

jct JOURNAL OF COATINGS TECHNOLOGY

JCTAX 55 (698) 1-83 (1983)

MARCH 1983

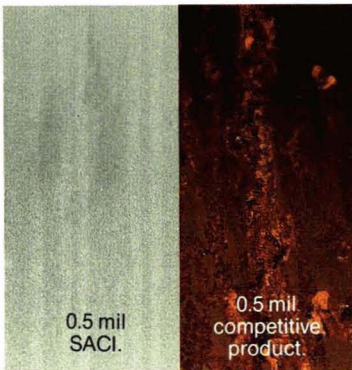


Effect of the Pigment-Vehicle Interaction on the Properties of Magnetic Coatings



SACI rust preventives: the best protection, test after test after test.

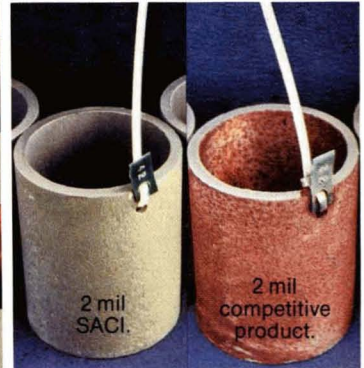
One thousand hours salt fog.



Pipes after three-year burial test.



Six-month atmospheric test. 8343



As these tests show, SACI® rust preventive provides better protection against corrosion.

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SACI is easy to apply. SACI coatings have strong bonding power, so you don't need extensive surface preparation. In fact, SACI will even adhere to rust without preliminary sandblasting.

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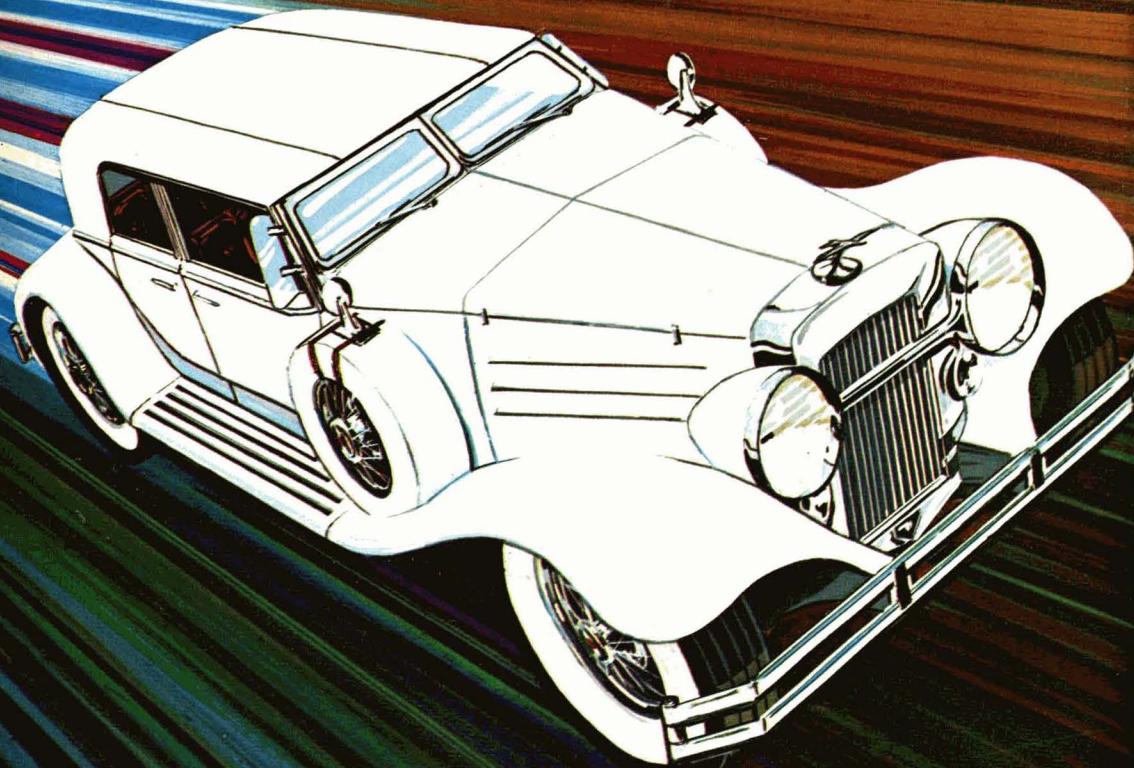
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MARCH 1983

jct JOURNAL OF
COATINGS
TECHNOLOGY
VOLUME 55 NUMBER 698

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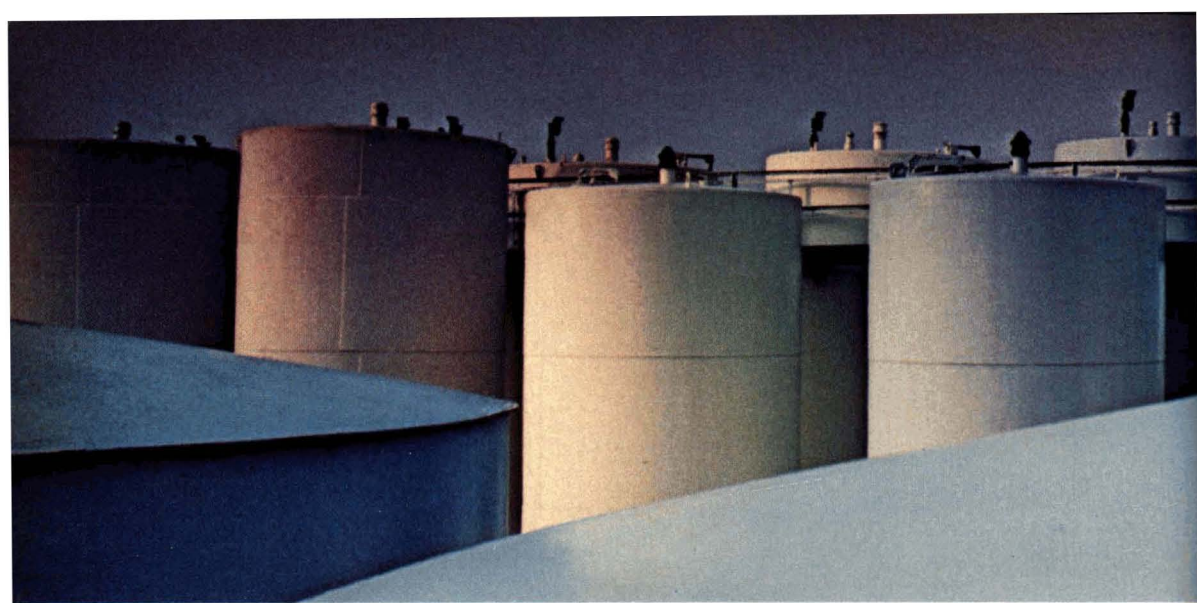
THE JOURNAL OF COATINGS TECHNOLOGY (ISSN 0361-8773) is published monthly by the Federation of Societies for Coatings Technology, 1315 Walnut St., Philadelphia, PA 19107. Phone: (215) 545-1507.

Second class postage paid at Philadelphia, PA and at additional mailing offices. POSTMASTER: Send address changes to JOURNAL OF COATINGS TECHNOLOGY, 1315 Walnut St., Philadelphia, PA 19107.

Subscriptions: U.S. and Canada—1 year, \$20; 2 years, \$37; 3 years, \$52. Europe (Air Mail)—1 year, \$40; 2 years, \$77; 3 years, \$112. Other countries—1 year, \$30; 2 years, \$57; 3 years, \$82.

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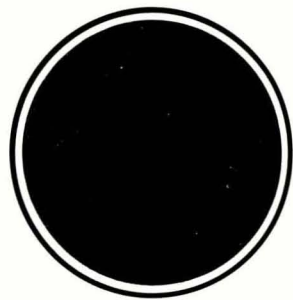


CIBA-GEIGY epoxy resins vs. the toughest applications around

Aggressive chemicals and organic solvents are tough on storage tank linings. Formulating a coating that resists them is not an easy job if you don't have the right components. Now, three new products from CIBA-GEIGY can help you change that.

Coatings based on XU-252.

Our new high performance novolac epoxy resin can take on many aggressive chemicals—including chlorinated solvents, ethanol, methanol, aromatic amines, acids, caustic and ammonia—under a variety of service temperatures.

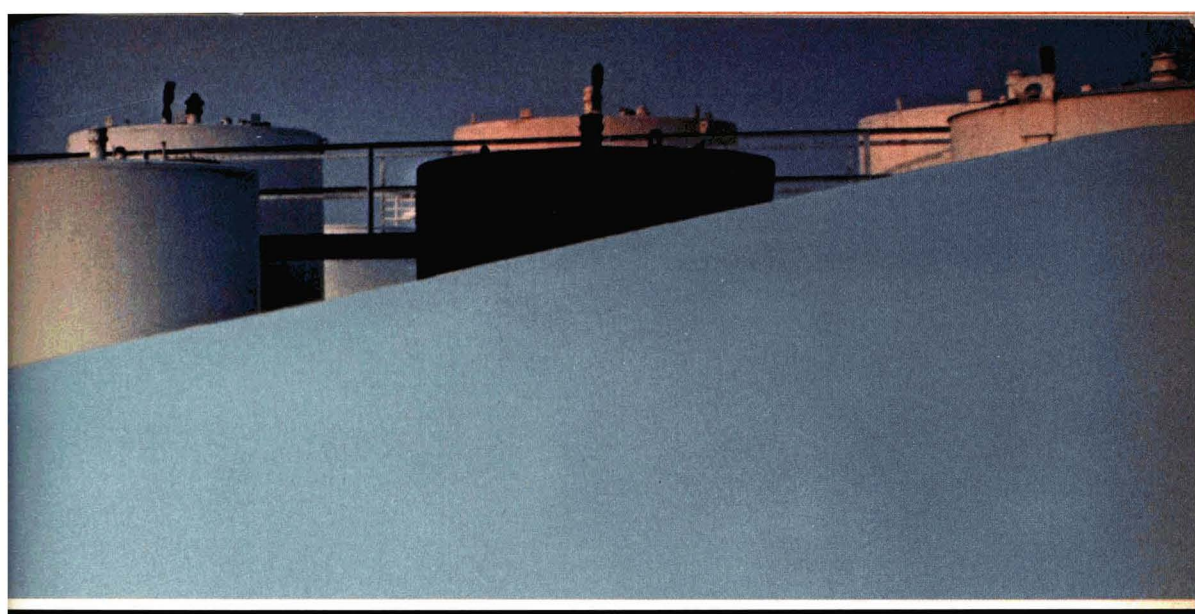


XU-252 based coating

Chemical exposure cell proves outstanding performance.

One of the most realistic tests for chemical resistance, the chemical exposure cell, is designed to simulate service conditions as closely as possible. A coated panel is attached to the end of a cylinder so that the chemical being tested makes direct contact with only the coated surface.

As you can see in the panels, an XU-252 based coating showed no sign of failure even against a solvent like methylene chloride, while one formulated with a standard bisphenol-A based epoxy resin softened and blistered.



Bisphenol-A based coating.

We also tested XU-252 based coatings for resistance against a range of other chemicals. The chart shows some of the toughest

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Two new hardeners increase chemical resistance.

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Chemical and solvent resistance of XU-252 based coatings							
Reagents	Months to date/test duration 8 months						
	1	2	3	4	5	6	7
Acetic acid (10%)							Failed
HCl (36%)							
NH ₄ OH (30%)							
Acetone							
Methylene chloride							
Methanol							
cure conditions: 10 hours @ 80°C (176°F)							

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THE JOURNAL OF COATINGS TECHNOLOGY is published monthly by the Federation of Societies for Coatings Technology at 1315 Walnut St., Philadelphia, Pa. 19107. Phone: (215) 545-1506.

Annual dues for Active and Associate Members of the Federation of Societies for Coatings Technology is \$15.00. Of this amount, \$10.00 is allocated to a membership subscription to this publication. Membership in the Federation is obtained through prior affiliation with, and payment of dues to, one of its 26 Constituent Societies. Non-member subscription rates are:

	U.S. and Canada	Europe (Air Mail)	Other Countries
1 Year	\$20.00	\$ 40.00	\$30.00
2 Years	\$37.00	\$ 77.00	\$57.00
3 Years	\$52.00	\$112.00	\$82.00

When available, single copies of back issues of the JOURNAL OF COATINGS TECHNOLOGY are priced as follows: \$3.00 each for current calendar year issues; \$4.00 each for all other issues.

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A Guide for Authors is published in each January issue. The JOURNAL OF COATINGS TECHNOLOGY is available on microfilm from University Microfilms, a Xerox Co., Ann Arbor, Mich. 48106.

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More About Our Roots

Mention was made on this page a year ago of the newly formed Ad Hoc Committee on Paint History, whose object is to trace our venerable industry's lineage and compile in-depth historical data for publication of a definitive work on the subject.

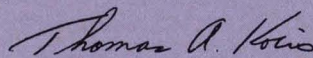
The project is noteworthy because it evolved as a voluntary commitment by a group of interested members who believe the paint industry's intriguing and fascinating past has been too long a well-kept secret. And news of the Committee's work has generated offers of assistance from a number of readers in various parts of the world, reflecting a wide-ranging interest in the undertaking.

Work is currently focused on the Ancient World (circa 4,000 BC to 400 AD), and the Committee is seeking input on several areas, namely, Greco-Roman and Byzantine Art, Bituminous Coatings, and Egyptian Tempera and Decorations.

Further down the road, assistance would be welcomed from anyone who has acquaintance with, or is interested in, early musical instrument manufacturers, early U.S. paint ingredients, and historical data on paint making machinery.

Those wishing to help with any of the above (or any other aspect of the project) are invited to contact Joe Boatwright, 6412 Mills Creek Lane, North Ridgeville, Ohio 44039 (216) 327-7700.

Help if you can, and be a part of history in the making!

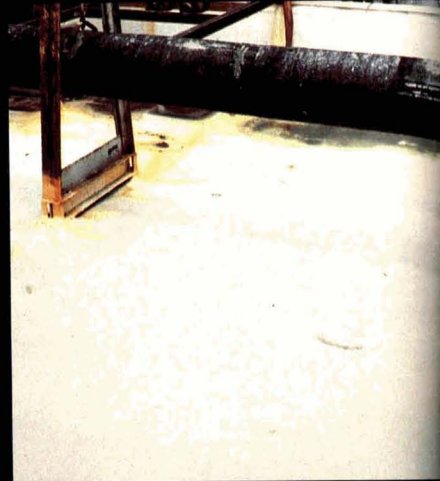
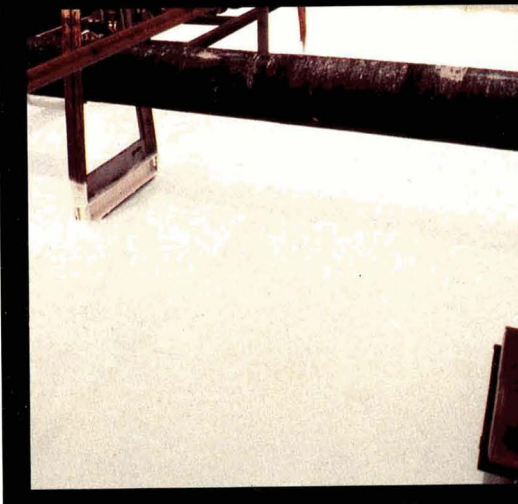
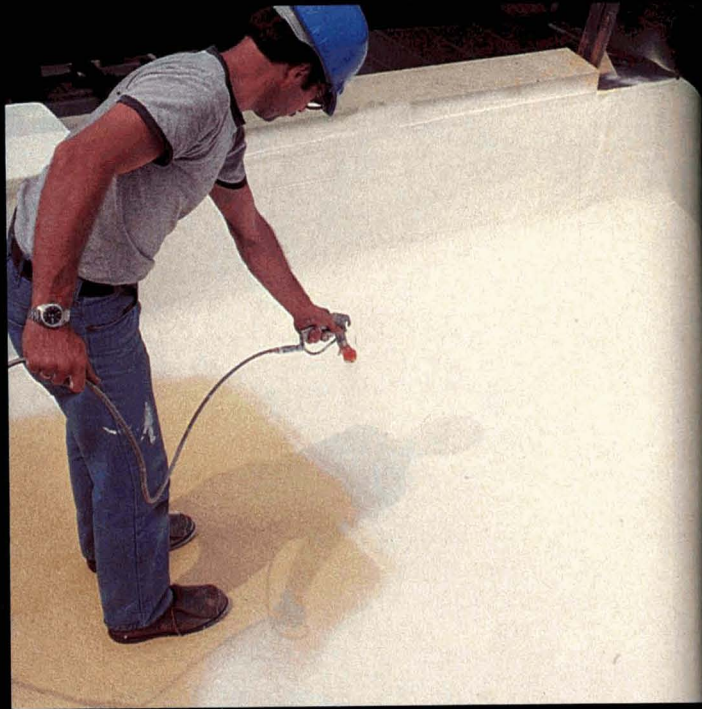


T. A. Kocis,
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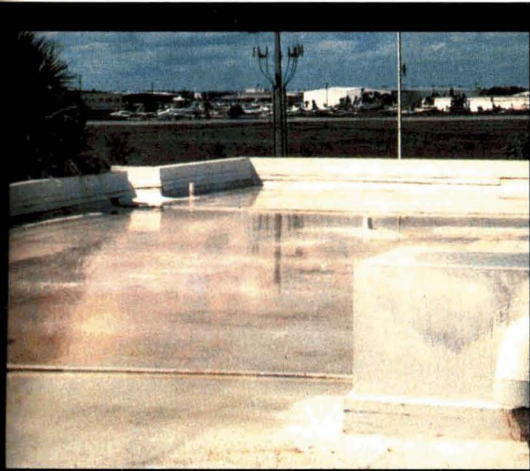
ACRYLIC BREAKTHROUGH

DO THE ROOFING

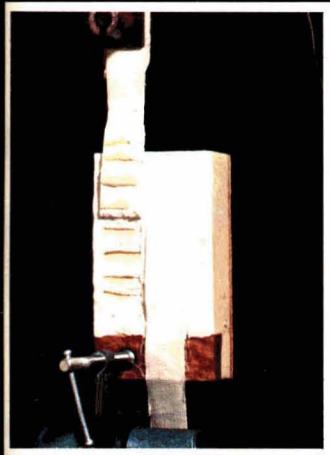
The reflective roof mastic based on RHOPLEX EC technology was spray applied on a roof in a heavy industrial environment in Pennsylvania. The photo at the lower right shows the same roof more than one year later.



INDUSTRY A BIG ACRYLIC FAVOR



This roof in Florida demonstrates how a roof mastic based on RHOPLEX EC-1895 acrylic retains its initial integrity under ponded water conditions.



The foam actually tore during peel adhesion testing on an Instron unit documenting adhesion of the mastic based on RHOPLEX EC-1791 acrylic.

Offer Roof Mastics Based on New RHOPLEX™ EC Technology

Introducing RHOPLEX® EC-1895 emulsion for superior resistance to water ponding conditions and RHOPLEX EC-1791 emulsion for superior adhesion to polyurethane foam. Acrylics from RHOPLEX EC technology are well known for:

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RHOPLEX EC-1685 acrylic is the standard, when water ponding and adhesion are not problems.

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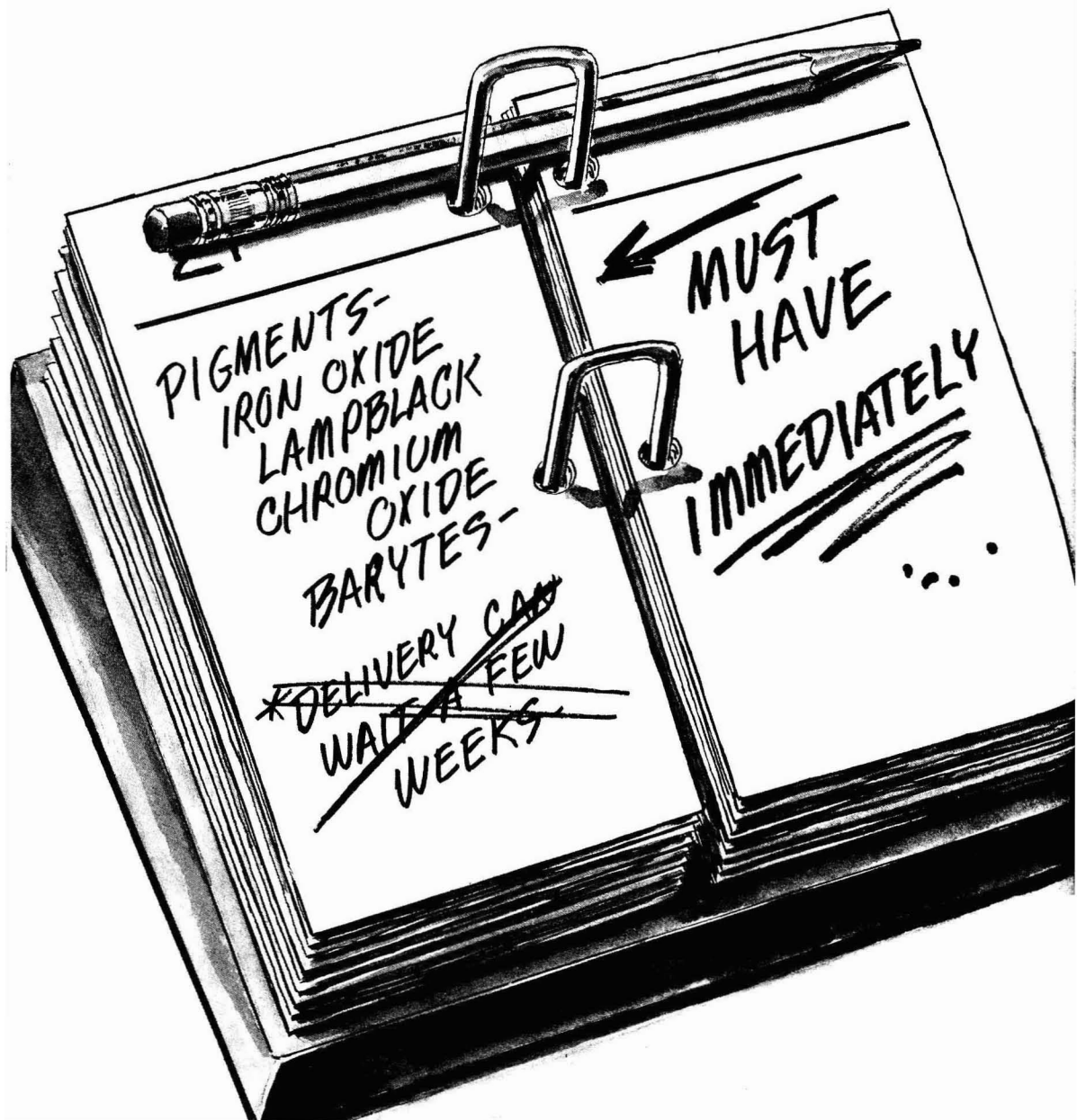
Another new roof mastic polymer, RHOPLEX EC-1791 provides elastomeric coatings with superior wet and dry adhesion to low and high density polyurethane foam.

Do your roofing contractors the favor of providing a seamless coating based on RHOPLEX EC technology. It goes on faster than sheets, eliminates hot tars, and reduces customer call backs. This saves time and money.

All you need to do to profit from this business opportunity is to combine your paint formulating know-how with RHOPLEX EC technology. Find out more about the product-line of acrylic polymers designed specifically for roof mastics. Write to Rohm and Haas Company, Marketing Services Department, Independence Mall West, Philadelphia, PA 19105.

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Abstracts of Papers in This Issue

EFFECT OF THE PIGMENT-VEHICLE INTERACTION ON THE PROPERTIES OF MAGNETIC COATINGS—Y. Isobe, K. Okuyama, A. Hosaka, and Y. Kubota

Journal of Coatings Technology, 55, No. 698, 23 (Mar. 1983)

Mechanical properties of coating films containing acicular $\gamma\text{-Fe}_2\text{O}_3$ and Co (cobalt)-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ were studied in comparison to TiO_2 . Dynamic viscoelasticity, stress-strain properties and water absorption of the coating films were measured. The thickness of the pigment-vehicle interfacial layer was estimated using the method proposed by K.D. Ziegel and also by the amount of polymer adsorbed on the pigment as measured by gel permeation chromatography. It was concluded that the interaction between Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ and the polymer was stronger than that between $\gamma\text{-Fe}_2\text{O}_3$ and the polymer. The composition of the adsorbed polymer on the pigment was determined by IR spectroscopy in order to study the affinity between the pigment and the polymer. Polyvinylchloride-vinyl acetate-vinylalcohol copolymer was adsorbed more strongly on Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ than polyurethane elastomer, but the reverse was true for $\gamma\text{-Fe}_2\text{O}_3$.

CROSSLINKED-CORE LATEX BY RADIATION-INDUCED EMULSION POLYMERIZATION—K. Makuuchi, A. Katakai, and H. Nakayama

Journal of Coatings Technology, 55, No. 698, 29 (Mar. 1983)

Copolymer latexes of self-crosslinking N-(n-butoxy-methyl) acrylamide (NBM) are prepared by radiation-induced emulsion polymerization using Co-60 gamma-rays. The latex, consisting of crosslinked polymers, is superior in water resistance, solvent resistance, and mechanical properties of films cured at 160°C for 30 minutes, but inferior in gloss of pigmented film to the latex consisting of low molecular weight polymers. The core-shell latex having a core of crosslinked polymers and a shell of low molecular weight copolymers of NBM exhibits excellent final properties. The weatherability of the cured film increased with increasing degree of crosslinking of core polymers. The effect of monomer feed rate and pre-emulsification of monomer on the final properties are investigated in connection with the formation of microgel and water-soluble acid bearing oligomers.

USE OF AC IMPEDANCE IN THE STUDY OF THE ANTICORROSIVE PROPERTIES OF CHLORINE-CONTAINING VINYL ACRYLIC LATEX COPOLYMERS—J.C. Padgett and P.J. Moreland

Journal of Coatings Technology, 55, No. 698, 39 (Mar. 1983)

Resistance, capacitance, and impedance data obtained from AC impedance measurements on coated test panels were found to give a very sensitive and quantitative assessment of both the permeation characteristics and

the deterioration of various latex and paint coatings. The measurements showed that films cast from chlorine-containing vinyl acrylic latex copolymers exhibited low uptake of liquid water and ions when the degree of particle coalescence was high. The addition of a block copolymer surfactant, introduced to ensure the stability of acidic paints based on such copolymers, was found to greatly increase the rate of latex particle coalescence due to a plasticization effect. AC impedance measurements supplemented by salt spray and outdoor exposure results showed a relationship between the permeation characteristics and the anticorrosive performance of latex films and latex paints, and showed the advantages to be gained by using a low permeability chlorine containing polymer.

CHARACTERIZATION OF PIGMENT VOLUME CONCENTRATION EFFECTS IN LATEX PAINTS—W.J. Culhane, D.T. Smith, and C.P. Chiang

Journal of Coatings Technology, 55, No. 698, 53 (Mar. 1983)

The relationship of the pigment volume concentration to the critical pigment volume concentration in latex paint films is characterized by traditional and new methods. Calculated and empirical critical pigment volume concentration determinations are shown to yield consistent results. Gloss, scrub resistance, staining and observed T_g of the films are correlated with scanning electron microscope observations for samples formulated over an extreme range of pigment volume concentrations. New insights into the role of the pigment/latex ratio are provided.

POPPING OF WATER-SOLUBLE ACRYLIC COATINGS—B.C. Watson and Z.W. Wicks, Jr.

Journal of Coatings Technology, 55, No. 698, 59 (Mar. 1983)

The tendency of water-soluble industrial baking enamels to show popping is a factor which significantly limits their commercial use in some applications. A test to determine the maximum film thickness of acrylic enamel which could be applied and cured under standardized conditions without popping was developed to compare various coatings. Glass transition temperature of the acrylic copolymer was found to correlate with popping. Critical film thickness decreased as glass transition temperature increased. The same trends were observed in solvent-reduced and water-reduced coatings. The critical film thickness was much thinner for water-reduced coatings. It was found that after initial losses, rate of volatile loss in a TGA furnace at 150°C decreased as T_g increased and was slower from water-reduced coatings than from 2-butoxyethanol-reduced coatings. Rate of temperature increase of the TGA samples from water-reduced coatings was slower than with 2-butoxyethanol-reduced coatings. The greater heat requirement to evaporate water may be a factor in the greater sensitivity to popping of the water-reduced coatings. Other factors which may affect popping are also discussed.

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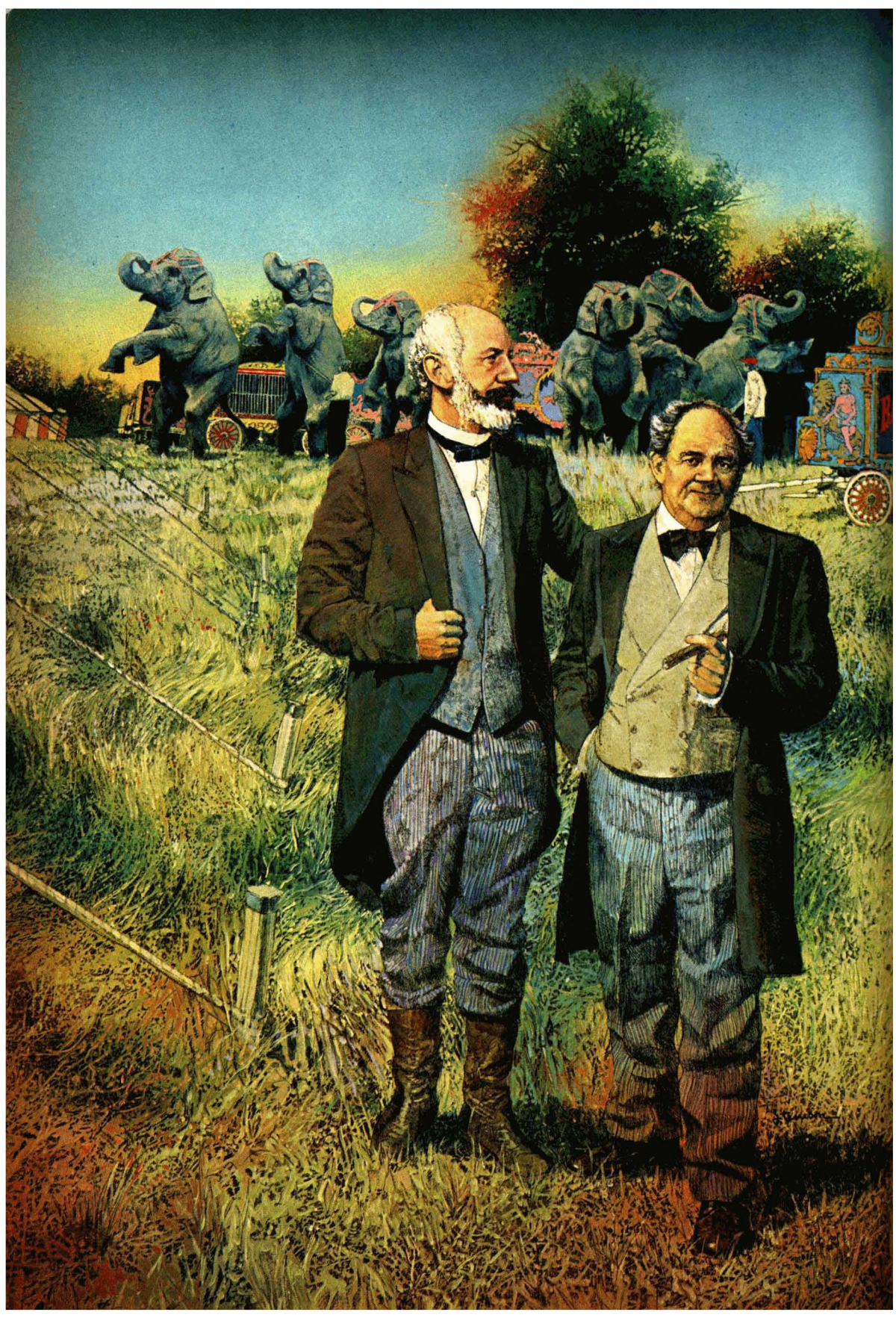


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SOLVENTS & INTERMEDIATES

FSCT Seminar to Focus on Efficient Use of Laboratories

"The Efficient Operation of an Up-to-Date Paint and Coatings Laboratory," will be the topic of the first seminar sponsored by the Federation, to be held at the Hilton Plaza Inn, Kansas City, MO, on April 26-27.

The 1½ day event is designed to help paint and coatings manufacturers re-evaluate the efficiency of their laboratory procedures. Well-known paint scientists will explain how they plan an R&D budget, how they develop cooperation with raw material suppliers, how they evaluate the effectiveness of their personnel, and how they communicate with the sales department and top management. Each session will conclude with an open-discussion period.

Moderated by Federation Past-President Howard Jerome, of Spatz Paint Industries, the seminar is designed for research and development, quality control, and management personnel from coatings manufacturing firms, and technical people from raw material suppliers and coatings users.

The following program is planned for presentation:

TUESDAY, APRIL 26

Keynote Address—"Designing the Laboratory to Fit the Business"—Dr. Orville H. Bullitt, Jr., Technical Manager—Finishes Div., E. I. du Pont de Nemours & Co., Inc., Wilmington, DE.

Because of the complex and sophisticated nature of present and emerging coatings technology, it is generally not economically practical to develop and market all types of products; hence, the R&D effort must be geared to producing those which will fulfill marketing goals.

"Planning the R&D Budget"—Warren O. Manley, Director of Research and Quality Assurance, Cook Paint and Varnish Co., Kansas City, MO.

Budget planning must include answering the question, "Will increased spending produce profitable results?" Among items to be considered are marketing goals, technical talent available, and emerging technology expected.

"Optimizing the Organization of an Industrial Coatings Laboratory"—Milton A. Glaser, Consultant, Glencoe, IL (Formerly Vice-President and Research

Director, Midland Div., Dexter Corp., Waukegan, IL).

Organizing technical foundations for laboratories is important, and human aspects may be equally vital. Presentation will include discussion of technical requirements and critical interfaces with other departments.

"Approach to Formulation—Architectural and Maintenance Paints"—John C. Ballard, Vice-President and Technical Director, Kurfrees Coatings, Inc., Louisville, KY.

Formulation of trade sales paint products demands a solid knowledge of pigments, vehicles, solvents, and additives by the paint chemist. Universal acceptability to do-it-yourselfers, as well as to professionals, is essential, as is unlimited shelf stability.

"Laboratory Instrumentation and Equipment"—Dr. Darlene Brezinski, Manager, Analytical and Computer Application Research, DeSoto, Inc., Des Plaines, IL.

Instrumentation and equipment for analytical and quality control work, for the smaller laboratory, as well as the larger, more sophisticated facility, will be explored, relative to meeting current product and governmental standards. A discussion of instrument and equipment cost, staffing cost, return on investment of larger, more expensive instrumentation, and operating expenses will be included.

"Use of Computers in Research and Development"—Dr. Mark E. Koehler, Polymer Research and Computer Scientist, Glidden Coatings and Resins Div., SCM Corp., Strongsville, OH.

R&D computer applications in the areas of instrument automation, sample tracking, data base management, personal computing, and process monitoring and control are discussed, in terms of both hardware and software implications.

Open Forum—Speakers will assemble as a panel for discussion period.

WEDNESDAY, APRIL 27

"Designing and Building a New Laboratory"—Dr. C. Malcolm Hendry, General Manager-Laboratory, Hempel Technology, Inc., Houston, TX.

The design and construction of a new laboratory involves myriad considerations. Space, equipment, and personnel needs, along with worker safety and health concerns, plus economic limitations, all require careful study. The creation of a recently built coatings laboratory is discussed.

"Quality Control/Quality Assurance"—Harold M. Werner, Consultant, Olmsted Twp., OH (Formerly Manager of Quality Assurance, Glidden Coatings and Resins Div., SCM Corp., Strongsville, OH).

Quality assurance begins with setting standards of excellence. Key factors are people, communication, formulations, materials specifications, process control, documentation and monitoring of compliance.

"Developing Cooperation with Your Raw Material Supplier"—John J. Oates, Manager of Technical Sales, Troy Chemical Corp., Newark, NJ.

The technical people and marketing specialists employed by raw material companies constitute a rich resource which is available to support coatings chemists in their work. Ideas and case histories will be presented which will indicate how this dialogue can be expanded and more effectively utilized.

"The Anatomy of Synthetic Resins"—James A. Hoeck, Laboratory Manager of Resin Development, Reliance Universal, Inc., Louisville, KY.

Resin and polymer technology continues to advance. Presentation will discuss resins currently used in the coatings industry, including their processing requirements and end uses, plus a look at future development objectives in this field.

