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JOURNAL OF
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TECHNOLOGY

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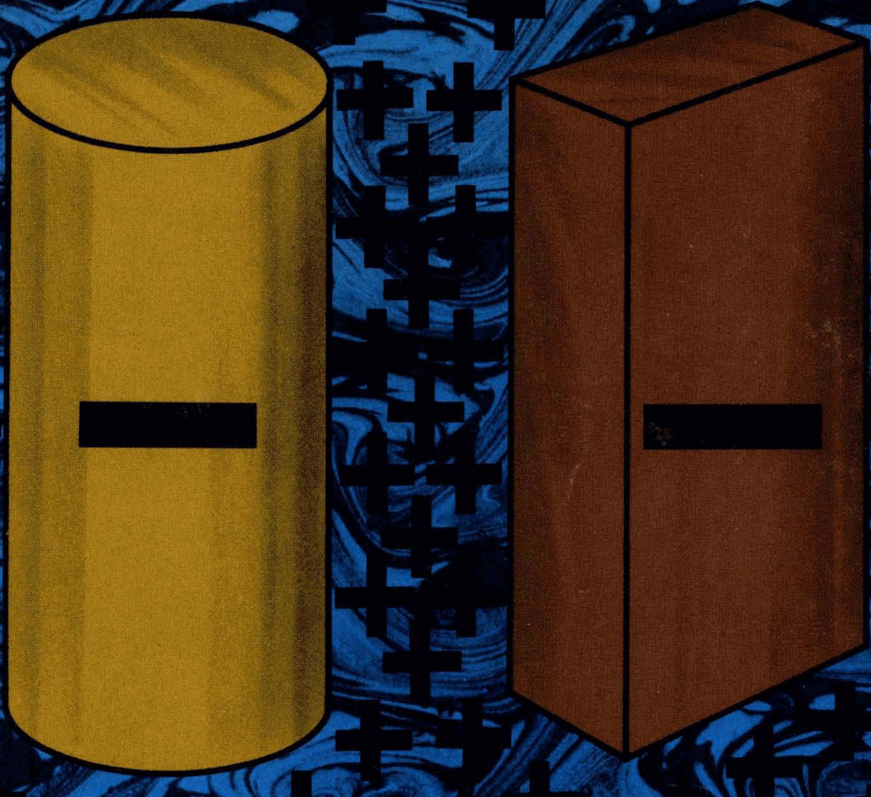
NOVEMBER 1978



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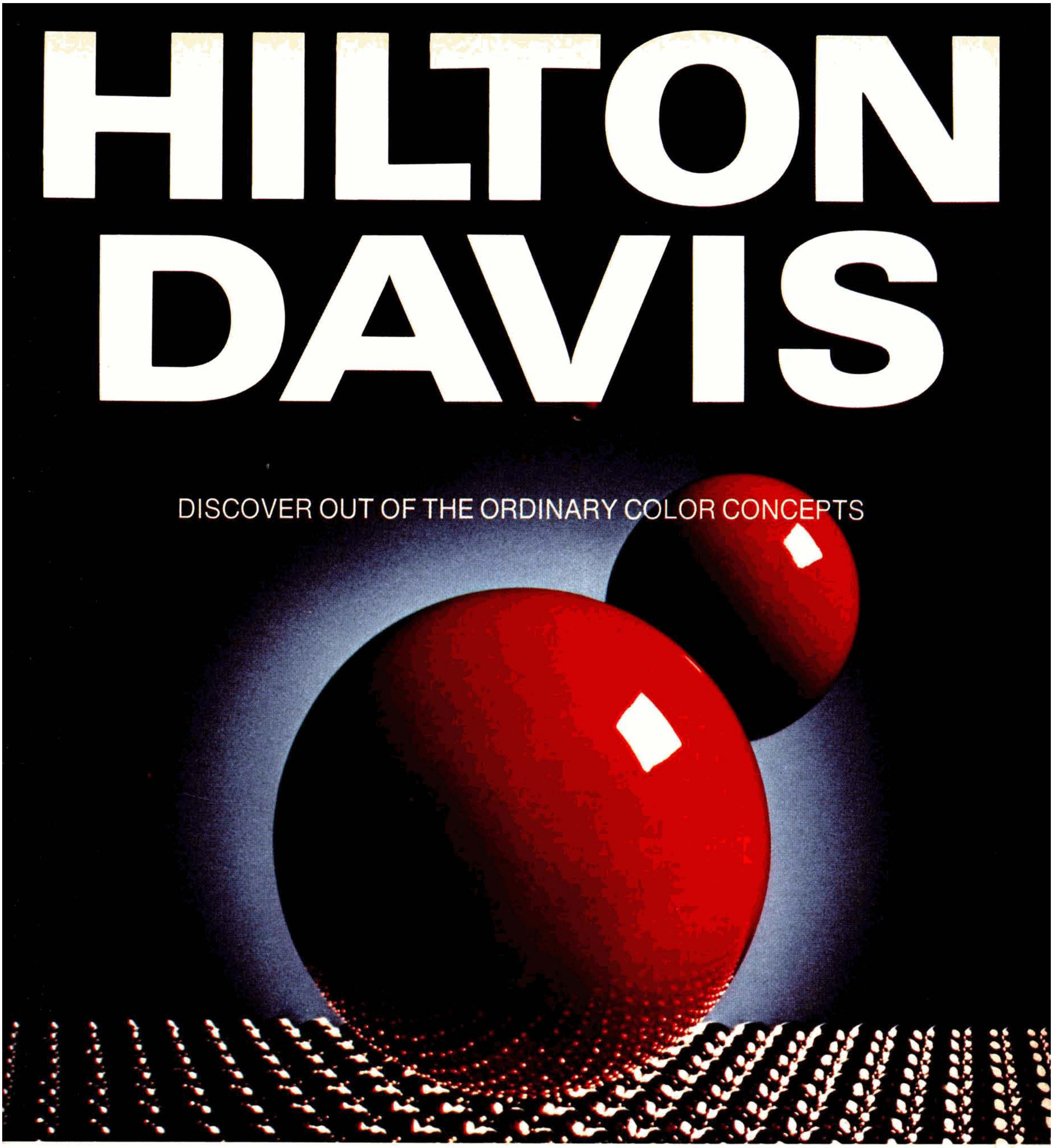
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NOVEMBER 1978

JOURNAL OF COATINGS TECHNOLOGY

Volume 50 Number 646

Features

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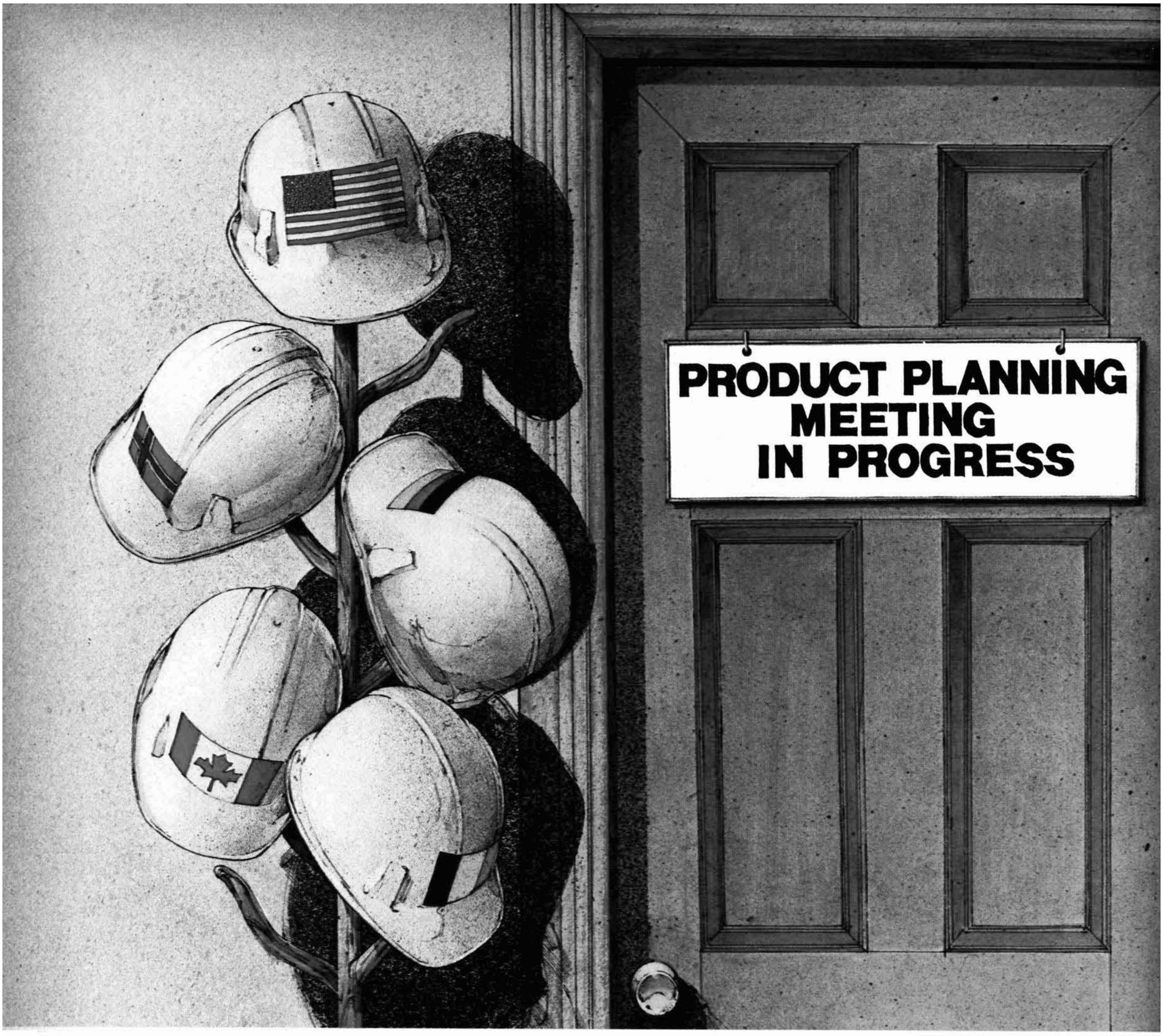
New Addition to This Edition

This issue of the JCT introduces a new editorial feature — the "Federation Newsletter," which will appear about six times per year.

The "Newsletter" has been published for eleven years as a special information tool for key Federation and Society personnel, to whom it was direct-mailed. More recently, it has been given wider distribution through special bulk mailings to Society Secretaries. But as interest and demand for copies have grown, it became apparent that the only effective means of bringing this special communication to all members is as a departmental feature in the JCT.

The "Newsletter" regularly highlights important Federation and Society happenings, as a reading of this month's edition will verify. So, if you want to keep abreast of what's going on at the national and local scene, make a point of checking the JCT and the "Newsletter" regularly.

And, as with any of the editorial material, we'd like to hear from you as to what you like or don't like about this new JCT feature. As they say, "keep those cards and letters coming." — TAK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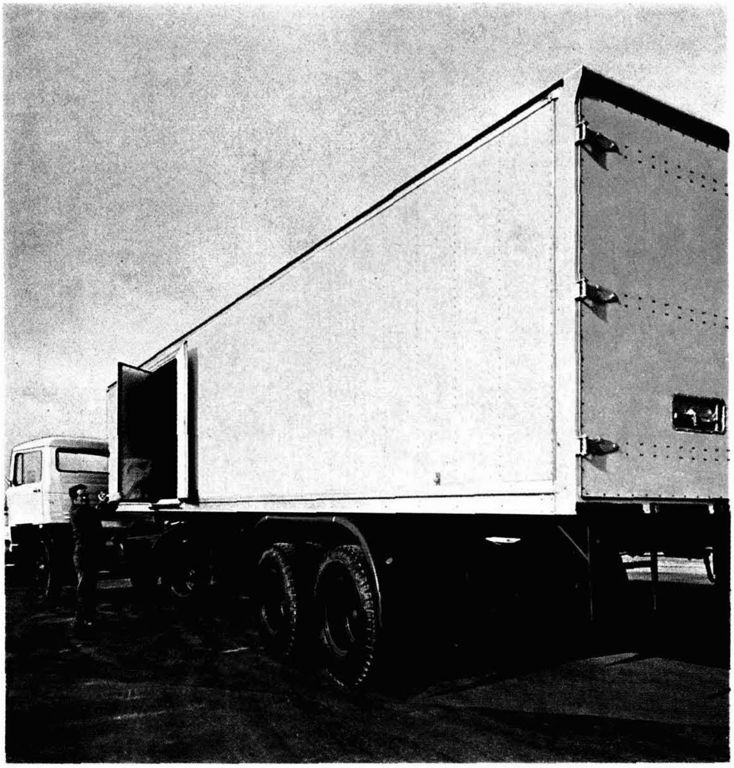

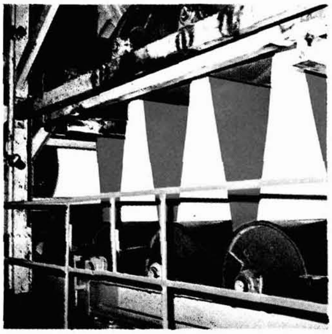

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Abstracts of Papers in This Issue

CATHODE REACTIONS AND METAL DISSOLUTION IN CATIONIC ELECTRODEPOSITION—D.G. Anderson, E.J. Murphy, and J. Tucci III

Journal of Coatings Technology, 50, No. 646, 38 (Nov. 1978)

In any electrochemical cell, reduction takes place at the cathode and, therefore, the metal surface does not ionize and remains passive during the deposition process. In theory, this proposed cathode passivity and the absence of included metallic ions portended virtual elimination of the typical anodic problems related to coating/substrate interactions. Because of this assumed passivity, most of the literature since the introduction of viable cationic systems, has been of a highly commercial nature, praising the new cationics as superior to the established anionics.

Approximately five years of commercial and laboratory experience, however, have taught cationic practitioners that cathodic systems do suffer from staining and film discoloration, and their cured film performance is still largely determined by the type and quality of substrate and pretreatment. Yet, there has been no published research during this period related to possible coating/substrate interactions in cationic electrocoat systems.

This paper studies possible cathode reactions which lead to substrate dissolution and inclusion of metallic ions in the deposited films.

EFFECT OF HUMIDITY AND OTHER AMBIENT CONDITIONS ON EVAPORATION OF TERNARY AQUEOUS SOLVENT BLENDS—A.L. Rocklin

Journal of Coatings Technology, 50, No. 646, 46 (Nov. 1978)

Evaporation of ternary blends of water, with a fast and a slow cosolvent at various ambient conditions, was investigated using an abbreviated method in which computer analysis of a limited number of carefully chosen experiments reveals the independent effects of each variable and permits prediction of evaporation behavior at any set of conditions within the range investigated. Relative humidity was found to have the greatest effect, with temperature and composition following, in that order. Response of solvent balance to humidity and temperature is shown for various compositions, and evaporation time is compared to that of water under the same conditions. For example, evaporation of the ternary water-organic blends is usually slower than water at low humidity, but faster at high humidity.

RHEOLOGICAL PROPERTIES OF STYRENE/ACRYLIC POLYMERS—H.P. Schreiber and G. Thibault

Journal of Coatings Technology, 50, No. 646, 56 (Nov. 1978)

Melt viscosities of a series of styrene/butyl acrylate/methacrylic acid polymers (80/15/5) have been studied by capillary and cone and plate viscometers. All members of the series display Newtonian viscosity plateaus, but at higher shear, viscosities reduce at rates dependent on molecular weight and weight distribution. Gel permeation chromatography shows these parameters to be interdependent. Zero shear viscosities and molecular weight (M_w) define a narrow range of M_w where chain entanglement and network structure occurs. Melt viscosities below about 190°C, however, are higher from entanglement theory than expected. Further, non-Newtonian flow is observed for specimens with M_w below the entanglement "point," and flow activation energies were found to depend both on temperature and shear stress. Network stabilization mechanisms due to the existence of hydrogen bonds are proposed to account for the complex rheology, and some consequences on the practical properties of the polymers have been suggested.

SINGLE-GRADE RUTILE TiO_2 CONCEPT FOR INTERIOR LATEX TRADE SALES SYSTEMS—C.C. Tatman

Journal of Coatings Technology, 50, No. 646, 64 (Nov. 1978)

The large number of rutile titanium dioxide grades commercially available in the United States present selection, inventory, and handling problems for the manufacture of interior trade sales finishes. The use of a single grade of rutile titanium dioxide in combination with extenders already on hand would serve to relieve that situation.

Based on an evaluation of commercial latex flat wall and gloss paints, comparable quality formulas were developed in which to examine general purpose, enamel, and high-dry-hide grades of rutile titanium dioxide for optical and physical performance. The tests showed that enamel grades of rutile titanium dioxide present the greatest potential to fulfill the requirements needed for broad trade sales application.

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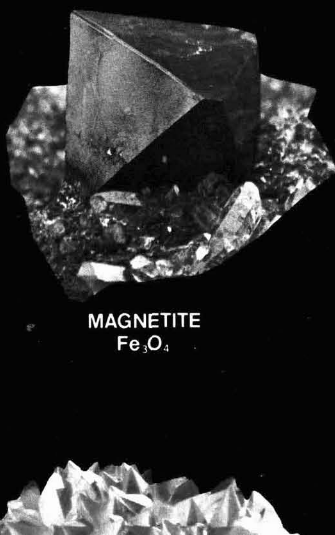

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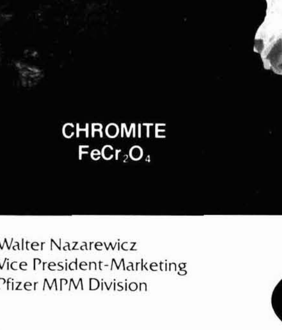

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Abstracts of Papers in This Issue (Continued)

WATER-DISPERSIBLE URETHANE POLYESTERAMIDE COATINGS FROM LINSEED OIL—W.J. Schneider and L.E. Gast

Journal of Coatings Technology, 50, No. 646, 76 (Nov. 1978)

Water-dispersible coatings from vegetable oils were easily prepared from products of the aminolysis reaction of linseed oil and diethanolamine, polybasic acid anhydrides, and tolylene diisocyanate. Polymers studied in detail to date were based on phthalic anhydride; but preliminary data indicate that pyromellitic and 3,3′,4,4′-benzophenone tetracarboxylic dianhydrides or trimellitic, maleic, succinic, and glutaric anhydrides also give polymers that result in satisfactory water-dispersible systems.

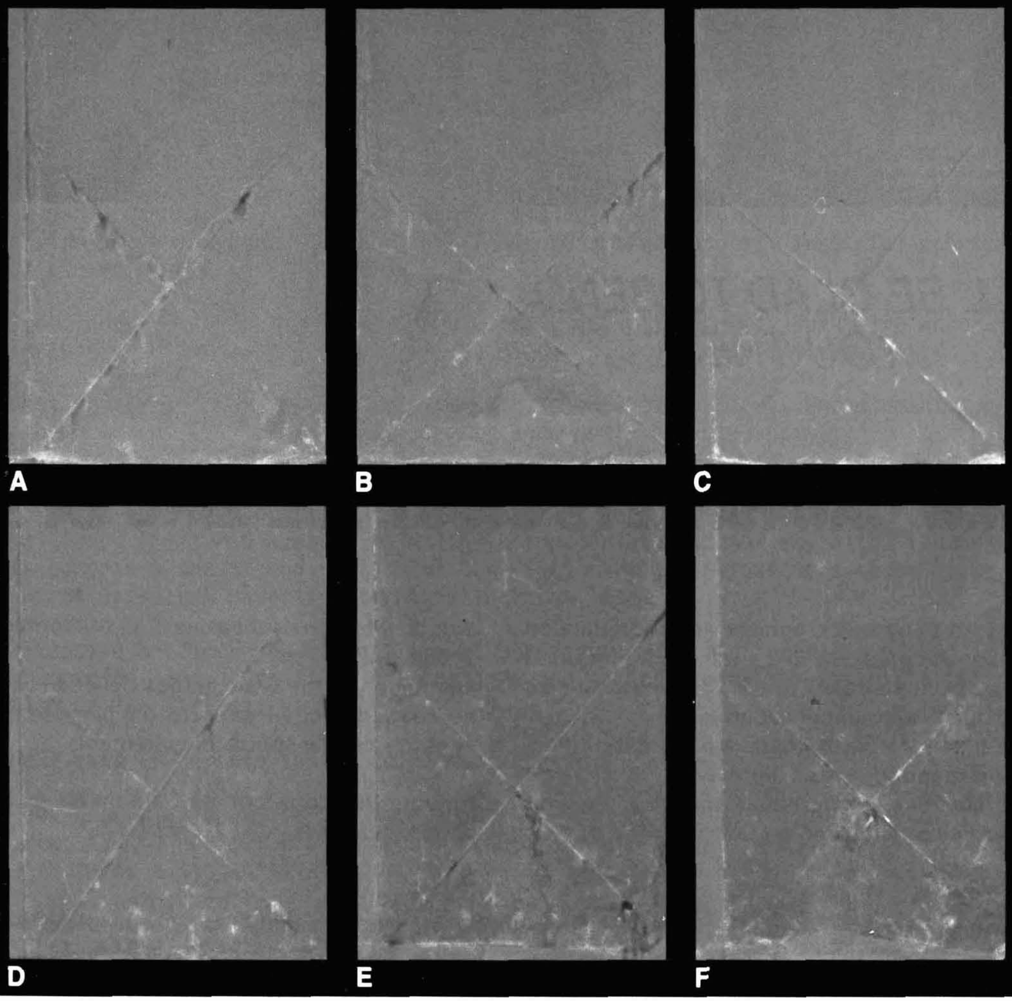
Acid value of the urethane polyesteramides, the resin/water/butyl Cellosolve® cosolvent ratio, and pH were related to dispersibility and stability of the products in aqueous solution and to their film properties, i.e., drying times, hardness, impact resistance and chemical, solvent, and water resistance. Polymers with acid values ranging from 30 to 70 were studied at 10, 20, or 30% resin concentrations in water/butyl Cellosolve. All samples dispersed readily to yield products which ranged from clear to slightly hazy solutions with Gardner viscosities of A to >Z6. Films prepared from the 30, 40, and 50 acid value polyesteramides without driers had rapid drying times (TF<1 hr), good hardness (Sward Rocker values of 34 to 62), excellent xylene resistance (> 1 wk), but poor to moderate resistance to 1% Spic and Span® solution (1.5 to 6 hr).

Cost savings could be substantial in these preparations since neither long processing times nor high temperatures normally used in alkyd technology were employed; reaction temperatures did not exceed 110°C in this process. Further savings could be realized because these materials air dry rapidly and only low baking schedules would be required for certain applications.

BENZENE—ANALYSIS AND IMPACT ON THE COATINGS INDUSTRY—D.R. Brezinski, R.C. Domingo, and J.P. Kelley

Journal of Coatings Technology, 50, No. 646, 82 (Nov. 1978)

Current statutory limits and mandatory compliance with regulatory agencies place responsibilities upon the coatings industry to guarantee product safety. The demand for low level benzene analysis has prompted the development of a simple gas chromatographic method using Siponate® DS-10 as the stationary phase. The analysis is rapid and efficient for the determination of benzene in the presence of solvents and monomers typically common to many coating formulations. Quantitation, using standard addition techniques or external calibration methods, is permitted at the low part per million level.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NUMBER 77 NOVEMBER 1978

FEDERATION NEWSLETTER

PUBLICATION OF "PAINT/COATINGS DICTIONARY" ANNOUNCED BY FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY

The Federation of Societies for Coatings Technology is pleased to announce publication of the "Paint/Coatings Dictionary," a comprehensive 632-page volume that defines the technical terms and jargon of the coatings industry and its interfacing technologies. The more than 5500 entries have been derived through consensus by the Federation's Definitions Committee over a 12-year period.

More than 4500 of the terms are defined and over 1000 additional entries are synonyms cross-referenced to the defined terms.

SI-approved units and spelling are used throughout.

The broad scope of terms included reveals the obvious usefulness of the dictionary to a wide audience, ranging from the layman, to artists and artisans, to technicians in all the coatings-related fields.

Included are the definitions for approximately 400 color terms, detailing color difference equations, optical phenomena, gloss, hiding, color instrumentation, etc.

Pigment terms have been classified by their Color Index numbers, and pigment synonyms have been extensively cross-referenced to a commonly accepted name.

A unique feature is the classification of all terms into one or more of 73 categories; these have been number coded and appear as superscripts at the end of each definition. The terms are listed in their appropriate categories in the thesaurus, which comprises the second section of the dictionary and serves as a check list for key words, research papers, literature searches, etc.

An extensive bibliography of more than 600 references of dictionaries, glossaries, encyclopedias, and journals of the coatings and allied industries forms the third section of the dictionary.

Several handy reference tables complement the text.

The 632-page dictionary (6 x 9 in.) is case-bound and sells for $30 to Federation members, $50 to non-members. Prepaid orders, add 5% to cover handling and postage; for orders requiring billing, postage plus a 50¢ handling charge will be added.

The dictionary is available from Federation of Societies for Coatings Technology, 1315 Walnut Street, Suite 832, Philadelphia, Pa. 19107

NEWS BRIEFS FROM SOCIETIES

C-D-I-C--Lew Larson, of Painteco, Inc., was named "Educational Man of the Year." Received "Ernest Mueller Memorial Education Award."

CLEVELAND--Very proud of its matching funds program begun in 1977 for the benefit of the Paint Research Institute. Last year, 22 outside contributions amounted to $735. In 1978, the total was $795 from 25 contributors. Society added $500 each year.

DALLAS--Educational and Manufacturing Committees will each be given responsibility of arranging one monthly meeting program....Plans a Technicians Course at a junior college, in cooperation with the local PCA.

DETROIT--Has proposed By-Laws changes which will give voting privileges to Associate Members and also permit one Associate to hold office at one time, and two to serve on the Board of Directors.

GOLDEN GATE--Past-Presidents in attendance at September meeting were: J.D. Beeby, R.E. Minucciani, L.F. Sanguinetti, A.G. Rook, B. Adler, A.L. Axelson, W. Sawyer L. Cummings, E. Kevin, E. Tengbergen, and E. Harmon....Due to the passing of Proposition 13, the coatings classes sponsored by the Society and the local PCA include a student tuition charge of $50.00 The Beginner and Advanced classes are taught by Bill Sawyer and Ted Favata....The Specifications Committee is working in conjunction with the Technical Committee to revise TT-P-1511A, a semi-gloss emulsion paint. The committee will test 10 leading brands, selecting their top quality semi-glosses to see if they meet the spec....Eric Tengbergren was the recipient of the Society-sponsored study grant to the summer course at the Polymer Institute at the University of Detroit.

HOUSTON--Has changed meeting night to first Wednesday and site to the Marriott, near Astroworld.

KANSAS CITY--In deference to the Federation's 1979 Annual Meeting and Paint Show in St. Louis, KC has postponed the annual joint meeting of the KC and St. Louis Societies (hosted by KC) until 1980. Board of Directors decided that this postponement will provide opportunity for more local members to attend and participate in the Federation meeting. Federation has expressed its thanks to KC for this cooperative gesture. (Houston did the same thing in 1977 when it cancelled its Southwestern Paint Convention in favor of the Federation AM & PS that year in the same city).....Twelve Society Educational Chairmen (in town for a national meeting) attend the September meeting.....Recent questionnaire to membership revealed the following program topics of greatest interest; Raw Material Technology, Formulating Techniques, Coatings Manufacturing, and Management Skills. Booking better speakers was also a suggestion for improving attendance.

LOS ANGELES--The 1979 edition of Society Year Book will include advertising....At the September meeting, Educational Committee awarded annual scholarships totalling $6,450 to children of members who can attend college of their choice.

LOUISVILLE--Coatings course--"Surface Coating Technology III, Quality Control"--is underway at University of Louisville. Jim Hoeck is instructor....Society, local PCA, and City of Louisville have joined in sponsorship of a new scholarship at University of Louisville to study "Industrial Waste Disposal"....Richard G. Fortener, who retired from Celanese after 36 years of service, was elected an Honorary Member.

MONTREAL--Fall course on "Organic Coatings I" is being given at Westmount High School. Society says this "new course is designed to meet the needs of persons entering the coatings industry for the first time." Instructors are Charles Craib and Walter Kolanitch.

NEW ENGLAND--Survey of Society membership, regarding monthly meeting programs, concluded that technical subject matter and quality of speaker are of primary importance.....Society will be 60 years old in 1979!

NEW YORK--In effort to increase service and communications to membership, Society has prepared a folder covering "Calendar of Events" for coming year - and - distributed a Newsletter, under the editorship of Jim Marshall....Attempting to reactivate Manufacturing Committee....Three courses underway by joint Education Committee of Society and local PCA: Fundamentals of Coatings Technology (NYC Community College Voorhees Campus), Color Technology (Seton Hall College), and Lab Course for Paint Technicians (at various industry laboratories)....Sponsored group flights to Federation's Annual Meeting in Chicago....The average meeting attendance for the past year was 132. Ted Young has attended all meetings for nine consecutive years; Joe Cantor for eight years....John Congleton, Louis Eromenok, and Morton Treade were elected to Honorary Membership.

PACIFIC NORTHWEST--15 are registered for the basic course in Coatings Technology at the British Columbia Institute of Technology, taught by Dave Cook.

PHILADELPHIA--As lead story indicates, the "Paint/Coatings Dictionary" has been completed and our hats are off to the Society committee consisting of: Chairman Stan LeSota, Dave Engler, Ruth Johnston-Feller, Dick Kiefer, Seymour Mark, John Landis, Mike McGroarty, Lothar Sander, and Frank Willard. A truly magnificent piece of work and contribution to the coatings industry....Has formed an Employment Service Committee, under the following statement--"It is the stated policy of the Philadelphia Society that the Employment Service is free and for the exclusive use of members of the Federation, with first preference to members of the Philadelphia Society, provided that the member is currently unemployed or has been informed of the projected date of unemployment; and that employers may use the Employment Service without charge provided that all offers of employment are for positions where vacancies exist or will exist because of retirement"....Educational Committee has surveyed membership for interest in any or all of following possible courses: a repeat of the ACS course on Coatings Technology, Color Matching and Computer Color Formulation, Laboratory Procedures, and Health and Safety Matters.... Technical Committee meetings feature speakers and Chairman Wayne Krause has released schedule for whole year....Will most likely join in with New York Society again in joint sponsorship of a spring seminar.

PITTSBURGH--Society will sponsor two students in High School Science Fair.

TORONTO--Manufacturing Committee met in September on subject of "Waste Disposal."

WESTERN NEW YORK--Working on a/v program on "Impact Testing"....Erie Community College is interested in establishing contact with industry and would offer a polymers course with sufficient enrollment.....Society offered a booth on the coatings industry at college's open house.....Will meet with local PCA on March 19.

THIS NEWSLETTER WILL BE INCLUDED

IN THE NOVEMBER JOURNAL OF COATINGS TECHNOLOGY

PROGRAM THEME FOR 1979 ANNUAL MEETING IN ST. LOUIS WILL BE "PROGRESS THROUGH INNOVATION"

The 1979 Annual Meeting of the Federation will have as its theme, "Progress Through Innovation," it was announced by Program Chairman Morris Coffino, of D.H. Litter Co., Inc. The Annual Meeting will be held in conjunction with the Paint Industries' Show at the Convention Center, St. Louis, Mo., October 3, 4, and 5.

The theme focuses on current demands upon the coatings industry, and the need for every member of the industry to explore and innovate new functions and applications for coatings, to be aware of changing regulations, and to respond to the dictates of new and exciting markets and raw materials. Accordingly, the committee is inviting speakers to present original papers which address the theme topic.

Authors wishing to present papers at the 1979 Annual Meeting are invited to submit abstracts for review to Morris Coffino, FSCT Program Chairman, c/o D.H. Litter Co., Inc., 116 E. 16th St., New York, N.Y. 10003. Deadline for receipt of abstracts is March 1.

Assisting Chairman Coffino is a Program Steering Committee composed of: William Mirick, of Battelle Memorial Institute, Columbus, Ohio (Vice-Chairman); Umberto Ancona, of McCloskey Varnish Co., Philadelphia, Pa.; Thomas Ginsberg, of Union Carbide Corp., Bound Broook N.J.; Colin D. Penny, of Hampton Paint Manufacturing Co., Inc., Hampton, Va.; and Richard E. Wolf, of DeSoto, Inc., Des Plaines, Ill.

The 1979 Annual Meeting will be hosted jointly by the St. Louis and Kansas City Societies for Coatings Technology. Chairman of the Host Committee will be Howard Jerome, of Vane Calvert Paint Co., in St. Louis.

COMING EVENTS

Feb. 12-14........Water-Borne and Higher-Solids Coatings Symposium. Sponsored by Southern Society and University of Southern Mississippi. Hyatt Regency Hotel, New Orleans.

Feb. 28-Mar. 2....Western Coatings Societies' Symposium and Show. Fairmont Hotel, San Francisco.

Mar. 14-17........Southern Society Annual Meeting. Dutch Inn, Buena Vista, Fla.

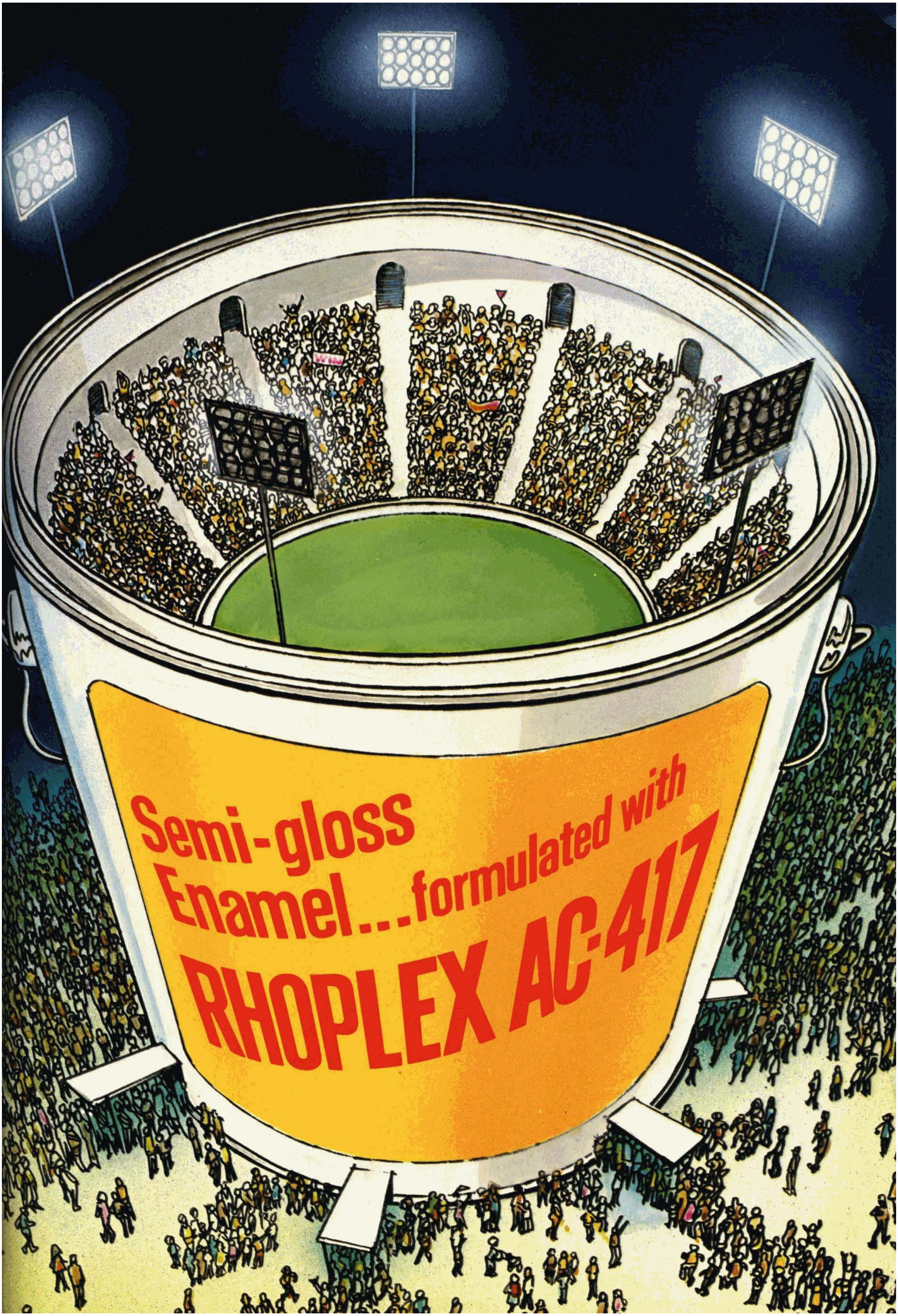
Mar. 20-21........Cleveland Society 22nd Annual Symposium. "Advances in Coatings Technology." Baldwin-Wallace College, Cleveland.

Apr. 5-7..........Southwestern Paint Convention of Dallas and Houston Societies. Shamrock Hilton Hotel, Houston.

May 3-5...........Pacific Northwest Society Annual Symposium. Bayshore Inn, Vancouver, B.C.

May 17............Society Third-ranking Officers Meeting)
May 18............Federation Board of Directors Meeting) Hilton Hotel, New Orleans.
May 19............Federation Executive Committee Meeting)

Oct. 3-5..........57th Annual Meeting and 44th Paint Industries' Show of Federation. Convention Center, St. Louis. Sheraton St. Louis and Stouffer's Riverfront Towers to serve as co-headquarters hotels.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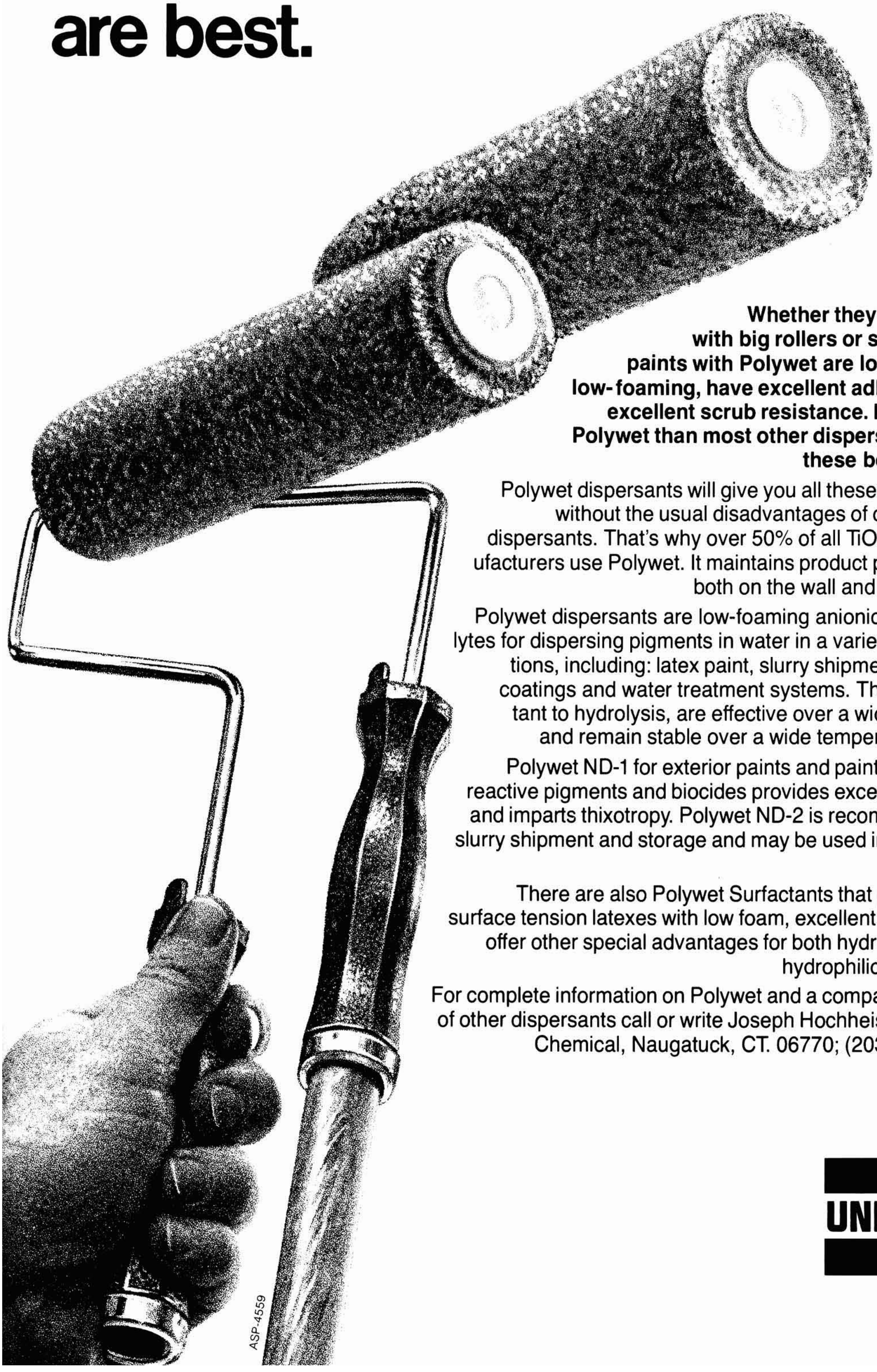
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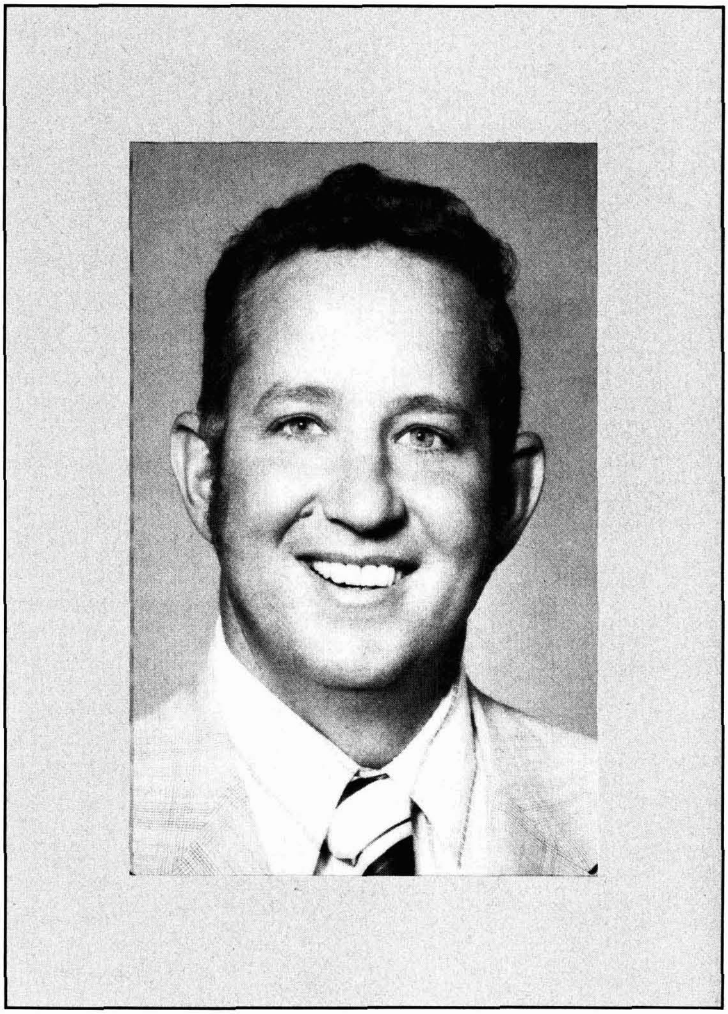
James McCormick, of Baltimore Society, Becomes Fifty-Seventh Federation President

James A. McCormick, Vice-President of Inland-Leidy, Baltimore, Md., became the 57th President of the Federation of Societies for Coatings Technology on November 3 at the Federation's Annual Meeting in Chicago, Ill.

Elder C. Larson, of Shell Development Co., Houston, Tex., was named President-Elect, and William H. Ellis, of Chevron Research Co., El Segundo, Calif., was elected Treasurer.



