be replaced.

On December 5, 1994, the United States Environmental Protection Agency[1] (EPA)

Figure 1—Volatile methylsiloxanes are built on a backbone of alternating silicon and oxygen atoms.

ruled that volatile methylsiloxanes (VMS) were now excluded from the classification as VOCs. Basically, the EPA said that VMS fluids do not contribute to declining air quality at ground level (or lower atmosphere), i.e., generate smog.

When released into the atmosphere, VMS products have a lifetime between 10 and 30 days. The oxidative degradation end products are carbon dioxide, silicic acid, and water. Recent studies demonstrate that VMS products have negligible potential to adversely impact urban air quality and do not contribute to the formation of ground-level ozone in urban settings.

This paper describes VMS fluids, solubility in selected silicone resins and silicone

alkyd copolymer resins. Aluminum, flat black, and medium-gloss gray paints with and without VMS fluids are discussed.
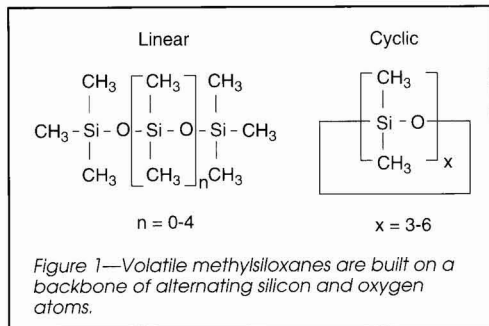
Volatile Methylsiloxanes

Compounds designated as volatile methylsiloxanes (VMS or VMS fluids) under the EPA ruling are cyclic, branched, or linear completely methylated siloxanes. These are organosilicon polymeric materials with a basic molecular structure built on a backbone of alternating silicon and oxygen atoms, formed into either a ring or linear chain containing from two to six silicon atoms. Methyl groups are attached directly to the silicon atom. The VMS fluids of choice have two to five silicon atoms as shown in *Figure* 1.

Volatile methylsiloxanes are pure distilled dimethylsiloxanes containing no additives. They are crystal clear and almost odorless. Although there are as many as seven different linear and cyclic VMS fluids available, two products (one linear and one cyclic fluid) will be evaluated in this study.

The linear product is octamethyltrisiloxane (designated L-3 for linear-three silicon) as shown in *Figure* 2, and the cyclic product is octamethyl-cyclotetrasiloxane (designated C-4 for cyclic-four silicon) as shown in *Figure* 3.

Typical physical properties of the two VMS fluids are summarized in *Table* 1. The linear L-3 product has the lower specific gravity, viscosity, and flash point. Both products have

low Kauri-Butanol (KB) values and are considered diluents based on solvent strength.

Figure 2—Octamethyltrisiloxane (L-3)

These two products and other VMS fluids are currently used in the personal care industry, by themselves or blended with other cosmetic fluids, to provide a fluid base for a variety of solid or liquid cosmetic ingredients. When used as a carrier in antiperspirants and deodorants, these fluids leave a dry feel and do not cool the skin when they evaporate. The lubricity and spreading properties of skin creams, lotions, bath oils, perfumes, colognes, sun care, preshaving, shaving, and stick products can be improved by the use of these products. Some VMS fluids are also used as solvents for precision cleaning operations.[2]

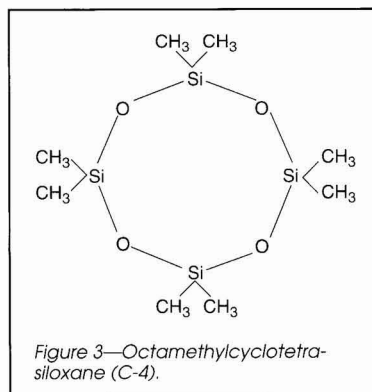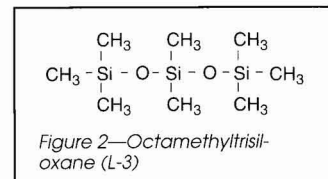VMS fluids have low oral and acute inhalation toxicity, and are safe to handle

Figure 3—Octamethylcyclotetrasiloxane (C-4).

Table 1—Typical Properties

	ASTM	L-3	C-4
Specific gravity	D 2935	0.82	0.95
Viscosity (cSt.)	D 445	1.0	2.5
Flash point (°F)(CC)	D 3934	94	131
Evaporation rate[a]	D 3539	1.0	0.2
Boiling point (°C/°F)	D 850	149/300	172/342
Kauri-Butanol value	D 1135	15	15

(a) n-butyl acetate = 1.

Table 2—Solubility Test Results

Resins	Phenyl/ Methyl Ratio	Mol. Wt.	% Solids	% Solubility[a] L-3	% Solubility[a] C-4
A	Low	Low	60	67	78
B	High	Low	60	48	59
C	High	High	50	43	53
D	High	Medium	70	45	55
E	Low	High	50	60	75
F	Silicone	Alkyd	60	60	70

(a) Based on total solvent.

Table 3—Aluminum Silicone Paint Formulation

Base Paint Formulation[a]

	Parts
Aluminum paste (65%)	45.1
Silicone resin (82%)	54.9
	100.0

(a) Reduced to 30 sec, No. 4 Zahn cup, or about 70 KU.

A = Density Paint
B = %wt Total Volatiles
C = %wt VMS Volatiles
D = Density VMS Volatiles

$$VOC = 100 - \frac{AC}{D} \quad \frac{(A)(B-C)}{D}$$

Figure 4—VOC determination— Federal Method 24.

Table 4—Aluminum Silicone Paint Properties

Solvent	% VMS (Total Solvent)	% Solids[a]	lb/gal	VOC lb/gal
Xylene	—	67.1	9.3	3.1 (3.1)[c]
L-3	30	67.2	9.6	2.6
C-4	38	65.2	9.7	2.5
Xylene[b]	—	58.4	9.1	3.8 (3.8)
C-4	47	54.6	9.4	3.0

(a) ASTM D 2369.
(b) Paint viscosity 30 sec, No. 2 Zahn cup.
(c) VOC determined by solid/density.

with little irritation to the skin and only temporary eye discomfort. Tests also show that these materials are not acutely toxic by dermal absorption.[3]

Research at the University of California's Statewide Air Pollution Research Center at Riverside formed the scientific basis for the petition to the EPA. Harwell Laboratories in England substantiated the University of California's findings. Harwell used computer modeling with European atmospheric conditions factored in the analysis. Similar substantiation came from analysis by researchers at the University of Kassel in Germany.

After reviewing the cumulative data on atmospheric fate and effects of VMS fluids, the EPA concluded that these materials demonstrated negligible potential for ozone formation at ground level. The agency granted the exemption as being consistent with its goal of improving air quality.

VMS fluids should not be confused with higher-molecular-weight polydimethyl-siloxanes (PDMS). Typical polydimethylsiloxanes used as paint and ink additives have viscosities of 50 to 350 centistokes and are not volatile at ambient temperatures. These products also have limited solubility and are known to provide reduced surface tension, thus improving leveling, flow, mar resistance, and reduced pigment floating. Viscosities above 350 centistokes are of little value in paint and ink applications. These products and compounds based on them may be the source of silicone contamination of surfaces to be painted, thus causing wetting problems. VMS fluids should not be considered in the same class as silicone "oils" or higher-viscosity fluids and should not contaminate or cause contamination problems.

Solubility

The KB values of both L-3 and C-4 VMS fluids are low, consequently, the fluids will not dissolve common solid resins such as polyesters, epoxies, acrylics, and silicones. They can, however, be used in combination with stronger solvents. The two fluids are soluble in alcohols, ketones, aliphatic, and aromatic solvents. They are not soluble in water.

Several silicone resins and silicone-modified copolymer alkyds were tested for maximum amounts of the two fluids in solution before incompatibility resulted. The procedure used was to titrate small amounts (40-50 grams) of the selected resins with the two fluids to a constant haze point. Results are shown in *Table 2* for six resin systems. Variables evaluated were phenyl-to-methyl ratio of the polysiloxane resin, relative molecular weight, and solids content. Percent solubility was the percent of VMS fluid based on the total solvent weight. All silicone resins (A-E) contained aromatic solvent. Resin F was a silicone alkyd

Table 5—Black Silicone Paint Formulation

Base Paint Formulation

	Parts
Inorganic Black	26.2
Mica	17.9
Silica	3.1
Silicone resin (71%)	40.5
Xylene	12.3
	100.0

Table 6—Black Silicone Paint Properties

Solvent	% VMS (Total Solvent)	% Solids[a]	lb/gal	VOC lb/gal
Xylene[b]	—	72.3	12.4	3.7 (3.4)[c]
L-3	27	71.4	12.2	3.2
C-4	33	70.7	12.3	3.1
Xylene[d]	—	67.9	11.6	4.3 (3.7)
C-4	42	62.5	11.4	3.6

(a) ASTM D 2369.
(b) Paint viscosity 30 sec, No. 4 Zahn cup.
(c) VOC determined by solids/density.
(d) Viscosity 30 sec, No. 2 Zahn cup.

copolymer resin supplied in naphtha mineral spirits.

Molecular weight and solvent content had little effect on the VMS fluid solubility. As would be expected, increasing the methyl content of the silicone resin did improve solubility. Polydimethylsiloxane gums and elastomers were very soluble in VMS fluids.

Between the two products, the cyclic C-4 product was more compatible with the resins than linear L-3 VMS fluid.

VOC Determination

Determination of VOC content is referenced in Federal Method 24 and allows for both water and exempt solvents. The formulation used in this study is found in *Figure* 4. Exempt solvent content was determined by the amount of exempt solvent added and not by an analytical method.

High-Solids Paint Systems

Aluminum and black paints were prepared based on formulations and high-solids silicone resins found in an earlier study.[4]

ALUMINUM PAINTS

Silicone aluminum paints consist of a very simple formulation and dispersion procedure. Leafing aluminum paste was mixed with a high-solids resin using a low-rpm blade (*Table* 3) and samples were reduced to 70 KU viscosity with xylene, L-3, and C-4 VMS fluids as shown in *Table* 4. VOC content values were determined by calculation. The sample cut with xylene was also determined for VOC content using percent solvent and paint density. Both methods yielded the same VOC content values. The amount of VMS fluid used was about 30%. This was much less than the determined maximum amount of 45-55%. VOC content levels were reduced about 0.5 lb/gal, or 16%.

Two additional paint samples were reduced to spray viscosity and properties determined. The C-4 VMS fluid was used and a larger concentration tested. The amount

used was close to the maximum amount. VOC content levels determined by calculation were 3.8 lb/gal for the control and 3.0 lb/gal for the sample containing C-4. VOC content reduction was 21%, and the calculated VOC content for the control was the same as the determined VOC content using paint density and volatile content. Cold-rolled steel panels were sprayed with the two aluminum paints and heat cured. There was no evidence of surface defects with either coating.

BLACK PAINT

Flat black high-solids silicone paint (*Table* 5) was prepared on a high-speed (15 min @ 3500 rpm) blade followed by further reduction with solvent to about 70 KU viscosity (*Table* 6). As with aluminum paints, the same three solvents were used and evaluated for VOC content and calculated by measuring solvent addition. The value using xylene was determined to be 3.7 lb/gal as compared to 3.4 lb/gal as determined by paint density and solvent content. The difference between the two numbers was attributed to solvent loss due to solvent evaporation during high-speed pigment dispersion. Using C-4 VMS fluid, VOC content was reduced 0.6 lb/gal, or 16%.

Two additional paint samples were reduced to spray viscosity using xylene and C-4 and the VOC content determined. Calculated and actual VOC content numbers differed by 0.6 lb/gal, and the loss of solvent was probably due to solvent evaporation dur-

ing the pigment grind. Using C-4 reduced the VOC content 16%. Cold-rolled steel panels were also sprayed with the flat black paints and heat cured. No surface defects were observed with either coating.

SILICONE ALKYD GRAY PAINT

Higher-solids silicone alkyd copolymer resins were demonstrated[5] about 10 years ago. It was found that lower viscosities could be obtained by replacing mineral spirits with more active solvents such as esters and ketones.

Six different solvents were tested in the silicone alkyd series as shown in *Table* 7. Solution viscosity varied from over 13,000 to 650 centistokes depending on solvent strength. Solubility of each silicone alkyd is also shown using both L-3 and C-4 VMS fluids. Solubility was found to be higher with the silicone alkyd than with the silicone resins, probably due to the aliphatic nature of the resin. It is of interest that the naphtha mineral spirit-based copolymer was less soluble which could be due to the poorer solvency of the solvent.

Medium-gloss gray paints were prepared to simulate a typical paint for the federal specification MIL-E-24635B. The paint formulation used in this study is shown in *Table* 8 and properties of three of these paints are listed in *Table* 9. Naphtha mineral spirits (NMS), propyl methyl acetate (PMA), and normal butyl propionate (n-BP) paints were reduced with the corresponding solvents or

Table 7—Silicone Alkyd Resins

Solvent	Viscosity[a] (cSt.)	Specific Gravity	% Solubility[b] L-3	L-4
Naphtha mineral spirits	13,574	1.005	49	63
SC-100	2,729	1.046	66	72
PM acetate	1,417	1.074	61	70
Isobutyl isobutyrate	1,342	1.042	64	73
N-butyl propionate	956	1.051	68	74
Methyl amyl ketone	652	1.030	68	74

(a) 70% solids; 30% silicone content.
(b) Resins reduced to 60% solids; % based on total solvent.

W.A. Finzel

Table 8—Silicone Alkyd Paint Formulation

	Parts
Titanium dioxide	24.1
Lampblack	0.4
Magnesium silicate	13.8
Mica	4.4
Dispersant	0.4
Resin (76%)	54.1

Disperse on high-speed blade, 15 min @ 3500 rpm

Cobalt octoate (6%)	0.4
Zirco drier (6%)	0.4
Calcium naphthanate (5%)	0.8
Exkin No. 2	0.6
11 additive[a]	0.6
	100.0

(a) Dow Corning

Table 9—Silicone Alkyd Paint Properties[a]

Solvent	% VMS	% Solids[b]	lb/gal	VOC lb/gal	Dry Time[d] (set to touch) hr
NMS	—	68.8	10.3	3.3(3.2)[c]	2.5
L-3	36.4	65.2	10.1	2.8	1.5
C-4	41.1	65.3	10.4	2.8	2.5
PMA	—	76.4	11.9	3.1(2.8)	2.7
L-3	36.5	74.5	11.4	2.4	3.0
C-4	37.3	73.2	11.6	2.6	2.7
n-BP	—	77.1	11.6	2.9(2.7)	2.3
L-3	38.1	74.7	11.2	2.3	2.5
C-4	38.9	73.5	11.3	2.4	2.7

(a) Viscosity 50 sec, No. 4 Zahn cup.
(b) ASTM D 2369.
(c) VOC determined by solids/density.
(d) Circular drytime recrder—2 mils dry film.

the two VMS fluids at 36-41% of the total solvent to about 80 KU viscosity, or 50 sec on a Zahn No. 4 cup. Paint VOC content was determined by calculations based on amount of solvent used. Each control paint was also checked for VOC content via paint density and solvent content. Differences between the numbers are probably due to solvent loss during pigment dispersion. Reduction of VOC was about 16% for the three paints using VMS fluids. Set-to-touch dry times were obtained for the three paint systems and found to be similar. Additional work on pigmentation and exempt solvent concentrations could possibly reduce the VOC content to about 2 lb/gal, which is the ultimate goal for low-VOC silicone alkyd copolymer paints.

Conclusions

Volatile methylsiloxanes, which were excluded from the definition of VOC by the EPA in late 1994, can now be considered alternative solvents for protective coatings. The decision by the EPA was based on research concluding that these products did not contribute to ground-level ozone formation.

Both linear and cyclic volatile methylsiloxanes (VMS) have low solvency when tested with silicone resins and should be classified as diluents. When added to selected silicone resins containing strong solvents, the VMS fluids either reduce viscosity with little change in VOC content or reduce VOC content by acting as a partial replacement with strong solvents.

