jct
JOURNAL OF
COATINGS
TECHNOLOGY

*UV CURING
OF ACRYLATE
COATINGS BY
LASER BEAMS*

CHICAGO '84
Annual Meeting
and
Paint Show
CONRAD HILTON HOTEL
OCTOBER 24, 25, 26

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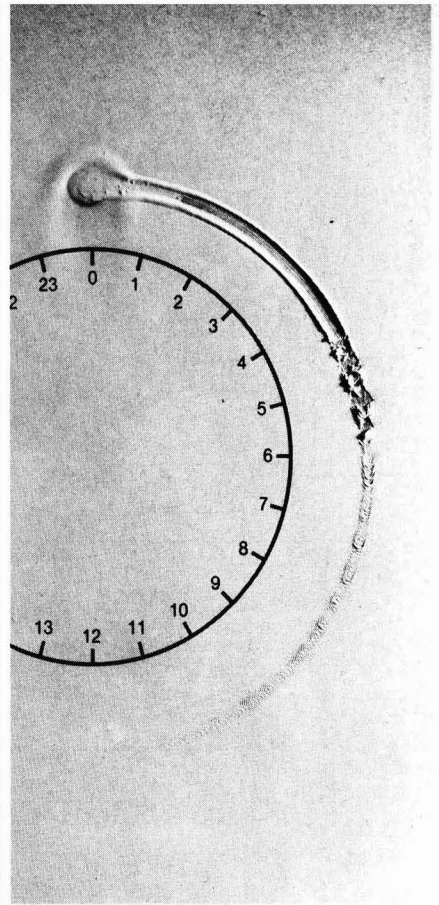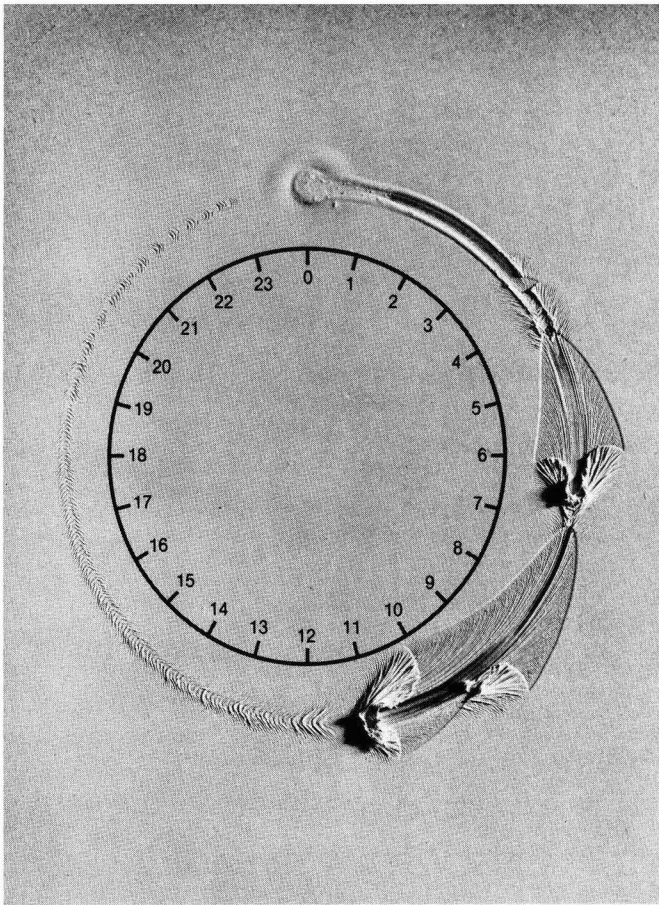
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Comment

Safety Net Cast Again
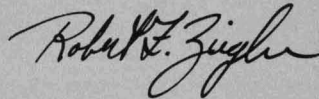
Speaking for the JCT in a "Comment" in the July 1983 issue, Technical Editor Tom Miranda requested readers to submit stories concerning safety-related incidents in the hope of preventing industrial accidents. Unfortunately, his request found little interest, and "Safety Net" made only one appearance in the JCT (Nov. 1983, p. 64).

Meanwhile, in their individual meetings this spring, the four major committees of the Federation (Technical, Manufacturing, Educational, and Publications) discussed the importance of safety and accident prevention in the coatings industry. Each recognized the importance of the topic and each developed their respective plans to address safety during the coming year.

This year we again make the request, not to recount accidents that have occurred, for tragedy serves little purpose, but to submit suggested ways to prevent tragedy from occurring.

From the plant to the lab, there are innumerable accidents waiting to happen—and just as many ways to prevent them. Your safety suggestion may help someone avoid painful injury—or worse.

Please participate.

Robert F. Ziegler,
Editor

Abstracts of Papers in This Issue

UV CURING OF ACRYLATE COATINGS BY LASER BEAM—C. Decker

The kinetics of the laser-induced polymerization of multifunctional acrylate coatings were investigated using I.R. spectroscopy. Both continuous (Ar$^+$) and pulsed (N$_2$) laser emissions in the near UV were used to initiate the curing. The large power output available allows extensive crosslinking to be carried out within a few microseconds. In the presence of air, typical S-shaped kinetic curves were observed; they result from an O$_2$ inhibition effect at the beginning of the laser exposure and from a reduced mobility of the polymer chains in the latter stages. The highest cure speeds were obtained with formulations based on triacrylate monomers, hexaacrylate polyester oligomers and acetophenone-type photoinitiators. The most promising applications of laser curing appear to be in microlithography for the fabrication of semiconductor electronic devices.

Special Feature Issue: Corrosion

Papers to Be Featured in the July Issue

"Resin Structure and the Corrosion Resistance of Organic Coatings: Epoxy-Alkanolamine Resins"—J.W. Holubka and R.A. Dickie, Ford Motor Co.

"Characterization of the Variability in Corrosion Resistance of Steel Using Electrochemical Techniques"—R.G. Groseclose, C.M. Frey, and F.L. Floyd, Glidden Coatings & Resins, Div. of SCM Corp.