President McCormick

Mr. McCormick has served as Treasurer of the Baltimore Society for Coatings Technology, and was Host Committee Chairman of the Federation's 1976 Annual Meeting. He is also a Past-President of the Baltimore Coatings Association.

He has been a member of the Federation Board of Directors, and is a Past-Chairman of its Public Relations Committee.

President-Elect Larson

Mr. Larson is a Past-President of both the Golden Gate and Houston Societies, and was Program Committee Chairman of the Federation's 1977 Annual Meeting.

He has been a member of the Federation Board of Directors and currently serves as a member of the Editorial Review Board of the Federation's Publication Committee.

Mr. Larson is a graduate of Washington University, St. Louis, Mo., and is a member of the American Chemical Society.

Treasurer Ellis

Mr. Ellis is a Past-President of the Los Angeles Society and has served as Federation Council Representative. He was General Chairman of the 1972 West Coast Societies' Symposium and has served on numerous Society committees.

He has been a member of the Federation Board of Directors, and has also served on the Program and Publicity Committees as well as the Ad Hoc Committees on Education and Federation Restructuring.

Mr. Ellis received the B.S. Degree in chemistry from Stanford University.

E.C. Larson

W.H. Ellis

'Progress Through Innovation' Is Theme of 1979 Annual Meeting

The 1979 Annual Meeting of the Federation of Societies for Coatings Technology will have as its theme, "Progress Through Innovation," it was announced by Program Chairman Morris Coffino, of D.H. Litter Co., Inc., New York, N.Y.

The Annual Meeting will be held in conjunction with the Paint Industries' Show at the Convention Center, St. Louis, Mo., October 3, 4, and 5, 1979.

President McCormick Announces 1978-79 Committee Chairman

Chairman of the 30 committees of the Federation of Societies for Coatings Technology for 1978-79 have been announced by President James McCormick. A complete roster of all committees will be published in the 1979 Year Book.

An asterisk (*) indicates reappointment for 1979.

A.F. VOSS/AMERICAN PAINT & COATINGS JOURNAL AWARDS — Horace Philipp, of Sherwin-Williams Co. of Canada Ltd., Montreal, Que., Canada

BRUNING AWARD — Ruth Johnston-Feller, of Pittsburgh, Pa.*

BY-LAWS — Howard Jerome, of Vane-Calvert Paint Co., St. Louis, Mo.*

CORROSION — Dean Berger, of Gilbert/Commonwealth Associates, Inc., Reading, Pa.*

DEFINITIONS — Stanley LeSota, of Rohm and Haas Co., Springhouse, Pa.*

EDUCATIONAL — John A. Gordon, Jr., of University of Missouri — Rolla, Rolla, Mo.*

ENVIRONMENTAL CONTROL — S. Leonard Davidson, of N L Industries, Inc., Hightstown, N.J.

FINANCE — John J. Oates, of Troy Chemical Corp., Newark, N.J.

HECKEL AWARD — E.E. McSweeney, of Union Camp Corp., Pooler, Ga.*

HOST (ANNUAL MEETING) — Howard Jerome, of Vane-Calvert Paint Co., St. Louis, Mo.

INTER-SOCIETY COLOR COUNCIL — Robert T. Marcus, of PPG Industries, Inc., Springdale, Pa.

INVESTMENT — Herbert L. Fenburr, of Columbus, Ohio

LIAISON — Milton A. Glaser, of Glencoe, Ill.

MANUFACTURING — Donald Fritz, of Superior Varnish & Drier Co., Merchantville, N.J.

MATTIELLO LECTURE — Thomas J. Miranda, of Whirlpool Corp., Benton Harbor, Mich.

MMA AWARDS — Thomas Cochran, of Bruning Paint Co., Baltimore, Md.

MEMBERSHIP — John Kenney, of Sinnett Lacquer Mfg. Co., Dothan, Ala.

MEMORIAL — Carroll M. Scholle, of Sherwin-Williams Co., Chicago, Ill.*

METRIC SYSTEMS — Ernest L. Humberger, of Schenectady Chemicals Ltd., Scarborough, Ont., Canada*

NOMINATING — John J. Oates, of Troy Chemical Corp., Newark, N.J.

PAINT INDUSTRIES' SHOW — Deryk Pawsey, of Rohm and Haas Canada Ltd., Vancouver, B.C., Canada

PROGRAM — Morris Coffino, of D.H. Litter Co., Inc., New York, N.Y.

PROGRAM AWARDS — Gordon Allison, of McCormick Paint Works Co., Rockville, Md.

PUBLICATIONS — Thomas J. Miranda, of Whirlpool Corp. Benton Harbor, Mich.*

PUBLIC RELATIONS — Harry Poth, of Dean & Barry Co., Columbus, Ohio.

ROON AWARDS — Umberto Ancona, of McCloskey Varnish Co., Philadelphia, Pa.

SPECIFICATIONS — John A.J. Filchak, of General Services Administration, Auburn, Wash.*

TECHNICAL ADVISORY — Colin D. Penny, of Hampton Paint Mfg. Co., Inc., Hampton, Va.

TECHNICAL INFO SYSTEMS — Helen Skowronska, of Sherwin-Williams Co., Cleveland, Ohio*

TRIGG AWARDS — Gus W. Leep, of Illinois Bronze Powder & Paint Co., Lake Zurich, Ill.*

Delegates to Other Organizations

NATIONAL ASSOCIATION OF CORROSION ENGINEERS — Tom Ginsberg, of Union Carbide Corp., New York, N.Y.

NATIONAL FIRE PROTECTION ASSOCIATION — Howard Horton, of Glidden Pigments, SCM Corp., Cleveland, Ohio*

NATIONAL PAINT AND COATINGS ASSOCIATION, SCIENTIFIC COMMITTEE — Theodore Provder, of Glidden Pigments, SCM Corp., Strongsville, Ohio*

NATIONAL PAINT AND COATINGS ASSOCIATION AND GOVERNMENT AGENCIES (Environmental Control) — S. Leonard Davidson, of N L Industries, Inc., Hightstown, N.J.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY — Percy E. Pierce, of PPG Industries, Inc., Allison Park, Pa.; Milton A. Glaser, of Glencoe, Ill.

Additional Contributions Advance PRI Research Efforts

Financial contributions in support of the research projects of the Paint Research Institute were increased during the third quarter of 1978, bringing to 71 the number of contributors to PRI for the 1978 research programs (an increase of seven over this period last year), and supplementing funds committed by the Federation.

Contributions received at Federation headquarters (January 1 to September 30) were made by the following:

Societies

Southern; New York; Baltimore; Rocky Mountain; Pacific Northwest; Golden Gate; C-D-I-C; Montreal; Toronto; and Cleveland.

Corporations

Rohm and Haas Co.; Harrison & Crosfield (Canada) Ltd.; Ohio Solvents & Chemicals Co.; Mameco International; Union Carbide Corp.; Midland Div., Dexter Corp.; Benjamin Moore & Co.; David Litter Labs.; Drew Chemical Corp.; Reed Decorative Products Ltd.; DeSoto, Inc.; Dow Chemical, U.S.A.; Nacan Products Ltd.; L.V. Lomas Chemical Co.; Benjamin Moore & Co. Ltd.; Dumar Paints & Chemicals Ltd.; Reichhold Chemicals Ltd.; Bate Chemical Co.; Ltd.; Mobil Chemical Canada Ltd.; Canadian Industries Ltd.; Shell Chemical Co.; Tioxide of Canada Ltd.; Inmont Canada Ltd.; Dar-Tech, Inc.; Donald McKay Smith, Inc.; Jamestown Paint & Varnish Co.; Body Bros., Inc.; The M.F. Cachat Co.; Gulf & Western Chem.-Div. Titanium; Kalcor Coatings Co.; Internat'l Minerals & Chemical Corp.; Ferro Corp.; Monsanto Co.; Palmer Supplies Co. of Cleveland; Q-Panel Co.; Seegott, Inc.; Davies Can Co.; Pfizer, Inc.; Mobay Chemical Corp; Canada Colors & Chemicals Ltd.; Gulf Oil Canada Ltd.; Celanese Canada, Inc.; Selectone Paints Ltd.; Canadian General Electric Co.; and PPG Industries, Inc.

Foundations

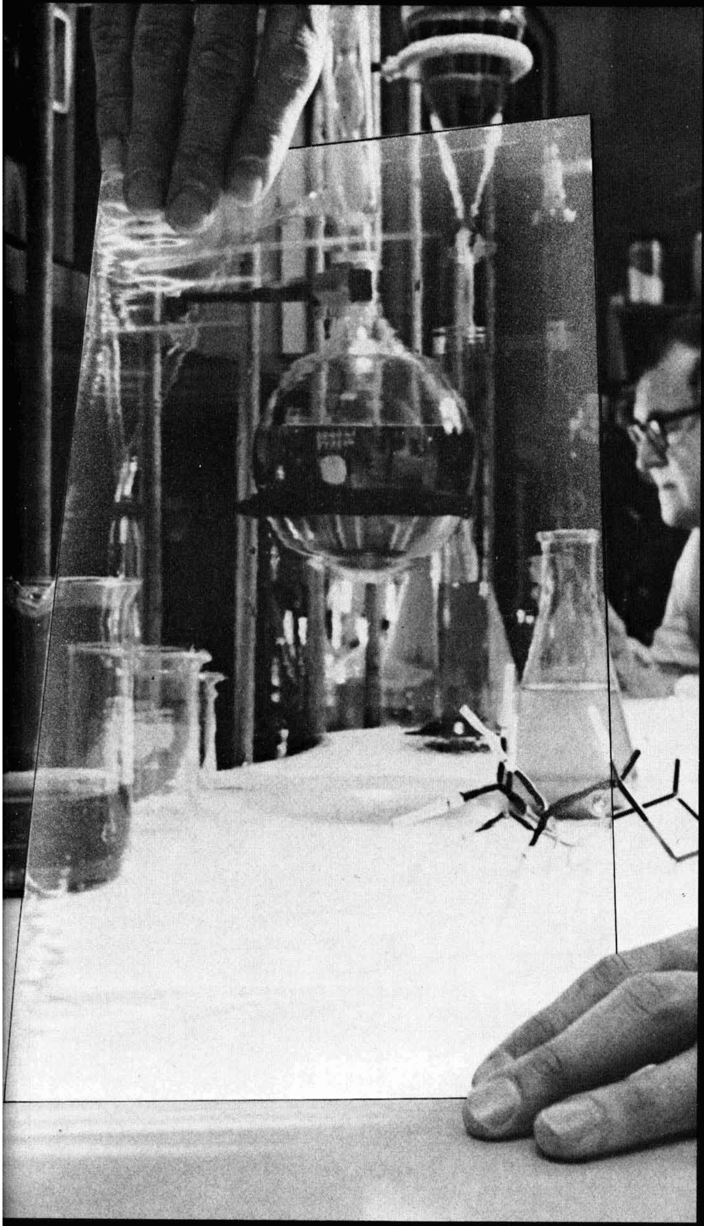
The N L Industries Foundation; and Henry Reichhold Foundation.

Associations

Baltimore Coatings Association; Ontario Paint Association; and Canadian Paint & Finishing Magazine.

Individuals

Mr. & Mrs. Flemming Kress; Mr. & Mrs. James Broggini; Ross Galati; Alan R. Hatter; Kenneth C. Waldo, Jr.; Helen M. Skowronska; Thomas D. Tuckerman; Charles A. Kumins; Fred Schwab; and Raymond R. Myers.



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Committee Activities

ENVIRONMENTAL CONTROL

NPCA Task Force Reviews Hazardous Waste Regulations

The Water Quality and Waste Management Task Force, of the National Paint and Coatings Association, met in Washington, D.C. recently to review the latest developments in regulatory action in the area of hazardous wastes.

Previously, Task Force members met with representatives of the Environmental Protection Agency (EPA) to discuss a draft of a test method (Sec. 3001) "Criteria Identification Methods and Listing of Hazardous Wastes." EPA is currently rewriting several test methods in an attempt to make them more accurate. Members anticipate that the draft will be concluded by the end of this year and will be followed by public hearings. Final rules are expected by the end of 1979. Meanwhile, samples of representative sludges will be analyzed to ascertain if possible exemptions exist.

Of increasing concern are polychlorinated biphenyls (PCB). They appear in a number of Phthalocyanine Blues and Greens and in Diaralyde Yellows. Pigment suppliers should be contacted to determine if shipments contain PCB, even in minute quantities.

Meanwhile, several nationally-known environmental groups have notified the EPA that they plan to sue the agency because they believe it is not moving fast enough in implementing the Resource Conservation and Recovery Act. Implementation of the Act in the coatings industry would require a massive effort by manufacturers.

●

Members of the NPCA Air Quality Task Force and NPCA staff met with New Jersey and New York state regulation writers to discuss drafts of proposed regulations and to suggest that the Federal EPA guidelines be followed with regard to Reasonably Available Control Technology (RACT). Both states were favorable to the suggestion and will proceed accordingly. New Jersey will probably adopt a RACT type regulation with compliance scheduled for 1980.

It was noted that individual plants may be exempted from RACT requirements if there is justification on particular exemptions based on individual plant studies. Small sources (less than 100 tons/year of Volatile Organic Compound) may be exempted. A Sub Task Force will study present questions of VOC definition and the determination of best test method.

In addition to the aforementioned states, the following are now drafting new or revised regulations: Colorado, Delaware, Illinois, Indiana, Maryland, Massachusetts, Michigan, Ohio, Oklahoma, Oregon, Pennsylvania, Tennessee, Texas, Virginia, Washington, and Wisconsin.

Members of the coatings industry in the above states are requested to monitor the activities of their respective state agencies, regulation changes, and public hearings regarding those changes, and to forward such notices to this delegate.

●

The EPA now has available the following volumes of Control Technique Guidelines: Vol. VI, "Surface Coating of Miscellaneous Metal Parts," and Vol. VII, "Surface Coating of Plat Woodstock." The EPA has also published Volumes I and II of "Air Quality Criteria for Ozone and Other Photochemical Oxidants."

GABRIEL MALKIN
Delegate to NPCA
and Governmental Agencies
(Environmental Control)

Government and Industry

Step-Down Approach Urged for CPSC Regulation Of Benzene as a Consumer Product Contaminant

NPCA filed comments with the Consumer Product Safety Commission (CPSC) urging the Commission to adopt a graduated step-down approach to its regulation of consumer products containing benzene as a trace impurity.

CPSC announced its intention to ban all consumer products, except gasoline and solvents or reagents for laboratory use, containing benzene as an intentional ingredient or as a contaminant at a level of 0.1% or more by volume in a *Federal Register* notice published on May 19, 1978 (See JCT, July 1978, p 64). The May 19 notice outlined several alternative ways of effecting the proposed ban.

NPCA requested CPSC to amend its proposed regulation by declaring consumer products containing benzene at levels of 0.5% or greater as banned hazardous products for a period of three years from the effective date of the regulation and then to step down the exclusion level to 0.1% or greater of benzene by volume.

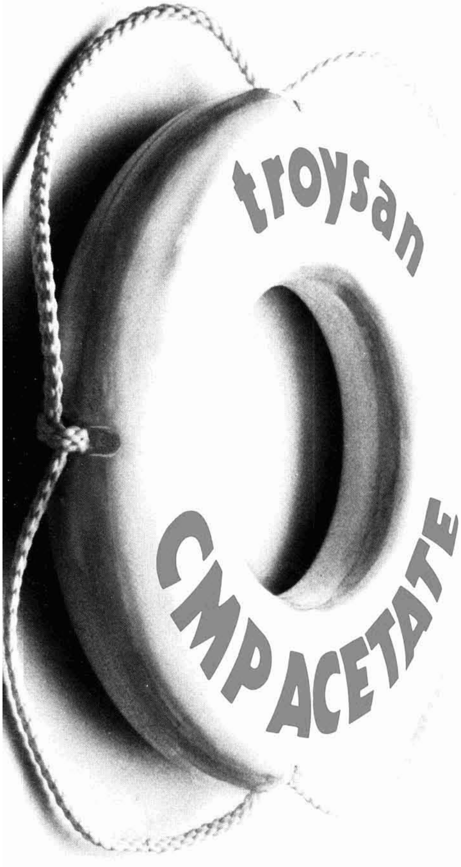
NPCA noted that the Occupational Safety and Health Administration has adopted this approach, based on extensive data from its rulemaking proceedings on occupational exposure to benzene. NPCA believes that since the basis of CPSC's proposed regulation is primarily data on workplace exposure, the Commission should provide for the same step-down approach taken by OSHA.

NPCA stated that exposure to benzene in consumer products is of an occasional rather than a chronic nature and, therefore, constitutes a lesser risk than workplace exposure.

NPCA also said that the pervasive nature of benzene in our environment and the impossibility of detecting trace amounts also justifies setting an exclusion level for exposure to trace amounts of benzene.

OSHA's record on benzene indicates that while not commercially available on a sufficiently large basis, materials with 0.1% or less benzene have been produced and are available on a limited basis, NPCA noted.

It was pointed out that the paint and coatings industry is dependent on the availability of raw materials to meet the proposed regulation's requirements.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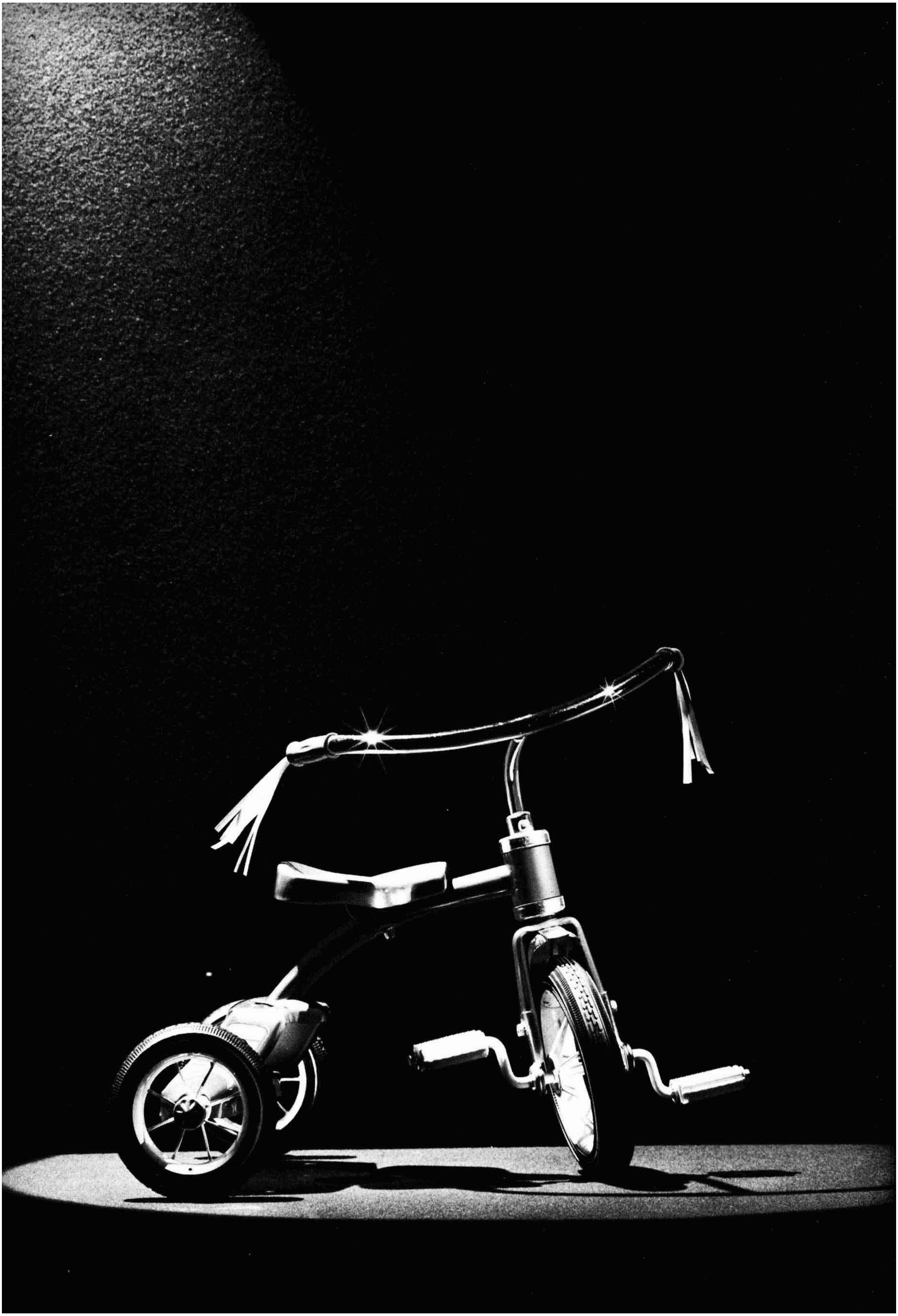

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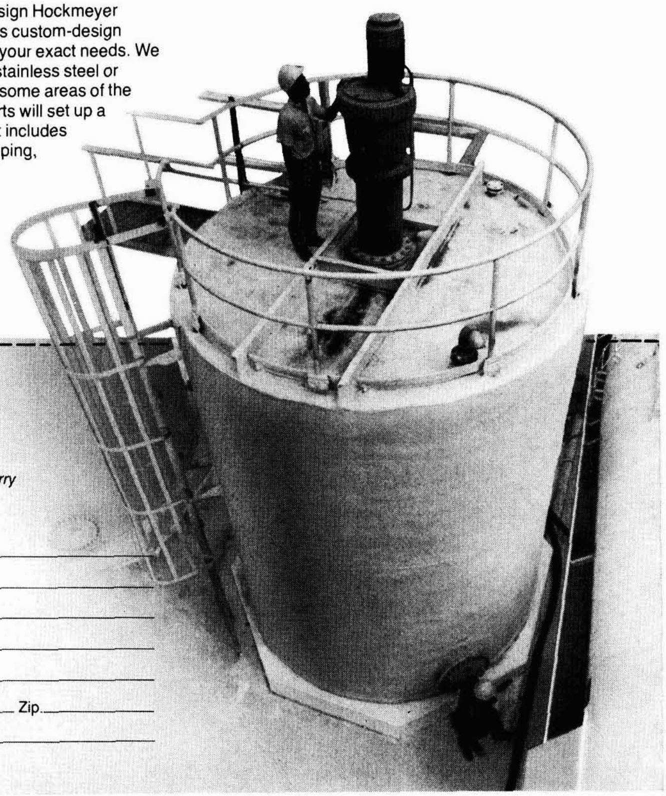

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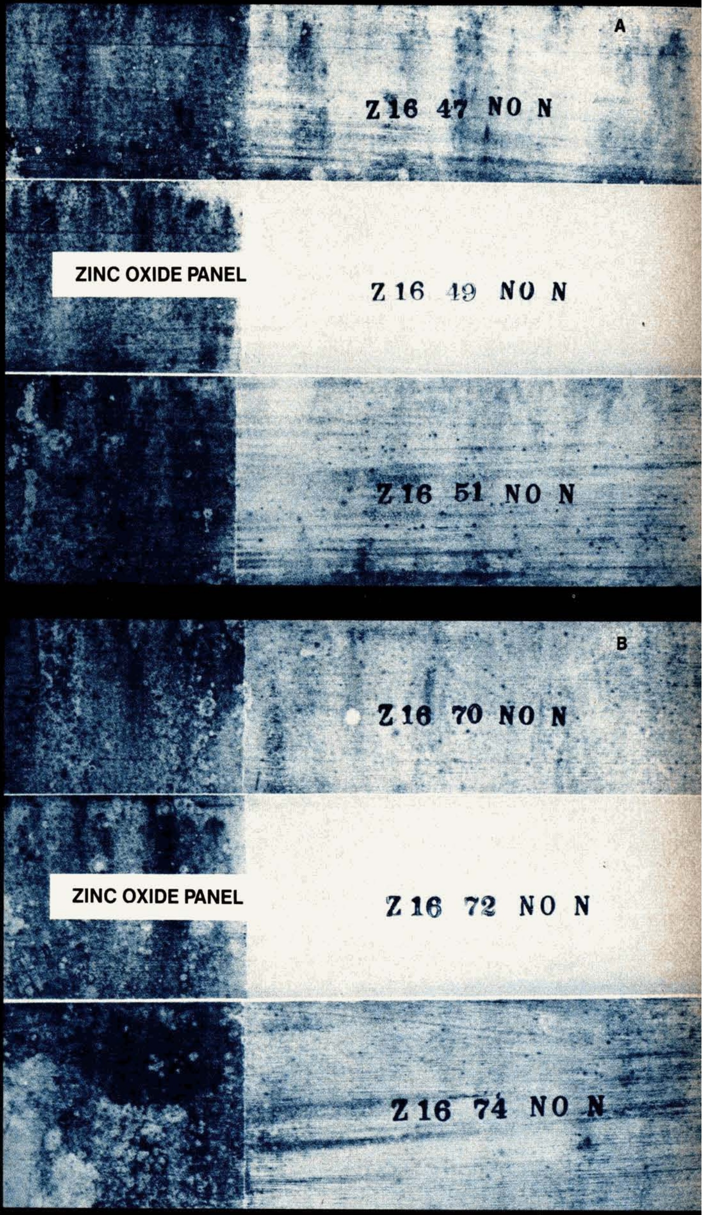
If you would like more information on the use of zinc oxide for mildew control, contact your zinc oxide supplier, or the Zinc Institute.



Test Z-16. 2 coats self-primed on yellow pine, north exposure. New Orleans.

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FOR APPLICATION TO EXHIBIT CONTACT:

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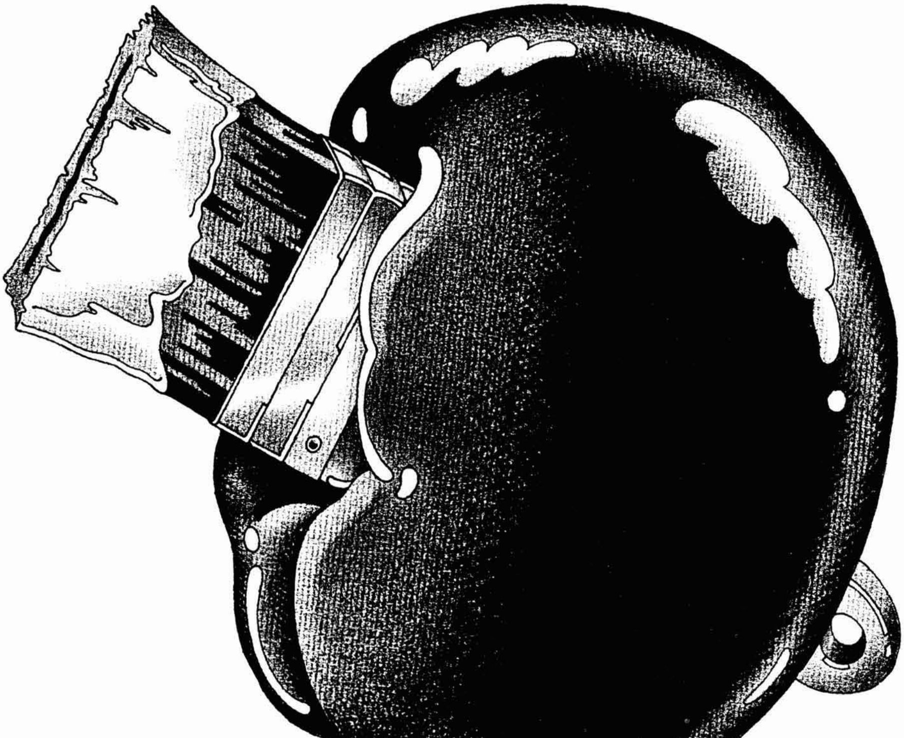

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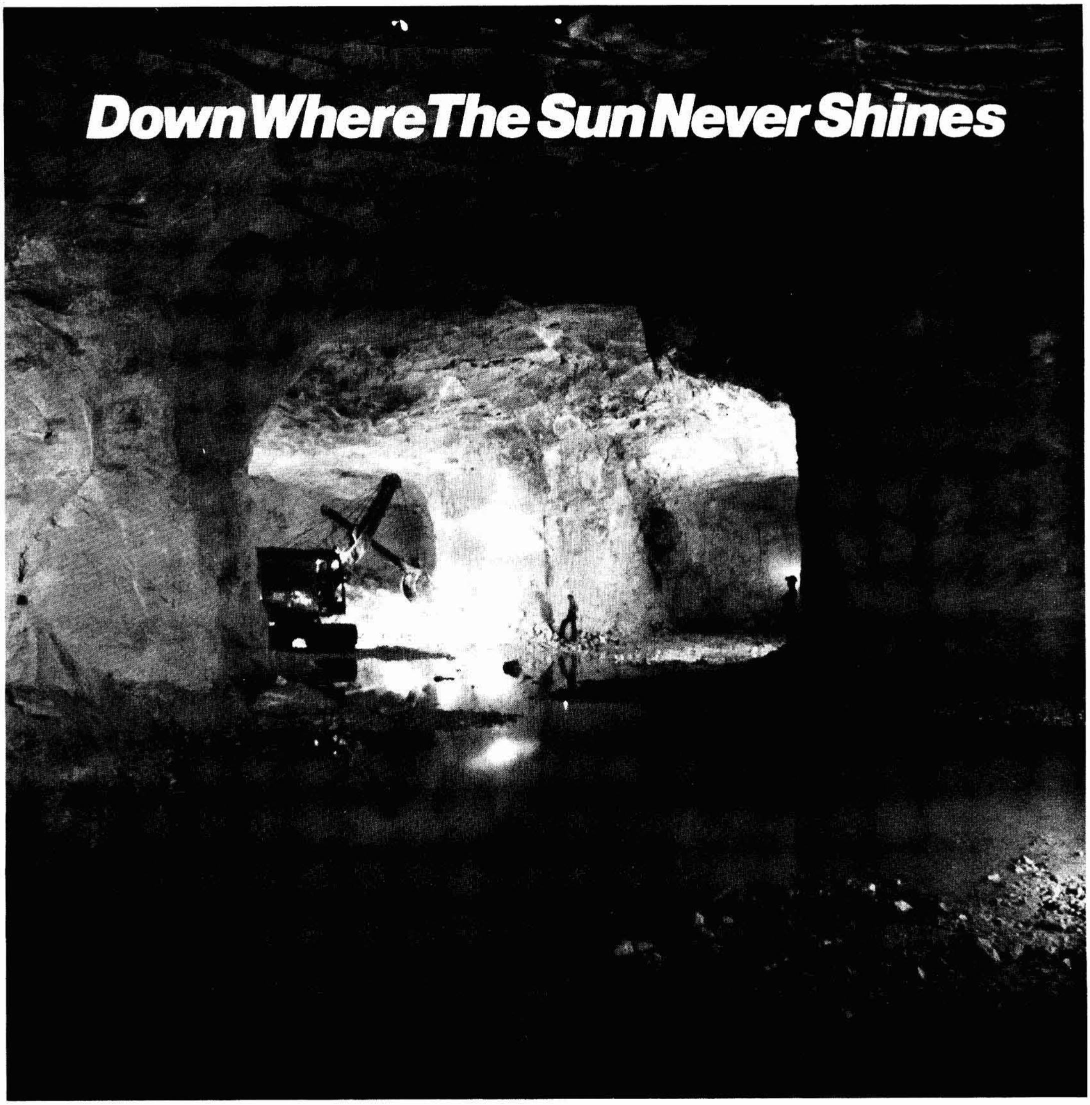
Down Where The Sun Never Shines

ROON FOUNDATION AWARDS

1978

Cathode Reactions and Metal Dissolution In Cationic Electrodeposition

Effect of Humidity and Other Ambient Conditions On Evaporation of Ternary Aqueous Solvent Blends

Rheological Properties Of Styrene Acrylic Polymers

Single-Grade Rutile TiO_2 Concept For Interior Latex Trade Sales Systems

THIS PAPER WAS AWARDED FIRST PRIZE OF $750 IN THE 1978 ROON AWARDS COMPETITION

Cathode Reactions And Metal Dissolution In Cationic Electrodeposition

D.G. Anderson, E.J. Murphy, and J. Tucci III
DeSoto, Incorporated*

In any electrochemical cell, reduction takes place at the cathode and, therefore, the metal surface does not ionize and remains passive during the deposition process. In theory, this proposed cathode passivity and the absence of included metallic ions portended virtual elimination of the typical anodic problems related to coating/substrate interactions. Because of this assumed passivity, most of the literature since the introduction of viable cationic systems, has been of a highly commercial nature, praising the new cationics as superior to the established anionics.

Approximately five years of commercial and laboratory experience, however, have taught cationic practitioners that cathodic systems do suffer from staining and film discoloration, and their cured film performance is still largely determined by the type and quality of substrate and pretreatment. Yet, there has been no published research during this period related to possible coating/substrate interactions in cationic electrocoat systems.

This paper studies possible cathode reactions which lead to substrate dissolution and inclusion of metallic ions in the deposited films.

INTRODUCTION

The commercial announcement of the cathodic electrodeposition of organic coatings in 1971 was a very significant event in the coatings industry.[1] It marked a potential quantum advance in the technology of providing corrosion protection to metallic substrates by means of the most efficient painting process known to date. Anodic electrodeposition had been commercially practiced for many years, and was a major advance in coatings practice over spray and dip application methods. The anodic process was extraordinarily clean and efficient, and the property of "throwpower" allowed hidden and recessed areas of the preformed workpiece to be coated uniformly.

However, as commercial practice and laboratory investigations were to reveal, the anodic process suffered from a singular process related problem, i.e., the electrochemical dissolution of the metallic workpiece and the inclusion of these dissolved metals into the organic film. A number of investigators have examined in-depth the causes and consequences of this metal dissolution.[2,3,4] As stated, the metal dissolution is process related. In any anionic electrocoat cell, the significant reactions can be summarized as follows:

1) ELECTROLYSIS OF WATER

$$2\,H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$

2) OXIDATION OF ANODE

$$M^0 \longrightarrow M^{n+} + ne^-$$

3) CARBOXYLATE POLYMER DEPOSITION

$$RCOO^- + H^+ \longrightarrow RCOOH$$

$$RCOO^- + M^{n+} \longrightarrow (RCOO)_n{-}M$$

The consequences of this electrochemical metal dissolution have been less extensively documented,[5,6] but are well known. They include: reduced corrosion and detergent resistance, nonuniform staining and discoloration of the cured films, reduced exterior durability, and sensitivity to variations in substrate and pretreatment quality.

Therefore, the announcement of the commercialization of a cathodic electrocoat system was received with great expectation. The singular cause of this elation is as follows. In any electrochemical cell, reduction takes place at the cathode and, therefore, the metal surface does not ionize and remains passive during the deposition process.[7] The cathode reactions which have been proposed for a typical cationic electrocoat cell are summarized below:

1) ELECTROLYSIS OF WATER

$$4H_2O + 4e^- \longrightarrow 4OH^- + 2H_2$$

2) AMINO POLYMER DEPOSITION

$$R_3NH^+ + OH^- \longrightarrow R_3N + H_2O$$

In theory, this proposed cathode passivity and the absence of included metallic ions portended virtual elimination of the typical anodic problems related to

---

*1700 S. Mt. Prospect Rd., Des Plaines, Ill. 60018.

Presented by Mr. Anderson at the 56th Annual Meeting of the Federation of Societies for Coatings Technology in Chicago, Ill., November 2, 1978.

Table 1—Changes in Dissolved Iron and Current Efficiency During Cationic Electrodeposition over Cold Rolled Steel

SUBSTRATE = COLD ROLLED STEEL
Neutralizing Acid = Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs / Gram	ppm Fe
65	25	90	145	35
65	80	90	78	27
65	80	20	75	45
90	25	90	282	262
90	80	90	97	46
90	80	20	94	49

Table 3—Changes in Dissolved Zinc and Current Efficiency During Cationic Electrodeposition over Zinc Phosphated Steel

SUBSTRATE = EP2
Neutralizing Acid = Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs / Gram	ppm Zn
65	25	90	115	101
65	80	90	65	86
65	80	20	66	209
90	25	90	172	23
90	80	90	95	20
90	80	20	92	30

coating/substrate interactions. Because of this assumed passivity, most of the literature since the introduction of viable cationic systems, has been of a highly commercial nature, praising the new cationics as superior to the established anionics. However, theoretical predictions and actual practice have not really correlated with one another. Roughly five years of commercial and laboratory experience have taught the cationic practitioners that cathodic systems do suffer from staining and film discoloration, and their cured film performance is still largely determined by the type and quality of substrate and pretreatment. And yet, there has been no published research, within this time, related to possible coating/substrate interactions in cationic electrocoat systems.

It was largely this experience and the lack of available literature, which led the authors to consider the possibility that, contrary to theory, the cathode workpiece in a cathodic system might not be totally passive with respect to electrolytic dissolution. Therefore, it was the purpose of this investigation to study possible cathode reactions which lead to substrate dissolution and inclusion of metallic ions in the deposited films.

Experimental Procedures

In brief, the basic experimental procedure was electrodepositing anionic and cationic clear coatings onto various substrates, removing the deposited films via solvent dissolution, and determining the dissolved metal content based on deposited film weight using atomic absorption spectroscopy.

Polymeric Vehicles Studied

The cationic resin used for these studies was a tertiary amine - hydroxy functional styrene/acrylate copolymer having an amine value of 58-60 on nonvolatile material and a hydroxyl value of 84-86 on nonvolatile content. The anionic vehicle used for the comparison studies was of identical composition except for being carboxylic acid-hydroxy functional. The acid value was 58-60 on nonvolatile and the hydroxyl value was also 84-86 on nonvolatile.

The coating baths were prepared using standard electrocoat practice, i.e., the resinous vehicle was mixed with the neutralizing agent and deionized water added slowly under constant agitation. All baths were reduced

Table 2—Changes in Dissolved Iron and Current Efficiency During Cationic Electrodeposition over Iron Phosphated Steel

SUBSTRATE = EP10
Neutralizing Acid = Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs / Gram	ppm Fe
65	25	90	159	143
65	80	90	68	74
65	80	20	70	104
90	25	90	303	36
90	80	90	103	33
90	80	20	96	56

Table 4—Changes in Dissolved Aluminum and Current Efficiency During Cationic Electrodeposition over Aluminum

SUBSTRATE = ALUMINUM
Neutralizing Acid = Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs / Gram	ppm Al
65	25	90	104	1500
65	80	90	66	3400
65	80	20	65	500
90	25	90	167	332
90	80	90	99	1165
90	80	20	89	301

Table 5—Changes in Dissolved Iron and Current Efficiency During Cationic Electrodeposition over Cold Rolled Steel

SUBSTRATE = COLD ROLLED STEEL
Neutralizing Acid = Hydroxy Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs/Gram	ppm Fe
65	25	90	116	167
65	80	90	93	141
65	80	20	82	265
90	25	90	308	335
90	80	90	108	105
90	80	20	103	316

to 10% nonvolatile content prior to electrodeposition. The cationic vehicles were neutralized to 65 or 90% with either an aliphatic, water-soluble carboxylic acid or a hydroxy-aliphatic acid. The pK_a of the neutralizing acids were identical at 4.75. The anionic baths were prepared in a similar manner employing diethylethanol amine as the neutralizing agent.

Substrates and Coating Methods

All substrates used for these studies were standard, commercially available, test panels. Three of the substrates were supplied by Parker Co.: EP-2 zinc phosphated cold rolled steel, EP-10 iron phosphated cold rolled steel, and untreated cold rolled steel (CRS). The fourth substrate tested was A412 untreated aluminum from the Q Panel Co.. Prior to electrodeposition of the organic films all panels were rinsed with deionized water and prebaked for 10 min at 350°F (177°C), and then weighed to the nearest milligram.

Electrodeposition of the organic films was performed out of 10% solids baths maintained at 85°F (29°C), employing standard electrocoating techniques at the stated deposition times and voltages. For the cationic systems a No. 20 cored carbon electrode from Atlas Electric Devices Co., was used as the anode, and for the anionic systems a heavy gauge 316 stainless screen was employed as the cathode. Coulomb measurements were made using a Model VT 1176 B coulometer from Vari-Tech Co. After deposition, all panels were rinsed with deionized water and heated for 1 min at 250°F (121°C) to accomplish drying of the deposited films. Panels were then reweighed to the nearest milligram to determine deposited film weights. The panels were then placed in glass jars and the films washed from the substrate with methyl ethyl ketone. The dimensions of the test panels were 3 in. × 6 in., and for all experiments a minimum of three panels were deposited for each methyl ethyl ketone solution prepared. As a control for the cationic systems and to determine background levels of dissolved metals, tests were run according to the above mentioned techniques employing a platinum screen as a cathode workpiece.

Table 6—Changes in Dissolved Iron and Current Efficiency During Cationic Electrodeposition over Iron Phosphated Steel

SUBSTRATE = EP10
Neutralizing Acid = Hydroxy Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs/Gram	ppm Fe
65	25	90	107	67
65	80	90	94	144
65	80	20	83	182
90	25	90	196	83
90	80	90	100	46
90	80	20	94	90

Table 7—Changes in Dissolved Zinc and Current Efficiency During Cationic Electrodeposition over Zinc Phosphated Steel

SUBSTRATE = EP2
Neutralizing Acid = Hydroxy Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs/Gram	ppm Zn
65	25	90	104	78
65	80	90	87	76
65	80	20	74	87
90	25	90	162	65
90	80	90	95	54
90	80	20	97	65

Atomic Absorption Spectroscopy

All atomic absorption spectrometric analyses were performed using a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Zinc and iron analyses were performed at 213.9 nm and 248.3 nm,[8] respectively, using an air-acetylene flame and a 10 cm single slot burner. Analyses for aluminum were ob-

Table 8—Changes in Dissolved Aluminum and Current Efficiency During Cationic Electrodeposition over Aluminum

SUBSTRATE = ALUMINUM
Neutralizing Acid = Hydroxy Aliphatic pKa = 4.75

% Neutral.	Voltage	Time (sec)	Coulombs/Gram	ppm Al
65	25	90	101	139
65	80	90	84	178
65	80	20	80	134
90	25	90	152	900
90	80	90	94	2138
90	80	20	96	445

Table 9—Iron Dissolution During Anionic And Cationic Electrodeposition over Cold Rolled Steel
Voltage = 90 (constant) 90% Neutralization

SUBSTRATE = COLD ROLLED STEEL

Deposition Time (Seconds)	Anionic ppm Fe	Cationic ppm Fe
10	425	419
15	500	146
30	628	119
40	756	70
50	945	68
60	1001	63
80	1728	60
90	2167	55

Table 11—Zinc Dissolution During Anionic And Cationic Electrodeposition over Zinc Phosphated Steel
Voltage = 90 (constant) 90% Neutralization

SUBSTRATE = EP2

Deposition Time (Seconds)	Anionic ppm Zn	Cationic ppm Zn
10	10800	203
15	10700	145
30	10800	101
40	10900	94
50	10700	86
60	12200	89
80	13200	84
90	13300	83

tained using a nitrous oxide-acetylene flame and a 5 cm single slot burner at 303.9 nm. Calibration was performed daily by dilution of 1000 ppm stock solutions of the metals prepared by Fisher Scientific Co. Analysis of the electrodeposited films was performed in the following manner:

(1) Methyl ethyl ketone solutions of the electrodeposited films were evaporated to dryness at 60°C and the weight of coating obtained to the nearest 0.2 mg using an analytical balance.

(2) All organic material was removed by dry ashing[9] at 450°C for 16 hr.

(3) The residue on ashing was dissolved in 25 ml concentrated hydrochloric acid with moderate heating.

(4) Following dissolution, the volume of each solution was diluted to 50 ml in a volumetric flask.

(5) These solutions were aspirated directly into the flame of the atomic absorption spectrophotometer and suitable dilutions made where appropriate.

DATA PRESENTATION

The data obtained during the investigation are presented in *Tables* 1 through 14 and in *Figures* 1 through 5.