Two specific products—octamethyltrisiloxane (L-3) and octamethylcyclotetrasiloxane (C-4)—were chosen as representative linear and cyclic VMS products. VOC content was reduced in three different paint systems using the two VMS products. Two paint systems were sprayed on steel substrates and did not show any evidence of wetting problems.

Based on solubility and cost, the cyclic product octamethylcyclotetrasiloxane is the VMS product of choice and should be considered when there is a need to reduce VOC content of solvent-based paint systems.

References

(1) *Federal Register*, Rules and Regulations, Vol. 59, No. 192, October 5, 1994, pp. 50693-50696.

(2) Burow, R.F., "Volatile Methylsiloxanes (VMS) as Replacements for CFCs and Methyl Chloroform in Precision Cleaning," Aerospace Hazardous Materials Management Conference, Changler, AZ, October 26-28, 1993.

(3) Dow Corning Corporation, "Position Paper for Ozone-Safe Fluids: A Summary of Toxicological and Environmental Information," Form No. 01-853-94.

(4) Finzel, W.A., "High-Solids Polyorganosiloxane Polymers for High Temperature Applications," JOURNAL OF COATINGS TECHNOLOGY, 64, No. 809, 47 (1992).

(5) Finzel, W.A., "Higher Solids Silicone Alkyd Copolymers for Lower VOC Maintenance Paints," *Proc. Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, February 5-7, 1986.

Recent Developments in Epoxy Resins and Curing Agents

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The continuing influence of various government regulations have resulted in the development of several new products which can allow protective coating formulators to meet these increasingly more stringent requirements.

This paper discusses and describes epoxy resins and curing agents that provide coating manufacturers the opportunity to develop high-solids, low VOC, and waterborne formulations.

Discussion
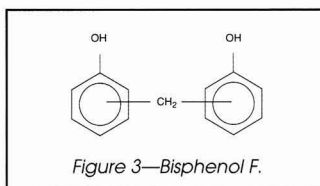
BISPHENOL A AND F EPOXY RESINS

The most commonly used type of epoxy resin today is based on the diphenol usually referred to as bisphenol A (see *Figure* 1).[1]

Figure 1—Bisphenol A.
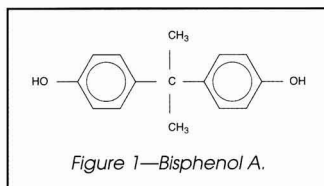
By reaction with epichlorohydrin, an epoxy resin commonly named the diglycidyl ether of bisphenol A is produced. A representative structure for this epoxy resin is shown in *Figure* 2.

Figure 2—Bisphenol A based epoxy resin.

Figure 3—Bisphenol F.
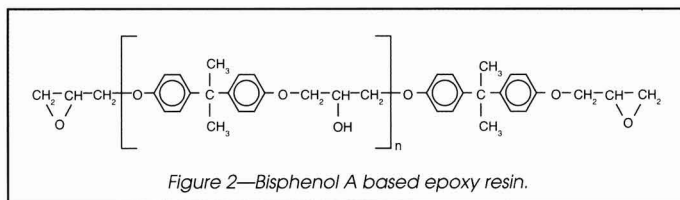
Liquid undiluted bisphenol A based epoxy resins typically have average values of "n" less than 0.2 and viscosities ranging from approximately 7,000 to 15,000 cP at 25°C. Standard epoxy resins, used in the largest quantities, usually range in viscosity from 11 to 16,000 cP at 25°C.

Another type of epoxy resin finding increasing popularity is based on a diphenol named bisphenol F whose structure is shown in *Figure* 3.

Bisphenol F is made by reacting phenol with formaldehyde.[2] Unlike bisphenol A, which is made by reacting phenol with acetone, bisphenol F is a mixture of isomers while bisphenol A is mainly all para-para. Bisphenol F epoxy resins are made, as is the case with bisphenol A epoxy resins, by reaction with epichlorohydrin. The resulting bisphenol F epoxy resin has the general structure given in *Figure* 4.

If "n" is less than about 0.2, the resins are called bisphenol F epoxides. If "n" is higher, they are referred to as EPN resins or epoxy phenol novolac resins. A comparison of bisphenol A to bisphenol F resin reveals several important differences.

Table 1—Liquid Bisphenol F Epoxy Resin Isomer Content

Isomer	Approximate Amount (Area %)
Ortho-ortho	14
Ortho-para	49
Para-para	37

Isomers—As mentioned earlier, bisphenol A is nearly all para-para in its structure. This is also true for the epoxy resin. Due to the various isomers of the precursor bisphenol F, the approximate distribution of isomers for liquid bisphenol-F based epoxy resins is shown in *Table* 1.

Repeat Unit—The repeat unit of epoxy resins based on bisphenol A is represented by the structure shown in *Figure* 5.[3]

Table 2—Bisphenol A Epoxy Resins

Approximate Average "n" Value	Epoxy Equivalent Weight Range
1	450-530
4	875-1025
7	1667-2500
9	2500-3575

This structure forms as a result of the reaction between an epoxy and a phenol group.

The higher the value for the repeat unit "n," the higher the molecular weight and viscosity of the resin and the higher the epoxy equivalent weight. This relationship is given in *Table* 2.

Regardless of the "n" value, this type of bisphenol A based epoxy resin can only have an epoxy functionality of two.

In contrast to the resin discussed previously, the repeat unit for bisphenol F epoxy resins and epoxy phenol novolac resins can be essentially represented by the structure shown in *Figure* 6.

D. Helfand

Table 3—Bisphenol F and EPN Epoxy Resins

Resin Designation	Viscosity cP	EEW
GY 285	2000-3000	164-172
GY 282	3000-4000	167-175
GY 281	5000-7000	159-172
PY 307-1	30,000-50,000	169-179
GY 1179	1100-1700 at 52°C	172-179
GY 1180	20,000-50,000 at 52°C	175-182

Table 4—Bisphenol A/F Epoxy Resin

Designation	GY 308
Viscosity at 25°C	6500-8000
EEW	173-182

Table 5—GY 281 Cured with Selected Hardeners

Component	Formulation Number (PBW)		
	1	2	3
Araldite GY 281	100	100	100
Hardener HY 837 (Aliphatic Amine Adduct)	38	—	—
Hardener HY 943 (Aliphatic Polyamine Adduct)	—	23	—
Hardener HY 2964 (Modified Cycloaliphatic Amine)	—	—	57

Formulation Properties	Formulation Number		
	1	2	3
Mix viscosity at 25°C (cP)	3230	4450	460
100 g gel time at 20°C (min)	15	11	23
Persoz hardness (sec) 7 days at 20°C	360	220	315
Dry through time at 20°C, 8 mil film (hrs)	4	5	8

Chemical Resistance (at 20°C)

Substrate: Sandblasted steel
Films thickness: c. 400 microns (16 mils)
Cure prior to testing: 7 days @ 20°C, 65% RH

+–Resistant
A–Affected
D–Destroyed

Test period (months of immersion)	1/4	1/2	1	2	3	4	5	6	7	8	9	10	11	12
Formulation 1														
Sulfuric acid 50%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
70%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hydrochloric acid conc.	+	+	+	A	A	A	A	A	A	A	A	A	A	A
Acetic acid 50%	D													
Caustic soda 30%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ammonia conc.	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methanol	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Ethanol 50%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
96%	A	A	+	+	+	+	+	+	+	+	+	+	+	+
Xylene		+	+	+	+	+	+	+	+	+	+	+	+	+
Formulation 2														
Sulfuric acid 70%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hydrochloric acid conc.	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methanol	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethanol 96%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Formulation 3														
Sulfuric acid 50%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
70%	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hydrochloric acid conc.	+	+	+	A	A	A	A	D						
Acetic acid 50%	D													
Caustic soda 30%	+	+	+					+	+	+	+	+	+	+
Ammonia conc.	+	+	+	A	A	A	D							
Methanol	D													
Ethanol 50%	+	+	+	D										
96%	A	A	D											
Xylene		+	+	+	+	+	+	+	+	+	+	+	+	+

Table 6—PY 322 Physical Properties

Property	Value
Gardner Color	3 maximum
Viscosity at 25°C	2000-5000 cP
WPE	317-357

Bisphenol-F Epoxy Resin

Figure 4—Epoxy phenol novolac (EPN).
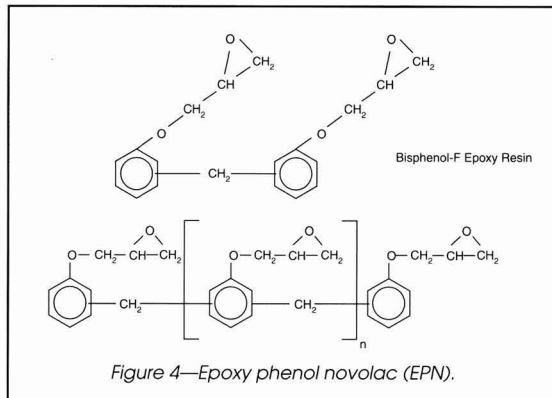
Table 7—Use of PY 322 with Bisphenol A Epoxy Resin (GY 6010)

	Parts by Weight				
Formulation No.	1	2	3	4	5
Araldite GY 6010	100	90	75	50	25
Araldite PY 322	—	10	25	50	75
Hardener HY 265	50	48	45	39	34
Physical Properties @ 25°C					
Gel time, min	39	45	64	118	289
Dry Time, hr					
Dust free	3.5	—	4.5	9.0	18.0
Through cure	5.0	—	7.5	8.0	11.0
Film Properties @ 25°C					
Substrate	Cold-rolled steel				
Film thickness	6-7 mils				
Cure schedule	7 days @ 25°C				
Persoz hardness, sec.	319	302	281	215	103
Pencil hardness	2H	F	F	F	F
Adhesion, cross-cut, %	0	50	50-75	90	100
Impact resistance, in-lb					
Direct	2	4	4	18	58
Reverse	0	<2	0	2	60
Chemical Resistance @ 25°C					
Substrate	Cold-rolled sandblasted steel				
Film thickness	10-12 mils				
Cure schedule	7 days @ 25°C				
Test period	8 months continuous immersion				

Formulation No.	1	2	3
Effect on Coating Number of Blisters			
Distilled water	none	none	none
NaOH, 50%	none	none	none
H$_2$SO$_4$, 30%	none	none	none
Xylene	none	none	none

Formulation No.	1	2	3	4	5
Resistance to Immersion in 100% Methanol, 4 Months, Number of Blisters					
Vapor phase	many	none	none	none	none
Liquid phase	many	many	few	none	none

In this case, the "n" unit is a result of the reaction between formaldehyde and phenol. Depending on the ratio of phenol to formaldehyde, the value of "n" can vary.

However, unlike the repeat unit of bisphenol A epoxy resins, increasing the repeat unit of a bisphenol F or epoxy phenol novolac resin does not significantly increase the epoxy equivalent weight although viscosity and functionality do increase.

Several bisphenol F based epoxy resins are available, and are briefly described in *Table 3*.

The last two resins in this table, GY 1179 and GY 1180, are usually referred to as epoxy phenol novolac resins although their chemical structures are the same as bisphenol F epoxies except for a higher "n" value. The first three resins, GY 285, 282, and 281, all have viscosities significantly lower than typical liquid unmodified bisphenol A-based epoxy resins which usually range from about 6500 to 14000 cP at 25°C. A major advantage of bisphenol F epoxy resins is their lower viscosity compared to bisphenol A-based resins which allow for higher filler loadings and reduced volatile organic content coating formulations.

When liquid bisphenol A based epoxy resins are subjected to temperature cycling, they will sometimes crystallize. The solid formed is the pure diglycidyl ether of bisphenol A (*Figure 2*, where n = o). This tendency can be significantly reduced by combining bisphenol A with bisphenol F based epoxy resins. An example of a resin of this type is described in *Table 4*.

Application—The examples given in *Table 5* illustrate the utility of the bis F epoxy resin GY 281. Similar results would be obtained with the other bis F-based resins. If unmodified bisphenol A epoxy resins were used, mix viscosities would be significantly higher which would limit filler loadings and processability. The chemical resistance of bisphenol F-based epoxy resins is

Table 8—PY 322 Amine Adduct Properties

Property	Value
Theoretical amine hydrogen equivalent weight	165
Brookfield viscosity at 25°C	6500-7500 cP
Gardner color	2
Amine value	200-230
Specific gravity	1.05

Table 9—PY 322 Amine Adduct—Cured Properties

Property	Value
100 g gel time at 25°C	52 min
Dust free time, 10 mil film, 25°C unpigmented	4 hr, 10 min
Dry through time, 10 mil film, 25°C unpigmented	4 hr, 30 min
Pencil hardness, 7 days cure at 25°C	F
Mandrel bend	Pass 1/8"
Crosshatch adhesion	5 (no failures)
Gardner impact	Direct 80 in-lbs
	Reverse 50 in-lbs
Glass transition temperature	49°C
Tensile elongation at 25°C	20%

Table 10—Chemical Resistance DGEBA/PY 322 Amine Adduct

Test Chemical/Reagent	Resistance Duration
Skydrol Xylene Unleaded gasoline Tap water 50% NaOH 50% H_2SO_4 30% H_2SO_4 10% HCl	One year resistance
100% Ethanol 10% Nitric acid 20% HCl	6 Months resistance
Methyl ethyl ketone 30% H_3PO_4 10% acetic acid	< 2 Months resistance

Table 11—XB 323 Typical Properties

Property	Value/Comment
Appearance	Uniform, milky
Apparent viscosity at 25°C (cP)	860 thixotropic
Solids (wt %)	75-78
WPE (as is)	222-250
Density at 25°C (g/ml)	1.16
Freeze thaw cycles	Fails 1 cycle
Flash point (°C)	> 200
Particle Size Distribution (%)	
< 1 micron	70
< 2 micron	95

Table 12—XB 323/HZ 340 Formulation

Components	Parts by Weight	Comment	
XB 323	100.0	75 wt%	Total solids 38% by weight
HZ 340	91.8	50 wt%	
TiO_2	80.9		
Water	257.8		

Table 13—XB 323/HZ 340 Film Properties

| Property	Value
Usable life (hr) at 23°C	4
Dust free time (hr)	6
Dry through time (hr)	
Soft gel	5.5
Hard gel	15
60° gloss 24 hr	Good
Flow/surface 24 hr	Good
Exudation	None
Whiteness vs calibrating panel (83.9%) (°%)	73
Persoz hardness (sec)	
24 hr	171
1 week	206
4 weeks	260
Distensibility (mm)	
14 days	6.2
8 weeks	0.2
Direct impact (in-lbs)	
7 days	180
8 weeks	90
Reverse impact (in-lbs)	
7 days	<10
8 weeks	<10
15 mm Mandrel bend after 8 weeks (°)	<10
Crosshatch adhesion after 10 days	0
	(0 = excellent, 5 = poor)

Figure 5—Bisphenol A epoxy resin repeat unit.
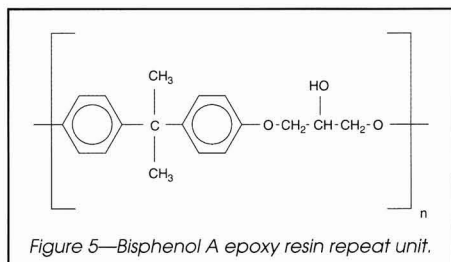
Table 14—Chemical Resistance XB 323/HZ 340

Substrate: Degreased pickled steel
Film Thickness: 4 mil
Cure: 14 days @ 20°C, 65% RH

Months	1/4	1	2	3	6	9	12
Water, deionized	+	+	+	+	+	+	+
Sodium chloride, 10%	+	+	+	+	+	+	+
Hydrochloric acid, 10%	D						
Sulfuric acid, 10%	D						
Lactic acid	D						
Sodium hydroxide, 50%	+	+	+	+	+	+	+
Ammonia, 10%	A	A	A	A	A	A	A
Xylene	+	+	+	+	+	+	+
Ethanol, 30%	+	+	+	+	+	+	+
Ethanol, 95%	+	+	+	A	A	A	A

D = destroyed; A = affected.

comparable to that of bisphenol A-based epoxies except that there is some improvement to acids depending on the curing agent used.