"Color Matching: Personnel, Instrument, Discipline Requirements"—Charles J. Sherman, Director, Color and Standards Laboratory, The Sherwin-Williams Co., Chicago, IL.

Proficient color matching begins with people who have a good working knowledge of color technology. Computers offer the most efficient method to match

(Please turn to page 19)

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with High
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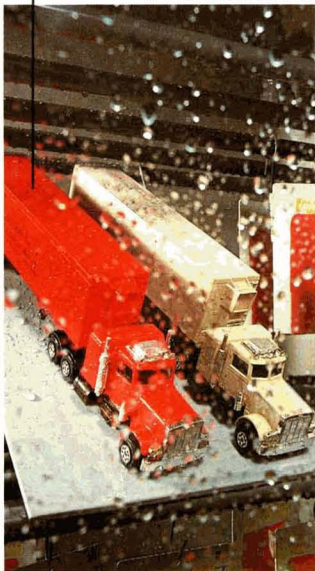
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Reference sample

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Reference sample

HEUCOTRON-Yellow 5



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To test for durability panels were coated with an alkyd-melamine resin varnish containing 20% for HEUCOTRON-Yellow 5 and 15% for HEUCOTRON-Red 23, then tested in accordance with DIN 50018 with 2 litres SO₂ in a Kesternich apparatus.

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FSCCT Seminar to Focus on Efficient Use of Laboratories

colors, provided the discipline required to minimize random error is followed.

Open Forum—Speakers will assemble as a panel for discussion period.

“Relationship of the Laboratory to Sales and Management”—Robert S. Bailey, Vice-President and Director of Marketing, Lilly Industrial Coatings, Inc., Indianapolis, IN.

The laboratory plays an important role in the success of a paint and coatings manufacturer. The greatest success is achieved with a high level of cooperation

among management, sales, and technical personnel. A speaker experienced in all of these areas tells how.

“Technical Service—Communication with Your Customers”—Dr. Thomas J. Miranda, Staff Scientist, Research and Engineering Center, Whirlpool Corp., Benton Harbor, MI.

When providing technical service, the coatings supplier must be acutely aware of the customer's needs. Developing this awareness can involve a maze of communications problems. Examples of communications among research centers, engineering groups, and division users will be discussed

“Training Programs for New Chemists and Technicians”—John A. Gordon, Jr., Adjunct Professor, Chemistry Dept., University of Missouri—Rolla, Rolla, MO.

A solid academic foundation in chemistry and/or chemical engineering is

important to a successful career in coatings development. The learning process, however, must continue at a high level once the graduate enters the industrial laboratory.

Open Forum—Speakers will assemble as a panel for discussion period.

REGISTRATION

Registration fee is \$80 for Federation members; \$90 for non-members; and \$100 for all after April 1. Included in registration is continental breakfast, luncheon, coffee breaks, and copies of the talks, as well as bus transportation to the airport at the conclusion of the seminar.

Housing requests for the Hilton Plaza Inn should be made through the Federation office.

For additional information, or to register, please contact the Federation office, 1315 Walnut St., Suite 832, Philadelphia, PA 19107; or call (215) 545-1506.

PRI Programs Supported by 1982 Contributors

The list of Federation Societies and Corporations which made financial contributions to the Federation's Paint Research Institute in 1982 (in addition to the annual grant from the Federation and the continuing Leo Roon Endowment Fund) is as follows:

1982 Contributors to PRI

Federation Societies

Golden Gate; Houston; Kansas City; Los Angeles; Louisville; New York; Pacific Northwest; and Southern.

Industries

M.F. Cachat Co.; Canada Colors & Chemicals Ltd.; Canadian General Electric Ltd.; Chemcentral/Cleveland; Celanese Canada, Inc.; C-I-L Inc.; Cook Paint & Varnish Co.; Daniel Products Co.; Dar-Tech, Inc.; Dominion Colour Co. Ltd.; Drew Chemical Co.; Dow Chemical Co.; Ferro Corp.; Jamestown Paint & Varnish Co.; Kalcor Coatings Co.; D/L Laboratories, Inc.; Midland Div., Dexter Corp.; Mooney Chemicals, Inc.; Benjamin Moore & Co. Ltd.; Nalcan Products Ltd.; NL Industries, Inc.; Q-Panel Co.; Reichhold Chemicals, Inc.; Rohm and Haas Co.; SCM Corp.; Seegott, Inc.; Shell Corp.; Sherwin-Williams Co.; Silberline Mfg. Co., Inc.; Donald McKay Smith, Inc.; Tioxide Canada, Inc.; Union Carbide Corp.; and Whirlpool Corp.

Industries Comprising The Mildew Consortium

Cosan Chemical Corp.; PPG Industries, Inc.; Rohm and Haas Co.; and SCM Corp., Glidden C&R Div.

Federation Publishes Southern Society's 'Consumer Guide to Trade Paint Quality'

A *Consumer Guide to Trade Paint Quality*, produced to help promote an appreciation of paint quality features and an understanding of paint application, has been published by the Federation of Societies for Coatings Technology.

The guide, entitled “Know Paint Quality Before You Buy,” focuses on latex interior flat paint and depicts the performance characteristics of low, average, and high-quality products.

Written and developed by the Southern Society for Coatings Technology, the pamphlet is designed for point-of-purchase use to help the consumer understand what to look for in paints. Full-color reproductions illustrate the effects of paint quality features on staining and washability-durability, as well as spreading rate, application, and wet & dry hiding.

Cooperating with the Federation in the distribution of the guide will be the National Decorating Products Association and its member paint store dealers.

The price of the guide is 10¢ each, minimum order of 100 copies. Order from the Federation of Societies for Coatings Technology, 1315 Walnut St. Philadelphia, PA 19107.

Proposed Amendments to Federation By-Laws and Standing Rules

TO BE PRESENTED FOR FIRST READING

The following amendment to the By-Laws will be presented for first reading at the May 20, 1983 Board of Directors meeting.

Re: Equal Voting and Office-Holding Privileges

WHEREAS the Pittsburgh Society has proposed that the existing Federation By-Laws and Standing Rules be amended to extend equal voting and office-holding privileges to all Federation Active and Associate members while still maintaining the existing classes of membership, and

WHEREAS the Federation Ad Hoc Committee on Federation Voting and Office-Holding Privileges studied this proposal and recommended to the Board of Directors that an orderly course of change be enacted, beginning with the right of each Constituent Society to determine the rights and privileges of its own members in the affairs of the Constituent Society, be it

RESOLVED that Article II, Section B, MANAGEMENT OF INTERNAL AFFAIRS, be amended to read as follows:

"(1) Subject to these By-Laws and the Standing Rules of the Federation, each Constituent Society shall have entire control of its own internal affairs.

"(2) The term Voting Member as used in these By-Laws and the Standing Rules of the Federation shall be construed to mean Active Member unless defined otherwise by the Constitution and/or By-Laws of the Constituent Society.

"(3) Each Constituent Society shall operate in accordance . . . violate these laws.

"(4) It shall be the duty . . . discussions held."

BE IT FURTHER RESOLVED that the By-Laws and Standing Rules of the Federation be amended as follows [deletions in parentheses, (), additions in italics]:

"IV A. (2) . . . Nominations for any elective office may also be made from the floor by any Society Representative at the Spring meeting, or by a petition signed by 25 (Active) *Voting* Members and forwarded to the Federation Executive Vice-President in time for publication in the August . . .

"IV B. (1) The (Active) *Voting* Members of each Constituent Society shall elect one Society Representative every third year who shall be an Active Member of said Society . . .

"XI A. ORIGINATION

Proposals to amend these By-Laws may be originated by:

"(6) The petition of ten or more (Active) *Voting* Members, each of two or more Constituent Societies being represented by at least five (Active) *Voting* Members in the petitioning group.

"SR II C. (1) An applicant for Active Membership must be proposed by (an Active) a *Voting* Member and be endorsed by another (Active) *Voting* Member . . . Election to membership shall be by a two-thirds favorable vote of the (Active) *Voting* Members present and voting at a regular Society meeting . . .

"(2) An applicant for Associate Membership must be proposed by (an Active) a *Voting* Member and be endorsed by another (Active) *Voting* Member. The application shall be processed in the same manner as an application for Active Membership.

"(3) An applicant for Educator and Student Membership must be proposed by (an Active) a *Voting* Member and be endorsed by another (Active) *Voting* Member. The applica-

tion shall be processed in the same manner as an application for Active Membership.

"(4) An applicant for Retired Membership . . . subject to election to membership by two-thirds vote of the (Active) *Voting* Members present and voting at any regular meeting of the Society. The application shall be processed in the same manner as an application for Active Membership.

"SR II D. Nominations for Honorary Membership may originate with any Constituent Society and shall require a 90 per cent favorable vote of all (Active) *Voting* Members present . . ."

Comment: The By-Laws Committee recommends adoption.

* * * * *

Note: The Executive Committee has approved a dues increase for 1985. The following amendments will be presented on May 20, 1983 if the Board of Directors approves this Executive Committee action.

TO BE PRESENTED FOR FIRST READING

Article VIII

DUES

WHEREAS the Federation Board of Directors has approved a dues increase from \$15.00 to \$20.00, beginning in 1985 (1984-85 Fiscal Year), for Active, Associate, and Society Honorary Members, be it

RESOLVED that By-Laws Article VIII, Sections A and C, be amended as follows:

"A. Active, Associate, and Society Honorary Members

Each Constituent Society shall pay to the Federation office annual dues in the amount set by the Board of directors for each Active, Associate, and Society Honorary Member of the Constituent Society."

"C. Educator and Student Members

The dues of Educator and Student Members shall be determined by the Board of Directors."

BE IT FURTHER RESOLVED that the By-Laws and Standing Rules of the Federation be amended as follows:

By-Laws — Article III

Article III, Section B, Paragraph (1)

"The duties of the Board of Directors shall be to:

o. Establish the annual Federation dues for Active, Associate, Society Honorary, and Educator and Student Members."

Standing Rules — Articles VIII and IX

Standing Rule Article SR VIII be renumbered as SR IX.

New Standing Rule Article SR VIII be added as follows:

"A. Active, Associate, and Society Honorary Dues

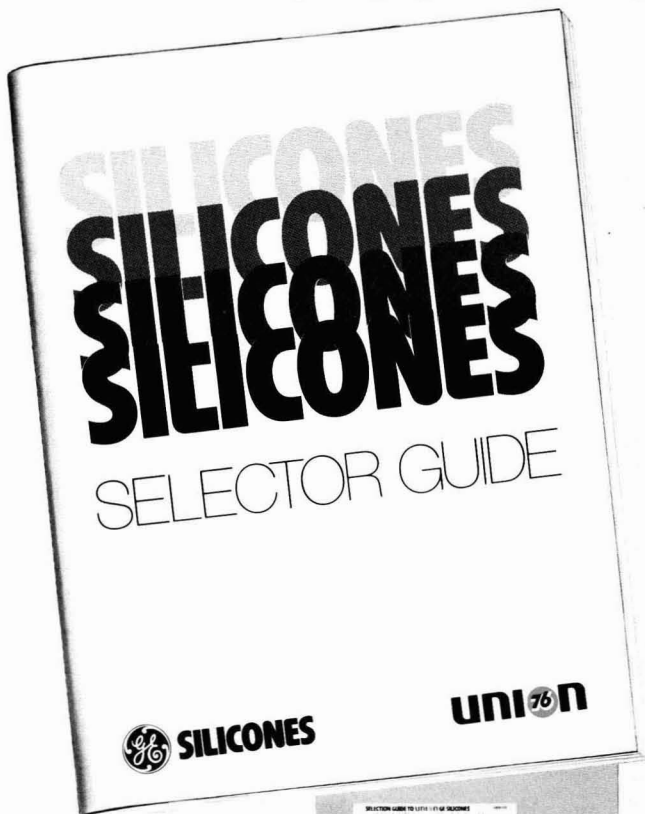
Annual Federation dues for each Active, Associate, and Society Honorary Member is \$20.00 in U.S. Funds.

"B. Educator and Student Members

Annual Federation dues for each Educator and Student Member is \$10.00 in U.S. Funds."

Comment: The By-Laws Committee recommends adoption.

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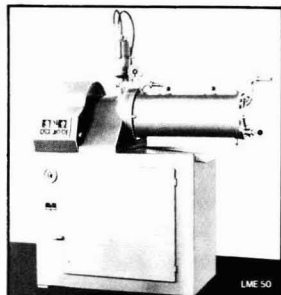
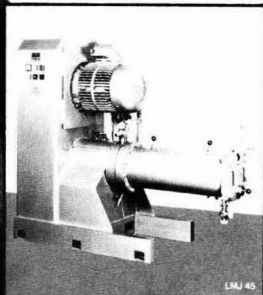
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Effect of the Pigment-Vehicle Interaction On the Properties of Magnetic Coatings

Yukihiro Isobe, Kiyotake Okuyama, Akihiko Hosaka, and Yuichi Kubota
TDK Electronics Company, Limited*

Mechanical properties of coating films containing acicular γ -Fe₂O₃ and Co (cobalt)-adsorbed γ -Fe₂O₃ were studied in comparison to TiO₂. Dynamic viscoelasticity, stress-strain properties and water absorption of the coating films were measured. The thickness of the pigment-vehicle interfacial layer was estimated using the method proposed by K.D. Ziegel¹ and also by the amount of polymer adsorbed on the pigment as measured by gel permeation chromatography. It was concluded that the interaction between Co-adsorbed γ -Fe₂O₃ and the polymer was stronger than that between γ -Fe₂O₃ and the polymer. The composition of the adsorbed polymer on the pigment was determined by IR spectroscopy in order to study the affinity between the pigment and the polymer. Polyvinylchloride-vinyl acetate-vinylalcohol copolymer was adsorbed more strongly on Co-adsorbed γ -Fe₂O₃ than polyurethane elastomer, but the reverse was true for γ -Fe₂O₃.

INTRODUCTION

Plastics are often mixed with fillers to improve their mechanical properties and reduce their cost. The interaction between filler and polymer matrix is complicated and has been discussed by many workers in the field.²⁻⁴ Magnetic recording tape consists of a coating layer filled with a magnetic pigment and a base film which supports

the layer. In this case the pigment differs from other commercial ones, such as TiO₂ and carbon black, from the standpoint of its acicular shape and magnetic properties. It is very important to investigate the interaction between the magnetic pigment and the polymer because it greatly affects the mechanical properties of the coating layer being stressed by the magnetic head during use.

Co-adsorbed γ -Fe₂O₃ has lately come into wide use for magnetic recording tape, because a tape coating filled with Co-adsorbed γ -Fe₂O₃ has higher recording capability than that filled with γ -Fe₂O₃.

In this paper, the influence of magnetic pigment such as γ -Fe₂O₃ and Co-adsorbed γ -Fe₂O₃ upon the mechanical properties of the coating is discussed.

EXPERIMENTAL

The properties of the pigments used in this study are listed in Table 1. The Co-adsorbed γ -Fe₂O₃ has Co²⁺ ion adsorbed on the surface of γ -Fe₂O₃.⁵ A mixture of 80% polyvinylchloride-vinyl acetate-vinylalcohol copolymer and 20% polyurethane elastomer was used for the polymer matrix. The polymers used in this study were: polyvinylchloride-vinylacetate-vinylalcohol copolymer: VAGH (Union Carbide Corp.); polyurethane: Estane® 5715 (B.F. Goodrich Chemical).

The sample films were prepared as follows: (1) Each pigment was blended with the solution of the polymer in methyl ethyl ketone and toluene by "Red Devil Mill" for two hours. The media used were glass beads having diameter of 1 mm; (2) The paint was coated on glass plates and dried at room temperature for two days; (3) The coated panels were then placed in a vacuum and the coatings pressed by a press machine.

The dynamic viscoelasticity was measured with a "Visco Elastic Spectrometer" (Iwamoto Seisakusho Co., Ltd.) at 10 Hz from 20° to 110°C. It was a direct reading type of apparatus, using a forced oscillation method.

Presented at the 59th Annual Meeting of the Federation of Societies for Coatings Technology in Detroit, MI, on October 29, 1981.

* Magnetic Recording Products R&D Dept., 113 Nenei, Saku shi, Nagano 385, Japan.

Table 1—Properties of Pigment

Pigment	Particle Size (μm)	Specific Surface Area (m^2/g) ^a	Density (g/cm^3)	Surface Treatment
$\gamma\text{-Fe}_2\text{O}_3$	0.45	19.7	5.0	none
Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$	0.45	18.3	5.0	Co 6%
TiO_2	0.23	14.6	4.2	Al 3%

(a) Measured by BET method.

The specimens used were 2.0 cm in length, 0.5 cm in width, and about 50 μm in thickness. The stress-strain curves were obtained by "Tensilon UTM III" (Toyo Baldwin Co., Ltd.) with an extension speed of 5 mm/min. The specimens used were 1 cm in width and 5 cm in length.

The water absorption of the films was measured by the following method: The films containing each pigment were immersed in distilled water for 24 hours and then were weighed (W). They were dried at 110°C for two

hours and weighed again (W_0). The water absorption was calculated by equation (1).

$$Q = 100 (W - W_0) / CW_0$$

where Q: Water absorption
C: Polymer content (wt) (1)

The polymer solutions were separated from the paints by a centrifugal method at 16,000 rpm. The solutions were injected into a GPC model LC-2 (Shimazu Seisakusho Ltd.). The analytical conditions were as follows: Gel: HSG-60,40,20; Temperature: 50°C; Flow Rate: 0.98 mL/min; and Detector: RI.

The polymer concentration of the solution was calculated from the area of the chromatogram obtained. The amount of the adsorbed polymer was determined by the difference of the calculated concentration of the solution between before and after milling.

The separated pigment was diluted with MEK and then a supersonic wave was passed through the solution to separate the polymer adsorbed firmly on the surface. The supernatant liquid after sedimentation was analyzed by IR spectrophotometer model IR-430 (Shimazu Seisakusho Ltd.).

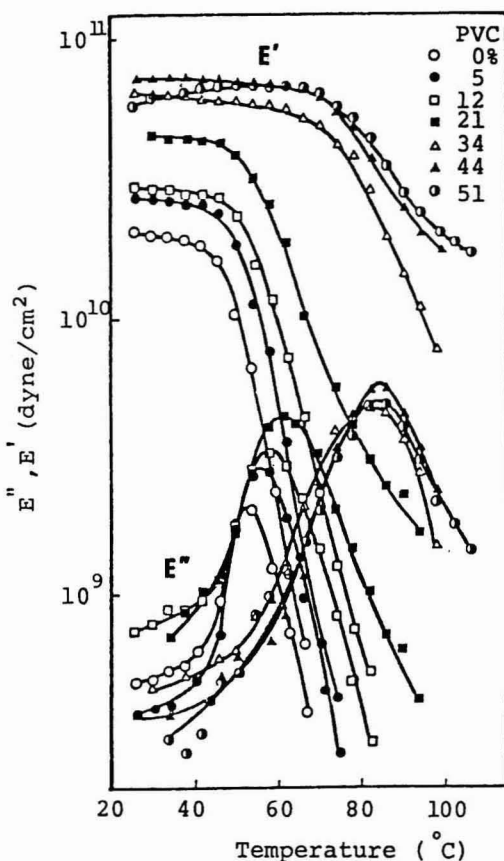


Figure 1—Dynamic viscoelasticity of coating films filled with $\gamma\text{-Fe}_2\text{O}_3$ (10 Hz)

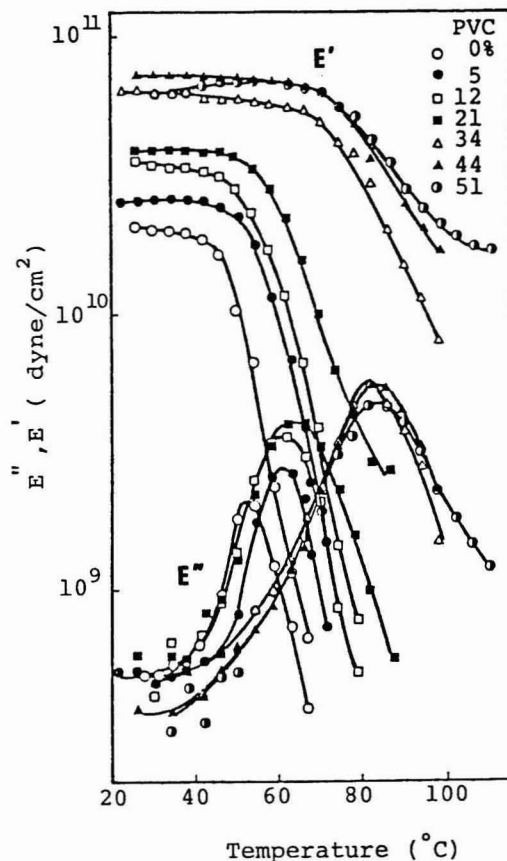


Figure 2—Dynamic viscoelasticity of coating films filled with Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ (10 Hz)

RESULTS AND DISCUSSION

Dynamic Viscoelasticity

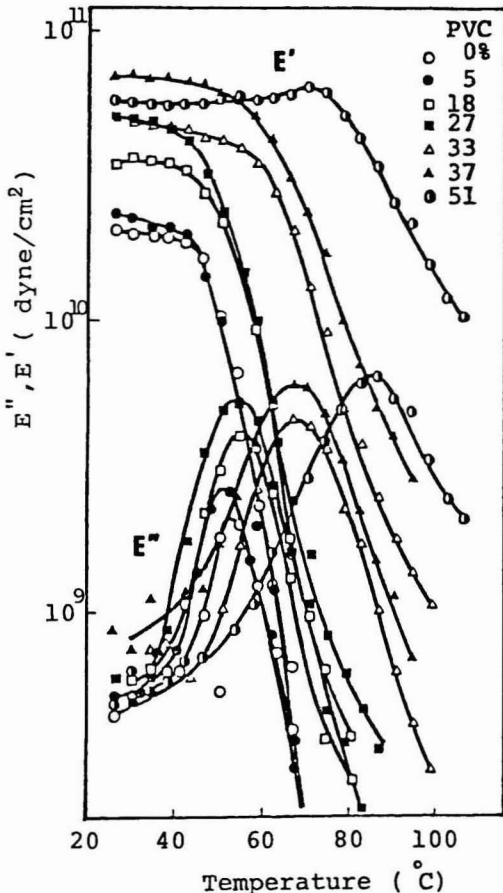
The temperature dependence of the dynamic viscoelasticity of the coating films for $\gamma\text{-Fe}_2\text{O}_3$ is shown in Figure 1. In this graph, the storage modulus (E') increases with the percentage of pigment volume concentration (PVC) in the film. The temperature of the maximum of the loss modulus (E'') shifts to a higher temperature with increasing PVC up to 21%, thereafter, remaining almost constant for the films of which PVC are high. The same relationship for Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ is shown in Figure 2.

For TiO_2 , in Figure 3, the storage modulus increases with increasing PVC, but the temperature of E'' maximum does not shift higher with PVC until 27%.

The relationship between the glass transition temperature (T_g) of the films and PVC is shown in Figure 4. The T_g was defined as the point of the maximum of E'' ; T_g of the unpigmented film was 52°C. For the films containing

the magnetic pigment, T_g increases somewhat in the low PVC range and then rises markedly at the higher pigment content. On the other hand, T_g of the coating films containing TiO_2 is nearly constant to 27% PVC and then rises suddenly at the higher percentage PVC. It is thought that the interaction between filler and polymer reduces the molecular mobility and flexibility of the polymer.³ However, C.A. Kumins and J. Roteman⁶ have reported that the T_g of polyvinylchloride-vinylacetate containing TiO_2 decreased at low PVC's. J. Seto⁷ also reported that the T_g of polyvinylchloride-vinylacetate filled with $\gamma\text{-Fe}_2\text{O}_3$ decreased at a certain PVC. They interpreted that the hydrogen bonding in the polymer was decreased by the interaction between TiO_2 and the acetate group. But the T_g did not decrease in this study. The copolymer having vinylalcohol can adhere tightly to the pigment because of its hydrophilic group and its mobility is diminished considerably. This is thought to be the reason why the T_g of the films in this study does not decrease with increasing PVC.

K.D. Ziegel¹ showed the following relation assuming that the adsorbed polymer on the pigment formed the immobilized layer and did not contribute to energy loss.



$$E''/E' = 1 - \phi B \quad (2)$$

where E'' : Loss modulus of matrix
 E' : Loss modulus of composite
 ϕ : Volume fraction of filler
 B : Interaction parameter

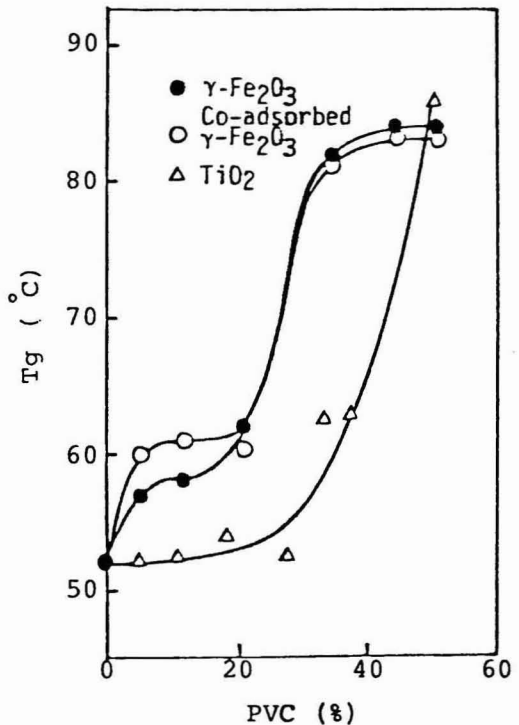


Figure 3—Dynamic viscoelasticity of coating films filled with TiO_2 (10 Hz)

Figure 4— T_g of films as a function of PVC (from Figures 1-3)

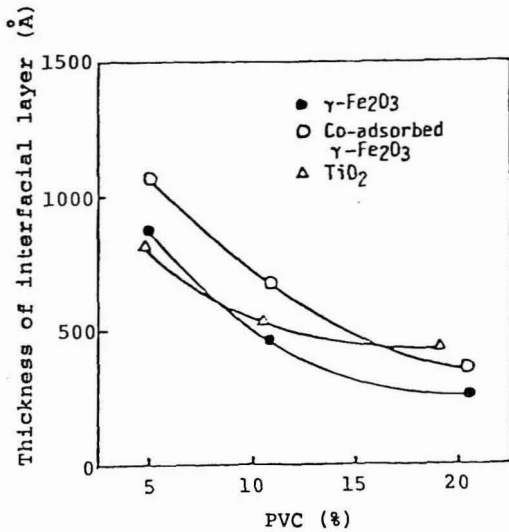


Figure 5—Calculated thickness of interfacial layer vs PVC

The thickness of the interfacial polymer layer, ΔR , on the pigment was estimated by equation (3).⁸

$$B = 1 + \rho S \Delta R \quad (3)$$

where ρ : Density of filler
 S : Specific surface area

Figure 5 shows the relationship between ΔR and PVC obtained by the calculation of the dynamic viscoelasticity. In this graph, ΔR decreases with increasing PVC, because parameter B approaches 1 with increasing PVC. The thickness of the interfacial layer on Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ was larger than that on $\gamma\text{-Fe}_2\text{O}_3$.

Stress-Strain Properties

Generally, rigid pigment in polymer increases the Young's Modulus of the system. Guth's⁹ or Kerner's¹⁰ equation on the modulus reinforcement is well known.

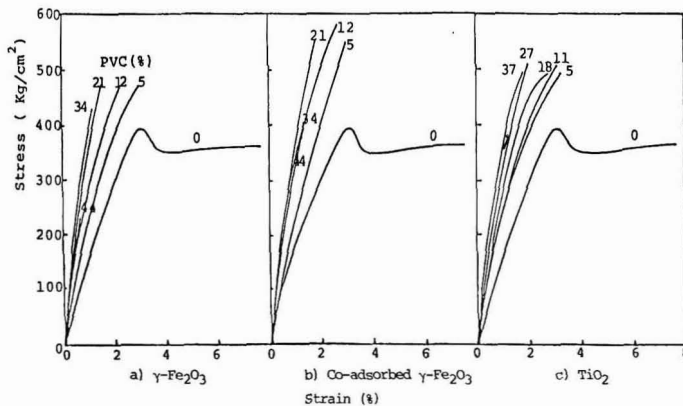


Figure 6—Stress-strain curves of films

The stress-strain curves of the films containing $\gamma\text{-Fe}_2\text{O}_3$, Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$, and TiO_2 are shown in Figure 6(a)(b)(c), respectively. In this graph, the curves become steeper for the samples of high PVC. It shows that the film modulus increases with increasing PVC. The relationship between tensile strength and PVC are shown in Figure 7. The tensile strength has its maximum from 10 to 15% PVC for $\gamma\text{-Fe}_2\text{O}_3$ and Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ and the maximum value of Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ is larger than that of $\gamma\text{-Fe}_2\text{O}_3$. This value is interpreted to be CPVC (critical pigment volume concentration) for tensile strength. Beyond this point, the pigments contact directly and the coating becomes brittle. Tubota, et al.¹¹ reported that the amount of the adsorbed polymer affected the mechanical properties of the coatings. It is considered that the difference of two curves depends on the difference of the amount of the adsorbed polymer indicated in Figure 5. However, the tensile strength for TiO_2 shows a plateau and its value is constant in the range of PVC from 5 to 37%. This result suggests the coating filled with TiO_2 has less air caused by aggregates.

Water Absorption of the Film

The water absorption of the coating film is thought to be related to the interaction between the pigment and the vehicle. W. Funke¹² explained that the water absorption increased with increasing PVC when the water permeated into the empty interstices of the pigment aggregates or flocculates.

Figure 8 shows the relationship between water absorption and PVC. The water absorption for $\gamma\text{-Fe}_2\text{O}_3$ and Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ increases at high PVC, but that for TiO_2 maintains almost the same value. This figure indicates that there is a lack of adhesion between the magnetic pigment and the polymer. It is thought that a great deal of aggregates occur because of the magnetic pigment's acicular shape and magnetic properties in the magnetic coating.

GPC Measurement

Table 2 shows the thickness of the adsorbed polymer layer on that pigment calculated from the chromatogram

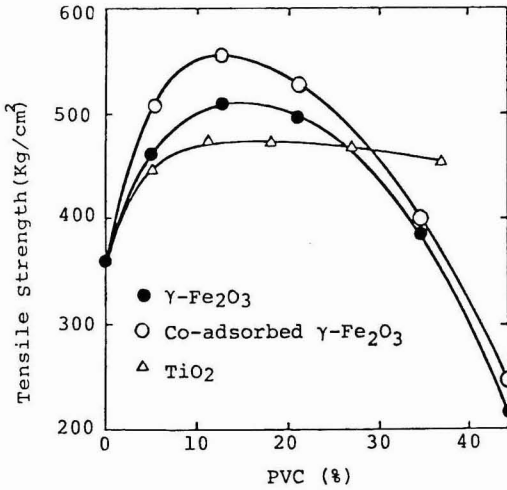


Figure 7—Tensile strength of films vs PVC

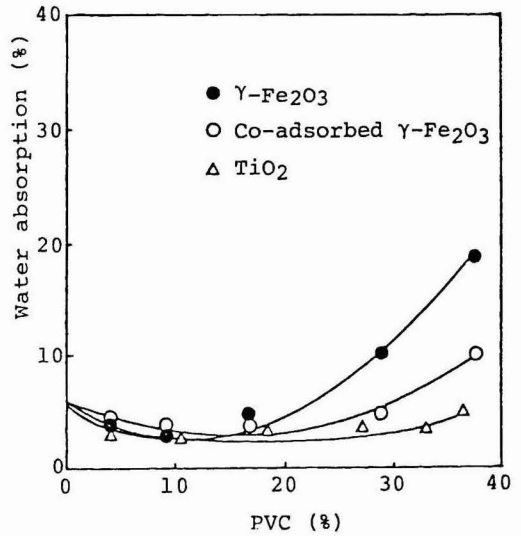


Figure 8—Water absorption of films vs PVC

of GPC. The concentration of the polymer solution was determined from the calibration curve.

$$A = \frac{M}{d \cdot S} \quad (4)$$

where A: Thickness of adsorbed layer
 M: Weight of adsorbed polymer solution
 d: Density of adsorbed polymer solution
 S: Specific surface area of pigment

The thickness of the adsorbed layer on Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ is 1.5 times larger than that on $\gamma\text{-Fe}_2\text{O}_3$. This is in accordance with the results in Figure 5.

IR Spectroscopy

Table 3 shows the result of IR analysis of the adsorbed polymer on the pigment. The proportion of the polymer, polyurethane, and polyvinylchloride-vinylacetate-vinylalcohol, is defined as the ratio of $1520\text{ cm}^{-1} / 612\text{ cm}^{-1}$. Here, the adsorption of 1520 cm^{-1} and 612 cm^{-1} are assigned to amide group in polyurethane and C-Cl bond in polyvinylchloride, respectively.

It is clear from Table 3 that the ratio of the original polymer matrix is 2.0 but that of adsorbed polymer on

$\gamma\text{-Fe}_2\text{O}_3$ is 3.3. This means that the polyurethane elastomer is adsorbed more than the copolymer including polyvinylchloride on $\gamma\text{-Fe}_2\text{O}_3$. On the other hand, the ratio for Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ is 1.6 which suggests the opposite for this case. For TiO_2 , the ratio is similar to the original one.

CONCLUSIONS

The results may be summarized as follows:

- (1) The thickness of the adsorbed layer on Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ is 1.5 times larger than that on $\gamma\text{-Fe}_2\text{O}_3$. Therefore, the interaction between Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ and the vehicle is larger than that between $\gamma\text{-Fe}_2\text{O}_3$ and the vehicle.
- (2) Each of films containing Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ show the strongest tensile strength in the PVC range from 10 to 15%.
- (3) Polyvinylchloride-vinylacetate-vinylalcohol copolymer is adsorbed to a greater extent on the surface of Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ than polyurethane elastomer. The opposite tendency is obtained for $\gamma\text{-Fe}_2\text{O}_3$.

Table 2—Calculated Thickness Of Interfacial Polymer Layer Adsorbed on Pigment

Pigment	Thickness (Å)
$\gamma\text{-Fe}_2\text{O}_3$	150
Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$	230
TiO_2	290

Table 3—Result of IR Analysis Of Adsorbed Polymer on Pigment

	Ratio of Absorbance $1520\text{ cm}^{-1} / 612\text{ cm}^{-1}$
Original	2.0
$\gamma\text{-Fe}_2\text{O}_3$	3.3
Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$	1.6
TiO_2	2.2

where the absorption of 1520 cm^{-1} and 612 cm^{-1} are assigned to amide group and C-Cl bond, respectively.

ACKNOWLEDGMENT

The authors wish to express their thanks to Prof. K. Ueki of Institute Vocational Training, and to President F. Sono; Managing Director S. Masujima; and General Manager of Magnetic Recording Products, R&D Dept., Dr. Y. Imaoka, of TDK Electronics Co., Ltd., for their continuous encouragement and support of this work.

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Crosslinked-Core Latex By Radiation-Induced Emulsion Polymerization

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Copolymer latexes of self-crosslinking N-(n-butoxymethyl) acrylamide (NBM) are prepared by radiation-induced emulsion polymerization using Co-60 gamma-rays. The latex, consisting of crosslinked polymers, is superior in water resistance, solvent resistance, and mechanical properties of films cured at 160°C for 30 minutes, but inferior in gloss of pigmented film to the latex consisting of low molecular weight polymers. The core-shell latex having a core of crosslinked polymers and a shell of low molecular weight copolymers of NBM exhibits excellent final properties. The weatherability of the cured film increased with increasing degree of crosslinking of core polymers. The effect of monomer feed rate and pre-emulsification of monomer on the final properties are investigated in connection with the formation of microgel and water-soluble acid bearing oligomers.

INTRODUCTION

The annual usage of paint in Japan has increased to 1.6×10^6 tons. About 6.5×10^5 tons of organic solvents were used in the paint industry, with almost all solvents being discharged into the atmosphere causing air pollution. Therefore, to prevent air pollution and to save oil

resources, the development of water-borne paints is a major priority, especially in the field of industrial coatings.

In previous papers,¹⁻³ the features of radiation-induced emulsion polymerization were studied to use the formed latex as vehicles for water-borne paints. Such features are, for instance, the absence of impurities derived from chemical initiators, the suppression of side reactions, such as hydrolysis of monomers, and formed polymers during polymerization because of low temperature polymerization. These features suggest the possibility of radiation processing for the preparation of latex suitable for thermosetting water-borne paints.

In a previous paper,⁴ it was also shown that a latex consisting of crosslinked polymers results in high water resistant films. The crosslinked latex, however, causes low surface gloss of pigmented films.

In this paper, core-shell latexes which had a core of crosslinked polymers and a shell of low molecular weight polymers were developed by a two-stage semicontinuous batch process⁵ with Co-60 gamma-rays.