"Effect of Zinc Oxidation on the Conductivity and Performance of Di-Iron Phosphide Augmented Zinc-Rich Primers"—N.C. Fawcett, C.E. Stearns, and B.G. Bufkin, University of Southern Mississippi.

"Ellipsometric Studies of Chelating Inhibitor Effects on the Cathodic Delamination of an Organic Coating on Iron"—J.J. Ritter, National Bureau of Standards.

"Pulsed Nuclear Magnetic Resonance Measurement of the Relative and Absolute Linseed Oil Content in Wood"—H. Peemoeller, et al., University of New Brunswick.

"Computer Formulation of Colors for Letterpress"—M.A. Genshaw, et al., Miles Laboratories.

KINETICS AND MECHANISM OF FILM GROWTH FOR THE CATHODIC ELECTRODEPOSITION PROCESS FROM EPOXY RESIN-CURING AGENT LATEXES—M.S. El-Aasser, J.W. Vanderhoff, A. Humayun, C.C. Ho, and M.F. Abdel-Bary

The kinetics of film growth by the cathodic electrodeposition process of a two component reactive latex mixture were investigated at constant voltage. The mass deposited increased linearly with deposition time suggesting an unimpeded film growth. Most of the deposition occurred in two stages: an initial fast growth stage in which the rate of film growth increased with the increase in applied voltage, followed by a much slower rate which represented consolidation of the deposited film. The initial fast growth stage became shorter as the applied voltage increased. The kinetic data can be explained by a concentration accumulation mechanism. According to this mechanism, the driving force for deposition is provided by the applied voltage and a two-layer deposit is formed at the cathode: an inner 'fixed' layer of coalesced latex particles and an outer 'fluid' layer of redispersible particles. The pressure required for initiation of flocculation of particles in the inner layer is determined by the coulombic electrical pressure in the redispersible layer.

INTERNAL STRESS OF CURED EPOXIDE RESIN COATINGS HAVING DIFFERENT NETWORK CHAINS—M. Shimbo, M. Ochi, and K. Arai

Epoxide resin coatings were cured with tertiary amine catalyst, and with aliphatic diamines with and without salicylic acid as an accelerator. The coatings formed a network structure composed of ether, amine, and both amine and ether linkages, respectively. The mechanism for the development of internal stress was investigated in detail for these coatings. For all cured systems, the internal stress was found to increase linearly with increasing shrinkage in the glassy region. Furthermore, both the internal stress and the shrinkage in the glassy region depended on the temperature difference between the glass transition temperature and room temperature. From these results, shrinkage is apparently converted directly to internal stress because the motion of the network segments is restricted in this region. The measured internal stress was in good agreement with the calculated value based on the magnitude of the shrinkage and the modulus of coatings.

THE SIMPLEX MIXTURE SCREENING DESIGN IN COATINGS RESEARCH—K.K. Hesler, J.R. Lofstrom, and J.A. Greenwald

The mixture screening design permits quick and efficient investigation of the effects of a large number of components. Determination of the coefficients of a linear equation model allows the calculation of component effects. With consideration of the component effects, the number of candidate components can be reduced to a reasonable number of essential components. Graphical analysis of the results of a mixture screening design can supplement or obviate the need for the mathematical determination of model coefficients and component effects. The simplex mixture screening design can result in the immediate application of a number of the particular components evaluated, or to the design of more comprehensive mixture studies.

INFLUENCE OF CO-SOLVENTS ON THE FILM PROPERTIES OF WATER-SOLUBLE ALKYDS—Toronto Society for Coatings Technology

The dry retention and pH stability of a water-soluble alkyd resin carried in butyl cellosolve and water was studied for nine months utilizing a variety of driers and methods of addition. Though some loss in tack-free time and film hardness was observed, the most significant observation was that the loss in pH was not a continuous phenomenon. It followed a two stage process, falling rapidly over the first three months, stabilizing for three months, and then continuing to fall from six to nine months.

Solutions of various glycol ethers in water demonstrate a loss in pH both in the presence or absence of amines in under three months suggesting an explanation for the observed discontinuity in pH loss behavior.

Dr. Thomas J. Miranda, of Whirlpool Corp., Will Present 1984 Mattiello Lecture At Federation Annual Meeting in Chicago

The Federation of Societies for Coatings Technology is pleased to announce that Dr. Thomas J. Miranda, Staff Scientist at Whirlpool Corp.'s Elisha Gray II Research and Engineering Center, Benton Harbor, MI, will present the 1984 Joseph J. Mattiello Memorial Lecture at the 62nd Annual Meeting of the Federation, to be held October 24-26 at the Conrad Hilton Hotel, Chicago, IL.

Dr. Miranda will speak on "Reading the Signals of Society: Technology Push or Market Pull," at the morning session on Friday, October 26.

The Lecture commemorates the contributions of Dr. Mattiello, who did much to expand the application of the sciences in the decorative and protective coatings field. Dr. Mattiello, who served as President of the Federation, 1943-44, was Vice-President and Technical Director of Hilo Varnish Corp., Brooklyn, NY, when he died in 1948.

The Lecturer is chosen from among those who have made outstanding contributions to science, and is selected to present a paper on a phase of chemistry, engineering, human relationships, or other science fundamental to paint, varnish, lacquer, or related protective and decorative coatings.

Early Career

Born in Hawaii, Dr. Miranda lived there until the age of 14, when his family moved to California. He attended San Jose State College, receiving a B.A. Degree, as well as a Secondary School Teaching Credential, in 1951. He taught chemistry at San Jose State while studying there for his M.A. Degree, which he received in 1953.

He was employed briefly as a Chemist with Eitel-McCullough, Inc., prior to joining the U. S. Army, where he served for two years.

Research Work

He entered the University of Notre Dame in 1955, as a W. R. Grace Research Fellow, and received the Ph.D. Degree in Organic Chemistry there in 1959.

After receiving his Doctorate, he joined The O'Brien Corp. as Director of Research.