EPOXY RESIN PY 322

A relatively recent development in flexibilizing epoxy resins is designated PY 322 and is patented under U.S. Patent Number 4,284,574.[4] *Figures* 7 and 8 show the chemical synthesis of this novel epoxy resin. The intermediate shown in *Figure* 7 is reacted with epichlorohydrin yielding PY 322 epoxy resin pictured in *Figure* 8. Selected typical physical properties of epoxy resin PY 322 are in *Table* 6. PY 322 can be used to improve the impact resistance of coatings based on standard liquid bisphenol A based epoxy resins cured with modified cycloaliphatic amines which tend to be very brittle without significantly affecting chemical resistance. This is demonstrated by the data given in *Table* 7.

Amine adducts of epoxy resins are well known as are the techniques for making them.[5] In the case of PY 322, various amines can be used to make useful amine adduct curing agents. One such curing agent, based on an aliphatic amine with a modifier added, is described in *Table* 8. Selected properties of this hardener, when cured using standard liquid bisphenol A-based epoxy resin, are tabulated in *Table* 9. Clear films, 10-12 mils thick, cured 10 days at room temperature based on this amine cured with liquid diglycidyl ether of bisphenol A epoxy resin were subjected to chemical resistance testing. These results are listed in *Table* 10.

Unlike typical aliphatic amine hardeners which provide brittle films, this PY 322 adduct gives the flexibility and impact resistance usually observed with polyamide type hardeners. However, the chemical resistance obtained from this hardener, while not superior, is still better than most polyamide type curing agents and is also better than epoxy systems flexibilized using epoxidized polyglycols.

WATERBORNE EPOXY RESINS

The use of waterborne coatings is increasing since it is widely recognized that these materials are ecologically friendly. Basically, it is possible to emulsify liquid epoxy resins and their curing agents through the use of suitable emulsifying agents sometimes adding small amounts of solvents with or without neutralizing acids or other reactants. Other techniques allow for the manufacture of solid resin dispersions in water. An interesting waterborne product recently introduced is based on the bisphenol F epoxy resin PY 307-1 which is described in *Table* 3. This product, designated XB 323, contains no solvents or neutralizing acids and has a resin content of 75 wt%. Typical properties of this emulsion are given in *Table* 11.

The small particle size of this emulsion is achieved through the use of optimized processing equipment and surfactant choice. Care must be taken to avoid freezing XB 323, since, primarily due to the lack of solvent, the emulsion will break.

A suggested starting point formulation using XB 323 and a polyamide type hardener HZ 340 is shown in *Tables* 12 and 13 with selected curing and physical properties of the coating. The data show that a good quality pigmented coating can be prepared using XB 323 cured with HZ 340. As is the case with most epoxy resin based formulations, further curing takes place with time.

This is reflected by the increased hardness and reduced impact and flexibility values reported. An equilibrium is finally reached when curing can no longer proceed due to steric hindrances and crosslink density factors. Depending on the temperature during and after curing, the equilibrium can be reached after a few days or several weeks.

Figure 6—Bisphenol F epoxy resin repeat unit.
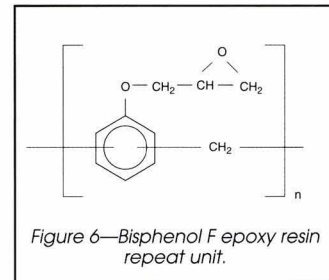
The chemical resistance of this formulation, while not exceptional, is typical for waterborne, polyamide cured formulations. Some chemical resistance data is given in *Table* 14.

The data show good resistance to water, salt solution, 50% caustic xylene, and 10% ammonia, but poor resistance to lactic, hydrochloric, or sulfuric acid.

Table 15—High-Solids Epoxy Resin Solutions

Property	Value	
	GZ 7488 N-50	GZ 7488 PMA-40
Main solvent	Methyl ethyl ketone	Propylene glycol monomethyl ether acetate
Viscosity at 25°C (cP)	3000-6000	3000-6000
Resin content (wt %)	50 ± 1	40 ± 1
EEW (on solids)	6670-10,000	6670-10,000
Flash point (°C)	≤ 0 (32°F)	36 (97°F)

Table 16—MDA and Non-MDA Hardener Comparison—Typical Properties

Property	MDA HY 2969	Non-MDA HY 3100	Non-MDA HY 3150
Active hydrogen weight	115	58	54.5
Viscosity at 25°C (cP)	600-900	1200	700
Pounds/gallons	9.3	8.8	8.7
Flash point (°F)..............................	212	> 200	> 200
Color/appearance	Dark brown/ clear	Dark brown/ clear	Dark brown/ clear

DAVID HELFAND has been employed by Ciba-Geigy for more than 30 years working in various fields of polymer applications, primarily epoxy resins and their curing agents. He is currently a Staff Scientist in the Coatings and Civil Engineering group of the Ciba Polymers Division.

Mr. Helfand graduated from the City College of New York with a B.S. Degree in Chemistry in 1969.

Table 17—Curing/Handling Properties— Non-MDA and MDA Hardeners

Formulation Component	Formulation No. (PBW) 1	2	3
Araldite GY 6010	100	100	100
HY 2969	60	—	—
HY 3100	—	30	—
HY 3150	—	—	30
Property			
25°C mixed viscosity cP	4300	4900	4600
100 g gel time at 25°C (min)	120	325	45
Dust free time 9-11 mil thick (hr)	6	> 18	10
Dry through time 9-11 mil thick (hr)	8	> 18	11

Table 18—Chemical Resistance of MDA vs Non-MDA Coatings

Formulation No.	1					2					3				
	Parts by Weight														
Araldite GY 6010	100					100					100				
Hardener HY 2969 (MDA-Amine)	60					—					—				
Hardener HY 3100 (Non-MDA)	—					30					—				
Hardener HY 3150 (Non-MDA)	—					—					30				
	Chemical Resistance														
Duration Months	1	2	4	8	12	1	2	4	8	12	1	2	4	8	12
Sea water, synthetic	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Sulfuric acid 10%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
70%	+	+	+	+	+	+	+	+	A	A	+	+	+	+	A
Hydrochloric acid 10%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
20%	+	+	+	+	+	+	+	+	D	D	+	+	+	+	+
37%	+	+	A	D		+	+	+	A	A	+	+	+	+	A
Acetic acid 5%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
10%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Lactic acid 10%	+	+	+	+	+	+	A	A	A	A	+	A	A	A	A
Caustic soda 50%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ammonia 10%	+	+	A	A	A	+	+	+	+	+	+	+	+	+	+
25%	A	D				+	+	+	+	+	+	+	+	+	+
Chlorox bleach	+	+	+	A	A	+	+	+	+	+	+	+	+	+	+
Ethanol 50%	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
96%	A	D				+	+	+	+	+	+	+	+	+	+
Butanol	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
MEK	A	D				D					D				
Acetone	D					D					D				
Ethylene glycol	D					+	+	+	+	+	+	+	+	+	+
Toluene	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Xylene	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Crude oil	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Unleaded gas	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Skydrol	+	+	+	+	+	A	D				A	D			

+ = resistant; A = attacked; and D = destroyed.
Skydrol is a registered trademark of Monsanto Co.

Figure 7—Bisphenol A and n-butyl glycidyl ether.

Figure 8—Epoxy Resin PY 322.
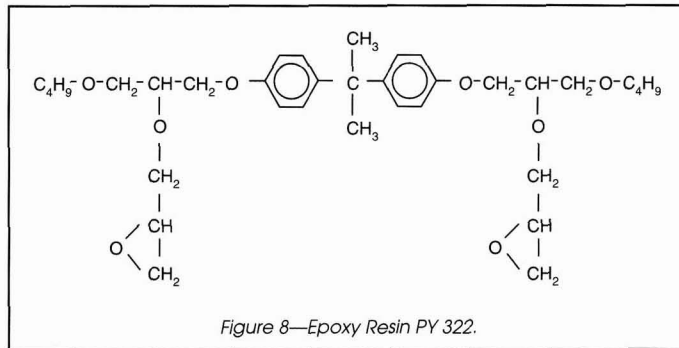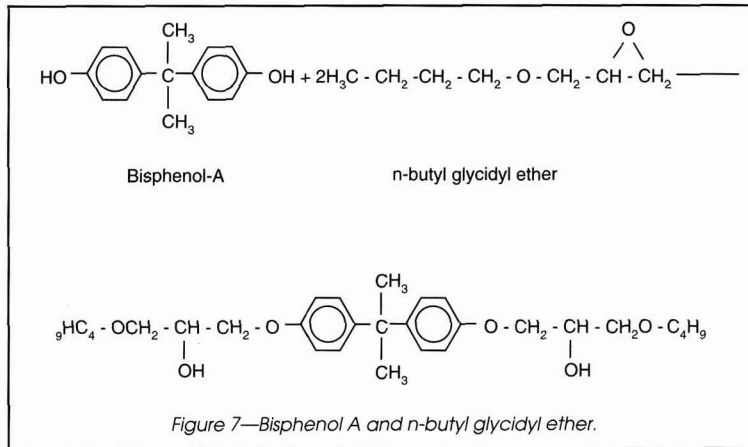
Heat curing and making the coating thicker will improve the chemical resistance.

HIGHER SOLIDS CONTENT EPOXY SOLUTIONS

Many applications such as can and coil coatings require the use of high molecular weight solid epoxy resins in solution.

Due to recent developments in the chemistry of preparing solid epoxy resins, the degree of branching has been significantly reduced. As a result, resin solutions with higher solids content can be prepared while still maintaining good viscosity for ease of processing. *Table* 15 describes two such resin solutions.

By contrast, the older high molecular weight solutions are 40 wt% in methylethylketone and 32 wt% in propylene glycol monomethyl ether acetate. Using these newer resin solutions can signifi-cantly reduce the overall volatile organic content of the formulation.

HARDENERS WITH NO MDA

It has long been recognized in the coatings industry that hardeners based on the aromatic amine methylene dianiline (MDA) provide the best overall chemical resistance especially to a wide variety of acids.

Due to recent OSHA regulations promulgated in 1992, strict monitoring and record keeping is required for personnel working with MDA containing materials. Since field operations are inherently difficult to control, it was decided by several manufacturers to withdraw MDA based hardeners from the coatings market in the USA.

As replacements, the hardeners HY 3100 and HY 3150 have been developed and commercialized. These hardeners are exempt from the OSHA regulation since they con-tain no MDA although another aromatic amine is present. Selected properties of the non-MDA containing hardeners in comparison to HY 2969, a hardener based on MDA, are given in *Table* 16.

Some typical curing and handling properties in comparison to HY 2969 are shown in *Table* 17.

Hardeners HY 3100 and HY 3150 have been designed so that they can be blended to achieve any gel time between 45 and 325 minutes depending on the application requirements.

As mentioned earlier, chemical resistance is the main advantage of MDA based hardeners. The data presented in *Table* 18 show the chemical resistance of the three formulations given in *Table* 16. In each case, clear films, approximately 15 to 20 mils thick, on a substrate of sand-blasted steel, cured 10 days at room temperature, were exposed to vapors and liquids of the various test fluids. The results of the testing indicate that in many cases the non-MDA containing hardeners can be substituted for the one containing MDA. However, specific testing must be carried out before substitution is made since some differences exist such as in the case of Skydrol.

Conclusions/Summary

Responding to the new requirements of environmental regulations and user safety, new products have been and are under development which can enable coatings formulators to satisfy these requirements without sacrificing the advantages of older formulations.

Acknowledgments

REFERENCES

(1) Lee, H. and Neville, K., *Handbook of Epoxy Resins*, McGraw-Hill, New York, NY, 1967.
(2) *Ibid*.
(3) *Ibid*.
(4) Bagga, M., U.S. Patent 4,284,574 (August 18, 1981).
(5) Lee, H. and Neville, K., *loc cit*.
(6) Wegmann, A., "Novel Waterborne Epoxy Resin Emulsion," JOURNAL OF COATINGS TECHNOLOGY, 65, No. 827 (1993).

Society Reports

CDIC—NOVEMBER

"Organic Modified Silicone Resins for Coatings"

Environmental Committee Chair, Philip Trew, of PPG Industries Inc., reported that House Bill #350, a Tort reform bill designed to lessen product liability suits, is under consideration. In addition, Mr. Trew also noted that filing for the Clean Air Act Title V Permits began on October 1, 1995.

Ohio Paint Council Representative, Hugh Lowrey, of Perry & Derrick, stated that the VOC regulations for architectural coatings, which were due to be released in September 1995 are still pending, and possibly will not be released until October 1996. According to Mr. Lowrey, there has been considerable protest to VOC restrictions placed on traffic paints due to increased cost of equipment.

Past-President Paul Guevin, of P.R. Guevin Associates, reported that 41 ballots regarding the proposed Bylaws change had been collected and the change was approved.

Technical Committee Chair Ken Pendleton, of K.A. Pendleton Co., Inc., announced that the Committee has been researching appropriate substrates for their waterborne coatings adhesion testing. Mr. Pendleton welcomed the following new members to the Committee: Gene Doll, of Schable Products; Bill Engelke, of Fischer Industrial Coatings; Jack Frost, of Ashland Chemical Co.; George Bless, of D.A. Campbell & Co., Inc.; and Barry Hoock, of Ashland Chemical Co.

Detroit Society member, Gerald Witucki, of Dow Corning Corp., delivered the evening's technical presentation on "ORGANIC MODIFIED SILICONE RESINS FOR COATINGS."

Mr. Witucki discussed a process that was discovered for synthesizing organic modified silicone polymers. This process allows for uniform incorporation of organic crosslinking throughout the resin matrix in a silsequioxane formation.

According to the speaker, the resulting polymers differ from traditional silicone/organic block polymers in that they have a more random structure and lower polydispersity. Other physical properties (previously unattainable) achieved include better solvent resistance, improvement in heat resistance, a narrower molecular weight distribution, and increased hardness and flexibility.

At the present, formulations using resins synthesized by the new process are being used to improve properties of coating systems for wood stoves. A patent on this process is pending.

TERESA CASE, Secretary

CLEVELAND—OCTOBER

Color Matching

The first speaker of the evening was John Mueller, of Datacolor International. He spoke on "COLOR MATCHING: PAST, PRESENT, FUTURE."

Mr. Mueller began by tracing the first recorded use of color to religious rites. He cited examples as those found in caves in France and Spain in 1800/1500 B.C. The materials used at that time included pigments and binders (chalk, charcoal, ore, and animal fat as a binder).

According to the speaker, Egyptians improved upon the French and Spanish by adding better color control and brushes.

Mr. Mueller stated that color matching in those early days was visual. Visual color matching is still used today; however it has

become increasingly difficult to find good visual color matchers. Therefore, computer color matching equipment was invented.

In conclusion, Mr. Mueller stated that color is not the same to all people, some of the things that affect color are light source, object, and observer.

Jeffrey Norris, of Engelhard Corp., delivered the next presentation entitled "TRENDS IN PIGMENT AND COLORANT TECHNOLOGY— COLOR AND COMPLIANCE."

Mr. Norris began with an overview of colorants in the 90s by focusing on their regulatory challenges and environmental friendliness, as well as the following: organic pigments vs. inorganic pigments, highsolids and solvent free, and globalization.

The speaker defined a heavy metal as a metal with an atomic weight greater than 22.9. Mr. Norris then discussed the regulatory issues facing heavy metals, stating that phthalocyanines and barium sulfate have been delisted, while a lead ban is still uncertain. He also noted that cadmium exposure is limited.

According to Mr. Norris, current trends in pigment technology are: heavy metal free, improved rheology, water stable grades, particle size optimization, and improved/easier dispersion.

He also explored industrial colorant technology trends. They are: VOC reduction, high-solids, universal in-plant colorants, and resin-free concentrates.

On the trade sales side, Mr. Norris said to look for solvent-free dispersions, higher pigment solids, improved resistance properties, and enhanced compatibility.