As stated previously, the working hypothesis for this investigation assumed that the cathode workpiece was not totally passive during the process of cathodic electrodeposition, but did in fact suffer dissolution, leading to the inclusion of metal salts in the cationic films. The experimental results are presented in the order of their chronological acquisition. An overall summary and conclusions will be presented later. It should be noted that the metal content of all the baths were obtained as a control measure and to establish background levels and instrument sensitivity. Metal concentrations for iron, zinc, and aluminum were found to be 5, 13 and 10 ppm, respectively, based on bath nonvolatiles.

The data presented in *Tables* 1-4 are results for the four separate substrates when coated for selected times and at selected voltages from a cationic bath neutralized at either 65 or 90% with an aliphatic carboxylic acid. An examination of this data immediately appears to con-

Table 10—Iron Dissolution During Anionic And Cationic Electrodeposition over Iron Phosphated Steel
Voltage = 90 (constant) 90% Neutralization

SUBSTRATE = EP10

Deposition Time (Seconds)	Anionic ppm Fe	Cationic ppm Fe
10	109	205
15	150	84
30	216	50
40	246	44
50	290	48
60	297	47
80	298	42
90	308	42

Table 12—Iron Dissolution During Anionic And Cationic Electrodeposition over Zinc Phosphated Steel
Voltage = 90 (constant) 90% Neutralization

SUBSTRATE = EP2

Deposition Time (Seconds)	Anionic ppm Fe	Cationic ppm Fe
10	155	88
15	147	70
30	179	54
40	216	40
50	228	35
60	247	32
80	253	30
90	249	30

Table 13—Aluminum Dissolution During Anionic And Cationic Electrodeposition over Aluminum
Voltage = 90 (constant) 90% Neutralization

SUBSTRATE = ALUMINUM

Deposition Time (Seconds)	Anionic ppm Al	Cationic ppm Al
10	320	210
15	440	300
30	2300	640
40	3050	930
50	3600	1290
60	4200	1580
80	5380	2070
90	6160	2470

Table 14—Iron and Zinc Content Of Cationically Electrodeposited Films over Platinum

SUBSTRATE = PLATINUM

Deposition Time (Seconds)	ppm Fe	ppm Zn
10	7	27
20	4	14
30	3	12
40	8	17
50	5	15
60	7	9
80	8	18
90	6	9

firm the working hypothesis. The data indicate, especially in the case of aluminum, that dissolved metal is being introduced into the deposited films. Substrate activity is also demonstrated because metal content is variable against all parameters of type of substrate, degree of neutralization, time, and voltage.

Tables 5-8 are again results for the four substrates coated for selected times and voltages from a cationic bath neutralized at either 65 or 90% with a hydroxy aliphatic acid. These data also clearly indicate that, contrary to theory, the cathode workpiece in cathodic electrodeposition is an active component in the process. Again, the dissolved metal content at all data points is much higher than would be expected based on the background levels, in fact, by two or three orders of magnitude in some cases.

Review of the data reveals several trends:

(1) Dissolved metal content for the ferrous substrates tends to be higher at the shorter deposition times and at the lower voltages.

(2) Dissolved aluminum is highest at longer deposition times and higher voltages.

(3) Untreated aluminum is much more active than the ferrous substrates.

(4) In most cases, more metal dissolution occurs when employing a hydroxy aliphatic acid as the neutralizing agent.

(5) A nominal trend appears to be an overall higher metal content at 65% neutralization than at 90%.

A second set of studies were conducted with anionic and cationic baths at 90% neutralization with diethylethanol amine and a hydroxy aliphatic acid, respectively. For these studies, a constant deposition voltage of 90 volts was employed, however, the deposition time was varied. The data are presented in *Tables* 9-14 and in *Figures* 1-5. The graphical depiction of the data shows the striking contrast in substrate activity between anionic and cationic systems. While all substrates have considerably less dissolved metal for the cationic system, it is obvious that they are not passive. In both anionic and cationic deposition, each type of substrate has its own behavior pattern. The most notable difference between the systems is that dissolved metal content based on deposited film weight con-

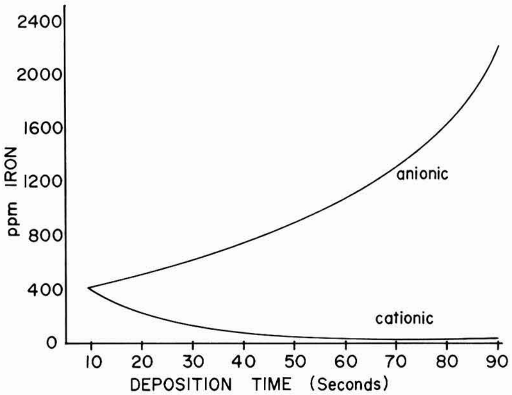

Figure 1—Changes in iron content of electrodeposited films on cold rolled steel with deposition time. Voltage = 90 (constant) 90% Neutralization

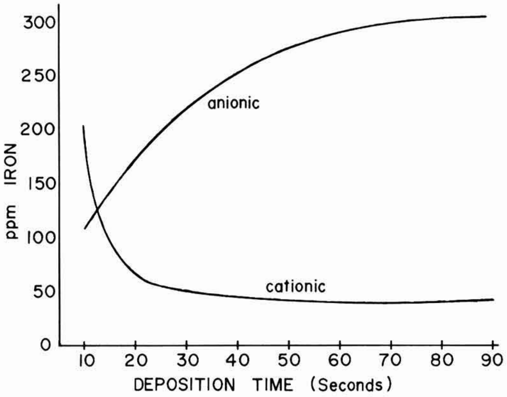

Figure 2—Changes in iron content of electrodeposited films on iron phosphated steel with deposition time. Voltage = 90 (constant) 90% Neutralization

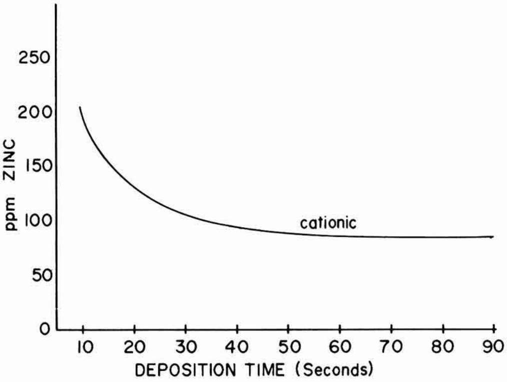

Figure 3—Changes in zinc content of electrodeposited films on zinc phosphated steel with deposition time. Voltage = 90 (constant) 90% Neutralization

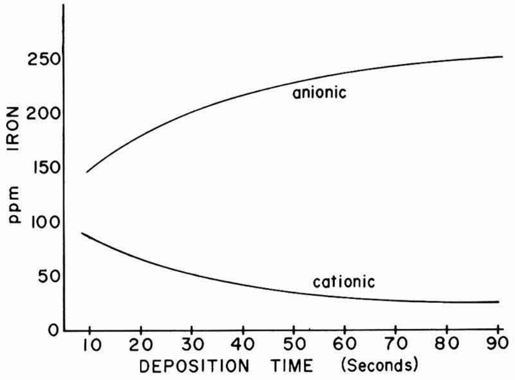

Figure 4—Changes in iron content of electrodeposited films on zinc phosphated steel with deposition time. Voltage = 90 (constant) 90% Neutralization

stantly increases with time in the anionic system, but decreases with time in the cationic, with the notable exception of untreated aluminum.

It is noted that the anionic data presented for zinc content over EP2 (*Table* 11) is higher than data presented by other investigators.[2,3] All other data points appear internally consistent and correlate with data presented by earlier investigators for anionic systems.[2,3]

CONCLUSIONS AND DISCUSSION

As stated previously, the mechanisms of the electrode reactions in anionic systems have been thoroughly investigated and are reasonably well understood. Apparently, dissolution of metal is continuous throughout the deposition process even after the insulating organic film has been deposited. This is because of the constant presence of water at the electrode surface which is available for ongoing electrolysis and subsequent oxidation of the anode. An excellent and highly quantitative examination of the anionic electrodeposition process has been presented by Beck.[10] The basic process of deposition involves the electrolysis of water at the anode to form high concentrations of hydrogen ions in a proximate boundary phase at the anode causing neutralization and coagulation of the polymeric carboxy anions which electrophoretically migrate into this highly acid boundary phase.

As the insulating organic film builds, the current density diminishes to the point where sufficient concentrations of hydrogen ion can no longer be maintained in a boundary phase and coagulation of the carboxy anions ceases. However, current density never decreases to zero and, therefore, water, which reaches the anode through simple occlusion or through film faults and fissures, is constantly electrolyzed providing the means for continuous metal dissolution. This mechanism accounts for the anionic experimental data in this investigation, which generally agrees with data derived by other investigators.

On the other hand, in examining the cationic data and the shapes of the time curves for the ferrous substrates, the above analysis does not at first appear to be accurately descriptive. It is known that the cationic deposition process involves similar mechanisms at the cathode. Electrolysis of water at the cathode forms a boundary phase with a high concentration of hydroxyl ions. Electrophoretically migrating polymeric amino cations are neutralized and coagulated upon entering this boundary phase, leading to deposition of the cationic films. Again, electrolysis of water is continuous throughout the process since current densities are always positive. However, the shapes of the cationic time curves in contrast to those of the anionics indicate that metal dissolution occurs in the early stages of the process and then diminishes significantly, or ceases, in the later stages, except in the case of untreated aluminum.

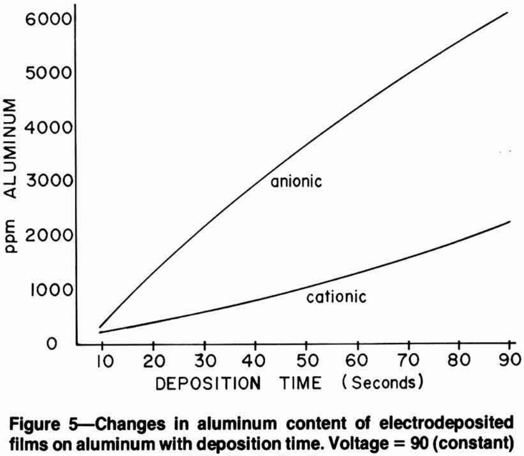

Figure 5—Changes in aluminum content of electrodeposited films on aluminum with deposition time. Voltage = 90 (constant) 90% Neutralization

This evidence leads to the postulate that ferrous metal dissolution, during the early stages of cationic electrodeposition, involves oxidation in an alkaline medium. While it is generally assumed that metals such as iron and zinc are not attacked by alkali, a review of the literature in the field of metal oxidation and corrosion reveals that this is not the case.[11] Most metals show a rise of corrosion rate at both ends of the pH scale, although the position of the rise in corrosion rate will vary from one metal to another. Pourbaix[12] states that the oxidation of iron wire is very slow at pH's up to 14.4 but increases linearly at alkali concentrations having pH's between 14.7 and 15.2. It was also noted by Evans[11] that, in contrast to iron, the oxidation rate of aluminum is very rapid, even under milder alkaline conditions. In fact, he makes special mention that the rapid attack of aluminum by washing soda was a serious matter in the early days of the aluminum saucepan.[11] The basic mechanism of alkaline metal oxidation involves the formation of soluble oxyanions according to the following equation illustrative of iron:

$$Fe + 4OH^- \longrightarrow [FeO_2]^{=} + H_2O + 2e^-$$

$$[FeO_2]^{=} \longrightarrow [FeO_2]^- + e^-$$

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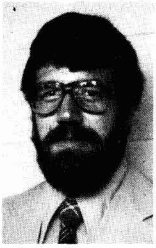

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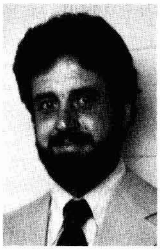

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Application of this theory to the case of cationic electrodeposition provides a rational account of the data generated in this investigation. During the early stages of the cathodic electrodeposition process the hydroxyl ion concentration in the cathode boundary phase is very high leading to metallic oxidation. Theoretically, it is possible that the pH at the site of a single molecule of water being electrolyzed could reach 15.8 which represents a hydroxyl ion concentration of 55 molar. As deposition proceeds, hydroxyl ions are converted to water via amino cation neutralization and fewer new hydroxyl ions are generated as the current density diminishes. This leads to a reduction of the excessive alkaline conditions necessary to oxidize the ferrous substrates and, therefore, one expects and finds that metal dissolution greatly diminishes, or ceases, in the latter stages of the cathodic process. In the case of aluminum, the degree of alkalinity necessary to provoke oxidation is much less than for ferrous materials because of its amphoteric nature. This leads to the positive slope of the aluminum time curves. As long as water is being electrolyzed, the hydroxyl ion concentration is sufficient to continuously dissolve aluminum into the cationic films.

It is not the purpose of this investigation to dampen the enthusiasm generated by the introduction of cationic electrodeposition systems. In general, these systems have provided significant advances in the protection of metallic substrates from corrosion and chemical attack. However, it is the purpose of this investigation to begin examination of the basic processes of cathodic deposition. It was felt that the nearly universal assumption of cathode passivity within the industry had led to a somewhat "tunnel-visioned" approach in coatings research in this area. It is felt that the results of this investigation lead to a revision of the potential cathode reactions in cationic electrodeposition to the following:

1) ELECTROLYSIS OF WATER

$$2H_2O + 4e^- \longrightarrow 4OH^- + 2H_2$$

2) METAL OXIDATION

$$M^0 + 4OH^- \longrightarrow [MO_2]^{n-} + 2H_2O + (4-n)e^-$$

3) POLYMER DEPOSITION

$$R_3NH^+ + OH^- \longrightarrow R_3N + H_2O$$

$$nR_3NH^+ + [MO_2]^{n-} \longrightarrow (R_3NH)_n-[MO_2]$$

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Effect of Humidity and Other Ambient Conditions On Evaporation of Ternary Aqueous Solvent Blends

Albert L. Rocklin
Shell Development Company*

Evaporation of ternary blends of water, with a fast and a slow cosolvent at various ambient conditions, was investigated using an abbreviated method in which computer analysis of a limited number of carefully chosen experiments reveals the independent effects of each variable and permits prediction of evaporation behavior at any set of conditions within the range investigated. Relative humidity was found to have the greatest effect, with temperature and composition following, in that order. Response of solvent balance to humidity and temperature is shown for various compositions, and evaporation time is compared to that of water under the same conditions. For example, evaporation of the ternary water-organic blends is usually slower than water at low humidity, but faster at high humidity.

INTRODUCTION

It has long been known that the performance of a coating is strongly affected by the evaporation characteristics of the solvent blend used in its formulation. For this reason, measurement and prediction of solvent evaporation have occupied an important position in coatings technology. Directed originally toward organic solvent systems, evaporation technology has been turning to aqueous blends, principally because environmental regulations, which are forcing the industry to cut back on organic solvents emissions, look with favor on coatings in which the main solvent component is water. Yet water-based systems can behave badly, and are subject to major ailments that rarely affect their organic rivals. For example, water-based coatings are sensitive to humidity. Not only does high humidity prolong drying time, it can also distort evaporation priority. Thus, an organic cosolvent which imparts a desirable film property may be lost by evaporation before it can become effective if high humidity has excessively slowed down the evaporation of water relative to that cosolvent. Consequently, coatings formulators are looking for answers to vital questions. Can drying time at high humidity be shortened by suitable cosolvents? How can film quality be maintained at high humidity? Can the same blend be effective at both high and low humidities? Can effectiveness be maintained over a wide temperature range? In short, can a formulator select a solvent blend for a coating that will give good film quality when it is cool and dry *and* when it is hot and humid?

This paper reports some of the results obtained in a survey of the effects of ambient conditions and blend composition on evaporation of selected ternary aqueous solvent blends, and shows how the results can be applied to answering those questions. For each ternary system, a set of a limited number of experiments was performed according to a central composite design involving ambient condition variables and composition variables centering on the 70-80% water range. Computer analysis revealed the separate effects of each of the variables. The main findings confirm that humidity, as expected, has a very large effect on evaporation, with temperature and composition following, in that order. At the low air flows used in these experiments (approximately 1 ft/min) variations in air flow were of little significance.

To make decisions on formulations for different ambient conditions, the technologist must have information on evaporation behavior of various compositions at the expected conditions. The method described in this paper untangles the complex pattern of the effects of composition and ambient condition variables on evaporation response. It can speed up the selection of formulations for optimum evaporation performance and prevent wasted effort in the laboratory because it gives the technologist an efficient method for screening formulations by calculation prior to actual laboratory testing. The calculations show that effectiveness of composition selection in coping with evaporation problems depends strongly on the cosolvents, but that there are practical limits to what the cosolvents can be expected to do.

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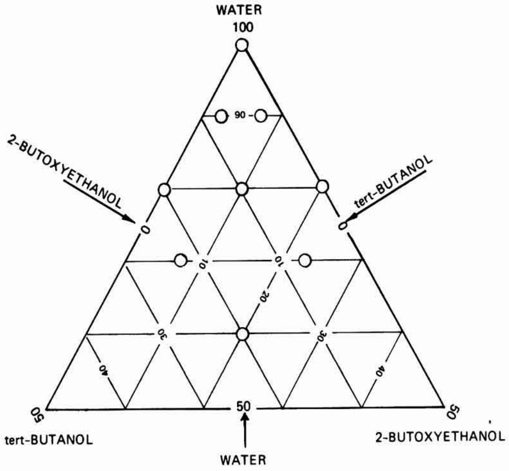
Presented by Dr. Rocklin at the 56th Annual Meeting of the Federation of Societies for Coatings Technology in Chicago, Ill., Nov. 2, 1978.

BACKGROUND

Of the three ambient conditions affecting evaporation, humidity is the most difficult to bring under experimental control. Temperature and air flow are easy to adjust but, as described in the experimental section, humidity control is harder to achieve. It is, perhaps, because of this that the literature on the effect of humidity on evaporation is not extensive, although it is certainly significant.

In their 1950 paper describing the earliest form of the Shell Evaporometer, Curtis, Scheibli, and Bradley[1] reported on the effect of humidity on solvent evaporation time. They found that higher humidity slowed down the evaporation of the water soluble solvents, ethanol, isopropanol, and methyl ethyl ketone, but that hydrocarbons were only slightly affected. Later, in a 1958 publication, Shur[2] reported a New York Society study in which the Shell Evaporometer was used to investigate evaporation of a nitrocellulose/methyl isobutyl ketone lacquer. The effect of relative humidity was noted but precise data were not obtained.

Recently, Calder[3] showed that humidity can have a controlling effect on the fate of a glycol ether coalescent during drying of a latex paint. At high humidity the evaporation of water can be so retarded that the coalescent evaporates from the applied coating before the water does. The result is poor film formation due to insufficient coalescence of latex particles. Calder's disclosure that humidity can affect the relative order of evaporation of water and a cosolvent leads to the conclusion that in these cases there must be a certain relative humidity at which the liquid composition does not change during the evaporation. This concept has been fully demonstrated by Dillon,[4] who showed that most binary blends of water and a cosolvent will evaporate without change in composition at certain humidities that are characteristic of the cosolvent and of its concentration in the blend. Dillon's article is also recommended for its comprehensive bibliography. The main thrust of the paper is on the useful concept of the relationship of humidity to constant composition evaporation of binary blends. However, no experimental details are reported; and although the principle is extended to multi-component systems, it is done so by calculation only.



VARIABLE	SET POINTS				
X1 RELATIVE HUMIDITY, %	10	30	50	70	90
X2 % TERT-BUTANOL IN ORGANIC	0	25	50	75	100
X3 % WATER	60	70	80	90	100
X4 TEMPERATURE, °C	20	25	30	35	40
X5 FLOW, ℓ/MIN	10	15	20	25	30
CODED VALUES	-2	-1	0	+1	+2

Figure 1—Ternary system for study by central composite design

Table 1—Five Variable Central Composite Experimental Design

Experiment No.	Coded Values X1	X2	X3	X4	X5
1	+1	−1	−1	−1	−1
2	−1	+1	−1	−1	−1
3	−1	−1	+1	−1	−1
4	+1	+1	+1	−1	−1
5	−1	−1	−1	+1	−1
6	+1	+1	−1	+1	−1
7	+1	−1	+1	+1	−1
8	−1	+1	+1	+1	−1
9	−1	−1	−1	−1	+1
10	+1	+1	−1	−1	+1
11	+1	−1	+1	−1	+1
12	−1	+1	+1	−1	+1
13	+1	−1	−1	+1	+1
14	−1	+1	−1	+1	+1
15	−1	−1	+1	+1	+1
16	+1	+1	+1	+1	+1
17	−2	0	0	0	0
18	+2	0	0	0	0
19	0	−2	0	0	0
20	0	+2	0	0	0
21	0	0	−2	0	0
22	0	0	+2	0	0
23	0	0	0	−2	0
24	0	0	0	+2	0
25	0	0	0	0	−2
26	0	0	0	0	+2
27	0	0	0	0	0
28	0	0	0	0	0
29	0	0	0	0	0
30	0	0	0	0	0
31	0	0	0	0	0
32	0	0	0	0	0

INVESTIGATING TERNARY SYSTEMS

A formulator may have many reasons for using cosolvents in combination with water. An obvious one is to speed up the evaporation of a water-reducible system by replacing some of the water by a volatile cosolvent. Another is to aid coalescence into continuous films; for this purpose the cosolvent must evaporate more slowly than the water. Since the same solvent cannot do both jobs, the formulator must use at least two if he wants both effects. In that case, the question arises as to how much of each cosolvent should be used. For a given water content, what is the maximum amount of low boiling cosolvent and the minimum amount of high boiling cosolvent that can be tolerated without sacrificing film quality? The choice is complicated by the obvious influence of humidity and temperature because these affect the evaporation rate and the solvent balance of the evaporating blend. To make an intelligent choice, the formulator needs to know how evaporation rate and solvent balance of the system under consideration are affected by ambient conditions and initial composition. It is particularly important to know how the evaporation response changes with changes in ambient conditions and initial composition. What are the trends as the variables are changed? How will a change in humidity, for example, affect evaporation of a blend that performs well under certain conditions, and how does one choose blends that are relatively insensitive to changes in ambient conditions?

To answer these and similar questions, information is needed on evaporation response under a very large variety of conditions. The effect of each variable has to be assessed separately. To do this by conventional experimentation would require, for example, measurement of evaporation time of a chosen initial composition at fixed temperature and air flow over a range of humidities. The series of experiments would have to be repeated at several different temperatures, and the compounded series would have to be done for a variety of compositions. It would be impossible to do the work in a reasonable time because the experiments would number in the thousands.

CENTRAL COMPOSITE EXPERIMENTAL DESIGN[5]

To overcome this problem an abbreviated method was used. A limited number of experiments were performed in which several variables were changed from one experiment to the next according to a regular pattern, and the results analyzed by computer. This method, called a Central Composite Experimental Design, allows a large number of variables to be investigated simultaneously and economically.

To illustrate, *Figure* 1 shows the selected values of the variables which will be used in setting up the experimental pattern for investigating the effects of these variables on evaporation time of the system water/tert-butanol/butoxyethanol*. There are three ambient condition variables, humidity, temperature, and air flow, and two composition variables. For convenience, one of the composition variables was chosen to be the percent of water in the blend and the other to be the percent of tert-butanol in the organic portion of the blend only.

Evaporations were done with each variable at five equally spaced settings. The settings depend on the chosen range of experimentation. In the illustration, the compositions being studied are confined to blends containing between 60 and 100%w water. Therefore, the water variable set points have the values 60, 70, 80, 90, and 100. Since relative humidity was investigated over the wide range from 10 to 90%, the set points of the humidity variable are placed at equal intervals between 10 and 90.

The actual values of the variables are not used in the computer analysis. Instead, coded values, which represent the position of the setting of the variable within the chosen range, are used. The center point of the range has the value 0, and the upper and lower limits of the range have the values 2 and −2. For example, the temperature of 30°C is in the center of the temperature investigative range, and so is given the coded value 0. Relative humidity of 50% has the coded value 0; 30% has the coded value −1; and 60% has a coded value of 0.5.

Only certain combinations of variables are used. These are shown in *Table* 1, which lists the coded values of five variables comprising a complete set of experiments. Looking only at the composition variables, the diagram in *Figure* 1 shows the nine compositions that were used in the set of evaporation experiments.

Each line in *Table* 1 designates a set of conditions under which an experiment is performed. In this case the experiment is the measurement of the 90% evaporation time in the Shell Automatic Thin Film Evaporometer.[6] To illustrate, the coded values on the first line of *Table* 1 represent a set of conditions in which the relative humidity is 70%, the concentration of tert-butanol in the organic portion of the blend is 25%w, the concentration of water in the blend is 70%w (this gives a blend with 70%w water, 7.5%w tert-butanol and 22.5%w 2-butoxyethanol), the temperature is 77°F (25°C) and the air flow is 0.53 cu ft (15 liters) per minute.

The 32 experiments of the set are not done in sequence as shown, but are performed in random order. This requires the instrument to be reset for every experiment, thereby avoiding systematic errors. Six of the measurements (Experiments 27-32) are made under identical conditions, and reliability assessed by calculation of the standard deviation. The results of the experiments, which in this case would be the measured 90% evaporation times under the various designated conditions, are processed by a computer program which fits a best curve among all the points. The method is based on the supposition that the evaporation time (or solvent balance) will vary smoothly with changes in composition and ambient conditions. The best fit is presented as a simple, although lengthy, equation which can calculate response as a function of ambient conditions and composition at any combination of values within the investigated range of variability.

It should be noted that this method is not based on solution theory, nor is there any attempt made to reconcile the results with, or justify them in terms of, any such theory. The method is entirely empirical. It is really an interpolation method, but its power is magnified enormously by the ability of the computer to analyze data from a minimum number of experiments involving five variables. That power is illustrated in the examples shown later, where the derived equation is used to calculate a large variety of correlations that can be of use to the coatings technologist.

The method is certainly a bargain. It gives a lot of value for a minimum investment. But like many bar-

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*Butyl Oxitol® is a registered trademark of the Shell Chemical Co.

Table 2—Relative Effects of Variables

SYSTEM: WATER, TERT-BUTANOL, BUTOXYETHANOL

	Initial Set		Modified Set	
Variable	**Range**	**Effect, %**	**Range**	**Effect, %**
X1, Rel. Hum.	10-90	60.2	10-80	44.8
X2, Org. Comp.[a]	0-100	4.5	0-100	11.7
X3, Water, %w	60-100	<0.1	50-90	0.2
X4, Temp., °C	20-40	20.2	20-40	17.8
X5, Air, *l*/Min	10-30	1.6	10-30	1.7
Other Effects[b]		10.2		21.2

(a) % tert-Butanol in the organic portion of the blend only.
(b) Includes quadratic terms, interaction of variables and estimated errors.

gains it has to be looked at carefully for hidden deficiencies. This one is no exception. The weakness is its diminished reliability in the upper and lower sections of the variability range. The best reliability is within that portion of the range between the 1 and −1 coded values. Beyond that, reliability drops off. For the system shown in *Figure* 1 in which, for example, the water concentration range is from 60 to 100%w, the most reliable calculations will apply to the narrower range between 70 and 90%w. For relative humidity, the range of greatest reliability is from 30 to 70%. Knowing this, an experimenter can choose the range of variability so that the area of greatest interest is close to the center. This is what was done for the water variable. The center of the range was chosen as 80% because that concentration is favored in certain existing, as well as proposed, solvents emissions regulations.

Calculations for which one or more variables go beyond the reliable central range (between the +1 and −1 coded values) should be interpreted with caution. Those calculations are useful for comparing trends, but ought not to be used for close predictions. This is pointed out in *Figures* 2-13 in which, for illustrative purposes, the calculations extend toward the limits of the variability range.

EXPERIMENTAL

Evaporation measurements were made using the Shell Automatic Thin Film Evaporometer. The standard procedures of the ASTM D3539 method were used except that the air humidity, temperature, and flow were adjusted to the values specified for each experiment. The observed evaporation time is the time required to evaporate 90% of a standard size sample of solvent deposited on a 9 cm disc of filter paper suspended in the air stream inside the instrument. This is called the 90% evaporation time, or t_{90}.

Composition of the solvent remaining on the filter paper at a given stage of evaporation was determined by removing the filter paper at the appropriate time, transferring it rapidly to a serum capped vial, extracting with a noninterfering solvent and analyzing the extract by gas chromatography.

Temperature and air flow control were no problem. The instrument was easily adjusted to the desired conditions. Humidity control, however, required careful attention. Air at high humidity was pumped out of a humidity chamber* and mixed with dry air to attain the desired humidity as indicated by the hygrometer† in the evaporometer. The humidity required continuous monitoring. Frequent readjustments had to be made because the evaporating aqueous samples would raise the humidity in the evaporometer chamber. However, after some experience, the operators were able to maintain the humidity to within ± 2%.

Relative Effects of Variables On Evaporation Time

Each set of experiments results in a set of 32 measured values of evaporation time ranging from low to high. The spread in these values is caused by the combined effects of all the variables. By computer analysis it is possible to calculate what proportion of the total effect can be ascribed to each variable. In *Table* 2, the figures under the heading "Initial Set" show this breakdown for the set of experiments pertaining to *Figure* 1. Relative humidity accounts for 60% of the effect, and temperature for 20%. These are the main influences. The evaporation time of the system appears to be insensitive to water concentration, but significantly sensitive to the relative proportions of the two organic solvents. The independent effects of the five variables account for most of the variability. The remainder, designated in the table as "other effects," includes those ascribed to interaction among the variables, and to estimated errors.

These results have to be interpreted with respect to the range of variability selected for study. The composition variables are fairly reasonable. They include those water and organic concentrations most likely to be used in an aqueous coatings system. The temperature range is perhaps a bit high. The upper limit of 40°C is about as high as could reasonably be expected, but the lower limit of 20°C is higher than some temperatures at which coatings might be applied. The reason the temperature range was not extended downward is that 20°C was the lowest temperature that could be conveniently maintained in the evaporometer without elaborate chilling equipment. The most severe instrument limitation was on air flow. The air flows which were used, and which ranged between the upper and lower practical limits for the instrument, correspond to linear flow rates of 0.007 to 0.020 mph. Since this is about 1/100 the air speed of a spray booth, it is not surprising that air flow appears to have minimal effect.

In this set of experiments the effect of humidity is somewhat exaggerated because the upper limit of the humidity range was chosen at the high value of 90%. High humidity has a disproportionately large effect on evaporation, and this might possibly mask other ef-

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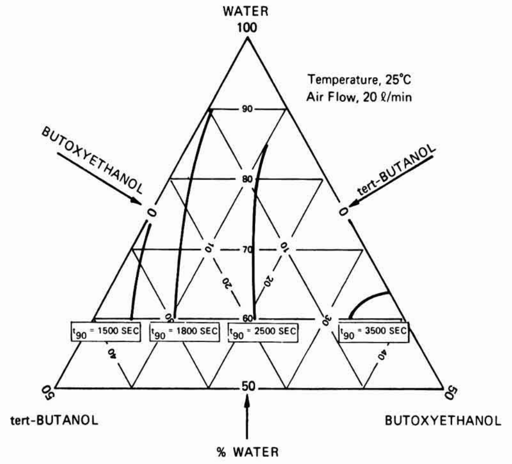
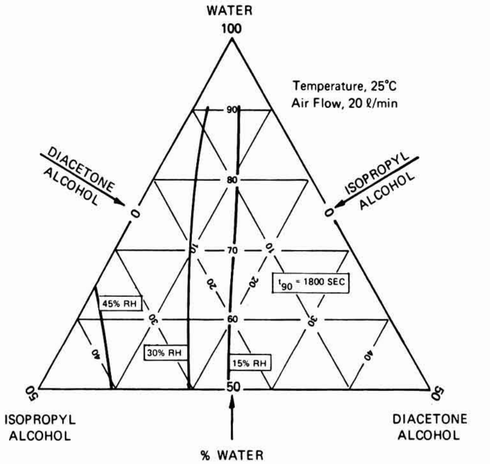
*Hotpack Temperature-Humidity Chamber, Philadelphia Pa.

†Durotherm Hygrometer, G. Lufft, Stuttgart, Germany. (Calibrated to ±2% between 32°F and 230°F).



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 2—Effect of composition on evaporation time at 50% relative humidity



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 3—Compositions having 90% evaporation time of 1800 sec at indicated humidity

fects. To see what the effect would be of a more conservative upper limit, a second set of measurements was made based on a relative humidity range of 10 to 80%. Also the water concentrations were shifted from the weight percent range of 60-100, to 50-90. The figures listed under the heading "Modified Set" in *Table* 2 show that relative humidity is still the most important factor, although the cutoff of the overly influential portion of the range between 80 and 90% had diminished the humidity effect from 60% down to 45%. Correspondingly, the effect of organic composition has increased. But the effects of the other variables are relatively unchanged. The total effect has been to modify some of the numbers, but not to change the pattern.

Effect of Humidity and Composition On Evaporation Time

With aqueous systems the formulator is striving for minimum evaporation time. Whatever can speed up the drying time can cut the applications cost. Therefore, information that can guide the formulator is of considerable value. *Figure* 2 shows how the 90% evaporation time of the system water/tert-butanol/2-butoxyethanol at fixed humidity is affected by composition. As expected, the fastest evaporating blends contain the most tert-butanol. The figure shows the approximate evaporation time limits that can be expected for this ternary system by adjusting the composition. Whether or not a formulator could get by with any selected composition might also depend on the solvent balance as the blend evaporates, especially if the solvent had to perform as a coalescent. In that case, the formulator would have to use the evaporation time data in conjunction with solvent balance data in order to make a practical choice.

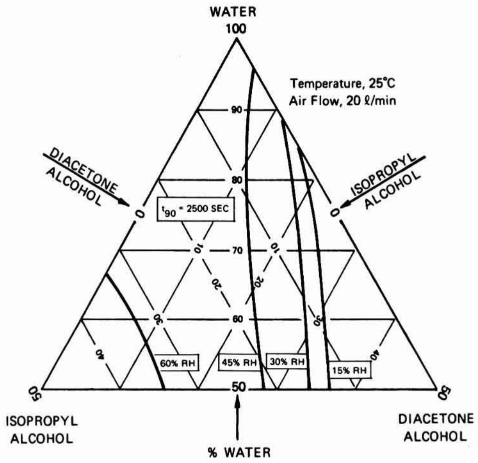
Figure 2 has given a picture of evaporation time behavior at fixed humidity. Since humidity has already been shown to have a large effect, it is instructive to look at the magnitude of that effect in a given case. *Table* 3 gives interpolated values of the 90% evaporation time at 30°C and at different humidities for three compositions of the ternary system water/isopropanol/diacetone alcohol. The compositions are related in that equal concentrations of both cosolvents are maintained as the water concentration changes, i.e., the organic composition variable remains fixed, although the water variable changes.

As with the previous system, this one is also sensitive to humidity and insensitive to water concentration. The two pairs of values at 20 and 50% relative humidity show no significant response when the water concentration is changed, but when the humidity of the 70%

Table 3—Effect of Humidity and Composition On Evaporation Time

System: Water, Diacetone Alcohol, Isopropyl Alcohol
Temperature: 30°C
Air Flow: 20ℓ/Min

	Composition, %w					
Water	80	70	70	70	60	60
Diacetone alcohol	10	15	15	15	20	20
Isopropyl alcohol	10	15	15	15	20	20
	Relative Humidity, %					
	20	20	35	50	50	70
	90% Evap. time, sec					
Calculated	1520	1537	1782	2201	2164	3330
Observed	1440	—	1720	2020	—	3072
Error, %	5.6	—	3.6	9.0	—	8.4
	Observed 90% Evap. Time (sec) for Water at Indicated Humidity					
	1285	1285	1760	2485	2485	4610



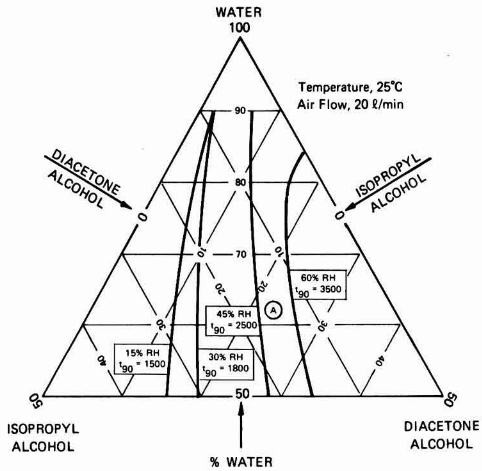
(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 4—Compositions having 90% evaporation time of 2500 sec at indicated humidity

aqueous system is changed from 20% to 35% and then to 50% there is a substantial increase in evaporation time. The 60% aqueous system shows a similar pronounced humidity effect in going from 50 to 70% relative humidity.

The effects of the cosolvents on evaporation time can be assessed by comparing the evaporation times of the blends with evaporation time of water under the same conditions. This is quite revealing. At lower humidities the blends evaporate more slowly than water, but at higher humidities they evaporate more quickly. With this information in hand, a formulator might be more confident about tackling the problem of designing a blend whose evaporation time changes less radically than that of water in going from a low to a high humidity.

Figures 3 and 4 show how and to what extent the formulator can offset the effect of humidity on evaporation time by adjusting the starting composition. Each curve in *Figure* 3 is for compositions with evaporation time of 1800 sec at the indicated humidity. The value of 1800 sec was chosen because that is the 90% evaporation time of water at 30% relative humidity at the same temperature. As expected, compensation for higher humidity requires increasing amounts of fast-evaporating isopropyl alcohol, and diminishing amounts of the slower evaporating diacetone alcohol. The figure shows that with this system it is not possible to stay below an 1800 sec evaporation time by composition adjustment if the humidity rises much above 45%. If the formulator who is using this system has to face higher humidities, he must lower his evaporation time demands. *Figure* 4 shows what can be expected if the formulator is willing to accept the longer evaporation time of 2500 sec, which corresponds to the evaporation time of water at 45% relative humidity. Here it is possible to allow for at least 60% relative humidity by appropriate composition selection.

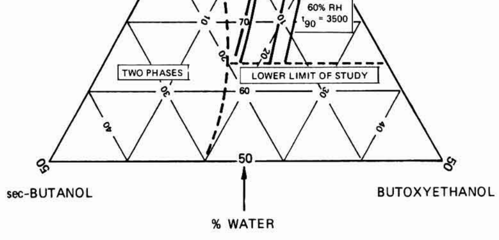


(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 5—Solvent blends having same 90% evaporation time as water at indicated relative humidity

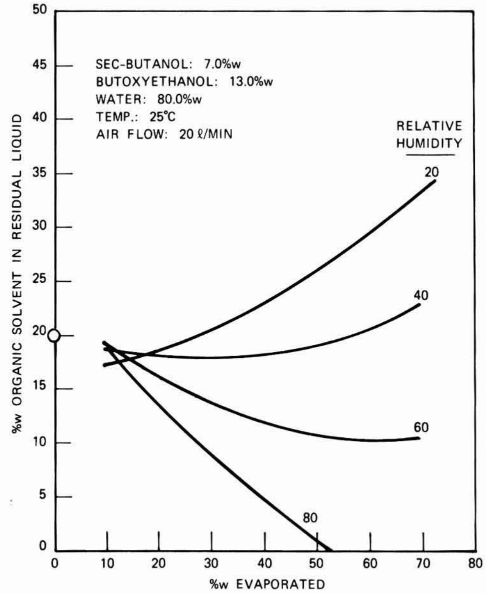
Comparison with Evaporation Time Of Water Under Same Conditions

For whatever reasons a formulator chooses cosolvents, it is desirable to have as much flexibility as possible in choosing their concentrations. If the evaporation time of water at any set of conditions is taken as a standard, compositions can be calculated which have the same evaporation time as the standard at the same conditions; this can show how much flexibility is possible in choosing compositions to meet evaporation time criteria. *Figure* 5 shows compositions in the system



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

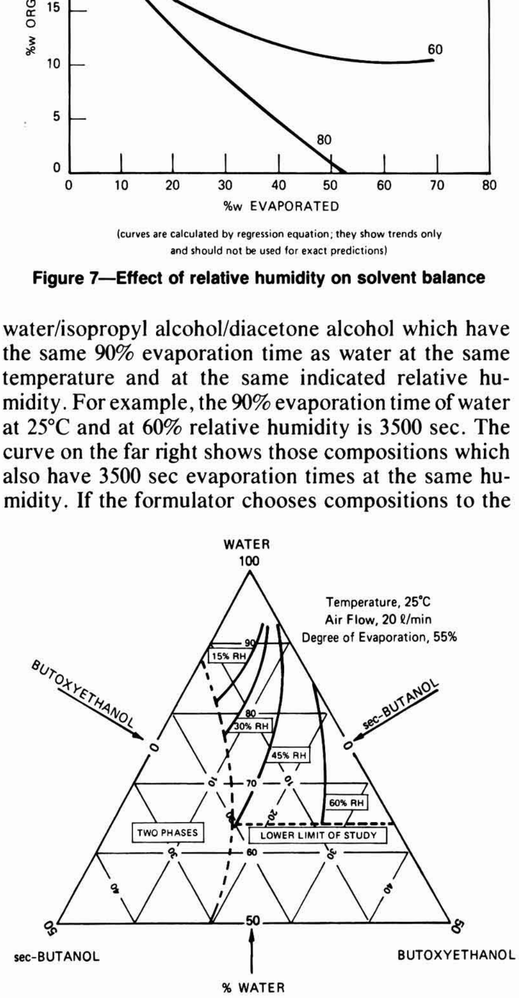
Figure 6—Solvent blends in alternate system which have same 90% evaporation time as water at indicated relative humidity



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 7—Effect of relative humidity on solvent balance

water/isopropyl alcohol/diacetone alcohol which have the same 90% evaporation time as water at the same temperature and at the same indicated relative humidity. For example, the 90% evaporation time of water at 25°C and at 60% relative humidity is 3500 sec. The curve on the far right shows those compositions which also have 3500 sec evaporation times at the same humidity. If the formulator chooses compositions to the left of that curve they will evaporate faster than 3500 sec because they will be richer in the faster evaporating isopropyl alcohol, and leaner in the slower evaporating diacetone alcohol.



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 8—Compositions for which water concentration in residual liquid is same as in original blend when 55% evaporated at indicated humidity

Since the region to the left of the 3500 sec curve is large, it means that the formulator has great flexibility in choosing compositions which are faster evaporating than water at 60% relative humidity. Suppose a composition is chosen, as indicated by point A, that is between the 3500 and 2500 sec curves. Since point A is to the left of the 3500 sec curve, the blend will evaporate faster than water at 60% or higher relative humidity, but since it is located to the right of the 2500 sec curve, it means that the same blend will evaporate more slowly than water if the humidity is 45% or lower.

This illustrates a general principle that applies to ternary aqueous blends containing fast and slow cosolvents: with these systems there is a good choice of compositions which evaporate more slowly than water at lower humidities, but more quickly than water at higher humidities. The flexibility and the options depend on the ternary system of choice. *Figure* 6 shows the pattern for the system water/sec-butanol/butoxyethanol. Here the lines are crowded together and the choice is more limited.

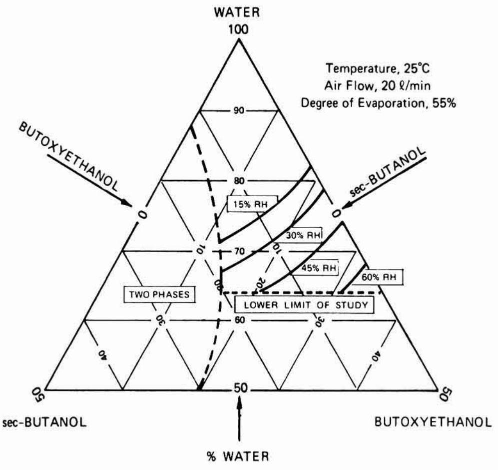
Effect of Relative Humidity On Solvent Balance

To include solvent balance in the experimental scheme, a new variable had to be introduced. The variable was degree of evaporation, and it was needed for following the solvent balance as the blend evaporated. Instead of going to a six-variable system, the relatively unimportant air flow variable was dropped, and degree of evaporation substituted in the five-variable plan. Air flow for all the solvent balance experiments was kept constant at 20 l/min, this being the center of the range for that former variable. The range for degree of evaporation was put at 10-70%. Thus, in different experiments in the set, water content of the residual solvent was measured after the weight of sample on the filter paper had dropped by 10, 25, 40, 55, or 70%.