In 1969, he joined the Whirlpool Corp. as Senior Research Material Scientist, and a year later was promoted to his current post of Staff Scientist. His responsibilities include developing and exploiting new material concepts for corporate use, as well as long-range project research in the areas of organic and polymer chemistry.

Over the years, his research studies have included water-soluble polymers, heterogeneous catalysis, oxazoline modified thermosetting acrylics, can coatings, ultraviolet absorbers, thermal analysis, emulsions, stabilization mechanisms of polymers, and radiation curable polymers. This work has resulted in 11 patents, and 45 publications on polymer chemistry and coatings.

His most recent efforts have focused on promoting water-based coating technology to reduce pollution, and on methods for reducing energy consumption in coatings processes.

Author and Lecturer

Dr. Miranda has lectured widely at local and national meetings of various organizations, including Annual Meetings of the Federation and the American Chemical Society, as well as Gordon Research Conferences. He has also lectured at the Universities of DePaul, Detroit, Indiana, and Utah.

He is currently Adjunct Professor of Chemistry at Indiana University, South Bend campus, where he received the M.B.A. in 1980. He is also Chairman of the Executive Lecture Series Committee of the Twin Cities Area Chamber of Commerce in Benton Harbor, MI.

A member of the American Chemical Society, he has served on the Advisory Board of the Organic Coatings and Polymer Chemistry Div. and on the Industrial Engineering Chemistry Product R&D Journal of ACS. He is also a member of American Society for Testing and Materials and Sigma Xi—he is the recipient of the Elisha Gray Award from the Whirlpool Chapter of Sigma Xi, for his outstanding scientific accomplishments.

Dr. Miranda was honored by the Federation with the 1980 George Baugh Heckel Award for his years of service as Chairman of the Publications Committee and Editorial Review Board, and as Technical Editor of the JOURNAL OF COATINGS TECHNOLOGY—positions he has held since 1972.

He was a member of the Federation Board of Directors (1978-80), and has served since 1982 as President of the Paint Research Institute. Currently Co-editor of the Federation Series on Coatings Technology, he has previously chaired the Trigg Awards, Program, Mattiello, and Heckel Awards Committees.

He is a member and Past-President of the Chicago Society for Coatings Technology, and a recipient of their Outstanding Service Award.

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Government and Industry

EPA/DOT Publish Final Rule on Use Of Uniform Manifest for Shipping Hazardous Waste

On March 20, 1984, the Environmental Protection Agency (EPA) and Department of Transportation (DOT) jointly published a final rule mandating the use of a uniform manifest for hazardous waste shipments. This rule is published in the *Federal Register*, pages 10490 through 10510.

This rule, which will make the paper work involved in shipping hazardous wastes less cumbersome, takes effect September 20, 1984. The salient points are listed below.

Under the current regulations, a transporter carrying hazardous waste in interstate commerce must carry manifests from the generating state, the state in which the wastes are being disposed of, and, possibly, a separate state-authorized manifest from every state through which wastes pass. It is possible for a transporter, under this system, to be required to carry as many as 12 different manifests for one shipment. In addition, multistate companies must use different manifests for every generating state, making central record-keeping difficult, if not impossible. Under the new regulation, "DOT's authority will be used to preempt all state manifest requirements so that under no circumstances will more than one manifest be required per shipment." (direct quote).

The new manifests will provide space for additional state-required information beyond the federally required items. States are not precluded from setting up another system of forms to solicit infor-mation not included on the Uniform Manifest form, so long as the system does not interfere with the actual shipment of wastes. While transporters would not be required to carry these forms, generators and treatment, storage, and disposal facility operators (TSD) could still be required to use them. States through which hazardous waste shipments pass are not allowed to place additional information requirements on the transporter as a condition of transportation.

The generator must obtain the blank manifest from the consignment state if that state supplies the form and requires its use; if not, then the shipper must obtain the form from the generator state—if that state supplies the form and requires its use; and, if not, the generator may obtain the form from any source (including printing it himself, so long as it is exactly the same as the form on page 10502 of the *Federal Register*). The form must be on 8½ × 11 in. paper, printed vertically, and contain all the information specified on pages 10497 through 10499 of the *Federal Register* in the order given. If the generator ships only one or two wastes, these products, as well as the EPA number and DOT classification, can be printed on the forms as well as all other information which will remain the same (name, address, EPA I.D. number, etc). Only the signature must be handwritten. Camera-ready copies of the form for printing can be obtained from the State, the EPA regional office, or EPA headquarters.

Sidney J. Rubin
Chairman
Environmental Control Committee

Sherwin-Williams Zinc Oxide Plant Purchased by T.L. Diamond

T.L. Diamond & Company, Inc., New York, NY, has purchased the assets of Sherwin-Williams' zinc oxide manufacturing facility at Hillsboro, IL.

The plant will complement the zinc dust manufacturing operations of T.L. Diamond's Meadowbrook Company Division in Spelter, WV. The company plans to market zinc oxide to the paint, rubber, petroleum, chemical, agricultural and animal feed markets. Raw materials sources will include zinc sludges, skimmings, residues, and concentrates.

Precoated Sheets and Coils to Be Evaluated by Battelle

A study to forecast the future market of precoated sheets and coils and to evaluate the market impact of new products has been proposed by researchers at Battelle Memorial Institute's Geneva Research Centres.

To be sponsored on a multiclient basis, the study is designed to benefit the producers and users of precoated sheets and coils, suppliers of basic materials such as steel and aluminum, producers of coatings and pretreatment chemicals, engineering companies, and equipment manufacturers in the U.S., Europe, and Japan. Products to be studied include general-purpose precoated sheets and coils, including zinc or zinc alloy coated steel; zinc or zinc alloy and organic coated steel; aluminized steel; organic coated steel; and organic coated aluminum.

In carrying out the study, Battelle staff will gather and analyze data on the current status of the industry, identify existing and potential applications, and evaluate the performance of new and existing products. In addition, technological trends and material selection based on a number of case studies will be analyzed. Battelle's quantitative market forecast will summarize all technical and economic trends in various segments of the market through 1995.