In conclusion, Mr. Norris predicted solvent-free latex paints, acceptance of solvent-free colorants, and European air and water regulations for the future of colorants. The forecast for pigments included medium performance organics, multiple suppliers, diluent scheme for high performance organics and safety coatings that are lead-free and water-based.
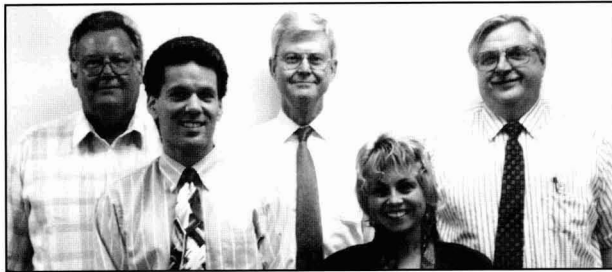
JAMES J. CURRIE, Secretary

DETROIT—SEPTEMBER

Chinese Coatings Industry

It was announced that a Program Committee is forming. The Committee will be comprised of members from different segments of the coatings industry.

The meeting's speaker was Frank N. Jones of the Coatings Research Institute at Eastern Michigan University. Dr. Jones discussed the "CHINESE COATINGS INDUSTRY."

Elected to serve as Officers of the Baltimore Society for 1995-96 are (from left): Secretary—Joseph C. Schilare; Society Representative—Joseph D. Giusto; Vice President—Connie Sauer; President—Albert Holder; and Treasurer—Jane B. Takesian.

Officers of the Cleveland Society for 1995-96 are (from left): Secretary—James J. Currie; President—Michael A. Wolfe; Lamar Brooks; Treasurer—Jennifer Rumberg; and Vice President—Richard A. Mikol.

Dr. Jones revealed that the Chinese are eager to jump into 21st century paint technology; however, they have much work to do in establishing a raw material infrastructure and ultimate customer base.

JOE LESNEK, *Publicity*

General Membership Meeting

President Lawrence Murphy, of Tnemec Co., Inc., recognized the Past-Presidents in attendance.

Randall Ehmer, of Walsh & Associates, reported that the Technical Committee Chair Monty Montgomery, of Tnemec Co., Inc., has several speakers lined up for the Kansas City/St. Louis meeting. He also said that Mr. Montgomery needs help with the other program and events.

Program Chair Bill Porter, of Hillyard Industries, Inc., announced that the January meeting will consist of a technical presentation.

CURRY SANDERS, *Secretary*

LOUISVILLE—SEPTEMBER

1995-96 Society Officers

Outgoing President Mike Moilanen, of Süd Chemie Rheologicals, passed the President's Gavel to Incoming Society President William Leightner, of C.L. McGuire, Co.

The Society Officers and Committee Chairs for 1995-96 were announced as follows: President-Elect and Program Chair—Andy Traister, of Courtaulds Coatings, Inc.; Treasurer—Dan Fortney, of American Dispersions, Inc.; Secretary—Paul Baukema, of Akzo Nobel Coatings, Inc.; Society Repre-

sentative—Larry Pitchford, of Reynolds Metals Co.; Membership Chair—Chris Lockhart, of Reynolds Metals Co.; Bylaws Chair—Don Collier, of Courtaulds Coatings; Educational Chair—Lloyd Browning, of Kelley Technical Coatings; Environmental Chair—Roy Funkhouser, of Law Environmental; Technical Chair—Ilona Duvall, of Red Spot Paint and Varnish; and Publicity Chair—James Flanagan, of Flanagan Associates, Inc.

Ken Hoy, retired from Union Carbide, spoke on "DECOMPRESSIVE SPRAY, A NEW SPRAY TECHNIQUE."

Spray application of paint, according to Dr. Hoy, dates back to the 1890s. He stated that spray application contributed to mass production by freeing the bottleneck of the paint shop in manufacture. The speaker also discussed several traditional air-assisted spray methods and the more modern methods of HPLV (high pressure low volume) sprayings, airless and air-assisted airless, electrostatic spraying, and super-critical fluid or decompressive spraying.

Another area covered by Dr. Hoy was the effect of particle size. He indicated that ideal sprays had particles in the 35-55 mi-

cron range. Sprays with lower particle sizes had more overspray (lower transfer efficiency) while sprays with higher particle sizes had orange peel. HPLV guns that virtually eliminate small particles have much better efficiencies, but they do tend to orange peel since a high number of larger particles are formed. Increasing the air pressure in an HPLV gun will improve orange peel, but reduces transfer efficiency.

The effect of solvent loss is also of importance. Using a Fickian diffusion model, Dr. Hoy modeled the solvent loss from the tip of the gun to the part. Large particles do not lose solvent as effectively, therefore, HPLV spraying will often result in sagging. HPLV spraying may lose only 60% of the solvent compared to conventional air spray. The speaker stressed the importance of selecting the proper solvent balance for application change.

The last area covered by Dr. Hoy was decompressive spray, a technique in which gas is heated and pressurized until it liquefies. The gas decompresses at the orifice and this expansion forms the droplets. According to the speaker, 89% of the droplets are in the ideal range. Only one percent are too large, and approximately 11% are too small. Therefore, the decompressive spray affords a high transfer efficiency and better appearance.

PAUL BAUKEMA, *Secretary*

LOUISVILLE—OCTOBER

Manufacturing Night

Carl Gerhiser, of Chesapeake Consulting, delivered the evening's presentation on "A BRIEF OVERVIEW OF THE THEORY OF CONSTRAINTS."

Elected as Officers of the Detroit Society for 1995-96 are (from left): President—Jane Allen; Vice President—Tedd Strobehn; Treasurer—Jan Hammond; and Secretary—Ray Stewart.

Constituent Society Meetings and Secretaries

BALTIMORE (Third Thursday—Martin's West, Woodlawn, MD). JOSEPH SCHILARE, The Valspar Corp., 1401 Severn St., Baltimore, MD 21230 .

BIRMINGHAM (First Thursday—Strathallan Hotel, Birmingham, England). DAVID C. MORRIS, PPG Industries (UK) Ltd., P.O. Box 359, Rotton Park St., Birmingham, B16 0AD, England.

CDIC (Second Monday—Location alternates between Cincinnati, Columbus, Dayton, and Indianapolis). THERESA CASE, Fibreglass Evercoat Co., Inc., 6600 Cornell Rd., Cincinnati, OH 45242.

CHICAGO (First Monday—Sharko's Restaurant, Villa Park, IL). GERRY K. NOREN, DSM-Desotech, Inc., 1122 St. Charles St., Elgin, IL 60120.

CLEVELAND (Third Tuesday—Monthly meeting site TBA). JAMES CURRIE, Jamestown Paint Co., 108 Main St., Jamestown, PA 16134.

DALLAS (Second Thursday following first Wednesday—Dallas Medallion Hotel, Dallas, TX). MIKE TEMPLIN, Hilton-Davis Co., 1696 Dickerson Dr., Arlington, TX.

DETROIT (Second Tuesday—meeting sites vary). RAY STEWART, Akzo Nobel Coatings, Inc., 1845 Maxwell St., P.O. Box 7062, Troy, MI 48007-7062.

GOLDEN GATE (Monday before third Wednesday—alternates between Francesco's in Oakland, CA, and Holiday Inn in S. San Franscisco). DON MAZZONE, Dowd & Guild, Inc., 14 Crow Canyon Ct., #200, San Ramon, CA 94583.

HOUSTON (Second Wednesday—Medallion Hotel, Houston, TX). KEN MUNDY, Ribelin Sales, Inc., 7786 Blankenship Dr., Houston, TX 77055.

KANSAS CITY (Second Thursday—Cascone's Restaurant, Kansas City, MO). CURRY SANDERS, Tnemec Co., Inc., 123 N. 23rd Ave., N. Kansas City, MO 64116.

LOS ANGELES (Second Wednesday—Steven's Steakhouse, Commerce, CA). ARTHUR W. LORENZ, Sinclair-Ameritone Paint Corp., 6100 S. Garfield Ave., Los Angeles, CA 90040.

LOUISVILLE (Third Wednesday—Executive West Motor Hotel, Louisville, KY). PAUL BAUKEMA, Akzo Nobel Coatings, Inc., R&D Div., 4730 Crittenden Dr., P.O. Box 37230, Louisville, KY 40233.

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— Restaurant Le Bifthèque, St. Laurent, Quebec). ROBERT BENOIT, KRONOS Canada Inc., 3390 Marie Victorin, Varennes, Que., J3X 1T4 Canada.

NEW ENGLAND (Third Thursday—Best Western TLC, Waltham, MA). RICHARD TWOMEY, Kronos, Inc., 68 Fisher St., Medway, MA 02053-2004.

NEW YORK (Second Tuesday—Landmark II, East Rutherford, NJ). ROBERT W. SCHROEDER, Daniel Products Co., 400 Claremont Ave., Jersey City, NJ 07304.

NORTHWESTERN (Tuesday following first Monday—Jax Cafe, Minneapolis, MN). MICHAEL D. COAD, McWhorter Technologies, 1028 S. Third St., Minneapolis, MN 55415.

PACIFIC NORTHWEST (PORTLAND SECTION—Tuesday before third Wednesday—Tony Roma's, Mall 205, Portland, OR; SEATTLE SECTION—Third Wednesday—Wyndham Gardes Hotel, Sea-Tac, WA; VANCOUVER SECTION—Thursday after third Wednesday—Abercorn Inn, Richmond, B.C.). KENNETH WENZEL, Chemical Distributors, Inc., P.O. Box 10763, Portland, OR 97210.

PHILADELPHIA (Second Thursday—DoubleTree Guest Suites, Plymouth Meeting, PA). PATRICIA M. PETERSON, ARCO Chemical Co., 3801 West Chester Pike, Newtown Square, PA 19073-3230.

PIEDMONT (Third Wednesday—Ramada Inn Airport, Greensboro, NC). ALEX BLAHNIK, Chemcraft Sadolin, Inc., P.O. Box 669, Walkertown, NC 27051.

PITTSBURGH (Second Monday—Montemurro's Restaurant, Sharpsburg, PA). JAMES GIAMMARCO, Lockhart Chemical Co., 2873 W. Hardies Rd., Gibsonia, PA 15044.

ROCKY MOUNTAIN (Monday following first Wednesday—Monthly meeting site TBA). JOHN ELVERUM, Hauser Chemical Research, 5555 Airport Blvd., Boulder, CO 80301.

ST. LOUIS (Third Tuesday—The Salad Bowl Restaurant, St. Louis, MO). ROBERT PHELPS, P.D. George Co., P.O. Box 66756, St. Louis, MO 63166.

SOUTHERN (GULF COAST SECTION—third Thursday; CENTRAL FLORIDA SECTION—third Thursday after first Monday; ATLANTA SECTION—third Thursday; MEMPHIS SECTION—bi-monthly on second Tuesday; and MIAMI SECTION—Tuesday prior to Central Florida Section). EVE DE LA VEGA-IRVINE, J.M. Huber Corp., One Huber Rd., Macon, GA 31298.

TORONTO (Second Monday—Speranza Restaurant & Banquet Hall Convention Centre, Brampton, Ont., Canada). MIKE MOLNAR, CIBA Pigments, P.O. Box 2000, Mississauga, Ont., L5M 5N3 Canada.

WESTERN NEW YORK—MARKO MARKOFF, 182 Farmingdale Rd., Cheektowaga, NY 14225.

Mr. Gerhiser began by defining synchronous manufacturing and the theory of constraints (TOC) as a process of continuing improvement for manufacturing. This theory was developed by Eli Goldratt after he observed that people often base business decisions on the wrong information or information based on wrong assumptions.

According to Mr. Gerhiser, an example based on the theory of constraints says that any system, usually manufacturing, will improve by maximizing the throughput of bottlenecks (i.e., constraints). He then contrasted to a decision based on traditional cost accounting. In a constrained system, TOC accounting increased profits by optimizing the utilization of the constrained resource. Optimizing nonconstrained resources increased operating expenses and inventory without increasing profits.

TOC accounting uses the following measures: throughput (T), inventory (I), and operating expenses (OE). Throughput equals the money generated through sales minus the totally variable expenses. Variable expenses equals raw materials, commissions, and freight (but not labor). Inventory is everything the company buys which it intends to sell (raw materials, the plant and property). Operating expenses include the money the company spends turning inventory into throughput (wages, direct labor, and overhead).

TOC works to improve profits through the "five focusing steps": (1) identify the constraint of the system; (2) decide how to exploit the constraint; (3) subordinate all else to the constraint; (4) elevate the constraint; and (5) if the constraint is broken, return to step one.

PAUL BAUKEMA, *Secretary*

NEW ENGLAND—NOVEMBER

Clean Air Act

President Chuck Shearer, of Zeneca Resins, presented Rich Green, of BFGoodrich, with an award from FSCT for having the largest increase in new memberships for 1994.

President Shearer was awarded the Hüls Gavel by outgoing President Joanne Monique, of Ashland Chemical.

George Frantz, of the Office of Technical Assistance spoke on "CLEAN AIR ACT AMENDMENTS AND ACETONE DELISTING REGULATIONS." Mr. Frantz discussed the program offered by his office. He stated that the program consists of walk through, confidential analysis of a specific manufacturing site's concern. This is then followed up with a specific report to any noncompliant activities.

At this point, the manufacturer is given the option as to whether he wishes to notify the E.P.A of his compliant and noncompliant concerns within the next 180 days.

Q. What is Federal enforcement?
A. It must come under Title 5 permitting.

The second speaker of the evening was Jim Bassett, of Eastman Corp., who addressed "SOLVENT SUBSTITUTION AS A SOLUTION TO THE REGULATIONS FOR THE 1990 CLEAN AIR ACT."

Mr. Bassett informed the members that acetone has now been exempted from being regulated as a VOC. At the present time, the primary concern under Title 3 is a listing of 189 chemicals that are allegedly hazardous air pollutants.

The speaker then presented slides that depicted a group of regulated solvents and then proceeded to show the substitute solvents that a manufacturer can use with some increased cost but with the net result that they will meet the new regulations of a non-hazardous solvent pollutant.

According to Mr. Bassett, the current object of the regulatory agency is to reduce the solvent levels between 33 and 50% of 17 specific solvents. While this objective might be obtainable, it may create shortages of the substitute solvents, leading to increases in cost for obtaining these replacement solvents.

Mr. Bassett also added that individual states can regulate these solvent restrictions, but they cannot regulate any levels less than those which the Federal government has set up as standards.

RICHARD TWOMEY, Secretary

NEW YORK—NOVEMBER

"Novel Hardeners for Polyurethane Powder Coatings"

Sheila Westerveld, of Standard Coating Corp., reported that the Technical Committee is currently working on a new project titled "Reactive Diluents."

Southern Society member, Ron Guida, of Hüls America Inc., delivered the evening's presentation, "NOVEL HARDENERS FOR POLYURETHANE POWDER COATINGS."

Mr. Guida acknowledged that the use of polyurethane in powders has been growing at approximately 12% per year, with the largest markets in the United States and Japan. Automotive hardware accessories, appliances, and lawn and garden equipment comprise the main polyurethane powder coatings market.

The speaker attributed externally blocked polyurethane hardeners toward this growth. Mr. Guida then explained the synthesis in

Officers of the Louisville Society for 1995-96 are (from left): Educational Chair—Lloyd Browning; Membership Chair—Chris Lockhart; Treasurer—Daniel Fortney; President—William Leightner; Vice President and Program Chair—Andy Traister; Past President—Mike Moilanen; Technical Committee Chair—Ilona Duvall; Secretary—Paul Baukema; Publicity Chair—James Flanagan; and Society Representative—Larry Pitchford.
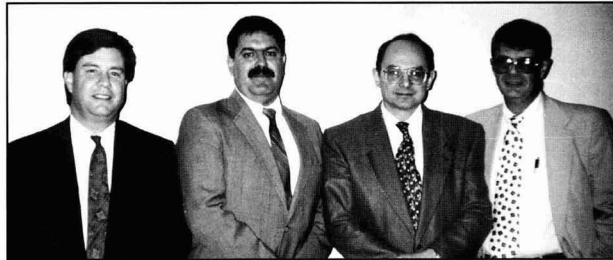
Elected to serve as Officers of the Piedmont Society for 1995-96 are (from left): President—Bob Bishop; Vice President—Roy Modjewski; Secretary—Alex Blahnik; and Treasurer—C. Dutch Hoffman.