In addition, a new self-crosslinking monomer, N-(n-butoxymethyl)acrylamide (NBM),⁶ was used as a functional monomer to facilitate thermosetting reaction products like N-(iso-butoxymethyl)acrylamide (IBMA).⁷

EXPERIMENTAL

Polymerization Procedure

The four kinds of monomer compositions used are listed in *Table 1*. Monomers used are n-butyl methacrylate (n-BMA), styrene (St), 2-hydroxyethyl methacrylate (HEMA), N-(n-butoxymethyl)acrylamide (NBM), acrylic acid (AAc), and 1,6-hexandiol dimethacrylate

* Presented at the Third International Meeting on Radiation Processing in Tokyo, Japan, October 1980.

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Table 1—Monomer Composition (wt%) for Semicontinuous Batch Emulsion Polymerization

	H	N	Hs	Ns
n-Butyl methacrylate (n-BMA)	88	78	78	68
N-(n-butoxymethyl)acrylamide (NBM)	0	11	0	11
2-Hydroxyethyl methacrylate (HEMA)	10	9	10	9
Styrene (St)	0	0	10	10
Acrylic acid (AAc)	2	2	2	2

(16HD); n-octylmercaptan (n-OMP) was used as a chain transfer agent. Polymerizations were carried out by semicontinuous batch process in the presence of a single anionic emulsifier, either sodium laurylsulfate (SLS) or sodium[nonylphenylpolyoxyethylene ($p = 2$)3-(sulfo), 2-(hydroxy)propylether] (H-E). These emulsifiers were supplied by Daiichi Kogyo Seiyaku Co. Ltd., Japan. Ammonium acetate (AcAm) was chosen to control the latex viscosity. All chemicals were used as received.

Figure 1 shows the schematic diagram of a polymerization system. Emulsion polymerizations were carried out by radiation in the following manner. Into a one-litre stainless steel (SUS 316) flask, 450g of deionized water, 3g of emulsifier (1 wt% based on total monomer), 0.7g of AcAm (20mM in water), and 30g of monomer mix (10 wt% of total monomer) were added. After mixing under nitrogen flow for 30 minutes at 40°C, the solution was irradiated with gamma-rays from 80kCi of Co-60 at a dose rate of 6.8×10^4 rad/hr. Polymerization temperature was kept at $40 \pm 2^\circ\text{C}$. The initiation of polymerization was observed from the outside of irradiation room by measuring the temperature in the flask with a thermocouple. The maximum rising of temperature was about 2°C, observed within 30 minutes. The remaining monomer mix was added continuously from the outside of irradiation room with a micro metering pump at a constant flow rate of 2mL/min (0.66% of total monomer/min). After adding the remainder of the monomer

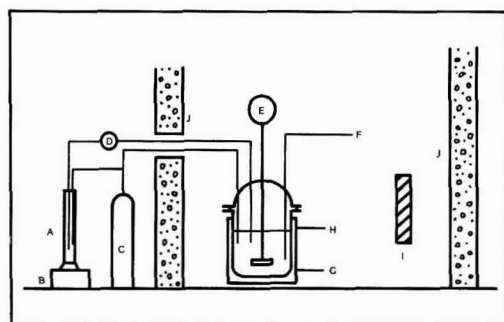


Figure 1—Schematic diagram of radiation-induced emulsion polymerization: A: monomer reservoir; B: magnetic stirrer; C: nitrogen gas bomb; D: micro metering pump; E: stirrer; F: thermocouple; G: water inlet; H: water outlet; I: Co-60 sources; J: shielding concrete

Table 2—Polymerization Recipe for Batch Process To Study Effects of Ammonium Acetate on Viscosity of Latex

Water	210.0 (g)
n-Butyl methacrylate (n-BMA)	70.2
N-(n-butoxymethyl)acrylamide (NBM)	9.0
2-Hydroxyethyl methacrylate (HEMA)	9.0
Acrylic acid (AAc)	1.8
n-Octylmercaptan (n-OMP)	0.45
Emulsifier H-E	0.90
Ammonium acetate (AcAm)	0.07–0.42

mix, polymerization was completed by irradiating for one hour.

Core-shell latex was prepared by two-stage emulsion polymerization. After complete polymerization of core monomer, which was observed by the temperature in the flask, shell monomer was added. Weight ratio of core to shell was 6 to 4, unless otherwise noted.

The effect of AcAm on the latex viscosity was studied by batch process. All ingredients listed in Table 2 were added to the flask before irradiation.

Characterization of Latex

The particle size of latex was determined by a photon correlation spectroscopy using a Coulter Nano-sizer.⁸

The viscosity of the latex was measured with a rotational viscometer model EMD, of Tokyo Keiki Co. Ltd., at a shear rate of 76.8 sec^{-1} at 30°C.

Distribution of acid groups in the latex was determined by conductometric titration of diluted latex before and after purification with ion-exchange resins. Acid groups originating from the acrylic acid are divided into three classes; these are: surface-bound, free, and buried acid groups, meaning chemically bound acid groups on the particle surface, acid-bearing water-soluble oligomers, and acid groups buried within the particle, respectively. The amount of surface-bound acid groups was determined by the titration of the latex purified with ion-exchange resins. The amount of free acid groups was found by subtracting the amount of surface-bound acid groups from the total amount of acid groups determined by the titration of the latex before the purification on the assumption that the purification procedure removes completely free acid groups and AcAm from the latex and that all acrylic acids added are completely polymerized.

Gel permeation chromatography (GPC) was used to find the molecular weight of polymers. A 5 g amount of latex was mixed with 50mL of tetrahydrofuran (THF), then centrifuged at 16,000 rpm for several hours at 5°C. The supernatant THF solution was used as a sample for GPC analysis. The amount of THF-soluble products was determined from the solid content of the supernatant. A standard GPC instrument (Toyo Soda) with four columns (G2500-H8, G3000-H8, G6000-H6, and GM-H6) was used with a R1 detector. The operating temperature was 40°C as solvent THF was applied. Figure 2 shows the calibration curve obtained by using standard mono-dispersed polystyrene.

Determination of Film Properties

For film preparation and curing, the latex was neutralized with a 30% aqueous solution of dimethylethanolamine amounting to 60% of the total acrylic acid used. It was then mixed with 25 phr of butylcarbitol which was used as a coalescent solvent to obtain a uniform film. This mix is described as latex blend. The latex blend contained a melamine resin Cymel® 350 (American Cyanamid) and a water-soluble acrylic polymer of which the monomer composition was n-BMA/St/HEMA/AAc = 69/10/15/6. The weight ratio of latex polymer, melamine resin, and water-soluble acrylic polymer, was 85/5/10. This mix is described as clear blend.

The latex blend and clear blend were cast with a draw-down bar on glass plates and steel plates. The cast plates were allowed to air-dry for 30 minutes at 40°C before being baked at 160°C for 30 minutes. The cured films from latex blend and clear blend are described as latex film and clear film, respectively.

To test for water resistance, the film on a glass plate was immersed in water at 80°C for four hours and checked for whitening and blistering. The water resistance was rated as 10 if whitening and blistering were not observed.

For testing solvent resistance, the film was rubbed with a cloth soaked with xylene. The solvent resistance was rated as 10 if it withstands 20 double rubs without mar.

The films were peeled from the plates after immersion in water at 70°C for two hours, dried at 100°C for 16 hours, and tested for water absorption, gel fraction, and mechanical properties. Water absorption of the film was measured from the increase of weight after immersion for 24 hours in water at 80°C. Gel fraction of the film was measured from the decrease of weight after extraction for 24 hours in boiling xylene. The tensile strength and elongation at break of the film were measured with a Instron model 1130 tester.

To test the gloss of the pigmented film, the latex was formulated into paint by a conventional manner using anatase titanium dioxide and latex blend at the following solid weight ratio; TiO₂/latex polymer/water-soluble acrylic polymer/melamine resin = 36/34/22/8. The gloss of the pigmented film, cured at 160°C for 30 minutes, was measured with a 60-degree gloss meter.

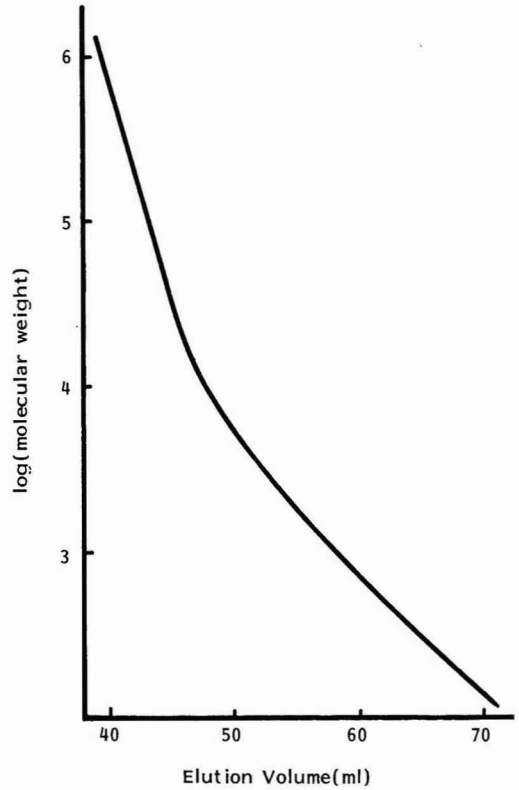


Figure 2—GPC calibration curve

Accelerated weathering test was conducted on the clear films using a Q-U-V tester, of Q-Panel Co. The test specimen prepared from the clear blend contained a 45/35/20 ratio of latex polymer, water-soluble acrylic polymer, and melamine resin. The tester was operated on the following schedule: (1) UV irradiation at 60°C for four hours, and (2) water condensation at 50°C for four hours.

Table 3—Effect of Ammonium Acetate on Properties of Latex

Emulsifier	Ammonium Acetate in Water (mM)	Amount of Coagulum % of Total Monomer	Particle Size (nm)	Viscosity (cP)	
				Polymerized	Neutralized
SLS	None	1.8	82	650	Very high
H-E	None	2.7	96	9.0	463
H-E	10	2.7	97	4.2	130
H-E	20	2.0	105	3.3	60
H-E	30	5.0	123	2.3	X ^a
H-E	40	11.0	X ^a	X ^a	X ^a
H-E	60	24.0	X ^a	X ^a	X ^a

(a) X: not measured due to excess coagulum.

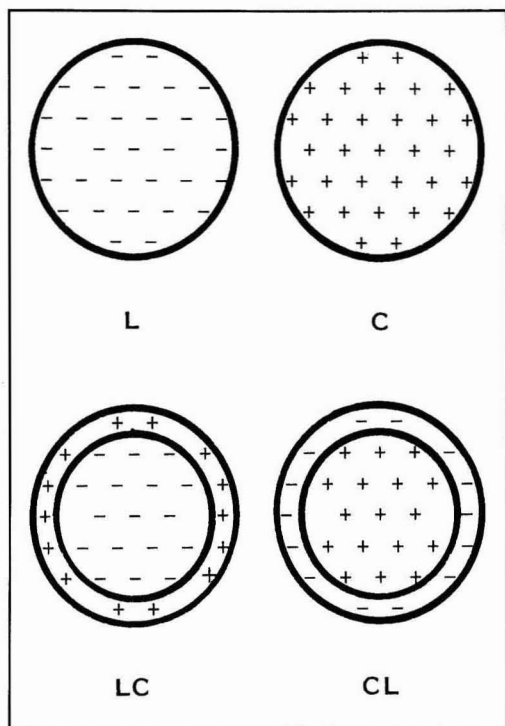


Figure 3—Design of particles: (-): low molecular weight polymers, (+): crosslinked polymers

RESULTS AND DISCUSSION

Viscosity Control with Ammonium Acetate

The viscosity of the latex prepared by radiation-induced emulsion polymerization depends on the emulsifier used, but generally it is higher than that of prepared by conventional chemical initiator method.^{3,4} The high viscosity is due to the lower concentration of electrolytes in the latex. The high viscosity, especially after neutralization to stabilize the latex, is a serious disadvantage from a practical viewpoint.

The viscosity could be reduced by addition of electrolytes into the initially charged water before irradiation. However, it must be taken into account that the water resistance of the latex film may be decreased by the presence of electrolytes in the film.

In this work, AcAm was selected as an electrolyte to reduce the viscosity without decreasing the water resistance of the film, because at 117°C, AcAm decomposes to ammonia and acetic acid and does not remain in the film after it is baked at 160°C. As an emulsifier, H-E was selected because the viscosity of the latex was lowest when several kinds of emulsifier were compared for radiation-induced emulsion polymerization.⁴

Table 3 shows the comparison of SLS and H-E and the effect of AcAm concentration on the polymerization stability, particle size, and the viscosities before and after

Table 4—Effect of Particle Structure on Properties Of Latex and Cured Film

	Latex No.			
	1	2	4	8
Structure of latex	L	C	LC	CL
Molecular weight modifier:				
Core ^a	n-OMP	16HD	n-OMP	16HD
Shell ^a	n-OMP	16HD	16HD	n-OMP
Latex Viscosity (cP):				
Polymerized	24	18	22	21
Neutralized	143	55	112	69
Latex film:				
Water resistance	4	8	8	9
Solvent resistance	8	9	7	9
Tensile strength (kg/cm ²)	306	314	311	348
Elongation at break (%)	10	16	13	11
Clear film:				
Tensile strength (kg/cm ²)	349	344	339	350
Elongation at break (%)	8	8	10	6
Pigmented film:				
60-Deg. gloss	88	79	86	86

(a) H type monomer with 2 of modifier, emulsifier: H-E.

neutralization. It is clear that the viscosity of the latex is lower when prepared with H-E than with SLS. However, the viscosity of the latex with H-E increased significantly after neutralization. The addition of AcAm was effective in reducing the viscosity of latex after neutralization. The amount of coagulum increased by increasing the amount of AcAm. This means that the polymerization stability decreased when the concentration of electrolyte was increased, as demonstrated by the increase of particle size. Adding electrolytes to the latex causes thinning of the electric double layer on the particles, which results in a decrease of viscosity and the stability of the latex. When the stability of the latex decreases, the particle size is increased to reduce the surface area to stabilize with a definite amount of emulsifier. The optimum concentration of AcAm was determined as 20 mM in initially charged water (Table 3).

Effect of Particle Structure On Viscosity of Latex

Four kinds of structurally different latexes were designed as shown in Figure 3. Latexes L and C consist of low molecular weight polymers and crosslinked polymers, respectively. To lower the molecular weight, n-OMP was used, and to crosslink, 16HD was used. The latexes LC and CL have core-shell structure. The latex LC consists of a core of low molecular weight polymers and a shell of crosslinked polymers. On the other hand, the latex CL has a crosslinked core and low molecular weight shell.

As shown in Table 4, the particle sizes and viscosities of the latexes prior to neutralization were in similar

Table 5—Effect of Styrene

	Latex No.	
	12	13
Structure of latex	CL	CL
Monomer mix:		
Core ^a	N	Ns
Shell ^b	N	Ns
Latex viscosity (cP):		
Polymerized	22	20
Neutralized	40	251
Latex film:		
Water resistance	3	3
Solvent resistance	7	7
Tensile strength (kg/cm ²)	302	348
Elongation at break (%)	14	13
Clear film:		
Water absorption (%)	4	4
Gel fraction (%)	14	13
Tensile strength (kg/cm ²)	303	350
Elongation at break (%)	11	9
Pigmented film:		
60-Deg. gloss	84	88

(a) containing 2% of 16HD.
(b) containing 2% of n-OMP.
Emulsifier: H-E.

Table 6—Effect of Location of NBM

	Latex No.	
	14	15
Structure of latex	CL	CL
Monomer mix:		
Core ^a	H	Ns
Shell ^b	Ns	H
Latex viscosity (cP):		
Polymerized	81	132
Neutralized	184	168
Latex film:		
Water resistance	8	4
Solvent resistance	9	8
Tensile strength (kg/cm ²)	288	173
Elongation at break (%)	27	2
Clear film:		
Water absorption (%)	4	8
Gel fraction (%)	80	70
Tensile strength (kg/cm ²)	294	251
Elongation at break (%)	15	9
Pigmented film:		
60-Deg. gloss	89	87

Emulsifier: SLS
(a) containing 2% of 16HD
(b) containing 2% of n-OMP

range. The viscosity after neutralization, however, depended strongly on the molecular weight of polymers. The highest viscosity was observed in latex L. On the contrary, latex C showed the lowest viscosity. The viscosity of latex LC after neutralization is high compared with latex CL. The high viscosity of latex LC suggests that n-OMP remained after polymerization of core and resulted in essentially no crosslinking in the shell. This assumption was confirmed by the fact that latex LC completely dissolved in excess acetone, meaning that the LC-type latex cannot be prepared by this process as long as chain transfer agent and crosslinking monomer are used for the core and shell parts, respectively.

Effect of Particle Structure On Properties of Cured Film

The particle structure also affects the properties of cured film, as shown in Table 4. By comparing L and C it is clear that the crosslinked particles are superior in resistance to water and solvent, and are inferior in gloss retention. One advantage of latex L was high value of gloss. Core-shell latex CL exhibited excellent properties in water resistance, solvent resistance, and mechanical properties, as well as gloss as a result of adequate combination of L and C. On the other hand, the film properties of latex LC were not good compared with latex CL, suggesting the failure of preparation of LC-type latex. It was concluded from these results that type CL latex is suitable for water-borne paints.

Effect of Monomer Composition

Styrene (St) is often incorporated in emulsion copolymers to improve the mechanical properties and surface gloss. The effect of St is shown in Table 5. When 10% of n-BMA is substituted with St, increases were found in the tensile strength (Tb) of latex film, from 303 kg/cm² to 350 kg/cm², and gloss of pigmented film, from 83 to 88, as expected. The addition of St increased the viscosity of the latex after neutralization, while the degree of thermal curing did not change as judged by water absorption and gel fraction. The mechanical properties of latex film and clear film were nearly identical which was due to the self-crosslinking capability of NBM.

As suggested by Bassett, et al.,⁷ it is reasonable to think that a self-crosslinking monomer is not necessary in the core part. To confirm this assumption two latexes were compared, No. 14, containing NBM only in the shell part, and No. 15, containing NBM only in the core part. These latexes were prepared using SLS as an emulsifier because the preparation of a latex having a core of H type monomer with H-E emulsifier was impossible. The stability of the latex was so low that it totally coagulated when H-E was used without NBM to prepare the core part. The reason for this phenomenon is not clear, but it seems that the copolymers of NBM have a stabilizing effect on the latex. As a result of using SLS, the viscosity of the latexes became high as discussed previously.

Water and solvent resistances and tensile strength of No. 15 are inferior to No. 14. From these data, it can be concluded that NBM moieties located near the particle surface facilitate crosslinking (See Table 6). Also, these

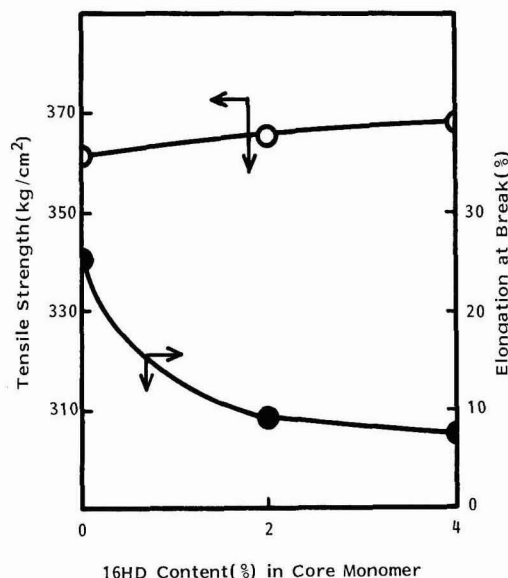


Figure 4—Effect of concentration of crosslinking monomer on mechanical properties of cured film

results suggest that the core-shell structure is successfully prepared in the case of crosslinked core-low molecular weight shell. Another fact showing the success of core-shell was obtained by measuring the particle size before and after polymerization of the shell monomer mix. For instance, when the particle size of the core was 78 nm and the weight ratio of monomer for core to shell was 6

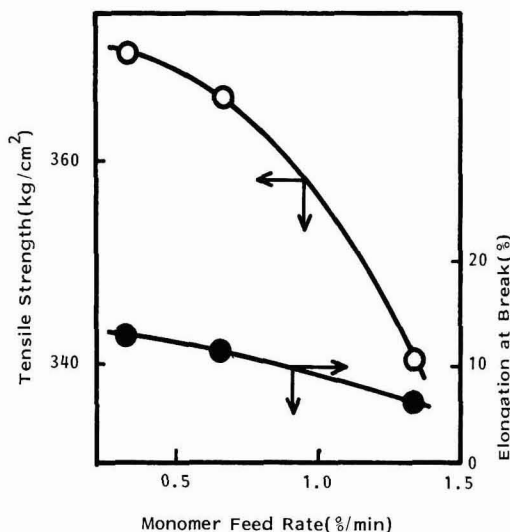


Figure 5—Effect of monomer feed rate on mechanical properties of cured film

to 4, the final size of the core-shell particle must be 92.5 nm if monomer for the shell polymerized only at the surface of the core. The observed size of the core-shell particles was 92 nm.

The effect of the concentration of crosslinking monomer, 16HD, in the core on the mechanical properties is shown in Figure 4. The tensile strength does not largely depend on the concentration of 16HD. The elongation at break, however, decreased with increasing of 16HD. Therefore, it seems that the tensile strength depends on the inter-particle crosslinking, whereas the elongation at break depends on the intra-particle crosslinking.

The effect of 16HD on the other properties of cured film is shown in Table 7. The film's water and solvent resistance increased with increasing concentration of 16HD. The gloss of pigmented film was independent of the concentration of 16HD.

Table 7—Effect of Crosslinking Monomer

	Latex No.		
	16	18	20
Structure of latex	CL	CL	CL
Weight ratio of core/shell	6/4	6/4	7/3
16HD In core monomer (%)	4	2	2
Latex viscosity (cP):			
Polymerized	93	93	96
Neutralized	294	239	309
Latex film:			
Water resistance	10	10	9
Solvent resistance	9	8	7
Tensile strength (kg/cm ²)	367	365	361
Elongation at break (%)	8	9	25
Clear film:			
Water absorption (%)	4	3	4
Gel fraction (%)	83	82	78
Tensile strength (kg/cm ²)	379	370	382
Elongation at break (%)	8	9	10
Pigmented film:			
60-Deg. gloss	91	90	89

Monomer mix: Hs for core and Ns with 2% of n-OMP for shell, emulsifier: SLS.

Table 8—Effect of Crosslinked Core on Weatherability Of Clear Film Cured at 160°C for 30 Minutes

	Testing Time (hours)				
	0	400	1,200	2,400	3,000
60-Deg. gloss:					
No. 16	98	97	93	80	57
No. 18	99	97	93	68	53
No. 20	98	97	95	70	29
Appearance:					
No. 16	EX ^a	EX	EX	EX	CK
No. 18	EX	EX	EX	SC	CK
No. 20	EX	EX	EX	SC	CK

(a) EX: excellent; SC: slight checking; CK: checking without blushing.

Weathering Properties of Core-Shell Latex

The latex having crosslinked core and reactive groups near the particle surface was expected to exhibit a high degree of weathering resistance which is essential in its evaluation as an automobile finish. Thus, the clear films were tested using an accelerated weathering tester. With the exception of No. 20, all latexes tested were previously described. The ratio of core to shell in latex No. 20 was 7 to 3. Latex No. 18 was selected as a control to evaluate the effects of (1) amount of crosslinking monomer, and (2) weight ratio of core to shell. The results are shown in Table 8. After 2,400 hours, No. 16, containing 4% of 16HD, showed no deterioration in appearance, whereas, No. 18, containing 2% of 16HD, showed checking. Also, gloss of No. 16 after 3,000 hours was higher than that of No. 18. Latex No. 20, containing a thicker shell than No. 18, showed lower gloss after 3,000 hours. These results indicated that the crosslinked core is considerably effective in increasing the weatherability of film.

Effect of Polymerization Process

In the above, polymerization monomer mix was added at a constant feed rate (0.66% of total monomer/min, 2mL/min) and all amounts of emulsifier were dissolved in initially charged water. It is well known that the properties of both the latex and the cured film from the latex depend largely on polymerization process factors,

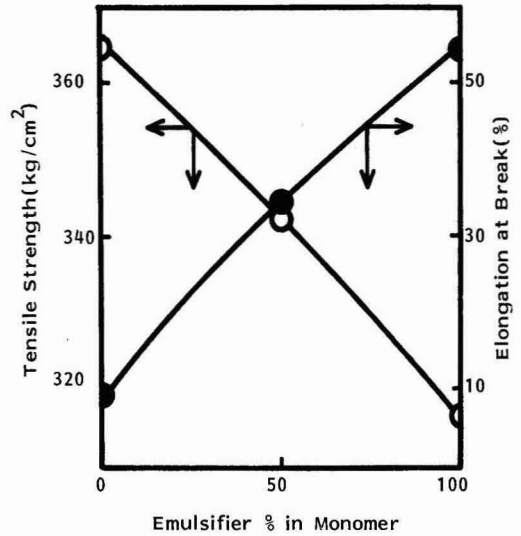


Figure 6—Effect of distribution of emulsifier in monomer on mechanical properties of cured film

such as monomer feed rate,⁹ and the distribution of emulsifier between water in reactor and monomer to be added even though the actual compositions are identical.¹⁰

Table 9—Effect of Monomer Feed Rate On Properties of Latex and Cured Film

	Latex No.		
	25	18	22
Monomer Feed Rate (mL/min) ...	1	2	4
Latex properties:			
Particle size (nm):			
At pH 6.0	89	93	94
At pH 10.5	90	94	96
Viscosity (cP):			
Polymerized	93	96	102
Neutralized	100	93	81
Acid groups (10 ⁻⁴ mol/g-solid)			
Surface-bound	117	239	very high
Water-soluble	1.42	1.27	1.19
	0.26	0.43	0.63
Latex film:			
Water resistance	9	10	8
Solvent resistance	8	8	8
Tensile strength (kg/cm ²)	370	365	340
Elongation at break (%)	12	9	6
Clear film:			
Water absorption (%)	3	3	5
Gel fraction (%)	80	82	79
Tensile strength (kg/cm ²)	329	370	332
Elongation at break (%)	12	9	13
Pigmented film			
60-Deg. gloss	90	90	90

Table 10—Effect of Pre-emulsification of Monomer On Properties of Latex and Cured Film

	Latex No.		
	18	23	24
Distribution of SLS in initial charge (%)			
	100	50	0
Particle size (nm)	94	104	123
Viscosity (cP):			
Polymerized	93	35	20
Neutralized	239	127	189
Acid groups (10 ⁻⁴ mol/g-solid):			
Surface-bound	1.27	1.33	1.33
Water-soluble	0.43	0.35	0.35
Latex film:			
Water resistance	10	9	9
Solvent resistance	8	9	9
Tensile strength (kg/cm ²)	365	342	317
Elongation at break (%)	9	35	54
Clear film:			
Water absorption (%)	4	3	4
Gel fraction (%)	83	80	79
Tensile strength (kg/cm ²)	370	346	331
Elongation at break (%)	9	23	9
Pigmented film:			
60-Deg. gloss	90	88	89

Monomer mix: Hs for core and Ns for shell; 2% of 16HD in core monomer and 2% of n-OMP in shell monomer; emulsifier: SLS.

Latex: CL type with Hs monomer for core and Ns monomer for shell; 2% of 16HD and n-OMP, respectively.

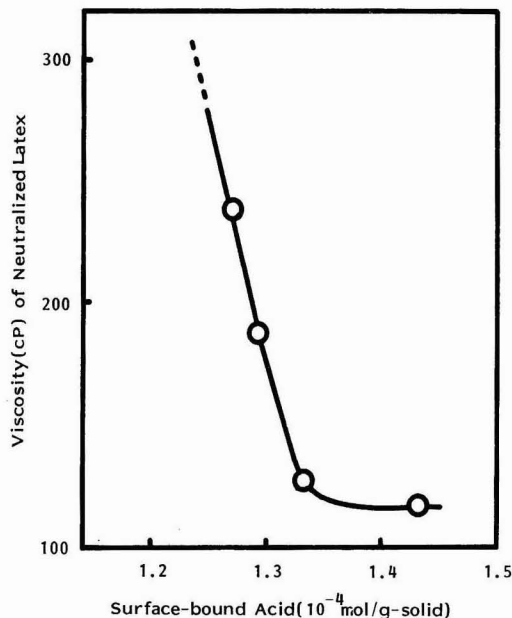


Figure 7—Relationship between amount of surface-bound acid groups on viscosity of neutralized latex

Figure 5 shows the effect of the monomer feed rate on the mechanical properties of cured latex film. The tensile strength and the elongation at break decreased with increasing monomer feed rate. This effect on mechanical properties is due to the nonuniform distribution of acrylic acid component in latex. It is well known that the thermal curing of N-(iso-butoxymethyl)acrylamide copolymer latex is promoted by the presence of copolymerized carboxyl groups.⁷ When the monomer feed rate is high, a large part of the acrylic acid tends to remain until the final stage of polymerization because the rate of polymerization of acrylic acid is lower than that of other monomers, such as n-BMA, HEMA, and St.³

Table 9 shows the acid distribution in latex. The water-soluble acid groups increased with increasing monomer feed rate. This result indicates that to be effective and to promote thermal curing acid groups must be buried and surface-bound.

Figure 6 shows the effect of emulsification of monomers on the mechanical properties of cured film. In these experiments, monomers were pre-emulsified with a definite amount of emulsifier and water. The distribution ratios of a constant amount of SLS between water in reactor and the monomer emulsion were 100/0, 50/50, and 0/100. The tensile strength decreased with increasing amounts of SLS in the monomer emulsion. On the other hand, elongation at break increased remarkably.

The striking effect of pre-emulsification of monomers was observed in the particle size, as shown in Table 10. The particle size increased with increasing amounts of SLS in the monomer emulsion. This is in accordance

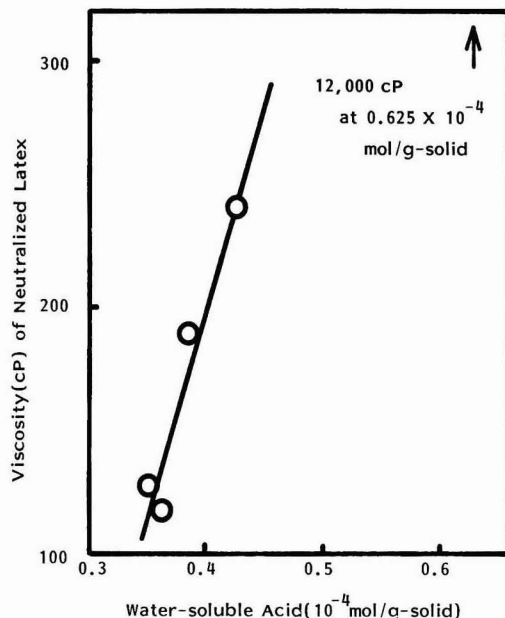


Figure 8—Relationship between amount of water-soluble acid groups on viscosity of neutralized latex

with the results of Snparek.¹⁰ This is due to the decrease of the number of micelles to initiate polymerization. Therefore, it seems reasonable to take into account the effect of particle size on the mechanical properties of cured film, but there is no evidence to support this concept.

The viscosity of the neutralized latex depended, to a great extent, on the monomer feed rate and did not depend on the pre-emulsification of monomer, as shown in Tables 9 and 10. The increase of viscosity by neutralization has been correlated to alkali-swelling and/or dissolving behavior.^{5,11,12} However, particle size determined at high pH indicated that particle expansion by neutralization is not high and independent of the monomer feed rate, as shown in Table 9.

Figure 7 shows the relation between the amount of surface-bound acid groups and the viscosity of neutralized latex. It is clear that the viscosity decreased with increasing amounts of surface-bound acid groups. On the other hand, as Figure 8 shows, the viscosity increased with increasing amounts of water-soluble acid groups. It can be concluded, therefore, that the water-soluble acid groups consisting of low molecular weight copolymers of acrylic acid are responsible for the increase in viscosity of neutralized latex.

The molecular weight of latex polymers is an important parameter in final properties. However, the whole molecular weight of the latex polymers prepared in this section could not be determined because the polymers in core part were crosslinked. Therefore, GPC measurements were carried out for the THF-soluble products of the latex isolated by means of centrifugation.

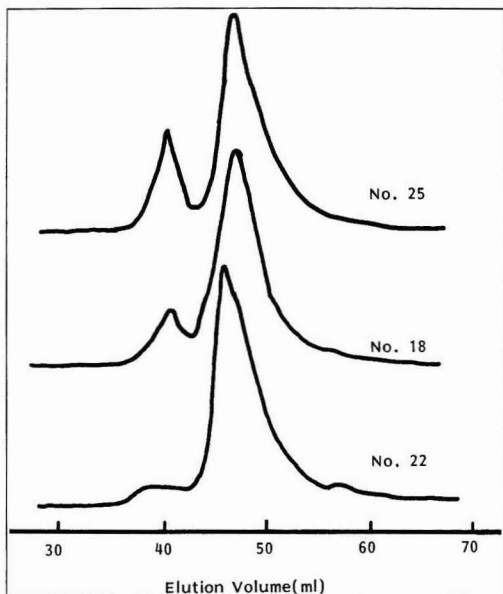


Figure 9—GPC curves of THF-soluble products isolated from latexes No. 25, 18, and 22

Figure 9 shows GPC curves of THF-soluble products of latex No. 25, 18, and 22, prepared with various monomer feed rates. As can be seen, the THF-soluble products of No. 22 consisted of low, middle, and high molecular weight components. The amount of low molecular weight component decreased with increasing monomer feed rate. The average molecular weight of this component was about 1×10^3 . Thus, it is reasonable to attribute this component to water-soluble acid-bearing oligomers described above. The molecular weight of middle-weight components coincide with that of polymers of shell monomers polymerized in the presence of chain transfer agent, n-OMP. The molecular weight of this component did not change with the monomer feed rate because the concentration of n-OMP in shell monomer was the same for these three latexes.

The amount of high molecular weight component increased with decreasing monomer feed rate. The average molecular weight was about 2×10^6 . This component can be attributed to "microgel", i.e., the cross-linked fine particles. The particle size of the microgel calculated from the molecular weight was about 20 nm. The centrifugation of these fine particles is not easy at 16,000 rpm. Since the number of micelles initiating the polymerization decreased with decreasing monomer feed rate, fine particles tend to form when the monomer feed rate is small. As shown in Figure 5, the tensile strength increased with decreasing monomer feed rate. These results indicate that the microgel is very effective in promoting the thermal curing of polymers, as reported by Bobalek, et al.¹³ and Funke.¹⁴

The pre-emulsification of monomer did not affect the

formation of the microgel and water-soluble acid-bearing oligomers.

CONCLUSION

In this investigation, the feasibility of radiation-induced emulsion polymerization was demonstrated in studies of the preparation of highly reactive self-crosslinking NBM latex. It was found that the cross-linked particle latex is superior in water resistance, solvent resistance, and mechanical properties of films cured at 160°C for 30 minutes, but inferior in the surface gloss of pigmented films to the low molecular weight latex. New latex consisting of a core of crosslinked polymers and a shell of low molecular weight NBM copolymers was developed by coating the crosslinked particles with the low molecular weight polymers by a two-stage semicontinuous batch process. The obtained core-shell latex exhibits excellent final properties.

Polymerization process factors such as monomer feed rate and pre-emulsification of monomer were also investigated. It was found that the formation of the microgel and water-soluble acid-bearing oligomers depended largely on the monomer feed rate. The mechanical properties of cured film increased with decreasing monomer feed rate. This is attributed to the formation of the microgel. The water-soluble acid-bearing oligomers brought about the increase in viscosity of neutralized latex which was formed when the monomer feed rate was large compared with that of polymerization of acrylic acid.

The formulation of the latex into a thermosettable coatings and the performance results will be reported elsewhere.

ACKNOWLEDGMENT

The authors wish to thank Mr. Takagi for his assistance with the experiments.

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Use of AC Impedance In the Study of the Anticorrosive Properties Of Chlorine-Containing Vinyl Acrylic Latex Copolymers

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Imperial Chemical Industries PLC*

Resistance, capacitance, and impedance data obtained from AC impedance measurements on coated test panels were found to give a very sensitive and quantitative assessment of both the permeation characteristics and the deterioration of various latex and paint coatings. The measurements showed that films cast from chlorine-containing vinyl acrylic latex copolymers exhibited low uptake of liquid water and ions when the degree of particle coalescence was high. The addition of a block copolymer surfactant, introduced to ensure the stability of acidic paints based on such copolymers, was found to greatly increase the rate of latex particle coalescence due to a plasticization effect. AC impedance measurements supplemented by salt spray and outdoor exposure results showed a relationship between the permeation characteristics and the anticorrosive performance of latex films and latex paints, and showed the advantages to be gained by using a low permeability chlorine containing polymer.