The study will be completed in March 1985.

For additional information on participation in the study in the U.S., contact H. Ronald Hamilton, Battelle Memorial Institute, 505 King Ave., Columbus, OH.

Union Carbide to Produce New Paint Thickeners

Union Carbide Corp. has announced the start-up of a new plant for commercial production of associative thickeners at its Specialty Chemicals Div. facility in Bound Brook, NJ.

The new plant, designed by Union Carbide's R&D and Engineering Depts., features a computer-controlled process for manufacturing nonionic, water-soluble urethane associative thickeners and rheology modifiers. The computerized process yields products of high uniformity. These thickeners, which modify rheology through an associative mechanism, add enormous value to formulated latex paints by improving application properties, appearance and durability.

Government and Industry

CMA Panel Urges Greater EPA Consideration Of Glycol Ethers in Rulemaking

In response to the Environmental Protection Agency's Advanced Notice of Proposed Rulemaking on 2-methoxyethanol, 2-ethoxyethanol, and their acetates, the Chemical Manufacturers Association's Glycol Ethers Program Panel urged the EPA to improve its data base before formulating regulatory options.

The panel discussed uses and exposures to the ethylene glycol ethers, interpretations of the extensive available toxicology data base, and possible regulatory options. The Panel stated that a ban on these compounds, which are used in commercial paints and stains and as industrial solvents, is not warrented. It urged the EPA to give further consideration to the widespread use of local ventilation, personal protective equipment and other workplace factors that already control exposure levels and the absence of any significant consumer use of these products, as found by the Consumer Product Safety Commission. In addition, the Panel cited the lack of scientific support for the attempt to quantify low exposure level reproductive risks and the difficulty, time, and expense involved in across-the-board substitution for the ethylene glycol ethers.

The Panel provided EPA with data which showed that actual worker exposure levels are lower than EPA's exposure model predicts and that "no-observed-effect levels" for reproductive effects are, in several cases, higher than those determined by EPA.

The CMA Glycol Ethers Panel was established in 1980 to improve the toxicological data base on ethylene glycol ethers and to cooperate with government agencies and others in reacting to the developing data base. Companies who participated in the preparation of the Panel's comments to the EPA include ICI Americas, Inc.; Olin Corp.; PPG Industries, Inc.; Shell Chemical Co.; Eastman Kodak Co.; Texaco Chemical Co.; and Union Carbide Corp.

Midland Opens Venezuela Facility

Midland Dexter de Venezuela, S.A. (Midevensa), a new facility designed to manufacture Midland's complete line of packaging products, officially opened on March 12 in Los Guayos (Valencia).

Midevensa is a joint venture with Inversiones Clefimar C.A. and the Midland Div., The Dexter Corp. The Midland Div. is a leading producer of specialty industrial coatings, with additional facilities in Europe, Japan, the United Kingdom and Mexico.

Napko Industrial/Marine Renamed Napko Protective Coatings

To avoid confusion regarding the Napko product line, the Napko Industrial/Marine Products Div. of The O'Brien Corp. has been renamed Napko Protective Coatings.

Lou Vincent, Vice-President of the product group stated that the "marine" connotation only covered some of Napko's capabilities. Their product line is also used for a wide range of industrial maintenance applications, including pulp and paper mills and storage tank farms. The new name designation will be incorporated into all future Napko products and literature.

York Castor Oil Co. Acquired by United Catalysts

The York Castor Oil Co., of Westfield, NJ, has been acquired by United Catalysts, Inc., Louisville, KY. The purchase included York's European manufacturing and sale facilities.

Both firms manufacture and market rheological control agents for the protective coating, ink, lubrication, cosmetic and associated industries. York also markets a broad range of castor oil grades and castor oil derivatives. United Catalysts manufactures organophillic clay products based on bentonite clays. The new association will combine expertise of the two firms to maximize service to industries served by both organizations.

Mr. L.J. Jubanowsky, the founder of York, will remain as President. National sales and distribution for both United Catalysts and York will continue in place.

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Government and Industry *(continued)*

PPG Dedicates Headquarters Complex

PPG Industries, Pittsburgh, PA, dedicated its new world headquarters complex, PPG Place, in a ceremony on April 11.

PPG broke ground for the six-building complex on Jan. 28, 1981. PPG Place includes a 40-story office tower, as well as office and retail space in four six-story structures and a 14-story building that surrounds a one-acre public plaza.

PPG established an office in the city in 1883, the year it began manufacturing flat glass at Creighton, PA. Headquarter offices were at the Creighton plant. In 1895, the company moved its corporate offices from the plant to the newly constructed Frick building in downtown Pittsburgh. The headquarters were moved to Gateway Center in 1953.

One PPG Place tower is the first structure built specifically to meet the company's headquarters requirements. It was designed to adapt to growth and continually changing space needs of PPG's operations, and provide cost-effective use of energy. The new structure has enabled the company to consolidate its 1700 headquarter employees at one location from five buildings in the downtown area.

ICI Acquires French Paint Company

Imperial Chemical Industries PLC (ICI) has purchased the Compagnie des Vernis Valentine SA, France.

ICI, one of the world's largest chemical companies, is seeking to broaden its base in the decorative and refinishing sectors of France in which Valentine is the market leader. The Valentine group offers a wide range of paints and varnishes for use in the home, in industry and commerce. Terms of the acquisition were not disclosed.

Toyo Ink Purchases Du Pont's CPC Pigment Technology

Toyo Ink Manufacturing Co., Ltd., of Tokyo, Japan, has purchased technology and related marketing information for copper phthalocyanine (CPC) blue pigment products from the Du Pont Co. Toyo Ink is a leading worldwide producer of CPC pigments.

The acquisition includes technical information, U.S. and international patents, and general sales and marketing information.

George C. Tunis, Director of the colored pigment products division of Du Pont's Chemicals and Pigments Dept., said that the sale is part of the company's planned withdrawal from the colored pigments business. Previously Heubach, Inc. of Newark, NJ, had purchased Du Pont's azo and chromate pigment product lines. CIBA-GEIGY Corp., the U.S. subsidiary of CIBA-GEIGY Ltd., Basel, Switzerland, has agreed to purchase the quinacridone red pigment product line.