Officers and Committee Chairs of the Pittsburgh Society for 1995-96 are (seated, from left): President—Brij Sharma; and Past-President and Educational Chair—Mark Harley. Standing: Secretary—Jim Giammarco; Technical Chair—Clifford Schoff; Vice President—Jim Rediske; Publicity Chair—Jeff Sturm; Treasurer—Joe Hunt; and Society Representative—Bill Spagenberg.

Elected to serve as Officers of the Northwestern Society for 1995-96 are (from left): Treasurer—Glen Vetter; Secretary—Michael Coad; Vice President—Jeff Gundry; and President—Joseph Mills.

forming the blocking compounds and the importance of selecting the right one.

The speaker said that ε-caprolactam blocking adducts based on IPDI (isophorone diisocyanate) are commonly used in polyurethane powder coatings. The 1990 Clean Air Act put ε-caprolactam on the raw material HAPs list. Their goal was to completely eliminate ε-caprolactam.

Mr. Guida next discussed new developments in polyurethane powder coatings. The first development was a product that used a lower level of ε-caprolactam, by 57%, by using an internally blocked group into the adduct. The second development actually reached the goal by making it fully internally blocked, using the isocyanate groups themselves to serve as blocking compounds through the formation of dimerized derivatives of IPDA. The speaker stated that the reaction product is then extended with low molecular weight polyols, resulting in a polymeric chain with potential reactive sites represented by the uretdione compound. These urethane crosslinkers are stable during processing into the formulated powders. It is at temperatures of > 160°C that thermal cleavage occurs and the isocyanate groups are regenerated to react with the polyesters' hydroxyl groups.

Mr. Guida summarized his topic by saying that uretdione chemistry polyurethane hardeners have reduced, if not eliminated, volatile blocking compounds. Other advantages over commercially available technologies are: shorter bake time at lower temperatures, superior detergent and hot water resistance, and as good exterior weathering as the established accepted products.

Q. *In the newer compound, the internally blocked structure, BF-1300 compared to the older version BF-1540, would it have a higher or lower melt viscosity than the BF-1540 and would you require lower melt viscosity polyester to maintain flow properties?*

A. BF-1300 has a slightly higher melt viscosity but the differences in viscosity are minor, a polyester with good flow is used. When you drop off in viscosity of the polyester, you start having mixing problems in the extruder.

ROBERT W. SCHROEDER, *Secretary*

PACIFIC NORTHWEST (VANCOUVER SECTION)— OCTOBER

"Wood Loves Water"

Society and Manufacturing Committee Chair, Valerie Braund, of General Paint Ltd., reported that she is working with the Portland and Seattle sections on the manufacturing seminars.

Environmental Committee Chair, Paul Andreassen, of Consolidated Coatings, stated that he recently spoke with the Canadian Paint and Coatings Association regarding meetings with industry representatives on VOC guidelines. A memorandum of agreement has been established, but no changes are predicted through the end of 1996.

In addition, Mr. Andreassen stated that B.C. Paint Care now has 53 members. A contractor depot is to open shortly and so far a total of one-million liters of waste paint have been collected.

Dick Stewart, of Firestop Systems Inc., motioned to retain the two reading format for membership. The applicant must also be in attendance at one of the two readings, unless the potential member is from out-of-town. The motion was carried.

Tom Fairley, of Calcoast Labs Canada Inc., updated members on the educational programs. He contacted the British Columbia Institute of Technology (BCIT) for information on their "Basic Paint Technology" course. Mr. Fairley recommended a hands-on program at BCIT since their venue seems best suited to a course on basic coating and application technology. Kwantlen College, on the other hand, is better suited to a technical program focusing on the science aspect of the subject, i.e., chemistry and coating physics.

Linda Smith, of Rohm and Haas, delivered the evening's presentation "WOOD LOVES WATER. WOOD FINISHING WITH WATERBORNE ACRYLIC LACQUERS."

KELVIN J. HUGET, *Secretary*

Rocky Mountain Society Officers for 1995-96 are (from left): Society Representative— Dick Mullen; Vice President—Paul Delmonico; President—Christine LesCamela; and Secretary—John Elverum.

INTERNATIONAL
COATINGS EXPO

CDIC

Active

Burnham, Tammy K.—Ashland Chemical Co., Columbus, OH.
Lubbers, Charles R.—Hilton Davis Co., Cincinnati, OH.

Associate

Roth, David A.—Deeks & Company, Cincinnati, OH.
White, James P. III—Shepherd Color, Cincinnati.

DALLAS

Active

Bixenman, Benny—Benco Sales Inc., Forney, TX.
Hendrix, Danny J.—Lockheed Martin, Fort Worth, TX.
Tramontana, Diane M.—Occidental Chemical, Dallas, TX.

DETROIT

Active

Bair, Daniel W.—The Sherwin-Williams Co., Troy, MI.
Caloia, Richard J.—Ford Motor Co., Detroit, MI.
Hamma, Diana Jean—The Sherwin-Williams Co., Inkster, MI.
Kramer, David L.—The Sherwin-Williams Co., Troy.
Musolf, Ginger S.—The Sherwin-Williams Co., Troy.
Portnoy, Etta—American Standox Inc., Oak Park, MI.
Sastry, Shyamy R.—The Sherwin-Williams Co., Troy.
Suriani, David M.—BASF Corp.,Crestview Dr., MI.
Szefi, Judith M.—Avery Dennison, Troy.
Ziegler, Rick W.—Harry Holland Co., Royal Oak, MI.

Associate

Grieves, Randolph C.—Kwality Equipment Co., South Haven, MI.
Kitchenmaster, Brian—Design & Finishing, Walled Laked, MI.
MacDonald, Daniel J.—Penn Color Inc., Hudson, OH.
Zorney, Peter A.—Shell Chemical Co., Plymouth, MI.

KANSAS CITY

Active

Habiger, Anthony F.—Nazdar, Shawnee, KS.
Hazlett, David E.—Tnemec Co., N. Kansas City, MO.
Kilpatrick, Perry D.—Tnemec Co., N. Kansas City.
Pandit, Shirish A.—Tnemec Co., N. Kansas City.
Richardson, Jon D.—Rich Paint Mfg., Inc., Olathe, KS.

Whiteside, Ross C.—Tnemec Co., N. Kansas City.
Yankee, Sam D.—Tnemec Co., N. Kansas City.

LOS ANGELES

Active

Bickel, Patricia A.—Hill Brothers Chemical, City of Industry, CA.
Crick, Denese R.—Major Paint Co., Torrance, CA.

Associate

Klopp, Frank M.—Kish Company, Oceanside, CA.
Zimmermann, Rick—Sinclair-Ameritone Paint Corp., Los Angeles, CA.

MONTREAL

Active

Cote, Marc A.—Glass Shield Paints, Chateauguay, Que.

NEW YORK

Active

Abelon, Leon—Tempil Industries, Inc., Morganville, NJ.
Belding, Sheila—Sika Corp., Lyndhurst, NJ.
Bialas, Kamila A.—Long Island Paint Co., Glen Cove, NY.
Navarro, Julian—M. Grumbacher, Cranbury, NJ.
Neithardt, William A.—Azon Corp., Randolph, NJ.
Krizan, Jeffrey F.—DataColor Corp., Southbury, CT.
Laakso, Thomas R.—Daniel Produts Co., Jersey City, NJ.
Mazzariello, Rick G.—SP Morell and Co., Sandy Hook, CT.
Rosner, Richard L.—DeGussa Corp., Rochelle Park, NJ.

Associate

Toomey, Robert F.—Rheox Inc., New York, NY.

Retired

Kustoff, Morris—Bayside, NY.

NORTHWESTERN

Active

Anderson, Stewart C.—H.B. Fuller Co., Vadnais Heights, MN.
Bell, David G.—Tomorrow River ROD, Almond, WI.
Hambrook, Ted M.—Ceramic Industrial Coatings, Osseo, MN.
Jensen, Steven C.—Ceramic Industrial Coatings, Osseo.

Associate

Benson, Frank R.—The Kenneth M. Rice Co., Des Plaines, IL.

Helbling, James F.—Zeelan Industries, Inc., St. Paul, MN.
Malone, Michael P.—Milsolv® Minn Corp., Roseville, MN.
Maslowski, Kurt—Pi-Con Chemicals Inc., Mequon, WI.
Schwich, James T.—Henkel Corp., Plymouth, MN.
Stein, Jon—Consolidated Container, Minneapolis, MN.

Educator/Student

Chen, Mao—North Dakota State University, Fargo, ND.
Weitzel, Wylie H.—North Dakota State University, Fargo.

PIEDMONT

Active

Huntington Clarence L. Jr.—Wikoff Color Corp., Fort Mill, SC.
Lodgek, Robert W.—Warlick Paint Co., Statesville, NC.
Van Remortel, Scott P.—Unimin Corp., Spruce Pine, NC.

Associate

Davis, Richard W.—Clariant Corp., Charlotte, NC.
Laird, Richard E.—Engelhard Corp., Harrisburg, NC.
Smith, Andre—Colorscope Corp., Columbia, SC.
Stenger, J. William Jr.—DuPont WPMP, Peachtree City, GA.

ROCKY MOUNTAIN

Active

Butera, Nick M. Jr.—Mesquite Valley Paint, Tuscon, AZ.
Simmons, W. David—Kemco Oil and Chemicals, Lehi, UT.
Raley, Gary L.—Sunlife Premium Paint, Phoenix, AZ.
Soberg, Orville A.—Soberg Industries Inc., Phoenix, AZ.

Associate

McCall, Michael J.—OMG, Houston, TX.
Muller, Jordan W.—Chemcentral, Tempe, AZ.
Stroud, David E.—Van Waters & Rogers, Phoenix, AZ.
Wool, Glenn O.—John K. Bice Co., Los Angeles, CA.

ST. LOUIS

Active

Brandt, Kenneth E.—U.S. Paint Corp., St. Louis, MO.
Daniels, Gary L.—U.S. Paint Corp., St. Louis.
Fischer, Louise—Carboline Corp., St. Louis.
Johnson, LaShawn R.—Carboline Corp., St. Louis.
Lian, Norman D.—Vanex Inc., Mt. Vernon, IL.

Future Society Meetings

Baltimore

(Feb. 15)—Joint Meeting (Outing)—Columbus Marine R & D Center.

(Mar. 21)—General Meeting—Mattye Reymont, Shell Chemical Co.

(Apr. 18)—"GOOD TESTS–BAD TESTING"—Saul Spindel, D/L Laboratories, Inc.

(May 16)—General Meeting and Elections.

Birmingham

(Feb. 1)—"SECURITY MARKING OF COATINGS"—M.G. Martindill, Glowbug Luminescent Colours.

(Feb. 29)—Symposium: Paint at the Crossroads—Strathallan Hotel.

(Mar. 28)—POWDER COATINGS: "WE MIGHT STILL BE GREEN BUT WE ARE NOT WET"—David Bate, H.B. Fuller Coatings.

(Mar. 30)—60th Anniversary Dinner Dance.

(May 2)—67th Annual General Meeting.

Chicago

(Feb. 5)—"PROBLEMS ASSOCIATED WITH WATERBORNE COATINGS FOR WOOD"—David Setzke, SC Johnson Polymer.

(Mar. 4)—"PIGMENTS FOR TRAFFIC MARKING SYSTEMS"—Mike Issel, Sino-American Pigments.

(Apr. 1)—"FIELD OBSERVATIONS AND LATEX CHEMISTRY"—Violete Stevens.

(May 10)—Annual Awards Banquet.

Los Angeles

(Mar. 10)—"AN ADDITIVES APPROACH TO DEFECT ELIMINATION IN THERMOPLASTIC WATERBORNE INDUSTRIAL MAINTENANCE COATINGS"—Joel Schwartz, Air Products & Chemicals Co.

(Apr, 10)—"RHEOLOGICAL MEASUREMENTS AND HOW THEY APPLY TO THE PAINT AND COATINGS INDUSTRY"—Scott Krane, Haake Instruments.

(May 8)—"THE LATEST TRENDS IN ACCELERATED CORROSION TESTING: PROHESION, QUV AND AUTOMOTIVE CYCLIC CORROSION TESTING"—Steve Grossman, Q-Panel Corp.

New York

(Jan. 9)—"PAINTING CONSERVATION"—Christopher McGlinchey, Metropolitan Museum of Art.

(Feb. 13)—Legislative Update.

(Mar. 12)—"NOVEL HARDENERS FOR POLYURETHANE POWDER COATINGS"—Ron Guida, Hüls America, Inc.

(Apr. 9)—"THE LOBBYING PROCESS: FROM BEGINNING TO END"—William Pascrell, Princeton Public Affairs Group.

(May 14)—PaVac Awards Night. "COLORED ORGANIC PIGMENTS FOR THE COATINGS INDUSTRY"—Peter Lewis, Sun Chemicals.

Pacific Northwest

(Mar.)—"AN ADDITIVES APPROACH TO DEFECT ELIMINATION IN THERMOPLASTIC WATERBORNE INDUSTRIAL MAINTENANCE COATINGS"—Joel Schwartz, Air Products & Chemicals Co.

(Apr.)—"RHEOLOGICAL MEASUREMENTS AND HOW THEY APPLY TO THE PAINT AND COATINGS INDUSTRY"—Scott Krane, Haake Instruments.

(May)—"THE LATEST TRENDS IN ACCELERATED CORROSION TESTING: PROHESION, QUV AND AUTOMOTIVE CYCLIC CORROSION TESTING"—Steve Grossman, Q-Panel Corp.

Philadelphia

(Feb. 8)—Manfacturers Night. "ADVANCES IN COLOR INSTRUMENTS"—Danny Rich, Data Color.

(Mar. 14)—"WHO BUYS TRADE SALES PAINTS, WHERE, AND WHEN"—Allen Irish, NPCA; Bill Cook, Wm. Cook & Co., and John Stauffer, Rohm & Haas Co.

(Apr. 26)—Awards Night

(May 8-10)—Eastern Training Conference and Technical Seminar.

Rocky Mountain

(Mar. 11)—"AN ADDITIVES APPROACH TO DEFECT ELIMINATION IN THERMOPLASTIC WATERBORNE INDUSTRIAL MAINTENANCE COATINGS"—Joel Schwartz, Air Products & Chemicals Co.

(Apr. 8)—"RHEOLOGICAL MEASUREMENTS AND HOW THEY APPLY TO THE PAINT AND COATINGS INDUSTRY"—Scott Krane, Haake Instruments.

(May 6)—"THE LATEST TRENDS IN ACCELERATED CORROSION TESTING: PROHESION, QUV AND AUTOMOTIVE CYCLIC CORROSION TESTING"—Steve Grossman, Q-Panel Corp.

Toronto

(Feb. 12)—Joint Meeting with OCCA—"THE IMPACT OF REGULATIONS ON THE PRINTING INKS AND COATINGS INDUSTRY"—Speaker from the Ministry of the Environment.

(Mar. 18)—"HEAVY DUTY MAINTENANCE COATINGS–THE CANADIAN EXPERIENCE"—Speakers from the Ministry of Transportation and the Corrosion Service Co., Ltd.

(Apr. 15)—Annual Technical Symposium.

(May 13)—"THE APPLICATION OF SCIENCE TO THE EXAMINATION AND CONSERVATION OF MUSEUM OBJECTS"—Sandra Lawrence, Ontario Gallery of Art.

New FSCT Members

(Continued from previous page.)

Price, David M.—Mamtc, Rolla, MO.
Rother, John H.—Borden Decorative Products, St. Louis.
Rush, Larry E.—Carboline Corp., St. Louis.
Tran, Tai T.—Nascote Industries, Nashville, IL.
Uang, Yuh-Jye—Colloid-Tech Inc., St. Louis.
Zak, Scott W.—Ultradec, Inc., Arnold, MO.

Associate

Collins, Douglas A.—Tioxide Americas Inc., O'Fallon, MO.
Gatti, Ralph J.—CL Smith, St. Louis.
Wasko, Joseph T.—Halox Pigments, Hammond, IN.
Williams, Warren O.—Archway Sales, Inc., St. Louis.

TORONTO

Active

Balkaransingh, Vishan—Plastcoat Ltd., Mississauga, Ont.