Figure 7 shows what happens when a blend of 80%w water, 7%w sec-butanol and 13%w butoxyethanol is evaporated at different humidities. At low humidity the blend becomes enriched in organic solvent but as the humidity rises the trend is reversed. At higher humidities organic solvent is lost, and the blend shows increasing water enrichment. The reason the curves do not all start squarely at the 20% point, which is the starting point of the real blend, is that these are calculated curves and, as explained previously, the fit of the regression equation at the extreme ends of the variability range is not close.

Combined Effects of Humidity And Composition of Solvent Balance

The previous example showed what happens during evaporation of a single sample at different humidities. It illustrates the effect of humidity on solvent balance, but to be useful to a coatings technologist, whose options



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

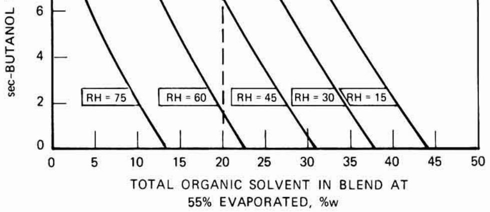
Figure 9—Compositions for which water content in residual liquid is 60%w when 55% evaporated at indicated humidity

DR. ALBERT L. ROCKLIN received the PhD Degree in Physical Chemistry from the University of Toronto. Following a period on the staff of Purdue University, and then at Dow Chemical Co., he came to Shell Development Co. in Emeryville, Calif. in 1958, where his interest in synthetic organic chemistry led to the development of phenolic oxidation inhibitors and solid propellants. Currently, he is a Senior Research Chemist in the Resins and Solvents Dept. at the Shell Westhollow Research Center in Houston. In 1976, Dr. Rocklin won a Roon Award for a paper on solvent evaporation.

are mostly limited to choice of cosolvents and their concentrations, a picture is needed of how these choices can cope with humidity effects. *Figure* 8 shows compositions which, when evaporated 55% of the way at the indicated humidity, will have the same water concentration as in the starting blend. This tells the technologist whether a chosen blend will tend to lose or gain water as it evaporates. A blend to the right of a line representing the humidity at which evaporation proceeds will become enriched in organic solvent because it will have started off with more slow solvent and less fast solvent than a blend which just holds its own at the same humidity. Blends to the left of the line will lose organic solvent.

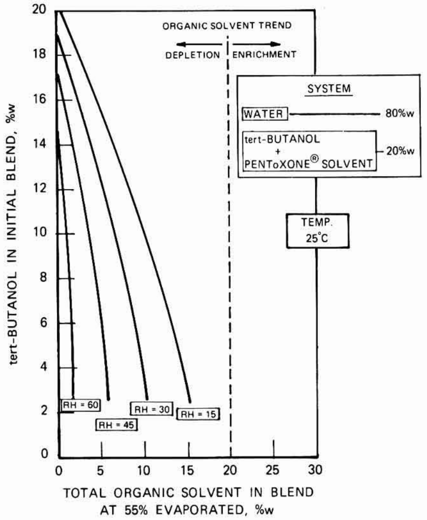
Once the experimental data have been obtained and processed by the computer, the technologist can examine any relationship that is pertinent to a coatings problem. If, for example, the coatings requirement is to have a blend whose water content must drop to at least 60%w during evaporation, calculations can produce a useful graph such as *Figure* 9 which shows those compositions whose water content will reach 60%w when 55% of the sample is evaporated at the indicated relative humidity.

If the initial solvent blend is restricted, as by legislation, to a maximum of 20%w organic solvent content, a graph such as *Figure* 10 shows how the proportions of fast and slow organic solvents affect the trend toward enrichment or depletion during evaporation at various humidities. As expected, organic solvent enrichment at higher humidities is achieved by increasing the proportion of slow solvent in the initial blend. The value of this



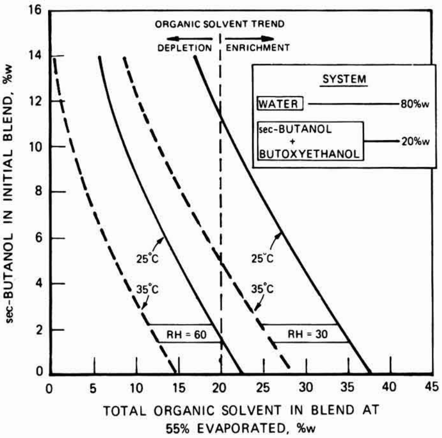
(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 10—Effect of humidity and of initial sec-butanol concentration on organic content of blend after partial evaporation



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 11—Effect of humidity and of initial tert-butanol concentration on organic content of blend after partial evaporation



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 12—Effect of temperature and humidity on organic content of blend after partial evaporation

graph is that it shows the trend clearly, and indicates the limits of the technologist's options for evaporation control. With these cosolvents there is not much hope of solvent enrichment above approximately 60% relative humidity for a starting blend containing no more than 20%w organic solvent, even if the blend contains no fast solvent at all.

The behavior of a system with a different pair of cosolvents is shown in *Figure* 11. With the cosolvents tert-butanol and Pentoxone® solvent* there is no hope of achieving solvent enrichment on evaporation of an 80%w aqueous blend at 25°C. Of course, it may be that solvent enrichment is not desired, and the cosolvents are used for some other purpose such as viscosity control. Whatever their purpose may be, the formulator can tell what will happen to them during evaporation.

Effect of Temperature on Solvent Balance

The evaporation behavior of the water/sec-butanol/butoxyethanol blends as shown in *Figure* 10 is at the fixed temperature of 25°C. In the case of evaporation time we know that rising temperatures hasten evaporation, but the effect on solvent balance is not obvious. If each component of a solvent blend had the same evaporation response to temperature there would be no change in solvent balance at different evaporation temperatures. This is not so, as is evident in *Figure* 12 which shows how a rise in temperature from 25 to 35°C affects the solvent balance of blends of 80%w water with sec-butanol and butoxyethanol evaporating at 30 and 60% relative humidity. The 25°C curves are taken from *Figure* 10. At both humidities the temperature rise sends the solvent balance strongly in the direction of organic solvent depletion. Presumably the opposite effect would be noted for a drop in temperature, and this suggests that if the goal is organic solvent enrichment, this system might be suitable for low temperature application.

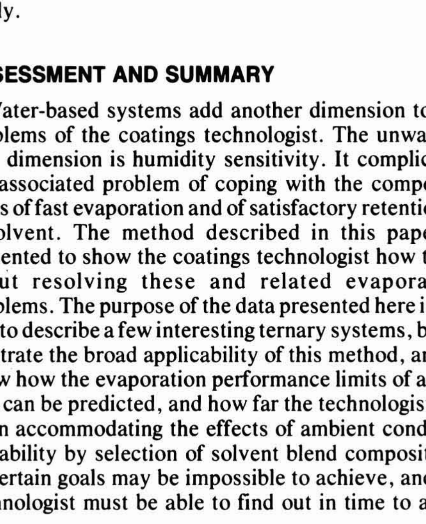
The response to temperature depends on the system. *Figure* 13 shows how a rise in temperature from 25 to 35°C affects the solvent balance of blends of 80% water with tert-butanol and Pentoxone solvent when they evaporate at 15 and 45% relative humidity. Here the response is the opposite of that of the previous system. A rise in temperature tends to move the solvent balance toward organic solvent enrichment.

These illustrations show that different systems have different temperature responses. Those which have been determined for one system will probably not apply to some other system. Each has to be examined separately.

ASSESSMENT AND SUMMARY

Water-based systems add another dimension to the problems of the coatings technologist. The unwanted new dimension is humidity sensitivity. It complicates the associated problem of coping with the competing goals of fast evaporation and of satisfactory retention of cosolvent. The method described in this paper is presented to show the coatings technologist how to go about resolving these and related evaporation problems. The purpose of the data presented here is not just to describe a few interesting ternary systems, but to illustrate the broad applicability of this method, and to show how the evaporation performance limits of a system can be predicted, and how far the technologist can go in accommodating the effects of ambient condition variability by selection of solvent blend composition.

Certain goals may be impossible to achieve, and the technologist must be able to find out in time to avoid



(curves are calculated by regression equation; they show trends only and should not be used for exact predictions)

Figure 13—Effect of temperature and humidity on organic content of blend after partial evaporation

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*Pentoxone is a registered trademark of the Shell Chemical Co. 4-Methoxy-4-methyl-2-pentanone.

wasted effort. For example, inspection of *Figures* 6 and 8, which apply to the system water/sec-butanol/butoxyethanol, shows that it is impossible to formulate a blend which becomes enriched in organic solvent during evaporation at 60% relative humidity, and which also has a 90% evaporation time of 2500 sec or less under those conditions. Blends can be chosen which will do one or the other, but not both.

In this study, a central composite experimental design was used for efficient investigation of the effects of ambient conditions and composition on evaporation time and solvent balance of several aqueous ternary systems containing both a fast and a slow evaporating cosolvent. For each system, computer processing gave a regression equation of a curve which was a best fit for the experimental data. In each case, the equation can be used to calculate evaporation behavior of any composition at any set of conditions within the experimental range. This allows the coatings formulator to examine proposed compositions from any point of view. Calculations can reveal which measures may be taken to stay within limits on solvent balance or evaporation time. They can uncover the effects of setting or changing any variable, or any combination of variables. In the hands of a knowledgeable technologist this can be a powerful tool for helping to solve formulation problems.

ACKNOWLEDGMENT

Computer analysis was performed by Joseph Levitan, of the Shell Information Center. I am indebted to him for his valuable guidance in applying the experimental design to this study, and for his prompt response in processing the data. I am also indebted to Mark F. Dante, of Shell Development Co., for his development of the method for determining solvent balance, and to Roy W. Tess, of Shell Chemical Co., and Granville D. Edwards, of Shell Development Co., for their advice and guidance.

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   c. The current model is described in the "Apparatus Number Series 109" bulletin, Roxana Machine Works, 300 Michigan Ave., South Roxana, Ill., 62087.

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Rheological Properties Of Styrene/Acrylic Polymers

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Melt viscosities of a series of styrene/butyl acrylate/methacrylic acid polymers (80/15/5) have been studied by capillary and cone and plate viscometers. All members of the series display Newtonian viscosity plateaus, but at higher shear, viscosities reduce at rates dependent on molecular weight and weight distribution. Gel permeation chromatography shows these parameters to be interdependent. Zero shear viscosities and molecular weight (M_w) define a narrow range of M_w where chain entanglement and network structure occurs. Melt viscosities below about 190°C, however, are higher than expected from entanglement theory. Further, non-Newtonian flow is observed for specimens with M_w below the entanglement "point," and flow activation energies were found to depend both on temperature and shear stress. Network stabilization mechanisms due to the existence of hydrogen bonds are proposed to account for the complex rheology, and some consequences on the practical properties of the polymers have been suggested.

INTRODUCTION

There are traditional and important links between the broad area of technology encompassed by the field of organic coatings and the science of rheology. Routine determinations of viscosity or flow times are frequently employed as a quality control datum for paints at the plant production level. The main impact of rheology to date, however, has reflected the fact that organic coatings generally involve dispersions of solids in complex fluid media, which often display non-Newtonian characteristics. Dispersion and agglomeration effects in pigmented systems and in latexes can have profound influence on the performance of coatings as well as on the economics of their production. The rheology of such systems (i.e., their viscous response to applied shear) has been studied in great detail in order to create a scientifically sound base for the interpretation and prediction of such diverse criteria as hiding power, durability, adhesion, etc. Numerous important publications have dealt with these subjects in recent years.[1-3]

The need for rheological characterization of coating systems appears to be increasing further as a result of recent constraints imposed by environmental protection standards and by stringent economic demands. These have led to the rapid development and use of polymers and procedures wherein a contiguous film is formed by the flow and coalescence of polymer particles at elevated temperatures. The viscoelastic properties of such polymers at high concentrations and in the molten state, therefore, are becoming criteria of applied importance. One motivation for the present work is to contribute to, as yet, scant literature on the viscoelastic properties of the complex polymer systems involved in such cases. A further motivation stems from the well established relationship between polymer melt rheology and molecular structure.[4,5]

In chemically simple polymers, such as polyolefins, rheological measurements can provide information on such important structure variables as molecular weight, weight distribution, and chain branch incidence.[5,6] In these simpler polymers, viscoelastic properties are dominated by the presence of networks due to the tendency of flexible polymer chains to entangle, i.e., to form temporary physical crosslinks, as proposed in the molecular theory of Bueche.[8] It would be useful to extend the search for similar relationships linking rheological and structural parameters to families of more complex polymers, typically those used as film formers. In such polymers, viscoelastic properties may well be influenced by the presence of specific interactions due to polar, hydrogen bond forces, etc., a consideration which has, in the past, created some controversy.[9-11] Recent studies of polyamides[5] have shown similarities in the rheological characteristics when compared with those of simpler chain polymers. Further, in preliminary work,[12] the viscous behavior of a styrene/acrylic terpolymer series showed several similarities when compared with series of simpler (e.g., polyolefin) melts. However, possible differences were also alluded to,[12] and these motivated more detailed studies of the polymers, with results given in this paper. It is hoped that the contribution being made to under-

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standing the rheological behavior of complex film-forming polymers may eventually lead to optimizing the formulation and processing variables in this category of polymers.

MATERIALS

Eight polymer samples were used in the present study. All were terpolymers of styrene (S), butyl/acrylate (BA), and methacrylic acid (MAA), and were synthesized by Paint Research Laboratories, Canadian Industries Ltd., Toronto. Through the control of synthesis variables, the materials were produced at varying degrees of polymerization but with uniform mole ratio compositions of S/BA/MAA = 80/15/5. The polymers were supplied as free-flowing powders.

The structural complexity of the polymers imposed limitations on the accuracy of structure characterization. They are typical, however, of film-forming polymers in contemporary use, and their choice is, therefore, pertinent to the present study.

Two sets of characterization data were obtained: Relative viscosities (RV) of the polymers were measured at 0.5% (w/v) concentrations in 95/5% (v/v) mixtures of ethylene dichloride/ethanol. Gel permeation chromatography of tetrahydrofuran solutions was the source of molecular size parameters reported along with the RV values in *Table* 1. The problem of converting elution volumes for such complex polymers into molecular size characteristics has already been noted.[12] As in the earlier work, calibration using polystyrene standards was carried out, so that the data in *Table* 1 are polystyrene equivalent (PSE) molecular weights.[13] Their absolute values are of indeterminate accuracy; though in view of the high styrene content of the series, the Mw and Mn values may be taken as good approximations. No reservations exist as to the relative validity of the molecular weight parameters.

It is evident from *Table* 1 that the molecular weight distribution in the resins broadens as the degree of polymerization increases. Since it is Mw that increases more rapidly, it follows that at higher degree of polymerization there is a broadening of the high molecular weight portion of the distribution. In the present work it is not possible, therefore, to separate the effects of molecular weight and of distribution on rheological behavior patterns. The relationship between M_n and M_w/M_n can be expressed quantitatively, as shown in *Figure* 1, the linear function corresponding to the statement

$$\log \frac{M_w}{M_n} = 0.13 + 1.12 \log (M_n - 4.0) \qquad (1)$$

Equation (1) is proposed to be valid in the range $10^4 < M_n < 10^5$.

Table 1—Molecular Structure Characterization Of S/BA/MAA Polymers

	R.V.	M_n 10^{-4}	M_w 10^{-4}	M_w/M_n
1	0.12	1.20	1.77	1.48
2	0.20	1.48	2.60	1.76
3	0.23	1.96	4.52	2.43
4	0.28	1.71	5.72	3.35
5	0.30	2.19	7.54	3.44
6	0.38	3.31	15.1	4.56
7	0.49	3.36	17.3	5.15
8	0.89	4.72	29.5	6.25

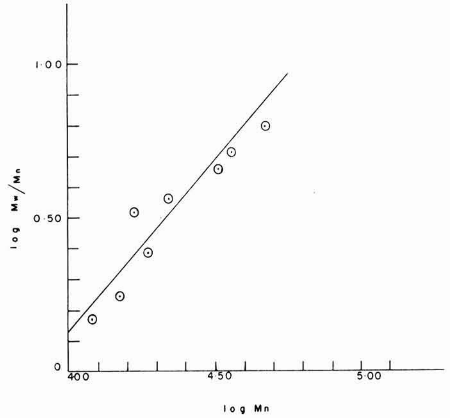

Figure 1—Interdependence of absolute molecular weight and molecular weight distribution in S/BA/MAA polymers

RHEOLOGICAL STUDIES

Two sets of flow data were obtained. One of these was measured with a gas-driven capillary high-shear viscometer (HSV), long familiar in the study of thermoplastic polymers.[14] This instrument is capable of furnishing viscosity data over a wide shear stress interval (typically $10^5 - >10^7$ (dynes/cm^2)) and, therefore, provides information which is useful for various processing operations such as extrusion, injection molding, etc. A single die was employed in this work; this had a length:radius (L/R) ratio = 7.673 and R = 0.0254 cm. Data were collected in the temperature range 150-200°C.

In capillary extrusion nonuniform velocity profiles are known to exist, and for non-Newtonian fluids corrections are often applied to calculate accurately the shear rate and shear stress variables. In this work, the shear stress at the capillary wall, τ_w, was calculated from the simple (ideal) expression.

$$\tau_w = \frac{P \cdot R}{2L} \qquad (2)$$

where P is the pressure applied to the molten polymer. This neglects pressure losses occurring in the die entry region,[14] but the magnitude of these losses was shown by calibration experiments to be less than the ± 5% reproducibility of individual experimental viscosity points. The shear rate at the wall, $\dot{\gamma}_w$, was calculated from the apparent $\dot{\gamma}_a$ via the Rabinowitsch equation[15]

$$\dot{\gamma}_w = \dot{\gamma}_a \left[\frac{3}{4} - \frac{1}{4} \frac{d \log \dot{\gamma}_a}{d \log \tau_a} \right] \ldots \qquad (3)$$

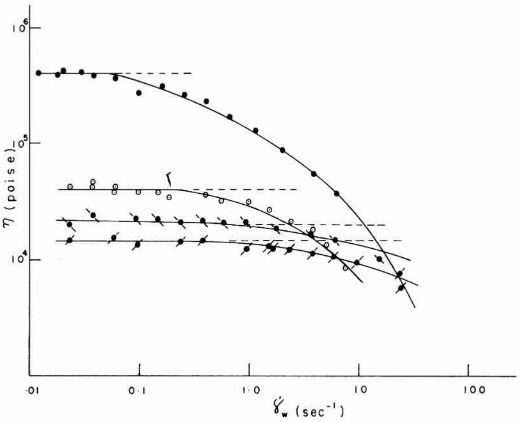

Figure 2—Typical cone and plate viscometer data at low shear rates and T = 150°C. Legend: • sample 6; ○ sample 4; ⟍ sample 2; and ⟋ sample 1

where $\dot{\gamma}_a = \frac{4.Q}{\pi R^3}$, Q being the volumetric output rate. The required melt densities were also calculated from HSV data, using the experimental method described by Terry and Yang.[16]

The HSV is of limited use for the measurement of viscosities at low or zero shear. These viscosities, however, are pertinent to many coatings applications, such phenomena as coalescence, sag, etc. occurring at shear rates near zero. In addition, the zero shear viscosity, η_0, is vital in forging the link between rehological parameters and molecular structure variables. Although empirical methods exist for extrapolations of η_0 from HSV data at higher rates of shear,[17] direct determination with cone and plate rheometers is preferable. A second set of data in the shear rate range 10^{-2} – approximately 10 sec^{-1} was, therefore, measured using the Mechanical Spectrometer, Model KMS-71C.* The temperature range again was 150-200°C. The thermal stability of the polymers in the chosen working range was confirmed by thermogravimetric studies which have been discussed in an earlier publication.[12]

RESULTS AND DISCUSSION

Zero Shear Viscosities

The determination of η_0 values is illustrated in *Figure* 2, which displays the steady-state (cone and plate) viscometer results for samples 1, 2, 4, and 6 at 150°C. It is clear that the molten terpolymers are non-Newtonian, shear thinning fluids, with a distinct "plateau" at low $\dot{\gamma}_w$, in which the melt viscosity is independent of shear rate. The shear rate value at which deviation from Newtonian flow begins decreases with increasing molecular weight, in a manner which is analogous to the behavior of homologous series of other polymers.[17-18] In the shear thinning range, the slope of the flow curve tends to increase with rising M and, if the behavior of simpler polymers is again followed, the broader distribution of the high molecular weight samples further contributes to the steepness of the flow curve in this region.[17,19] One interesting consequence is the tendency of the flow curves to cross over, as in the case of samples illustrated in *Figure* 2. This incident points to a danger inherent in the use of parameters like the melt flow index,[20] often the sole commercially available characterization datum for polymer processing. The melt flow index is a function of melt viscosity at a fixed temperature and a fixed, moderate, shear stress (τ_w). While it will place polymers in the right order of "processability" when that processing takes place at shear stresses near the melt indexing condition, it can be quite misleading as a guide to performance when the processing conditions are far removed from the melt indexing point. The situation illustrated in *Figure* 2 is typical: At moderate shear stresses such as in low speed extrusion, samples 4 and 6 will have melt viscosities not far different from those of the lower molecular weight specimens. In coalescence or other flow effects occurring at low $\dot{\gamma}_w$ (e.g., < 1 sec^{-1}), the melt viscosities of samples 4 and 6 will be, in fact, significantly higher than those of samples 1 and 2. The materials should, therefore, be processed under adjusted conditions (e.g., higher temperature) if their performance is to match that of their lower molecular weight analogues.

Zero shear viscosities, determined over the experimental temperature range, were plotted against M_w on double logarithmic coordinates, with typical results shown in *Figure* 3. The data follow a familiar pattern[6] in

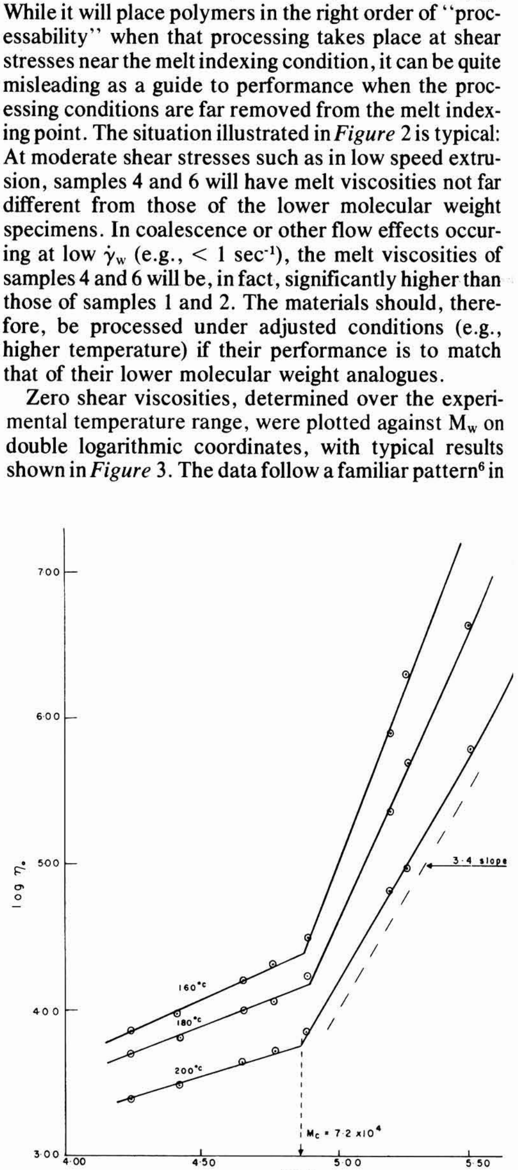

Figure 3—Illustrating variation of Newtonian melt viscosity with M_w at 160, 180, and 200°C, and definition of M_c value

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*We thank the staff of the Chemical Engineering Dept., McGill University for permission to use their instrument for this purpose.

displaying a distinct transition from low to higher slope, which occurs in a narrow molecular weight interval, centered on a "critical" value, $M_c \simeq 7.2 \times 10^4$. The M_c value is essentially independent of melt temperature.

According to the chain entanglement theories of Bueche[5] and of Graessley,[21] M_c denotes the molecular weight above which a polymer chain becomes sufficiently flexible to entangle with other chains, giving rise to an elastically deformable network structure. The present polymer series, therefore, follows the patterns established by many homologous polymer series; the M_c value, however, appears high relative to $M_c \simeq 3.8 \times 10^4$ for polystyrene,[6] a point arguably associated with the presence of acid moieties in the terpolymer, and consequently with the existence of H bond interactions, which would tend to stiffen (crosslink) the polymer chains. This subject is further discussed later on.

Another unusual feature of *Figure* 3 is the evident variation in the slope of the plotted function, particularly above M_c. While theory is not fully quantitative on this point,[22] frictional and steric hindrance effects associated with the entanglement concept call for η_0 and M ($>M_c$) to be related through a power-law relationship with a 3.4 exponent. At temperatures above the 180-190°C interval, the behavior of the terpolymers conforms with these expectations (see *Figure* 3). At lower temperatures the power law dependence rises. The specific values being as follows:

T (°C):	150	160	170	180	190	200
$\frac{\delta \log \eta_0}{\delta \log M(>M_c)}$	5.9	5.4	5.0	4.4	3.6	3.4

Once again the suspicion is raised that mechanisms other than physical chain entanglements are operative in determining the melt viscosity and, furthermore, that these mechanisms are significantly temperature dependent, most particularly so in the 180-190°C interval.

The ability to predict temperature variations of melt viscosity is an important one, and in many systems it is possible to apply simple Arrhenius expressions of the form:

$$\eta(T) = A \exp. (E_T/RT) \ldots \quad (4)$$

where A is a constant, R is the gas constant, and E_T is the activation energy for viscous flow at stated shear stress. Using this procedure to calculate the activation energy for flow at zero shear, E_0, leads to results exemplified by *Figure* 4 for samples 3, 5, and 7 (see also *Table* 1). In contrast with a number of polymers, including those containing polar groupings,[23] the E_0 datum is not independent of temperature. The relationships exemplified in *Figure* 4 are curved, and may be approximated by two linear sections, as shown. As a consequence, for any given polymer of the series, two E_0 values are defined, with a "dividing line" in the vicinity of 180°C between the two values. A summary of E_0 data is given in *Table* 2.

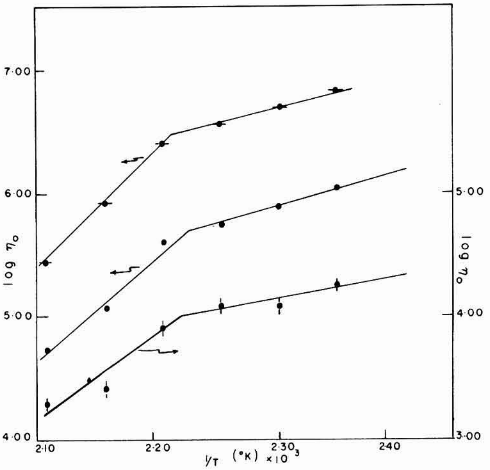

Figure 4—Arrhenius plot of log η_0 vs. 1/T for samples 3 (ɸ), 5 (•), and 7 (-•-)

There seems to be no significant molecular weight dependence of E_0 on either side of the M_c boundary, but the E_0 values below M_c (in the area of sample 5) are characteristically lower than their higher M homologues. This appears to be consistent with the suggestions made earlier that two district mechanisms determine the viscous response of these materials. One of these is the presence (or absence) of entanglement networks, and the other is the existence of thermolabile hydrogen bonds arising from the presence of acid groups. Since there is little evidence for temperature dependence of E_0 in polymers where entanglement structures dominate viscosity variations,[6,23] it is suggested that the apparent "shift" in E_0 near 180°C corresponds to a distinct reduction in the effectiveness of hydrogen bonds as supplementary network stabilizers or quasi-crosslinks. Thus, the present series represents the interesting case of a polymer in which melt (and processing) behavior is essentially that of a simple network polymer when at sufficiently high temperature, but which assumes the characteristics of a more viscous, quasi-crosslinked fluid when processed below the crosslink dissolution temperature. The experimental E_0 datum is then the sum of at least two terms,

$$E_0 = (E_0)_e - (E_0)_H \ldots \quad (5)$$

Table 2—Activation Energies, E_0, For S/BA/MAA Series Of Polymers

	E_0 in Kcal/g mole:		
Sample	**T > 180° C**	**T < 180°C**	
1	9.5	6.5	
2	9.5	8.5	
3	11.0	8.0	
4	11.5	8.0	
5	16.5	9.5	Region of M_c
6	18.0	11.0	
7	19.5	11.0	
8	18.5	10.5	

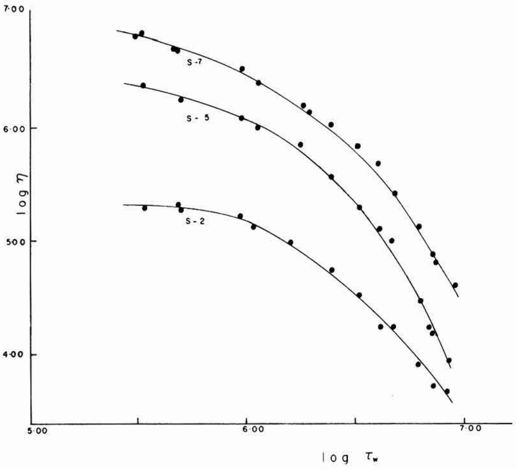

Figure 5—High shear (capillary) viscometer flow data at 160°C

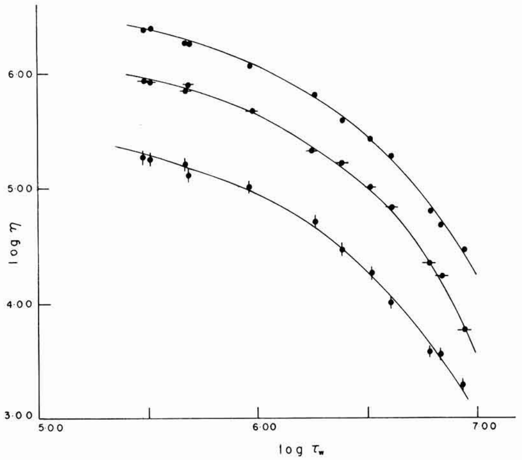

Figure 6—Temperature dependence of flow data at high shear: sample 6 at 150°C (●), 170°C (-●-) and 190°C (⧫)

the subscripts e and H referring to entanglement and H-bond origins of the activation energy.

The nature of the hydrogen bond has been studied extensively.[24] Its contribution to the viscoelastic behavior of such polymers as ethylene-acrylic copolymers,[23] carboxy-terminated polybutadienes,[25] and low molecular weight styrene-acrylic copolymers[26] has been noted. According to Blyler and Haas,[23] the contribution per mole of acrylic acid groups to the activation energy of ethylene/acrylic acid copolymers is about −1.5 Kcal. In their earlier work, Longworth and Morawetz[26] found a contribution of roughly −3 Kcal/mole of acid in the activation energy of styrene/methacrylic acid polymers, and also noted that the magnitude of the effect decreased sharply with increasing temperature. The total contribution to E_0 in our higher M_w materials (i.e., where $M > M_c$) is about −8 Kcal. Assuming that a relationship between E_0 and mole % acid is roughly linear, this would amount to a contribution of about −1.6 Kcal/g mole, in very good agreement with the earlier findings noted here,[23,26] though lower than the −5 Kcal/mole proposed for H-bonds in basic considerations[24] of this linkage. If, in the vicinity of 200°C, the network stabilizing influence due to H-bonds is completely absent, then $E_0 = (E_0)_e \simeq 15$ Kcal/g mole, a value which is similar to flow activation energies in many nonpolar polymer series.[6,18]

The given hypothesis also accounts for the apparently high M_c value, commented on earlier. The presence of H-bonds would act to stiffen the polymer chain and to increase the size of flow "domains." This would be expected not only to raise M_c but to contribute to the absolute melt viscosity value. The presumed enhancement of η_0 due to H-bonds is of course reflected in *Figure* 3, and may be expressed empirically as

$$\eta_0 = KM^{(3.4+\alpha)} \quad . \; . \; . \; . \; . \qquad (6)$$

when $M > M_c$. The parameter α will have non-zero values when $T \leqslant 180°C$. This argument, however, would call for M_c to reduce somewhat at temperatures above the suggested 180°C boundary, an expectation apparently not met by the results in hand.

A further anomaly in the data is the behavior of E_0 for samples with $M < M_c$. Two sets of E_0 values persist, although the difference between them on either side of the "shift" temperature has been reduced. If the same mechanism of H-bond "dissolution" is proposed here, then it must be concluded that the "effectiveness" of H-bonds as flow inhibitors is considerably less in the low than in the high molecular weight samples of this series.

Shear Dependence of Viscosity

A preliminary discussion of capillary viscometer data for these polymers noted[12] that the terpolymers form non-Newtonian fluids, even when $M < M_c$. Typical flow curves for the polymers are given in *Figures* 5 and 6. The former shows representative flow behavior at 160°C, while Figure 6 shows the (typical) temperature dependence of capillary flow data for sample 6. The tendency to approach a Newtonian flow "plateau" is again clearly marked in the lower molecular weight members of the series. Because of shortcomings associated with low shear, capillary extrusion data, already discussed, these apparent "plateau" values of viscosity do not correspond to steady-state η_0 results, reported in the preceding section. Non-Newtonian flow is evident, as is the tendency for this to begin at lower wall stresses as polymer molecular weight increases. In this respect the S/BA/MAA polymers follow well established patterns of behavior.[5,17,27] It is not advisable, at this time, to attempt correlating an index of shear thinning flow with molecular weight because of the related shift in M_w/M_n.

It is well known that molecular weight distribution also influences the shape of the flow curve;[17,18,22,27] consequently, independent control of M_w and M_n will be needed to separate the effects of absolute molecular weight and weight distribution on the rheological be-

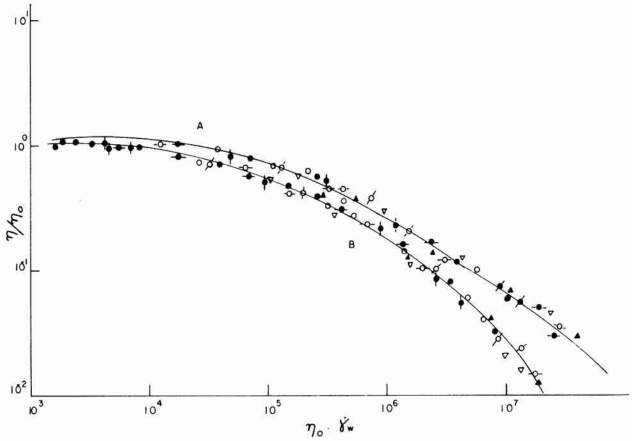

Figure 7—Master flow curves for S/BA/MAA polymer series (A) reduced variables plot at 150°C (B) reduced variables plot at 190°C, Legend: • sample 1; -●- sample 2; • sample 3; ○ sample 4; -○- sample 5; ⌀ sample 6; ▽ sample 7; and ▲ sample 8

havior of the polymers. This is the subject of work now underway in these laboratories. Appreciable non-Newtonian flow is observed in samples with $M < M_c$ (viz., sample 2, *Figure* 5). Clearly, changes in entanglement spacing or entanglement density cannot account for this effect. This phenomenon is also tentatively ascribed to the existence of specific interactions in these polymers and, hence, to the existence of flow "domains" or networks below M_c. The interesting inference to be drawn from *Figure* 5 is that the stability of the specific interaction (H-bond) linkages is shear sensitive as well as being temperature dependent. The matter is again raised later on. The complex temperature dependence of melt viscosity is also evident in *Figure* 6. The overall shape of the flow curves further suggests complications in the combined effects of temperature and shear on polymer melt viscosity.

The prediction of rheological and processing behavior for any member of a series of polymers is possible if a master flow curve can be constructed for the polymer family. Various receipes exist for the definition of reduced variables, the most widely used being those based on the entanglement concepts of Bueche and Graessley.[22] Thus, reduced viscosity may be defined by η/η_0, where η is the melt viscosity at finite shear, and reduced shear rate by $\eta_0 \cdot \dot{\gamma}_w$. Superposition of flow data obtained at various temperatures is also widely practiced through use of the temperature shift factors defined by the WLF expression.[27] The complex temperature dependence of melt viscosities in this work precludes the definition of a single WLF factor capable of producing temperature independent master curves. Isothermal master curves may be obtained readily, however, as shown in *Figure* 7, at 150°C by curve A and for data at 190°C by curve B. The reduced data fall into relatively narrow bands, permitting reasonably accurate predictions (about ± 15%) of the η vs. $\dot{\gamma}_w$ function for any polymer in the series provided η_0 is known, either from experiment or from calculation using the previously established relationship between η_0 and M_w.

The variation of melt viscosity with temperature at higher shear stresses is frequently analyzed by the activation energy parameter, as in the case of E_0. Accordingly, Arrhenius functions of the type shown in *Figure* 4 were constructed, using viscosity data at constant wall stresses in the range $\sim 7 \times 10^5 - 10^7$ dynes/cm^2. As before, curvilinear functions were generated and these were again depicted as two linear segments, one employing data at 190° and 200°C, the other joining data points collected at $T \leq 180°C$. Consequently, analogous to equation (5), two activation energies are again involved, the presumed result of distinct relaxation (flow) processes due to H-bond and entanglement effects. The shear stress dependence of the higher temperature value, previously associated with entanglement effects, $(E_\tau)_e$, is illustrated in *Figure* 8 (l.h. ordinate) for representative samples. The slight decrease in (E_τ) is similar to that reported for ethylene/acrylic acid copolymers by Blyler and Haas.[23] Similar variations have been observed for a variety of polymers.[6,9,11,25]

At lower temperatures the variation of E_τ, now containing the $(E_\tau)_H$ contribution, is quite unusual. The evident upward shift in E_τ is in keeping with the behavior of the E_0 function as shown in *Table* 2, and is particularly noticeable for samples with $M > M_c$. Their initial low activation energies have already suggested the network stabilization influence of persistent H-bonds. *Figure* 8 now indicates that $(E_\tau)_H$ is also shear sensitive, that is, the effectivenss of H-bond crosslinks in the melt network decreases as the shear stress is increased. This suggestion appears to be reasonable when viewed against the known properties of H-bond linkages and the known nature of capillary flow in the non-Newtonian regime. It is well known that H-bond and related associative forces are short-range;[24] they tend to act over radii of the order of 5Å, and they are highly sensitive to the orientation of bonding groups.

In viscous flow, on the other hand, it is well known that more or less parabolic flow profiles are set up in the capillary, with zero flow velocity at the wall and maximum velocity at the center of the flow stream. Since melt lamina near the center of the capillary travel

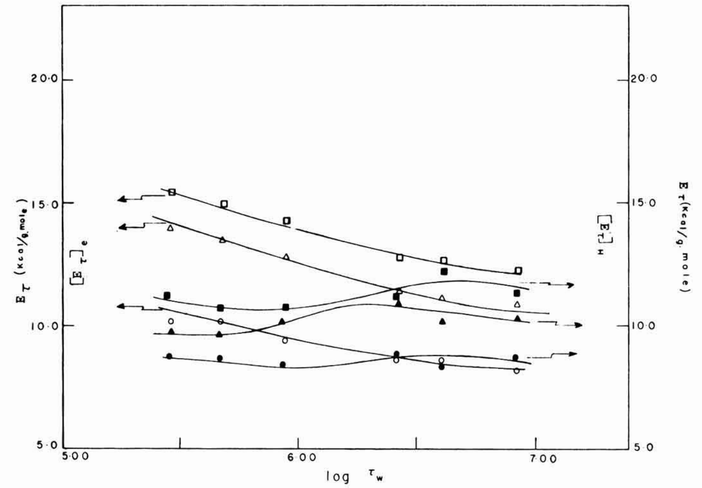

Figure 8—Stress dependence of flow activation energy, typical behavior for samples 3 (○, ●), 5 (△, ▲), and 7 (□, ■). Open symbols depict $(E_T)_e$, closed symbols for $(E_T)_H$

at higher speeds than those near the capillary wall, there must be considerable displacement (slippage) of polymer chains past each other. Under these conditions the effectiveness of H-bonds as network stabilizers must be seriously reduced, if not destroyed. The tendency of polymer chains to rotate and align parallel to the flow direction[22] at higher shear stresses must also be noted, since this tendency will change the morphology of the polymer system from its state at zero shear stress. An impact on the effectiveness of H-bonds is indicated. Moreover, the orientational effect is as applicable to polymer chains above M_c as it is below. Thus, the manifestation of non-Newtonian flow below M_c, already noted above and in a preceding publication,[12] may have its origin in this aspect of the associative force mechanism.

Much emphasis has been given in this discussion to the concurrent network stabilization mechanisms of chain entanglements and associative forces operative in the S/BA/MAA polymer series. They provide a good, qualitative rationale for the interesting and complex shear and temperature responses of melt viscosity: Nevertheless, additional effects may also be operative; these are mentioned here, though a detailed investigation of their existence was beyond the scope of present work.

Table 3—Young's Modulus, G, For S/BA/MAA Films Pressed at Various Temperatures

All films molded at 500 psi/5 min
G (dyne.cm^{-2}) × 10^{-9}

Press Temp. (°C)	150	160	190
Sample 1	1.23	1.26	1.05
Sample 2	1.26	1.21	—
Sample 3	1.20	1.30	1.12
Sample 4	1.31	1.34	1.10
Sample 5	1.13	1.25	1.10
Sample 6	1.08	1.10	0.95
Sample 7	1.09	1.05	1.05
Sample 8	0.96	1.05	1.05

SHEAR HEATING: True melt viscosities may be higher than the apparent values, due in part to frictional heating generated by the viscous liquids in their flow at high shear stress. In addition, the proposed response of H-bonds to applied stress would also contribute a thermal effect which may not dissipate fully in the time span of transit through the extrusion capillary. Such shear-heating effects, while certainly present,[22,23] are regarded as being of second order importance, though more detailed studies will be needed to settle the point.

MORPHOLOGICAL DETAIL: It is not known whether the proposed H-bonds in the polymer melts are distributed randomly, whether they tend to cluster in distinct "domains," or, finally, whether transitions between the two states take place under specific conditions of T and τ_w. The degree of viscosity enhancement and the steepness of the flow curve in the non-Newtonian region may well depend strongly on such considerations,[25] which will be targets for subsequent studies.

RELATIONSHIP TO SOLID-STATE POLYMER PROPERTIES: The rheological characteristics of the present polymer series may be taken as indicators of the way these materials will process. Such performance criteria as coalescence rates, gloss development, and flow-out will undoubtedly correlate with the melt flow properties given here. It is intuitively suggested that solid-state properties of these polymers may also depend on whether the solid film was formed under conditions favoring the presence or absence of network stabilization effects ascribed to H-bonds. A preliminary scouting of this suggestion was made through measurements of the elastic (Young's) modulus (G) on polymer strips compression molded against copper foil at 500 psi and at temperatures on either side of the H-bond "dissolution boundary." The metal was removed by amalgamation with Hg, and the free films were tested in an Instron

Table Model Tester (jaw separation speed = 0.5 cm/min). The results of this sequence are given in *Table* 3.

The data in *Table* 3 give qualitative support to the suggested relationship between solid-state properties and film formation temperature. At lower temperatures, where H-bonding is assumed to persist, relatively high values of G in materials below M_c reflect the existence of frozen-in strains, presumably arising from deformation of equilibrium spacings between interacting groups. Lower G values are obtained for these materials at 190°C—an indication that these strains are reduced or absent. For all practical purposes, G for materials above M_c is independent of film formation temperature: Evidently, the modifying influence of entanglement couplings is predominant. Entanglement networks are inherently deformable, hence the strain building effects felt in their absence are now reduced to the point where present measurements are insufficiently sensitive for their detection. The interrelation between processing (rheological) conditions and use properties will warrant further study.