Objective of Superfund Should be Waste Cleanup, Not Punishment of Generators, Says NPCA's Thomas

A beefed-up Superfund should be adequate to pay the costs of cleaning up hazardous waste disposal sites without exacting punitive repayments from identified waste generators, Larry L. Thomas, Executive Director of the National Paint and Coatings Association, said during recent Congressional subcommittee hearings.

Testifying before the Subcommittee on Commerce, Transportation and Tourism of the House Committee on Energy and Commerce, Thomas said that hazardous waste sites "must be cleaned up, and cleaned up now." He also contended that a proposed annual tax should be adequate to pay for the cleanups, without attempts to recoup additional payments from generators of waste in the individual sites.

Thomas testified at the request of Rep. James J. Florio (D-NJ), sponsor of a bill (H.R. 4813) to reauthorize the Comprehensive Environmental Response, Compensation and Liability Act, commonly known as Superfund. While calling for annual taxes amounting to $1.8 billion on chemical feedstocks and $600 million on wastes, the bill also calls for joint and several liability on the part of contributors to waste sites.

Noting the EPA has estimated that enforcement actions against generators would only produce from $2 to $44 million annually, Thomas said, "Pursuit of such a relatively small amount through costly, time-consuming negotiation and litigation hardly seems worthwhile." He added that transaction costs such as legal fees for both government and industry could exceed the amount generated for the fund.

He also pointed out that more than half of NPCA's member companies have less than $5 million in annual sales, and said that for small to mid-size companies, the current Superfund enforcement process, which calls for joint and several liability of generators, poses a very real hardship.

If the eventual reauthorization legislation continues to call for recovery of costs from generators, rather than paying all costs from taxes, Thomas asked that at a minimum, the "joint and several liability" provision be deleted in favor of language that would allow contributors to sites to pay their fair share, and only their fair share, of cleanup costs. "If apportioned responsibility were permitted, rather than joint and several liability," he said, "there would be many more voluntary and expeditious site cleanups. This would serve the national interest of preventing problem sites from becoming worse and further jeopardizing the environment and the public."

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1984 ADVANCE REGISTRATION

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY

1315 Walnut St., Philadelphia, PA 19107

Please fill out this form and mail with a check in the correct amount (made payable to the FSCT) to the Federation address shown above. All checks must be payable in U.S. Funds. Any that are not will be returned. DEADLINE DATE FOR ADVANCE REGISTRATION IS SEPTEMBER 17. NONE WILL BE ACCEPTED AFTER THAT DATE.

A $10.00 charge will be made for cancellations received prior to September 17. No refunds will be made after that date.

INDUSTRY REGISTRATION FEES:

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

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Federation Constituent Society

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YOUR COMPANY (CHECK ONE BLOCK ONLY)

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BB ☐ Manufacturers of Raw Materials

CC ☐ Manufacturers of Equipment and Containers

DD ☐ Sales Agent for Raw Materials and Equipment

EE ☐ Government Agency

FF ☐ Research/Testing/Consulting

GG ☐ Educational Institution/Library

HH ☐ Paint Consumer

JJ ☐ Other

YOUR POSITION (CHECK ONE BLOCK ONLY)

KK ☐ Management/Administration

LL ☐ Manufacturing and Engineering

MM ☐ Quality Control

NN ☐ Research and Development

PP ☐ Technical Sales Service

QQ ☐ Sales and Marketing

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SS ☐ Educator/Student/Librarian

TT ☐ Other

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1984 Annual Meeting
Paint Industries' Show
October 24, 25, 26
Conrad Hilton Hotel
Chicago, Illinois

Federation of Societies for Coatings Technology

YE OLDE PAINT STONE
1737

TO OUR MEMBERS AND FRIENDS:

It is a pleasure for me to invite those associated with the coatings manufacturing industry *everywhere* to the Federation's 62nd Annual Meeting and 49th Paint Industries' Show in Chicago, October 24–26.

These significant coatings events have been held in Chicago more than any other city and we are glad to return after a six-year absence.

The theme of the Program Sessions—"Appearance and Protection—Essential to Our Lifestyle"—*recognizes that a thin coating film is the unheralded protector of all surfaces to which it is applied. Dr. Darlene Brezinski directs the Program Committee which is arranging a quality selection of papers, seminars, and other presentations which will address the theme. Speakers will come from throughout the world of coatings science.

The Paint Show grows a little each year and I am proud to say, as have many of my predecessors, that this year's will be the biggest. The exhibit halls of the Conrad Hilton Hotel will be chock full of the traditionally outstanding and colorful exhibits of more than 180 companies.

There will be much to learn and see at the Federation's 1984 big event in Chicago. Please do come.

Terryl Johnson
President
Federation of Societies
for Coatings Technology

FSCT 1984 ANNUAL MEETING AND PAINT INDUSTRIES' SHOW
CONRAD HILTON HOTEL, CHICAGO, ILLINOIS
OCTOBER 24, 25, 26 (Wednesday, Thursday, Friday)
APPLICATION FOR HOTEL ACCOMMODATIONS

MAIL TO:	Fed. Socs. Coatings Tech. 1315 Walnut St.—Dept. H Philadelphia, PA 19107

Please indicate below the type of accommodations requested and choice of hotels. All reservations will be processed by the Housing Bureau of the Chicago Convention & Visitors Bureau. Hotel assignments will be made in accordance with prevailing availability. The Housing Bureau will send you an acknowledgment, noting the hotel to which you have been assigned. The confirmation of your reservation will come to you directly from the hotel, to whom you must direct all inquiries.

All reservations will be held until 6:00 p.m. and none can be guaranteed after September 28.