Becker, Gil—St. Clair Paint., Concord, Ont.
Garrido, Joe A.—Lorama Chemicals Inc., Milton, Ont.
Greer, Lucy—Imperial Oil Ltd., Toronto, Ont.
Lam, Christina G.—Lorama Chemicals Inc., Milton.
Racota, Maria—KUB Coatings Corp., Kingston, Ont.
Randman, Steven—St. Clair Paint, Concord.
Rozomiak, Andrew J.—Polycon Industries, Guelph, Ont.

Associate

Hall, Sue E.—BDH Inc., Toronto, Ont.
MacKay, John R.—KUB Coatings Corp., Kingston, Ont.
Maj, Stephen—Ashland Chemical, Mississauga, Ont.
Stock, Jeffrey D.—Stochem, Inc., Brampton, Ont.
Thompson, Edward W.—L.V. Lomas, Brampton.
Wickett, Craig—Anachemia Solvent, Mississauga.

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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

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City _____ State____ Zip _____

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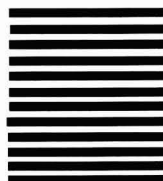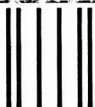
Zeneca Resins, Wilmington, MA, has appointed Dallas Society member **Michael L. Templin** Account Manager for the Southwest territory. In his new position, Mr. Templin will sell the company's line of advanced polymers to the paints and coatings, adhesives and sealants, and graphic arts markets.

Don Landes, a member of the Kansas City Society, has been appointed Sales Representative, Central Region for RHEOX, Inc., Hightstown, NJ. Based in Schaumburg, IL, he is responsible for the sale of the company's products in Nebraska, Kansas, Iowa, Missouri, and Illinois.

Fusion Systems Corp., Rockville, MD, has hired **Roger McCartney** as Director of Chemistry and Process Development for its UV Curing subsidiary. Mr. Mc-Cartney has more than 25 years of experience in the industrial application of UV curing technology.

BASF Corp., Mt. Olive, NJ, has promoted **Andrew G. Mueller** to Group Vice President, Colorants. Mr. Mueller joined the company in 1973 and has held positions in research, development, and manufacturing.

CDF Corp., Plymouth, MA, has appointed **Michael Basel** Quality Assurance Director. Mr. Basel is responsible for directing the company's Total Quality Management.

The National Association of Printing Ink Manufacturers, Inc., Hasbrouck Heights, NJ, has presented the following awards: the Technical Associate Member Service Award to **Ludwig P. Horn**, Lawter International; and the Award for Technical Achievement to **Robert T. Peters**, Kohl & Madden.

The Association also honored its Technical Director, **Paul F. Volpe**, for his 20 years of service to the ink industry.

Mary E. McKnight, a Research Chemist with the National Institute of Standards and Technology in Gaithersburg, MD, has been named a 1995 recipient of the Award of Merit by the American Society for Testing and Materials, West Conshohocken, PA. Ms. McKnight, a member of the Baltimore Society, was cited for administrative and technical leadership in the development of standards for the abatement of hazards from leaded paint in buildings.

Terryl F. Johnson, FSCT Past-President, Passes Away at 70

Terryl F. Johnson, 62nd President of the Federation of Societies for Coatings Technology, passed away at age 70, on December 10, 1995.

Born in Lockwood, MO, Mr. Johnson was graduated from the University of Missouri in 1947. Upon graduation, he started in the coatings industry as a Research Chemist at Cook Paint & Varnish Company, in Kansas City, MO. Remaining with Cook for his entire career, Mr. Johnson served as the company's Quality Assurance Manager prior to his retirement in 1992

Among his many significant contributions to the Federation over the years, Mr. Johnson served as FSCT President in 1983-84, and was a member of the FSCT's Executive, Finance, Liaison, Nominating, Planning, Professional Development, and Program Committees.

Very active locally, Mr. Johnson was a Past-President of both the Kansas City Society and the Kansas City PCA. He also served as the Kansas City Society's Representative to the Federation Board of Directors from 1977-1983.

In recognition of his outstanding contributions and support, Mr. Johnson was elected an Honorary Member of both the Kansas City Society and the Federation.

Mr. Johnson is survived by his wife, Bonnie; a stepson; and a stepdaughter.

T.F. Johnson

Witco Corp., Greenwich, CT, has named **Radu Bacaloglu** as its Outstanding Scientist for 1995 for his fundamental research in polyvinyl chloride degradation. Dr. Bacaloglu is Group Leader for vinyl research at the company's Oakland, NJ, technical center.
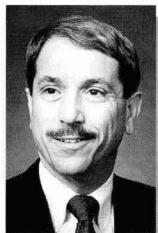
Kenneth H. Brown has been named Executive Director of Paint Research Associates (PRA Laboratories, Inc.), located at the research facilities at Eastern Michigan University, Ypsilanti, MI. He will direct the laboratory operations of PRA.

K.H. Brown

The Board of Directors of Minerals Technologies Inc., New York, NY, elected **Anton Dulski** a Vice-President of the company and appointed him President of Minteq International Inc., a wholly owned subsidiary. Mr. Dulski will succeed **James C. O'Donoghue**, who is retiring in February 1996.

In a related move, **David Rosenberg** will succeed Mr. Dulski as Vice President, Minteq Europe. Mr. Rosenberg has been with the company since 1980, when he was hired as Finance Director in South Africa.

Claudia G. Reich has been named Acting President, Standard Brands Paint Stores for Standard Brands Paint Co., Torrance, CA. Her priorities lie with the re-engineering of 54 stores located throughout California, Arizona, New Mexico, and Texas.

ISA, The International Society for Measurement and Control, Research Triangle Park, NC, has announced its new officers for 1995-96. Elected are: President—**Ronald B. Jones**, of Dow Chemical Co.; President-Elect—**Paul T. Arbuckle**, of CavCon Systems; Vice President of the Industries and Sciences Department—**Robert M. Bailliet**, of Shell Offshore, Inc.; Vice President-Elect of the Industries and Sciences Department—**Terry L. Tolliver**, of Monsanto Co.; Vice President-Elect of the Automation and Technology Department—**Al Iverson**, of Lyondell Petrochemical Co.; Vice President of the Strategic Planning Department—**James Conboy**, of Malcolm Pirnie, Inc.; Vice President-Elect of the Strategic Planning Department—**Pierguiseppe Zani**, of Aero Products International S.A.S.; Vice President of the Professional Development Department—**Sheldon Weatherby**, of Northern Alberta Institute of Technology; and Vice President-Elect of the Professional Development Department—**Lowell E. McCaw**, Consultant.

Edson P. Peredo has been elected to the Board of Directors of Buckman Laboratories, Inc., Memphis, TN. An employee of Buckman since 1972, Mr. Peredo currently serves as Executive Vice President of Buckman Laboratorios Ltda. (Brazil).

Parker Hannifin Corp., Ravenna, OH, has promoted **John Fox** to Marketing Manager for the company's Parflex Division. Mr. Fox will hold U.S. and international responsibility for marketing of all products in this division.

R.H. Lance   **R.M. Pauwels**

Robert H. Lance has been promoted to Vice President, Mobile Operations for Hüls America Inc., Somerset, NJ. In his new position, Mr. Lance will be responsible for all operations at the company's flagship manufacturing facility in Mobile, AL.

The company has also hired **Robert M. Pauwels** as Senior Technical Service Chemist in its Coatings Raw Materials Group. He will provide technical assistance to customers on the use of aliphatic isocyanate raw materials for polyurethane coatings.

In other news, **Joseph G. Sapone** has been promoted to Market Development Manager for the Silicones and Silanes Business Group of Hüls America Inc. In his new position, Mr. Sapone will develop new markets and applications to support growth in specialty silanes.

Randy V. Johnson has assumed the position of Director of Strategy and Market Planning for The Dexter Corp.'s Packaging Products Division, Waukegan, IL. Mr. Johnson will oversee global technology planning and marketing, including alliance development.

Pratt & Lambert United, Inc., Buffalo, NY, has appointed **Brad K. Wooten** as Plant Manager of its Sumter, SC, plant. Mr. Wooten formerly held various operations positions with Ameron's Protective Coatings Group.

Barry Reynolds has been named Site Administrator of the same plant. In this capacity, Mr. Reynolds will direct Accounting and MIS and will assume responsibility for all other general administrative functions.

North American Packaging Corp., Inc., Atlanta, GA, has announced that **Kenneth Williams** has been appointed Midwestern General Manager. He will manage all regional sales and operations, including production facilities in Indiana, Missouri, and Texas.

K. Williams

Peter W. Johnson, of ICI Surfactants, Wilmington, DE, has been named Regional Director, Americas. Mr. Johnson is responsible for the growth of the household, personal care, industrial, and textiles businesses with a stronger focus on North and South America.

The company has also hired **Michele K. Cinti** as MSDS and Label Coordinator. In this capacity, she is responsible for preparation and maintenance of MSDS and labels, and their respective databases.

Senior-level management appointments have been made by the Atlas Weathering Services Group, Chicago, IL, formed by the alliance of South Florida Test Service and DSET Laboratories. **Larry W. Masters** is President of the Group; **John L. Scott** will continue in his position of Vice President and Technical Director; **William J. Putman** has been promoted to Vice President of Quality Assurance and Research; **Laurence F. Bond** has been named Vice President of Sales and Client Technical Services; **Jack. L. Martin** has been promoted to Site Manager of the Miami, FL location; and **Russell W. Lane** has been named Site Manager of the Arizona locations.

Michael E. Growney has joined Kusumgar & Nerlfi, Inc., North Caldwell, NJ, as a Partner. Mr. Growney brings 10 years of consulting experience and 10 years of chemical industry experience to the firm.

Andrew D. Swanston has accepted the position of President and Chief Executive Officer of Inland Leidy, Inc., Baltimore, MD. Mr. Swanston joined the company in 1993 as Chief Financial Officer.

Joseph P. Kennedy, Distinguished Professor of Polymer Science and Chemistry at the University of Akron, Akron, OH, was selected by the American Chemical Society's Rubber Division as the recipient of its 1996 George Stafford Whitby Award for Teaching and Research. The award honors teachers and scientists for distinguished, innovative, and inspirational teaching and research in chemistry and polymer science.

Classified Advertising

Services

Chemical Searching

World Wide Chemnet Inc. offers Chemnet, an Internet service that sets up prospective buyers and sellers of chemicals, oils, and petrochemicals, bypassing difficult searches for new sources of raw materials and hard-to-find chemicals. The company has direct access to worldwide manufacturers via the Internet, and there is no charge if the product is not located. The service is accessible through any on-line Internet service as well as Prodigy, CompuServe, America Online, or Delphi.

Circle No. 30 on Reader Service Card

Container Cleaning

A new cryogenic container cleaning system for viscous materials has allowed Recycle Inc. to expand its service capabilities and offer on-site container cleaning. The system also enables users to recapture any residual viscous material which might remain in RCRA empty containers. The company can now accept drums which originally contained products traditionally requiring a burn or solvent wash products.

Circle No. 31 on Reader Service Card

Internet Presence

The International Society for Measurement and Control introduces its Home Page on the World Wide Web. Information is available on ISA activities and services, including industry news and events, technology updates, membership news and information, training opportunities, industry standards, ISA journals, the ISA Directory of Instrumentation, ISA services and staff contacts, forums, and mail. New information and opportunities are added daily.

Circle No. 32 on Reader Service Card

Raw Materials

Adhesion Promoters

Chartwell International, Inc. has announced the availability of two new metal organic adhesion promoters, each of which has a combination of both hydroxy and carboxy functionality. Chartwell B-523.2W is synthesized in water and supplied at a pH of 5.5. Chartwell C-523.2 is supplied in propylene glycol and is recommended for high-solid polyesters and alkyds.

Circle No. 33 on Reader Service Card

Tackifying Agent

A new resin dispersion developed by Hercules Resins Division is designed for tackifying polychloroprene latex for water-based contact adhesives. Tacolyn® 5001 reportedly provides high-temperature performance for postforming and dispersion stability when used with nonionic polychloroprene. This dispersion is clear in appearance and is compatible with anionic polychloroprene.

Circle No. 34 on Reader Service Card

Polyether Polyols

ARCO Chemical Co. has developed a new class of high performance, high molecular weight, liquid polyether polyols that are designed to offer improved physical properties and processing. Reported benefits of Acclaim™ polyols include higher tensile strength and elongation, improved tear strength and dynamic properties, and reduced compression set and hysteresis. The polyols are recommended for use in urethane coating, adhesive, sealant, and elastomer applications.

Circle No. 35 on Reader Service Card

Sample Kit

Daniel Products Co. offers a Dapro defoamer and interfacial tension modifier (ITM) kit. Contained in the kit are 15 defoamers and three interfacial tension modifiers for water and solvent-borne industrial and architectural coatings, overprint varnishes, and flexographic and gravure inks, as well as a laminated properties/recommended use chart and MSDS in booklet form. The samples are packaged in plastic bottles with single-drop dispenser caps.

Circle No. 36 on Reader Service Card

Emulsion Polymer

A new emulsion polymer, Rohamere® 4096-D, is designed for use as a binder in a variety of applications to give materials high levels of wet abrasion resistance and wash fastness performance. Rohm Tech reports strong holding power when the product is used as a binder in applications such as flocking, label coatings, and textile flushing, especially where a material is subjected to high wear. This emulsion is a self-crosslinking styrenated acrylic polymer.

Circle No. 37 on Reader Service Card

VAE Technology

Two new products based on advanced vinyl-acetate ethylene technology, designed to help formulators manufacture low VOC/low odor water-based paints and coatings, are available. Airflex® 808 EXP and 809EXP emulsions have been designed for use in interior architectural paint formulations. Air Prod-

ucts and Chemicals, Inc. reports scrub resistance, freeze-thaw stability, and low temperature coalescence and touch-up properties without the need for coalescing agents.

Circle No. 38 on Reader Service Card

Black Dispersion

CDI Dispersions announces the availability of a jet black dispersion for use in nitrocellulose inks and coatings. The compound, BS 16238, contains 32% pigment, along with a plasticizer/dispersant combination in an n-propyl alcohol/n-propyl acetate solvent system. The dispersion is designed to offer compatibility, rheology, blackness, and viscosity stability.

Circle No. 39 on Reader Service Card

Additive

A silicone/organic copolymer additive for inks, paints, and coatings is designed to provide mar resistance and other benefits to water-based and solvent-based systems. Dow Corning® 55 Additive, from Dow Corning Corp., is engineered for mar, rub, and abrasion resistance of high-solids formulations. Other reported features include minimization of pigment separation and improvement of coating flow-out, wetting, leveling, and gloss.

Circle No. 40 on Reader Service Card

Amino Alcohol

An amino alcohol is available to replace ammonia in industrial latex coatings. When ammonia is replaced with AMP-95® (2-amino-2-methyl-1-propanol containing 5% water) in a formulation, savings in overall additive costs are reported to be up to 30%. The ANGUS Chemical Co. additive is designed to provide gloss and weathering performance and accelerated overall cure response.

Circle No. 41 on Reader Service Card

Miscellaneous

Thermocouple

Series 9000 noble metal thermocouple assemblies from Tudor Technology, Ltd. feature platinum/rhodium elements in simplex or duplex designs that can withstand temperatures to 3,200°F. Available with a variety of ceramic primary and ceramic or metal secondary protection tubes, these pre-tested thermocouple assemblies are engineered to stand up to oxidizing and reducing atmospheres. A number of head designs are available.

Circle No. 42 on Reader Service Card

Overflow Prevention

An overflow prevention switch/alarm monitors tank fluid levels and automatically shuts off flow in overfill situations. The Model 712 mounts on top of the tank and measures liquid levels via an ultrasonic probe. An averaging circuit prevents this Bernard, Inc. device from tripping upon misleading contact with splashing or shifting materials.

Circle No. 43 on Reader Service Card

Temperature Regulator

Ocean Optics, Inc. has introduced the TR-1, a new temperature regulator that maximizes system stability and alleviates the need for frequent reference calibrations for its miniature spectrometers. Featured is a Peltier thermoelectric cooler that controls the temperature of the optical bench and the detector. The regulator is applicable for on-line process control applications, long-term field or laboratory experiments, and uses requiring spectrometer stability.