INTRODUCTION

In recent years, latex-based trade sales paints have steadily replaced oil- and solvent-based products for a variety of well documented reasons. However, in anticorrosive primer paints a similar move to latex-based systems has been slower to occur, despite the advantages of such systems in terms of low flammability, solvent costs, and legislation on pollution and toxicity. The low penetration of latex-based paints into the anticorrosive market has been largely due to a number of recognized

limitations in the present generation of acrylic-rich copolymers commercialized for this duty, notably poor performance in accelerated tests and flash rusting.

Some of the binder polymers, such as chlorinated rubber, used for the preparation of accepted high performance solvent-borne anticorrosive primers, are notable in that they exhibit good water barrier properties. On the other hand, the current classes of latex copolymers sold as water-borne anticorrosive paint binders generally contain, as at least one of the principal comonomers, an ester of acrylic acid, and in consequence, the polymers are highly water permeable. This paper describes a study of the anticorrosive performance of highly water-impermeable chlorine-containing vinyl acrylic latex copolymers, and of an air drying primer paint based on one such latex copolymer. Particular attention was focused on: (1) the effect of the intrinsic permeability characteristics of the polymeric binder on the anticorrosive characteristics of latex and paint coatings; and, (2) the effect of one particular surfactant on coating permeability and on the latex particle coalescence process. Conventional tests of anticorrosive performance were used to supplement an AC impedance technique which gave information relating to coating permeability and to the deterioration of various coatings.

REQUIREMENTS FOR THE PROTECTION OF STEEL

To be effective, an anticorrosive coating system must possess a range of attributes such as good mechanical properties, good adhesion under exposure conditions, and good weathering properties. Most important, however, must be its ability to prevent corrosion of the metal substrate. Corrosion is a consequence of anodic and cathodic reactions, both of which take place at the metal surface. In principle, corrosion can be prevented by

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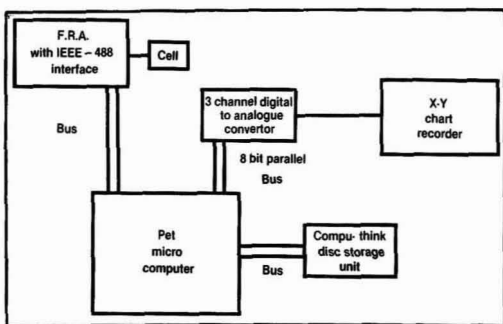


Figure 1—Equipment used for AC impedance measurements

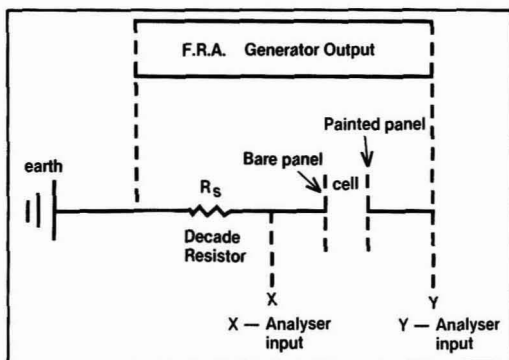


Figure 2—Circuit for AC measurements

suppressing either the anodic or cathodic reactions, or by hindering the passage of electrons or ions between the anodic and cathodic sites through the electrolyte. It must be the aim, therefore, to achieve at least one of these effects in the design of an anticorrosive coating system. When the metal surface is steel, the principal anodic and cathodic reactions are: Anodic—(1) $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$; and (2) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ in the presence of oxygen. The cathodic reaction depends upon pH: $2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^-$, in neutral or basic solutions; or, $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ in acidic solutions.

A protective coating can in principle influence corrosion by: (a) limiting the access of oxygen and hence, polarizing, i.e., retarding the cathodic reaction which occurs at neutral or basic pHs; (b) impeding ionic transport between anodic and cathodic sites through the electrolyte/coating system; (c) limiting the access of water through the film and hence, polarizing the cathodic reaction; and, (d) providing anticorrosive species capable of polarizing either the anodic or cathodic reaction; anti-corrosive pigments are generally assumed to function in this manner.

In practice, the reduction in water permeability is particularly important because, even when water permeation cannot be reduced to the extent that the cathodic reaction is directly prevented, the conductivity and resistance of the coating is highly dependent upon the water content of the coating because the latter quantity strongly influences solubilization of ions and the ionic diffusion characteristics of the film. Moreover, Funke¹ has pointed out that the adhesion of many paint films decreases significantly on prolonged exposure to high humidity. If, as one might expect, this is due to water displacing the film from the substrate, corrosion should then be able to occur readily. The rate determining step for any such loss of adhesion will be related to the water permeability of the coating. This contributory mechanism for the corrosion process provides another reason for attempting to reduce the water permeability of an anticorrosion coating.

The achievement of water impermeable films from aqueous latex polymers presents an additional problem not encountered in solvent-borne polymer systems. Not only must the polymer itself exhibit low permeability to water, but the film forming process of latex particle

coalescence must occur to a high degree of completion so that well integrated films are obtained. Failure to obtain such well integrated films gives rise to a situation in which water penetration can occur even when the polymer itself exhibits an intrinsically low water permeability. One purpose of the paper is to describe certain aspects of the development and performance of a system which satisfies these two requirements of low permeability and good coalescence.

A further consideration for a low permeability coating system is that the permeability to water and the penetration of water should be low when coated on to the substrate to be protected. In this situation, additional factors not present when considering detached films become important, notably the osmotic driving force for the diffusion of water through the film arising from the presence of ionic impurities on the metal surface. It was, therefore, important to establish whether the chlorine-containing vinyl acrylic copolymer latex and derived paints, developed in our laboratories, exhibited good barrier and protective properties when coated on to a metal substrate.

USE OF AC IMPEDANCE

Although the salt spray test is the most common accelerated technique for the evaluation of the performance of organic coatings to chloride related environments, it suffers both from its qualitative appraisal as well as its long test duration and uncertain relevance. To overcome these features, electrical and electrochemical type measurements such as resistance, capacitance, polarization resistance, potential, and potentiodynamic response have been utilized. Leidheiser² has reviewed many of these techniques. However, the traditional DC methods have long suffered from the inclusion of undesirable 'IR' voltage drops across the films, as well as polarization produced at the metal/film interface. AC bridge techniques for impedance measurements offered some solutions to these problems as early as the 1940's. However, the complexity of the instrumentation of the AC bridge technique together with tedious data analysis limited its application in this area. More recent electronic instrumentation, in the form of frequency response analysers using digital correlation techniques, has, however, over-

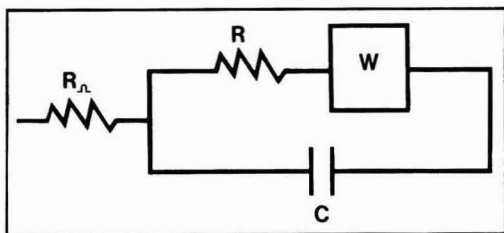


Figure 3—Randles Equivalent Circuit

come such problems and the technique is seeing vigorous application to this area.^{3,4} One strength is seen to be in the small perturbation signal required, i.e., 10–100 mV and the fast data analysis. Moreover, the analysis over a wide frequency range allows a broad range of electrochemical rate processes for activation, diffusion, and adsorption/desorption of species to be examined. The technique is sensitive and capable of giving a quantitative assessment of a paint film as well as being admirably suited to automation and the use of a modeling approach.

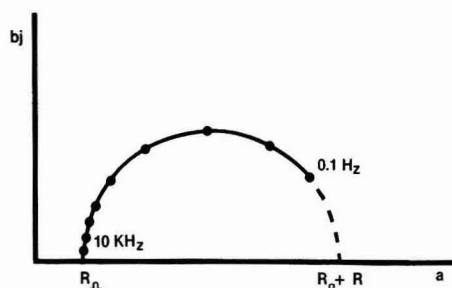
CHLORINE-CONTAINING VINYL ACRYLIC LATEX COPOLYMERS AND PAINTS

A very effective method of reducing the water vapor permeability of a polymer is to incorporate a high proportion of chemically bound chlorine.⁵ For example, the low water vapor permeability of chlorinated rubber⁶ and the excellent anticorrosive properties of the derived solvent-borne paints are well documented.⁷

The design of chlorine-containing vinyl acrylic copolymer latexes has been recently disclosed.^{8–10} Water vapor permeability measurements on solvent cast films showed a very low permeability which decreased with increasing chlorine content. The chlorine-containing vinyl acrylic latex copolymers were based on vinyl chloride and vinylidene chloride as the principal comonomers, and a proportion of an acrylic comonomer introduced in order to exercise fine control over film formation and to split up VDC sequences in the polymer chain.

The latex was prepared by emulsion polymerization in the absence of colloid, which can impair film coalescence, and in the presence of an extremely low concentration of surfactant. Colloid stability of the latex was provided in part by charged polymer end groups arising from the polymerization initiator system.

However, for a variety of reasons, it was necessary to introduce surfactants and dispersants when formulating the latex into a practical paint. In view of the tendency of such chlorine-containing latex copolymers to dehydrochlorinate at alkaline pHs, the paint was formulated at an acidic pH of 5; at this pH (and below) the rate of dehydrochlorination was shown to be negligibly small. It was found that certain ethoxylate based nonionic surfactants, when used as latex stabilizer and pigment dispersant, were capable of giving storage stable acidic paints which maintained their state of pigment dispersion

Figure 4—Determination of film resistance R from Nyquist impedance diagram

during storage. One very effective class of surfactant was found to be the ethylene oxide/propylene oxide/ethylene oxide block copolymer type such as Pluronic F87 or Synperonic PE 39/70 which was capable of stabilizing the latex, and dispersing and stabilizing the pigment. The anticorrosive pigment was zinc phosphate because of its particular effectiveness at acidic pHs and its nontoxic nature. A typical paint formulation is given in the Appendix.

The acidic pH of 5 is an important feature of the paint formulation since it was found that at acidic pHs, the tendency to give flash rusting was surprisingly very much reduced.¹¹ In formulating such an acid paint, it was found that the nature and purity of the pigments utilized should be chosen with care so that the optimum paint pH of 4–5 was obtained; basic pigments or pigments containing basic impurities were found to cause the paint pH to rise above 5, with a consequent increase in the tendency to give flash rusting.

The effect of the block copolymer surfactant, introduced to ensure stability of the acid paint, is clearly of importance. The effect of this surfactant on the latex particle coalescence process and on film permeability was studied as an important part of this work.

EXPERIMENTAL

Electron Microscopy

Latex films were cast on to clean mica sheets using a Sheen film applicator. The films were allowed to dry for the stated period of time in a dust proof cabinet at 25°C. The films were then shadowed at an angle of 45° with a gold/palladium heated wire in an Edwards E12 evaporation unit. The shadowed film was then replicated by carbon deposition in the evaporation unit at 10^{-4} – 10^{-5} torr to give a carbon coating of 400–500 Å. The pre-shadowed and carbon coated film was placed in a petri dish containing THF to dissolve the polymer, allowing the carbon raft to float to the surface. After several THF washings to completely remove the polymer, the carbon replicas were mounted on specimen grids and examined by transmission electron microscopy.

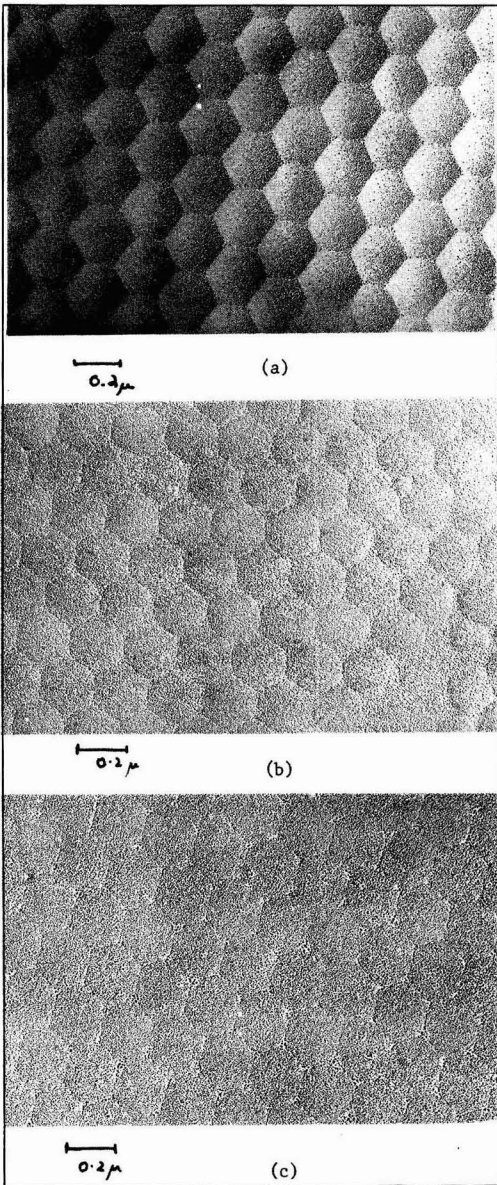


Figure 5—Transmission electron micrographs of preshadowed replicas showing the effect of drying time of chlorine-containing vinyl acrylic latex films: (a) 4 hours, (b) 6 days, and (c) 9 days

Water Vapor Permeability

Films were cast on glass at 25°C from latex containing 0.6% methyl vinyl ether/maleic anhydride copolymer as a thickener. Measurements were made on detached films at 38°C/90% RH according to BS 3177.

Panel Preparation

Latex and paint films were cast on to 6" × 4" degreased mild steel Pyrene test panels using an applicator bar. The films were dried for 24 hours at 25°C and 50% RH between coats and for a further seven days after application of the final coat. Particular attention was given to preparing pinhole free films since this is critical to AC impedance measurements. The preferred technique was to apply four coats to minimize the risk of pinholing. Total dry film thickness was measured using an Elcometer eddy current thickness meter.

AC Impedance Technique

After coating the test panel, a 1.6 mm diameter copper wire was soft soldered to a bare patch provided on the top of the panel to serve as an electrical connection. Both faces of the panel were then heavily waxed with the exception of a selected area of 5 cm² or 25 cm² of the paint film. The waxed panel was then immersed in a large screened tank containing 3% NaCl at room temperature. The panel was mounted parallel to a standard bare mild steel panel (separation 2") which served as a counter electrode in the two electrode cell. The much larger area of the bare mild steel panel ensured that the measured impedance of the cell was virtually that of the high impedance paint panel.

AC impedance measurements were made using the set up shown in Figure 1 using a Frequency Responses Analyser (FRA), Solartron Model 1174. The FRA was used with a sinusoidal output of between 10 to 100 mV (rms) and a frequency sweep between 10 KHz to 100 mHz. The logarithmic frequency sweep was initiated at 10 KHz. This ensured that the shorter duration higher frequency measurements were not influenced by mass transfer processes associated with the longer duration lower frequency measurements. The electrical circuit for the measurements on the two electrode cell is shown in Figure 2. The cell was coupled in series to a decade resistance box R_s which acted as a multiplier on the measured impedance $|Z|$ which can be expressed in terms of a real (a) and an imaginary (bj) component using standard complex number notation. These components were given directly by the FRA. The data was obtained in the form of a, bj, $|Z|$, $\log Z$, ϕ , and $\log f$, where ϕ is phase angle and f the frequency. Software allowed the data to be analyzed and plotted in the form of Nyquist (a vs bj) or Bode ($\log f$ vs $\log Z$) diagrams; or to be modeled in terms of a Randles¹² equivalent circuit, i.e., parallel resistance R, series resistance R_n , parallel capacitance C_p , and Warburg Impedance W (Figure 3).

The AC impedance data was used in three different forms to assess and compare the performance of the coatings:

(1) Nyquist impedance diagrams, i.e., plots of a vs bj over the frequency range 10 KHz to 100 mHz.

(2) The film resistance R. For Nyquist impedance diagrams of a semicircular nature and responding like a parallel RC circuit with time constant < 3.2 sec, the film resistance R value was readily determined from extrapolation of the impedance diagram to the value on the real

(a) axis at low frequencies (*Figure 4*). For impedance diagrams showing limited circular behavior, i.e., high resistance film ($R > 10^8 \text{ ohm/cm}^2$) typical of films upon initial exposure, the films were modeled using in-house prepared software based upon a Randles type equivalent circuit in order to determine the film resistance R .

(3) Capacitance C was calculated from the imaginary component (b_j) of the cell impedance at 1 KHz. For an RC circuit it can be shown that:

$$b = \frac{\omega CR^2}{1 + \omega^2 R^2 C^2}$$

where $\omega = 2\pi f$. The value of b approaches $\frac{1}{\omega C}$ as f approaches 1 KHz, allowing the capacitance C to be calculated.

RESULTS AND DISCUSSION

Effect of Block Copolymer Surfactant On Latex Coalescence

The nonionic block copolymer surfactant was introduced to ensure stability of the acidic paint. Its effect on the film forming properties of a chlorine-containing vinyl acrylic latex was studied by electron microscopy, AC impedance, and a distilled water soak technique. In all cases, 0.2% of hydroxy propyl methyl cellulose was added to the latex to ensure good application properties. *Figure 5* shows the very gradual coalescence of the latex at room temperature over a period of time. Even after nine days the coalescence of the latex can be seen to be incomplete since the identity of the separate latex particles can still be distinguished. Vanderhoff¹³ described this process as "further gradual coalescence." *Figure 6* illustrates a far greater extent of coalescence after nine days when 1% block copolymer surfactant was added to the latex before the film was cast. The effect of the addition of the surfactant on film coalescence is even more dramatically revealed in *Figure 7* which shows the condition of the film after only four hours drying. At a concentration of 3% nonionic surfactant, the coalescence appears to be essentially complete after four hours (*Figure 7c*). Close inspection of the micrograph of the sample containing 5% nonionic surfactants (*Figure 7d*) shows the appearance of surface exudations similar to those previously reported by Vanderhoff¹³ who attributed the effect to exudation of the surfactant to the film surface. Evidence was obtained to support this explanation by measuring the adsorption isotherm of nonionic surfactant on to the latex particle surface (*Figure 8*) which clearly shows that at total surfactant concentrations of <3% there was little surfactant present in the aqueous phase (i.e., mainly adsorbed on to the particle surface). Whereas, when the surfactant concentration was increased to 4%, all the additional surfactant was present in the aqueous phase of the latex. For the sample containing 3% surfactant (*Figure 7c*), exudations on the surface of the film can just be discerned, which is consistent with the small proportion of surfactant present in the aqueous phase

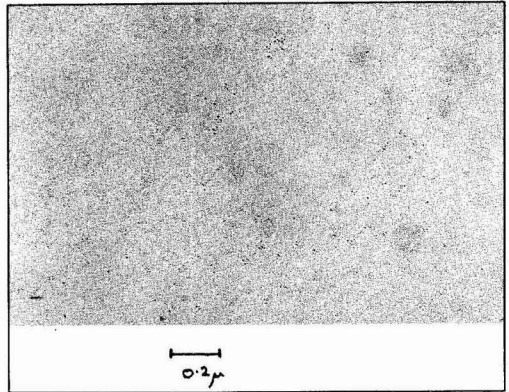


Figure 6—Transmission electron micrograph of preshadowed replica of chlorine-containing vinyl acrylic latex film containing 1% block copolymer surfactant and dried for 9 days

of the latex (*Figure 8*). The results therefore suggest that it was only that surfactant which was present in the aqueous phase of the latex which was exuded to the surface of the final film during the four-hour drying period. Whereas, surfactant which was adsorbed on to the latex particles was not exuded to the surface of the

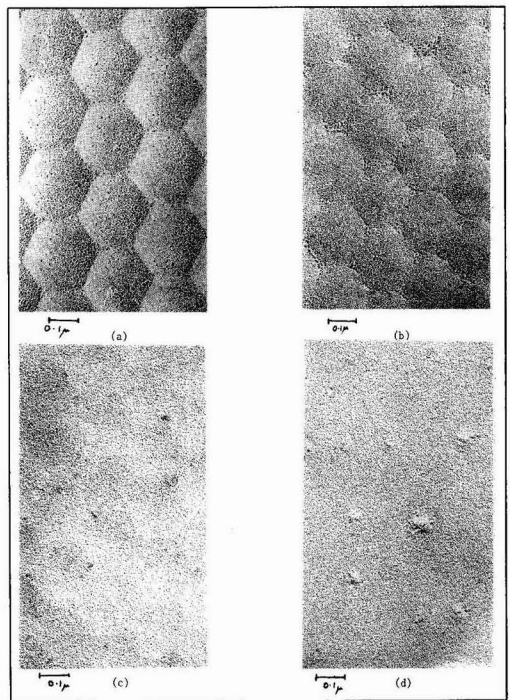


Figure 7—Transmission electron micrographs of preshadowed replicas of latex films showing the effect of the block copolymer surfactant concentration after four hours drying: (a) 0%, (b) 1%, (c) 3%, and (d) 5%

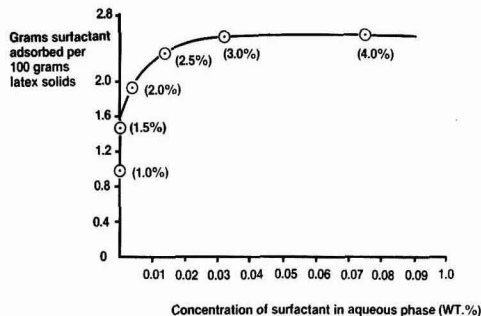


Figure 8—Adsorption of block copolymer surfactant on to the chlorine containing vinyl acrylic latex. The figure in parenthesis is the total weight of added surfactant expressed as a weight percentage of the total latex solid weight

film over this same time scale. The most important of the results was the pronounced increase in the rate of coalescence with increasing nonionic surfactant concentration.

Latex samples containing different proportions of added nonionic surfactant were cast on to mild steel test panels in two coats to give a total dry film thickness of 60 μm , dried for eight days at 25°C/50% relative humidity, immersed in distilled water for seven days, and then inspected. It was observed that the surfactant-free film exhibited water blushing, i.e., a white haze was present in the film which was presumed to be due to the effects of water penetration. This water blushing effect was found to decrease progressively as the surfactant concentration was increased progressively in the range 0–3%; in the latter case (i.e., 3%) blushing was virtually absent. A further increase in surfactant concentrations to 4% reintroduced the water blushing effect, although to a much smaller extent than was obtained in the surfactant-free film. These results are consistent with the finding of improved coalescence with increasing surfactant concentrations given by electron microscopy (Figure 7).

AC impedance measurements were performed on similar coated mild steel test panels to those used for the water blushing work. The coated panels (dry film thickness = 60 μm , exposed area = 25 cm^2) were immersed in 3% sodium chloride solution. It was found that in all four cases the capacitance increased with increasing immersion time. Such an increase in capacitance has been reported by other workers who have attributed the capacitance increase to the presence of water in the film, with a consequent increase in dielectric constant. Brasher and Kingsbury¹⁴ derived an expression for calculating the water uptake of coatings from capacitance data. Their expression involved the assumption that the water within the coating is both random and uniform, although as Leidheiser² points out, water penetration into a coating will take place by some form of diffusion process. Hence, this assumption is unlikely to be strictly valid. However, Brasher and Nurse¹⁵ found reasonable agreement between water uptake calculated from capacitance measurements and determined gravimetrically, provided

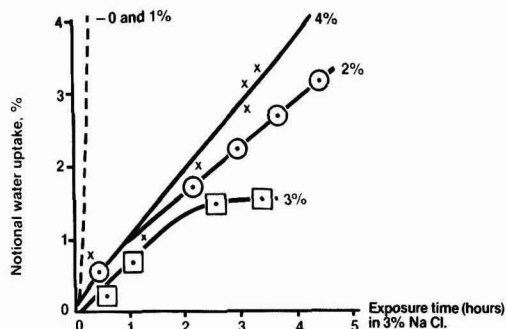


Figure 9—Notional water uptake as a function of percentage added block copolymer surfactant for a chlorine-containing vinyl acrylic latex film

that the water uptake was small. Therefore, Brasher and Kingsbury's expression was used to calculate what we term the "notional water uptake" as a function of immersion time.

The notional water uptake during immersion calculated from capacitance data (Figure 9) was found to decrease dramatically as the surfactant concentration was increased in the range 0–3%. Thus, the water uptake results followed exactly the same pattern as the water blushing observations, and confirmed the increase in the rate of coalescence of the latex particles caused by the introduction of the block copolymer surfactant. At a concentration of 3% surfactant the film properties were at optimum. At the higher concentration of 4% surfactant both capacitance measurements and water blushing observations showed that there was a deterioration from the optimum. This deterioration corresponded to the presence of surfactant in the aqueous phase of the latex. The electron micrographs suggest at least a proportion of this excess surfactant was exuded to the film surface. The capacitance and water blushing results suggested a proportion of the excess surfactant was also retained within the well coalesced film, where it gave rise to an increase in water penetration.

Even when the electron micrograph of the latex film indicated good coalescence, as for example in Figure 6 which shows the film containing 1% surfactant after nine days drying, the coalescence process could be far from complete. This is evidenced by the finding that for films dried for approximately the same period of time a further increase in surfactant concentration gave a significantly lower capacitance change (Figure 9) and smaller extent of water blushing. Thus, the AC impedance derived measurement of the capacitance of immersed films represented a more sensitive indication of the extent of the later stages of film coalescence than did electron microscopy. One contributory reason for this situation is probably that the electron microscopy technique reflected only the extent of coalescence at the surface of the film, while coalescence in the interior of the film may have been less complete.

The addition of the surfactant was, of course, not essential for the achievement of a high degree of particle

Table 1—Effect of Surfactant on the Tensile Properties Of Dry Films of Chlorine-Containing Vinyl Acrylic Latex Films

% Added Surfactant ^a	Tensile Modulus kg/cm ²	Yield Stress kg/cm ²	Ultimate Tensile Stress kg/cm ²	Extensibility %	MFT °C
0	3.6	13	33	710	15 ± 2
1	2.6	16.5	19	1250	16 ± 2
2.5	1.7	4	11	1400	16 ± 2
4	1.6	3	6	>1500	16 ± 2

(a) Expressed as a percentage of the latex solids.

coalescence since introduction of coalescing solvent or increasing the drying time or drying temperature had a similar effect. The main significance of the results was that the presence of the surfactant accelerated coalescence and, provided its concentration did not exceed surface coverage of the latex particles, did not have a deleterious effect on the rate and extent of water uptake. This conclusion is supported by earlier work in our laboratory⁸ which showed that the water vapor permeability of a detached film, obtained by casting latex containing 3% added block copolymer surfactant, was very close to that of the corresponding solvent cast, surfactant-free polymer film.

The large increase in the rate of coalescence of the latex polymer caused by the post addition of the nonionic surfactant is thought to be attributable to a plasticization of the polymer by the surfactant. Tensile measurements on dry latex films which had been dried for seven days after casting (Table 1) showed a pronounced physical softening, as manifested by an increase in extension to break, and a decrease in modulus, yield stress, and ultimate tensile stress.

Interestingly, the block copolymer surfactant did not significantly affect the minimum film forming temperatures (MFT) of the latex. Although the surfactant was strongly plasticizing in the dry polymer film and during the late stages of latex coalescence when water is essentially absent, it was not plasticizing during the early coalescence period of the MFT measurement when water is present. It is postulated here that the reason for this observation is that in the aqueous latex the polyethylene oxide chain in the nonionic surfactant was strongly hydrated and hence was unlikely to be polymer compatible, explaining the unchanged MFT. On the other hand, in the dry polymer film, the polyethylene oxide will lose its water of hydration, and, hence, change its polymer compatibility characteristics, the evidence being that, from glass transition temperature measurements on solvent cast systems, the surfactant became polymer compatible in the absence of water. Evidence that it was the polyethylene oxide component of the nonionic surfactant which was polymer compatible was provided by the observation that pure polyethylene oxide was also capable of plasticizing the dry polymer.

Table 2—Comparison of Latex Types and Latex Properties

Hard Monomer	Soft Monomer	Water Vapor Permeability g/25μ/m ² /day	Film Resistance (ohm/5 cm ²)			
			Initial	1 hour	1 day	14 days
Methyl methacrylate	Butyl acrylate	1270	5 × 10 ⁸	8 × 10 ⁷	2 × 10 ⁵	*
Acrylonitrile	Butyl acrylate	1290	> 10 ⁹	7 × 10 ⁴	*	*
Vinyl chloride	Vinylidene chloride + acrylate	11	> 10 ⁹	> 10 ⁹	> 10 ⁹	> 10 ⁹

(a) Film resistance had fallen to <10⁴ ohm/5 cm² with visible corrosion of the panel.

Comparison of Latex Types

Virtually all latex polymers currently sold as anti-corrosive paint binders contain as at least one of the principal comonomers an ester of acrylic or methacrylic acid. Examples of two of the currently available latex types are listed in Table 2 along with that of a chlorine-containing vinyl acrylic copolymer which contained vinylidene chloride and vinyl chloride.

It can be seen that the water vapor permeability (WVP) of the chlorine-containing vinyl acrylic latex was approximately 100-fold lower than that of the acrylate ester based latexes. Since the WVP measurement was performed at 38°C, (i.e., about 20°C above the MFT of the latexes involved) it was presumed that in all cases the films were well coalesced.

The AC impedance technique was used to establish whether there was a similar difference in water uptake when the films were applied to a mild steel substrate and immersed in 3% brine. In view of the results given in the previous section, the chlorine-containing vinyl acrylic latex was stabilized with block polymer surfactant (3% on latex solids) to ensure good coalescence after the seven-day drying period. The other latexes were tested in the already surfactant stabilized form in which they are sold for the preparation of air drying paints. In all cases, 0.2% hydroxy propyl methyl cellulose (on latex solids) was added to the latex to ensure good application properties. The film was applied in four coats to reduce the risk of pinholes with a No. 7 Mayer bar to give a total dry film thickness of 115 μm. The total area exposed by the waxing process was 5 cm².

In this case, the equation of Brasher and Kingsbury¹⁴ was not used to calculate water uptake from capacitance measurements because the assumption of random and uniform water uptake was considered to be invalid for the large extent of water uptake obtained for the acrylic latexes. Thus, the results were expressed as capacitance vs time plots (Figure 10); these plots being used as a nonquantitative measure of water uptake. It can be seen from Figure 10 that the rate and extent of capacitance increase was considerably less for the chlorine-containing vinyl acrylic latex film than for the acrylic-based latexes, as had been anticipated from the water vapor permeabil-

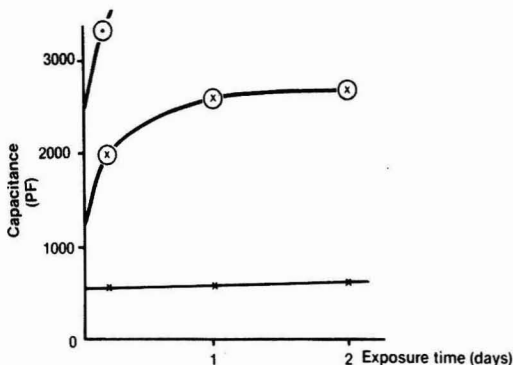


Figure 10—Capacitance as a function of exposure time in 3% NaCl for latex films. x—chlorine-containing vinyl acrylic latex; X—methacrylate-butyl acrylate latex; and •—acrylonitrile-butyl acrylate latex. Exposed area = 5cm²

ity measurements (Table 2). The far greater capacitance increase for the acrylonitrile-butyl acrylate latex than for the methyl methacrylate-butyl acrylate latex, despite their very similar water vapor permeabilities, was presumably due to failure of the former latex to coalesce perfectly under the drying conditions employed during the panel coating operation (25°C), despite the presence of surfactant. On the other hand, the temperature at which the water vapor permeability was measured (38°C) would ensure coalescence in all cases.

The influence of the chlorine content of the polymer is demonstrated in Figure 11 which shows a lower rate and extent of capacitance increase during immersion for the copolymer having the higher chlorine content. This result is consistent with the water vapor permeability measurements previously reported⁸ which showed a progressive decrease in water vapor permeability with increasing chlorine content for a set of detached films which had been cast from solvent.

The variation in resistance with time for the various latex films is included in Table 2. The results show a rapid loss of resistance for the two acrylate ester based films from an initially high resistance. The fall of resistance was the precursor to the onset of corrosion of the panel which could be readily seen through the clear film. On the other hand, the chlorine-containing vinyl acrylic copolymer retained a very high resistance (>10⁹ ohm) with no detectable decrease throughout the period of the test (14 days) and with no visible change in the condition of the substrate. A similar conclusion regarding the superior protective properties of high resistance coatings has been reported in a number of previous publications.¹⁶⁻¹⁸

By way of comparison with a more conventional accelerated test method, duplicate metal panels similar to those used in the AC impedance tests were subjected to 1000 hours of continuous salt spray performed under the conditions laid down in BS 3900 Part F4:1968. Since the films were transparent the condition of the substrate could be readily seen. The acrylic ester based latex films were seriously blistered and the underlying panels were

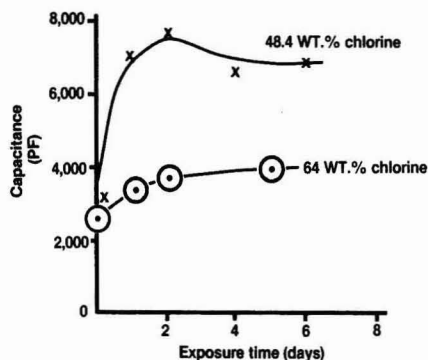


Figure 11—Capacitance as a function of exposure time—effect of chlorine content of latex polymer. Exposed area = 25cm²

extensively corroded, whereas the chlorine-containing vinyl acrylic latex film was found to be remarkably intact with very little underfilm corrosion (Figure 12).

It is interesting to note that the capacitance, resistance, and salt spray measurements used to compare the protective properties of the various latex films were in agreement in showing the chlorine-containing vinyl acrylic copolymer to be substantially more effective than the acrylic-based copolymers. The capacitance measurements, which indicate water uptake by the film, and the resistance measurements, which indicate ion ingress into the film, had the advantage that they detected at an earlier stage the deterioration which was eventually observed over longer time scales in the salt spray test. This early indication of deterioration by AC impedance measurements is an important advantage of this technique.

Performance of Paints

The results obtained for latex films showed that well coalesced chlorine-containing vinyl acrylic latex films gave highly water-impermeable films which were capable of giving remarkably good protection of steel. However, it has been reported that one effect for formulating latex into paint is to change its water and oxygen permeability.¹⁹ It was therefore necessary to establish whether the good performance of the latex films could be translated into corresponding advantages in a practical paint. The results given in previous sections showed that the block copolymer surfactant, introduced in order to ensure colloid stability of the latex and pigment components of the acidic chlorine-containing vinyl acrylic latex paint, would ensure a high degree of latex particle coalescence in the paint after the seven-day drying period employed in this work, especially as the paint formulation (Appendix) also contained a small proportion of coalescing solvent.

In each case, the formulation used was a proprietary air drying anticorrosive primer formulation for the polymer in question.

To minimize the risk of pinholes, the paints were each tested as a four coat system of total dry film thickness

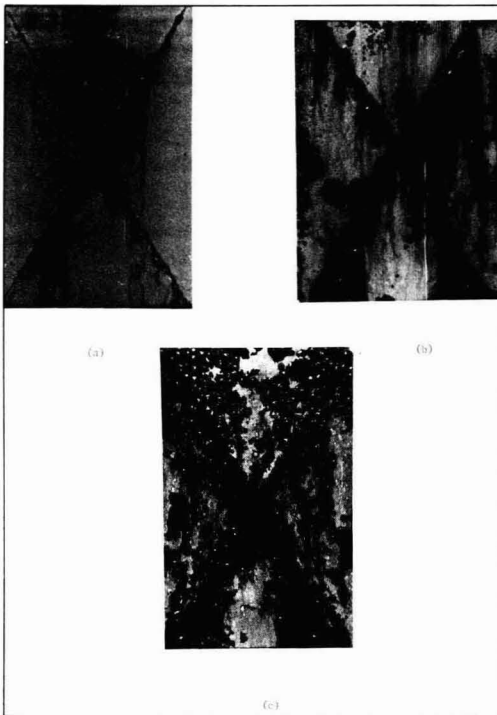


Figure 12—1000 hour salt spray results on simple thickened latex coatings: (a) chlorine-containing vinyl acrylic latex; (b) methyl methacrylate-butyl acrylate latex; and (c) acrylonitrile-butyl acrylate latex

140 μm using an exposed area of 5 cm^2 . The Nyquist impedance behavior was measured periodically (Figure 13). The measurements on the chlorinated rubber and the chlorine-containing vinyl acrylic based paints indicated these two systems to be the most protective of those tested. The Nyquist impedance diagram for the chlorinated rubber system showed little change over three days exposure and exhibited behavior consistent with a highly protective film, i.e., large values for a and b relating to an equivalent RC circuit with a large film resistance (R) value $> 10^9$ ohms. The chlorine-containing vinyl acrylic paint film showed slightly more curvature and only slightly decreased film resistance of the order of 6×10^8 ohm after three days of immersion.