CONCLUSIONS

The results of this study show first of all that standard rheological apparatus, including familiar capillary and cone-and-plate viscometers, are useful in characterizing the viscous properties of complex film forming resins over ranges of temperature and shear which are consistent with processing conditions. Specific points arising from the study show that:

(1) The dependence of melt viscosity of an S/BA/MAA (80/15/5) polymer series on temperature and shear stress (shear rate) is complex, depending both on absolute molecular weight and molecular weight distribution.

(2) Following a limited range of shear rate or stress where melt viscosity is constant, the polymers become shear thinning, the degree of non-Newtonian flow being a function of molecular weight parameters. Therefore, practical characterization parameters, like the melt flow index, should not be relied upon to provide an accurate prediction of polymer processability, unless the shear and temperature conditions in processing and in melt indexing are similar.

(3) While the rheological properties of the S/BA/MAA series resemble those of simpler polymers in certain respects, important distinguishing features are also noted. In particular, the melt viscosity at low shear is higher than expected from chain entanglement concepts, non-Newtonian flow is observed for samples with molecular weights below the entanglement "point," and the activation energy of viscous flow is dependent on both temperature and shear stress. These findings imply the existence of a crosslink mechanism, allegedly due to the presence of H-bonds in the polymers. The effectiveness of the H-bond structures has been assumed to vary with both T and τ_w.

Use properties of the polymers and their optimization should reflect strongly on the above points. Thus:

(1) Coalescence of molten particles at low shear should occur very slowly due to the viscosity enhancement effects of H-bonds, unless that coalescence occurs above the temperature of H-bond "dissolution" (180-190°C).

(2) Dimensional stability (sag, etc.) of molten polymer will be enhanced under T and τ_w conditions favoring the persistence of H-bonds.

(3) Films formed under conditions where the persistence of H-bonds is favored should be subject to greater frozen-in strains due to the deformation of these linkages. Consequences are modifications of elastic moduli and may also include reduced clarity, reduced impact resistance, but a tendency for these properties to change with aging, as the strains are relaxed.

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Single-Grade Rutile TiO_2 Concept For Interior Latex Trade Sales Systems

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The large number of rutile titanium dioxide grades commercially available in the United States present selection, inventory, and handling problems for the manufacture of interior trade sales finishes. The use of a single grade of rutile titanium dioxide in combination with extenders already on hand would serve to relieve that situation.

Based on an evaluation of commercial latex flat wall and gloss paints, comparable quality formulas were developed in which to examine general purpose, enamel, and high-dry-hide grades of rutile titanium dioxide for optical and physical performance. The tests showed that enamel grades of rutile titanium dioxide present the greatest potential to fulfill the requirements needed for broad trade sales application.

INTRODUCTION

Since its inception in the United States in 1916, the titanium dioxide industry has shown outstanding growth so that today we find six domestic manufacturers producing in excess of 600,000 tons annually. Better than 50% of this production is consumed by the coatings industry. Along with this high growth in titanium dioxide manufacture came an equally staggering number of grade types. The development and marketing activities were so prolific that today the marketplace is saturated with over 90 dry and wet grades of titanium dioxide.

In the early years, with the types of resins and extenders available to the paint formulator, it may have been necessary to develop a number of different grade types to provide the reflectivity and hiding power we have come to associate with this white hiding pigment. In response to the question, "Why not design a single pigment to perform all tasks?", Kampfer says that those pigmentary properties designed and built into a given grade of TiO_2 by the manufacturer for one coatings application may well mitigate against its successful performance in another area.[1] Sagely, he observes that "skillful formulating actually provides for greater degree of universality for a given pigment than is ever possible for a manufacturer to achieve by production techniques." In light of the present state of the art in TiO_2, extender, and resin technology, are the large number of TiO_2 grades currently available a technical necessity? Accepting the fact that a single grade of TiO_2 can be used in a wide range of coatings formulations, it is unclear as to the grade to choose so we can apply our "formulating skills" to the problem of single grade use in interior pigmented trade sales systems.

The 50's and 60's saw publication begin in earnest on pigments and extenders,[2] particle size,[3,4] CPVC,[5,6] and high-dry-hide[7,8,9] as they pertain to hiding power in flat latex paints. (These articles are readily available in the referenced sources and since they deal thoroughly with each of the concepts involved that material will not be repeated here.) Suffice it to say that all this theory (and sometimes practical treatment of theory) serves to reinforce the feeling that a single grade of TiO_2 might well be used to formulate a broad range of interior trade sales coatings. The purpose of this project was to put those theories to work. First, we wanted to determine the grade of TiO_2 that would fit the single grade performance criteria of quality commercial optical, physical, and economic properties. Then, we would develop a set of interior trade sales formulations—flat through gloss—covering the use of that single grade.

EXPERIMENTAL PROCEDURES

Commercial Paint Evaluation

To make certain the information developed would be practically useful, the first step was to purchase and evaluate commercially available latex flat, semi-gloss, and gloss paints. The paints purchased were representative of products manufactured by national and regional (mideastern and southeastern U.S.) trade sales houses. This study included developing formula composition (through label analysis as well as wet chemical and instrumental analysis of the paints themselves), evaluation of physical properties, and establishment of optical performance. The results of that testing are found in LFW-COM. PTS. (*L*atex *F*lat *W*all *P*aints) and

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GL-COM. PTS. (*G*loss *L*atex *P*aints) in the Appendix-Data Sections No. 1 and 2.

Laboratory Evaluation Formulas— Latex Flat Wall Paints

Having established the physical and optical performance property ranges of the latex flat commercial products involved, formulas were developed that displayed those characteristics. In order to cover the commercial product property ranges involved, the laboratory formulas [see Appendix-Formulas Section (1)] used to screen candidate TiO_2 grade types for single grade application covered PVC's from 50-70% and TiO_2 levels from 0.5 lb/gal up to 2.0 lb/gal in 0.5 lb increments. The PVC changes were made keeping pigmentation constant while adjusting latex solids and bulking out to 100 gal with water/thickener as needed. As TiO_2 levels were changed in the above range, pigment volume was maintained by appropriate adjustments in the volume of natural $CaCO_3$ (Snowflake®) in the formula.

Three different types of TiO_2 were evaluated in those formulas: enamel, general purpose, and high-dry-hide. Typical physical and chemical properties of these grades are given in *Table* 1.

A broad range of optical and physical performance properties were evaluated on those formulas. It appeared, though, that three properties could be used to screen the candidate grades to determine the one grade to work with: tinting strength, porosity, and scrub resistance.

Tinting Strength

To develop this information, a fixed weight of the white paint was tinted with a fixed weight of universal black colorant. The levels were such that light grey paints with reflectance values ranging from 70-85 (as evaluated using a Hunter Color Meter, D-25-3, ANLab Scale) were obtained. Tint tones (b-values) were also taken on these same tints to determine the blueness-yellowness differences in undertone. On this basis, then, the higher the brightness level, the stronger the TiO_2; the more positive the b-values, the yellower the tint tone, and vice versa.

Table 1—Typical Physical and Chemical Properties Of TiO_2 Grades Evaluated

	Enamel[a]	General Purpose[b]	High-Dry-Hide[c]
% TiO_2, min	94	90	84
Specific gravity	4.1	4.0	3.8
Oil absorption	12-16	16-20	36-40
pH	6.8-7.5	6.5-7.5	7.0-8.5
Specific resistance, ohms, min	7,000	7,000	6,000
Chalk-resistance	Medium/high	Medium/high	Medium/high
ASTM D-476-73	II, III	III, IV	III

(a) Zopaque® RCL-9
(b) Zopaque RCL-2
(c) Zopaque RCL-3
(Examples, similar grades from other manufacturers may work equally as well.)

more staining ⟵ Control ⟶ less staining

-3	-2	-1	0	+1	+2	+3

Note: The ratings are set such that each point value represents a <u>just</u> visible difference from the point on either side of it.

Figure 1—Paint porosity rating system

Porosity

Porosity measurements were made using ASTM Method D3258, "Test for Porosity of Paint Films," except for the method of rating. The test consisted of staining a dried drawdown of the white paint with a blue-grey stain (K&N Special Test Compound), removing as much of the stain as possible, and in our work, rating resistance to staining relative to the control paint. The rating was done visually on the point system basis shown in *Figure* 1.

Scrub Resistance

Scrub resistance was determined by subjecting preweighed 10-mil wet film thickness drawdowns of the white paints on black plastic scrub panels to a maximum of 1,000 cycles (or until just before wear-through to the substrate occurs) using an abrasive scrub medium and a 500 g weighted small pore sponge in conjunction with a Gardner Straight Line Scrub Tester. The panel was then rinsed, dried, weighed, and the resulting milligram weight loss per 100 cycles obtained. The greater the weight loss found, the poorer the scrub resistance was judged to be.

The above baseline performance properties on the three TiO_2 types evaluated were studied. From this a control formula and control TiO_2 grade were selected. They served as a basis of comparison for further flat wall paint formula modifications to evaluate single grade performance possibilities and evolve a formula exhibiting the performance obtainable using that single grade of TiO_2.

Latex Semi-Gloss and Gloss Paints

The four formula types listed in *Table* 2 were involved in this portion of the project [detailed formulas are presented in the Appendix-Formulas Section (2, 3, 4, 5)]. These formulas are within the performance/economic range of the commercial paints tested. The first two formulas represent conventional formulation approaches to latex gloss paint production. The two

Table 2—Laboratory Semi-Gloss and Gloss Paint Formulas

Formula 2—Acrylic Latex-Based Semi-Gloss Paint, Dry TiO_2
Formula 3—Acrylic Latex-Based High Gloss Enamel, Dry TiO_2
Formula 4—Acrylic Latex-Based, Supergloss Texigel Formula, Dry TiO_2
Formula 5—Acrylic Latex-Based, Competitive Texigel Formula, Dry TiO_2

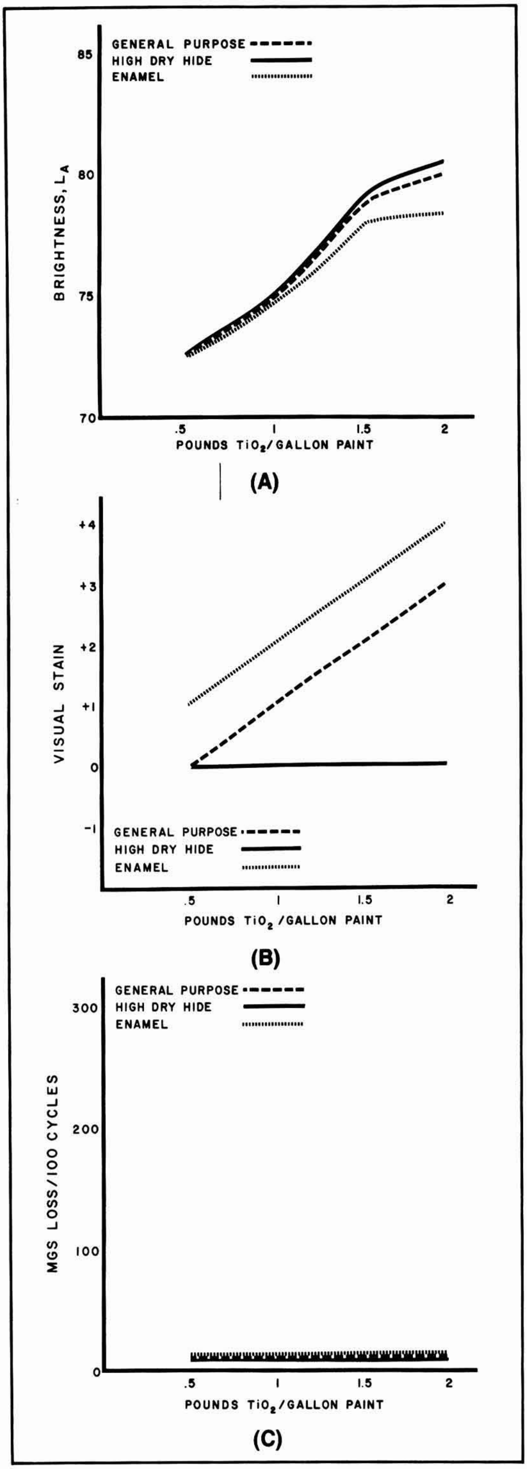

Figure 2—Tint strength (A), porosity (B), and scrub resistance (C) at 50 PVC for enamel, general purpose, and high-dry-hide grades

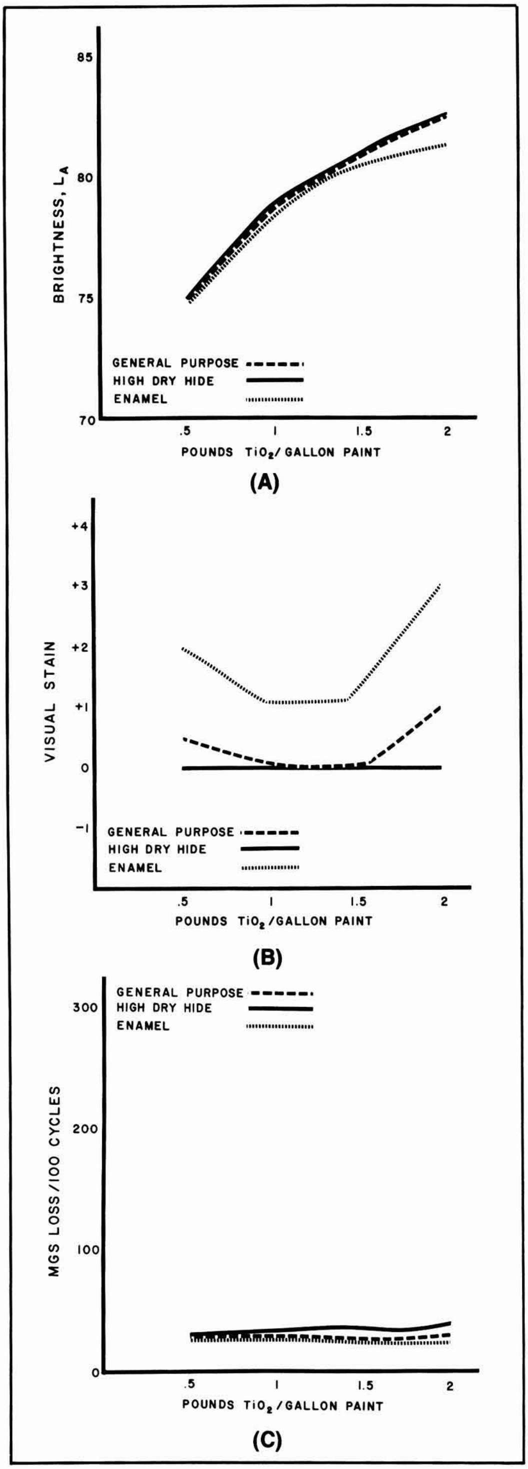

Figure 3—Tint strength (A), porosity (B), and scrub resistance (C) at 60 PVC for enamel, general purpose, and high-dry-hide grades

Texigel® formulas illustrate the possibilities of gloss additive use for gloss paint development.

For the purpose of this work, gloss and hiding power were the principal criteria for single grade TiO_2 evaluation and selection. As noted in the Attachments-Data Section, more extensive testing was carried out. The enamel and general purpose grades used in the latex flat wall paint work were evaluated in these four formulas on an equal weight basis; the highly surface-treated, high binder demand, high-dry-hide grade was not included in this phase of the project since it yields too low a gloss to be useful in these types of paint systems.

RESULTS AND DISCUSSION

Latex Flat Wall Paints

Figures 2, 3, and 4 graphically present the tinting strength, porosity, and scrub resistance data obtained at 50, 60, and 70 PVC equal weight comparisons of enamel, general purpose, and high-dry-hide grades. In interpreting this data, one should keep in mind the following guidelines as to the significance of the data presented. Significance is defined in this case as values of data such that the difference is visible and equals or exceeds normal test variability. Within (or smaller than) those values, comparative performance is considered to be equal.

SIGNIFICANCE FACTOR

Tint strength:	± 0.5%
Tint tone:	± 0.1 unit
Porosity:	± 0.5 unit
Scrub resistance:	*Good* up to 80 mg wt loss/100 cycles. *Moderate* 80 to 120 mg wt loss/100 cycles. *Poor* > 120 mg wt loss/100 cycles.

In the equal weight comparisons, the three grades were ranked as shown in *Table* 3. At 50 and 60 PVC no significant difference was assigned in tinting strength until the TiO_2 level reached about 1.5 lb of TiO_2/gal; at 70 PVC differences became apparent at 1 lb of TiO_2/gal. In tint tone, the enamel grade showed the bluest undertone and the high-dry-hide type was yellowest in undertone; the general purpose grade fell between those two grades. No significant differences in scrub resistance attributable to TiO_2 grade selection were noticed at 50 and 60 PVC, regardless of the level employed. The results parallel those that theory predicts. The high-dry-hide, high binder demand grade develops

Table 3—Equal Weight TiO_2 Performance Ranking

Property	Rank (order high to low)
Tint strength	High-Dry-Hide, General Purpose, Enamel
Porosity	High-Dry-Hide, General Purpose, Enamel
Scrub resistance	Enamel, General Purpose, High-Dry-Hide

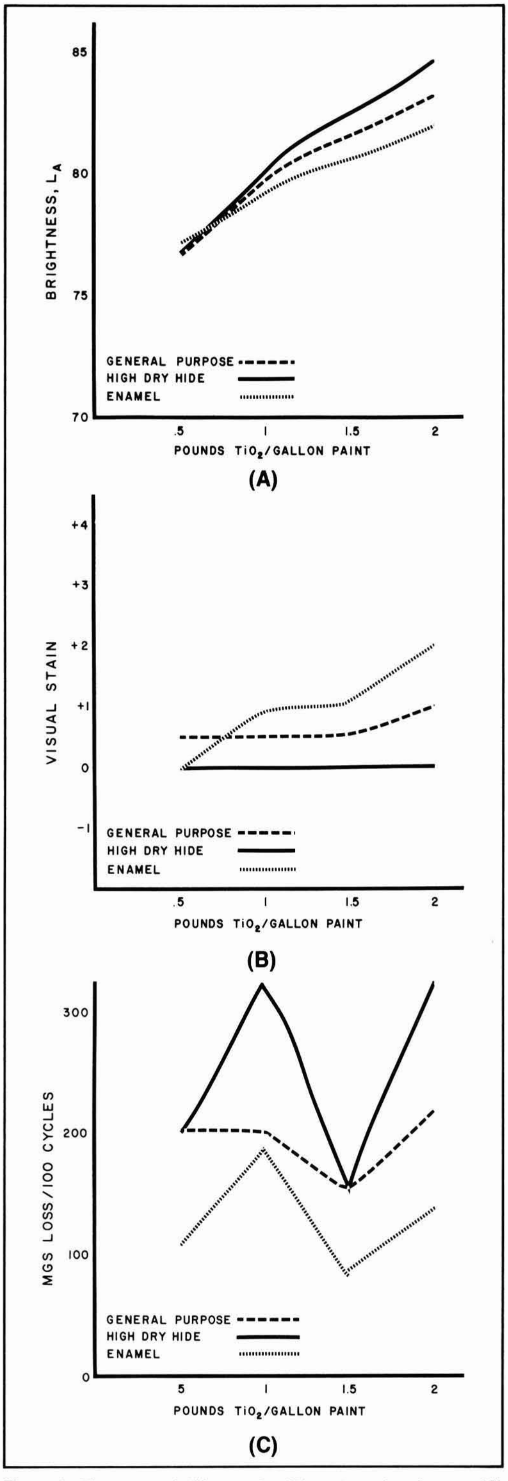

Figure 4—Tint strength (A), porosity (B), and scrub resistance (C) at 70 PVC for enamel, general purpose, and high-dry-hide grades

Table 4—Extender Modification-Precipitated $CaCo_3$

	TiO_2 Type		
	High-Dry-Hide Control	Enamel Grade	General Purpose
PVC	60	60	60
Tint strength (% of control)	100	99.6	100
Tint tone (difference from control)	0	0.5 B	0.4 B
Porosity (relative to control)	0	+2	+1
Scrub test (mg loss/100 cycles)	45	70	85
Pigment/Vehicle RMC/gal	\$1.62	\$1.62	\$1.62

Table 5—Extender Modification-Calcined Clay

	TiO_2 Type		
	High-Dry-Hide Control	Enamel Grade	General Purpose
PVC	60	60	60
Tint strength (% of control)	100	100	100.4
Tint tone (difference from control)	0	0.1 B	0.2 B
Porosity (relative to control)	0	−1	−½
Scrub test (mg loss/100 cycles)	45	53	61
Pigment/Vehicle RMC/gal	\$1.62	\$1.62	\$1.62

Table 6—Extender Modification-ppt. Silica/Amorphous Silica Blend

	TiO_2 Type		
	High-Dry-Hide Control	Enamel Grade	General Purpose
PVC	60	60	60
Tint strength (% of control)	100	99.8	100.8
Tint tone (difference from control)	0	0.3 B	0
Porosity (relative to control)	0	+½	−½
Scrub test (mg loss/100 cycles)	45	65	102
Pigment/vehicle RMC/gal	\$1.62	\$1.60	\$1.60

Table 7—Formula Modification-PVC Adjustment

	TiO_2 Type		
	High-Dry-Hide Control	Enamel Grade	General Purpose
PVC	60	70	70
Tint strength (% of control)	100	100.2	101.1
Tint tone (difference from control)	0	0.3 B	0
Porosity (relative to control)	0	0	−2
Scrub test (mg loss/100 cycles)	45	184	278
Pigment/vehicle RMC/gal	\$1.62	\$1.54	\$1.54

the greatest strength; because (at least in part) it does so at the expense of the free binder in the system, it also has the highest level of stain retention and poorest scrub resistance. At the other end of this spectrum lies the lower binder demand enamel grade. This grade exerts the least effect of the grades tested on high-dry-hide related effects and so doesn't develop the strength of the high-dry-hide grade. Because it doesn't tie up as much of the free binder, it displays better film integrity as shown by a low level of staining and high scrubbability. The general purpose TiO_2 fell between the high-dry-hide and enamel grades in these same performance and optical properties. As was to be expected, and shown by *Figures* 2, 3, and 4, as TiO_2 level and PVC increased, absolute reflectance (tint strength) increased as did porosity; scrubbability dropped under these same conditions but not to the magnitude one might have expected based on the porosity data.

Reviewing the flat commercial paint evaluations and lab work done to this point, it was decided to use the 60 PVC, 2 lb TiO_2/gal formula as the control for the remainder of the latex flat wall paint work. Further, since the high-dry-hide TiO_2 is designed to give maximum performance in the PVC area involved with flat interior latex wall paints, that TiO_2 type was established as the grade to match for performance and economics. It seemed highly probable that if cost/performance matches could be made using either the enamel or general purpose grades, successful matches at other PVC and TiO_2 levels could also be realized. This control formula/TiO_2 type and level combination provided a paint that performed as well as the commercials.

Formula modifications chosen for study to achieve the performance/economic balance of the control pigment involved both the use of high oil absorption extender pigments and PVC adjustment (the latter as outlined by Stieg[9]). The extenders evaluated included: precipitated calcium carbonate; calcined clay; and precipitated silica/amorphous silica blend.

Starting with the basic pigmentation of the 60 PVC, 2 lb TiO_2/gal formula each extender was worked into the control pigment composition individually. Adjustments in TiO_2, $CaCO_3$, clay, and extender levels were made to achieve the cost/performance data found in *Tables* 4, 5, and 6. With the 58 oil absorption, 0.06μ precipitated calcium carbonate, that adjustment meant reducing TiO_2 and natural calcium carbonate levels; calcined clay remained unchanged. The calcined clay modification consisted of an increase in the clay level coupled with a decrease in TiO_2 and calcium carbonate. The introduction of a 1:1 blend by weight of the amorphous and precipitated silicas in conjunction with an increase in calcined clay was coupled with decreases in TiO_2 and calcium carbonate.

While any of the high binder demand extenders could be used individually with either the general purpose or enamel grade to formulate acceptable tint strength, porosity, and scrub relative to the control formula/control pigment, there were some deficiencies. They all provided high sheen; the least amount of sheen was found with the precipitated silica/amorphous silica blend, the most occurred with the precipitated calcium

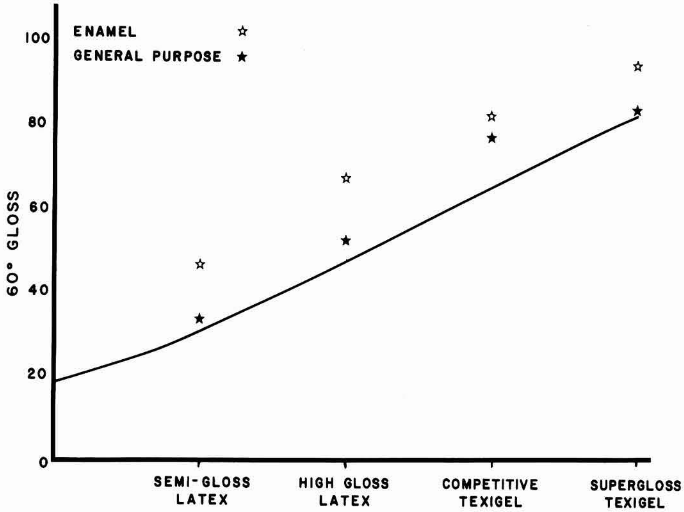

Figure 5—Comparison of enamel and general purpose grades in four latex gloss formulas

carbonate followed closely by the calcined clay. The latter two extenders also displayed high burnish tendencies on scrub testing. The PVC adjustment gave the strength predicted by Stieg[9] at significantly lower raw material cost (R.M.C.) than the control formula/pigment. This was offset by higher film porosity and noticeably poorer scrub resistance (*Table* 7).

Of the two TiO_2 grade types, the general purpose grade required lesser modification with the extenders than did the enamel grade to attain high-dry-hide TiO_2 type tint strength. This difference was not such, though, that the use of general purpose over enamel grade would overcome the extender shortcomings noted above.

Latex Gloss and Semi-Gloss Paints

Comparisons of enamel and general purpose grades in the four latex gloss formulas (data graphed in *Figure* 5) found the enamel grade provided higher gloss than the general purpose type TiO_2. The data also indicate that the gloss of the enamel grade pigmented formulas exceeds that of the commercial paints tested. The general purpose grade did give, as seen in *Figure* 5, gloss performance in line with that of the commercial paints. Even the use of gloss modifiers was not totally satisfactory, though, in improving the general purpose gloss to the point where it would be comparable to that of the enamel grade. The detailed data in the Appendix-Data Sections No. 3 and 4 didn't reveal any other significant differences in performance between these two TiO_2 grade types.

SUMMARY

The foregoing work shows that an enamel grade TiO_2 can serve as the only grade needed to produce latex flat wall and gloss paints—paints that compare favorably in performance and economics with commercial paints now on the market. Such a move will require a break with previous thinking on TiO_2 grade use and may require some innovating on the part of the formulator, but it *can* be done. For the most part, it appears the greater challenge lies with the formulation of the latex flat systems. However, opportunities also exist to produce better gloss systems with the enamel grade than presently marketed, or to produce current quality gloss levels at lower R.M.C.

Formula No. 6 (a) (Appendix) provides a latex flat wall paint starting point formula pigmented with enamel grade TiO_2. This formula was developed from the high-dry-hide extender/PVC modification work already discussed. It minimizes the sheen and burnish problems evident with the use of the individual extenders discussed earlier and gave the performance and economics of the commercially equivalent control formula. Starting Point Formula data appear in Appendix-Data Section 5 (a).

The enamel grade, in conjunction with the laboratory latex semi- and gloss systems included in the Appendix, gave superior gloss levels. Alternately, through the use of selected extenders, along with a slight reduction in TiO_2, current commercial gloss levels can be obtained at lower R.M.C. It is the enamel grade/Texigel® 23-555 gloss modifier combination, however, that presents the

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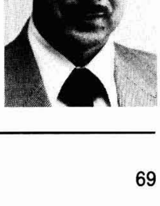

most intriguing possibilities for a new generation of gloss latex enamels. The R.M.C. is high, rivaling that of the most expensive commercials tested, but 20° gloss levels of 75 and 60° gloss levels of 90 are possible.

To those interested in slurry TiO_2, the same possibilities displayed by the dry enamel grade also exist for its slurry counterpart. Using the techniques applied to the dry grades in this report to their slurry versions provided the same relative performance. Formula No. 6 (b) (Appendix) gives a slurry enamel grade starting point formula equivalent to that shown for the dry enamel grade Formula No. 6 (a). Slightly higher extender modification was required to produce the optical performance of the control formula. In gloss systems, the substitution of slurry for dry TiO_2 essentially requires adjustment for the water and surfactant portion of the slurry and the addition of the gloss paint materials to the slurry under agitation. Alternately, one can compound the "let-down" and meter this under agitation to the slurry. Formula 7 (Appendix) illustrates this latter technique using the interior high gloss latex enamel formula given in the Appendix.

This combination of performance, then, makes the enamel grade of TiO_2—either the dry or wet form—a prime candidate for evaluation as a single grade TiO_2 for interior paint use.

ACKNOWLEDGMENT

The author thanks the management of Chemical/ Metallurgical Div. of SCM Corp. for permission to publish this paper.

Appreciation is also extended to W. L. Dean who performed much of the pigment selection and evaluation work, as well as R. K. Morrison who assisted in the lab work and preparation of the illustrations.

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Trademark References

Busan	Buckman Laboratories, Inc.
Celite	Johns-Manville Corp.
Colloids	Colloids, Inc.
Cosan	Cosan Chemical Corp.
Dapro	Daniel Products Co.
Dowanol	Dow Chemical Co.
Drew	Drew Chemical Co.
HiSil	PPG Industries, Inc.
Imsil	Illinois Minerals Co.
Metasol	Merck & Co., Inc.
R&R	Ross and Rowe, Inc.
Resyn	National Starch Products, Inc.
Rhoplex, Tamol, Triton	Rohm and Haas Co.
Satintone Special	Engelhard Minerals Corp.
Snowflake	Thompson, Weinmann & Co., Inc.
Tergitol NPX, Carbitol, Cellosize	Union Carbide Corp.
Texanol	Eastman Chemical Products, Inc.
Texigel	PVO International
Zopaque	Glidden Pigments, Div. of SCM Corp.

(Note: The raw materials used in this work are identified with the intent that such information may make the results more meaningful to the reader. The identification of these materials does not constitute the author's endorsement of their use; equivalent materials from other sources may provide the same benefits reported here.)

APPENDIX
FORMULAS SECTION

Formula 1—Equal Weight Dry TiO_2 Comparisons
Latex Flat Wall Paints

Grind Materials	Pounds/Approx. 100 Gal		
	50 PVC	60 PVC	70 PVM
Water	100.0 (130.0)[a]	100.0 (130.0)[a]	100.0 (130.0)[a]
KTPP	1.5	1.5	1.5
Water dispersible lecithin R&R® 551	4.0	4.0	4.0
Wetting agent, Tergitol® NPX	1.0	1.0	1.0
Ethylene glycol	25.0	25.0	25.0
Carbitol® acetate	11.0	11.0	11.0
Busan® 25	1.0	1.0	1.0
Rutile TiO_2, dry	200.0	200.0	200.0
Calcium carbonate, Snowflake	136.0	136.0	136.0
Calcined clay, Satintone® Special	104.5	104.5	104.5

Disperse on high speed dissolver, then add the following, in order listed, under mild agitation.

Let-Down	50 PVC	60 PVC	70 PVM
Water	165.6 (135.6)[a]	226.0 (196.0)[a]	267.0 (237.0)[a]
Vinyl acetate copolymer Emulsion, Resyn® 1255	310.0	208.0	133.2
Defoamer, Colloids® 683	1.5	1.5	1.5
3% Cellulosic thickener Soln., Cellosize® QP-4400	102.0	135.0	161.8
Total formula	1163.1	1154.5	1147.5

Note: Only the 2 lb TiO_2 level is given here; these were the base formulas modified to obtain the 0.5, 1.0, 1.5 lb/gal TiO_2 levels discussed in the report.

(a) Figures in parentheses indicate levels used with the high-dry-hide TiO_2; other figures were used with the enamel and general purpose grades.

Formula 2—Semi-Gloss Latex-Based Paint

Grind Materials	Pounds/Approx. 100 Gal
Propylene glycol[a]	65.0
Tamol® 731 or Colloid 111	10.5
Drew® L-475	2.0
Metasol® TK-100	0.5
Rutile TiO_2	250.0
Barytes #1[b]	40.0

Sift in pigments at low speed on Cowles type dissolver. Increase speed and disperse for 20 min. Under agitation add let-down ingredients in order given.

Let-Down	Pounds/Approx. 100 Gal
Propylene glycol[a]	90.0
Dowanol® DE	58.0
Acrylic latex, Rhoplex® AC-490	500.0
Drew L-475	2.0
Triton® GR-7M	1.5
Cellosize® QP-4400 (2.5% soln.)	38.0
Water	29.2
Total formula	1086.7

(a) Supplied by Union Carbide Corp.
(b) Supplied by Pfizer, Inc.

Formula 3—Interior High Gloss Latex Enamel

Grind Materials	Pounds/Approx. 100 Gal
Tamol 731 or Colloid 111	10.0
Colloid 681F	2.0
Propylene glycol[a]	65.0
Rutile TiO_2	250.0

Sift in pigments at low speed on a high speed disperser. Increase speed and disperse for 20 min. Under agitation add let-down ingredients in order given.

Let-Down	Pounds/Approx. 100 Gal
Propylene glycol[a]	83.0
Hexylene glycol[a]	32.3
Cosan® 635W	0.5
Acrylic latex, Rhoplex AC-490	580.0
Colloid 681F	2.0
Triton GR-7	2.0
Cellosize QP-4400 (2.5% soln. in H_2O)	9.7
Water	25.0
Total formula	1061.5

(a) Supplied by Union Carbide Corp.

Formula 4—Supergloss Texigel

Grind Materials	Pounds/Approx. 100 Gal
Texigel 23-555	115
Rutile TiO_2	225

Disperse on high speed dissolver, then add the following slowly, in order, under gentle agitation:

Let-Down	
Propylene glycol[a]	65
Cellosize QP-4400 (3% soln. in deionized water)	56
Acrylic latex, Rhoplex AC-490	580
Texanol®	6
Total formula	1047

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[a] Supplied by Union Carbide Corp.

Formula 5—Competitive Texigel

Grind Materials	Pounds/Approx. 100 Gal
Texigel 23-555	58
Rutile TiO_2	225
Water (Deionized)	47

Disperse on high speed dissolver, then add the following slowly, in order, under gentle agitation:

Let-Down	
Propylene glycol[a]	65
Dapro® DF-911	2
Cellosize QP-4400 (3% soln. in deionized water)	61
Acrylic latex, Rhoplex AC-490	580
Texanol	8
Total formula	1046

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[a] Supplied by Union Carbide Corp.

Formula 6—Latex Flat Wall Paint Starting Point Formula

	Pounds/Approx. 100 Gal	
Grind Materials	(a) Dry Enamel Grade TiO_2	(b) Slurry Enamel Grade TiO_2
Water	115.0	120.0
KTPP	1.5	1.5
Water dispersible lecithin, R&R 551	4.0	4.0
Wetting agent, Tergitol NPX	1.0	1.0
Ethylene glycol	25.0	25.0
Carbitol acetate	11.0	11.0
Busan 25	1.0	1.0
Enamel grade rutile TiO_2, dry	189.4	—
Calcium carbonate, Snowflake	44.3	44.3
Calcined clay, Satintone Special	139.3	139.3
Precipitated silica, Hi-Sil® 422	20.0	20.0
Amorphous silica, Imsil® 1240	25.0	25.0
Diatomaceous silica, Celite® 499	13.5	13.5

Disperse on high speed dissolver, then add the following, in order listed, under mild agitation:

Let-Down		
Water	215.4	150.6
Vinyl acetate copolymer emulsion, Resyn 1255	202.7	202.7
Defoamer, Colloids 683	1.5	1.5
3% Cellulosic thickener soln., Cellosize QP-4400	135.0	135.0
Enamel grade rutile TiO_2, slurry	—	249.2
	1144.6	1144.6

Formula 7—Slurry Enamel Grade TiO_2 High Gloss Latex Enamel Starting Point Formula

Let-Down Base Materials	Pounds/Approx. 100 Gal
Tamol 731 or Colloids 111	9.7
Propylene glycol[a]	59.3
Colloids 681-F	3.9
Hexylene glycol[a]	31.4
Cosan 635-W	0.5
Cellosize QP-4400 (2.5% Soln.)	33.7

Charge above ingredients, in order listed, to a high speed disperser; disperse 5 min. Then, under mild agitation, add:

Acrylic latex, Rhoplex AC-490	564.2
Triton GR-7M	1.9

Slurry Let-Down	Pounds/Approx. 100 Gal
Charge into a mixing tank:	
Slurry TiO_2, rutile enamel grade (66.5% solids)	317.9
Slowly add:	
Water	29.6
Mix well, then add slowly under mild agitation:	
Let-down base, above	704.6
Total Formula	1052.1
Mix until uniform.	

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[a] Supplied by Union Carbide Corp.

DATA SECTION

Table I—Commercial Latex Flat Wall Paints Optical and Physical Properties

LFW—COM. PTS.

	Low	High	Average
Weight per gal (lb)	10.8	12.2	11.3
% Nonvolatile (wt)	43.6	55.0	49.6
PVC (%)	34	74	53
Consistency (KU)	82	116	97
Color, L (brightness)	89.9	97.1	93.6
b (tone; –blue; + yellow)	+12.2	– 0.4	+ 2.1
Contrast ratio (2-mil wet film)	0.981	0.997	0.988
85° Sheen	3	22	7
Scrub resistance (mg wt loss/100 cycles)	12.9	746	113.5
Burnishing (85° change after scrub test)	4/5	22/50	7/23
Freeze-Thaw (cycles passed)	—	3	3
Roller application: Spattering	V. low	V. low	V. low
Foaming	Mod.	Mod.	Mod.
Leveling	Good	Good	Good
Brush application: Leveling	Good	Excellent	
Lapping	Good	Good	Good
Touch-up	Good	Excellent	
Accelerated storage (50°C, 21 days)			
Settling	Soft	Soft	Soft
Separation	Slight	Slight	Slight
Seeding	None	None	None
Porosity; K&N stain test	> + 3	< – 3	—
# TiO_2/gal	0.5	2.8	1.8
Pigment/vehicle RMC/gal[a]	$ .70	$2.75	$1.64

(a) Based on published prices as of April 1978.

Table II—Commercial Interior Latex Gloss And Semi-Gloss Paints Optical and Physical Properties

GL—COM. PTS.

	Low	High	Average
Weight per gal (lb)	10.1	11.4	10.6
% Nonvolatile (wt)	44.5	60.3	50.5
PVC (%)	16.4	26.0	20.9
Consistency (KU)	72	97	85
Sag, Baker Sag Liner	None	V. Sl.	—
Hegman	5 Sl. d.	7+ V.s.d.	6-Sl.d
Color, L (brightness)	91.1	97.9	96.0
b (tone; – blue; + yellow)	– 1.2	+ 4.1	+ 0.9
Contrast ratio	0.974	0.989	0.981
Gloss, initial; 20°	$2^b/30^c$	$27^b/69^c$	$14^b/41^c$
60°	$14^b/69^c$	$68^b/87^c$	$48^b/76^c$
Adhesion	Good	Good	Good
Water-Resistance	Marginal	Pass	—
Leveling (Leneta)	2	10	5
Freeze-Thaw (cycles passed)	3	3	3
Roller application: Spattering	Heavy	Mod.	—
Foaming	Heavy	Mod.	—
Leveling	Poor	Good	—
Brush application: Foaming	Heavy	Mod.	—
Leveling	Poor	Good	—
Lapping	Poor	Good	—
Touch-up	Poor	Good	—
Scrub resistance (mg wt loss/100 cycles)	8	107	26
Accelerated storage (50°C, 21 days)			
Settling/separation	Sl. sep.	None	—
Viscosity, KU	70	100	85
Seeding	None	None	None
Pigment/vehicle RMC[a]	$ 1.99	$ 3.27	$ 2.72

(a) Based on published prices as of April 1978.
(b) Semi-gloss latex values.
(c) High gloss latex values.

Table III—Laboratory Formulas Interior Latex Semi-Gloss and Gloss Optical and Physical Data

	Semi-Gloss Latex		High Gloss Latex	
	En. Grade	Gen. Purp.	En. Grade	Gen. Purp.
Weight per gal (lb)	10.9	10.9	10.5	10.5
% Nonvolatile (wt)	48.0	48.0	48.2	48.2
PVC (%)	25.4	25.4	21.3	21.3
Consistency (KU)	73	73	80	80
Sag, Baker Sag Liner	None	None	None	None
Hegman	6 V.s.d.	6 V.s.d.	7 Sl.d.	7 Sl.d.
Color, L (brightness)	98.0	97.7	97.8	98.2
b (tone; – blue; + yellow)	+ 0.6	+ 0.3	+ 0.6	+ 0.4
Contrast ratio	0.979	0.976	0.980	0.976
Gloss, initial; 20°	10	6	22	14
60°	46	35	65	55
Adhesion	Good	Good	Good	Good
Water-Resistance	Pass	Pass	Pass	Pass
Leveling (Leneta)	5	5	6	6
Freeze-Thaw (cycles passed)	3	3	3	3
Roller application: Spattering	Moderate	Moderate	Moderate	Moderate
Foaming	Moderate	Moderate	Moderate	Moderate
Leveling	Good	Good	Good	Good
Brush application: Foaming	Moderate	Moderate	Moderate	Moderate
Leveling	Good	Good	Good	Good
Lapping	Good	Good	Good	Good
Touch-up	Good	Good	Good	Good

Table III—(Continued)

	Semi-Gloss Latex		High Gloss Latex	
	En. Grade	Gen. Purp.	En. Grade	Gen. Purp.
Scrub resistance (mg wt loss/100 cycles)	11	11	11	11
Accelerated storage (50°C, 21 days)				
Settling & separation	None	None	None	None
Viscosity, KU	83	83	90	90
Seeding	None	None	None	None
Pigment/vehicle RMC/gal[a]	$ 2.90	$ 2.90	$ 2.84	$ 2.84

(a) Based on published prices as of April 1978.

Table IV—Laboratory Formulas Interior Latex Gloss Paint Optical and Physical Data

	Super Gloss Texigel		Competitive Texigel	
	En. Grade	Gen. Purp.	En. Grade	Gen. Purp.
Weight per gal (lb)	10.5	10.5	10.4	10.4
% Nonvolatile (wt)	50.4	50.4	49.0	49.0
PVC (%)	17.1	17.1	17.9	17.9
Consistency (KU)	72	72	79	79
Sag, Baker Sag Liner	V.sl.	V.sl.	None	None
Hegman	7½	7½	7+	7+
Color, L (brightness)	97.8	97.9	98.3	98.1
b (tone; – blue; + yellow)	+ 0.7	+ 0.4	+ 0.7	+ 0.4
Contrast ratio	0.980	0.977	0.982	0.977
Gloss, initial; 20°	75	50	48	36
60°	92	80	81	76
Adhesion	Good	Good	Good	Good
Water-resistance	Pass	Pass	Pass	Pass
Leveling (Leneta)	8	8	4	4
Freeze-Thaw (cycles passed)	3	3	3	3
Roller application: Spattering	Moderate	Moderate	Low	Low
Foaming	Heavy	Heavy	Moderate	Moderate
Leveling	V. good	V. good	Good	Good
Brush application: Foaming	Heavy	Heavy	Moderate	Moderate
Leveling	V. good	V. good	Good	Good
Lapping	Fair	Fair	Good	Good
Touch-up	Good	Good	Good	Good
Scrub resistance (mg wt/loss/100 cycles)	25	27	25	19
Accelerated storage (50°C, 21 days)				
Settling & Separation	Sep./Sl. Stlg.	Sep./Sl. Stlg.	None	None
Viscosity, KU	72	72	82	82
Seeding	None	None	None	None
Pigment/vehicle RMC/gal[a]	$ 3.12	$ 3.12	$ 2.72	$ 2.72

(a) Based on published prices as of April 1978.