Circle No. 44 on Reader Service Card

Metering Pump

A compact, portable in-barrel metering pump is available in corrosion resistant materials of construction. The submersible barrel pump, supplied by Iris Engineering, Inc., is engineered for accurate metering of acids or caustic liquids from barrels directly to a process.

Options include check valves, relief valves, custom lengths, explosion-proof motors, and various control interfaces.

Circle No. 45 on Reader Service Card

Spray Gun

An EPA-compliant, palm-sized gun is designed to provide a professional quality finish for the metal fabricator or professional finisher. Capable of handling high-solid, low VOC formulations, industrial, marine, enamels, water, or solvent coatings, the Protouch is applicable for detailing, spotting, stenciling, matching, striping, touch-up, or blending. AirVerter® reports a reduction in paint consumption by as much as 40%.
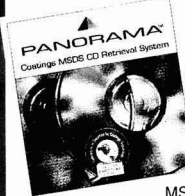
Circle No. 46 on Reader Service Card

Software

Color Measurement

BYK-Gardner USA offers the new auto-QC Windows™ software and auto-color color spectrophotometer family. Auto-QC, which can be configured for flexible development or to restrict access and options for repeatable production use, is a tool for color measurement and color quality control. Auto-color spectrophotometers are available in both sphere and 45/0 geometries in both large and small aperture sizes.

Circle No. 47 on Reader Service Card

Maintenance

MasterTrend software is the control center for CSI's Reliability-Based Maintenance® strategy, uniting technologies including vibration monitoring, alignment and balancing, tribology, electric motor testing, and infrared thermography into a single tool for analyzing and trending data. The software provides automatic problem detection, diagnostics, and a library of fault frequencies and machine history. A report generator feature and standard reports are included.

Circle No. 48 on Reader Service Card

Color Analysis

MetalliX-QC, a software package developed by X-Rite, Inc. for users of its multi-angle spectrophotometers for the measurement of special effects pigments, pearlescents, and metallics, features the *Job Function*. This capability allows the user to program a series of prompts and steps for color measurement and download those instructions from the computer into a portable spectrophotometer. This program reportedly facilitates tangible, consistent collection of color data.

Circle No. 49 on Reader Service Card

FEDERATION MEETINGS

(CSI) *For information on FSCT meetings, contact Federation of Societies for Coatings Technology, 492 Norristown Rd., Blue Bell, PA 19422 (610) 940-0777, FAX: (610) 940-0292.*

1996

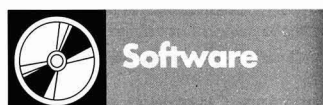(May 3-5)—FSCT Spring Week. Held in conjunction with the Pacific Northwest Society's Annual Spring Symposium. Seminar on the 3rd and 4th. Incoming Society Officers Meeting on the 4th. Board of Directors Meeting on the 5th. Doubletree Suites Hotel, Seattle, WA.

(Aug. 15-17)—Pan-American Coatings Expo. Co-sponsored by Federation of Societies for Coatings Technology, ANAFAPYT, and Instituto Mexicano de Técnicos en Pinturas y Tintas. Sheraton Maria Isabel Hotel, Mexico City, Mexico.

(Oct. 23-25)—International Coatings Technology Conference and Expo (Formerly Annual Meeting and Paint Industries' Show). McCormick Place North, Chicago, IL.

1997

(Nov. 5-7)—International Coatings Technology Conference and Expo (Formerly Annual Meeting and Paint Industries' Show). Georgia World Congress Center, Atlanta, GA.

SPECIAL SOCIETY MEETINGS

1996

(Feb. 14-16)—23rd Annual International Waterborne, High-Solids, and Powder Coatings Symposium. Sponsored by the Southern Society 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).

(Mar. 20-22)—Southwestern Paint Convention. Sponsored by Houston and Dallas Societies. Del Lago Resort, Conroe, TX. (Thomas Fitzgerald, Monarch Paint Co., P.O. Box 55604, Houston, TX 77255; (713) 462-5313).

(Apr. 16)—FOCUS '96—"Driving Technology to Meet New Challenges." Sponsored by the Detroit Society. Michigan State University Management Center, Troy, MI. (Rosemary Brady, Akzo Nobel Coatings, Inc., 1845 Maxwell St., P.O. Box 7062, Troy, MI 48007-7062; (810) 637-8565).

(May 3-4)—49th Annual Spring Symposium. Sponsored by the Pacific Northwest Society. Doubletree Suites Hotel, Seattle, WA. (Richard C. Tomczak, Specialty Polymers, Inc., 8531 Juanita Dr., Kirkland, WA 98034; (206) 979-3875).

(May 8-9)—Eastern Training Conference and Show. Sponsored by the Philadelphia Society for Coatings Technology. Valley Forge Convention Center, Valley Forge, PA. (Wayne Kraus, Hercules Incorporated, Research Center, 500 Hercules Rd., Wilmington, DE 19808; (302) 995-3435. Booth reservations: Sam Firestone, S.E. Firestone Associates, Inc., 101 Surrey Rd., Melrose Park, PA 19207-2931).

(May 8-10)—Southern Society Annual Meeting. Hyatt Regency-West Shore, Tampa, FL. (Walter R. Naughton Jr., Scott Paint Corp., P.O. Box 10218, Sarasota, FL 34278-0218; (813) 371-0015).

(June 14-15)—Joint Meeting of the St. Louis and Kansas City Societies. Holiday Inn, Lake of the Ozarks, MO. (Randall Ehmer, Walsh & Associates, Inc., 500 Railroad Ave., N. Kansas City, MO 64116; (816) 842-3014).

1997

(Feb. 18-20)—Western Coatings Societies' 23rd Biennial Symposium and Show. Sponsored by the Golden Gate, Los Angeles, Pacific Northwest, and Rocky Mountain Societies. Disneyland Hotel and Convention Center, Anaheim, CA. (Bruce Cotton, Pluess-Staufer (California), Inc., P.O. Box 825, Lucerne Valley, CA 92356; (619) 248-7306; or Ron Elliott, J.R. Elliott Enterprises, Inc., 300 Thor Pl., Brea, CA 92621; (714) 529-0711).

OTHER ORGANIZATIONS

1996—North America
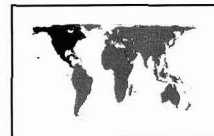
(Feb. 2-4)—"Spring Decor '96." Sponsored by the National Decorating Products Association (NDPA). The Opryland Hotel, Nashville, TN. (Teri Flotron, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132-2994).

(Feb. 5-7)— SPI Composites Institute's 51st Annual Conference and Exhibition. Cincinnati Convention Center, Cincinnati, OH. (Peggy Stabach, SPI Composites Institute, 355 Lexington Ave., New York, NY 10017).

(Feb. 6-7)—BatchMaster Inventory/Production Course. Sponsored by Batchmaster Software Corp. Chicago, IL. (Elizabeth Phillips, BatchMaster Software Corp., 1500 Pacific Coast Hwy., Ste. E, Seal Beach, CA 90740).

(Feb. 6-8)—"Color Pigments 1996: Trade, Technology, and Regulation in the Americas." Sponsored by the Color Pigments Manufacturers Association, Inc. (CPMA). Hotel Presidente Inter-Continental Mexico, Mexico City, Mexico. (CPMA, P.O. Box 20839, Alexandria, VA 22320-1839).

(Feb. 14-15)—IBC USA. Conference and exhibition sponsored by Baltic Communications. Sheraton Astrodome, Houston, TX. (David Wall, Baltic Communications, 32 W. Burlington Ave., Ste. 5, Westmont, IL 60559).

(Feb. 15-16)—"Coatings Application Training Seminar." Sponsored by Madison Chemical Industries Inc. Milton, Ont. (Madison Chemical Industries Inc., 490 McGeachie Dr., Milton, Ont. L9T 3Y5).

(Feb. 24-26)—"Interiors Decor Showcase '96." Sponsored by the National Decorating Products Association (NDPA). Toronto Congress Center, Toronto, Ontario. (Teri Flotron, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132-2994).

(Feb. 25-28)—Fifth Annual International Zinc Conference. Sponsored by the American Zinc Association. Palm Springs, CA. (Cricket Forster, American Zinc Association, 1112 Sixteenth St., N.W., Ste. 240, Washington, D.C. 20036).

(Feb. 26-28)—"Basic Coatings for Sales, Marketing, and General Personnel." Short Course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (UMR Coatings Institute, 1870 Miner Circle, Rolla, MO 65409-0010).

(Feb. 28-Mar. 1)—"Inherently Conductive Polymers: An Emerging Technology." Short course sponsored by Advanced Polymer Courses. Ocean Resort Hotel & Conference Center, Deerfield Beach, FL. (Matt Aldissi, Advanced Polymer Courses, 536 Main St., Unit #1, Falmouth, MA 02540).

(Mar. 4-6)—"Toughening of Polymers." Sponsored by The American Chemical Society: Division of Polymeric Materials: Science and Engineering. Hilton Head, SC. (Angelos V. Patsis, Director, Institute for Materials Science, State University of New York, New Paltz, NY 12561).

(Mar. 5)—Steel Water Tank seminar. Sponsored by Steel Plate Fabricators Association. Anaheim, CA. (Steel Plate Fabricators Association, 3158 Des Plaines Ave., Des Plaines, IL 60018).

(Mar. 11-13)—Ninth Annual Industrial Lead Paint Abatement and Removal Conference. Sponsored by Steel Structures Painting Council (SSPC). Pittsburgh Hilton and Towers, Pittsburgh, PA. (Dee Boyle, SSPC, 40 24th St., Pittsburgh, PA 15222).

(Mar. 11-14)—24th Annual Symposium and Equipment Exhibition. Sponsored by American Vacuum Society (AVS). Orlando, FL. (Margaret Stringer, AVS, 120 Wall St., 32nd Floor, New York, NY 10005).

(Mar. 11-15)—27th Annual Spring Program in Polymers. Sponsored by the Institute of Materials Science. The Grosvenor Resort Hotel-Disney World Village, Lake Buena Vista, FL. (Angelos V. Patsis, Institute of Materials Science, State University of New York, New Paltz, NY 12561).

(Mar. 12-14)—Advanced Productivity Exposition. Sponsored by the Society of Manufacturing Engineers (SME). New Charlotte Convention Center, Charlotte, NC. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).

(Mar. 13-14)—17th Annual Equipment Exhibition. Sponsored by American Vacuum Society (AVS). San Jose, CA. (Margaret Stringer, AVS, 120 Wall St., 32nd Floor, New York, NY 10005).

(Mar. 18-22)—"The Basic Composition of Coatings." Short Course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (UMR Coatings Institute, 1870 Miner Circle, Rolla, MO 65409-0010).

(Mar. 19-22)—BatchMaster Training Course. Sponsored by BatchMaster Software Corp. (Elizabeth Phillips, Batchmaster Software Corp., 1500 Pacific Coast Hwy., Ste. E, Seal Beach, CA 90740).

(Mar. 20-22)—"Electrocoat '96." Conference sponsored by *Products Finishing*. Clarion Plaza Hotel, Orlando, FL. (Cindy Goodridge, Gardner Management Services, 6600 Clough Pike, Cincinnati, OH 45244).

(Mar. 24-29)—NACExpo/96. Colorado Convention Center, Denver,CO. (NACE International, P.O. Box 218340, Houston, TX 77218-8340).

(Mar. 25-28)—ARMA Spring Committee Meetings. Sponsored by Asphalt Roofing Manufacturers Association (ARMA). Atlanta, GA. (ARMA, 6000 Executive Blvd., Ste. 201, Rockville, MD 20852-3803).

(Mar. 25-28)—Westec Advanced Productivity Exposition. Sponsored by the Society of Manufacturing Engineers (SME). Los Angeles Convention Center, Los Angeles, CA. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).

(Mar. 26-29)—"Experiment Design Made Easy." Sponsored by Stat-Ease Corp. Raleigh, NC. (Rich Burnham, Stat-Ease Inc., Hennepin Square, Ste. 191, 2021 E. Hennepin Ave., Minneapolis, MN 55413-2723).

(Apr. 13-14)—"Eastern Education & Trade Fair." Sponsored by the National Decorating Products Association (NDPA). Sturbridge Host Hotel, Sturbridge, MA. (Teri Flotron, NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132-2994).

(Apr. 14-17)—The American Ceramic Society's 98th Annual Meeting and Exposition. Indiana Convention Center and RCA Dome, Indianapolis, IN. (The American Ceramic Society, 735 Ceramic Place, Westerville, OH 43081-8720).

(Apr. 16-18)—1996 Annual Forum. Sponsored by The Conference on Safe Transportation of Hazardous Articles (COSTHA). Atlanta Airport Hilton and Towers, Atlanta, GA. (COSTHA, 9053 Shady Grove Ct., Gaithersburg, MD 20877).

(Apr. 16-19)—"Introduction to Coatings Science." Short course sponsored by The University of Southern Mississippi (USM), Hattiesburg, MS. (Shelby F. Thames, Director, USM, Box 10037, Hattiesburg, MS 39406).

(Apr. 22-23)—"Practical Chemistry of Polyurethanes and Diisocyanates." Seminar sponsored by Technomic Publishing Co., Program Division. Sheraton Colony Square Hotel, Atlanta, GA. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(Apr. 22-26)—"Basic Coatings for Sales, Marketing, and General Personnel." Short Course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (UMR Coatings Institute, 1870 Miner Circle, Rolla, MO 65409-0010).

(Apr. 22-26)—23rd International Conference on Metallurgical Coatings and Thin Films (ICMCTF '96). Sponsored by the American Vacuum Society. Town & Country Hotel, San Diego, CA. (Mary Gray, Conference Secretary, 1090 G Smallwood Dr., Ste. 502, Waldorf, MD 20603).

(Apr. 23-25)—Fabtech East. Sponsored by the Society of Manufacturing Engineers (SME). Pennsylvania Convention Center, Philadelphia, PA. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).

(Apr. 23-25)—Rapid Prototyping and Manufacturing Conference & Exposition. Sponsored by the Society of Manufacturing Engineers (SME). Hyatt Regency Hotel, Dearborn, MI. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).

(Apr. 24-25)—"Advances in Polyurethane Foam Formulation." Seminar sponsored by Technomic Publishing Co., Program Division. Sheraton Colony Square Hotel, Atlanta, GA. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(Apr. 28-May 1)—American Oil Chemists' Society (AOCS) Meeting. Indiana Convention Center and RCA Dome, Indianapolis, IN. (AOCS Education/Meetings Dept., P.O. Box 3489, Champaign, IL 61826-3489).

(Apr. 28-May 2)—Radtech North America. Exhibition and Conference sponsored by RadTech International North America. Nashville, TN. (Christine Dionne, RadTech International North America, 60 Revere Dr., Ste. 500, Northbrook, IL 60062).

(Apr. 30-May 1)—"Thermoplastic Foams." Seminar sponsored by Technomic Publishing Co., Program Division. Sheraton Colony Square Hotel, Atlanta, GA. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 1-2)—"Paint Volatile Organic Compounds (VOC)." Training course sponsored by the American Society for Testing and Materials (ASTM). Cleveland, OH. (Tina Falkenstein, ASTM, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959).

(May 1-2)—Automotive Finishing Conference & Exposition. Sponsored by the Society of Manufacturing Engineers (SME). Cobo Center, Detroit, MI. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121).

(May 5-7)—1996 ISCC Annual Meeting and Joint Symposium. Sponsored by the Inter-Society Color Council. Doubletree Guest Suites Resort at Walt Disney World Village, Lake Buena Vista, FL. (Robert T. Marcus, ISCC Publicity Chairman, c/o Pantone, Inc., 590 Commerce Blvd., Carlstadt, NJ 07072-3098).

(May 6-10)—"Dispersion of Pigments and Resins in Fluid Media." Short course sponsored by Kent State University, Kent, OH. (Carl J. Knauss, Director, Professional Development Institute, P.O. Box 1792, Kent, OH 44240).

(May 8-9)—ARMA Executive Committee Meeting and Board of Directors Meeting. Sponsored by Asphalt Roofing Manufacturers Association (ARMA). Baltimore, MD. (ARMA, 6000 Executive Blvd., Ste. 201, Rockville, MD 20852-3803).