TYPE OF ACCOMMODATION	NUMBER	RATE REQUESTED
Single (1 person)		
Double (2 persons)		
Twin (2 persons)		
Suite (parlor and 1 bedroom)		
Suite (parlor and 2 bedrooms)		

CHOICE OF HOTELS:
1st
2nd
3rd
4th

NAMES AND ADDRESSES OF ROOM OCCUPANTS AND DATES OF ARRIVAL/DEPARTURE

Type of Room	Name	Address	Dates Arrive	Depart

Please Type Additional Reservations on a Separate Sheet and Attach to This Form

SEND CONFIRMATION FOR ALL RESERVATIONS TO:

Name_____

Company_____

Address_____

City _____ State or Province _____

Country _____ Mailing Code _____

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Note: Requests for accommodations at the Conrad Hilton will be limited to five rooms per company. A parlor counts as one room.

HOTEL INFORMATION AND RATES

All Room Rates Are Subject to a City and State Tax of 9.1%.

Hotel	Singles	Doubles Twin	Parlor & 1 Bedroom	Parlor & 2 Bedrooms
*Conrad Hilton	65-71-82-86-97	81-97-98-102-113	100 to 355	255 to 475
*Conrad Hilton Towers	82-102	98-118	"	"
Americana Congress	55	65	85 to 300	175 to 400
Continental	70	85	175 to 240	240 to 450
Essex Inn	46-54-60-66	56-64-70-76		
Hyatt Regency	94-104-114-124	109-119-129-139	175 to 525	275 to 625
McCormick Center	68-78-86-96-104	80-90-98-108-116		
†Palmer House	75-90-105-115-130	95-110-125-135-150	165 &up	395 & up

 * Requests for accommodations at the Conrad Hilton will be limited to five rooms per company. A parlor counts as one room. Additional reservations will be assigned to other cooperating hotels.

 † Reservations for the Palmer House will be accepted for arrival beginning Wednesday only.

CHICAGO '84
FSCT
Annual Meeting
and
Paint Show
CONRAD HILTON HOTEL
OCTOBER 24, 25, 26
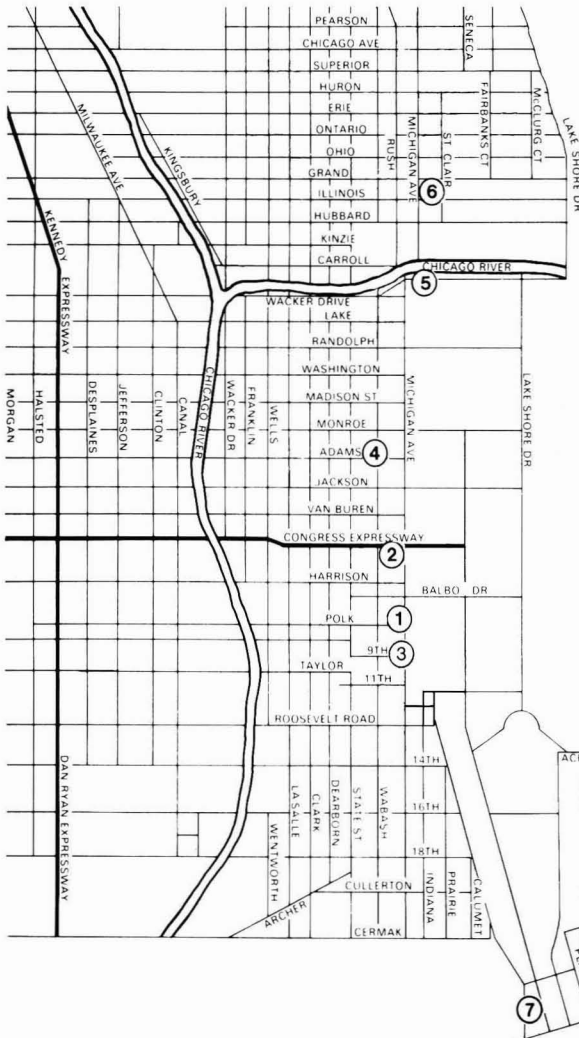
DOWNTOWN MAP CHICAGO

1 Conrad Hilton
2 Americana Congress
3 Essex Inn
4 Palmer House
5 Hyatt Regency Chicago
6 Continental
7 McCormick Inn

UV Curing
Of Acrylate Coatings
By Laser Beams

Christian Decker
Université de Haute-Alsace*

The kinetics of the laser-induced polymerization of multifunctional acrylate coatings were investigated using I.R. spectroscopy. Both continuous (Ar⁺) and pulsed (N₂) laser emissions in the near UV were used to initiate the curing. The large power output available allows extensive crosslinking to be carried out within a few microseconds. In the presence of air, typical S-shaped kinetic curves were observed; they result from an O_2 inhibition effect at the beginning of the laser exposure and from a reduced mobility of the polymer chains in the latter stages. The highest cure speeds were obtained with formulations based on triacrylate monomers, hexaacrylate polyester oligomers and acetophenone-type photoinitiators. The most promising applications of laser curing appear to be in microlithography for the fabrication of semiconductor electronic devices.

INTRODUCTION

The photopolymerization of multifunctional monomers is known to be a convenient and very efficient method to produce highly crosslinked polymers.[1-3] These insoluble materials are mostly used as decorative and protective coatings because of their remarkable mechanical and optical properties, together with their excellent resistance to chemical attack and weathering. Crosslinking-poly-merization also allows production of high-resolution relief images in polymeric films and has, therefore, found new applications in microlithography. The main reason for the fast development of UV curing over the last decade lies in the outstanding advantages of this technique with respect to the conventional thermal treatment: a much higher cure speed, a lower energy consumption, reduced solvent emissions and an improved product quality. The source of UV radiation most commonly used is the medium pressure mercury lamp which can operate at 80 W per linear centimeter for over 2000 hours; power densities of 30 W/cm^2 are easily reached in UV curing equipment by means of semi-elliptical focusing reflectors. If needed, higher light-intensities and, therefore, higher cure rates, can still be attained by replacing the mercury lamps by powerful lasers that emit in the UV range and that are now commercially available.