In comparison to these two films which maintained a high value of resistance after three days of immersion, the alkyd paint, although having an initially high resistance ($R > 10^9$ ohm), underwent a fall off in performance after only one hour of immersion as depicted by the small semi-circular behavior from which a film resistance R value of 2.5×10^8 ohm was derived. After one day of exposure the resistance had fallen to 4×10^6 ohm. After three days, the Nyquist impedance diagram developed a "tail" at low frequencies, indicating Warburg impedance or the existence of a diffusion process within the film as major ingress of ions occurred. Small blisters

Table 3—Summary of Primer Paints Tested

System	Paint Type	Polymer Type	pH	PVC %
1	Latex	Chlorine-containing vinyl acrylic	5	20
2	Latex	Methyl methacrylate/butyl acrylate	9	20
3	Latex	Methyl methacrylate/butyl acrylate	9	30
4	Latex	Methyl methacrylate/butyl acrylate	9	40
5	Solvent-borne	Chlorinated rubber	—	35
6	Solvent-borne	Alkyd	—	40

were also observed at this stage. In contrast, the chlorinated rubber and chlorine-containing vinyl acrylic based coatings showed no visible signs of deterioration or significant change in impedance properties after 10 days.

The two paint coatings based on the methyl methacrylate/butyl acrylate copolymer, and having PVCs of 20% and 30%, behaved very similarly to each other, and deteriorated more quickly than the systems described above (Figure 13). Within one hour the resistance of the films was $< 2 \times 10^7$ ohms. A substantial Warburg "tail" was present after three days, by which time the resistance had decreased to a value of the order of 10^4 ohms. Micro blistering was observed after three days, although the impedance data had changed significantly after the earlier time of one day.

Paint system 4, also based on a copolymer of methyl methacrylate and butyl acrylate, proved to be interesting in that it demonstrated the AC impedance behavior of a very poor protective coating (Figure 13), presumably due to its high PVC of 40%. It was consistently found that even after a very early period of approximately 10 minutes of immersion the values of a and b were extremely low ($\sim 10^3$ ohms), with a linear Nyquist plot of approximately 45° slope. Thus, in effect, the diffusion tail dominated the behavior of the system, with no part of the semi-circle being within the test frequency range. This behavior is consistent with a high ingress of ions into the coating.

The Nyquist impedance behavior described above differentiated clearly between the performance of the various paint formulations. The capacitance behavior of the painted panels during immersion is shown in Figure 14. It can be seen that all the paint films had a similar initial value of capacitance in the region of 300–500 pF. However, the capacitance increase during immersion differentiated between the systems and gave an identical order of performance to that discussed above from the Nyquist plots, with the rate of capacitance increase being in the order acrylic copolymer (systems 2, 3, 4) $>$ alkyd (system 6) $>$ chlorine-containing vinyl acrylic (system 1) $>$ chlorinated rubber (system 5).

Outdoor exposure results have recently been published⁸ for paint systems 1, 2, 3, and 6. For this outdoor exposure testing, panel preparation differed slightly from that used for AC impedance measurements in that the

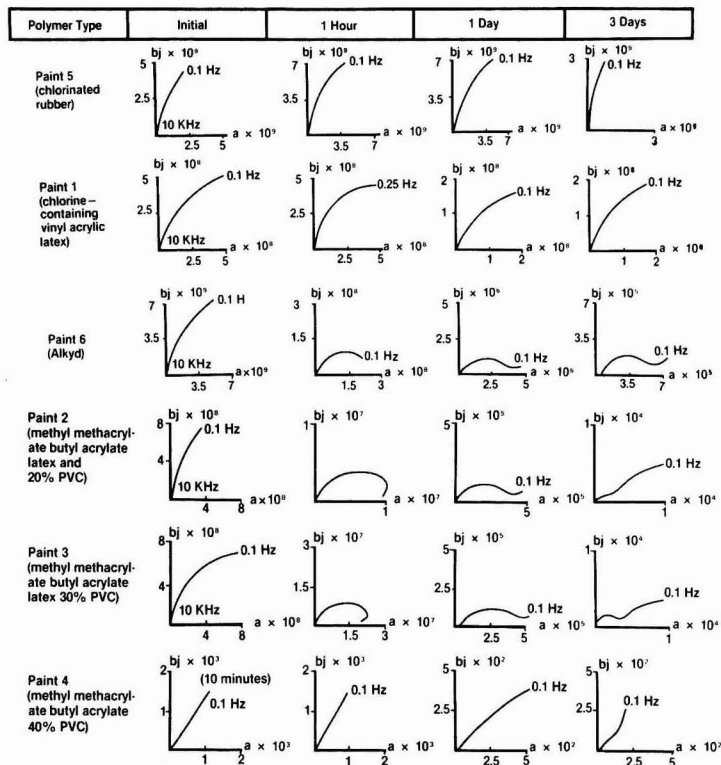


Figure 13—Nyquist impedance diagrams for paint films on mild steel after various periods of exposure in 3% NaCl. a and bj values are expressed in ohms for exposed area of 5cm²

primer paints listed in Table 3 were brush applied to blast cleaned steel in two coats, each giving a dry film thickness of 30 μm. For each system, the primer was overcoated with a corresponding white top-coat based on the same latex polymer utilized in the preparation of the primer, the top-coat being applied by brush in two coats, each giving a dry film thickness of 30 μm. Thus, the total dry film thickness of 120 μm was very similar to that used in the AC impedance tests. At each of the three exposure sites (coastal, industrial, and rural) the two paints based on a conventional acrylic latex copolymer (paints 2 and 3) had deteriorated significantly. Neither paint 1 (chlorine-containing vinyl acrylic) nor paint 6 (alkyd) had deteriorated after the period of exposure of 1.5 years, although the prediction from the AC impedance results was that the latter system would deteriorate more rapidly than the former over longer time scales.

Identical panels to those used for the AC impedance measurements were scored with a cross cut and subjected to a standard salt spray test conducted according to ASTM B117-75. The panels were examined after 500 hours immersion and rated according to ASTM D714-56. Results are shown in Table 4.

The salt spray results on the various systems can be seen to rank the paints in the same order of performance as the AC impedance Nyquist plots and capacitance data. Taking together the outdoor exposure, AC impedance, and salt spray results, it can be concluded that when the

chlorine-containing polymers were formulated into optimized paint systems the low permeability characteristics of this class of polymeric binder were highly advantageous in terms of corrosion protection. The rate of uptake of water and ions was considerably lower than was the case for comparable paint systems based on more permeable polymeric binders, and the coatings retained their protective properties for considerably longer periods of time.

From the AC impedance data on the various coatings studied, it is clear that the shape and magnitude of the Nyquist impedance plots allow the changing performance of paint films to be examined. The deterioration of a paint film falls clearly into five characteristic Nyquist impedance diagrams, as illustrated in Figure 16. Stage I is an impedance diagram of little curvature with large impedance values (> 10⁹ ohm) which changes to a curved plot in Stage II as ions ingress the film and R falls to 10⁹ ohm. Further deterioration (Stage III) yields a reasonably shaped semi-circle with R now of the order of 10⁷ ohm. In Stage IV, the impedance plot develops a "tail" due to the presence of Warburg impedances through the operation of rate controlling diffusion processes in the film with R values now of the order of 10⁶ ohm. Finally, in Stage V the impedance diagram has low impedance values (< 10⁴ ohm) and is often linear with a slope of 45° relating to complete control by diffusion (Warburg) related processes. Physical defects in the film can often be observed at this stage.

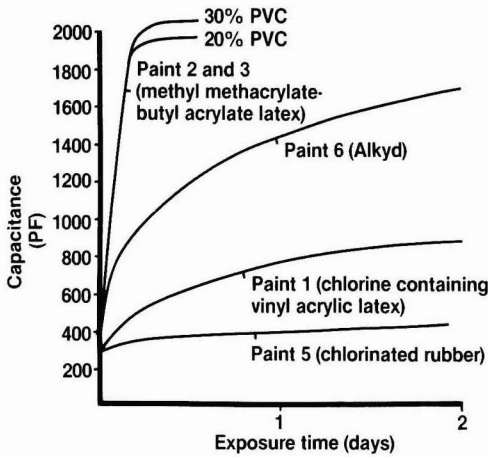


Figure 14—Capacitance vs exposure time in 3% NaCl for various paint systems. Exposed area = 5cm²

It was found that the observance of these characteristic curves is highly dependent upon the absence of insidious pinholes.²⁰ Even very small fractional areas of bare metal due to such features can produce completely overriding results because of their much smaller RC characteristics. This will be discussed in a future paper. An inadequately prepared film (i.e., pinholed) immediately exhibited a Stage V impedance diagram, whereas a well prepared nonpinholed film exhibited a Stage I or Stage II behavior immediately on immersion. Thus, in practice, it was always clear whether panel preparation for the AC impedance measurements was satisfactory.

Comparison of Latex and Paint

Figure 15 compares the capacitance behavior of a 15% PVC paint based on the chlorine-containing vinyl acrylic latex and the corresponding well integrated film cast from the latex itself. The results show a greater rate and extent of capacitance increase during immersion for the paint when compared to the corresponding latex, presumably reflecting the influence of the pigments in the paint.

From the impedance measurements on latex and paints, it would be anticipated that the chlorine-containing vinyl acrylic latex would exhibit even better anticorrosive performance as an unpigmented latex film than as a paint film. The salt spray results supported the excellent performance of unpigmented latex films, while a range of tests demonstrated the good anticorrosive properties of a derived paint. It was anticipated that there could be applications for which the performance of unpigmented clear films could be usefully exploited, but, in general, it was considered that a carefully formulated paint, such as that described in the Appendix, is to be preferred. The reason not least being because its better mechanical properties provide superior protection from corrosion arising from mechanical damage, better

Table 4—Salt Spray Performance of Paints

Paint System	Polymer Type	Paint Type	Paint PVC	Blister Rating	Comments
1	Chlorine-containing vinyl acrylic	Latex	20	None	
2	Methyl methacrylate/butyl acrylate	Latex	20	4D	No rusting from blisters
3	Methyl methacrylate/butyl acrylate	Latex	30	2D	No rusting from blisters
4	Methyl methacrylate/butyl acrylate	Latex	40	2D	Severe rusting from blisters
5	Chlorinated rubber	Solvent	35	None	
6	Alkyd	Solvent	40	None	Severe lifting of film

hiding power, superior film build, and a surprisingly low tendency to flash rust.

It is likely that the mechanism of protection in the unpigmented latex film differs somewhat from that in the corresponding paint. Despite the exceptionally low water vapor permeability of the chlorine-containing vinyl acrylic copolymer film, it is considered unlikely that the mechanism of protection is one of directly polarizing the cathodic reaction by limiting access of water to the cathodic sites on the steel surface. This conclusion is based on a simple comparison between the measured water vapor permeability of the unpigmented polymer film (Table 2) and data quoted by Corti and Fernandez-Prins²¹ on water consumption during corrosion of steel in various environments. This comparison shows that the film cannot act as a sufficiently effective barrier to water permeation to prevent corrosion. It is far more likely that the protective properties of the unpigmented latex film were attributable to the high value of film resistance maintained during exposure which would limit corrosion by providing a high resistance between anodic and cathodic sites on the steel surface. This high resistance was in turn attributable to the low penetration of water and ions into the film.

The impedance measurements showed that the paint based on the chlorine-containing vinyl acrylic latex was more susceptible to the penetration of water and ions than the latex itself, although the paint was still remarkably resistant to ingress by these species when compared to the other paint systems tested. It is likely that in the case of the paint coating, protection was provided only in part by the high film resistance mechanism, with a further contribution from the presence of the anticorrosive pigment.

SUMMARY

Chlorine-containing vinyl acrylic latex polymers based on vinylidene chloride and vinyl chloride as the principal monomers were shown to exhibit a low water vapor permeability. AC impedance measurements showed such polymers to exhibit low water uptake when cast on to a mild steel substrate. As expected, both water vapor permeability and water uptake decreased with increasing chlorine content of the polymer.

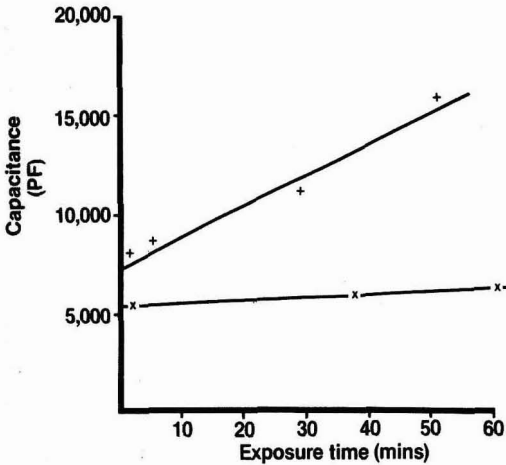


Figure 15—Capacitance as a function of exposure time in 3% NaCl. x—chlorine-containing vinyl acrylic latex film + 3% block copolymer surfactant; +—paint based on chlorine-containing vinyl acrylic latex. Exposed area = 25cm²

It was found that latex films which exhibited such low water uptake were only obtained when the degree of particle coalescence was high. Both the AC impedance technique and electron microscopy showed that the addition of a block copolymer surfactant of the ethylene oxide-propylene oxide-ethylene oxide type significantly increased the rate and extent of particle coalescence of a chlorine-containing vinyl acrylic latex film and decreased the water uptake of films dried for seven days at 25°C in the absence of coalescing solvent. This increase in coalescence was shown to be due to plasticization of the latex polymer by the surfactant in the absence, but not in the presence, of water. The AC impedance measurement of the capacitance change proved to give a more sensitive indication of the degree of coalescence during the later stages of coalescence than did electron microscopy.

The increase in rate of particle coalescence with increasing surfactant concentration and the corresponding decrease in water uptake was only observed at surfactant concentrations up to surface coverage of the latex particles. At higher surfactant concentrations, the excess surfactant present in the latex aqueous phase caused both an increase in water uptake and an exudation of surfactant to the coating surface. The addition of the block copolymer surfactant, however, was not essential for obtaining a high degree of coalescence, since addition of coalescing solvent or increasing the drying time/temperature has a similar effect. The significant point is that the addition of surfactant, provided that it was not present at a concentration exceeding surface coverage and provided that it was compatible with the latex polymer, ensured good coalescence and gave a film with good permeability characteristics and low water uptake.

Typical acrylic ester based latex copolymers of the type currently used for the preparation of anticorrosive paints gave films with a 100-fold greater water vapor permea-

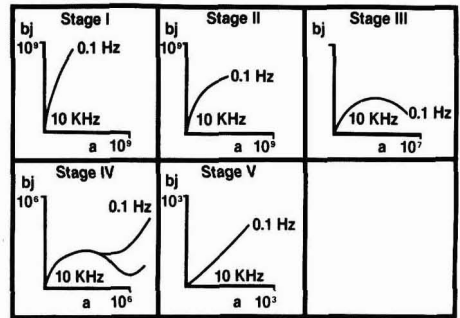


Figure 16—Five stages of impedance behavior during deterioration

bility than a chlorine-containing vinyl acrylic latex. When coated on to a mild steel substrate, these copolymers showed a far greater rate of water and ion penetration as assessed by AC impedance tests, and a far lower degree of protection as assessed by AC impedance, salt spray, and water immersion tests.

A chlorine-containing vinyl acrylic latex was formulated into a primer at a pH of 5 to eliminate dehydrochlorination reactions which take place at a more alkaline pH. The presence of both block copolymer surfactant and coalescing solvent in the paint ensured good coalescence of the latex particles. AC impedance and salt spray tests were conducted on mild steel panels coated with this acidic paint. The system was compared to more conventional acrylic ester based anticorrosive latex paints and to two selected solvent-borne paints. Formulation of the chlorine-containing vinyl acrylic latex into a paint significantly increased the rate and extent of water penetration into the coating as assessed from the capacitance change during immersion. Nevertheless, paints based both on the chlorine-containing latex and on chlorinated rubber showed both an appreciably lower rate of capacitance increase and a lower rate of resistance decrease during immersion in 3% sodium chloride solution than did an alkyd paint and a number of conventional acrylic ester based anticorrosion latex paints. Corresponding salt spray tests confirmed the much higher level of protection afforded by the paints based on the two chlorine-containing polymers, while outdoor exposure results demonstrated the superior performance of the chlorine-containing vinyl acrylic latex paint compared to paints based on conventional acrylic latexes.

The Nyquist plots obtained from AC impedance measurements during immersion of test panels gave a rapid and very sensitive indication of the deterioration of the various paint systems, and provided a quantitative tool for assessing and ranking the performance of coatings on a metal surface. The deterioration of the coatings were found to pass through a series of stages each characterized by its own distinctive Nyquist plot. For example, in the first stage the impedance diagram had little

curvature and corresponded to a high impedance value. The plot then became curved due to the ingress of ions into the coating; film resistance fell progressively until rate controlling diffusion processes were apparent and the film had a very low impedance.

The assessment from the AC impedance studies was generally in line with more traditional performance tests such as outdoor exposure and salt spray. The assessment by AC impedance, however, could be made sooner and gave a much clearer quantitative picture.

It should be emphasized, however, that AC impedance cannot replace practical exposure testing. The information given by AC impedance can complement exposure testing by rapidly giving information which allows the deterioration processes to be better understood and, hence, serve as an aid to formulation design.

Notwithstanding the increase in water penetration found on formulating a polymer into a practical paint, the results obtained in this work clearly show that highly water impermeable chlorine-containing polymers, whether they be solvent-borne or water-borne, were excellent binders for the preparation of anticorrosive paints with good performance in various tests. More permeable polymeric binders were found to give paints with inferior protective properties. The paints based on the chlorine-containing polymer binders exhibited a smaller change in capacitance and resistance during exposure than the other coatings tested, and it is likely that they owe their excellent protective properties to a lower rate of ingress of water and ions into the coating.

ACKNOWLEDGMENTS

The authors wish to acknowledge R. Satgurunathan and S. Champaneri for much of the experimental work, R. Oldman for supervising the electron microscopy,

D. Caldwell for his contribution to the paint formulation development, A. J. Burgess for his part in the work on polymer synthesis, and Miss C. C. Taylor (ICI Paints Div.) for refinements to the panel waxing procedure and for discussions on AC impedance.

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APPENDIX

PRIMER FORMULATION BASED ON CHLORINE-CONTAINING VINYL ACRYLIC LATEX

Ingredient	% w/w
Chlorine-containing vinyl acrylic latex ^a	59.7
Synperonic PE39/70 (30% w/w solution) ^b	3.1
Methocel J12MS ^c	0.2
Zinc phosphate PZ40 ^d	5.8
Micronized barytes	15.6
Micronized red iron oxide	2.6
'Bevaloid' 642 ^e	0.2
Butyl Ethoxol ^f	2.0
Water	10.8

PVC	20%
Volume solids	44%
pH	5
Viscosity	2 poise (180 s ⁻¹)

- Chlorine-containing vinyl acrylic binder (60% solids)—Haloflex 202 —ICI UK
- Synperonic PE39/70 stabilizer/dispersant —ICI UK
- Methocel J12MS—thickener —Dow Corning, USA
- Zinc phosphate PZ40 —Société Des Couleurs Zincique, France
- Bevaloid 642—defoamer —Bevaloid Ltd, UK
- Butyl Ethoxol—coalescing solvent —ICI UK



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Chemicals



Characterization Of Pigment Volume Concentration Effects in Latex Paints

W.J. Culhane, D.T. Smith, and C.P. Chiang
The Sherwin-Williams Company*

The relationship of the pigment volume concentration to the critical pigment volume concentration in latex paint films is characterized by traditional and new methods. Calculated and empirical critical pigment volume concentration determinations are shown to yield consistent results. Gloss, scrub resistance, staining and observed T_g of the films are correlated with scanning electron microscope observations for samples formulated over an extreme range of pigment volume concentrations. New insights into the role of the pigment/latex ratio are provided.

INTRODUCTION

The importance of the pigment volume concentration (PVC) on a paint's properties was first shown by Calbeck¹ over a half century ago. Since then PVC has provided a basis for explaining a wide range of optical, mechanical, and physical test results. The introduction of the critical pigment volume concentration (CPVC) concept² greatly enhanced the usefulness of these models. Several *a priori* empirical methods of determining CPVC have been reported.³⁻⁵

The PVC at which the void volume of the packed pigment is just filled with the polymer vehicle is defined as the CPVC. Bierwagen, *et al.*⁶⁻⁸ developed a method for calculating a theoretical CPVC from a paint's pigment composition. In that method, particle size distribution of the pigments and extenders (including oil adsorption) is considered and the void volume at closest random packing of these ingredients is calculated. It is convenient to characterize paints by the ratio between PVC and the theoretical CPVC, Λ . Many basic properties of paints can be correlated to these Λ values.

One of the objectives of the present paper is to provide a systematic picture on how the experimental gloss, scrub resistance, and paint porosity data depend on Λ values, so that the empirical and calculated CPVC determinations can be compellingly tied together.

Another objective of this paper is to complement the customary experimental methodology of studying the effects of PVC and CPVC, that is Λ . Dynamic mechanical analysis (DMA) data show that the observed glass transition temperature (T_g) of the polymer present in the paint film is shifted due to interactions with pigments. The magnitude of this effect is studied below and above $\Lambda = 1$.

The experimentally observed variation of physical measurements with increasing Λ can be mechanistically explained from studying the microstructure of the paint films by scanning electron microscopy (SEM). An additional objective of this paper is to go beyond the previous studies which have used SEM⁹⁻¹¹ to examine the effects of PVC and to correlate the physical property variations to the microstructure of the films.

EXPERIMENTAL

Eight latex paints were prepared with calculated Λ values ranging from zero to 1.54. The Λ calculations were carried out in a manner similar to that described by Bierwagen and co-workers.⁶⁻⁸ Table 1 shows the compositions of two premixes, each having 37% volume solids, which were used for blending the paints described in Table 2. These vinyl acrylic latex paints have compositions simulating commercial flat latex paints.

The paints were applied with an automatic drawdown machine and dried for at least one week under ambient conditions. Since the volume fraction solids of the samples were alike, the differences between the total film thickness and void thickness was constant. For gloss and scrub resistance smooth black Mylar® substrates were used. All drawdowns were applied with a 5 mil bar. No pigment flocculation was evident in any of the resulting films. The excellent dispersion can be seen in the SEM photomicrographs of Figure 2.

Presented by Mr. Culhane at the 60th Annual Meeting of the Federation of Societies for Coatings Technology in Washington, D.C., November 3, 1982.

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Table 1—Composition of Premixes

Latex Premix	Weight (grams)
Wallpol 40-136® VA Latex (Reichhold)	2000
Texanol® (Eastman)	108
Natrosol® H4BR HEC (Hercules)	10
2315 Defoamer (Nalco)	6
Water	915
Pigment Premix	
TiPure R-940® TiO ₂ Slurry (DuPont)	1090
Optiwhite-P® Clay (Burgess)	500
Emtalc® 41 Talc (Englehard)	450
Silica 1240 (Illinois Mineral)	450
Natrosol® H4BR HEC (Hercules)	20
AMP-95® (Commercial Solvent)	18
Trinton N-57® (Rohm and Haas)	18
Ammonium Hydroxide, Reagent Grade (Fisher Scientific)	13
Ethylene Glycol, Industrial Grade (Union Carbide)	5
2315 Defoamer (Nalco)	5
Proxel GLX® Biocide (ICI America)	2.5
Water	1040

Table 2—Latex Paint Compositions

Sample	Pigment Mix (g)	Latex Mix (g)	Calculated Δ
1	0	500	0.00
2	240	292	0.60
3	350	266	0.80
4	400	242	0.90
5	400	191	1.00
6	500	148	1.20
7	500	83	1.40
8	500	50	1.54

The 60° gloss values were measured with a Hunter D48D Glossmeter and the values reported are an average of four individual readings. The range of the individual readings was 0.2 units for each sample except sample 1. For sample 1 the range was 0.5 units. The scrub resistance was measured by a slight modification of ASTM test D2486-74a (tap water was used to presoak the brush, not a 1% detergent solution). This test is not meaningfully applicable to the unpigmented sample due to difficulty in determining the end point.

For the Gilsonite stain test a coated panel was placed in a near vertical position and a 5% solution of Gilsonite stain in naphtha was brushed over the paint on the white section of a Morest chart. The stain was left for 10 seconds and then rinsed off with naphtha applied from a squirt bottle. After drying for one hour the Y value (CIE,

1931, 2° observer, illuminant c) was measured and the drop in reflectance (DIR) percentage was calculated.

A DuPont Model 981 dynamic mechanical analyzer (DMA) was used to study viscoelastic properties. The principle and operation of DMA is described elsewhere.¹² An aluminum coupon with a thickness of seven mil was used as a sample support. The aluminum (0.5" × 0.75") with the dried latex paint film was clamped in a configuration perpendicular to the top of the furnace. The instrument was operated at an A/Z gain (voltage stability) of 40% and an oscillation amplitude of 0.2 millimeters. The experiment was run with a temperature range of -120°C to 100°C in a nitrogen atmosphere. Resonance frequency and damping versus temperature were automatically recorded by a DuPont 1090 Thermal Analyzer. The onset of frequency is used for the determination of the glass transition temperature of the latex paints.

The SEM examination was done with a Cambridge Stereoscan 250. Both the surface and liquid nitrogen fractured cross-sections were sputter coated with gold. Details of sample preparation and the operation of the SEM as applied to paint films can be found in the literature.^{13,14} The areas chosen for illustrations were selected only after extensive scanning of the samples to ensure that representative data was obtained.

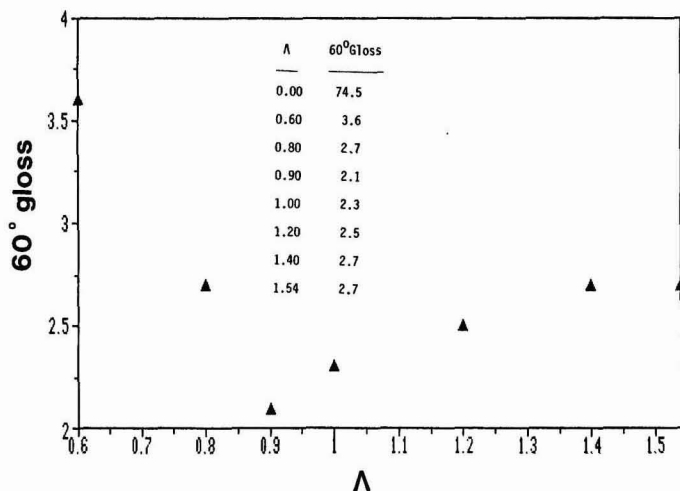


Figure 1—Effect of Δ on 60° gloss of latex paints

RESULTS AND DISCUSSION

Gloss

Variations of gloss with pigment concentration is a classical method of determining CPVC.² The advantages of this test include ease of measurement and the relative sharp definition of the critical point. The gloss of films pigmented exclusively with small particles (less than one micron in diameter) have been shown by several researchers to pass through a minimum near their CPVC¹⁵⁻¹⁷ while films pigmented with large particles (greater than one micron in diameter) have been described as reaching a minimum at the CPVC and remaining approximately constant at $\Lambda \geq 1$.^{17,19} Studies of systems pigmented exclusively with TiO₂ have shown some deviation from this behavior near the CPVC but the anomalies have been ascribed to the high refractive index of the pigment.²⁰⁻²³

Zorll,²⁴ discussing high gloss paints, has stated the following: "The pigment-free layer features a smooth surface and therefore a very high gloss. A slight degree of pigmentation will then produce some distortion of the surface, owing to some pigment particles just beneath it. The result is a decrease in gloss. When the pigmentation is increased further, the number of scattering sites becomes much greater, but their effective size diminishes drastically. This is the reason for the observed stronger scattering at shorter wavelengths. If the scattering sites become so closely crowded that their size is much smaller than the wavelength, the effect to be observed visually is comparatively small, and an increase in gloss can again occur." In a later paper, Funke and Zorll²⁵ proposed the existence of a thin layer of binder covering the pigment tops in high Λ paints, although no evidence of this layer was seen in their electron photomicrographs of paint film cross-sections.

Samples 2-8 are representative of most commercial flat paints in that they contain both small (TiO₂) and large (clay, talc) particles. An explanation similar to

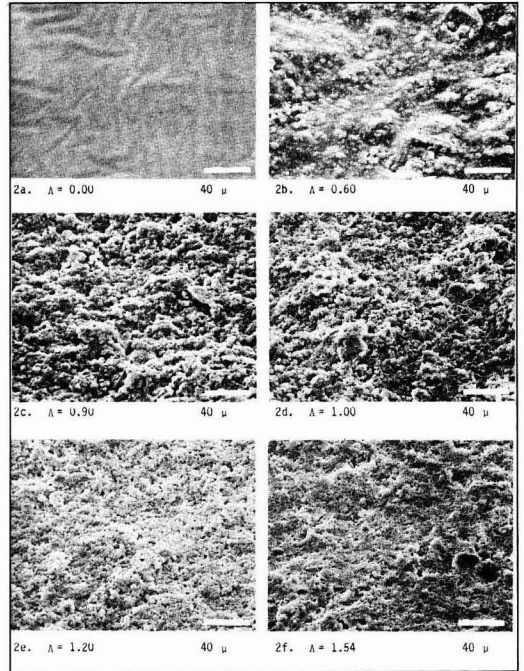
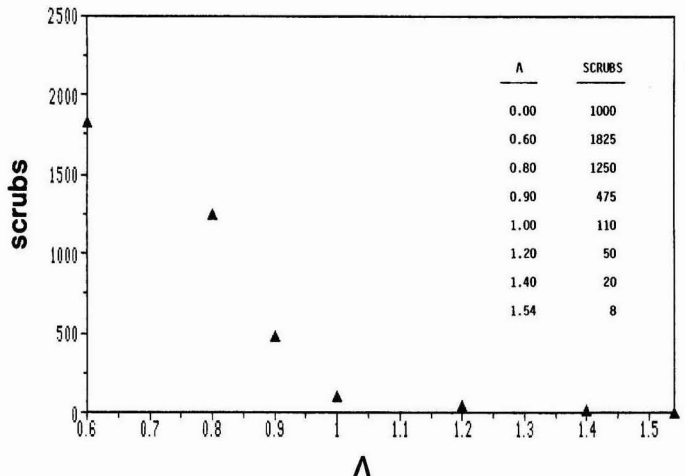


Figure 2—SEM photomicrographs of paint surfaces

Zorll's could be used to describe their gloss behavior. The gloss reaches a minimum at $\Lambda = 0.90$ (Figure 1), a fact which can be explained by viewing the films' surfaces with the SEM. Paints with a $\Lambda \leq 0.80$ exhibit a continuous layer of latex which covers all the pigment and provides a relatively smooth surface (Figures 2a and 2b). A smooth surface allows for maximum reflection at the specular angle, hence gloss. Paints near the CPVC do not possess a smooth surface (Figures 2c and 2d). The change from a

Figure 3—Effect of Λ on the scrub resistance of the latex paints



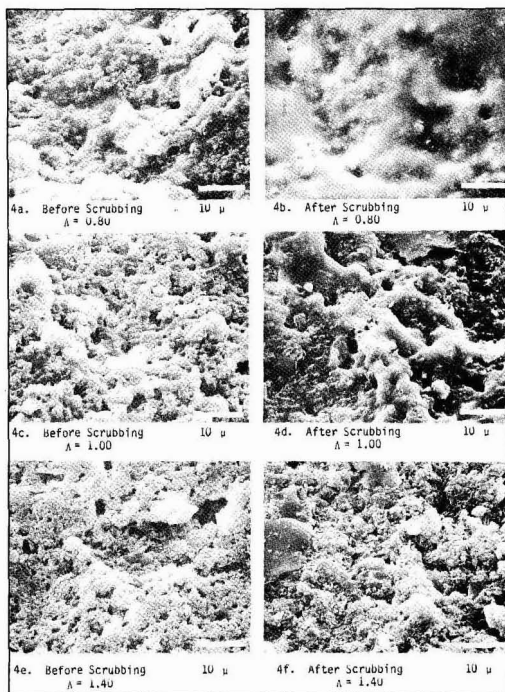


Figure 4—SEM photomicrographs of paint surfaces before and after scrubbing

smooth to a rough surface is dramatic enough that Colling, et al.,²⁶ in studying acrylic and alkyd systems below the CPVC, were able to use a spectrogoniometer to actually measure the increase in surface peak height as the PVC was increased in their samples.

Paints with a $\Lambda \geq 1.2$ (Figures 2e and 2f) lack sufficient latex to engulf the pigment particles or even bind the particles together in craggy chunks and produce films consisting of individual particles “glued together” by the

latex. An uneven surface exists but the magnitude of the peaks and valleys caused by the single particles is often too small to reduce specular reflection at visible wavelengths of light. Instead, an effectively smooth surface results and the films have a higher gloss than those formulated at the CPVC.

Scrub Resistance

Though individual scrub ratings are subject to some error,²⁷ the plot of scrub resistance versus PVC has been shown to change slope in the region of $\Lambda = 1$.^{17,18} This test has been used to determine CPVC. Figure 3 shows the scrub resistance of samples 2–8 versus calculated Λ values and, indeed, there is a change in slope at $\Lambda = 1$. Figure 3 thus goes beyond the present literature in that it proves that the slope change is at the predicted $\Lambda = 1$.

The literature does not give a mechanistic interpretation of the observed trends. Comparison of SEM pictures of paint surfaces before and after scrubbing, shown in Figure 4, may give some new insights. In paints with Λ below 1 the scrubbing action seems to pluck pigment particles from the exposed layer, leaving behind a smooth surface of latex to withstand the next pass of the brush. This phenomena can be seen in Figures 4a and 4b. In higher Λ paints the mechanism for film removal is quite different. Without a matrix of latex to protect and cement it in place, the particles can be uprooted at a rapid rate allowing the abrading bristles to progress rapidly through the film. This can be seen in Figures 4e and 4f. Not surprisingly, a paint with a calculated Λ of 1 exhibits a hybrid of these two mechanisms as shown in Figures 4c and 4d.

This result was surprising since it could have been expected that the pigment would play a more active role in low Λ paints, providing some protection for the latex. The predominant role of the latex helps to explain the general experience of this laboratory that in architectural paints the use of an abrasion resistant latex is usually more effective in improving wet scrub resistance than pigment substitution.

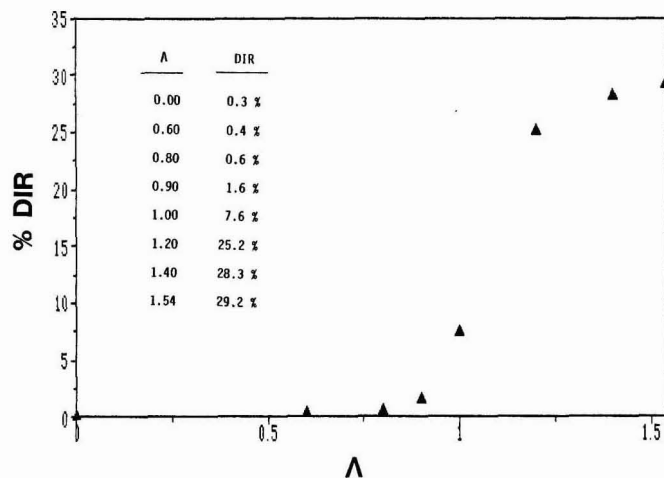


Figure 5—Effect of Λ on percent drop in reflectance caused by staining

Stain Test

Gilsonite stain tests provide a simple measure of film porosity. Results similar to those in *Figure 5* have been reported in the literature^{17,18,28} as a means of identifying CPVC. *Figure 5* shows the soundness of the experimental procedure in that it shows a well-defined inflection point near the calculated Λ of 1. By examining a fracture of the films with the SEM one can see the reason for this. Low Λ paints (*Figures 6a* and *6b*) show an absence of pores thus preventing the penetration of the stain medium. Without the pores the observed drop in reflectance after staining is very small. The appearance of a few voids at a Λ of 0.9 (*Figure 6c*) corresponds to the first significant stain retention. The presence of voids at this Λ is not a shortcoming of the calculations but a natural result of the film formation process in latex coatings.²⁹ The calculated CPVC is based upon the minimum amount of binder needed to fill the interstitial voids left by the closest random packing of the pigment. The likelihood that every latex particle would happen to fall in its optimum location is infinitesimally small, especially when one considers the force at work during film formation. The $\Lambda = 1.00$ sample (*Figure 6d*) shows a considerably higher pore density and a larger stain retention.