(May 8-9)—"Surgical Tissue Adhesives." Seminar sponsored by Technomic Publishing Co., Program Division. Westin Hotel, San Francisco, CA. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 12-17)—42nd Annual Technical Meeting and Exposition of the Institute of Environmental Sciences. Radisson Twin Towers Hotel, Orlando, FL. (Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, IL 60056).

(May 13-17)—"Physical Testing of Paints and Coatings." Short Course sponsored by University of Missouri-Rolla (UMR), Rolla, MO. (UMR Coatings Institute, 1870 Miner Circle, Rolla, MO 65409-0010).

(May 13-18)—"Interpretation of IR and Raman Spectroscopy." Short course sponsored by the Fisk Infrared Institute. Vanderbilt University, Nashville, TN. (Clara Craver, Fisk Infrared Institute, 1000 17th Ave., N., Nashville, TN 37208).

(May 14-17)—"Practical Emulsion Polymerization." Short course sponsored by The University of Southern Mississippi (USM), Hattiesburg, MS. (Shelby F. Thames, Director, USM, Box 10037, Hattiesburg, MS 39406).

(May 20-24)—"Adhesion Principles and Practice for Coatings and Polymer Scientists." Short course sponsored by Kent State University, Kent, OH. (Carl J. Knauss, Director, Professional Development Institute, P.O. Box 1792, Kent, OH 44240).

(May 21-23)—Eastec Advanced Productivity Exposition. Sponsored by the Society of Manufacturing Engineers (SME). Eastern States Exposition Center, West Springfield, MA. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).

1996—Africa

(Mar. 25-29)—"Coatings for Africa '96." Sponsored by Oil & Colour Chemist's Association (OCCA). Cape Town Civic Centre, Cape Town, South Africa. (Chris Pacey-Day, SURFEX Ltd., Priory House, 967 Harrow Rd., Wembley HA0 2SF, England).
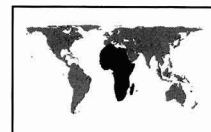
1996—Asia

(Mar. 12-13)—Middle East Coatings Show. Exhibition and conference sponsored by FMJ International. Hyatt Regency Hotel, Dubai, United Arab Emirates. (Mike Tarrant, FMJ International Publications Ltd., Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS).

(May 28-31)—China Coat. Exhibition sponsored by Sinostar International Ltd. Guangzhou, China. (Sinostar International Ltd., 1001 Shiu Lam Bldg., 23 Luard Rd., Wanchai, Hong Kong).

(June 5-6)—Asia-Pacific Coatings Show. Exhibition and Conference sponsored by FMJ International. Hong Kong Convention and Exhibition Centre, Hong Kong. (Mike Tarrant, FMJ International Publications Ltd., Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS, England).

(June 5-8)—The International Exposition for Coatings & Paints. Sponsored by Chinese Chemical Society (CCS) and Chemical Industry and Engineering Society of China (CIESC). Shanghai Exhibition Center, Shanghai, P.R. China. (Worldwide Exhibitions Service Co., Ltd. (WES), 4/F, Bldg. 2, 1486 Nanjing Rd. (W), Shanghai 200040, P.R. China).

(July 9-12)—Autofact Asia Conference. Sponsored by the Society of Manufacturing Engineers (SME). Singapore International Convetion and Exhibition Center (Suntec City), Singapore. (SME, One SME Drive, P.O. Box 930, Dearborn, MI 48121-0930).
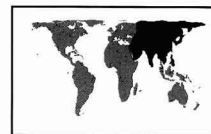
1996—Australia

(Jan. 18-25)—International Schools and Conference on X-ray Analytical Methods—AXAA '96. Sponsored by the Australian X-ray Analytical Association (AXAA), Inc. Sydney, Australia. (The Secretariat, AXAA '96, GPO Box 128, Sydney, NSW 2001, Australia).

(Aug. 11-16)—Third International Hydrocolloids Conference. Cosponsored by the CSIRO and the Cooperative Research Centre for Industrial Plant Biopolymers. Landmark Park Royal Hotel, Potts Point, Sydney, Australia. (Gail Hawke, Third International Hydrocolloids Conference, P.O. Box N399, Grosvenor Place, Sydney, NSW 2000, Australia).
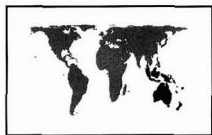
1996—Europe

(Feb. 5-7)—"Printing Ink Technology." Training course sponsored by Paint Research Association (PRA). Teddington, Middlesex, England. (Sue Benjamin, PRA, 8 Waldegrave Rd., Teddington, Middlesex TW11 8LD England).

(Feb. 19-23)—"Paint Technology." Training course sponsored by Paint Research Association (PRA). Teddington, Middlesex, England. (Sue Benjamin, PRA, 8 Waldegrave Rd., Teddington, Middlesex TW11 8LD England).

(Mar. 4-6)—Carbon Black '96. Conference sponsored by Intertech. Le Meridien Hotel, Nice, France. (Melanie Briggs, Intertech Conferences, 411 U.S. Route One, Portland, ME 04105).

(Mar. 11-13)—"Design of Experiments." Training course sponsored by Paint Research Association (PRA). Teddington, Middlesex, England. (Sue Benjamin, PRA, 8 Waldegrave Rd., Teddington, Middlesex TW11 8LD England).

(Mar. 18-22)—"Globec '96." Sponsored by Maack Business Services. Davos, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804 AU/Zürich, Switzerland).

(Mar. 26-28)—"Pressure Sensitive Adhesives: Materials, Testing, and Applications." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(Mar. 27-28)—"Practical Chemistry of Polyurethanes and Diisocyanates." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(Apr. 11-12)—"Polymer Structure and Practical Properties." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(Apr. 15-17)—"Color Measurement and Color Control." Training course sponsored by Paint Research Association (PRA). Teddington, Middlesex, England. (Sue Benjamin, PRA, 8 Waldegrave Rd., Teddington, Middlesex TW11 8LD England).

(May 7-8)—"Hydrogels: Specialty Plastics for Biomedical and Pharmaceutical Applications." Seminar sponsored by Technomic Publishing AG. Basel Hilton Hotel, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 8-10)—"Medical Packaging Technology and Validation of the Packaging Process." Seminar sponsored by Technomic Publishing AG. Zurich Hilton Hotel, Zurich, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 21-22)—"Thermoforming: Process and Design." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 23-24)—"Thermoplastic Foams." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(May 30-31)—"Nanomaterials: Design, Preparation, Characterization, and Applications." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(June 3-5)—"Styrenics '96." Sponsored by Maack Business Services. Zürich, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804 AU/Zürich, Switzerland).

(June 4-5)—"Sealing Technology: Materials, Design, and Applications." Seminar sponsored by Technomic Publishing AG. Hotel International, Basel, Switzerland. (Program Division, Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604).

(June 10-14)—FATIPEC. Conference sponsored by the Belgian Association of Coatings Technicians. Brussels, Belgium. (Michael Kuhn, Vincentz Verlag, Postfach 6247, 30062 Hannover, Germany).

(June 11-13)—European Coatings Show '96. Exhibition and conference sponsored by Vincentz Verlag. Brussels, Belgium. (Michael Kuhn, Vincentz Verlag, Postfach 6247, 30062 Hannover, Germany).

(June 10-13)—"Science and Technology of Pigment Dispersion." Vitznau (Luzern), Switzerland. (Angelos V. Patsis, Director, Institute for Materials Science, State University of New York, New Paltz, NY 12561).

(June 17-19)—18th International Conference in Stabilization and Controlled Degradation of Polymers. Luzern, Switzerland. (Angelos V. Patsis, Director, Institute for Materials Science, State University of New York, New Paltz, NY 12561).
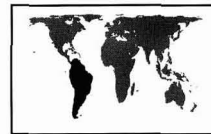
(July 1-3)—Ninth International Symposium on Polymer Analysis and Characterization. Keble College, Oxford University, United Kingdom. (John Dawkins, Dept. of chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, United Kingdom).

(July 1-5)—22nd International Conference in Organic Coatings—Waterborne, High-Solids, Powder Coatings. Vouliagmeni (Athens), Greece. (Angelos V. Patsis, Director, Institute for Materials Science, State University of New York, New Paltz, NY 12561).

(Sept. 18-20)—"Polypropylene '96." Sponsored by Maack Business Services. Zürich, Switzerland. (Maack Business Services, Moosacherstrasse 14, CH-8804 AU/Zürich, Switzerland).

1996—South America

(July 10-11)—Latin American Coatings Show '96. Sponsored by FMJ International. Sheraton Hotel, Buenos Aires, Argentina. (Mike Tarrant, FMJ International Publications Ltd., Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS, England).

Humbug from Hillman

Wishing all my loyal Humbugians a glorious New Year reminds me that as you read this, Christmas was not so long ago. Which reminds me that Bennett Cerf once wrote: "Milton Berle once told his radio audience that his sponsor had gifted him at Christmas with a one hundred piece after dinner set ... a box of tooth picks. Berle went on to admit that when he hung his stocking on Christmas Eve the only thing he found the next morning was a summons from the health department.

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Happily, my files are clogged with columns from Joe Koleske's favorite writer, West Virginia columnist Terry Marchal. To lighten my file load and to tickle your funny bone, here are some more of my favorites:

➡ "I've been trying to see you for a week. When may I have an appointment."
"Make a date with my secretary."
"I did. We had a wonderful time. But I'd still like to see you."

➡ A fellow walked into a Huntington tavern and sat at the bar next to four guys from across the river. He and the Ohioans were having a friendly conversation when a sailor entered the tavern. The sailor had a patch over his left eye.
"Look at the sailor with one eye," the West Virginia told the Ohioans.
Each of the four visitors put a hand over one eye and turned to look.

➡ "Hey, Janie, I heard you got a new little brother. What's his name?"
"I don't know. We can't understand a word he says."

➡ Three guys were sharing a taxi in Chicago. During the ride, one of the men said that his son was a lawyer and a very good one. "It cost me a bundle to get my son educated," he said, "but he makes in excess of 100 grand a year now."
"My son is a doctor," the second man said. "I also spent a fortune putting him through school. But now he is a surgeon and makes more than $300,000 a year."
The third guy said, "My son didn't go to college, didn't cost me anything but he sends me a lot of money because he became a millionaire as an athletic repairman."
"What in the world is an athletic repairman?" One of the others asked.
"I'm not exactly sure. All I know it has something to do with fixing football games, basketball games..."

➡ What's your name, private?"
"Robert Jones."
"When you talk to me, private, you say, 'sir.' Now, what's your name?"
"Sir Robert Jones."

Some of my veteran Humbug readers may remember that when I started writing this nonsense, I promised, faithfully, to publicly give my contributors credit (or blame). However, as many of you know, my unreliable filing system faithfully loses or mixes up stuff, as in this case. Some months ago an alert contributor picked the following out in the *Pipe Line and Gas Industry* (sic) magazine. Thanks, whoever you are!

Family has a male cat. Every night the cat leaves the warmth and comfort of family and home to tom around with female felines. Typically, it returns home in early hours before dawn.
After a number of years of this routine, the family decided the cat was getting too old for such reckless activity. Took the cat to the veterinarian to be fixed.
Cat returns to the comfort of family and home. But instincts take over. Each night he stills leaves home ... now, as a consultant.

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Another unrecognized contributor sent in a clip from the February 7, 1994 *C&E News* of K.M. Reese's "Newscripts." Two items caught my eye and I hope amuses yours.

The Quarterly Review of Doublespeak for January illustrates progress in the field with a set of definitions. Some examples:

—Fired: repositioned.
—Bag of ice cubes: thermal therapy kit.
—Bribes and kickbacks: sales credits.
—Used: owner pretested.
—A bar: age controlled environment.
—Down payment: customer capital cost reduction.
—Car salesman: transportation counselor.

And—the column mentions the death of the inventor of the Burma Shave road signs, Allan G. Odell, at age 90. A sample is quoted:
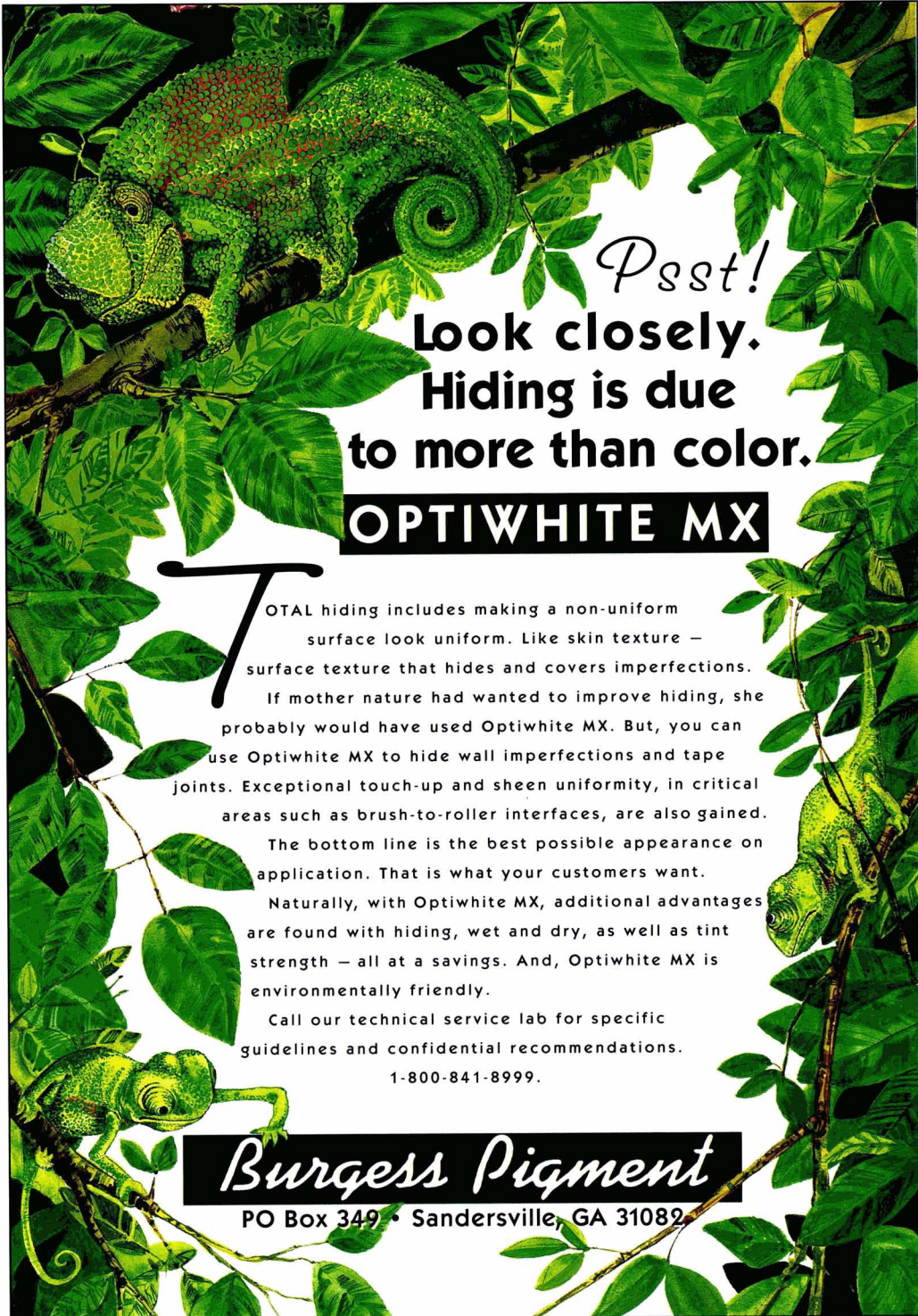
> Within this vale
> Of toil and sin
> Bald but not
> Your chin.
> Use Burma Shave

And from the columns of the aforementioned Terry Marchal:

> What woman wants
> To dance and dine
> Escorted by
> A porcupine.
> Burma Shave.

> The hobo lets
> His whiskers sprout
> But he takes trains
> Not girls, out.
> Burma Shave.

—Herb Hillman, Humbug's Nest,
P.O. Box 135, Whitingham, VT 05361.

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