Lasers have several advantages over conventional light sources that make them very attractive for curing applications: (1) a narrow wavelength spread,which can be matched with the maximum absorption of the photoinitiator thus making laser curing an energy efficient process; (2) a very large power output that induces an instantaneous polymerization of the photoresist; and (3) a spatial coherence of the emission which contributes to the high directivity of the laser beam and permits sharp focus of the light-pencil down to a tiny spot with a diameter of a few microns. In consideration of the limited area that can be treated by laser beams, the most likely applications of laser curing should concentrate in the field of high-definition photoimaging for the manufacture of microcircuits or microprinting plates. Several authors have already examined the feasibility of this new technique and its potential application in semiconductor microlithography.[4-10] Here we present new kinetic results
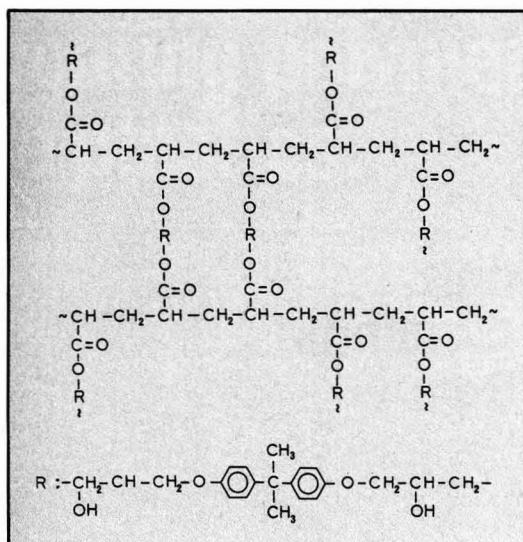
Figure 1—Chemical structure of an epoxy-acrylate network formed by crosslinking-polymerization

on the curing of multiacrylate photoresists that were induced by laser irradiation carried out on a continuous or pulsed wave mode.

EXPERIMENTAL

The photosensitive resins used in this work consisted of three main components:

(1) A triacrylate monomer acting as a reactive diluent—trimethylolpropanetriacrylate (TMPTA) or pentaerythritoltriacrylate (PETA)—both from UCB.

(2) A multiacrylate oligomer containing three possible types of backbone chain—a polyurethane (Actilane® 20 from SNPE), an aliphatic polyester (Ebecryl® 830 from UCB), or an epoxy chain derived from bis-phenol A and epichlorohydrin (Ebecryl® 605 from UCB).

(3) A photoinitiator selected among the following: Irgacure® 184 and Irgacure® 651 from CIBA-GEIGY; Darocure® 1173 and Darocure® 1664 from Merk; 2-chlorothioxanthone (CTX) and dodecylthioxanthone (DTX) from Sherwin-Williams; benzophenone and benzoquinone from Aldrich.

The photosensitive formulations contained equal proportions of monomer and oligomer, and 5 to 10% of photoinitiator with the amount used depending on the film thickness and on the type of photoinitiator used. These multiacrylate systems undergo very rapid polymerization under laser irradiation with formation of an insoluble network. Thus, they can be used as negative photoresists.

The resin was applied as a uniform layer of 10 to 20 μm thickness on a quartz plate or on a NaCl disk and exposed for a short time to the laser beam. Two types of laser were employed:

First, an argon-ion laser (Spectra Physics, Model 170) tuned to its emission lines at 363.8 nm or at 488.0 nm; the maximum power available in the continuous wave (cw) mode was 80 mW and 5 W, respectively; the corresponding light-intensity (I_o) of the unfocused laser beam was calculated to be 1.2×10^{-5} E*s^{-1} cm^{-2} for the emission line in the UV range and 1.02×10^{-3} E s^{-1}cm^{-2} for the green blue emission line. For imaging applications, the laser beam was focused by means of a microscope objective down to a cross-section of a few microns; the light-intensity increases accordingly to attain extremely high values: 0.24 and 20.4 E s^{-1}cm^{-2} for a 10 μm spot of the laser emission lines at 363.8 and 488 nm, respectively.

The second type of laser used was a pulsed nitrogen laser (Sopra 804 C) which has a coherent emission at 337.1 nm. The output power of the pulse, 8 ns wide, was tunable between 0.05 and 0.6 MW; the instantaneous light-intensity was evaluated to be 1.45 E s^{-1}cm^{-2}, at the maximum. The laser was operated in a multiple pulse mode at repetition rates in the range of 6 to 20 Hz.

The fraction (f) of the incident laser radiation absorbed by the sample was determined from the optical density of the coating at the wavelength of the considered laser emission; f varies between 0.05 and 0.63, depending on the film thickness e, the type of photoinitiator used and the concentration of the latter. The number of photons absorbed by the coating per time unit (I_a) was calculated from the equation:

$$I_a \ (E \ L^{-1}s^{-1}) = \frac{10^7 \ f \ I_o \ (E \ s^{-1}cm^{-2})}{e_{(\mu m)}} \qquad (1)$$

For the emission in the UV range, I_a values were typically in the order of 1 E L^{-1}s^{-1} for the unfocused argon ion laser beam, 10^4 E L^{-1}s^{-1} for the focused beam (spot of 10 μm), and 10^5 E L^{-1}s^{-1} for the pulsed nitrogen laser.

The extent of the cure of the photoresist was evaluated quantitatively either from the thickness of the insoluble polymer film, which is recovered on the quartz plate after laser exposure and solvent development, or from the decrease of the infrared absorption of the reactive double

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*1 Einstein (E) = 6.02×10^{23} photons.
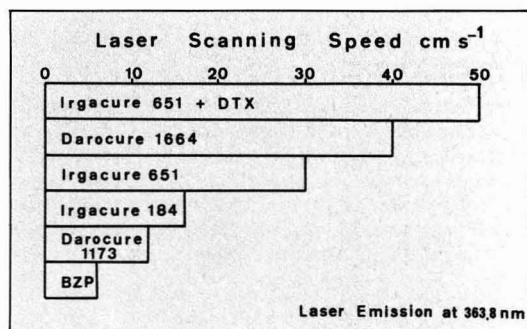
Figure 2—Influence of the photoinitiator on the scanning speed in the UV curing of an epoxy-acrylate photoresist by an argon-ion laser beam (λ = 363.8 nm)

bond at 810 cm^{-1}. The amount of acrylate function polymerized or of crosslinks formed was then calculated from the initial acrylate concentration of the formulation ($[A]_0 \simeq 8$ mol L^{-1}) and from the ratio of the optical densities at 810 cm^{-1} before and after irradiation. S values correspond to the scanning speed at which 50% conversion is attained.