The films of high Λ paints (*Figures 6e* and *6f*) are a virtual maze of pores. The preponderance of voids in these high Λ paints is even greater than one might first realize since the sample fracture splits many voids and masks their original size. These pores provide ready passages which permit penetration of the stain and result in the sizeable drop in reflectance which is observed. At $\Lambda \geq 1.2$ there are so many passages available that the system is nearly saturated with stain and a shift toward higher PVC's has little effect on the test results.

Glass Transition Temperature

The glass transition temperature (T_g) is one of the most important parameters in polymer characterization and often determines the suitability of a vehicle for a given

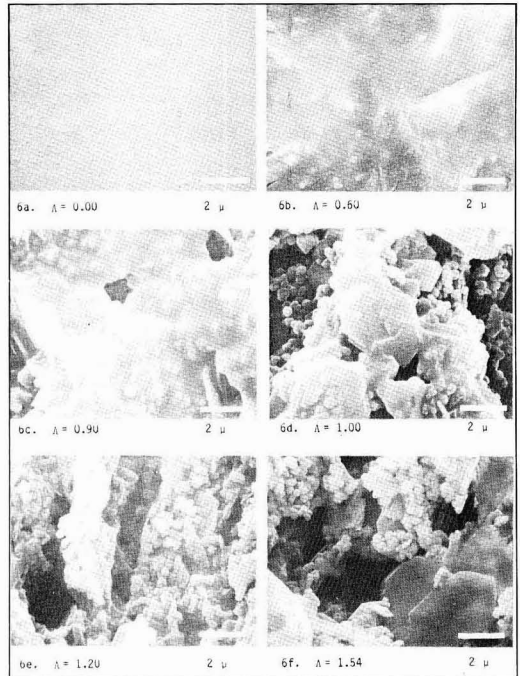
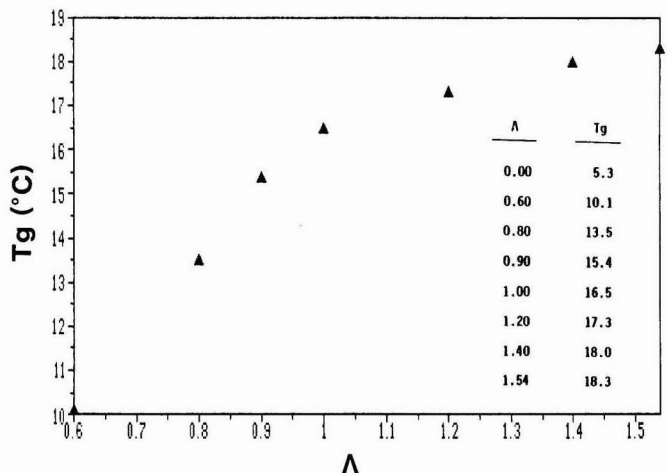


Figure 6—SEM photomicrographs of paint fractures cross-sections

application.³⁰ A polymer's T_g is the temperature above which its segments are relatively free to move about in a manner analogous to single molecules in a liquid. Below T_g the segments are "frozen in", much like a glass, with minimal vibrational amplitude. Sorption of polymer segments at a rigid surface changes the T_g if enough sorbed segments are present so that the ratio of attached to unattached segments is high.³¹ A recent review³² lists several papers which have shown that the PVC of a

Figure 7—Effect of Λ on the observed T_g shift of the latex paints



coating can affect its T_g . Others have suggested the observed behavior is due to physical bonding,³³ or a combination of physical and chemical bonds.³⁴ The literature contains no information on the T_g shift in latex paint films at PVC values above CPVC.

The data of Figure 7 show how the observed T_g is modified by the pigment loading. The slope of observed T_g versus PVC is greater for paints below a Λ of 1 than for paints above a Λ of 1. Although the overall increase in observed T_g with PVC was expected in view of the previous references, the change in slope was not. There is no obvious explanation for this transition though viewing the SEM photomicrographs gives some qualitative insights. In low Λ samples (Figures 6a and 6b) sorption of the latex polymer on the pigment can account for the change in observed T_g . Since the surface area of the pigment available for sorption increases proportionally with PVC, a linear relationship is observed. At about a Λ of 1 (Figures 6c and 6d) the incorporation of air voids into the film begins to mitigate the sorption effect. It is unknown whether the change in rate of observed T_g shift with PVC is due to an increased polymer/air interface area or if it is an anomaly of the testing procedure resulting from the discontinuity of the film caused by air voids. A third concept that would explain the mechanical behavior is to think of the air voids as a flexible filler. Modulus, T_g , and strength are functions of the matrix and fillers. Since air is "soft", it will mitigate the hardening effects of adsorption of the matrix material onto the pigment fillers. This is the essence of impact modification (though greatly over-simplified) and foam strength of brittle polymers (e.g., styrofoam).³⁵ For all of these theories it is clear, however, that in high Λ paints the quantity of air involved in the film increases (Figures 6e and 6f) and the modification of the observed T_g effect is maintained.

SUMMARY

A series of latex paints with varying pigment volume concentrations (PVC) are evaluated. The theoretical critical pigment volume concentration (CPVC) is calculated from first principles, based on close packing of the pigments and fillers whose particle size distribution is known. The calculated values are presented in terms of the ratio, $\Lambda = \text{PVC}/\text{CPVC}$. The variation of physical properties (gloss, scrub resistance, paint porosity) by the Gilsonite test and shift of observed glass transition temperature of the polymer with increasing Λ is shown to have a different pattern below and above calculated $\Lambda = 1$. This proves that the concept of CPVC based on conventional intuitive interpretation of the dependence of the experimentally determined properties on PVC has sound theoretical basis. Conversely, these results prove the validity of calculations of CPVC based on first principles. Additionally, new insights are provided on how PVC affects the properties of paint films. The shift in observed glass transition temperature shows how pigments and air voids change the physical structure of the polymer in the paint film at the molecular level. Scanning electron photomicrographs provide evidence as to the

changes in the morphology of the paint films when the pigment loading is increased.

ACKNOWLEDGMENTS

The authors wish to thank the Sherwin-Williams Company for its support and for permission to publish this work. We are also grateful to the many individuals at the Research Center who helped us, especially Dr. John Gardon, Mrs. Shirley Chandler, Dr. Robert Vance, and Mr. James Koesema.

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Popping of Water-Soluble Acrylic Coatings

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The tendency of water-soluble industrial baking enamels to show popping is a factor which significantly limits their commercial use in some applications. A test to determine the maximum film thickness of acrylic enamel which could be applied and cured under standardized conditions without popping was developed to compare various coatings. Glass transition temperature of the acrylic copolymer was found to correlate with popping. Critical film thickness decreased as glass transition temperature increased. The same trends were observed in solvent-reduced and water-reduced coatings. The critical film thickness was much thinner for water-reduced coatings. It was found that after initial losses, rate of volatile loss in a TGA furnace at 150°C decreased as T_g increased and was slower from water-reduced coatings than from 2-butoxyethanol-reduced coatings. Rate of temperature increase of the TGA samples from water-reduced coatings was slower than with 2-butoxyethanol-reduced coatings. The greater heat requirement to evaporate water may be a factor in the greater sensitivity to popping of the water-reduced coatings. Other factors which may affect popping are also discussed.

INTRODUCTION

While use of water-soluble baking enamels for industrial coatings has grown, popping has been identified as a problem which significantly limits this growth.^{1,2} Use of water-soluble topcoats for some applications is reported to have required adaptation of application conditions to minimize popping. Problems are generally most severe when relatively high film thicknesses are required on lines where flash-off time is limited. For example, for

automotive topcoats the changes included: humidity control of spray booths, longer spray booths with an increase in the number of spray applications, and longer ovens with lower temperature in the initial zones.³ Popping results from formation of bubbles within a drying film which expand with heat to form blisters retained by a partially rigid surface layer. Sometimes the blisters rupture leaving imperfections on the film surface. It has been stated that popping is more severe in water-soluble coatings than in solvent-borne coatings.⁴

The principal resins in water-soluble enamels are acrylic or polyester resins with an acid number in the range of 35–100 and with free hydroxyl groups. The polymer solutions in a cosolvent are partially neutralized with an amine and melamine-formaldehyde resins are used as crosslinkers. Pigment is dispersed into the vehicle system. The coating is diluted with water to application viscosity. At this stage, the coatings contain on the order of 20–25% polymer and 250–380 grams of volatile organic compounds per liter of coating excluding water. It has been established that the water-soluble polymers are not really soluble under these conditions but that aggregates, which are swollen by cosolvent and water, are formed.⁵

The greater severity of popping in water-soluble coatings has been attributed to a wide variety of factors: boiling of water in the film,^{3,6} high heat of vaporization of water,^{7,8} entrapped air,^{4,6–8} and loss of amine from the film surface⁹ have been specifically cited. In addition to the published work on popping, there have been many unpublished trial and error studies in industrial laboratories to overcome or minimize the problem. However, since substantial uncertainty about the causes of popping remained, this work was undertaken to attempt to gain a more basic understanding of the phenomenon.

EXPERIMENTAL

Copolymer Synthesis

Acrylic copolymers were prepared by free radical polymerization in 2-butoxyethanol under N_2 with 2,2'-azobisisobutyronitrile (AIBN) as initiator. The poly-

Presented by Dr. Wicks at the 60th Annual Meeting of the Federation of Societies for Coatings Technology in Washington, D.C., November 4, 1982.

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Table 1—Copolymer Compositions - Mole % (Wt %)

Copolymer	AA	HEMA	BA	MMA
1	12.4 (7.8)	8.8 (10.0)	54.8 (61.2)	24.0 (21.0)
2	12.1 (7.8)	8.6 (10.0)	45.1 (51.6)	34.2 (30.6)
3	11.8 (7.8)	8.4 (10.0)	34.7 (40.8)	45.1 (41.4)
4	11.5 (7.8)	8.2 (10.0)	25.3 (30.5)	55.0 (51.7)
5	11.3 (7.8)	8.0 (10.0)	18.1 (22.2)	62.6 (60.0)

merizations were carried out at 100°C in a four-neck one-liter breakaway flask fitted with agitator, thermometer, condenser, gas inlet, and a dropping funnel. For example, dropwise addition of a solution of acrylic acid (AA) (23.4 g; 0.32 mole), hydroxyethyl methacrylate (HEMA) (30.0 g; 0.23 mole), butyl acrylate (BA) (183.6 g; 1.43 mole), methyl methacrylate (MMA) (63.0 g; 0.63 mole) and AIBN (3.0 g; 0.018 mole) in 2-butoxyethanol (33.67 g; 0.28 mole) was carried out over 1.5 hr while maintaining the temperature at 100°C. The reflux condenser was replaced with a distillation condenser after the monomer addition and the temperature was held at 100°C for an additional hour to complete the polymerization and remove unreacted monomers.

This procedure was used to prepare a series of copolymers shown in Table 1.

Molecular weights were determined by gel permeation chromatography (GPC) using Waters ALC/GPC 501 Styragel columns of 10⁵, 10⁴, 10³, and 500 Å pore sizes with THF at a flow rate of 2 mL/min. Calibration was done with polystyrene standards. Nonvolatile contents were determined by weight loss of approximately one gram samples in aluminum dishes at 105°C under a vacuum of 67 Pa. Viscosities were determined with a Wells-Brookfield RVT cone and plate viscometer at 25° ± 0.05°C. Glass transition temperatures were determined using a du Pont 990 Thermal Analyzer with a differential scanning calorimetry (DSC) Cell Base Module II. Apparent T_g values with heating rates of 5, 10, and 20°/min were determined as the extrapolated onset of the transition and the data was extrapolated back to 0°C/min heating rate.¹⁰

Characteristics of the copolymers are given in Table 2.

Coatings Preparation

A typical formulation was as follows:

Acrylic resin solids	13.36
Cymel® 303 crosslinker	2.67
Tipure® R960 TiO ₂	14.32
Dimethylaminoethanol (DMAE)	1.11
p-Toluene sulfonic acid (p-TSA)	0.03
2-Butoxyethanol	8.68
Water	25.00
	65.17

The pigment was dispersed in the acrylic resin using a

Table 2—Copolymer Characteristics

Copolymer	Non-Volatile		Acid No.	T _g , °C
	Wt. %	\bar{M}_n		
1	81.6	15,600	53	-28
2	79.5	14,200	52	-13
3	78.6	14,000	55	-8
4	73.5	15,100	55	14
5	62.3	16,800	54	32

Dispensator high speed disperser. The PVC was 20%. Equal equivalents of DMAE and carboxylic acid were used. The coatings were reduced to 33.3% nonvolatile by volume (NVV) using 2-butoxyethanol or water. When water was used for reduction, the resulting weight ratio of water to 2-butoxyethanol was 74 to 26.

Popping Evaluation

Coatings were allowed to stand 24 hr without agitation before application. Films were drawn down on untreated cold rolled steel panels using wire-wound applicators. After a five minute flash-off time, the coated panels were placed in a Blue M Convection Oven (OV-490A-2) for 20 min at 150°C. Many panels were prepared with each coating with different dry film thicknesses from 5 μm to 120 μm. Film thicknesses were determined by General Electric Film Thickness Gauge. Panels were selected at 5 ± 1 μm intervals. Baked panels were inspected for popping. Popping increased as film thickness increased, the maximum film thickness that did not result in popping was recorded as the critical film thickness. All determinations were done in triplicate.

Weight Loss Studies

A duPont 990 Thermal Analyzer with a duPont 950 Thermogravimetric Analyzer (TGA) was used for solvent loss studies. A modified isothermal thermogravimetric technique¹¹ was used in which the TGA furnace was held at 150°C. Approximately 9 μL (11 mg) volumes of test samples with the same NVV were introduced into a flat bottom dish (diameter 0.6 cm) which was put in the instrument boat suspended from the horizontal balance beam. The sample and balance assembly were at 25°C when inserted into the 150°C furnace and measurements were started immediately. A nitrogen flow rate through the unit of 100 mL/hr was maintained. Both weight loss and temperature were recorded as a function of time. Since the thermocouple was not actually in the sample, the temperature readings could be somewhat higher than the actual temperature of the sample. Samples were inspected after the run. In a few cases, the coating had flowed to the edges of the dish during drying exposing the dish bottom. Data on these cases were discarded.

RESULTS AND DISCUSSION

Popping Test Method

In order to evaluate the effect of possible variables on popping, it was felt that a reproducible test was needed to

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Table 3—Copolymer Characteristics

Copolymer	\bar{M}_n	\bar{M}_w	Viscosity (poises) 50% Solutions	$T_g, ^\circ\text{C}$
1	15,600	51,800	19.4	-28
2	14,200	108,300	52.9	-13
3	14,000	64,600	22.7	-8
4	15,100	73,100	281.0	14
5	16,800	61,100	1,273.0	32

Table 4—Application Viscosities of Coatings

Copolymer	Viscosity (poises)	
	Water	Solvent
1	8.3	1.6
2	18.4	6.0
3	9.4	1.8
4	75.9	8.3
5	109.0	17.3

give a basis for numerical comparisons. While air entrapment has been shown to be a factor in popping, it was felt that, at least initially, it would be best to minimize this factor. Therefore, samples of coatings were not agitated for 24 hours before application and wire-wound draw-down bars were used to apply films. Applications were made during times when relative humidity was in the range of 48–52% and temperature was in the range of 22–25°C. After a five minute flash-off time, the coatings were placed in a convection oven for 20 minutes at 150°C. Panels with dry film thicknesses at intervals of $5 \pm 1 \mu\text{m}$ were selected for evaluation. All tests were run at least in triplicate. The maximum film thickness where no panels showed any popping was designated as being the "critical film thickness." This film thickness was reproducible. At the next higher film thickness, there were a relatively few pops per unit area. As film thickness increased further, the number of pops increased.

Catalyst concentration (p-toluene sulfonic acid, p-TSA) was varied from 0.1 to 1.25% of total resin solids. An increase in catalyst level resulted in increased film wrinkling as reported by others.¹² Wrinkling prevents accurate popping evaluation. The balance of the studies was done with 0.2% p-TSA, since it was the maximum concentration that gave no wrinkling within the film thickness range of interest.

Effect of Variables on Popping

Initially, a wide range of variables were evaluated. Popping increased as flash-off time was decreased. Water-reduced coatings consistently showed more popping than the same coatings reduced with 2-butoxyethanol. No correlation was observed between popping and application viscosity or nonvolatile volume content of the coatings. Unpigmented samples showed less popping than corresponding pigmented samples. Preliminary results indicated an increase in popping with a series of amines: triethanolamine < N,N-diethylaminoethanol < N,N-dimethylaminoethanol (DMAE). DMAE was used in all other studies.

Effects of other variables over the ranges tested were relatively small except for glass transition temperature of the copolymer. A pair of acrylic copolymers with comparable acid numbers and molecular weights but with different T_g 's gave coatings in which the higher T_g system showed a marked increase in popping. Since T_g had not been previously reported as being a factor influencing popping of water-soluble coatings, the primary goal of this research became to test the

hypothesis that copolymer T_g has a significant influence on popping in this type of system.

A series of five copolymers having 7.8 wt % acrylic acid (AA) and 10.0 wt % hydroxyethyl methacrylate (HEMA) with different percentages of butyl acrylate (BA) and methyl methacrylate (MMA) was made. The weight percent BA was varied from 61.2 to 22.2 while the weight percent of MMA was varied from 21.0 to 60.0 (composition of all copolymers is given in the experimental section). All copolymers had acid numbers between 52 and 55. The molecular weights (as determined by GPC), viscosities of 50 wt % solutions in 2-butoxyethanol determined at 25°C and a shear rate of 5 sec^{-1} , and T_g of solvent free copolymer (as determined by DSC) are given in Table 3.

In general, the viscosities of the copolymer solutions increase as T_g of the copolymers increase. This trend is in line with other observations and predictions.^{13,14} Copolymer 2 solution has a higher viscosity than copolymer 3 solution in spite of its lower T_g . Copolymer 2 is significantly higher in weight average molecular weight (\bar{M}_w) than the other copolymers. It has been reported that the viscosity of polymer solutions vary more nearly with \bar{M}_w instead of number average molecular weight (\bar{M}_n).

White coatings with and without water were formulated with each of the copolymers. A highly methylated highly methylolated melamine resin crosslinker was used at 20% by weight of polymer solids and rutile TiO_2 was dispersed into the acrylic copolymer. p-TSA (0.2% of total resin solids) was used as a catalyst and equal equivalents of DMAE to carboxylic acid were added. The coatings were diluted to 33.3% NVV with either 2-butoxyethanol or water. The water-reduced coatings had a 26/74 weight ratio of 2-butoxyethanol/water. Table 4 shows the viscosities of the coatings determined at 25°C and a shear rate of 5 sec^{-1} .

The critical film thicknesses for popping of the coatings are shown in Table 5. As can be seen, the film thickness which can be applied without having popping under the standard conditions decreases substantially as T_g of the copolymer increases. Also the film thickness which can be applied without popping with any one copolymer is substantially less with water-reduced systems than with solvent-reduced systems. (Film thickness greater than 120 μm was not evaluated). Popping might be expected to vary with viscosity. However, the viscosities of the coatings made with copolymer 2 are higher than the viscosities of the coatings made with copolymer 3, yet the popping of the water-reduced

Table 5—Critical Film Thickness for Popping

Copolymer	Copolymer T_g (°C)	Critical Dry Film Thickness (μm)	
		Water	Solvent
1	-28	50	≥ 120
2	-13	30	$\text{IV} \text{ } 70 < 95^a$
3	-8	20	$\text{IV} \text{ } 70 < 95^a$
4	14	10	55
5	32	5	25

(a) Did not show popping at 70 μm but did pop at next higher film thickness applied, 95 μm .

coatings of the higher T_g copolymer 3 is greater than with 2. The difference, if any, between the two solvent coatings from polymers 2 and 3 was not detected since neither gave popping at 70 μm and both gave popping at the next greater film thickness tested, 95 μm .

Air entrapment has been proposed as an important factor in popping.^{4,6-8,15} The results shown in Table 5 were obtained with draw-downs of samples which had not been agitated for 24 hr. When the coatings were stirred immediately before application, the amount of popping at any given dry film thickness increased but popping was still a function of T_g . Air could also be entrapped during spray application. Therefore, the water-reduced coatings made with copolymers 1 and 3 were also applied by spray after each was further reduced with water to 2.2 poises at 5 sec.⁻¹ These reduced coatings were also applied by draw-down. At a given dry film thickness, the spray applied coatings contained more pops per unit area than the corresponding draw-downs. However, the coating based on the higher T_g copolymer had a lower critical film thickness regardless of the application technique. Thus, air entrapment increased popping but popping remained a function of T_g . It should be noted that the difference in popping persisted despite the adjustment to equal application viscosity.

Volatile Loss

A possible reason for the relationship between copolymer T_g and popping is that T_g could affect the rate of solvent and water loss from the film. The relative rates of evaporation of water-cosolvent mixtures have been studied both in the absence and presence of polymers with 25°C air flowing over the samples and during spraying.¹⁶⁻¹⁹ We felt it would be desirable to study volatile loss under conditions more nearly approaching those encountered in baking a panel. The nearest approach available to us was to use a TGA while maintaining the furnace at a constant temperature of 150°C and constant nitrogen flow rate. As described in the experimental section, the dish containing the coating at 25°C was inserted into the furnace. Weight loss from the sample and temperature near the dish were followed with time. Such determinations were made with coatings of all five copolymers reduced with water and reduced with 2-butoxyethanol. As can be seen in Table 6, the volatile loss (expressed as a weight % of the initial volatile

Table 6—TGA Analyses of Initial Weight Loss Of Coatings When Room Temperature Coatings Are Put In 150° C TGA Furnace

Coating	Copolymer T_g °C	Volatile Loss, Weight % Time, sec	
		15	30
1S ^a	-28	0	3
1W ^a	-28	1	6
2S	-13	0	4
2W	-13	1	6
3S	-8	0	1
3W	-8	1	6
4S	14	0	3
4W	14	1	4
5S	32	0	3
5W	32	1	6

(a) S indicates reduced with 2-butoxyethanol, W indicates reduced with water.

present) in the first 30 seconds is independent of T_g and consistently greater from the water-reduced coatings than from the solvent-reduced coatings.

In the first stage of drying of a coating, solvent loss is independent of polymer and controlled by boundary layer resistance.^{20,21} T_g , thus, should not affect initial solvent loss. The more rapid weight loss from the water system is in accord with evaporation rates of water, 2-butoxyethanol and 2-butoxyethanol-water mixtures reported by McEwan.¹⁶

As weight loss continues, however, loss becomes less for water-reduced systems than for solvent-reduced systems and less for higher T_g polymer systems than for lower T_g polymer systems. The effects are shown graphically in Figures 1 and 2 for water-reduced and solvent-reduced coatings. (For clarity only data for coatings from copolymers 1, 3, and 5 are shown. Data for coatings from copolymers 2 and 4 were intermediate). Hansen, among others, has shown in many studies of solvent evaporation from films at room temperature that in the second stage of drying the rate controlling step becomes the rate of diffusion through the film rather than boundary layer resistance as in the first stage.^{20,21} It is clear that in these systems, similar changes occur. As T_g of the polymer increases, volatile retention at the transition from first stage to second stage drying increases. Similarly with any given T_g copolymer, water-reduced systems reach this transition with greater amounts of volatiles retained within the films. That is, diffusion control of solvent loss becomes rate controlling earlier as copolymer T_g increases and in water systems as compared with solvent systems.

While conditions in the TGA technique are not identical to those encountered when panels are baked in ovens, there is a clear correlation between the amount of volatiles retained in the film when second stage drying is reached in the TGA and popping of panels in the oven. Popping apparently does not occur during the early stages when volatile loss is boundary layer controlled and there is not a volatile gradient within the film. It apparently occurs in the second stage (or transition

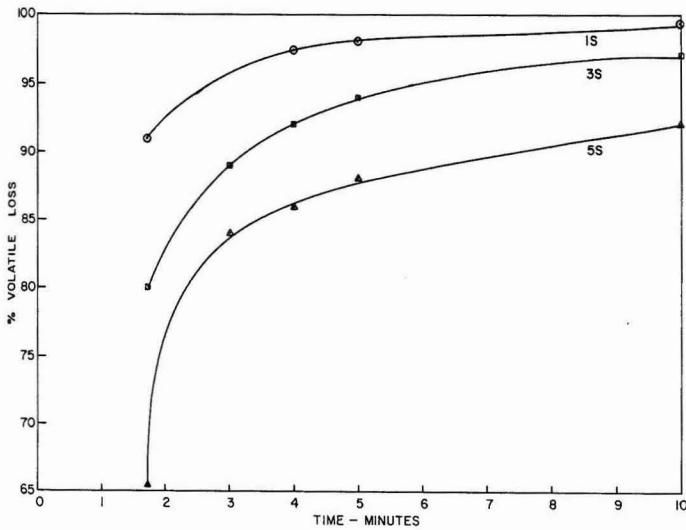


Figure 1—Weight loss expressed as percentage of total volatiles initially present from water-reduced coatings as a function of time. Samples at 25° C were put into a TGA furnace preheated at 150° C

between first and second stage), which is a condition where the top layer of the film contains essentially no volatiles, while volatiles are still present in the lower layers of the film.²⁰ This top layer would be expected to have rheological properties that could aid in bubble stabilization as well as prevent reflow once a bubble has ruptured.²² Since solvent loss during the diffusion stage becomes dependent on the square of the film thickness, the strong dependence of popping on film thickness is also consistent with the relation between popping and solvent retention at the transition to second stage of drying.

The relation between T_g of the copolymers and solvent and water diffusion rates presumably is due to differences in free volume. Free volume of polymers is related to $T-T_g$, the larger the difference, the greater the free

volume.²³ The diffusion rate would be related to the free volume of the drying films at the temperature at which popping occurs. Higher T_g copolymers would be expected to have lower free volumes at any given temperature above T_g and slower diffusion rates. The presence of water, cosolvent, amine, crosslinking agent, the degree of crosslinking reaction which has occurred, and pigment would also affect free volume in the film.

While the data show that volatile retention during second stage drying for any given T_g system is higher with water-cosolvent containing systems than cosolvent only systems, they do not provide any information as to the composition of the retained solvent.

One potential reason for increased volatile retention in the presence of water is the fact that water can lead to self condensation of the melamine resin.²⁴ This might

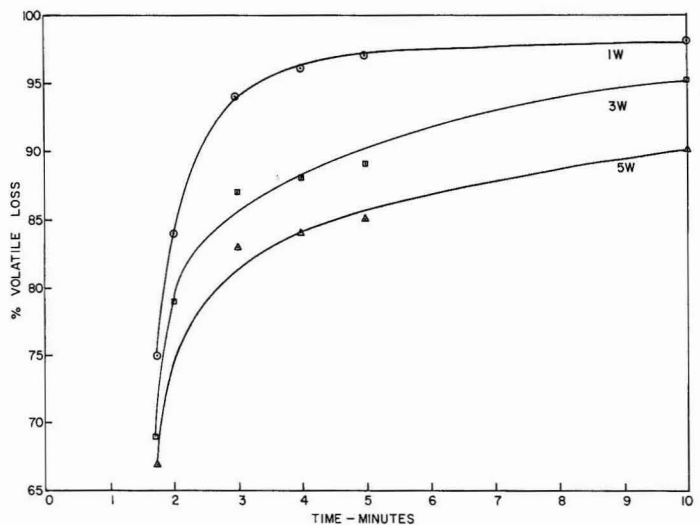


Figure 2—Weight loss expressed as percentage of total volatiles initially present from butoxyethanol-reduced coatings as a function of time. Samples at 25° C were put into a TGA furnace preheated to 150° C

Table 7—Evaporation of Solvents in TGA At 150°C Expressed as % Loss

	Time (Minutes)							
	0.5	0.75	1.00	1.25	1.50	1.75	2.00	2.50
2-Butoxyethanol .	2	4	14	30	52	76	99	—
Water	3	9	19	30	42	55	66	94*
26/74 Blend	4	11	20	33	48	62	78	99

(a) 99% after 2.6 min.

Table 8—Temperature During Solvent Evaporation in TGA at 150°C

	Time (Minutes)			
	0.75	1.0	1.25	1.5
2-Butoxyethanol	110	130	142	150
Water	107	125	135	140
26/74 Blend	102	122	135	142

result in greater crosslinking at the surface of the water containing films leading to earlier formation of a barrier. However, TGA analyses of corresponding systems not containing melamine resin showed the same general behavior as the complete coatings systems.

Another factor which may be important is the effect of volatile loss on the rate of temperature increase. All systems containing water increased in temperature more slowly than those not containing water. Since the thermocouple was not actually in the sample, the temperature differentials could have been somewhat greater than read. The heat capacity of water is higher than the heat capacity of 2-butoxyethanol and more importantly, the heat of vaporization of water is 2,260 J/g at its boiling point¹⁶ and that of 2-butoxyethanol is 373 J/g.²⁵ To demonstrate the possible effect of evaporative cooling, the same TGA conditions were used with 2-butoxyethanol, water, and a 26/74 solution of 2-butoxyethanol in water. The weight loss data are shown in Table 7. The water evaporates faster than 2-butoxyethanol at the early times and slower after 1.25 min. Also, initially the blend evaporates faster than either of the components, as has been previously reported at 25°C air temperature.¹⁶ After 0.75 min some cooling (that is slower heat rise) of the water and blend samples was observed relative to 2-butoxyethanol as shown in Table 8. As noted earlier, the thermocouple was not actually in the samples so the differences might be larger than recorded. Similar temperature differences were observed between cosolvent diluted and water diluted coatings systems. Thus, evaporative cooling appears to be at least one difference between solvent and water diluted systems.

Still another factor which may be related to slower weight loss when water is present is the possibility that water molecules may associate strongly with polar groups such as the salt groups. Hill and Lu have shown that water absorption by films from amine salts of similar acrylic copolymers is substantially greater than in the absence of salt groups.²⁶ Obviously, the conditions are drastically different from the conditions under which popping occurs but do illustrate the potential importance of this factor.

Consideration of the solvent loss behavior of these systems is made even more complex because, at least initially, the polymer is aggregated. It has been shown in a similar system that the aggregates are highly swollen by cosolvent and water.⁵ Furthermore, the cosolvent/water

ratio in the aggregates is higher than the average and in the external phase it is lower than the average. It was also demonstrated with a t-butanol/H₂O "solution" of an acrylic of this type that the cosolvent/water content of vapor was in equilibrium with the external phase with its lower t-butanol/H₂O ratio. Thus, early stages of evaporation would be from a lower cosolvent content system as compared to the total. Furthermore, as cosolvent/water ratio changes during evaporation, degree of swelling of aggregates and very possibly degree of aggregation change. Brandenburger and Hill have studied this phenomenon through the spraying and flash-off stage.¹⁷ Imai and Tsubouchi followed loss of water and solvent in baking systems but did not relate the results to morphology.¹ Morphology and changes in morphology may be important factors affecting relative rate of volatile loss in the water versus solvent-reduced systems but no obvious technique is available to study these effects. It should be pointed out that the changes in ratios of BA to MMA, made to change T_g , may also change the degree of aggregation of the polymer and the effect of changes in cosolvent/water ratio on the degree of aggregation and/or swelling of the aggregates with cosolvent and water.

Other Factors That May Affect T_g and Popping

The results of these experiments demonstrate that T_g of the copolymer is an important factor affecting popping. While in this case, the variation was made by changing the BA/MMA ratio, the effect of other monomers should also be investigated. There undoubtedly are limitations as to how great a change in copolymer T_g can be practically made because T_g is an important factor affecting many other properties such as viscosity, curing rate, hardness, flexibility, and permeability among others.

A preliminary experiment demonstrated that blending of compatible polymers with different T_g 's gives an intermediate critical film thickness for popping. The data are shown in Table 9.

As was noted earlier, pigmented films showed worse popping than unpigmented films. Few studies of the effect of pigmentation on T_g of polymers have been reported in the literature; increases, decreases, and no effect have been reported. TiO₂ has been shown to increase the T_g of poly(methyl methacrylate).²⁷ T_g 's of these copolymers containing rutile TiO₂ were determined. The data are given in Table 10. Pigmentation of

Table 9—Popping of Copolymers 1 and 3 And Their Blend

Copolymer	T _g	White Coatings Popping Critical Film Thickness
1	-28°C	50 μm
3	- 8	20
50% 1 - 50% 3		35

these copolymers does increase T_g. This could further affect the diffusion of volatiles out of the film. Also the physical effect of having part of the volume of the film occupied by pigment could be a factor in reducing diffusion of volatiles.

SUMMARY

Copolymer glass transition temperature was found to be a major factor affecting the popping tendency of water-reduced and solvent-reduced water-soluble acrylic enamel films. The water-reduced systems had a greater popping tendency than solvent-reduced systems. It is proposed that copolymer T_g affects free volume in the second stage of volatile evaporation. Free volume in turn would be expected to affect the rate of diffusion of volatiles out of the film.

Thermogravimetric analysis of the coatings showed that initially weight loss was higher for water diluted than solvent diluted systems and was independent of T_g. These results fit in with predictions based on first stage solvent loss from polymer films. However, as drying proceeded, weight loss became dependent on copolymer T_g; the higher the T_g, the lower the weight loss. Also in comparing water-reduced systems with solvent-reduced systems with the same T_g polymer, weight loss after the initial stages was slower from the water-reduced systems. These results parallel the results of critical film thickness for popping. It was observed that the rate of temperature increase measured when samples were put into the TGA furnace at 150°C was slower for the water diluted than for the 2-butoxyethanol diluted systems. Parallel results as to both temperature and evaporation times were obtained by following weight loss of water, 2-butoxyethanol, and a blend of 2-butoxyethanol and water. Thus, evaporative cooling may be a factor in slower weight loss from water-reduced systems and in popping.

It was shown that blending two water-soluble copolymers with different T_g's gave an intermediate degree of popping and that pigmentation with TiO₂ increases both T_g and popping tendency in this type of system.

T_g has been shown to be an important factor in popping. Use of this concept may be useful in reducing popping problems. Certainly other factors are also important. Very obviously, film thickness and flash-off time are critical as has been observed by many workers. Evaporative cooling appears to be one factor affecting volatile loss and hence popping. Other possible factors affecting water loss are identified. Air entrapment did increase popping but the T_g still had a significant effect even when air was entrapped in the coating.

Table 10—Effect of Pigmentation on T_g's of Copolymers

Copolymer	Copolymer	Pigmented Copolymer
1	-28°C	-12°C
2	-13	7
3	- 8	16
4	- 14	17
5	32	39

ACKNOWLEDGMENT

The financial support as well as use of instrumental facilities of The Sherwin-Williams Co. is gratefully acknowledged. We also thank Dr. Loren Hill for his help in the initial planning of the work and for his constructive criticisms of this paper.

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Society Meetings

BALTIMORE VIRGINIA SECTION

DEC.

"The Role of Paint and Color In Modern Design and Decorating"

Bonnie Seitz, of Larivey-Teichert, Inc., discussed "THE ROLE OF PAINT AND COLOR IN MODERN DESIGN AND DECORATING."

Augmented by collage board representations of blending different design and decorating materials such as carpet, paint, fabric, and wallcoverings, the presentation focused on the main color schemes. Ms. Seitz discussed the available tones and shades of decorating materials and pointed out their advantages and disadvantages in application uses.

MICHAEL J. BECKER, *Secretary*

BIRMINGHAM

DEC.

"Micronized Waxes and Wax Dispersions"

Past-President John Green presented the MMA Award plaque and check to Technical Committee Chairman John Hitchin in recognition for the society's production of the audio-visual program entitled, "Introduction to the Paint Industry."

Ralph Kochler, of G.M. Langer, spoke on "MICRONIZED WAXES AND WAX DISPERSIONS."

A short history was given by Mr. Kochler describing the difficulties in obtaining ultra-fine dispersions of the hard waxes used in coatings.

The micronizing process was explained by Mr. Kochler. He listed the general properties which are obtained from micronized wax in coating systems: high mar resistance and resistance to metal marking; resistance to polishing and unwanted gloss in matt and semi-matt finishes; silky and soft feel; good anti-blocking effect; improved slip and anti-scurf properties; prevention of hard sedimentation of silica gels; and high matting efficiency. According to Mr. Kochler, it is possible to produce these properties in a stir-in grade of wax by accurate control of particle size and size distribution.

Examples of the use of micronized waxes and wax dispersions as post additives to coatings in a range of applications including wood finishes,

powder coatings, paints, and printing inks were discussed.

Q. Does addition of wax affect recoatability and intercoat adhesion?

A. This depends on the binder and the level of addition, e.g., the addition of 1.5 - 2% wax to achieve 30-40% gloss will give intercoat adhesion problems, but a 2:1 silica:wax mixture will achieve the result without problems. Ten to 20% micronised wax on silica stops settlement without affecting intercoat adhesion.

Q. What wax:PTFE ratio is needed to bring the mixture to the surface?

A. Not too high. A special process prevents separation in the medium of a 90:10 mixture.

Q. What is the affect or cure temperature on the migration of wax to the surface?

A. This depends on wax type. For waxes melting at 106-118°C, problems will occur at cure temperatures greater than 180°C. To achieve higher temperature one can use 140° or 186°C melting point waxes, produced at 250°C.