Table V—Latex Flat Wall Paint Enamel Grade TiO_2 Starting Point Formulas Performance Data

	(a) Dry TiO_2	(b) Slurry TiO_2
Weight per gal (lb)	11.4	11.4
% Nonvolatile (wt)	47.4	—
PVC (%)	60 (60.1)	—
Consistency (KU)	77	78
Color; L (brightness)	Equal to control	—
b (tone; – blue; + yellow)	Equal to control	—
Contrast ratio (2-mil wet film)	Equal to control	—
Tint strength, L (brightness)	Equal to control	—
b (tone; – blue; + yellow)	V.sl. blue vs. control	—
85° Sheen	+1 to control	—
Scrub resistance (mg wt loss/100 cycles)	Equal to control	—
Burnishing (85° change after scrub test)	Equal to control	—
Freeze-Thaw (cycles passed)	3	—
Porosity (rel. to control formula/pigment)	+1	+1½
Pigment/vehicle RMC/gal[a]	$ 1.62	—

Note: Unless otherwise shown, the values under (5)(a) are the same for (5)(b).

Control - high-dry-hide TiO_2, 2 lb/gal, 60 PVC formula

(a) Based on published prices as of April 1978.

Water-Dispersible Urethane Polyesteramide Coatings From Linseed Oil

Wilma J. Schneider and Lyle E. Gast
United States Department of Agriculture[*]

Water-dispersible coatings from vegetable oils were easily prepared from products of the aminolysis reaction of linseed oil and diethanolamine, polybasic acid anhydrides, and tolylene diisocyanate. Polymers studied in detail to date were based on phthalic anhydride; but preliminary data indicate that pyromellitic and 3,3′,4,4′-benzophenone tetracarboxylic dianhydrides or trimellitic, maleic, succinic, and glutaric anhydrides also give polymers that result in satisfactory water-dispersible systems.

Acid value of the urethane polyesteramides, the resin/water/butyl Cellosolve® cosolvent ratio, and pH were related to dispersibility and stability of the products in aqueous solution and to their film properties, i.e., drying times, hardness, impact resistance and chemical, solvent, and water resistance. Polymers with acid values ranging from 30 to 70 were studied at 10, 20, or 30% resin concentrations in water/butyl Cellosolve. All samples dispersed readily to yield products which ranged from clear to slightly hazy solutions with Gardner viscosities of A to >Z6. Films prepared from the 30, 40, and 50 acid value polyesteramides without driers had rapid drying times (TF<1 hr), good hardness (Sward Rocker values of 34 to 62), excellent xylene resistance (> 1 wk), but poor to moderate resistance to 1% Spic and Span® solution (1.5 to 6 hr).

Cost savings could be substantial in these preparations since neither long processing times nor high temperatures normally used in alkyd technology were employed; reaction temperatures did not exceed 110°C in this process. Further savings could be realized because these materials air dry rapidly and only low baking schedules would be required for certain applications.

INTRODUCTION

Our previous work has shown that urethane polyesteramides derived from linseed and soybean oils have good film properties with respect to drying, hardness, chemical resistance, impact and abrasion resistance,[1,2] and exterior durability on wood.[3] With increased emphasis towards the use of nonpolluting coatings, we initiated work on preparation of urethane polyesteramide products that could be adapted to aqueous systems. This paper describes the synthesis of water-dispersible anionic urethane polyesteramides, via the phthalate half-ester intermediate, the polymer and film properties.

EXPERIMENTAL

Preparation of Polymers

A three-necked, round-bottomed flask fitted with a nitrogen ebulator, dropping funnel, and stirrer is charged with dry, distilled diethanolamine (0.2 mole) and heated to 100-105°C. After addition of sodium methoxide catalyst (0.035 mole), linseed oil (0.1 mole) is added dropwise over 15-20 min. The reaction is maintained at approximately 100°C during oil addition and is held at this temperature for an additional 15 to 20 min. By titration, <0.25% unreacted diethanolamine remained in the reaction mixture, 98.7% of it reacted. Thin-layer chromatography on pre-coated silica gel plates with a 70% diethyl ether-30% hexane solvent system indicated two major components were formed, N,N-bis(2)-hydroxyethyl linseed amide and linseed monoglyceride, while only a trace of linseed diglyceride was observed. Thus, the aminolysis reaction product is essentially a mixture of difunctional hydroxy materials, approximately two-thirds of which is the amide and one-third monoglyceride. After cooling to 85°C, phthalic anyhydride is added to the reaction mixture. Opening of the anhydride ring to form the half-ester is complete in approximately 0.5 hr. At this point the reaction media should be clear. Titration with standard 0.1 N sodium hydroxide gives an acid number[†] consistent with half-ester formation. Product acid values are varied by altering the quantity of phthalic anhydride added. Stoichiometric quantities of triethylamine are then added to form the amine salt of the carboxyl

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[*] Northern Regional Research Center, Federal Research, Science and Education Administration, Peoria, Ill. 61604.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Dept. of Agriculture over other firms or similar products not mentioned.

[†] Acid number as used throughout the paper is defined as mg KOH/g sample.

present. Neutralization of the carboxyls at this time is necessary, otherwise the medium is too acidic and the subsequent tolylene diisocyanate (TDI) reaction becomes very slow. Dry toluene (70 ml) is added to the reaction mixture and the temperature is lowered to 50°C. Theoretical quantities of TDI (a mixture of 80% 2,4- and 20% 2,6-isomers) are added in another 70-ml portion of toluene to react with all the remaining hydroxyls to form the urethane derivative. The reaction is held at 50°C for approximately two hours or until complete, as judged by the disappearance of the NCO band in the infrared at 2270 cm^{-1}. Acid values, molecular weights, and degree of polymerization of urethane polyesteramides prepared are shown in *Table* 1.

Table 1—Urethane Polyesteramide Properties

Acid Values			
Theory	Found	Molecular Weight[a]	n[b]
29.9	30.2	3710	5.3
40.0	42.0	2650	3.3
50.0	50.3	2230	2.5
60.3	61.2	1835	1.8
70.4	70.7	1585	1.3

(a) Calculated from acid value as determined by carboxyl titration.
(b) Degree of polymerization.

Aqueous Dispersions

Butyl Cellosolve (bp 170.6°C), used as the cosolvent in the dispersions, is added at the desired level to the polymer in toluene solution. The toluene (bp 110.8°C) is preferentially removed by distillation under reduced pressure, leaving the polymer in butyl Cellosolve. Deionized water is added and the polymers can be dispersed by using either a Waring Blendor® or a mechanical shaker, followed by pH adjustment to 8-8.5 with triethylamine. All samples dispersed readily and, depending on acid value and quantity of cosolvent, gave clear to slightly hazy dispersions.

Film Casting and Testing

Chemical resistance, hardness, impact, abrasion, and drying tests were run on films cast on steel Q-Panels® (4 × 8 × 0.032 in. cold rolled steel) and spread with a drawdown bar machined to give a dried film approximately 0.8 mil thick. All films including commercial controls were prepared without drier and air-dried at 25°C and 50% relative humidity or baked at 80°C or 125°C for 15, 30, or 45 min. Tack-free times, as defined by Gardner,[4] were determined on air-dried films by manually placing a small amount of sand on the film periodically. Hardness tests were made by the Sward Rocker technique. Chemical and solvent resistances were carried out as previously described.[1] Impact tests were run with a Gardner impact tester (cat. no. IG-1120). The value reported is the maximum impact the film would withstand without failure. Elongation data were determined with the conical mandrel apparatus by ASTM Method D 522-60. Adhesion was determined by the cross-hatch tape test.

DISCUSSION

Polymer Preparations

A three-step "one-kettle" process is used for the preparation of the water-dispersible urethane polyesteramides. A ratio of two moles of dry distilled diethanolamine to one mole of linseed oil in the sodium methoxide-catalyzed aminolysis reaction at 110°C gives a reaction mixture that contains essentially difunctional hydroxy materials, i.e., dihydroxyethyl linseed amide and linseed monoglyceride. High purity phthalic anhydride (recrystallized from benzene† and analyzed for anhydride content,[5] >99.9%) was used. Technical grade phthalic anhydride which is 99.0% pure, or better, is suitable. Carboxyl groups are introduced into the polymer only, via opening of the anhydride ring, at temperatures that do not exceed 85°C.[6] Phthalic acid will not react at this temperature and remains insoluble, causing cloudiness in the final product. The acid value of a product depends on the quantity of phthalic anhydride used. TDI reacts readily at 50°C in toluene solution with the remaining hydroxyls to tie the components together into the polymer (*Figure* 1). For simplicity, the formula illustrates a polymer molecule which contains only linseed dihydroxyamide units; however, linseed monoglyceride units would also be present. The formula shows further that the polymer molecules contain end groups derived from phthalic anhydride and that the acid value of the polymer controls the molecular weight.

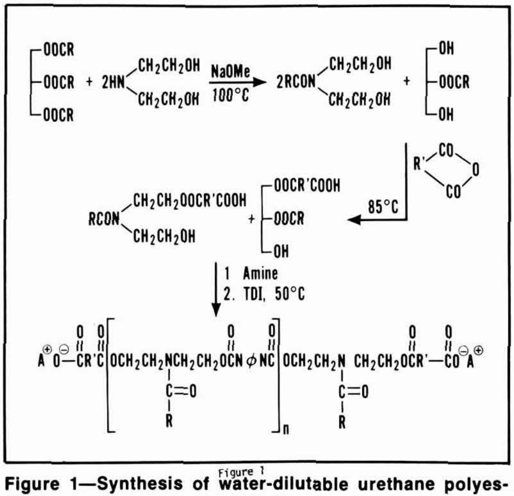

Figure 1

Figure 1—Synthesis of water-dilutable urethane polyesteramides

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†Caution in handling triethylamine and benzene is recommended.

Cellosolve is a registered trademark of Union Carbide Corp.
Spic and Span is a registered trademark of Proctor and Gamble.
Waring Blendor is a registered trademark of Waring Products Div., Dynamics Corp. of America.
Q-Panel is a registered trademark of the Q-Panel Co.

Table 2—Relationship of Solution Viscosity to pH

Resin[a]/Butyl Cellosolve Ratio	pH	Gardner Viscosity[b]
85/15	6.8	A
	7.0	C
	7.1	X
	7.5	Z6
67/33	6.4	F
	6.5	O
	6.7	Y
	7.3	Y

(a) Resin acid value = 40; resin concentration 30% in solution.
(b) Determined at 25°C.

In alkyd resin technology, 10 hr processing time at temperatures of 210-232°C, or higher, is common.[7] Other water-reducible polyester resins, i.e., those made with glycols (trimethylpentanediol, neopentyl, or cyclohexanedimethanol) and acids (isophthalic, trimellitic, and adipic) need processing times of 8-12 hr at 195-215°C to achieve acid values of 55; often these higher temperatures (>215°C) lead to glycol losses, and decomposition becomes appreciable.[8] The total time involved in our process for preparing the water-dispersible urethane polyesteramides is less than four hours. The highest temperature required is 110°C for approximately 0.5 hr in the aminolysis reaction; half-ester preparation is at 80-85°C for approximately 0.5 hour, and the urethane modification requires 2 hours heating at 50°C. Thus, substantial time is saved and consumption of processing energy is reduced considerably over typical alkyd processes.

A series of 45 linseed-phthalic anhydride-urethane polyesteramide dispersions were prepared for polymers listed in *Table* 1 and were studied in detail to relate carboxyl content of the polymer, polymer/water/butyl Cellosolve cosolvent ratio and pH to dispersibility, viscosity, and stability, as well as to film properties, i.e., drying times, hardness and impact, chemical, solvent, and water resistance.

Polymers with acid values ranging from 30 to 70 were studied at 67/33, 75/25, and 85/15 polymer/butyl Cellosolve ratios at 10, 20, and 30% polymer concentrations in the final water-butyl Cellosolve dispersion. Literature references indicate that generally one milliequivalent of carboxyl per gram of resin, or an acid value of 56, is needed for water dispersibility. Unexpectedly, it was found that urethane polyesteramides with acid values as low as 30 will disperse readily to yield clear, light amber-colored products.

Gardner viscosities of these aqueous systems are pH dependent particularly in the 6.5 to 7.5 range as shown in *Table* 2. At high resin to butyl Cellosolve ratios (85/15 composition) and at a pH of 7.0 or below, very fluid products result. Viscous syrupy solutions result with only a very slight increase in pH 7.1. This dramatic change in viscosity was not observed for the 67/33 composition, i.e., from slightly acid to basic conditions, no change in viscosity occurs. Again, the viscosity has increased with pH but to a lesser extent than did the 85/15 composition.

All dispersion compositions form good to excellent films that "wet" the metal substrate well, and after drying, continuous coatings are obtained (*Table* 3). Film properties of two commercially available water-dispersed resins (P and Q)* were evaluated along with our experimental resins. Film properties such as hard-

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*Resin P = Kelsol® 3901, Resin Q = Kelsol® 3902. Kelsol is a registered trademark of Spencer Kellogg Div. of Textron, Inc.

Table 3—Physical and Film Properties of Urethane Polyesteramide Dispersions[a]

Formulation	Acid Value	Resin/Butyl Cellosolve Ratio	Gardner Viscosity[b]	Wetability	Tack Free Time (hr)	Rocker Hardness Days Aging 1	4	7	14	21	Spic and Span Resistance[c,d] (hr)	Xylene Resistance[d] (hr)
A	70	67/33	<A	Good	21	<1	12	14	14	16	D <0.25	1
B		75/25	E	Good	21	<1	<1	16	18	17	D <0.25	2.25
C		85/15	X	Good	21	<1	<1	11	14	14	D <0.25	2.25
D	60	67/33	B	Good	20	<1	17	20	21	19	P 0.17	2.25
E		75/25	<A	Good (some crowfooting)	>20	<1	<1	<1	8	8	P 0.17	2.25
F		85/15	W	Fair	20	<1	<1	17	20	22	P 0.17	>6 <21
G	50	67/33	H	Very good	0.75	10	26	30	36	40	P 3.75	>240
H		75/25	Z5	Very good to excellent	0.33	14	21	27	28	29	P 2	>240
I		85/15	Z3-4	Very good	0.42	9	18	34	38	34	P 1.5	>240
J	40	67/33	V	Fair	0.58	30	36	34	43	36	P 2.5	>240
K		75/25	Z3	Good	0.42	12	16	27	35	39	P 1.25	>240
L		85/15	>Z6	Very good	0.58	14	30	42	48	51	P 3	>240
M	30	67/33	Z5	Good	0.42	40	47	50	54	56	P 6	>240
N		75/25	>Z6	Good	0.33	36	52	54	60	62	P 5.75	>240
O		85/15	>>Z6	Good	0.33	21	45	49	56	53	P 5.75	>240
P[e]	37	75/25	F	Good	0.83	—	32	34	38	40	P 26	<1
Q[e]	41	75/25	G	Good	13	—	23	24	26	29	P 8	<1

(a) 30% by weight urethane polyesteramide in dispersion.
(b) Determined at 25°C.
(c) D = dissolved; P = puckered.
(d) See reference 1.
(e) P = Kelsol 3901; Q = Kelsol 3902.

ness and drying times are directly related to the acid values or molecular weights (determined by COOH titration) which range from 1586 to 3710 for the 70 and 30 acid value polymers, respectively. Better film properties result from the high molecular weight resins. Low molecular weight polymers (A-F) form films which air dry slowly and become tack free in 21 hr; however, the films derived from the high molecular weight polymers (G-O) are tack free in 45 min or less, a significant improvement. Moderate to hard films with Sward Rocker values of 29-62 were obtained after the films had aged three weeks at 25°C and 50% relative humidity. Initial hardness values for these films are also good, whereas those from the low molecular weight polymers are soft. These results are remarkable in view of the fact no drier metals were used. Butyl Cellosolve does appear to influence the drying of films initially. When dispersed at high levels of butyl Cellosolve (G, J, and M), viscosities are reduced considerably, the films flow out better, and volatiles are lost more rapidly. However, after aging two to three weeks, differences in hardness values for given resin-acid value-butyl Cellosolve combinations are not significant. Most films increase in hardness on aging due to oxidative crosslinking of the linseed acryl groups. High molecular weights (and low acid values) likewise contribute to improve resistance to Spic and Span or xylene. Films from the 60 or 70 acid value resins either dissolved readily or puckered in 1% Spic and Span solution or xylene, whereas the 50, 40, or 30 acid value polymer films showed excellent xylene resistance and were unaffected after 10 days. Spic and Span resistance improved to 5.5-6 hr for films of the 30 acid value composition. The most notable difference in film properties was in the xylene resistances of the commercial samples. They were extremely sensitive and swelled almost immediately on contact.

Water sensitivity of air-dried films was determined by the same method as for the Spic and Span or solvent resistances. Test results were obtained on films dried and aged at room temperature for one and four days and one, two, three, and five weeks. Failure was defined as when the film first became hazy, cloudy, or showed other visible changes. As the films aged, they did become slightly more water resistant, but did not change significantly after one week. No air-dried film, even after aging five weeks, had water resistance time greater than two hours. The 30 acid value resin films were more water resistant than the films from the 40 or 50 acid value resins. Negligible permanent damage occurs to the films by water. After it is removed and the test spot is allowed to dry, the films recover to their original clarity. When compared to the commercial resins, P and Q (*Table* 3), which had water resistance times of 8 and 24 hr, respectively, the experimental films were much more water sensitive.

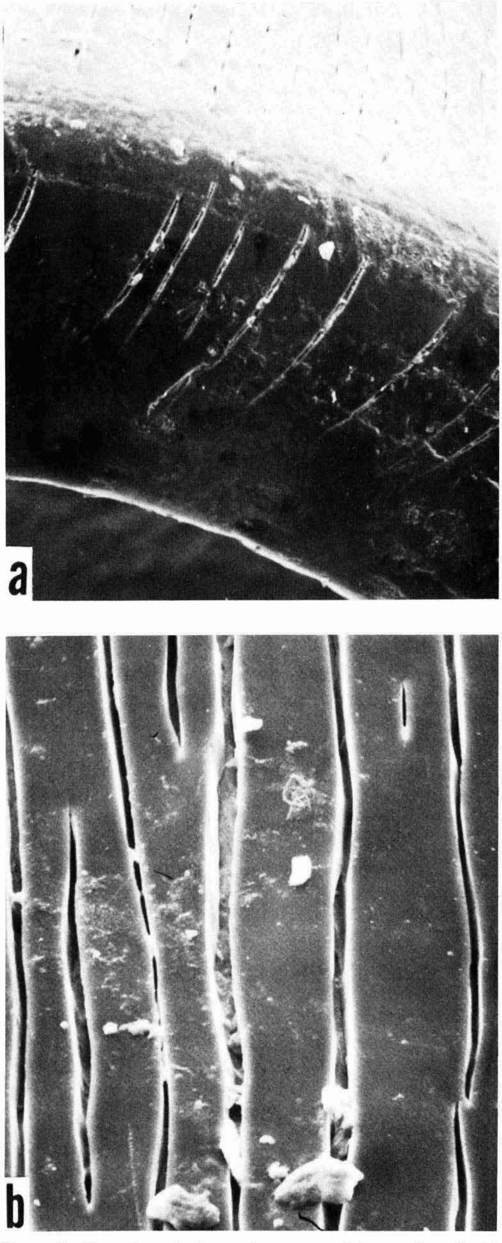


Figure 2—Scanning electron microscope pictures of urethane polyesteramide films from conical mandrel tests. a—Edge-on view, 30X. b—Close up view of micro-cracking, 300X

The urethane polyesteramide films compare favorably with the commercial resin films in the impact test. The commercial resin films withstood 0.115 and 0.230 m-kg (10 and 20 in.-lb) direct impact respectively, but <0.115 m-kg (<10 in.-lb) reverse impact. All experimental films failed regardless of molecular weight or resin/butyl Cellosolve composition when subjected to the impact test. They passed 0.115 m-kg (10 in.-lb) direct impact, but failed at 0.230 m-kg (20 in.-lb) as well as at 0.115 m-kg (10 in.-lb) reverse impact. Failure of the 30 acid value samples was characterized by loss of adhesion and peeling of the film at

Table 4—Hardness Study on Baked Films Of Water Dispersed Urethane Polyesteramides[a]

Dispersion Composition	Baking Schedule		Sward Hardness Days Aging				
	Temperature (°C)	Time (min)	1	2	4	7	14
75/25	80	15	16	—	54	60	65
	80	30	15	—	54	59	59
	80	45	16	—	57	61	59
	125	15	20	—	48	56	57
	125	30	30	—	44	57	61
	125	45	35	—	47	57	65
	RT - Air Dried		36	—	55	59	62
85/15	80	15	31	54	58	58	57
	80	30	33	54	58	57	58
	80	45	41	54	56	56	59
	125	15	24	38	37	44	47
	125	30	25	35	36	50	51
	125	45	31	40	35	50	51
	RT - Air Dried		26	48	49	50	48

(a) 50 acid value resin.

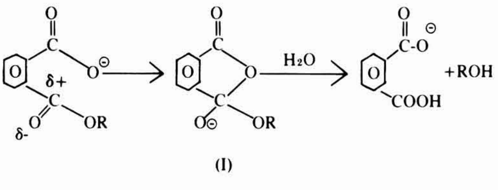
the outer circumference of the impact area; all other samples showed a circular, minute hairline cracking pattern, but the film retained adhesion to the Q-Panel substrate. This same type of failure by cracking was also observed in the conical mandrel tests. Films from the 30 and 40 acid value resins lost adhesion over the entire length of the bend. These films are also brittle and show almost no flexibility. The 70 acid value films passed the conical mandrel test; however the 50 and 60 acid value films showed minute parallel cracks, but no loss of adhesion. The area of sharpest curvature from one of the films that failed in the conical mandrel was examined by scanning electron microscopy. *Figure* 2 shows an edge-on view of a segment of this film magnified 30 diameters. The dark portion is the coated edge of the Q-Panel, while the light portion is the upper film surface on the panel. Interestingly, the film at the juncture of the top surface and edge did not crack, suggesting flexibility in this area. However, the top surface and edge of the film suffered extensive cracking that appears to extend down to the metal substrate. In agreement with visual observations, the film remains firmly attached to the metal (*Figure* 2b). For comparison, the films from the commercial resins passed the conical mandrel test and show excellent elongation.

For certain industrial applications, such as coil coatings and appliance finishes, low-temperature baking cycles may be desired to rapidly cure these films. Films from a 30% dispersion of a 50 acid value resin at two resin/butyl Cellosolve compositions were baked at either 80°C or 125°C for 15, 30, and 45 min. Hardness values were determined after additional curing at 25°C and 50% RH. Two air-dried films were evaluated at the same time for comparative hardness values. Generally, baking improves the hardness of urethane coatings. We did not find this to be entirely true with the urethane polyesteramides. The hardness data (*Table* 4) show that these films are not fully "cured" at the baking times and temperatures we selected, since rocker hardness values continue to increase with aging. After one day significant differences in hardness values were observed. Increased temperatures and longer baking times produce harder films with the 75/25 resin butyl/Cellosolve composition, while an air-dried film was nearly as hard as one baked at 125°C for 45 min. After two weeks aging, all films of this composition are almost equal in hardness. Neither the air-dried film nor the 125°C baked films were as hard as those baked at 80°C for the 85/15 resin/butyl Cellosolve composition. Thus, a low-temperature baking cycle in combination with a high resin/butyl Cellosolve composition gives the harder films.

Product Stability

The formulations listed in *Table* 3 were adjusted to a pH of 8.0-8.5 immediately after they were prepared. To assess the long-term stability of these dispersions they were stored at room temperature, their pH was measured periodically, and a visual evaluation of their condition was made. The pH of all samples was found to decrease with time; as the pH of 6-7 was reached, polymeric material separated slowly from the dispersions over a period of days or weeks. A comparison of acid values of the initially dispersed polymer and the precipitated polymer showed that loss of acidity had occurred. When fractions were collected, the acid value of the polymers which came out of solution at first were essentially the same as those which finally precipitated. A polymer dispersion was prepared and allowed to precipitate over a three-month period in an apparatus designed to measure evolution of CO_2. None was detected, but the acid value of the precipitated polymer was reduced to 25.1 from an initial value of 51.6. Esterification of an oil isolated from this aqueous layer after acidification with dilute HCl and examined by GLC showed that 11.8% was butyl Cellosolve and 80% had a retention time identical to dimethyl phthalate. Infrared spectra of the oil prior to esterification showed it to be mostly o-phthalic acid plus some butyl Cellosolve. By titration of this aqueous layer, the amount of phthalic acid found was in agreement with that expected from the loss of acidity of the precipitated polymer.

The formation of phthalic acid from these polymers when dispersed in aqueous solutions of amines is not surprising. The preparative method used requires that the phthalic half-esters become end groups and



(I)

R = polymer chain

cannot occur elsewhere along the polymer chain (see *Figure* 1). According to Turpin,[9] a carboxylate ion situated close to and in the same molecule as the ester group assists in the attack by an external nucleophile (H_2O or OH^-) via a cyclic intermediate, I.

Turpin refers to the intramolecular catalytic action of the neighboring group as the anchimeric effect and, with our dispersed polymer systems, this mechanism would produce phthalic acid in the aqueous layer and precipitate a low acid value polymer. These data suggest that polymers prepared from other anhydrides, i.e., maleic, succinic, and glutaric, where the anchimeric effect might not operate, may form much more stable aqueous dispersions. The effect of alternative anhydrides has been studied[10,11] and will be the subject of a future publication.

SUMMARY

Water-dispersible urethane polyesteramide coatings were developed from linseed oil by an economical method consuming less time and energy than conventional alkyd processes. When deposited on metal substrates, films are obtained which dry tack-free in <1 hr at ambient temperatures without driers. These air-dried films are hard and glossy and also show moderate to good chemical and solvent resistance.

ACKNOWLEDGMENT

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Benzene — Analysis and Impact On the Coatings Industry

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DeSoto, Incorporated*

Current statutory limits and mandatory compliance with regulatory agencies place responsibilities upon the coatings industry to guarantee product safety. The demand for low level benzene analysis has prompted the development of a simple gas chromatographic method using Siponate® DS-10 as the stationary phase. The analysis is rapid and efficient for the determination of benzene in the presence of solvents and monomers typically common to many coating formulations. Quantitation, using standard addition techniques or external calibration methods, is permitted at the low part per million level.

INTRODUCTION

Current literature has not yet begun to reflect technological changes being made daily to keep apace with government regulations. The list of health hazards appears to be increasing logarithmically with time. As the number of regulated toxic materials approaches infinity and acceptable exposure limits approach zero, industrial response to meet demands becomes more critical, more taxing, and more costly. The present paper is concerned with benzene, its toxicity, its regulation history, and its quantitative analysis in coatings systems.

Historically, benzene has been recognized as toxic since the turn of the century. In the late 1930's, the Division of Occupational Hygiene of the State of Massachusetts established a maximum acceptable limit of 75 ppm benzene. The American Conference of Governmental Industrial Hygienists (ACGIH), in 1946, recommended a threshold limit value (TLV) of 100 ppm[1] for benzene exposure. This level was reduced to 50 ppm and to 35 ppm in 1947 and 1948, respectively. It was not until 1974 that the ACGIH adopted a TLV of 10 ppm.[1]

Between 1974 and 1977 the "benzene issue" was growing as the subject of increasing legislative recommendation, and consideration as a suspected leukemogen. An excellent review of the health effects of benzene was prepared for the Environmental Protection Agency by the National Research Council, Advisory Center on Toxicology.[2] Based on an accumulation of data and information supplied by NIOSH, the Occupational Safety and Health Administration (OSHA) on January 14, 1977, issued a voluntary benzene guideline recommending that exposure to benzene in air not exceed an 8-hour time-weighted average to 1 ppm in any 8-hour shift of a 40 hour week.[1] An Emergency Temporary Standard for Occupational Exposure to Benzene was issued in May 1977, followed by a proposed permanent standard.

Public hearings were held on the proposed permanent standard in July and August 1977 with representative witnesses from a wide variety of concerned industries. Based on all accrued data, OSHA, in the *Federal Register* of February 10, 1978 (43 FR 5918), published the permanent benzene standard. The compliance program became effective May 13, 1978.

For the coatings industry, the benzene standard contains two critical areas of importance. First, the regulation limits the benzene exposure to 1 part benzene per million parts of air (1 ppm) as an 8-hour time-weighted concentration, with a 5 ppm ceiling for any 15-minute period during the 8-hour day. Secondly, the standard regulates that products containing *any* amount of benzene carry a label indicative of a cancer hazard. Quite obviously, the economic impact and the rigorous analytical demands becomes enormous.

The term "any" amount of benzene can quite literally denote one molecule. The state of the art in analytical chemistry, while progressing in the direction of ppb

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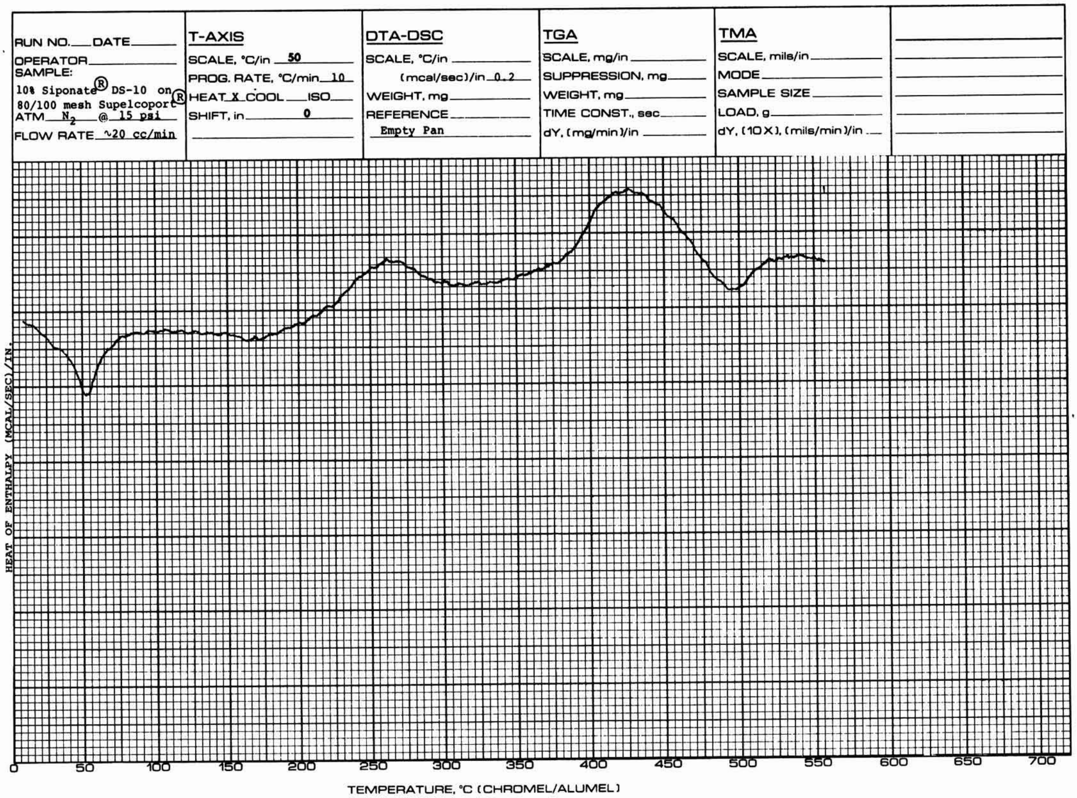

RUN NO.___ DATE___
OPERATOR___
SAMPLE:
10% Siponate® DS-10 on 80/100 mesh Supelcoport®
ATM N$_2$ @ 15 psi
FLOW RATE ~20 cc/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT X COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in 0.2
WEIGHT, mg ___
REFERENCE
Empty Pan

TGA
SCALE, mg/in ___
SUPPRESSION, mg ___
WEIGHT, mg ___
TIME CONST., sec ___
dY, (mg/min)/in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

Figure 1—DSC thermal analysis curve of Siponate DS-10

and ppt detection levels, is still removed from quantitative molecular analysis. In keeping with the permanent standard however, the manufacturer bears the burden of labeling the product as carcinogenic, or, more importantly, by not labeling the product effectively guaranteeing the absence of "any" benzene. It is important to bear in mind that while benzene may not be incorporated into the formulation, traces of benzene may be found in a wide variety of solvents and monomeric raw materials. Ironically, OSHA has also stated that it is clear that certain quantities of benzene are present in the ambient environment as a result of natural phenomena and as artifacts of human activity.[3]

Following publication of the permanent standard, OSHA was innundated with requests for the issuance of an amendment to exclude from the standard liquid mixtures containing 0.1% or less benzene. A temporary stay was issued in the *Federal Register,* Vol. 45, No. 60, for Tuesday, May 23, 1978.

As analytical chemists in the coatings industry, the burden of regulation lies upon us to constantly refine methods, techniques, and analyses to meet stringent demands. The literature in the past few years concerned with benzene analysis, centers primarily on the determination of the organic vapor from industrial ambient air.[4,5] The current paper is concerned with the separation of benzene in liquid samples and its subsequent quantitative analysis.

COLUMN SELECTION

The past three to five years has witnessed significant change in column technology and availability for the analyst. Five years ago, the majority of analytical laboratories relied almost exclusively on relatively few polar (DEGS, Carbowax®, OV-275) and nonpolar (SE-30, Apiezon L, OV-101) columns for general chromatographic purposes. These columns were certainly sufficient for most analyses required of those in the coatings industry, satisfying both qualitative and quantitative solvent and residual monomer analysis.

The increasing use of a wide variety of monomeric starting materials, and low level additives to achieve new formulations with desirable film properties, has prompted the investigation of other stationary phases. In addition, government regulatory agencies continually impact all industry with the issuance of lists of toxic organic species allowable in plant ambient air and in products. The proverbial "vicious circle" syndrome is in operation: the state-of-the-art in instrumentation

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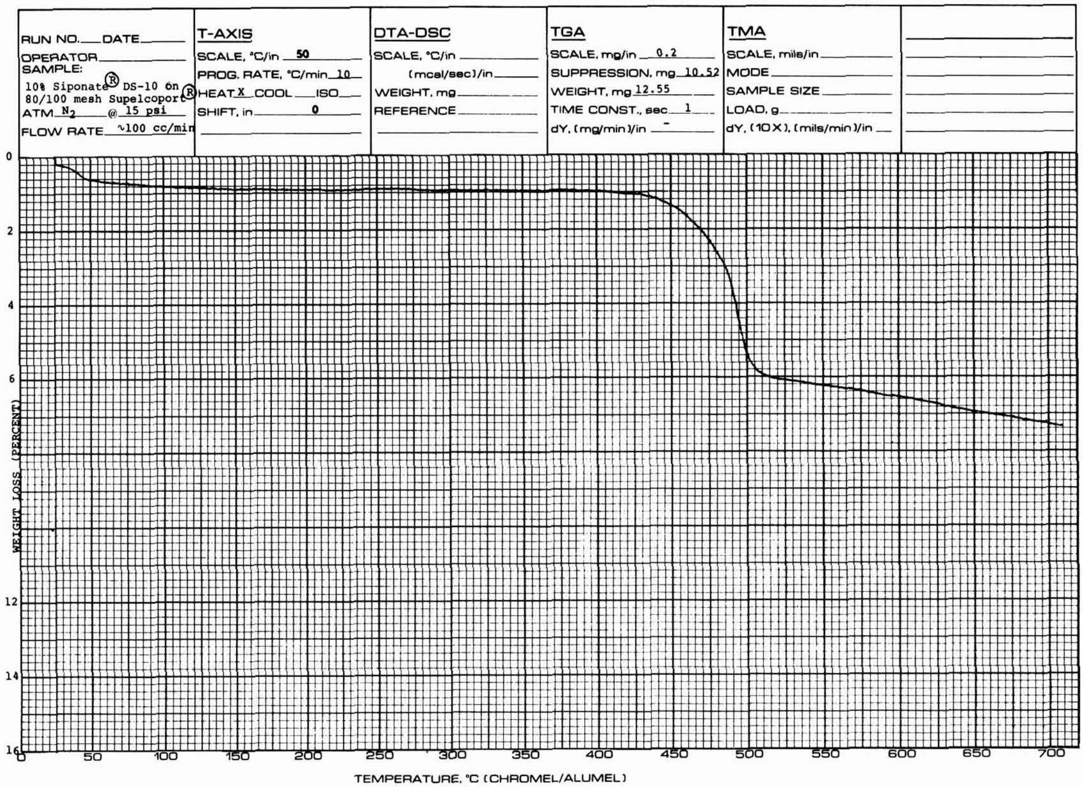
Carbowax is a registered trademark of Union Carbide Corp.



RUN NO.___ DATE___
OPERATOR___
SAMPLE: 10% Siponate® DS-10 on 80/100 mesh Supelcoport®
ATM N$_2$ @ 15 psi
FLOW RATE ∿100 cc/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT X COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, mg/in 0.2
SUPPRESSION, mg 10.52
WEIGHT, mg 12.55
TIME CONST., sec 1
dY, (mg/min)/in -

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

Figure 2—TGA thermal analysis curve depicting the onset of weight loss of Siponate DS-10

allows the separation and detection of lower levels of organic species which in turn prompts the regulation agencies to review and adjust acceptable levels to meet analytical capabilities which in turn prompt further analytical refinements, and so forth. Analysts are confronted with a helix spiraling downward in pursuit of molecular detectability.

As product line and solvent blend samples were received for analysis, separation problems became more apparent and, as importantly, sample turnover time was increasing. Typically, incoming product line samples demanded method development because of interference from the solvent, residual monomer, and, in many cases, the resin itself. For the analyst this meant evaluating most available on-the-shelf columns, establishing a method for that sample type, and proceeding with the analysis. It became quickly apparent that this approach was problematic in that (a) a considerable time-factor was needed to evaluate columns and program conditions for each sample, and (b) there were some sample systems in which resolution could not be achieved using the standard laboratory columns.

At this point in time, confronted with the OSHA Benzene Standard, selectivity for benzene—or, more accurately, *non-selectivity*— becomes the keyword. A column selective for any component retains that component in the liquid phase longer than most other components in the sample being analyzed. Hence, the sought component elutes separated from most interfering volatile species. Therefore, one must label an ideal column for trace level gas chromatography as "non-selective."

Ideally, in trace level gas chromatographic analysis the component of interest should elute before all other major components because of the following points:

(1) Baseline drift often becomes significant due to temperature programming.

(2) Analysis time can be considerably shortened because, following elution of the component of interest, one can increase the oven temperature and clean out the column.

(3) More accurate quantitative data for all modes of integration (disc, electronic, manual) is obtained if near base line resolution has been accomplished. It becomes much more difficult to accurately integrate peak areas which are eluting on the shoulder of another peak.

(4) The resolution of any two peaks can be affected if the concentration of the two components is not similar. This is primarily due to band spreading and column overload.

Column selection for the analysis of benzene was made based on tables of McReynolds Constants avail-

Table 1—Retention Data Determined On Siponate DS-10

Component	Kovats Index	Retention Time (Sec)	Boiling Point (°C)
Methyl acrylate	860	189	80.5
Ethyl acrylate	925	243	99.6
Isobutyl acrylate	1025	327	137.9
Butyl acrylate	1110	408	148.8
2 Ethyl hexyl acrylate	1390	671	—
Acetone	800	150	56.1
Methyl ethyl ketone	875	199	79.6
Methyl isobutyl ketone	990	288	116.2
Cyclohexanone	1295	579	155.8
Ethyl acetate	895	213	77.2
Propyl acetate	990	288	101.6
Butyl acetate	1080	374	126.0
Cellosolve® acetate	1300	522	156.3
Methanol	895	217	64.5
Ethanol	960	265	78.3
Isopropanol	960	265	82.3
Propanol	1050	348	97.2
Butanol	1160	446	117.7
BENZENE	735	111	80.1
Toluene	840	173	110.6
Xylol	930-940	246-259	137-140
Ethyl benzene	930	246	136.2
Chlorobenzene	955	277	131.0
Styrene	985	300	145.2
Cumene	985	300	152.0
o-Dichlorobenzene	1215	514	180.5
Methyl methacrylate	910	230	100.0
Ethyl methacrylate	965	282	117.0
Isobutyl methacrylate	1100	407	155.0
Butyl methacrylate	1145	444	160.0
2 Ethyl hexyl methacrylate	1450	709	—
Solvent Description			
VM&P naphtha	775-986	132-286	
SC-85	905-1360	224-644	
Mineral spirits	870-1280	198-571	
Solvesso® 100	1020-1275	330-565	

Cellosolve is a registered trademark of Union Carbide Corp.; Solvesso is a registered trademark of Humble Oil & Refining Co.

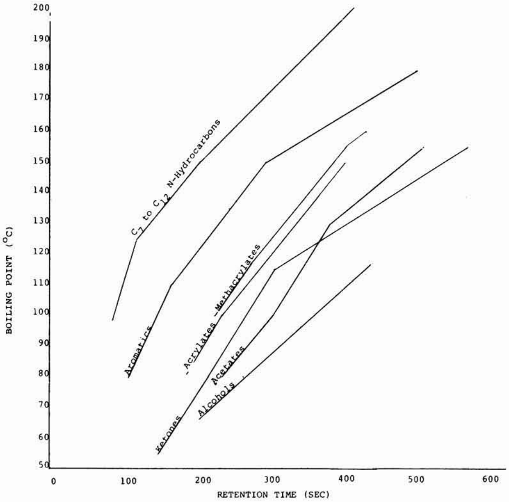


Figure 3—Plot of boiling point vs retention time for different classes of compounds

able for a number of stationary phases.[6,7] The McReynolds Constants are directly related to retention time for the respective stationary phase, i.e., the larger the McReynolds Constant, the greater the retention time for that compound. Typically, McReynolds Constant differences of 100 or larger between compounds indicate significant separation ability. Although there are limitations, use of the McReynolds Constants provide rapid, and perhaps the best, information currently available for comparing the selectivity of gas chromatographic stationary phases.[6] A number of references are available providing more detailed discussion and complete listings of the McReynolds Constants.[8-11] Based on the constants, Siponate® DS-10 became the separation phase of choice.

Characterization of Siponate DS-10

Siponate DS-10, a sodium dodecylbenzene sulfonate, is familiar to the emulsion polymer chemist being typically used as a surfactant in many styrene-acrylic, vinyl acetate, vinyl chloride, and styrene-butadiene systems. Various application information is available from the supplier.[12]

Thermal analysis techniques were employed to characterize the stability of the Siponate for practical gas chromatographic usage. Differential scanning calorimetry (DSC), monitoring enthalpy changes of a polymer as a function of temperature, in an inert nitrogen atmosphere indicated phase transition onset temperatures in the Siponate occurring at 195°C and 355°C. Thermogravimetric analysis, monitoring weight change as a function of temperature, indicated no noticeable weight loss until 415°C. Based on the data obtained from the thermal analysis curves, *Figures* 1 and 2, Siponate for gas chromatographic purposes can be used up to 195°C without risking degradation of the column packing. However, the Siponate appears to be able to withstand much higher temperature before detector contamination becomes a problem.

Boiling point and experimental retention time data for compounds of particular interest are listed in *Table* 1. *Figure* 3, a plot of the data contained in *Table* 1, graphically illustrates how the liquid phase separates and provides information on retention indices. One can readily discern from the plot that benzene can be chromatographically free from interferences most often found in typical coating systems. It is important to note that the separation ability of Siponate is not based upon boiling point or molecular weight, but rather appears to be a function of the polarity of the compound.

Siponate is a registered trademark of Alcolac Chemical Corp.

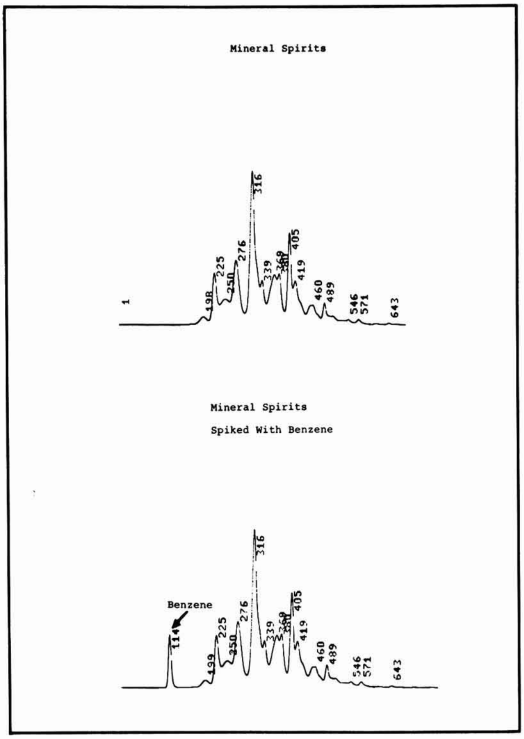


Figure 4—Chromatograms showing the separation of benzene in mineral spirits

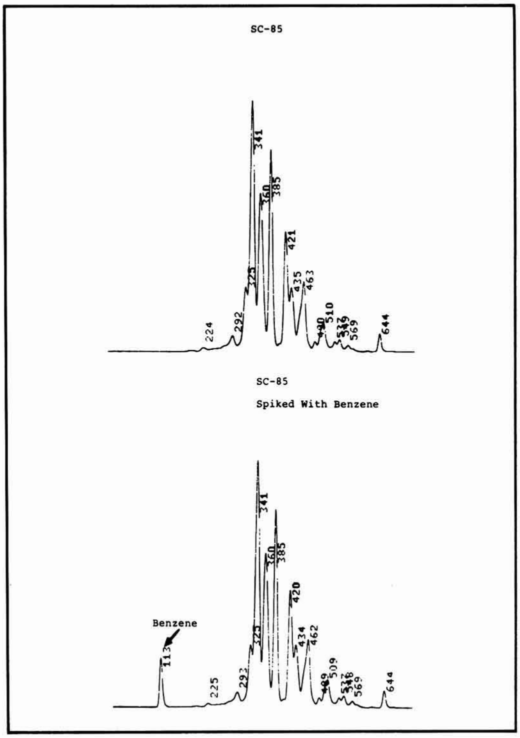


Figure 5—Chromatograms showing the separation of benzene in SC-85

EXPERIMENTAL APPLICATIONS

All chromatographic data were generated using a Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector and operated in conjunction with a Spectra Physics Model SP-4000 computing data system. A 12′ ⅛″ O.D. SS column was packed with 10% Siponate DS-10 on 80/100 mesh Supelcoport®. Prior to packing, the stainless steel tubing was cleaned thoroughly.[13] Helium, operated at a flow of 30 cc/min, was used as the carrier gas. The hydrogen/air ratio was optimized for maximum detector sensitivity. The column was conditioned for a 12-hr period at 190°C prior to performing any analysis.

Both inlet and detector temperatures were set at 250°C. All sample reference materials listed in *Table* 1 were analyzed using the following temperature program:

INITIAL TEMPERATURE	70°C
RATE	10°C/min
FINAL TEMPERATURE	185°C

All product line evaluations used the following programming conditions:

INITIAL TEMPERATURE	70°C
INITIAL TIME	4 min
RATE	80°C/min
FINAL TEMPERATURE	185°C
FINAL TIME	20 min

Because injection technique and, consequently, reproducibility is so critical to trace level analysis, a $3\ \mu l$ solvent backflush injection technique was used for analysis of all coatings samples.[14] With this type of technique and the above indicated temperature programs, an electrometer range setting of 10^{-11} amps/mv

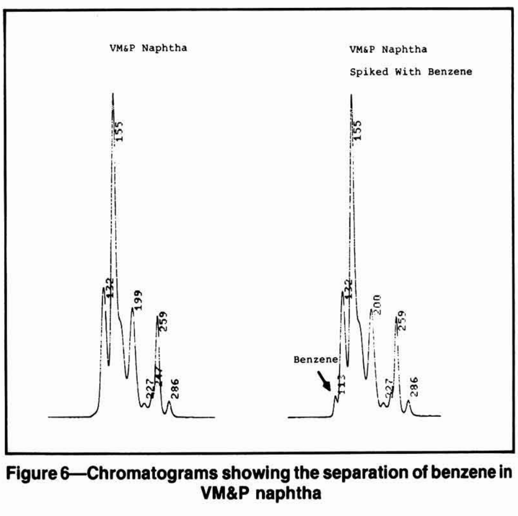


Figure 6—Chromatograms showing the separation of benzene in VM&P naphtha

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Supelcoport is a registered trademark of Supelco, Inc.

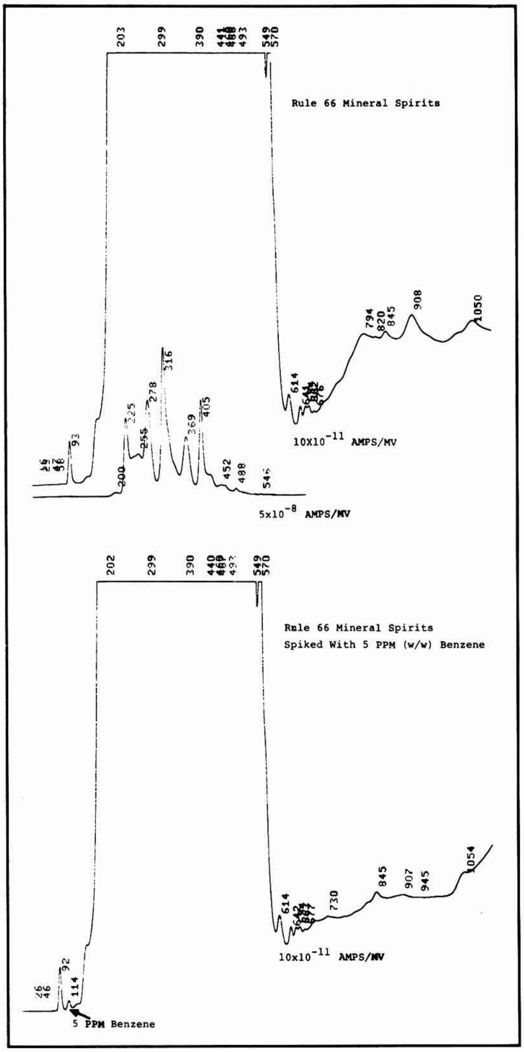

Figure 7—Chromatograms showing the detection of 5 ppm benzene in "Rule 66" mineral spirits

and attenuation 10 was suitable to detect benzene at the 5 ppm level.

Solvent Blend Applications

Solvent blends frequently encountered in the coatings industry are mineral spirits, SC-85 and VM&P naphtha. Each of these solvent blends was run "on scale," an amount of benzene added, and the sample rerun to illustrate the column separation capabilities.

Figures 4-6 show gas chromatograms of these aromatic and aliphatic solvents before and after the addition of benzene. The chromatograms clearly illustrate that trace level benzene determination is possible, even in the presence of solvent blends with wide boiling ranges, either by using the chromatographic conditions outlined or by optimizing the parameters to obtain the desired separation.

Figure 7 shows "Rule 66" mineral spirits analyzed "on scale" to display the separation of the different components present and expanded 2000-fold to illustrate that benzene can be readily detected and quantitated even at the low ppm level. Quantitation of benzene in this type of sample can be accomplished by the standard addition method using the component eluting at 92 seconds as the reference peak.

The chromatogram shown in *Figure* 8 illustrates the elution order which might be expected from aromatic solvents commonly used in the paint and coatings in-

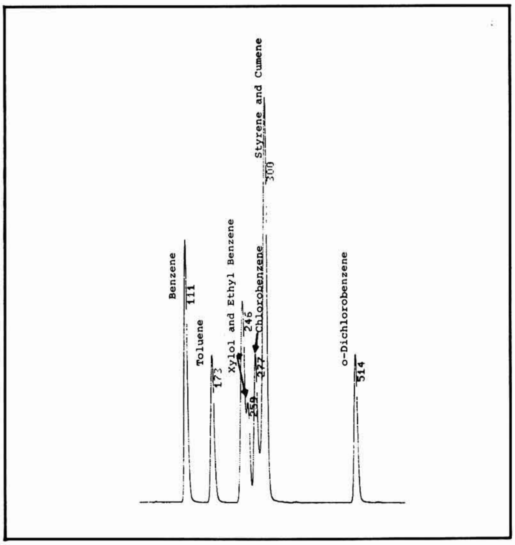

Figure 8—Chromatogram showing elution times of some aromatic compounds using Siponate DS-10

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ROLANDO C. DOMINGO graduated with a B.S. Degree in Chemical Engineering and has over 10 years of experience in Analytical Chemistry. He is a Research Chemist at DeSoto, Inc. and engaged in various aspects of chromatographic separations and ancillary techniques including those related to Industrial Hygiene. He currently is a Governing Board member of the Chicago Chromatography Discussion Group.

JAMES P. KELLY currently is an Analytical Project Chemist in the Research Services Department of DeSoto, Inc. and a member of the American Chemical Society. He received the B.S. Degree in Chemistry from Loyola University of Chicago and is pursuing a Master's Degree. In his present position, he is primarily concerned with GC, PGC, and GC/IR analytical techniques related to the coatings industry. He has also investigated analytical procedures in the liquid chromatography and wet chemical areas.

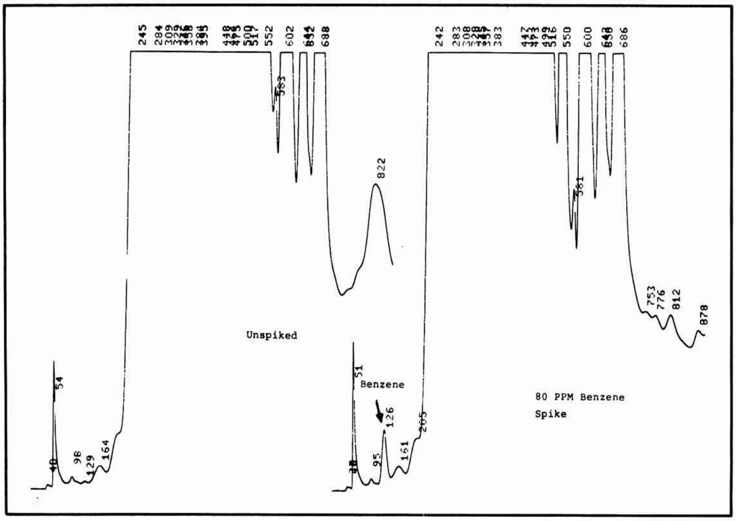


Figure 9—Chromatograms of an uncatalyzed alkyd melamine wetting varnish

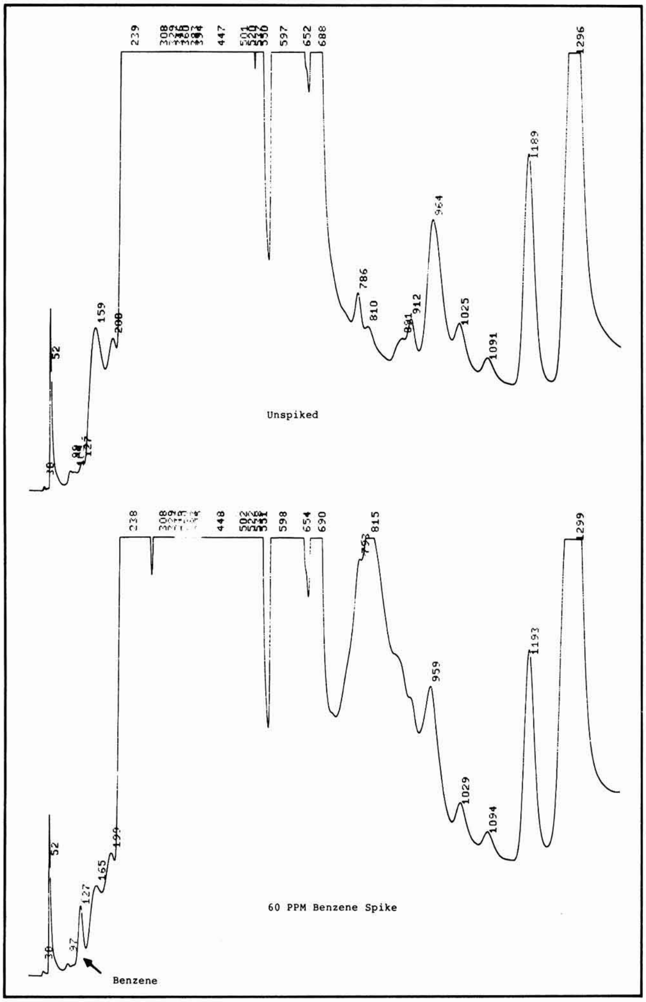


Figure 10—Chromatograms of a catalyzed alkyd melamine wetting varnish

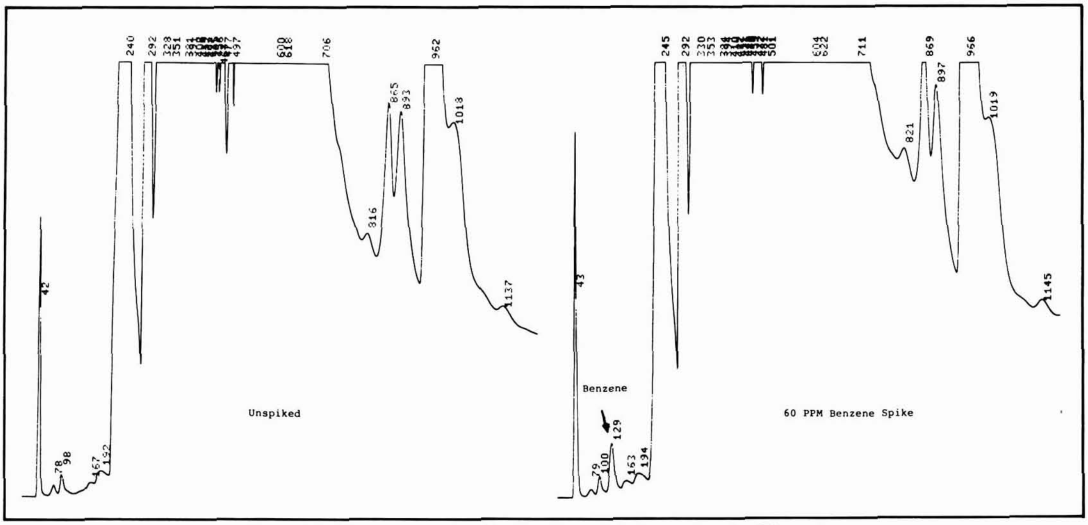


Figure 11—Chromatograms of an appliance/electrocoat replenishment

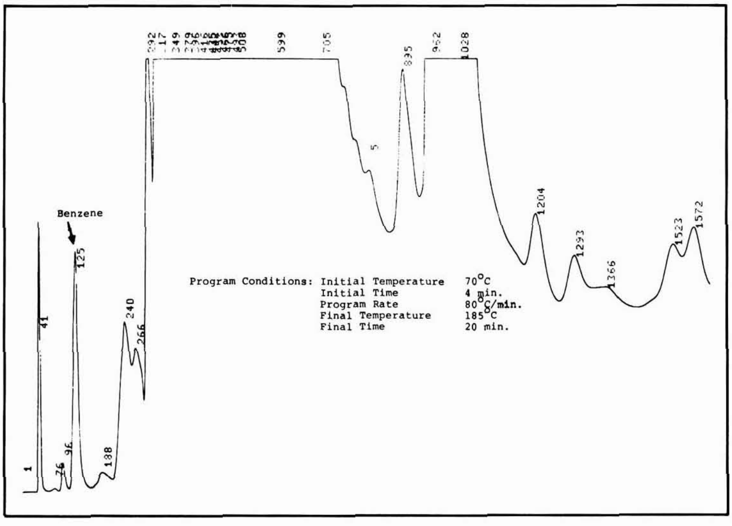
dustry. Although any of these aromatic solvents appear to be a good choice for use as a sample diluent because they elute following the benzene peak, they are not recommended for this purpose since benzene might be present as an impurity.

Sample Application

All industrial coatings samples were diluted with MEK and run as received using either of two accepted quantitative techniques, a standard addition method or an external calibration method. The Spectra-Physics SP-4000 data system employed facilitated peak integration and provided quantitative information using either method.

The use of the SP-4000 data system allowed the use of either method without manually preparing the calibration plots usually associated with these techniques. When an external calibration method was used, daily instrument calibration was performed to ensure utmost precision and accuracy. This method was used for samples suspected to contain copious amounts of benzene, while the standard addition techniques were employed for samples containing 0.01 to 0.10% by weight of benzene. Since the amount of benzene in the samples illustrated below contained less than 100 ppm, a simple "spiking" technique provided a relatively fair estimation of the level of benzene present.

Figures 9 and 10 illustrate the applicability of the described procedure to the analysis of actual samples without modification of the column oven temperature program. *Figure* 9 shows the chromatograms of an un-



Program Conditions:

Initial Temperature	70°C
Initial Time	4 min.
Program Rate	80°C/min.
Final Temperature	185°C
Final Time	20 min.

Figure 12—Chromatogram of an appliance/electrocoat replenishment with different programming conditions

catalyzed alkyd melamine wetting varnish before and after the addition of 60 ppm benzene. *Figure* 10 shows the chromatograms of a catalyzed varnish system. Close examination of the chromatograms clearly indicates that benzene, if present in this sample, is at a concentration below 30 ppm.

Figure 11 demonstrates the same procedure applied to the analysis of an appliance/electrocoat replenishment sample. Again, based on two chromatograms, one can safely conclude that the benzene level in the sample is less than 60 ppm.

Figure 12 shows the same appliance/electrocoat sample spiked with a few hundred ppm benzene and re-analyzed via the same Siponate column but using different temperature program conditions. Note that the benzene peak was baseline resolved but analysis time was lengthened.

It is not the intention of the authors to show aesthetically pleasing chromatograms but rather chromatograms typically observed by the analyst for trace level analysis.

CONCLUSIONS

By using Siponate DS-10, the demands usually placed upon the analyst when involved in trace level analysis can be considerably decreased. Most importantly a gas chromatographic method of analysis is today a universal technique—a technique which can be employed inexpensively in virtually all analytical laboratories. A simple chromatograph equipped with a flame ionization detector is sufficient to satisfy all needs; neither a dedicated chromatograph nor electronic integrator is necessary. Advantages of the above described method include an increase in sample turnover time, a straight forward analysis and the elimination of method development on a per sample basis. It should be noted that most analyses were performed using one program; a great deal of flexibility is available using different temperature programming conditions. The method of analysis also lends itself to automation.

Despite the fact that benzene is not directly used in formulation, it is introduced into products via contamination in monomeric and solvent raw materials. Accountability for benzene is being demanded by regulatory agencies for all—including those in the coatings industry.

ACKNOWLEDGMENT

The authors wish to acknowledge the contribution of A.M. Deihl for assistance in the preparation of this paper and M.L. Hanninen for providing the thermal analysis.

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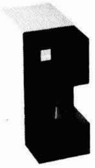

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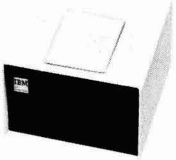

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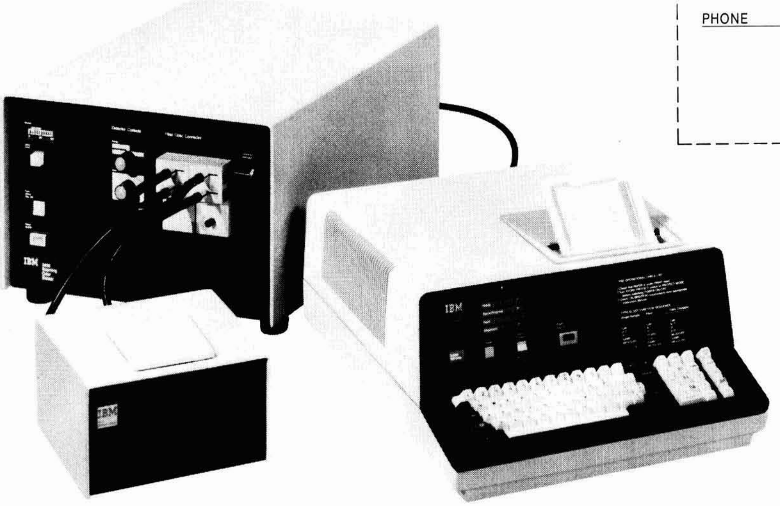


Society Meetings

Baltimore — Sept. 21

President Thomas Cochran was presented the Tenneco Gavel by Don Miller, of Tenneco, Inc.

Martin Freidman, of Rohm and Haas Co., spoke on "CRITICAL VIEW OF LABORATORY EVALUATION PROCEDURES FOR TRADE SALES PAINTS."

Mr. Freidman discussed a number of tests and procedures for appearance, resistance application, and stability with a special emphasis on planning and the need for comparison controls.

GORDON ALLISON, *Secretary*

Cleveland — Sept. 14

Charles K. Beck, of Premier Industrial Corp., was presented the Tenneco Gavel upon his installation as Society President for 1978-79.

Other Society officers installed were: President-Elect — Paul Houck, of Morgan Adhesives Co.; Secretary — Jack S. Malaga, of Body Bros, Inc.; Treasurer — Thomas D. Tuckerman, of Coatings Research Group, Inc.; and Council Representative — Fred G. Schwab, of Coatings Research Group, Inc.

R. Drew Baker, of Reichhold Chemicals, Inc., spoke on "COATINGS FOR CORROSION PROTECTION: PAST, PRESENT, AND FUTURE."

Mr. Baker's talk spanned his 40 years in the paint industry — from the early days when vehicles were oils and natural gums, through the alkyds of the 1940's, the epoxies of the 50's, and the complex vehicles of today.

JACK S. MALAGA, *Secretary*

Dallas — Sept. 16

Honored guests in attendance included Federation Treasurer Harry Poth and Executive Vice-President Frank J. Borrelle.

Society officers for 1978-79, formally installed for the first time, were: President — Samuel F. Biffle, of Sherwin-Williams Co.; Vice-President — William F. Holmes, of DeSoto, Inc.; Secretary — Richard Williamson, of Trinity Coatings; Treasurer — Ray Marett, of Western Specialty Coatings Co.; and Society Representative — Carlos Dorris, of Jones Blair Co.

Roland Duncan of the Industrial Div. of Kelco, Div. of Marck & Co., Inc., spoke on "ZANFLO — A UNIQUE, NEW CELLULOSE STABLE THICKENER."

Mr. Duncan related that the product, when incorporated into a paint, did not interfere with the gloss, flow, and leveling, and that it was compatible with a wide range of cationic and anionic materials.

SAM BIFFLE, *President*

Executive Committee of the C-D-I-C Society for Coatings Technology for the year 1978-79. Seated (left-to-right): Vice-President—Robert A. Broerman; President—Lloyd J. Reindl; Secretary—William J. Frost. Standing: Treasurer—Robert D. Thomas; Council Representative—William Mirick; and Past-President—Raymond R. Schomaker

Golden Gate — Sept. 18

Designated "Past-Presidents' Night", this meeting was attended by several previous G.G. Society Presidents, including: J.D. Beeby (1952), R.E. Minucciani (1962), L.F. Sanguinetti (1963), A.G. Rook (1965), B. Adler (1966), A.L. Axelson (1967), W. Sawyer (1972), L. Cummings (1973), E. Kevin (1975), E. Tengbergen (1976), and E. Harmon (1977).

It was announced that 25 students have enrolled in the beginning and advanced coatings courses.

Eric Tengbergen, the June recipient of the Study Grant Program, reported on his attendance at the University of Detroit, Polymer Institute.

Society officers for the year 1978-79 were installed. They are: President — Ken Probst, of San Jose Regional Vocational Center; Vice-President — Fred Apfel, of International Paint Co. (Cal.), Inc.; Treasurer — Ted Favata, of Triangle Paint Co.; Secretary — Sharon Vadnais, of E.T. Horn Co.; and Council Representative — A. Gordon Rook, of Napko Corp.

Ken Probst was presented the Tenneco Gavel by Robert Cole, of Abbot, Cole & DeGraf.

The Past President's Gift was presented to the guest of honor, Joyce Ballinger, widow of the immediate Past President, Walter Ballinger.

Paul C. Stievater, of Spencer-Kellogg Div. of Textron, Inc., spoke on "CORROSION RESISTANCE IN WATER-REDUCIBLE COATINGS."

Mr. Stievater made a comparison of emulsions and water-reducible solution coatings and showed how the particle size of the water reduced coating can affect the properties of the finished coating. Several other formulating variables concerned with resin structure and their influence on corrosion resistance were discussed. He showed how these variables are comparable in a new series of water-reducible alkyd resins which perform as well as solvent alkyds used in similar applications.

SHARON VADNAIS, *Secretary*

Kansas City Sept. 14

A moment of silence was observed in memory of Norbert Mann, who died on August 31, 1978.

Honored guests included Thomas Kocis, Federation Field Director, and John Gordon, National Education Committee Chairman.

The following slate of officers was elected for the year 1978-1979: President — William J. Fitzpatrick, of Cook Paint & Varnish Co.; Vice-President — Hugo Manco, of Davis Paint Co.; Secretary — William A. Smith, IV, of Conchemco, Inc.; and Treasurer — Richard Warren, of Cook Paint & Varnish Co.

Wade Martin, of Abner Hood Inc., presented President Fitzpatrick with the Tenneco Gavel.

Michael Smith, of Gemini Lacquer Co., spoke on "PREVENTATIVE SAFETY PROGRAMS FOR SMALL PLANTS."

Mr. Smith's talk was geared toward small plants of 15-25 people. He suggested that when developing a safety program, the order of the companies goals should be (1) to guard the employee, (2) to protect the plant, and (3) to satisfy OSHA requirements.

WILLIAM A. SMITH, IV, *Secretary*

Los Angeles Sept. 13

A moment of silence was observed in memory of Hal Palmer, of Zynolyte Corp., and K.C. Johnson, of CIBA-GEIGY Corp., who died recently.

The following officers of the 1978-1979 year were introduced: President — Fred Croad, of Engard Coatings Corp.; Vice-President — Albert Seneker, of Ameron Corp.; Secretary — Jan P. Van Zelm, of McCloskey Varnish Co.; and Treasurer — Donald Jordan, of Cargill, Inc.

The Tenneco Gavel was presented to President Croad by Jim Dye, of Tenneco Chemicals, Inc.

Paul Stevater, of Spencer Kellogg Div., Textron, Inc., spoke on "CORROSION RESISTANCE IN WATER-REDUCIBLE COATINGS."

Mr. Stevater presented comparisons of emulsions and water-reducible solution coatings, and showed how the particle size of the water reduced coating can affect the properties of the finished product.

Q. Why is the drier added to the grind in water-soluble alkyd formulations?

A. Driers will go in better when added in coupling solvent but could be added anyplace.

Q. Most producers of W.D. resins do not include an anti-sag agent in their suggested formulas. Do you assume that all your resins impart sag resistance without an anti-sag agent?

A. Our formulations are not to be expected to be final formulations. We do show, in some experimental formula, an anti-sag agent.

JAN P. VAN ZELM, *Secretary*

Montreal Sept. 6

Albert Gowen, of DuPont of Canada Ltd., spoke on "CURRENT CONCEPTS OF PRODUCT RESPONSIBILITY."

Mr. Gowen's presentation featured the manufacturer's responsibility for safety of the coatings products as they affect the environment and the consumer.

C.A. MCWADE, *Recording Secretary*

New England Sept. 21

Don Aikman, of D.H. Litter Co., presented the Tenneco Gavel to Martin L. Davis, of Sterling-Clark-Lurton Corp., the new President.

William J. Stewart, of Tenneco Chemicals, Inc., spoke on "HEAVY METAL ADDITIVES FOR COATINGS — A PROSPECTUS."

Mr. Stewart reviewed, on a broad basis, the utility of additives and offered suggestions for the future in terms of environmental, economic, and political problems. He said that mercury is an effective biocide, acting as a preservative (interior) and as a fungicide (exterior). Some alternatives to the use of mercury as a fungicide are ethylene sulfone types and thio phthalimide types in solvent systems. These, however, hydrolize in aqueous systems and are ineffective. It is possible, said Mr. Stewart, to reduce the level of these items by using them in combination with zinc oxide.

Alternatives to mercury as a preservative run into difficulty, particularly where marginal quantities are used. Lack of adequate level, poor housekeeping, and use of recycling wash water contribute to bacteria growth.

Mr. Stewart concluded by saying that the formulation response to the problems of the day must be to use materials in combination, to reduce levels, and to watch for color problems.

R.G. MODRAK, *Secretary*

New York Sept. 12

Honored guests included John Oates, Federation President.

Saul Spindel, of D/L Laboratories, Inc., was presented with the Tenneco Gavel by Fred Holtzman, of D.H. Litter Co.

Dr. Stephen Cantor, of Uniroyal, Inc., spoke on "THE ROLE OF POLYELECTROLYTE DISPERSANTS IN PREPARATION OF TITANIUM DIOXIDE SLURRIES."

Dr. Cantor began by discussing the importance of titanium dioxide in providing hiding, gloss, and other paint properties, and the need for chemical dispersants to maximize these properties. He indicated the mechanism of dispersion as involving three steps - wetting of the pigment, mechanical disruption, and stabilization of the dispersed particles to prevent flocculation. He pointed out that dispersion involves neutralization of charges on the pigment particles by adsorption of oligomeric dispersants, forming a shell around the particles. Stokes' Law was discussed, stressing the importance of minimizing the effective particle size of dispersed pigments by means of improving dispersion, in order to reduce pigment settling.

MARVIN J. SCHNALL, *Secretary*

Philadelphia Sept. 14

A moment of silence was observed in memory of William McFarland, of Richardson Paint Co., and John Williams, Jr., who died recently.

It was announced that the Philadelphia Society has formed an Employment Service Committee, the purpose of which is stated as follows:

> *"It is the stated policy of the Philadelphia Society for Coatings Technology that the Employment Service is free and for the exclusive use of members of the Federation of Societies for Coatings Technology, with first preference to members of the Philadelphia Society, provided that the member is currently unemployed or has been informed of the projected date of unemployment; and that employers may use the Employment Service without charge provided that all offers of employment are for positions where vacancies exist or will exist because of retirement."*

It was also announced that the society will offer again this year the American Chemical Society's Short Course on Organic Coatings.

Society officers for the year 1978-79 were installed. They are: President — Lothar Sander, of Amchem Products, Inc.; President-Elect — Carl W. Fuller, of Reichard-Coulston, Inc.; Secretary — Barry Oppenheim, of McCloskey Varnish Co.; Treasurer — Matthew J. Hanrahan, of Lilly Industrial Coatings, Inc.; and Council Representative — Richard J. Kiefer, of McCloskey Varnish Co.

Mr. Sander, as the incoming President, was presented the Nuodex Gavel and he, in turn, presented the Past-President's pin to Mr. Wood.

Steven Malaga, of Hercules Incorporated, spoke on "EASY DISPERSING PIGMENTS."

A new pigment treatment has been developed to meet the demand that water-borne coatings have made on the industry, said Mr. Malaga. The end product of this process is a dry, dispersable pigment which does not aggregate. It offers unusual stability, broad compatibility, formulating-flexibility, easy storage-handling, and is moisture insensitive in a cured film. When using this pigment, the batch must contain sufficient water for both the resin and the dry colorant; simple stirring yields the primary particle, he said.

Mr. Malaga related that in two samples of a white water-borne coating where this new colorant (a phthalocyanine blue) was added, there was equal color development with no streaking or specking. He said this was true despite the fact that one was power mixed for three minutes and the other was hand mixed for eight minutes. This new class of pigments has a high tinting strength, approximately 70-85% of conventional pigments. The following colors are now available, he said: hansa yellow, dinitro orange, and phthalocyanine blue and green. Work is progressing on jet black and napthol red. To date, only transparent iron oxides seem to present a problem in applying this new technology.

Q. Are there many colors available now?

A. The number of colors now available are somewhat limited.

Q. Is the pigment treatment water soluble?

A. No, surface treatment remains on pigment.

Q. Is there a difference in tint effect with conventional pigments?

A. That depends on pigments and dispersing equipment. In some systems it is better.

Q. Is there a loss in gloss?

A. There is usually an improvement in gloss.

Q. Is there a moisture pickup problem?

A. No, packaging takes care of it.

BARRY OPPENHEIM, *Secretary*

Future Society Meetings

Chicago

(Jan. 8) — "HIGH SOLIDS RESINS AND COATINGS" — Speaker to be announced; and "MICROBIAL PROBLEMS IN PLANTS" — William Machemer, of Troy Chemical Corp.

(Feb. 5) — "FSCT SLIDE PRESENTATION" — Federation Officers; and "SURFACTANTS AS RELATED TO THE PAINT INDUSTRY" — Julius Deutsch, of Stepan Chemical Co.

(Mar. 5) — "AMINE SOLUBILIZERS FOR WATER-SOLUBLE INDUSTRIAL COATINGS" — Dr. Zeno W. Wicks, Jr., of North Dakota State University; and "MARKETING - RESEARCH INTERACTIONS" — Dr. Robert Bumb, of Dow Chemical Co.

(Apr. 2) — "ACCELERATED WEATHERING" — George Grossman, of Q-Panel Co.; and "YOU CAN'T AFFORD TO BE WITHOUT SAFETY" — Gilbert Cain, of Hercules Incorporated.

C-D-I-C

(Dec. 11) — "ROLE OF POLY ELECTROLITE AS A DISPERSANT FOR TiO_2 SLURRIES AND LATEX PAINTS" — Stephan Cantor, of Uniroyal Chemical.

(Jan. 8) — "CONVERSION ENAMELS — ENERGY SAVERS" — Paul W. McCurdy, of Reichhold Chemicals, Inc.

(Feb. 12) — PLANT TOUR - Inland Manufacturing, GM Div.

(Mar. 12) — FSCT SLIDE PRESENTATION — Federation Officers.

(May 14) — "A NEW, IMPROVED THICKENER SYSTEM" — R.J. Duncan, of Kelco Div., Merck & Co., Inc.

Cleveland

(Jan. 23) — Annual joint meeting with Cleveland Paint & Coatings Association. "LIVING WITH GOVERNMENT REGULATIONS" — Panel Discussion.

(Feb. 21) — Joint meeting with Cleveland Section of American Chemical Society. "METAL CLUSTERS;" "SURVEY OF COATINGS AND POLYMER CHARACTERIZATION TECHNIQUES;" "WHAT DOES A (PAINT) CHEMIST DO? WHAT ARE THE CAREER OPPORTUNITIES IN (PAINT) CHEMISTRY?;" and "WOMEN IN CHEMISTRY."

(Mar. 13) — "FSCT SLIDE PRESENTATION" — Federation Officers; Panel Discussion on "NEW CONCEPTS IN PAINTS/COATINGS APPLICATION TECHNOLOGY."

(Apr. 12) — Meeting to be held at Ohio Edison Nuclear Power Plant, Perry, Ohio.

(May 17) — "ART OPENS WAY FOR SCIENCE" — Dr. Jon B. Eklund, of Smithsonian Institution.

Golden Gate

(Jan. 15) — "SURFYNOL NONIONIC SURFACTANTS" — Noshir F. Chinoy, of Air Products & Chemicals, Inc.

(Mar. 19) — "NEW DEVELOPMENTS IN THE FIELD OF GLOSS EMULSION PAINTS" — John Bax, of Scott-Bader.

(Apr. 16) — "ACCELERATED WEATHERING AND FADING" — R. Metzinger, of Atlas Electric Devices Co.

(May 14) — "USE OF ORGANO TITANATES IN COATINGS" — Salvatore J. Monte, of Kenrich Petrochemicals, Inc.

Los Angeles

(Nov. 8) — "COLOR COMMUNICATIONS" — George Lorditch, of Macbeth, Div. of Kollmorgen.

(Jan. 10) — "SURFYNOL NONIONIC SURFACTANTS" — Noshir F. Chinoy, of Air Products and Chemicals, Inc.

(Feb. 14) — "SLEUTHING WITH A MICROSCOPE" — Dr. Walter C. McCrone, of Walter C. McCrone Associates.

(Mar. 14) — "NEW DEVELOPMENTS IN THE FIELD OF GLOSS EMULSION PAINTS" — John Bax, of Scott-Bader.

(Apr. 11) — "ACCELERATED WEATHERING AND FADING" — R. Metzinger, of Atlas Electric Devices Co.

(May 9) — "USE OF ORGANO TITANATES IN COATINGS" — Salvatore J. Monte, of Kenrich Petrochemicals, Inc.

Constituent Society Meetings and Secretaries

BALTIMORE (Third Thursday—Eudowood Gardens, Towson). GORDON ALLISON, McCormick Paint Works, 2355 Lewis Ave., Rockville, Md. 20851.

BIRMINGHAM (First Thursday—Warwickshire County Cricket Ground). R.G. SMITH, Arthur Holden & Sons Ltd., Bordesley Green Rd., Birmingham, England.

CHICAGO (First Monday—meeting sites in various suburban locations). RICHARD M. HILLE, United Coatings, Inc., 3050 N. Rockwell, Chicago, Ill. 60618.

C-D-I-C (Second Monday—Sept., Nov., Jan., Mar., May in Columbus; Oct., Dec., Feb., Apr. in Cincinnati, Kings Island Inn). WILLIAM J. FROST, Ashland Chemical Co., P.O. Box 2219, Columbus, Ohio 43216.

CLEVELAND (Second Tuesday—meeting sites vary). JACK S. MALAGA, Body Brothers, Inc., 214 Northfield Rd., Bedford, Ohio 44146.

DALLAS (Thursday following second Tuesday—Vic's Gallery Restaurant). RICHARD WILLIAMSON, Trinity Coatings Co., P.O. Box 721, Fort Worth, Tex. 76101.

DETROIT (Fourth Tuesday—Rackham Memorial Bldg.). GARY VAN DE STREEK, Wyandotte Paint Products, Inc., 1430 Sycamore, Wyandotte, Mich. 48192.

GOLDEN GATE (Monday before third Wednesday—Sabella's Restaurant, San Francisco). SHARON VADNAIS, E.T. Horn Co., 7700 Edgewater Dr., Oakland, Calif. 94621.

HOUSTON (Second Wednesday—Marriott Hotel, Astrodome). SAMUEL L. LOE, JR. Samuel Loe Co., Inc., 4715 S. Main St., Houston, Tex. 77002.

KANSAS CITY (Second Thursday—Washington Street Station). WILLIAM SMITH IV, Conchemco, Inc., P.O. Box 37, Kansas City, Mo. 64141.

LOS ANGELES (Second Wednesday—Steven's Steak House). JAN P. VAN ZELM, McCloskey Varnish Co., 5501 E. Slauson Ave., Los Angeles, Calif. 90040.

LOUISVILLE (Third Wednesday—Essex House). P.W. HARBAUGH, Reliance Universal, Inc., 4730 Crittenden Dr., Louisville, Ky. 40221.

MEXICO (Fourth Thursday—meeting sites vary). EMILIO SANTILLAN, Industrias Resistol, S.A., Apartado Postal 44-997, Mexico 12, D.F.

MONTREAL (First Wednesday—Bill Wong's Restaurant). B. MCWADE, Stahl Finish (Canada) Ltd., 380 Des Lauriers St., Montreal, Que., P.Q.

NEW ENGLAND (Third Thursday—Fantasia Restaurant, Cambridge). ROBERT G. MODRAK, Benjamin Moore & Co., P.O. Box 416, Milford, Mass. 01151.

NEW YORK (Second Tuesday—Landmark II, East Rutherford, N.J.). MARVIN J. SCHNALL, Troy Chemical Corp., One Ave. L, Newark, N.J. 07105.

NORTHWESTERN (Tuesday after first Monday—Jax Cafe). ROGER ANDERSON, 3M Company, 3M Center, St. Paul, Minn. 55101.

PACIFIC NORTHWEST (Portland Section—Tuesday following second Wednesday; Seattle Section—the day after Portland; British Columbia Section—the day after Seattle). CURTIS BAILEY, Parker Paint Co., 3302 S. Junett St., Tacoma, Wash. 98409.

PHILADELPHIA (Second Thursday—Valle's Steak House). BARRY OPPENHEIM, McCloskey Varnish Co., 7600 State Rd., Philadelphia, Pa. 19136.

PIEDMONT (Third Wednesday—Howard Johnson's Coliseum, Greensboro, N.C.). WILLIAM J. CUNANE, Sherwin-Williams Co., P.O. Box 4528, High Point, N.C. 27263.

PITTSBURGH (First Monday—Skibo Hall, Carnegie-Mellon University Campus). RAYMOND C. UHLIG, Technical Coatings Co., 1085 Allegheny Ave., Oakmont, Pa. 15138.

ROCKY MOUNTAIN (Monday prior to second Wednesday). F.H. MEYERS, Kwal Paints, Inc., P.O. Box 5231 T.A., Denver, Colo 80217.

ST. LOUIS (Third Tuesday—Salad Bowl Restaurant). FLOYD THOMAS, JR., Thomas & English, Inc., 108 Mullanphy St., St. Louis, Mo. 63102.

SOUTHERN (Gulf Coast Section—Second Tuesday; Central Florida Section—Thursday after third Monday; Atlanta Section—Third Thursday). FRANKLIN D. RECTOR, Indurall Coatings, Inc., 3333 Tenth Ave., N., Birmingham, Ala. 35234.

TORONTO (Second Monday—Great Canadian Beef Co.). A.G. MORRIS, L.V. Lomas Chemical Co., 6365 Northwest Dr., Mississauga, Ont., Canada.

WESTERN NEW YORK (Second Tuesday—Holiday Inn, Cheektowaga, N.Y.). GEORGE C. REID, Spencer Kellogg Div., P.O. Box 210, Buffalo, N.Y. 14225.

Montreal

(Dec. 6) — Technical Committee report "FREEZE-THAW AND ADHESION OF LATEX PAINTS."

(Jan. 10) — "UPDATE ON WATER-BORNE FINISHES": *Latex Stains* — M. Belanger, of Union Carbide Canada Ltd.; *Interior Gloss Paints* — A. Marchetti, of Nacan Products Ltd.; and *Air Dry Maintenance* — R. Fraser, of C.N.R. Research Centre.

(Feb. 7) — "FLOW IMPROVEMENT IN LATEX GLOSS AND SEMI-GLOSS PAINTS" — Panel discussion.

(Mar. 7) — Annual joint meeting with Quebec Paint Industry Association. "MARKETING OF CONSUMER PAINT PRODUCTS" — B. Wayne, of International Paints (Canada) Ltd.; and "THE PROFESSIONAL CHEMIST IN THE COATINGS INDUSTRY" — F. Bonnier, of Carter White Lead.

(Apr. 11) — "FSCT SLIDE PRESENTATION" — Federation Officers.

(May 2) — WORKSHOP NIGHT: *Color Matching, Metrification, Quality Control,* and *Technical Service.*

New York

(Jan. 9) — "PAINT ADDITIVES AND THE CHANGING PAINT TECHNOLOGY" — John Oates, of Troy Chemical Corp.

(Feb. 8) — Joint meeting with New York Paint and Coatings Association. "LEGISLATIVE UPDATE" (Tentative).

(Mar. 13) — MINIWORKSHOPS — Speakers to be announced.

(Apr. 10) — "CLASSES OF WATER DISPERSIBLE BAKING FINISHES" — Nicholas Roman, of Rohm and Haas Co.

(May 8) —PAVAC AWARD NIGHT.

Philadelphia

(Dec. 15) — "CAN COATINGS — YESTERDAY, TODAY, AND TOMORROW" — Anthony Rossi, of Campbell Soup Co.

(Jan. 18) — "THE EFFECTS OF SOLVENTS ON FILM CLARITY — A PRACTICAL TEST" — T.E. Parsons, of Eastman Chemical Products Co.

(Feb. 15) — "THE TRANSITION FROM LABORATORY TO SALES" — Donald Denny, of E.W. Kaufman Co.

(Mar. 15) — "NEW TECHNOLOGY IN ANTI-FOULING PAINTS" — Dr. Dodd Carr, of International Lead Zinc Research Organization.