Q. Does wax addition affect oxidation in air drying systems?

A. This is negligible at the addition levels needed.

Q. Is there any affect on clarity and sanding times in two pack finishes?

A. There is no affect on clarity. Amorphous amide type waxes are used to avoid extending times to reach sandibility.

Q. What is the maximum incorporation in solvent for a wax dispersion?

A. This depends on the solvents. Langers' standard dispersions are 20%, the absolute maximum is around 27-30%.

Q. Are there any storage problems with these types of waxes?

A. We have no low temperature figures. Figures are available at 30, 40, and 50°C.

Q. Can one prevent blocking in warm coatings without loss of gloss?

A. Yes. 0.1% of a PE/PTFE wax prevented blocking in a test while reducing gloss from 96% to 95%.

Q. Is it a good practice to incorporate waxes in systems needing exterior durability?

A. We have specialized in other fields and lack the data to answer the question.

DON H. CLEMENT, *Secretary*

C-D-I-C

DEC.

"Use and Abuse of Additives"

"SOME OBSERVATIONS ON THE USE AND ABUSE OF ADDITIVES" was presented by Marvin J. Schnall, of Troy Chemical Corp.

Mr. Schnall began by defining an additive as a powerful chemical, which, in small amounts, will substantially alter the properties of a paint. The additive should function as a part of the paint system and may interact with any of the other components. The additive may even react to variations of the same component such as a surface treated pigment or a broad range molecular weight vehicle. In order to avoid problems caused by unwanted interactions of this kind, Mr. Schnall suggested that additive suppliers should provide all relevant technical data to the paint chemist, point out all known possible problem areas, and provide continuing technical service to the customer. The paint chemist, in turn, has the responsibility to carefully study the data provided, thoroughly lab test the additive in the paint systems to be used, and, finally, make the decision of which additive to use.

In conclusion, Mr. Schnall said for best results in choosing an additive, one must (1) know the problem; (2) know the additive; (3) know the system; and (4) check the additive's effect on the system.

An educational presentation was given by Thomas Breed, of Schwartz Manes & Ruby Co. He discussed recent tax developments involving federal estate taxes, gift taxes, and income taxes.

DAVID C. KINDER, *Secretary*

GOLDEN GATE

NOV.

"Digital Batch Control"

Manufacturing Committee Chairman Louie Sanguinetti reported on the committee's symposium entitled "Paint Man-

ufacturing Methods Update" scheduled for June 13. This all-day symposium will include eight papers and a panel discussion.

President Robb Holt presented a 25-year pin to Roy Cohen, of the O'Brien Corp.

"DIGITAL BATCH CONTROL—FRIEND OR FOE" was presented by John E. O'Meara of E.M.C. Controls, Inc.

Mr. O'Meara discussed the various aspects one should know when purchasing and using process control computers, especially in relation to the paint and coatings industry. The steps for process control computerization were given as: system definition; vendor selection; system specifications; communications source; training; system checkout; installation; start-up; and maintenance.

Cost of computerization was discussed. Mr. O'Meara stressed that automation is not cheap, but it can be done in steps. Always use equipment which can be expanded, said Mr. O'Meara.

ROBERT MILLER, *Secretary*

MONTREAL

JAN.

"New Methods in Coatings Rheology"

Dr. Richard Eley, of Glidden Coatings & Resins Div., SCM Corp., discussed "NEW METHODS IN COATINGS RHEOLOGY."

All aspects of rheology and the various measurement techniques which can be used were explained. According to Dr. Eley, the following rheological parameters may have to be considered for any given product or application: shear viscosity; dynamic viscosity/elasticity; normal stress; elongational viscosity; and surface dilational modulus.

Dr. Eley classified coatings as newtonian, non-newtonian, or viscoelastic.

Dr. Eley advised against the use of single point instruments such as a flow cup or Stormer. Flow cup results, for example, said Dr. Eley, frequently do not give a good indication of sag resistance. It is much better to use a more sophisticated instrument such as one of the cone and plate type, stressed Dr. Eley.

The flow-cure characteristics of two component coatings were also discussed.

M. MEGELAS, *Secretary*

PACIFIC NORTHWEST

NOV.

"Batch Computer Control"

John Nicholson, of EMC Controls, Inc., spoke on the topic of "BATCH COMPUTER CONTROL—FRIEND OR FOE."

Mr. Nicholson stressed that with

computerized controls becoming a part of our daily lives, it is only natural that the use of such a system for the operation of our processing equipment in the paint industry should be investigated. Benefits of using computer controls were lower operating costs, lower hardware expense, greater throughput with a higher degree of accuracy, and a higher safety aspect.

Before installing a computerized system, Mr. Nicholson advised that attention should be given to the projected expectations, such as degree of accuracy required, repeatability, complexity of

the control mechanisms, and control enforcement.

The presentation was concluded with a slide presentation on the EMCON D system.

OTTWIN SCHMIDT, *Secretary*

PHILADELPHIA

DEC.

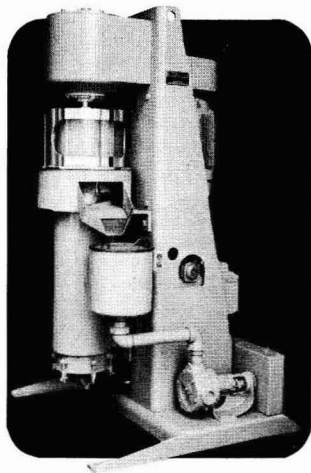
"Water-Borne Epoxy Materials"

Honored guests in attendance were Federation Executive Vice-President

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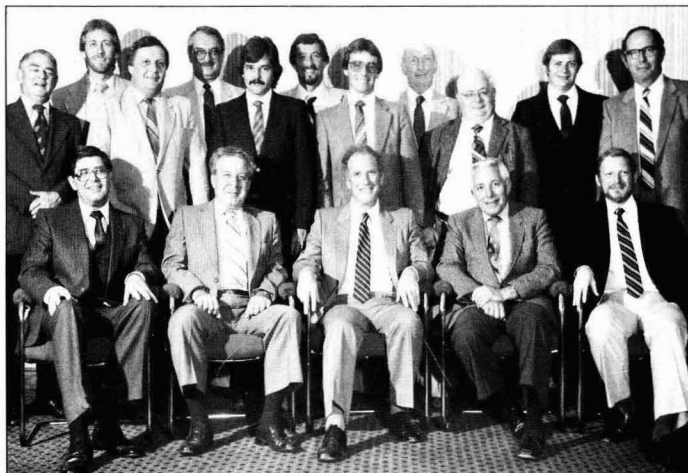


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1982-1983 Officers and Board Members of the Toronto Society. (Seated from left to right): Society Representative—Kurt Wertz; Secretary—Ted Stevenson; President—Frank La Roche; Federation President—A. Clarke Boyce; and Vice-President—Peter Hiscocks. (Standing left to right): Andrew Jones; Membership Chairman—Phil Read; Educational Chairman—Roy Donnelly; Immediate Past-President—Paul Cooper; Frank Krause; Larry Ham; Victor Langley; Manufacturing Chairman—Alun Morris; Frank Reckless; John Pitt; and Ernie Humberger. Not shown: Treasurer—Rob Kuhnen; Steve Balmer; Gordon Major; and Technical Chairman—Stamatis Kambanis

Frank Borrelle and Field Services Director Thomas Kocis.

Jack Avery, of Celanese Plastics & Specialities Co., presented a talk entitled, "TWO COMPONENT WATER-BORNE EPOXY MATERIALS FOR INDUSTRIAL MAINTENANCE COATINGS SYSTEMS."

Using slides, Mr. Avery discussed an update on water-borne epoxy and industrial maintenance systems. He gave a brief history of resins systems leading to current technology. He also covered the pros and cons of each resin system. The various ways to convert resins and the good and bad points of each system were examined. A review of five typical systems and a particular highlight of each system was given. They are: liquid epoxy/polyamide gives excellent solvent resistance; liquid epoxy/amine adduct gives versatility; great weathering is found with liquid epoxy/acrylic/acid; mmw epoxy/amine adduct gives very fast dry and abrasion resistance; and resistance properties are highlighted by mmw epoxy/polyamide adduct. The right system has to be used, stressed Mr. Avery.

According to Mr. Avery, water-borne epoxies are preferred because of: environmental reasons; reduced fire hazard; low odor; and cost and cost stability.

WILLIAM GEORGOV, *Secretary*

PIEDMONT

"Organic Pigments"

"ORGANIC PIGMENTS: PAST, PRESENT, AND FUTURE" was presented by Dr. H.M. Smith, of Sun Chemical Corp.

Dr. Smith divided the organic pigment production period into three distinct phases. The first phase, 1856-1896, involved mainly in synthesis of dye type chemicals with the exception of the introduction of para-red in 1885. The second phase, 1900—pre World War II, produced pigments such as the hansas and the phthalo blues which are still widely used today, said Dr. Smith. The third phase encompassed the post World War II era which largely introduced high performance pigments for the automobile industry. These are the quinacridones, the benzimidazolone oranges, and the perylene Reds.

Dr. Smith discussed five present day trends in organic pigment technology: (1) Synthesis of novel pigment structures, chromophors, or molecular rearrangements to impart intense color; (2) Tacking on chemical groups to make existing pigments more inert, insoluble, heat resistant, and light fast; (3) Product development to upgrade properties for enhanced value in use; (4) Hybridization of dye-stuffs and pigment technology to achieve quality improvements such as flocculation resistance and migration

resistance; and (5) Response to environmental pressures or compliance.

In the coming years, because of TOSCA and PMN, pre-manufacture notification, Dr. Smith predicted that fewer new pigments will be introduced. However, he said that no shortages in the supply of organic pigments were predicted there is an ample supply of petrochemicals which the organic pigment industry is heavily dependant upon. Due to the accelerated rate of company mergers and purchases by European organizations at the present, a strong European influence will take place. There will be a growing focus on high solids and pigments that can be packaged more efficiently for the end-users. Process knowledge will be emphasized so that effective use and control of by-products could be gained, explained Dr. Smith.

PHILIP WONG, *Secretary*

PITTSBURGH

JAN.

"Factors Affecting Coatings Performance On Metal Surfaces"

Bruno Perfetti, of U.S. Steel Research Laboratories, presented a talk entitled, "SOME FACTORS AFFECTING COATINGS PERFORMANCE ON METAL SURFACES."

Mr. Parfetti pointed out that a metallic surface is dynamic rather than static. It continuously undergoes chemical change as it interacts with its environment. He indicated the importance of understanding the chemistry of the metal surface as well as that of the coating. The best approach considers the whole system, the composite of substrate, and coating. If the surface of the metal changes, then the coating must be changed, the surface modified, or both.

Mr. Perfetti then described the general characteristics of steel surfaces which are complex matrices of materials: adsorbed water, mixed oxides, hydrated oxides, metallic fines, etc. These surfaces are normally cleaned, pretreated, and painted. The most important property of the substrate and the paint is paintability, that is, the degree of paint adherence and the corrosion resistance that the paint imparts. Both of these are surface dependent. Mr. Perfetti pointed out that surface properties differ from the bulk properties of a solid, and that this was especially true of steel. One surface property, cleanliness, was especially critical to adhesion and corrosion resistance of coatings. Steel suffers from a lack of cleanliness with a large number of contaminants, including surface carbon, various oils, lubes, metal fines, and other extraneous materials. With most contaminants there will be little or no

problem if the concentration is low enough, said Mr. Perfetti. Oxidized oils and salts are objectionable at very low levels, however.

Effective cleaning reduces or removes contaminants, stressed Mr. Perfetti, but that cleaning baths must be carefully controlled to be effective. If the steel is not coming out clean enough, then the bath temperature and/or dwell time must be increased. Alkaline cleaners remove oxidized oils, but surface carbon can only be removed with pickling acids. Surface carbon can be a serious problem. At or above a level of 1 mg/ft² it interferes with deposition and development of zinc phosphate conversion coatings. Surface carbon originates from various sources, a major one being decomposition of rolling oils. High surface carbon leads to low salt spray resistance of the painted surface. Low surface carbon does not guarantee good paintability, however, said Mr. Perfetti.

Mr. Perfetti described the steps in preparing metal for painting: clean/rinse/pretreatment/rinse/final rinse. He pointed out that iron phosphate pretreatments are used for general industrial, coil, and some appliance applications, whereas zinc phosphates are used on automotive steel. Paint adherence to pretreatments usually is quite good.

Paint appearance was then discussed. Mr. Perfetti pointed out that the determinants of appearance are substrate roughness and the paint system itself. The texture of steel sheet is a function of the rolling process. A bumpy surface is not a problem with appliance applications where orange peel and texture are acceptable. Automotive steel, on the other hand, must be very smooth because the coated surface must have very high gloss and reflectivity (distinctness of image). The dominant factor in controlling distinctness of image (D.O.I.) is the paint quality and thickness, but metal topography also is important, stressed Mr. Perfetti. The phosphate conversion coating tends to telegraph the steel surface, but increased thickness does improve the D.O.I.

Mr. Perfetti summarized his talk. He emphasized that the metal surface had a great influence on the appearance of a finished article, and that the surface and its chemistry must always be considered.

Q. How does surface carbon interfere with the deposition of a zinc phosphate pretreatment?

A. Surface carbon isolates the area it covers from interaction with the acidic phosphate. It interferes with the oxidation-reduction reactions necessary to

propagate the zinc phosphate layer. The result is nonuniform deposition with thin spots surrounded by clumps of large plate-like crystals.

Q. How do you measure surface carbon?

A. Several techniques are available, but I use a method of my own. A piece of fiberglass filter paper is dipped in 50% HCl, then rubbed across the surface. The surface carbon that is removed is determined after the fiberglass filter is ashed in a furnace.

CLIFFORD SCHOFF, *Secretary*

ROCKY MOUNTAIN DEC.

"PAST-PRESIDENTS' NIGHT"

President Don Bagge called for self-introductions by the past-presidents and certificates of appreciation were presented to them by Vice-President Don Shillingburg. Society Representative James E. Peterson gave a brief history of the society.

"THE USE AND APPLICATION OF SPECIALTY COATINGS ON WATER STORAGE TANKS AND BRIDGES" was discussed by John Matouk, of Caliber Coatings.

LUIS O. GARCIA, *Secretary*

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Future Society Meetings

Birmingham

(Apr. 14)—"TRANSPORT AS IT APPLIES TO THE PAINT INDUSTRY"—O. Thomas, Freight Transport Assoc.

(May 5)—"USE OF ANTI-STATIC DEVICES IN THE PAINT INDUSTRY"—G. Wheatcroft, 3M Co.

Chicago

(Apr. 4)—"ACID RAIN TRENDS IN THE U.S."—Dr. Gary Stensland, University of Illinois. "ASPECTS OF RHEOLOGY IN COATINGS"—Dr. J.E. Glass, North Dakota State University.

Cleveland

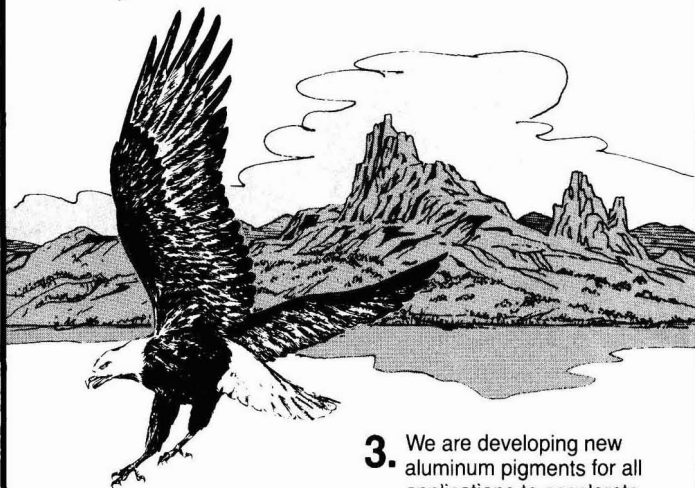
(Apr. 19)—"ATTRITOR GRINDING AND DISPERSING EQUIPMENT"—Arno Szegvari.

(May 17)—"A FUNNY THING HAPPENED ON THE WAY TO THE COATINGS TECHNICAL MEETING"—Frank Borrelle, FSCT Executive Vice-President.

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Golden Gate

(Apr. 18)—"CHLORINATED SOLVENTS IN COMPLIANCE COATINGS"—Hank George, Consultant.

(May 16)—"BENEFITS OF COMPOSITE DISPERSANTS IN COATINGS AND COLORANTS"—Elio Cohen, Daniel Products Co.

(June 13)—MANUFACTURING COMMITTEE'S SEMINAR.

Houston

(Apr.)—"PAST PRESIDENT'S NIGHT."

(May 11)—"IMPACT OF THE SUPERFUND LAW ON THE PAINT INDUSTRY"—Tom Graves, NPCA Legal Staff.

Kansas City

(Apr. 14)—"HIGH SOLIDS COATINGS—PAST, PRESENT, AND FUTURE"—Speaker from Spencer Kellogg, Div. of Textron, Inc.

(May 12)—FEDERATION OFFICERS' VISIT. Update on Federation Activities; Education Committee will present Science Pioneer Awards; and Election of Officers.

(June 10-11)—JOINT MEETING of the Kansas City/St. Louis Societies.

Los Angeles

(Apr. 13)—"CHLORINATED SOLVENTS IN COMPLIANCE COATINGS"—Hank George, Consultant.

New England

(Mar. 17)—"FORMULATING WITH MICROSOPHERES."

(Apr. 14)—ANNUAL WESTERN MEETING. "REVIEW OF THE ALYCOL ETHER SITUATION."

(May 20)—BIENNIAL SYMPOSIUM ON COATINGS TECHNOLOGY.

Constituent Society Meetings and Secretaries

Northwestern

(Apr. 5)—"EDUCATION NIGHT"—James Lawlor, Chairman.

(May 3)—"MANUFACTURING PROGRAM"—Richard Munding, Chairman.

Philadelphia

(Apr. 15)—AWARDS NIGHT.

(May 12)—"NEWER TECHNOLOGICAL AREAS OF WATER-BORNE RESINS"—Don Hogan, Polyvinyl Chemical Corp.

Piedmont

(Mar. 16)—FEDERATION OFFICER VISIT.

(Apr. 20)—"PLANT SAFETY—HANDLING SOLVENT AND NITROCELLULOSE"—Speaker from Hercules, Inc.

(May 18)—"SOLVENTS FOR HIGH SOLIDS COATINGS"—R. Readshaw, Union Carbide Corp.

(June 15)—"FINISHING POLYOLEFIN PLASTICS"—T.E. Parsons, Eastman Chemical Products, Inc.

Pittsburgh

(Apr. 4)—"CHLORINATED SOLVENTS—AN ALTERNATIVE TECHNOLOGY IN COATINGS"—Jed Fulkerson, Dow Chemical Co.

(May 2)—"WHAT IS THE STRUCTURAL STEEL PAINTING COUNCIL?"—John Keane, Mellon Institute.

St. Louis

(Mar. 15)—"HIGH SOLIDS COATINGS"—Speaker from Freeman Chemical Co.

(Apr. 19)—"EDUCATION NIGHT."

(May 17)—"MANUFACTURING NIGHT."

BALTIMORE (Third Thursday—Eudowood Gardens, Towson, MD).

BIRMINGHAM (First Thursday—Westbourne Site, Edgbaston). D. H. CLEMENT, Holden Surface Cts. Ltd., Bordesley Green Rd., Birmingham B94TQ, England.

CHICAGO (First Monday—meeting sites in various suburban locations). FRED FOOTE, U.S. Gypsum Co., 700 N. Rte. 45, Libertyville, IL 60048.

C-D-I-C (Second Monday—Sept., Jan., Apr., June in Columbus; Oct., Dec., Mar., May in Cincinnati; Nov., Feb., in Dayton). ROBERT A. BURTZLAFF, Potter Paint Co. of Ind., P.O. Box 265, Cambridge City, IN 47327.

CLEVELAND (Third Tuesday—meeting sites vary). RAY PODLEWSKI, Mansfield Paint Co., P.O. Box 998, Mansfield, OH 44901.

DALLAS (Thursday following second Wednesday—Steak & Ale Restaurant). T. LEON EVERETT, Dan-Tex Paint & Ctg. Mfg., Inc., P.O. Box 18045, Dallas, TX 75218.

DETROIT (Fourth Tuesday—meeting sites vary). PETER BURNETT, Wyandotte Paint Products, Inc., 650 Stephenson Hwy., Troy, MI 48084.

GOLDEN GATE (Monday before third Wednesday—Alternate between Sabella's Restaurant on Fisherman's Wharf and the Sea Wolf at Jack London Square, San Francisco). ROBERT MILLER, Frank W. Dunne Co., 1007 41st St., Oakland, CA 94608.

HOUSTON (Second Wednesday—Sonny Look's, Houston, TX) RICHARD D. BATCHELOR, Valspar Corp., 2503 W. 11th St., Houston, TX 77008.

KANSAS CITY (Second Thursday—Cascone's Restaurant, Kansas City, MO). GENE WAYENBERG, Tnemec Co., Inc., P.O. Box 1749, Kansas City, MO 64141.

LOS ANGELES (Second Wednesday—Steven's Steak House, Commerce, CA). MICHAEL GILDON, Guardsman Chemicals, 9845 Miller Way, Southgate, CA 90280.

LOUISVILLE (Third Wednesday—Howard Johnson's, Louisville, KY). W. JERRY MORRIS, Celanese Plastics & Specialties Co., P.O. Box 99038, Jeffersonville, KY 40299.

MEXICO (Fourth Thursday—meeting sites vary). GEORGE CARRINGTON, Nuodex Mexicana, Mexico, D.F., Mexico.

MONTREAL (First Wednesday—Bill Wong's Restaurant). M. MEGELAS, International Paints Ltd., P.O. Box 190, Outremont, Que., Can., H2V 4M9.

NEW ENGLAND (Third Thursday—Fantasia Restaurant, Cambridge). CHARLES J. HOAR, Union Chemicals Div., 67 Walnut Ave., Clark, NJ 07066.

NEW YORK (Second Tuesday—Landmark II, East Rutherford, NJ). MICHAEL ISKOWITZ, Koppers Co., Inc., 480 Frelinghuysen Ave., Newark, NJ 07114.

NORTHWESTERN (Tuesday after first Monday—Boulevard Cafe, Golden Valley, MN). ROBERT MADY, George C. Brandt, Inc., 2975 Long Lake Rd., St. Paul, MN 55113.

PACIFIC NORTHWEST (Portland Section—Tuesday following second Wednesday; Seattle Section—the day after Portland; British Columbia Section—the day after Seattle). WILLIAM SHACKELFORD, Gaco-Western, Inc., P.O. Box 88698, Seattle, WA 98188.

PHILADELPHIA (Second Thursday—Valle's Steak House. WILLIAM GEORGOV, J.M. Huber Corp., P.O. Box 310, Havre de Grace, MD 21078.

PIEDMONT (Third Wednesday—Howard Johnson's, Brentwood exit of I-85, High Point, NC.) JAMES E. HUSTED, Mobil Chemical Co., P.O. Box 2438, High Point, NC 27261.

PITTSBURGH (First Monday—Skibo Hall, Carnegie Mellon Univ.). CLIFFORD SCHOFF, PPG Industries, Inc., R&D Center, P.O. Box 9, Allison Park, PA 15101.

ROCKY MOUNTAIN (Monday following first Wednesday—Gusthaus Ridgeview, Lakewood, CO). LUIS O. GARCIA, Kelly-Moore Paint Co., 3600 E. 45th Ave., Denver, CO 80216.

ST. LOUIS (Third Tuesday—Salad Bowl Restaurant). WILLIAM TRUSZKOWSKI, Mozel Chemical Products Co., 4003 Park Ave., St. Louis, MO 63110.

SOUTHERN (Gulf Coast Section—Various Dates; Central Florida Section—Third Thursday after first Monday; Atlanta Section—Third Thursday; Memphis Section—Second Tuesday; Miami Section—Tuesday prior to Central Florida Section). S.G. SANFILIPPO, Reichhold Chemicals, Inc., Technical Services Lab., P.O. Box 1610, Tuscaloosa, LA 35401.

TORONTO (Second Monday—Cambridge Motor Hotel). R. H. STEVENSON, Tenneco Chems., Canada Ltd., 235 Orenda Rd., Bramalea, Ont., Can., L6T 1E6.

WESTERN NEW YORK (Third Tuesday—The Red Mill, Clarence, NY). DONALD M. KRESSIN, Spencer Kellogg Div., Textron, Inc., P.O. Box 210, Buffalo, NY 14225.

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Elections

NEW ENGLAND

Active

KORETSKY, DIANA R.—Samuel Cabot, Inc., Chelsea, MA.

Associate

BENING, P. SCOTT—Spencer Kellogg, Div., Textron, Inc., Malden, MA.
COSGROVE, THOMAS J.—BASF Systems, Wakefield, MA.
PARESKY, PAUL S.—Cypress Color & Chemical Inc., Westwood, MA.

NEW YORK

Active

ARESTY, ROBERT J.—Solar Energy Corp., Princeton, NJ.
BERMAN, STEVEN H.—Chromatic Paint Corp., Garnerville, NY.
BRYTUS, VINCE—Ciba Geigy Corp., Ardsley, NY.
CALBO, LEONARD J.—King Industries, Norwalk, CT.
FRANKLIN, EUGENE—Kay-Fries, Inc., Stony Point, NY.
JOSHI, AJAY—Hoboken Paints, Inc., Lodi, NJ.
MARKOWITZ, JOEL—R & A Specialty Chemical Co., Brooklyn, NY.
MENDOZA, CARLOS—Absolute Coatings, Inc., Bronx, NY.
MILLER, MARTIN C.—R & A Specialty Chemical Co., Brooklyn.
MINASSIAN, STEVEN S.—Benjamin Moore & Co., Newark, NJ.
MORVAY, RUDOLF C.—Metal Film Co., Inc., North Bergen, NJ.
NAUGHTON, FRANK C.—Caschem Inc., Bayonne, NJ.
PUGLISI, JOSEPH S.—CIBA-GEIGY Corp., Ardsley, NY.
TSUCHIYA, YOSHINORI—Toyota Motor Corp., Secaucus, NJ.
YUSTER, JANE—Troy Chemical Co., Newark.

Associate

BUDMAN, THEODORE M.—Superior Materials, Inc., Garden City, NY.
COLASURDO, CYNTHIA—Rhone Poulenc, Inc., Monmouth Junction, NJ.
CURTIS, CARL L.—ISIS Chemical, Somerville, NJ.
FLYNN, JAMES B.—EM Chemicals, Hawthorne, NY.
FRUHMANN, JOHN F.—Pfizer, Inc., MPM Div., Clifton, NJ.
GAN, BARBARA M.—Drew Chemical Corp., Boonton, NJ.
GIBBONS, THOMAS J.—Diamond Shamrock Chemical Co., Morristown, NJ.
GOLDEN, VICTOR J.—Shamrock Chemicals Corp., Newark, NJ.

HOLTZER, MITCHELL T.—Rohm and Haas Co., Piscataway, NJ.
JAFFE, HAROLD L.—Chemical Consultant, Millburn, NJ.
JANICKI, DAVID E.—Spencer Kellogg Div., Textron, Inc., Newark.
KAFKA, STEVEN M.—Superior Materials, Inc., Garden City.
KARLSON, JAMES—Caschem Inc., Bayonne.
LIGHT, DEBRA—Dow Chemical USA, Saddle Brook, NJ.
LITRIN, JAMES N.—Pfizer, Inc., MPM Div., Clifton.
MAGLIOCCO, JOHN—Allied Chemical Corp., Morristown.
MINATO, ICHIRO—Takeda Chemical Ind., New York, NY.
NASSBERG, BERNARD—Kikuchi Color & Chemical, Paterson, NJ.
PETERSON, WILLIAM M.—EG & G Princeton Applied, Princeton.
ROHLER, RICHARD P.—Pfizer, Inc., MPM Div., Clifton.
SCHIMMEL, BRUCE S.—Alcan Ingot & Powders, Elizabeth, NJ.
SHAFFER, J. SCOTT—Celanese Specialty Resins, Madison, NJ.
STOWE, JAMES A.—Inland Leidy, Union, NJ.

Retired

TUROW, ABRAHAM—Brooklyn, NY.

NORTHWESTERN

Active

FOSTER, ROSEMARY—Cargill, Inc., Minneapolis, MN.
HANCOX, SHARI L.—Cargill, Inc., Minneapolis.
TRIEN, TAN DAO—Plastic Dip International, Minneapolis.

Associate

JENNINGS, DAVID R.—Applied Color System, Westmont, IL.
TROST, DOUGLAS C., JR.—Hercules Inc., Naperville, IL.

PHILADELPHIA

Active

ADAMCHUK, MARK R.—Arco Chemical Co., Newtown Square, PA.
ARMISTAD, WILLIE L.—Air Products & Chemicals, Inc., Allentown, PA.
CAMILLETTI, ROBERT C.—RCA Corp., Camden, NJ.
CHRISTHIEF, HAROLD H.—Witco Chemical Corp., Trailer, PA.
DENIGAN, EDWARD P., JR.—Arco Chemical Co., Philadelphia, PA.

DURANTE, JOSEPH P.—Gilbert Spruance Co., Philadelphia.
FRACK, STERLING, JR.—Reichard-Coulston, Inc., Bethlehem, PA.
JUNKER, L. JOSEPH—McCloskey Varnish Co., Philadelphia.
KLOTZ, JAMES M.—Coatings For Industry, Souderton, PA.
KLOTZ, WILLIAM R.—Coatings For Industry, Souderton.
KRAUS, WAYNE A.—Chemcoat Inc., Montoursville, PA.
LANCASTER, WILLIAM—McCloskey Varnish Co., Philadelphia.
MAIDEN, NEIL A.—Congoleum Corp., Marcus Hook, PA.
MAIR, JOHN C.—Coyne Chemical Co., Philadelphia, PA.
MARINO, CHARLES P.—Markel Corp., Norristown, PA.
MATHEWS, ROBERT H.—McCloskey Varnish Co., Philadelphia.
MCMANUS, DANIEL—Finnaren & Haley, Inc., Conshohocken, PA.
NIEFCZURA, PAUL W.—Witco Chemical Corp., Trainer.
O'CONNOR, BRIAN—McCloskey Varnish Co., Philadelphia.
OTTER, JAMES W.—Gulf & Western Industries, Bethlehem.
PAEHL, BALDEN K.—Stulb Paint & Chemical Co., Norristown, PA.
PRESSLEY, HILLIE, JR.—Gilbert Spruance Co., Philadelphia.
RICH, RAMON D.—Stulb Paint & Chemical Co., Norristown.
SHABLIN, DONALD—Congoleum Corp., Marcus Hook.
TIBBETTS, KENNETH C.—Finnaren & Haley Inc., Conshohocken.

Educator and Student

GRANATA, RICHARD D.—Lehigh University, Bethlehem.
VANDERHOFF, JOHN W.—Lehigh University, Bethlehem.

PITTSBURGH

Active

CASEY, TOM—PPG Industries, Inc., Springdale, PA.
FEDEROFF, DONNA L.—Mobay Chemical Co., Pittsburgh, PA.
JOHNSON, WILLIAM C.—KTA-Tator, Inc., Pittsburgh.
KOSIOREK, RAYMOND S.—Drakenfeld Colors, Washington, PA.
WILLIAMS, JOHN L.—Mobay Chemical Co., Pittsburgh.

Associate

JIULIANO, JOSEPH P.—Jewell Chemical Co., Pittsburgh.
SHIELDS, WILLIAM T.—Neville Chemical Co., Pittsburgh.

Meetings/Education

47th Annual Meeting To Be Held by Southern Society, March 23-25

The Southern Society for Coatings Technology will host its 47th annual meeting entitled, "From Laboratory to Customer—Bridging the Gap Through Creativity," on March 23-25 at the Peabody Hotel, Memphis, TN.

Chairman William Early, of Piedmont Paint Mfg. Co., announced the following program:

Thursday, March 24

SSCT Annual Business Meeting.

The Keynote Address entitled, "It Takes More than Thinking to Be Creative," will be presented by Royal A. Brown, Technical Advisor of the Federation of Societies for Coatings Technology.

"The Economics of Quality Trade Sales Paints"—Abel Banov, Co-Publisher/Editorial, *The American Paint Journal*.

Panel: "Microcomputers—No Arcade Games, Please"—Moderated by Stanley Harshfield, United Paint Co.

"Ten Rules for Success"—Craig Larson, Chemical Specialties.

"Word Processing and Report Analysis"—Stanley Harshfield.

"Label Analysis and Inventory Control"—Joe Budash, Scott Paint Corp.

"Mini-Microcomputers"—Jim Stanley, Rico Chemicals, Inc.

"Basic Concepts of Electrodeposition"—Joe Lucas, PPG Industries, Inc.

"Robotic Finishing"—Ken Close, DeVelbiss Co.

"Gadget and Gimmick Contest"—Moderated by Bob Link, R.T. Vanderbilt Co.

"The Wings of Eagles" will be presented at the Society's Annual Luncheon by Norris L. Johnston, of The Warren Rupp Co.

Friday, March 25

Panel: "Applications of Industrial Coatings"—Moderated by Terry Walsh, Kinsmen Corp.

"Coil Coating—Past, Present, and Future"—Bob Rodger, Whittaker Corp.

"Electrostatic Applications"—James Wright, PPG Industries, Inc.

The afternoon session will feature presentations given by students of the University of Southern Mississippi.

Registration and housing information is available from Terrence J. Walsh, Kinsmen Corp., 214 Permalume Place, N.W., Atlanta, GA 30318.

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Baltimore, MD / Pittsburgh, PA

WPTG To Sponsor 23rd Annual Symposium in D.C.

"Coatings—On the Move" will be the theme of the Washington Paint Technical Group's 23rd annual symposium to be held at the Marriott Twin Bridges Motel in Washington, D.C., April 11 and 12.

Dr. Henry Leidheiser, Professor of Chemistry and Director of the Center for Surface and Coatings Research at Lehigh University, Bethlehem, PA, will present the keynote address, "A Better Understanding of the Metal-Coating Interface."

The program will also feature the following topics and speakers:

"The Quality Assurance Approach"—James V. Parish, The Sherwin-Williams Co.

"Maritime R&D in Coatings, Abrasives, and Surface Preparation"—John W. Peart, Avondale Shipyards.

"Advantage of Developing Coatings with Industrial Hygiene Considerations"—Patrick J. Hurd, National Paint & Coatings Association.

"Chlorinated Vinyl-Acrylic Latices for Steel Protection"—Marvin L. Caine, ICI Americas, Inc.

"Optimizing Performance of Field Applied Industrial Coatings"—V. Scott Pignolet, E.I. du Pont de Nemours & Co., Inc.

"Hydrophobic Fumed Silica Control of Epoxy Coatings Rheology"—Dennis G. Miller, Cabot Corp.

"Improvements in Adhesion and Durability Testing"—Mary E. McKnight, National Bureau of Standards.

"Microprocessors in Pigment Dispersion Equipment"—Roland E. Swett, Morehouse Industries, Inc.

"Water-Dispersible Crosslinking Urethanes"—Peter Loewrigkeit, Witco Chemical Co.

"New GSA Procedures for Procurement of Paints"—Speaker from General Services Administration.

"Replacement Solvents for Ethylene Glycol Monoethyl Ether and Acetate"—Richard L. Smith, Eastman Chemical Products.

"Formulating UV Curable Coatings"—Eli Levine, Celanese Chemical Co.

For further information, contact Washington Paint Technical Group, P.O. Box 12025, Washington, D.C. 20005, or Hing Dear at (301) 279-4215 or Mildred Post at (301) 530-1664.

HunterLab Announces Color Workshop, Apr. 6-8

HunterLab, Reston, VA, will present a 2-½ day workshop on "Colorimetry and Other Aspects of Appearance Science," on April 6-8, at the Sheraton International Conference Center in Reston.

The workshop will provide appearance technologists, and others interested in the measurement of appearance, with a basic knowledge of color and appearance science. It is an introductory course for those having little previous formal education in the field. Emphasized will be the practical aspects of measuring the ap-

pearance of products of industry. Topics such as color theory, colorimetry, metamerism, and spectrophotometry will be thoroughly explained. The effect of geometric attributes such as gloss and haze on the color and overall appearance of the product will also be covered in detail.

The workshop fee of \$295 includes course material, a hard bound copy of R.S. Hunter's book, "The Measurement of Appearance," and lunches.

For additional information, contact Dorothy C. Miner, HunterLab, 11495 Sunset Hills Rd., Reston, VA 22090.

Call For Papers Issued For World Coatings Conference On Bridges, Steel Structures

Papers are currently being solicited for the Third World Congress on Coatings Systems for Bridges and Steel Structures to be held November 2-3, at the Breckenridge Concourse Hotel in St. Louis, MO.