(Apr. 19) — "METAL FINISHES —YESTERDAY, TODAY, AND TOMORROW" — Pat Hunt, of Gilbert Spruance Co.

(May 17) — Philadelphia Society TECHNICAL SEMINAR.

(All of the above will be presented at the Society's Technical Committee meetings.)

Technical Articles in Other Publications

Compiled by the Technical Information Systems Committee—H. Skowronska, Chairman

Progress in Organic Coatings

Published by Elsevier Sequoia S.A., P.O. Box 851, 1001 Lausanne 1, Switzerland

Vol. 6 No. 1 — August 1978

Simpson, L.A.—"Factors Controlling Gloss of Paint Films;" 1-30.
Chromy, L. and Kaminska, E.—"Relationship Between the Optical Properties of Coloured Pigments and Their Morphology and Crystalline Structure;" 31-48.
McKelvie, A.N.—"Measurement of Paint Consistency of Flow Cups;" 49-64.
Hatano, M. and Tanikawa, K.—"Recent Developments in Polymeric Photo-conductors;" 65-104.

Product Finishing

Published by Sawell Publications Ltd., 127 Stanstead Rd., London SE23, England

Vol. 31 No. 7 — July 1978

Bassett, G.T.—"Ultra-Violet Radiation Cured Finishes and Equipment;" 27-8, 31-2.

Pigment and Resin Technology

Published by Sawell Publications Ltd., 127 Stanstead Rd., London SE23, England

Vol. 7 No. 6 — June 1978

Ryan, P.J.—"Daylight Fluorescent Pigments and Their Applications;" 4-8.
Anon.—"Coatings Update 1977: Energy" (Literature review); 9-10.

Vol. 7 No. 7 — July 1978

Troughton, G.E.—"A New Approach to Bulk Production;" 10-13.

Coatings and Plastics Preprints

Preprints of Papers Presented before the ACS Division of Organic Coatings and Plastics Chemistry

Miami Beach, Fla. — September 1978 — Vol. 39

Decreasing Energy Requirements in Coatings and Plastics Processing (13 papers); pp 1-30, 62-90.
Epoxy Resins (20 papers); pp 31-61, 91-119, 139-171, 192-217.
Sorption and Transport in Glassy Polymers (35 papers); pp 120-138, 172-191, 218-247, 282-311, 336-364, 441-472.
New Developments in Foundry Binders (10 papers); pp 254-281, 312-335.
Marine and Antifouling Paints (17 paints); pp 365-393, 473-505, 567-589.
High Solids Coatings (6 papers); pp 394-440.
New Concepts in Coatings and Plastics (11 papers); pp 506-566.
Macromolecular Secretariat Symposium on "Chemical and Physical Lifetime Limits and Macromolecular Materials," ACS Div. of Organic Coatings and Plastics Chemistry Session (8 papers); pp 599-640.
Inquiries regarding price and availability of this preprint book should be sent to G.G. Schurr, Sherwin-Williams Co., Research Center, 10909 S. Cottage Grove Rd., Chicago, Ill. 60628.

Polymer Preprints

Preprints of Papers Presented before the ACS Division of Polymer Chemistry

Miami Beach, Fla. — September 1978 — Vol. 19 No. 2

Advances in Condensation Polymerization (22 papers); pp 1-120.

Matrix Controlled Polymerization (18 papers); pp 121-214.

Ion-containing Polymers (41 papers); pp 215-429.

Plasma Polymerization (24 papers); pp 429-552.

Special Topics in Polymer Chemistry (45 papers); pp 553-793.

Macromolecular Secretariat Symposium on "Chemical and Physical Lifetime Limits of Macromolecular Materials," ACS Div. of Polymer Chemistry Session (7 papers); pp 799-830.

Inquiries regarding price and availability of this preprint book should be sent to J.C. Salamone, Dept. of Chemistry, University of Lowell, Lowell, Mass. 01854.

West Coast Symposium to Feature Two and One-Half Day Program

The Western Coatings Societies' Symposium and Show will present 20 papers and a panel discussion, as well as a product display of supplier companies at the Fairmont Hotel, San Francisco, Calif., February 28 to March 2, 1979.

Centering around the Symposium topic, "A Bold Look into the 80's," the technical program consists of the following presentations:

February 28

"Coping with Government Regulations"—Austin C. Abbott, of Sherwin-Williams Co.

"Can the Modern Spectrophotometer Replace Color Standards?"—S. Upton Jenkins, of Hunter Associates Laboratory.

"A Pigment Slurry System - Circulating Through the Usage Areas"—Milton Golden, of Major Paint and Varnish Co.

"Switch From Bag to Slurried Clay; Formulating Parameters Effecting the Paint Manufacturer"—Thomas G. Brown, of Engelhard Minerals and Chemicals Div.

March 1

"Investigation into Causes of Mudcracking of Latex-Based Paints"—Anton K. DeMik of Reichhold Chemicals, Inc.

"Viscosity Loss in Hydroxy-Ethyl Cellulose Thickened Paint Caused by Chemical Oxidants: Methods of Detection and Their Possible Application in the Paint Industry"—Vaughn L. Irwin, of Celanese Polymer Specialties Co.

"Evaporation Behavior of Organic Cosolvents in Water-Borne Coating Formulations"—R.F. Eaton and F.G. Willeboordse, of Union Carbide Corp.

"Trimethylolpropane or Pentaerythritol in Water-Soluble Air-Dry Industrial Coatings"—Thomas M. Powanda, of Celanese Chemical Co.

"Foaming and Crawling in Aqueous Industrial Coatings"—Marvin Schnall, of Troy Chemical Corp.

"New Technology in Water-Borne Coatings Useful for Automotive, Appliance, and General Metal Finishing"—J.D. Crowley, of Eastman Chemical Products, Inc.

"Water-Borne and High Solids Coatings for Use in Low Energy Demand Finishing Applications"—Robert N. Price, of Ashland Chemical Co.

"Copper Phthalocyanine Pigments in Industrial Water-Borne Systems"—Paul G. Schmidt, of E.I. du Pont de Nemours & Co., Inc.

"Effective Use of Titanium Dioxide Pigments in Emulsion Flat Paints"—Dwight A Holtzen, of E.I. du Pont de Nemours & Co., Inc.

"Surface Modification of Inorganic Pigments and Extender Pigments"—J.E. Moreland, of Malvern Minerals Co.

"New, Improved Light-and Weather-Fast Organic Yellow Pigments"—Albert E. Medas, of American Hoecht Corp.

"Flaked Aluminum Pigments for Today's Metallescent Coatings"—Harry E. Bell, of Alcan Metal Powders, Inc.

March 2

"Appliance and General Industrial Polyester Oligomer Enamels for Application at 80% Volume Solids"—R.B. Pywell, of E.I. du Pont de Nemours & Co., Inc.

"Weatherable Epoxy Resins"—Constantine S. Demos, of Shell Chemical Co.

"Film Erosion Studies of Silicone Modified Copolymer Paints"—William A. Finzel, of Dow Chemical Co.

"Effect of Catalyst Structure on the Properties of Coatings Crosslinked with Hexamethoxy-Methylmelamine"—Leonard J. Calbo, of King Industries, Inc.

PANEL DISCUSSION on "Dealing with Government Agencies and Regulations"—Louie F. Sanguinetti, of Jasco Chemical Corp.—Moderator; Panelists: Leo Ryan, Congressman, 11th Congressional District, California; Robert Minucciani, of Glidden Pigments, SCM Corp.; Eveleth Hayden, of Bay Area League of Industrial Associations, Inc.; Frank Martin, of PPG Industries, Inc.; Larry Thomas, Executive Director, National Paint and Coatings Association; and Harry D. Williams, of Ashland Oil Co.

The Show will run concurrent with the symposium and will also be held at the Fairmont Hotel.

Complete details on the event and information on registering or exhibiting are available from Ed Kelvin, The O'Brien Corp., 450 E. Grand Ave., S. San Francisco, Calif. 94080.

Hunterlab to Continue Seminar/Mini-Shows in 1979

Hunter Associates Laboratory, Inc., Fairfax, Va., will continue its series of exhibits, held in conjunction with its traditional area seminars, during 1979.

Lectures and discussions during the first day will focus on appearance measurement and will be supplemented by visual aids, demonstrations, and hands-on use of instruments for color, gloss, haze, whiteness, etc. Fee for the first day is $75, which includes reference material and lunch.

The second day will feature Hunterlab personnel and instruments in an informal day-long Mini-show exhibit. There will be an opportunity for interested individuals to discuss, at no cost, their color problems and possible instrument solutions.

The Mini-Show/Seminar 1979 schedule is:

Toronto, Canada — Dec. 6-7, 1978.
Houston, Tex. — Jan. 17-18.
Pittsburgh, Pa. — Jan. 31-Feb. 1.
Chicago, Ill. — Feb. 14-15.
Northern California
(Location TBA) — Mar. 1-2.
Los Angeles, Calif. — Mar. 5-6.
Philadelphia, Pa. — Apr. 4-5.
Detroit, Mich. — Apr. 18-19.
Montreal, Canada — May 2-3.
Saddlebrook, N.J. — May 16-17.
Boston, Mass. — June 6-7.

Two Service Seminars will be conducted in Fairfax, Va. These are one-day seminars aimed at personnel who are interested in learning "trouble-shooting" servicing of their Hunterlab instrument.

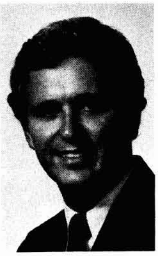
Additional information and application forms for all Seminars may be obtained from the Marketing Dept., Hunter Associates Laboratory, Inc., 9529 Lee Highway, Fairfax, Va. 22031.

People

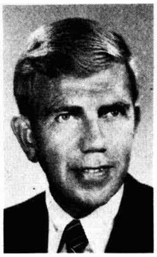
Larry L. Thomas has been named Executive Director of the National Paint and Coatings Association. He succeeds **Robert A. Roland** who was named President of the Manufacturing Chemists Association. Mr. Thomas joined NPCA's Legal and Government Relations Division in 1971 and most recently served as General Counsel.

The Manufacturing Chemists Association has appointed **David W. Carroll** Assistant General Counsel. Mr. Carroll previously worked with the EPA as Chief of the Regional Liaison Section I, Div. of Stationary Source Enforcement.

The Harshaw Chemical Co. has named **Donald H. McBride** Director of Marketing for the Color Dept. Prior to this appointment, he was Chicago Regional Sales Manager for the company. Mr. McBride has been with the company for 22 years. He is a member of the NPCA.



L.L. Thomas



J.F. Lawrence

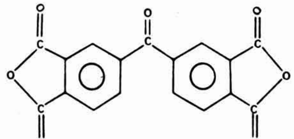
Cargill, Inc., Minneapolis, Minn., has promoted **James F. Lawrence** to Assistant Vice-President of its Chemical Products Div. Mr. Lawrence will continue with his responsibilities as General Manager for resins.

Stanley M. Elman has been promoted to Director, Product Development, for the Specialty Chemicals Div., Lonza, Inc., Fair Lawn, N.J.

Daubert Chemical Co. has appointed **George R. Stevens** President and Chief Operating Officer. **George A. Daubert,** who served as President since he founded the company in 1935, has become Chairman and Chief Executive Officer.

Meanwhile, the following executive promotions have been made: **Clemens A. Hutter** to Executive Vice-President, Paper Div.; **M. Lawrence Garman** to Executive Vice-President/Marketing, Chemical Div.; **William A. Erby** to Vice-President/Research and Manufacturing, Chemical Div.; and **John R. Cosbey** to Vice-President/Finance and Treasurer.

John T. Williamson has been named President of Freeport Kaolin Co., New York, N.Y. He replaces **Edward C. Stebbins, Jr.,** who has become Director of Operations Review for the parent company, Freeport Minerals Co.



People (Continued)

Aluminum Company of America has named **Kenneth L. Millican,** formerly Marketing Manager — powder and pigments, to General Manager of the newly created Powder and Pigments Division. Mr. Millican has held both domestic and international sales and marketing positions with the company, which he joined in 1952. Mr. Millican is a member of Metal Powder Producers' Association, National Paint and Coatings Association, and the Pittsburgh Society for Coatings Technology.

James E. DiGuglielmo has been appointed a sales representative for the specialty chemicals division of ICI Americas, Inc. Based in Houston, Texas, he will be responsible for sale of division products in that region of the southeastern United States.

International Minerals & Chemicals Corp., Des Plaines, Ill., has announced the following key management responsibilities for its Chemical Group: **O. Wayne Chandler,** Vice-President and General Manager, NP Div.; **James A. Wylie,** Vice-President and General Manager, Electrochemicals Div.; **Lyle A. Holmes,** Vice-President and General Manager, Industrial Minerals Div.; **James J. Roveda,** Vice-President and General Manager, Industrial Chemicals Div.; **Paul E. Sullivan,** Vice-President and General Manager, Explosives Div.; **Glen R. Hamrick,** Vice-President and General Manager, Carbon Black Div.; and **Herman Reerink,** Vice-President and General Manager of NYMA in the Netherlands. **Roger E. Secrist** is the IMC Chemical Group President.

Ronald Bolen has been named Advertising and Promotion Manager for Kelco, a division of Merck & Co., Inc. He will be responsible for advertising and public relations activities for the San Diego-based firm.

Robert A. Roland, President of the Manufacturing Chemists Association and Past-President of NPCA, was presented with the Key Award, the highest honor of the American Society of Association Executives. ASAE annually presents the award to its members who have demonstrated the highest qualities of leadership in their associations, industries, and professions, as well as their civic and community activities.

Lawrence Kytassari has been named General Manager—Manufacturing of the Tnemec Co., Kansas City, Mo. He succeeds **J.C. Leslie,** Vice-President, who will devote his full attention to the purchase of raw materials.

The Industrial Chemicals Div. of NL Industries, Inc., Hightstown, N.J., has appointed **James D. Wilson** Marketing Manager, Industrial Paint Chemicals. In his new position he will be responsible for the commercial development of industrial chemicals to paint and ink markets. Mr. Wilson was formerly a Southeast Regional Sales Representative, and is a member of the Piedmont Society for Coatings Technology.

Meanwhile, the division has named **Michael E. Masterson** Marketing Manager, Coatings Chemicals. He was formerly a Midwest Regional Sales Representative for the company's plastics and specialty area.

Dr. George B. Kauffman has received the 1978 Dexter Award for "outstanding contributions to the history of chemistry" at the fall meeting of the American Chemical Society. Dr. Kauffman, Professor of Chemistry at California State University, Fresno, has concentrated his research and publications in the areas of inorganic synthesis, coordination chemistry, and unusual metal oxidation states. Following the award presentation, he delivered an address entitled "Alfred Werner's View of Valence."

Hugo Grayden has been appointed Central Regional Sales Manager for the Industrial Coatings Div. of the O'Brien Corp. He has been with the company for 17 years, serving most recently in the Nason Automotive Div. as OEM Sales Manager. Mr. Grayden has been a member of the Federation of Societies for Coatings Technology for 26 years.

Also, in a series of promotions, the company has named **James J. Kelly** National Sales Manager, Container Coatings Div.; **Albert L. Williams** Industrial Sales Manager, for Washington, Oregon, and Idaho; **Walter E. Gruver** Western Regional Sales Manager, Industrial Coatings Div., headquartered in San Francisco, Calif.; **John K. Lansingh** National Products Manager, Industrial Metal Coatings; and **Sandra Gute** Production Supervisor.

Spencer K. Harris, Technical Director of the William Armstrong Smith Division of Prismo Universal, has retired after nearly 50 years in the paint industry. Mr. Harris entered the industry in 1929 with the Sherwin-Williams Co., Newark, N.J., while attending Pratt Institute in Brooklyn, N.Y., where he graduated in Industrial Chemical Engineering in 1931. After 10 years of industrial development and sales service work, he joined the Frank Bownes Co. (Modene Paint) in Chelsea, Mass. as technical director in 1941. In 1951, he joined the William Armstrong Smith Co., in East Point, Ga., as technical director. Mr. Harris has been a member of the American Chemical Society and active in the Federation of Societies for Coating Technology for many years. He is a Past-President and honorary member of the New England Society and is currently a member of the Southern Society for Coatings Technology and the Gallows Birds. Mr. Harris is one of the organizing and initial members of the Atlanta Section and a past chairman of that Section. He and Mrs. Harris plan to move to the Ft. Meyers area of Florida.

Gerhard J. Pietsch has been appointed Product Manager for Polymer Surfactants and Specialties at Henkel, Inc.

The Sherwin-Williams Co., in an executive realignment, has announced that **Ronald F. Curley,** as Chairman and Chief Executive Officer, will take direct charge of the company's Canadian operations. He will relocate to the Montreal headquarters. Mr. Curley has also been elected a Senior Vice-President of the parent company and will continue to serve on the President's Committee. In the U.S. organization, **William Moonan,** as Senior Vice-President, will direct the operations of the four divisions of the former Coatings Group.

Meanwhile, **Richard A. Mulcahy** has been appointed General Manager of the company's Chicago manufacturing facility. He replaces **Arthur D. Maine,** who has been elected Vice-President, Human Resources.

Mary G. Brodie, formerly Associate Director of the Sherwin-Williams' research center in Chicago, has been appointed Vice-President and Technical Director of Coatings. She succeeds **Harold E. Spitzer,** who will serve as Technical Advisor until his retirement later this year. Ms. Brodie is a member of the American Chemical Society, the Society of Plastics Engineers, and the Cleveland Society for Coatings Technology.

The Rust-Oleum Corp., Evanston, Ill., has promoted **Orville E. Brown** from Senior Chemist to Manager, Coating Products Laboratory. Mr. Brown is a member of the American Society for Testing and Materials and the American Chemical Society. He succeeds **David Campbell,** who has been assigned to the position of Manager, Solvent-Based Coatings, in the company's Research and Development Group.

Duane H. Miller has been appointed Senior Chemist/Technical Manager, Coatings Resins, by Callaway Chemical Co., Columbus, Ga. He will be responsible for the development and marketing of resins for coatings applications. Mr. Miller is a member of the Chicago Society for Coatings Technology and the National Paint and Coatings Association.

The J.M. Huber Corp. has announced the promotion of **Burney Baldwin** to the position of Production Manager and Assistant Operations Manager for the Huber, Ga. operation. Mr. Baldwin has been with the company for 12 years and was previously Mine Superintendent. He is a member of the Society of Mining Engineers of the AIME.

Obituary

Dr. Stanley J. Buckman, founder and chairman of the board of Buckman Laboratories, Inc., died on September 9, 1978. He was 69 years old.

Dr. Buckman received the University of Minnesota's Oustanding Achievement Award in 1951. He was elected a Fellow of the American Association for the Advancement of Science in 1967 and a Fellow of the American Institute of Chemists in 1969. He also held membership in numerous other professional and technical associations, including the American Chemical Society, American Society for Microbiology, American Wood-Preservers Association, Canadian Pulp and Paper Association, Forest Products Research Society, National Paint, Varnish and Lacquer Association, New York Academy of Science, Paper Industry Management Association, Society of American Foresters, Society for Industrial Microbiology, and Technical Association of the Pulp and Paper Industry.

Dr. Buckman is survived by his wife, Mertie W. Buckman, and two sons, Robert H and John D. Buckman.

Literature

Horizontal Bead Mill

A continuous horizontal bead mill for fine wet dispersing and pulverizing applications in the dye, ink, paint, and chemical industries is described in literature now available. Small diameter media filling the grind chamber are agitated by discs rotating on a central shaft, while the horizontal design permits easy access for inspection and cleaning. For more information about the Torrance Roto Mill write Bowers Machine Co., P.O. Box 719, New Cumberland, Pa. 17070.

Solvent-Control System

A 7-page Memo describes the application of a new solvent-control system to industrial paint-drying ovens. The memo provides schematic diagrams and a complete description and an itemized list of the components of the system, which includes temperature and oven-pressure control as well as lower flammable limit control. Application Memo E3.2002-AM can be obtained by contacting Leeds & Northrup Co., North Wales, Pa. 19454.

Colorimeter

A new optical colorimeter that uses sphere geometry for color measurement is introduced in literature now available. The unit is a complete system that allows inter-instrument agreement between colorimeters and between colorimeter and spectrophotometer. Technological advantages are discussed. For further information, contact Marketing Manager, Color Data Products, Macbeth, Little Britain Rd., Drawer 950, Newburgh, N.Y. 12550.

Spectroscopy

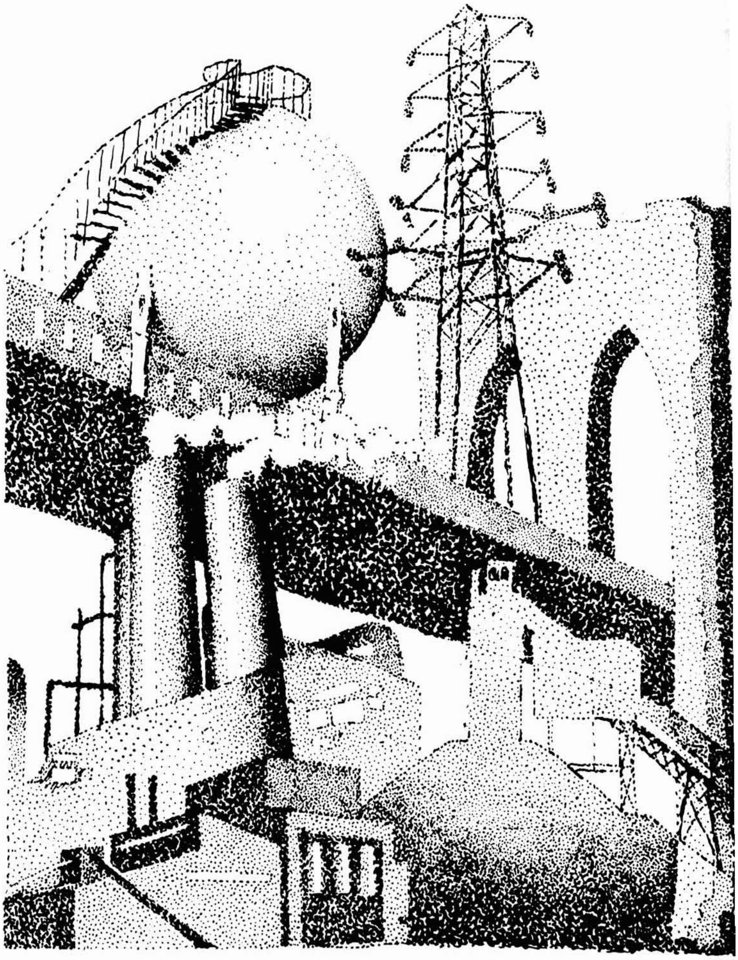
"Advances in Infrared and Raman Spectroscopy, Volume 4," edited by R.J.H. Clark and R.E. Hester, the latest in a series of books, contains articles on fundamental and applied aspects of infrared and Raman spectroscopy. Volume 4 includes chapters on the measurement of optical constants in the infrared by attenuated total reflection, infrared emission spectroscopy, and band shapes and molecular dynamics in liquids. The 320-page book is listed at $44.00, and is available from Heyden & Son Inc., 247 S. 41st St., Phila., Pa. 19104.

Particle Size Monitor

A new monitor designed to provide continuous, on-line measurement of particle size in dry powder streams is described in literature now available. Its operation and uses in such areas as the dry grinding of cement are also covered. For more information about the Microtrac Monitor, write Leeds & Northrup Co., Advanced Business Development Dept., Dickerson Rd., North Wales, Pa. 19454.

Chlorinated Rubber

Thirty typical case histories of maintenance paints made with chlorinated rubber are reviewed in a four-color booklet now available. The literature contains information on surface preparation, application sequence, service life, corrosive environment, and other details. For copies of bulletin 764-22, write to Specialty Chemicals Div., ICI Americas Inc., Wilmington, Del. 19897.



Closed Cycle Drying

A new four-color brochure covers closed cycle flash and fluid bed and spray drying systems designed to fulfill numerous safety, energy and/or environmental considerations. Flow charts illustrate basic variations in closed cycle designs. Copies of the brochure are available from D.L. Partyka, Adv. Manager, Stork-Bowen Engineering Inc., P.O. Box 898, Somerville, N.J. 08876.

Coil Coating

Facts and figures on coated coil, the new engineered material that can be fabricated after finishing, are presented in a new six-page booklet. Highlights include growth of coil coating, what it is and how it is done, major end-use industries and their current tonnage use, coil coating and the environment/energy. "Coil Coating: The Better Way" is available from NCCA, 1900 Arch St., Phila., Pa. 19103.

Antifoams

Literature is available which describes two improved antifoam products designed to prevent foaming of paints, adhesives, and paper coatings based on polymers such as acrylics, latex, and polyvinyl acetate. Further information about PX-31 and PX-108 can be obtained by contacting Hodag Chemical Corp., 7247 N. Central Park Ave., Skokie, Ill. 60076.

Proton and C-13 NMR

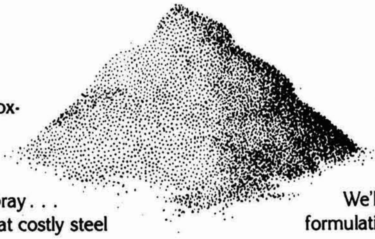
"Proton and Carbon-13 NMR Spectroscopy, An Integrated Approach," by R.J. Abraham and P. Loftus, provides a comprehensive introduction to NMR spectroscopy as it applies to the two most important nuclei studied by this technique. The book begins with a discussion of basic principles, and contains chapters on chemical shift, spin-spin coupling, analysis of NMR spectra, pulse Fourier transform techniques and relaxation mechanisms, and applications of NMR spectroscopy. The book is available at a cost of $13.50 from Heyden & Son, Inc., 247 S. 41st St., Phila., Pa. 19104.

Load Scales

A new line of fabricated steel axle load scales for motor truck weighing is described in literature now available. The pit type scales are available in capacities of 20, 30, and 50 tons. For further information, write Martin-Decker Co., 1928 S. Grand Ave., Santa Ana, Calif. 92705.

Moisture Analyzer

Literature is available which describes a new automatic moisture analyzer which determines the moisture content of organic and inorganic materials. Materials with moisture contact from 0 to 100% can be tested, and final results will be displayed within 7 to 10 minutes when testing material with moisture content of 5 to 20%. Moisture percentage (dry basis) or moisture ratio (wet basis) are displayed on three large digits, and accuracy is guaranteed to ± 0.1% moisture. Further information on Compa-Trac is available from Motorola Process Control., Inc., 1711 West 17th St., Tempe, Ariz. 85281.



Elections

LOS ANGELES

Active

ALEXANDER, CYRIAC P. — Cargill, Inc., Lynwood, Calif.

DREW, ROBERT C. — Guardsman Chemicals, Inc. - P.C. Div., South Gate, Calif.

FULTON, LARRY T. — Ameritone Paint Corp., Long Beach, Calif.

GAYNES, NORMAN I. — Lupton Paint Mfg. Co., Inc. of Arizona, Phoenix, Ariz.

GLEICKE, HERBERT E. — Altawood, Inc., Gardena, Calif.

HARDING, DANA A. — Hughes Paint Co., Los Angeles, Calif.

HASTINGS, JAMES E. — Guardsman Chemicals, Inc. - P.C. Div., South Gate.

HAYAG, POMPOSA B. — Advanced Coatings & Chemicals, Inc., South El Monte, Calif.

JENKINS JR., VERGIL C. — Reliance Universal, Inc., Brea, Calif.

JESSUP, BYRON L. — Jessup Industries, Oceanside, Calif.

LINDROTH, THOMAS A. — Kelco, Div. of Merck & Co., San Diego, Calif.

MARUYAMA, ROBERT T. — Pacific Dispersions Company, Inc., Cudahy, Calif.

MATSUI, KEN — Major Paint & Varnish Co., Torrance, Calif.

MECHAM, LORRIE E. — Advanced Coatings & Chemicals, Inc., Buena Park, Calif.

MILICI, STEPHEN G. — Advanced Coatings & Chemicals, Inc., South El Monte.

MINAMYER, MARK A. — Devoe & Raynolds, Inc., Riverside, Calif.

VAN ZELM, JAN P. — Byk-Mallinckrodt, Redondo Beach, Calif.

VELASQUEZ, ANTONIO A. — Deft, Inc., Chemical Coatings, Irvine, Calif.

WESTPHALEN, DONALD E. — Dutch Boy Inc., Synkoloid, Compton, Calif.

Associate

BENEDICT, DAVID M. — John K Bice Co., Los Angeles, Calif.

DEARMAN, RHODA C. — Uniroyal Chemical Co., Commerce, Calif.

ENGERT, DAVID M. — Nalco Chemical Co., Long Beach, Calif.

GIORDANO, AL D. — Harrisons & Crosfield (Pacific), Inc., Newport Beach, Calif.

MARTZ, SHIRLEY C. — E.T. Horn Co., La Mirada, Calif.

MEARDON, PAUL H. — A.J. Lunch & Co., Los Angeles.

ODUM, MILTON D. — E.I. du Pont de Nemours & Co., Inc., Arcadia, Calif.

WARFE, SHIRLEY R. — Cities Service Co., Fullerton, Calif.

NEW YORK

Active

EHRET, ALLAN T. — E. J. Gaisser, Inc., Stanford, Conn.

KENNY, WILLIAM L. — Pride Solvents & Chemical Co., Inc., West Babylon, N.Y.

KLEVEDAL, OLE M. — O.K. Chemical, Inc., Brooklyn, N.Y.

RYBNY, CHARLES B. — Penn Color, Doylestown, Pa.

TRACTON, ARTHUR A. — National Starch & Chemical Corp., Bridgewater, N.J.

Associate

BOGNAR, DAVID B. — The Goodyear Tire & Rubber Co., New Brunswick, N.J.

GOLDHAMMER, JOHN A. — Titanium Div., N.L. Industries, Inc., South Amboy, N.J.

TIGNER, ROBERT E. — R.E. Tigner & Co., Stamford, Conn.

Book Review

COATINGS TECHNOLOGY ANNUAL, 1978
First Edition

Edited by
M.T. Gilles
Noyes Data Corp.
Park Ridge, N.J.
353 pages
$40.00

Reviewed by
Thomas J. Miranda
Whirlpool Corp.
Benton Harbor, Mich.

This book is a continuation of a series published by Noyes Data Corp. which presents critical reviews of patent literature significant to the coatings industry. This book covers 306 patents issued in 1977. Each patent is covered on a single page in a simple, clear manner devoid of legal jargon. Each patent description is followed by at least one example for preparation of the material.

Topics covered in this textbook include:

- Metal Coatings
- Powder Coatings
- Electrodeposited Coatings
- Radiation Cure Coatings
- Paints, Lacquers and Varnishes
- Fire-retardant and Corrosion Resistant Coatings
- Anti-fungal/Anti-fouling Coatings
- Coatings for Plastics and Glass
- Wood and Paper Coatings
- Specialty Applications

It also includes a company, inventor, and U.S. patent number index. The author claims that this textbook covers material that is not ordinarily found in journal literature, and in that he may be correct. Readers should also know that the data presented cannot be used without proper permission, since it is taken from the patent literature, and therefore, should be used carefully. A disclaimer is published in the back of the book.

The main value of the book is that it is a relatively good update of recent literature and current thinking in the coatings industry for practical finishes. The disadvantage is the high cost of the book, $40, which may limit its use by individuals, but would be good for coatings research libraries and other information centers.

Coming Events

FEDERATION MEETINGS

(Oct. 3-5)—57th Annual Meeting and 44th Paint Industries' Show. St. Louis Convention Center, St. Louis, Mo. (FSCT, Suite 830, 1315 Walnut St., Philadelphia, Pa. 19107).

SPECIAL SOCIETY MEETINGS

(Feb. 12-14)—Sixth Annual Water-Borne and Higher-Solids Coatings Symposium. Hyatt Regency Hotel, New Orleans, La. Sponsored by Southern Society and University of Southern Mississippi. (Dr. B. George Bufkin, Dept. of Polymer Science, University of Southern Mississippi, Southern Station, Box 276, Hattiesburg, Miss. 39401).

(Feb. 28-Mar. 2)—Western Coatings Societies' Symposium and Show. Fairmont Hotel, San Francisco, Calif. (Ed Kevin, The O'Brien Corp., 450 E. Grand Ave., South San Francisco, Calif. 94080).

(Mar. 14-17)—Southern Society Annual Meeting. Dutch Inn, Buena Vista, Fla.

(Mar. 20-21)—22nd Symposium of the Cleveland Society, "Advances in Coatings Technology." Baldwin-Wallace College, Berea, Ohio. (Sid Lauren, Coatings Research Group, Inc. 2340 Hamilton Ave., Cleveland, Ohio 44114).

(Apr. 5-7)—Dallas and Houston Societies. Southwestern Paint Convention. Shamrock Hilton Hotel, Houston, Tex. (Don Webb, Jones-Blair Co., P.O. Box 35286, Dallas, Tex. 75235).

(May 3-5)—Pacific Northwest Society. Annual Symposium. Vancouver, B.C., Canada.

OTHER ORGANIZATIONS

(Jan. 7-12)—National Association of Corrosion Engineers Courses, "Basic Corrosion" and "Corrosion Prevention by Cathodic Protection," Charlotte, N.C. (NACE, P.O. Box 986, Katy, Tex. 77450).

(Jan. 21-24)—ASTM Committee D-1 on Paints and Related Coatings and Materials, Shoreham Hotel, Washington, D.C. (J.H. Bystrom, ASTM, 1916 Race St., Philadelphia, Pa. 19103.)

(Jan. 21-Feb.2)—National Association of Corrosion Engineers Courses, "Basic Corrosion," "Corrosion Prevention by Cathodic Protection," and "Corrosion Prevention by Coatings,"—Jan. 21-26, Amarillo, Tex.—Jan. 28-Feb. 2, Chicago, Ill. (NACE, P.O. Box 986, Katy, Tex. 77450).

(Jan. 31-Feb. 2)—Society of Plastics Engineers, Western Sections RETEC, "Plastics Technology—Recent Developments and Trends." South Coast Plaza Hotel, Costa Mesa, Calif. (John C. Moricoli, West Coast Plastics Equipment, Inc., 7571 Alpine Way, Tujunga, Calif. 91042).

(Feb. 5-9)—Third Annual Gulf Coast Corrosion Seminar. Dunfey's Royal Coach Inn, Houston, Tex. (NACE, 1440 South Creek, Houston, Tex. 77084).

(Feb. 11-14)—"Judd Memorial Conference on Color Metrics," sponsored by Inter-Society Color Council. Williamsburg Lodge, Williamsburg, Va. (S. Leonard Davidson, c/o N L Industries, P.O. Box 700, Hightstown, N.J. 08520).

(Feb. 13-16)—Conference on "Control of Specific (Toxic) Pollutants," sponsored by the Air Pollution Control Association. Hilton Hotel, Gainesville, Fla. (Leo Weitzman, IERL, EPA, Cincinnati, Ohio 45268).

(Mar. 5-9)—30th Pittsburgh Conference on "Analytical Chemistry and Applied Spectroscopy," Pittsburgh Section, Analytical Group, et al., Convention Center, Cleveland, Ohio, (PCAC & AS, P.O. Box 2128, Lower Barrell, Pa. 15068).

(Mar. 12-13)—Conference on "Quality Assurance in Air Pollution Measurement," sponsored by the Air Pollution Control Association. Grand Hotel, New Orleans, La. (Gus Von Bodungen, Air Quality Section, Louisiana Air Control Commission, P.O. Box 60630, New Orleans, La. 70160).

(Mar. 12-16)—National Association of Corrosion Engineers Annual Conference and Materials Performance and Corrosion Show, CORROSION/79. Atlanta Hilton, Atlanta, Ga. (NACE, P.O. Box 986, Katy, Tex. 77450).

(Mar. 22-23)—Coatings - 79: International Symposium on Coatings. Carillon Hotel, Miami Beach, Fla. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont., K6H 5V7, Canada).

(Mar. 27-29)—1979 Industrial Pollution Conference. Philadelphia, Pa. (Alan Krigman, ICON Inc., 211 S. 45th St., Philadelphia, Pa. 19104).

(Mar. 29-30)—International Conference on Spectroscopy. Konover Hotel, Miami Beach, Fla. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont. K6H 5V7, Canada).

(Apr. 1-6)—Pacific Chemical Conference: 1979. Honolulu, Hawaii. (A.T. Winstead, ACS, 1155 - 16th St., N.W., Washington, D.C. 20036).

(Apr. 3-6)—OCCA-31. Oil and Colour Chemists' Association 31st Annual Technical Exhibition. Alexandra Palace, London, England. (The Director & Secretary, Oil and Colour Chemists' Association, Priory House, 967 Harrow Rd., Wembley, Middlesex, HAO 2SF, England).

(Apr. 4-5)—NPCA Marine Coatings Conference. Omni International Hotel, Norfolk, Va. (Georgene Savickas, National Paint and Coatings Association, 1500 Rhode Island Ave., N.W., Washington, D.C. 20005).

(Apr. 19-20)—Second Canadian Chromatography Conference. Hampton Court Hotel, Toronto, Canada. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont. K6H 5V7, Canada).

(Apr. 23-24)—Inter-Society Color Council. Annual meeting. Roosevelt Hotel, New York, N.Y.

(Apr. 25-May 3)—70th Annual Meeting of the American Oil Chemists' Society. Fairmont Hotel, San Francisco, Calif.

(May 7-10)—Society of Plastics Engineers, 37th Annual Technical Conference, "Plastics—Efficient Use of Resources." Hyatt Regency Hotel, New Orleans, La. (SPE, Eugene E. Wilson, 656 W. Putnam Ave., Greenwich, Conn. 06830).

(May 15-17)—Powder and Bulk Solids Conference and Exhibition. The Civic Center, Philadelphia, Pa. (Industrial & Scientific Conference Management, Inc., 222 W. Adams St., Chicago, Ill. 60606).

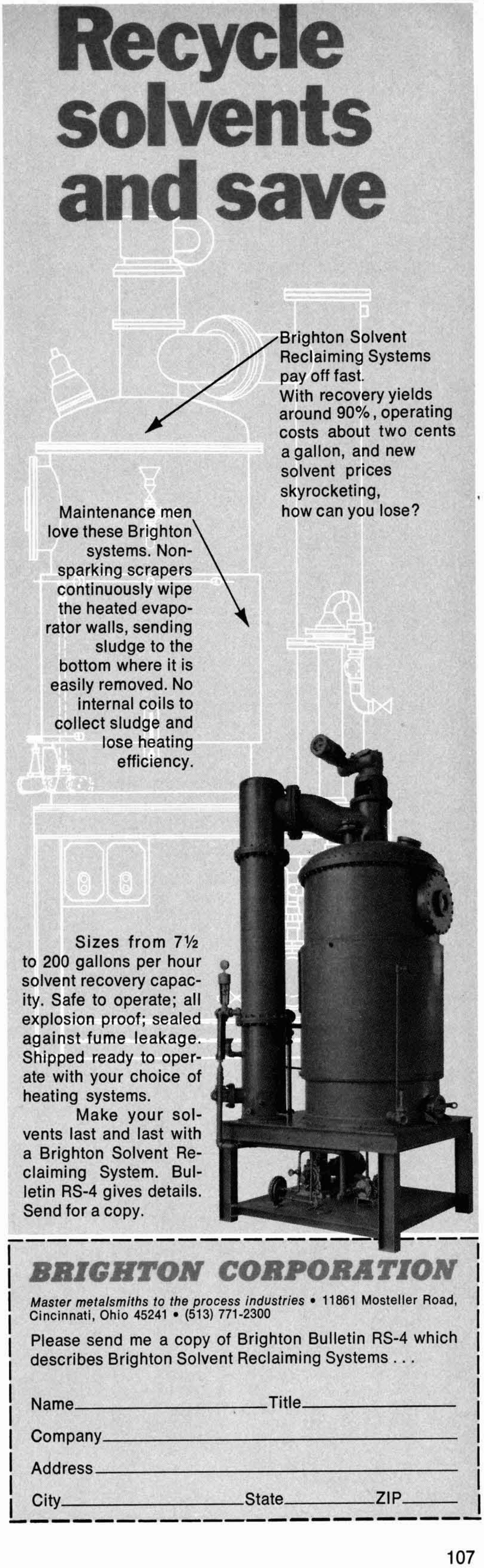
(May 18-19)—International Symposium on "Flammability and Fire Retardants." Maria Isabel Sheraton Hotel, Mexico City, Mexico. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont. K6H 5V7, Canada).

(May 21-25)—"Colloids and Surfaces." Carnegie-Mellon University. (Mrs. Gerry Cohen, Course Coordinator, Post College Professional Education, Carnegie Institute of Technology, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pa. 15213).

(June 10-13)—ASTM Committee D-1 on Paints and Related Coatings and Materials, Shoreham Hotel, Washington, D.C. (J.H. Bystrom, ASTM, 1916 Race St., Philadelphia, Pa. 19103.)

(June 14-15)—Society of Plastics Engineers, European Sections RETEC, "Lastest Improvements in the Development and Processing of Polyolefins." Ghent, Belgium, (Jacques de Craene, RIGI p.v.b.a. Noorderlaan 98/36 2030-Antwerpen-Belgium).

(June 17-20)—Dry Colors Manufacturers Association, Annual Meeting. The Greenbrier, White Sulpher Springs, W. Va. (J.L.



Coming Events (Continued)

Robinson, DCMA, Suite 100, 1117 N. 19th St., Arlington, Va. 22209).

(June 20-23)—Oil and Colour Chemists' Association Conference, "The Challenge to Coatings in a Changing World." Stratford Hilton Hotel, Stratford-on-Avon, England. (The Director and Secretary, OCCA, Priory House, 967 Harrow Rd., Wembley, Middlesex HAO 2SF, England).

(June 25-26 and 28-29)—European Conference on Paints and Coatings, "Eurocoatings-79." Excelsior Hotel, Rome, Italy. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont. K6H 5V7, Canada).

(July 2-3)—World Spectroscopy Conference. Sheraton Hotel, Lisbon, Portugal. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont. K6H 5V7, Canada).

(July 5-6)—World Chromatography Conference. Sheraton Hotel, Lisbon, Portugal. (V.M. Bhatnagar, Alena Enterprises of Canada, P.O. Box 1779, Cornwall, Ont., K6H 5V7, Canada).

(July 17-20)—"Fifth Annual International Conference in Organic Coatings Science and Technology," Athens, Greece. (Angelos V. Patsis Institute in Science & Technolgoy, State University of New York, College at New Paltz, Department of Chemistry, New Paltz, N.Y. 12562).

STATEMENT OF OWNERSHIP, MANAGEMENT AND CIRCULATION

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  President-Elect—James A. McCormick, 900 S. Eutaw St., Baltimore, Md. 21230
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A. Total No. of Copies Printed *(Net Press Run)*	9508	9500
B. Paid Circulation		
1. Sales Through Dealers and Carriers, Street Vendors and Counter Sales	0	0
2. Mail Subscriptions	8943	8947
C. Total Paid Circulation	8943	8947
D. Free Distribution by Mail, Carrier, or Other Means. Samples, Complimentary, and Other Free Copies	132	278
E. Total Distribution	9075	9225
F. Copies Not Distributed		
1. Office Use, Left Over, Unaccounted, Spoiled After Printing	433	275
2. Returns From News Agents	0	0
G. Total	9508	9500

I certify that the statements made by me above are correct and complete. (signed) Thomas A. Kocis, Editor

Advertisers Index

Comparison of Busan® 11-M1 (middle) with zinc phospho oxide (left) and calcium borosilicate (right) in latex emulsion primer. Each primer topcoated with two coats of latex emulsion paint without inhibitor. Panels exposed 200 hours in salt fog cabinet. Panels shown before and after paint was removed.

Comparison of Busan® 11-M1 with zinc chromate in an oil-alkyd primer. Primer on top panel contains 0.7 lb. Busan® 11-M1 per gal. Primer on bottom panel contains 0.7 lb. zinc chromate per gal. Both primers topcoated wth alkyd finish coat without inhibitor. Panels exposed for 10 years.

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. . . or solvent-thinned paints.

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