The conference, presented by the University of Missouri-Rolla, the Federal Highway Administration, and the Steel Structures Painting Council, will bring together new skills and technologies to aid in the recovery, repair, and maintenance of bridges and steel structures.

Papers on the following topics will be considered for presentation: surface preparation methods, disposal of removed materials to conform with environmental regulations, evaluation and field experience of alternative pigments and coatings, new specifying methods, inspection and quality assurance.

Abstracts should be submitted to Dr. Lloyd Smith, program chairman, Materials Technology and Chemistry Div., HNR-40, Federal Highway Administration, Washington, D.C. 20590. Authors of selected papers will be required to submit a complete manuscript by August 1 so that it may be included in the proceedings available at the conference.

For further information on the conference contact John A. Gordon, Jr., conference director, or Norma R. Fleming, conference coordinator Arts & Sciences Continuing Education, UM-Rolla, Rolla, MO 65401.

Seven Sessions Announced for 'Radcure '83', May 9-11

The Association for Finishing Processes of the Society of Manufacturing Engineers (AFP/SME) has announced that seven conference sessions have been scheduled for "Radcure '83" to be held May 9-11 at the Palais de Beaulieu, Lausanne, Switzerland.

This first international conference on radiation curing will be user-oriented and will cover case histories, new applications, and research in a wide spectrum of radiation curing technologies and operations.

The scheduled conference sessions include: Radiation Curing Overview; Paper and Film Converting; Wood and Building Materials; Printing and Varnishing in Radiation Curing; Finishing of Metals and Plastics; Advances in Technology; and Electronics and Communications. Plant tours to examine these technologies also are planned.

A spouse's program is scheduled during the conference.

For registration and housing information, contact Susan Buhr, AFP/SME

Administrator, Technical Activities Dept., SME, One SME Dr., P.O. Box 930, Dearborn, MI 48128.

KSU To Present Spring Coatings Courses

Kent State University's Rheology and Coatings Division of the Chemistry Department will present three short courses this spring. Designed for polymer and coating specialists, these courses will cover the subjects of diversion, adhesion, and rheology.

The courses and dates are as follows: (May 16-20)—"Dispersion of Pigments and Resins in Fluid Media."

(June 6-10)—"Adhesion Principles and Practice for Coatings and Polymer Scientists."

(June 20-24)—"Applied Rheology for Industrial Chemists."

Information can be obtained from Carl J. Knauss, Chemistry Dept., Kent State University, Kent, OH 44242.

People

J. Richard Kiefer, Jr. has been named Corporate Director-Environment, Safety and Health at McCloskey Varnish Co., Philadelphia, PA. Mr. Kiefer will assume responsibility for security, compliance with governmental regulations, and the establishment and maintenance of safety and health preservation programs for company employees. A past-president of the Philadelphia Society, Mr. Kiefer serves as Honorary Director and Handbook Editor. He has been awarded its Liberty Bell and Technical Committee awards, as well as a silver plate commemorating his completion of 19 consecutive years as an officer on the executive committee and Board of Directors.

Kathleen A. McGuire has been appointed Product Marketing Manager of trade paints for PPG Industries' Coatings and Resins Div. Mrs. McGuire joined PPG at the firm's Springdale, PA research center in 1970 as a chemist in the automotive coatings group. She has held various research posts including senior development chemist and project leader for interior consumer coatings. In 1980, she was named technical manager of interior consumer products. Mrs. McGuire is a member of the Pittsburgh Society.

Craig M. Davis, George Tipton, Jr., and **Ronald Lee Younts** have been appointed Senior Marketing Representatives by Eastman Chemical Products, Inc. Mr. Davis will represent the Raleigh, NC area, while Mr. Tipton will serve the Western Michigan region. Based in the Atlanta, GA area is Mr. Younts who is a member of the Southern Society.

Premier Mill Corp., New York, NY, was recently purchased by its President, **Myron Segal**, who has served the company for 18 years. Mr. Segal is a member of the New York Society. Corporate offices will be located at 220 E. 23rd St., New York, with manufacturing offices based in Reading, PA.

Union Camp Corp., Wayne, NJ, has announced the appointment of **Susan R. Young** as a Sales Representative for the Inks, Adhesives, & Coatings Group, Chemical Products Div. Ms. Young will be headquartered in Des Plaines, IL.



J. R. Kiefer, Jr.



K.A. McGuire



R. Marderosian



S.L. Davidson

Robert Marderosian has been appointed to the position of Manager, Equipment Sales, for Cypress Color and Chemical, Inc., Westwood, MA. Mr. Marderosian is a member of the New England Society.

Thibaut and Walker has announced the appointment of **Robert C. Gasman** as Technical Director/Emulsion Polymers.

SCM Pigments has named **John T. Gallagher** Senior Sales Representative for its northern Illinois and southern Wisconsin areas. Mr. Gallagher will be based in Chicago, and is a member of the Chicago Society.

Premier Coatings, Inc. has named **Michael Miskewitch** Vice-President of Manufacturing and **Duane DeYoung** Technical Director. Both are members of the Chicago Society.

Nuodex Inc., Piscataway, NJ, a newly formed company headed by a group of former Tenneco Chemicals, Inc. management employees, has announced the following appointments. **Frank X. Dwyer**, most recently Executive Vice-President and General Manager of Tenneco, was named President and Chief Executive Officer. The Nuodex management group also includes **Joseph Fath, Dr. Lawrence A. Wigdor, and Lawrence Okun**.

Robert Lockwood has been appointed Product/Market Manager—Airless and Coaters for the Finishing Equipment Div. of Nordson Corp., Amherst, OH.

Robert J. Zilli was promoted to the position of Market Manager, Technical Services, for Manville Products Corp., a subsidiary of Manville Corp.

S. Leonard Davidson retired March 1 from NL Industries, Inc., Hightstown, NJ, after a 40-year career in the coatings industry. He served the company most recently as Regulatory Affairs Specialist. Mr. Davidson is a Past-President of the Federation and has also served as Chairman of the Environmental Control Committee.

ODC Inc., a joint venture formed by Oak Industries and Dow Corning, has announced the following appointments. **Don Solar**, formerly an Account Manager at Dow Corning, was named Director of Marketing and Sales. **Bernie Van Wert** was appointed Director of Development. He previously served as a Senior Technical Service and Development Specialist for Dow Corning. Promoted to the position of Director of Engineering and Manufacturing is **Lloyd Rain**, formerly Manager of Special Products at Oak Industries. **George Levey**, previously Controller of Mass Laminates at Oak Industries, was named Controller for the new venture.

Barry Douglas has been appointed Executive Vice-President of Red Devil Paints & Chemicals, Mount Vernon, NY.

Jerry Hall, Director of the Chemical Coatings Division of the National Paint and Coatings Association for the past 25 years, has announced an early retirement for the end of this year. Mr. Hall has been the staff liaison to the NPCA's Chemical Coatings Steering Committee and its subgroups, the Chemical Coatings Industry Committee, and the Furniture Finishes Industry Committee. He has been involved in the planning of many conferences and in the development of case studies used in committee-sponsored seminars. Mr. Hall joined the NPCA staff in 1957, following three years as a White House military aide during the Eisenhower Administration.

Lawrence B. Moss has been appointed Product Manager for Urethane and Acrylic Polymers for the Organics Div. of Witco Chemical Corp.

Dr. William C. Spitzer has retired as Research Director of PRA Laboratories, Inc., a position he has held since 1966. His duties will be assumed by **Gerald K. Delves**. Dr. Spitzer, a member of the Chicago Society, will continue to serve the organization as a Technical Consultant.

James C. Hendershot has retired as Chairman and Chief Executive Officer of Reliance Universal, Inc., a subsidiary of Tyler Corp. He will continue as a member of the Tyler Board. **Charles J. Fisher** has been named President of the company, and assumed the position of Chief Executive Officer upon Mr. Hendershot's retirement.

Kenneth R. Lawson, Manager, Market Development at DeSoto, Inc., Des Plaines, IL, has been re-elected as President of the Association for Finishing Processes of the Society of Manufacturing Engineers (AFP/SME). Also, elected to the position of President-Elect was **George Paulus**, Manager, Technical Department, Acheson Colloids Co., Port Huron, MI. Mr. Paulus is a member of the Detroit Society.

The Minerals & Chemicals Div. of Engelhard Corp., Menlo Park, NJ, has appointed **John C. Hirschman** Product Manager, Paint and Coatings Pigments, in its Pigments & Extenders Group.

Negley Paint Co., San Antonio, TX, has announced the appointment of **Caryl J. Swann** to the position of Controller.

EM Chemicals, an EM Industries Co., Hawthorne, NY, has named **Sigrid Teaney** Technical Chemist in Pigment Applications for its Plastics & Coatings Group.

Ralph J. Bellrose has been appointed Product Sales Manager for Coatings Solvents in the Solvents & Coatings Materials Div. of Union Carbide Corp., Danbury, CT.

A. Blair Battistini has been named National Sales Manager for the pigments department of the Hilton-Davis Chemical Co., Cincinnati, OH.

Steve Inman has been appointed Account Supervisor for the Union Chemicals Div., Union Oil Co. of California.

Literature

Quinacridones

Literature has been published announcing the introduction of two new Quinacridones, specifically developed for different segments of the coatings industry. Featured are No. 228-0594, a Sunfast® Quinacridone Red Y, developed for automotive and industrial coatings, and Sunfast® Quinacridone Magenta, No. 228-0605, designed for trade sales paint manufacturers and aqueous dispersion manufacturers. For further information, write Sun Chemical Corp., Pigments Div., 411 Sun Ave., Cincinnati, OH 45232.

Lid Closer

Literature is available featuring a new semi-automatic lid closer for plastic and steel pails. Failsafe operator protection and low PSI operation are described. Additional data with photo call-outs explains pail size adjustments, interchangeable crimper head, and general construction features. Contact Beltron Corp., P.O. Box 893, Red Bank, NJ 07701 for additional information.

Non-Residential Coatings

A recently completed study entitled "High Performance Non-Residential Coatings" has been published and is now available. The study is a comprehensive business report which covers both new construction and maintenance segments, both industrial and marine applications, and both high performance and conventional coatings. It analyzes and projects critical market factors such as high solids, preconstruction primers, guaranteed maintenance contracts, buying influences, painting contractors, and prices per gallon. It employs finely tuned market definitions and is current, using 1982 as a base year, with 1987 and 1992 as projection years. One emphasis of the study involves a ranking of the 14 high performance markets by their growth over the coming half-decade, allowing subscribers to position themselves properly. Another emphasis centers on a grid of end-users versus coating producers, showing for 1982 the shares of the top 23 suppliers for each of 14 high performance markets, allowing subscribers to know their competition. The study is available for \$4,900 and can be obtained from WEH Corp., P.O. Box 40066, San Francisco, CA 94140.

Resins

Modified and unmodified ketone formaldehyde resins for the paint and ink manufacturing industries, generally used as supplementary resins for the specific improvement of covering properties, are the subject of new literature. The resins are non-saponifiable and neutral with market brightness and light-fastness and are generally combined with binders and increase the gloss, solids content, and coloring capacity of paint systems. Properties and practical applications, such as paints for wood and paper, flexographic and photogravure printing inks, road marking paints, ball-point pen pastes, inks, or spray paints, are detailed. For a copy of "Ketone Formaldehyde Resins and Modifications," contact Huels Corp., 750 Third Ave., New York, NY 10017.

Coating

Literature is available featuring Uni-Prime cationic coating, a product which is expected to become the preferred coating for electrodeposition priming. Discussed are the application uses of the coating, which involves advanced chemistry that permits the application of a thicker protective primer to the metal bodies of new cars. Its benefits, such as improved quality and versatility, and better appearance and durability, are listed. For information, contact PPG Industries, Inc., One Gateway Center, Pittsburgh, PA 15222.

Rheometer

The new Carri-Med controlled stress rheometer is featured in recent literature. Discussed is its wide range of applications, which include the paint and printing ink industries, where it is required to study deformation and flow properties of thixotropic and other liquids, semi-solids, emulsions, suspensions, and polymeric systems. Its key features and benefits are also detailed. Write Sheen Instruments Ltd., Nine Sheendale Rd., Richmond, Surrey, TW9 2JL England for information.

Optical Sensor

An optical sensor which is suitable for both transmission and reflection measurements is the subject of recently published literature. Its uses and measurement capabilities are detailed. For information, contact HunterLab, 11495 Sunset Hills Rd., Reston, VA 22090.

Viscosity Sampling System

Literature introducing a new, low-cost sample chamber for the Viscosel Automatic Viscosity Control System is now available. Features and uses of the chamber are described. For more information, contact Brookfield Engineering Laboratories, Inc., Dept. NR 41, 240 Cushing St., Stoughton, MA 02072.

Measurement System

Literature is available featuring a new Positioning Color-Eye® On-Line Color Measurement System. Described are the instrument's ease of operation, standard features, and measurement capabilities. For information, write Color Communications, Macbeth, Div. of Kollmorgen Corp., P.O. Box 950, Newburgh, NY 12550.

Life Support Apparatus

A two-page brochure is available which describes the recently introduced five-minute escape hood, ELSA (Emergency Life Support Apparatus), designed for escape from smoke fumes and other dangerous environments. Its unique features are detailed. Contact International Safety Instruments, Inc., P. O. Box 846, Lawrenceville, GA 30246, for additional information.

Industrial Cleaning

The National Association of Corrosion Engineers has announced the publication of *Industrial Cleaning Manual*. Industrial cleaning is an important factor in both start-up and maintenance of plants and equipment. Proper cleaning schedules, techniques, and equipment are critical to the efficient and safe operation of industrial equipment. This new manual addresses chemical, manual, and mechanical cleaning, as well as the safety factors to be considered in all cleaning operations. Among the chemical cleaning techniques considered in TPC Publication #8 are acid baths and acid slugging. Types of acids used and their compatibilities with materials of construction are covered in detail. Hydraulic jetting, hand lancing, and mechanical scraping are among the non-chemical cleaning techniques covered in the manual.

Offered in soft cover format, *Industrial Cleaning Manual* has nine chapters in 42 pages with a foreword, introduction, list of definitions, and a detailed index. The manual is available for \$5 for NACE members and \$7 for nonmembers from NACE, P.O. Box 218340, Houston, TX 77218.

APCA Proceedings

The Air Pollution Control Association (APCA) has published the proceedings of a specialty conference on "Emission Inventories and Air Quality Management" which was conducted by APCA in April, 1982.

The illustrated, 390-page publication contains 27 original technical presentations, and introductory and summary remarks. The presentations address the topic through five major areas of discussions: emission inventory applications; data adequacy, uncertainties and policy implications; data base development and management; inventories, models and reality; and continuing activities and development techniques.

The hard-bound publication contains all graphs and charts submitted by the authors as well as a complete subject index.

Prices are: APCA Members, \$24.00; Nonmembers, \$28.00. All orders should be mailed to: Publications Dept., APCA, P.O. Box 2861, Pittsburgh, PA 15230.

Resource Recovery Service

A resource recovery service designed to capture by-product value from hazardous wastes generated by the paint and coatings industry has been introduced in new literature as a cost-saving alternative to several on-site and off-site disposal techniques currently used. Discussed is the service's objective and the means used to accomplish this objective. Actual implementation of the service is detailed as are its results. For further information, write Stauffer Chemical Co., Environmental Venture Div., Westport, CT 06881.

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Book Review

THE WORLD PAINT INDUSTRIES: A REVIEW, 1980-81

Published by
Paint Research Association

Middlesex, England
£ 100

Reviewed by
R. M. Christenson
PPG Industries, Inc.

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Dynacoat LH Series

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coil coating and spray coatings.

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Dynacoat P Series

Thermoplastic and thermoset polyester resins for use as binding agents for electrostatic and fluidized bed powder coating formulations. Thermal stability, chemical resistance, weatherability, elasticity in the coating of metal substrates.

As the foreword indicates, this is a compilation based entirely on published sources of statistical information on the paint industry. The book has done a good job in assembling all these statistics in one place. It would be very difficult to independently arrive at such a worldwide thorough compilation of data. Types of products, markets, sales volumes, market distribution and other pertinent statistics are covered country by country. The names, business activities, principal markets, and types of products are given for the paint companies in these various countries. The acquisition and merger history of organizations is also included. Financial data and recent developments in facilities, where available, are given.

A bibliography of the original sources is also furnished for the reader who wishes to secure still more details for given situations. A large number of publications have been consulted, including many foreign language publications that are not easily accessible.

The work should be especially valuable to those individuals concerned in international selling and exporting, licensing agreements, or considering acquisitions. One subject which receives some attention, but is not gone into thoroughly, is the relationship of technical excellence to the companies' businesses. This is, perhaps, too much to ask for such a review, but areas of specialization and technical excellence very often have a great deal to do with the success of the organization.

The book is not without some error. For example, PPG Industries is listed as having acquired Celanese's container coating business. This is not true. There are some discrepancies, for example, both Kansai and Nippon are indicated to have 600 people in an R&D capacity, but the R&D expenditures are listed at \$1800 million yen for Kansai and \$410 million yen for Nippon Paint. I would expect that this is due to numbers reported in two separate publications with somewhat different definitions of R&D.

This book should be present and available in every major paint company library. It is especially valuable to those that are engaged in international paint production, sales, and licensing.

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Coming Events

FEDERATION MEETINGS

(Apr. 26-27)—Federation Seminar on "The Efficient Operation of an Up-to-Date Paint and Coatings Laboratory." Hilton Plaza Inn, Kansas City, MO. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

(May 19-20)—Spring Meetings. Society Officers on 19th; Board of Directors on 20th. Terrace Hilton Hotel, Cincinnati, OH. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

(Oct. 12-14)—61st Annual Meeting and 48th Paint Industries' Show. Place Bonaventure, Montreal, Quebec, Canada. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

1984

(May 17-18)—Spring Meetings. Society Officers on 17th; Board of Directors on 18th. Galt House, Louisville, KY. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

(Oct. 24-26)—62nd Annual Meeting and 49th Paint Industries' Show. Conrad Hilton Hotel, Chicago, IL. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

SPECIAL SOCIETY MEETINGS

(Mar. 16)—Louisville Society Spring Symposium on Coatings Plant Safety. Marriott Inn, Clarksville, IN. (Don Collier, Porter Paint Co., 400 S. 13th St., Louisville, KY 40203).

(Mar. 23-26)—Southern Society Annual Meeting. Peabody Hotel, Memphis, TN. (William G. Early, Piedmont Paint Mfg. Co., P.O. Box 6223, Stn. B, Greenville, SC 29606).

(Apr. 13-15)—Southwestern Paint Convention of the Dallas and Houston Societies. Lowe's Anatole Hotel, Dallas, TX.

(Apr. 19-20)—Chicago Society for Coatings Technology Symco '83—"E.T.—Emerging Technologies: A Closer Encounter." Knickers Restaurant, Des Plaines, IL. (Chairman Ross Johnson, The Enterprise Companies, 1191 S. Wheeling Rd., Wheeling, IL 60090).

(Apr. 26-27)—"Advances in Coatings Technology." 26th Annual Technical Conference of the Cleveland Society for Coatings Technology. NASA-Lewis Research Center, Cleveland, OH. (Dr. Richard R. Eley, Glidden Coatings & Resins, P.O. Box 8827, Strongsville, OH 44136).

(May 2)—Philadelphia Society for Coatings Technology. "Substrate Technology" Seminar. Philadelphia College of Textiles and Science, Philadelphia, PA. (Robert Sonntag, Superior Varnish & Drier Co., P.O. Box 1310, Merchantville, NJ 08109).

(May 4)—Detroit Society for Coatings Technology FOCUS—"Corrosion Resistance." Michigan State University Education Center. (Peter Burnett, Wyandotte Paint Products Co., 650 Stephenson Hwy., Troy, MI 48084).

(May 5-7)—Pacific Northwest Society Symposium. Thunderbird Inn, Portland, OR. (Chairman Gerry McKnight, Lilly Industrial Ctg. Inc., 619 S.W. Wood St., Hillsboro, OR 97123).

(June 10-11)—Joint meeting of Kansas City and St. Louis Societies. Holiday Inn, Lake of the Ozarks, MO.

(June 13)—Golden Gate Society for Coatings Technology. Manufacturing Committee Symposium on "Paint Manufacturing Methods Update." (Louie Sanguinetti, Jasco Chemical Co., P.O. Drawer J. Mountain View, CA 94042).

1984

(Apr. 12-14)—Southwestern Paint Convention of Dallas and Houston Societies. Shamrock Hilton Hotel, Houston, TX.



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For technical literature and detailed information write: Jerry Walter, **Sherwin-Williams, Chemical Division**, 501 Murray Road, St. Barnard, Cincinnati, Ohio 45217.



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OTHER ORGANIZATIONS

(Mar. 14-18)—"Composition of Coatings" Short Course. University of Missouri-Rolla, Rolla, MO. (Norma Fleming, Arts & Sciences, Continuing Education, G-6 H/SS, UMR, Rolla, MO 65401).

(Mar. 24-25)—"Fundamentals of Color" Seminar. Charlotte, NC. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(Mar. 26-27)—Western Decorating Products Show. Disneyland Hotel, Anaheim, CA. (NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).

(Mar. 28-31)—"Cutting Costs with Computers and Automated Systems"—National Plant Engineering & Maintenance Conference and Exhibition. McCormick Place, Chicago, IL. (Clapp & Poliak, A Cahners Exposition Group Co., 708 Third Ave., New York, NY 10017.)

(Apr. 4-8)—8th Annual Introductory Short Course on "Paint Formulation." University of Missouri-Rolla, Rolla, MO. (Arts & Sciences, Continuing Education, UMR, Rolla, MO 65401).

(Apr. 10-12)—Inter-Society Color Council Annual Meeting. Louisville, KY. (Fred W. Billmeyer, Dept. of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181).

(Apr. 11-12)—23rd Annual Symposium of the Washington Paint Technical Group. Marriott Twin Bridges Motel, Washington, DC. (Mildred A. Post, Publicity Chairperson, WPTG, P.O. Box 12025, Washington, DC 20005).

(Apr. 12-14)—ASTM Committee C-22 on Porcelain Enamel and Related Ceramic-Metal Systems Meeting. ASTM/Philadelphia Centre, Philadelphia, PA. (Drew Azzara, ASTM, 1916 Race St., Philadelphia, PA 19103).

(Apr. 14-15)—"Fundamentals of Color" Seminar. Seattle, WA. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(Apr. 17-20)—National Coil Coaters Association Annual Meeting. Marriott's Marco Beach Hotel, Marco Island, FL. (NCAA, 1900 Arch St., Philadelphia, PA 19103).

(Apr. 18-21)—"Fundamentals of Chromatographic Analysis." Kent State University, Kent, OH. (Dr. Carl J. Knauss, Chemistry Dept., Kent State University, Kent, OH 44242).

(Apr. 18-22)—"Corrosion/83 sponsored by the National Association of Corrosion Engineers. Anaheim, CA. (NACE, P.O. Box 218340, Houston, TX 77218).

(Apr. 19-21)—Chemical Coaters Association. "Surface Coating 83." Milwaukee, WI. (Chemical Coaters Association, Box 241, Wheaton, IL 60187).

(Apr. 20-22)—ASTM Committee C-3 on Chemical Resistant Nonmetallic Materials Meeting. Galt House, Louisville, KY. (Jim Dwyer, ASTM, 1916 Race St., Philadelphia, PA 19103).

(Apr. 24-28)—"Nuclear Quality-Assured Coatings Work" Course. Pittsburgh, PA. (Carmen A. Rivera, IAT, P.O. Box 32331, Washington, DC 20007).

(Apr. 28-29)—"Fundamentals of Color" Seminar. Don Mills, Ont., Can. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(May 8-12)—74th Annual Meeting of the American Oil Chemists' Society. Chicago Marriott Hotel, Chicago, IL. (American Oil Chemists' Society, 508 S. Sixth St., Champaign, IL 61820).

(May 9-11)—RADCURE '83 Conference sponsored by AFP/SME. Palais de Beaulieu, Switzerland. (Susan Buhr, Society of Manufacturing Engineers, One SME Drive, P.O. Box 930, Dearborn, MI 48128).

(May 10-12)—Paint Research Association's Fifth International Conference, "Technological Advances in the Coatings Industry." London Penta Hotel, London, England. (PRA, Waldegrave Rd., Teddington, Middlesex TW11 8LD, England).

(May 11-13)—23rd Annual Marine and Offshore Coatings Conference. Hyatt Regency Hotel, Baltimore, MD. (National Paint & Coatings Association, Inc., 1500 Rhode Island Ave., NW, Washington, DC 20005).

(May 12-13)—"Fundamentals of Color" Seminar. Newton Lower Falls, MA. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(May 19-20)—"Fundamentals of Color" Seminar. Cherry Hill, NJ. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(May 23-25)—ASTM D-33 Coatings for Power Generation Facilities Committee Meeting. Galt House, Louisville, KY. (Phil Lively, ASTM, 1916 Race St., Philadelphia, PA 19103).

(May 24-26)—8th Annual Powder and Bulk Solids Conference/Exhibition. Georgia World Congress Center, Atlanta, GA. (Cahners Exposition Group, Cahners Plaza, 1350 E. Touhy Ave., Des Plaines, IL 60018).

(June 1-2)—"Color Technology for Management" Course. Rochester Institute of Technology, Rochester, NY. (Val Johnson, T&E Center Seminar Coordinator, Rochester Institute of Technology, P.O. Box 9887, Rochester, NY 14623).

(June 6-10 & 13-17)—"Principles of Color Technology" Course. Rochester Institute of Technology, Rochester, NY. (Val Johnson, T&E Center Seminar Coordinator, Rochester Institute of Technology, P.O. Box 9887, Rochester, NY 14623).

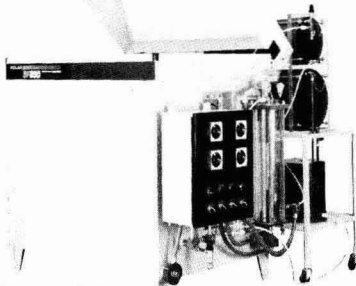
(June 2-3)—"Fundamentals of Color" Seminar. Rosemont, IL. (Jeanne M. Dolan, Macbeth, Div. of Kollmorgen Corp., Little Britain Rd., P.O. Box 950, Newburgh, NY 12550).

(June 15-18)—Oil & Colour Chemists' Association Biennial Conference on "The Efficient Use of Surface Coatings." Viking Hotel, York, England. (R.H. Hamblin, Director and Secretary, OCCA, Priory House, 967 Harrow Rd., Wembley, Middlesex, HA0 2SF, England).

(June 19-22)—Dry Color Manufacturers' Association Annual Meeting. The Greenbrier, White Sulphur Springs, WV. (P.J. Lehr, DCMA, Suite 100, 117 N. 19th St., Arlington, VA 22209).

(June 20-24)—"Advances in Color Technology" Course. Rochester Institute of Technology, Rochester, NY. (Val Johnson, T&E Center Seminar Coordinator, Rochester Institute of Technology, P.O. Box 9887, Rochester, NY 14623).

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(June 26-27)—ASTM Committee E-12 on Appearance of Materials Meeting. Hyatt Regency Nashville, TN. (Bob Morgan, ASTM, 1916 Race St., Philadelphia, PA 19103).

(June 26-29)—ASTM Committee D-1 on Paint and Related Coatings and Materials Meeting. Hyatt Regency Nashville, Nashville, TN. (Phil Lively, ASTM, 1916 Race St., Philadelphia, PA 19103).

(Aug. 26-30)—International Colour Association's Forsius Symposium on Colour Systems. Kungälv, Sweden. (Fred W. Billmeyer, Jr., Dept. of Chemistry, MRC 217, Rensselaer Polytechnic Institute, Troy, NY 12181).

(Aug. 31-Sept. 8)—20th Commission Internationale de l'Eclairage Congress. RAI Congress Center, Amsterdam, The Netherlands. (U.S. National Committee, CIE, c/o National Bureau of Standards, Washington, D.C. 20034).

(Sept. 27-28)—Pulp Chemicals Association's 11th International Naval Stores Conference and Technical Symposium. Westin Peachtree Plaza Hotel, Atlanta, GA. (Pulp Chemicals Association, 60 E. 42nd St., New York, NY 10165).

(Sept. 27-30)—National Coil Coaters Association Fall Technical Meeting. Hyatt Regency O'Hare, Chicago, IL. (NCCA, 1900 Arch St., Philadelphia, PA 19103).

(Sept. 28-Oct. 1)—Oil & Colour Chemists' Association's Silver Jubilee Convention and Exhibition. Southern Cross Hotel, Melbourne, Australia. (O.C.C.A.A., 1983 Pacific Coatings Convention, C/- Tioxide Australis Pty. Ltd., Private Bag 13, Ascot Vale, Victoria, 3032, Australia).

(Oct. 11-13)—"Finishing '83" sponsored by the Association for Finishing Processes of the Society of Manufacturing Engineers. Cincinnati Convention Center, Cincinnati, OH. (Susan Buhr, AFP/SME Administrator, One SME Dr., P.O. Box 930, Dearborn, MI 48128).

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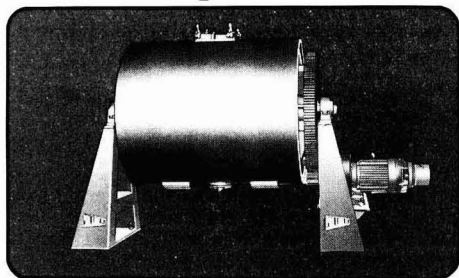
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Comments From Our (now) Second Time Conventioneer

How great it was to get back to the convention this year—wiser, more experienced, and full of enthusiasm. I had decided to reserve my room early, register in advance, and plan my agenda on a day-by-day basis. I determined to limit my visits to only a few hospitality suites, imbibe conservatively, and concentrate on the important lectures and Paint Show exhibits. I confess a "dutch uncle" and "or else" talk from my boss helped me reach that conclusion. The results of my careful preparation were moderately successful. At least my boss seemed somewhat satisfied when I submitted a long, detailed report of what I had learned at the convention. (Thank goodness for the lecture abstracts and exhibit descriptions in the program booklet).

I was much encouraged when the hotel check-in and pre-registration went well giving assurance that my long range planning had worked. However, my wonderful intentions showed signs of slipping seriously right after I pinned on my badge at the registration desk.

A gentleman who seemed vaguely familiar was giving my name tag the side long, casual glance that is expertly done only with long experience. He then greeted me with an outburst of enthusiasm. "Pete, how great to see you again," he said. I tried to maneuver my eyes toward his badge as discreetly as possible. Without my glasses in place, I had to squint a little but managed a confident—"Wonderful to see you, too, er-er-Jim."

"John", he corrected.

Well, it turned out that he was the new assistant district sales manager of our principal pigment supplier and had just been transferred to our territory. I guess we had met in the haze of the 1981 convention. It felt good to have met a friend (friendships come quickly and easily) so early in the convention and we proceeded to the lobby bar which was filling up rapidly. So were the standees who were clutching glasses in one hand and juggling tiny cracker gold fish in the other. Time passed rapidly as the happy talk at the bar was carried along on the wings of those flying cocktails. At least, we were all flying. I suddenly noticed that John seemed to have disappeared. Well, no matter because a number of my new friends were comparing hospitality suites and making plans for a series of visits. So "wot de hell". I decided to go along.

I got to my room several hours later and set my travel alarm for 7 A.M. I had decided on putting no more reliance on hotel wake-up calls after my agonizing experience of last year.

It felt as though I had just put my head on the pillow when the darn alarm went off. As a matter of fact my aching head had not been resting very long. It appeared that I had set the alarm for 5 A.M. No

wonder it was dark as I was putting on my tie. Well, I dozed and rested until about 10 o'clock and then rushed down to a cup of coffee and the keynote speaker. Bergman must have been great. I stayed awake through the whole thing. The Wednesday afternoon program was a problem when I was arranging my agenda. It was difficult to decide between "Computer Utilization" and the Formulation Symposium. In reality it turned out to be agony. I had decided to do both lectures even though they were in conflict, by sitting in the rear on the rooms and running back and forth between each discussion. In my hung-over condition, by 5 o'clock I was in a state of mental, physical, and emotional exhaustion.

I staggered back to my room in order to get some rest before my 7 P.M. dinner appointment. The appointment should have been set for 7 A.M. for that's when I woke up.

(to be continued)

• • •

Frank Borrelle, in recognition perhaps of his Federation reports, forwarded the following from *AEUNY News*:

"Short and Sweet is better than long gone

The Lord's Prayer—56 words

The Gettysburg Address—266 words

The Ten Commandments—297 words

The 23rd Psalm—118 words

The 1966 U.S. Gov't Order on Cabbage Prices—26,911 words"

Sid Lauren and son David continue to be our most dependable and valued contributors. This, from father, Sid who chose it from some of Prof. Ross K. Baker's gems:

"Finding what goes on in the C.I.A. is like performing acupuncture on a rock."

"The confusion of a staff member is measured by the length of his memos."

And from "Newsprints" in *C&E News* he sent—"Applications (of an analytical method) include analysis of pigments used in paintings. If chlorine shows up in a supposed 16th century painting, it is most likely a fraud because chlorine wasn't even discovered until much later." (Max Saltzman - please note.)

—Herb Hillman

Color-matching Aptitude Test



Color-matching Aptitude Test Set was created by the Inter-Society Color Council and sponsored by the Federation. It is in world-wide use as a means for estimating color-matching skill. The 1978 edition contains minor refinements over the previous editions (1944, 1953, 1964), and these bring it closer to the original ISCC plan, making it a still more successful tool for evaluating color-matching skill.

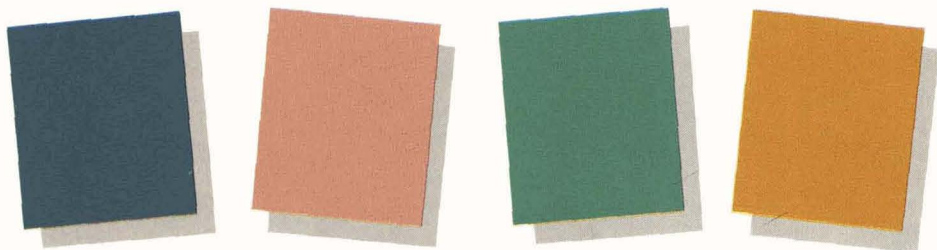
The basic aim of the Test is to provide an objective measure that will aid in determining an individual's ability for performing color-matching tasks accurately. Changes in a person's color-matching skill may occur over a period of time, improving due to training, experience, and motivation, or lessening when removed from practice, or as a result of health disorders. Retesting at regular intervals will provide an indication of any such changes in an individual's ability.

The Test is not designed to indicate or measure "color-blindness" (anomalous color vision). Special tests designed for this purpose should be used.

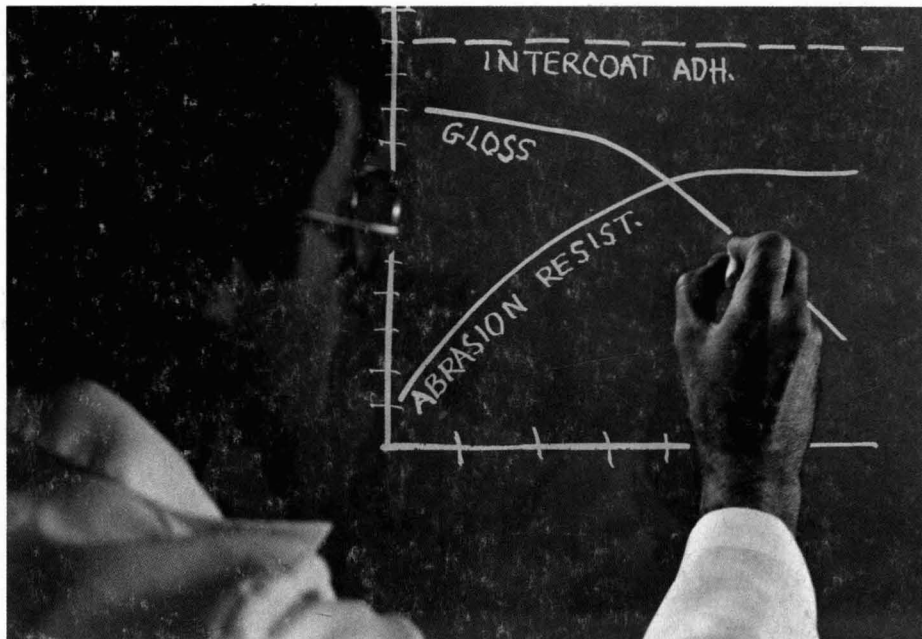
The Color-matching Aptitude Test Set consists of a carrying case, an easel on which are mounted 48 color chips, a dispenser which holds 48 matching chips, score sheets, and a scoring key.

Brochure available upon request. Price: \$400.

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