BASIC PRINCIPLE OF CROSSLINKING-POLYMERIZATION

UV curable systems always contain a photosensitive molecule that, after becoming electronically excited by illumination, yields reactive species which in turn initiate a polymerization or crosslinking process by reacting with the substrate. If each monomer or oligomer molecule contains more than one reactive double bond, the polymerization will proceed simultaneously in the three directions to give ultimately a polymer network of infinite molecular weight and very high crosslink density (up to 10 mol L^{-1}). The chemical structure of such a network is schematically represented in *Figure* 1 for an epoxy-diacrylate oligomer.

It is apparent from this figure that the network chain length, i.e., the number of chain links between two consecutive branch joints in the network, is very short in these tightly crosslinked coatings. Its value is only 2 if the crosslinks considered are located on the same growing polymer chains, and 22 if they are located on two different polymer chains. The average molecular weight between crosslinks was, therefore, calculated to be 170 for a completely crosslinked material. Because of their extremely high branch densities, UV cured coatings exhibit
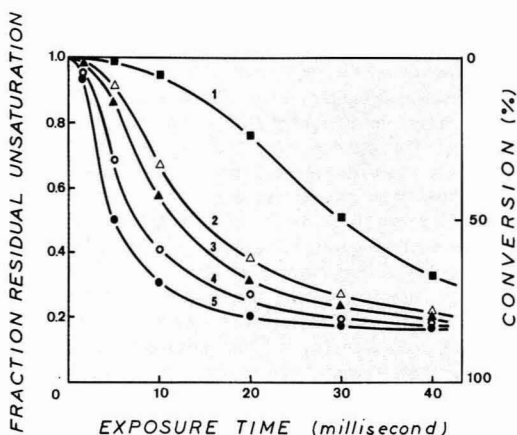
Figure 3—Kinetics of the polymerization of an epoxy-acrylate photoresist (Ebecryl 605 + TMPTA) under laser irradiation at 363.8 nm in air. Influence of the photoinitiator (5%): (1) Benzophenone, (2) Darocure 1173, (3) Irgacure 184, (4) Irgacure 651, (5) Irgacure 651 + 2-CTX

properties that are quite different from those of conventional networks formed by a coupling reaction of two polymer radicals. In particular, there will be no swelling by the solvents used for the development in photoimaging and the contrast is therefore markedly improved. The network formation is also developing faster in this polymerization process, which means higher sensitivity and shorter exposure times than are obtained for conventional photocrosslinking. Typical values of some characteristic parameters are given in *Table* 1 for both types of networks.

CURING WITH UV-LASER RADIATIONS

Unfocused Laser Beam

When the coated photoresist is exposed to the 25 mW beam of an argon ion laser emitting in a c.w. mode at 363.8 nm, the crosslinking-polymerization develops rapidly, once the initial induction period due to oxygen inhibition is over. For the epoxy-acrylate formulation containing Irgacure 651, 85% of the original resin deposit was recovered as insoluble polymer after 5 ms of exposure to the unfocused laser beam; it was previously shown that half of the acrylate functionality has then polymerized.[8] Complete insolubilization usually requires up to 10 ms of irradiation. The laser scanning speed (S) was found to vary between 6 and 50 cm s^{-1}, depending on the formulation and primarily on the type of photoinitiator used, as described in *Figure* 2. The formulation which appears to be the most sensitive to the laser emission line at 363.8 nm contains as photoinitiator, Irgacure 651, in combination with a thioxanthone derivative.

By monitoring the disappearance of the acrylate unsaturation upon laser exposures, the kinetics of the photopolymerization may be followed accurately. *Figure* 3 shows the reaction profile for an epoxy-acrylate

Table 1—Comparison of Conventional and Crosslinked-Polymerized Networks

Process	Conventional Crosslinking	Crosslinking-Polymerization
Reaction	$P^{\bullet} + P^{\bullet} \rightarrow P - P$	$P^{\bullet} + {}_nM \rightarrow P^{\bullet}{}_n$
Structure		
Crosslink distribution	Randomly	Along a chain
Number of branches	4	3
Crosslink concentration (mol L^{-1})	<0.5	2–10
Degree of crosslink[a] (Γ)	1 to 100	10^5
Number-average molecular Weight between crosslinks ($\overline{M}_n)_c$	>3000	100–500
Contrast (γ)	<1	$\geqslant 2$
Cure speed (m s^{-1})	<1	up to 10

(a) Number of crosslinked monomeric units per primary chain or per initiating radical.

photoresist (Ebecryl 605 + TMPTA) containing different types of photoinitiator at a concentration of 5%. The induction period observed in the early stages disappears if the irradiation is performed under N_2 blanketing and can, therefore, be attributed to the well-known inhibition effect of the oxygen dissolved in the formulation. Diffusion of air during the exposure is not expected to play a significant role in consideration of the very short exposure times to the laser beam (a few ms). The rate reduction observed in the latter stages results from the gelation of the resin which greatly restricts the chain mobility, thus preventing free access of the acrylate double bonds to the reactive sites. Therefore, the amount of residual unsaturation in the cured coating is strongly dependent on the crosslink density of the network as well as on the flexibility of the oligomer chain. The fraction of remaining acrylate double bonds in the laser-irradiated photoresist is typically on the order of 30% for epoxy-acrylate + TMPTA formulations, but goes down to 10% for polyurethane acrylates; it can even drop to almost 0%, i.e., a 100% conversion, by using monofunctional monomers such as ethyl-diethyleneglycol monoacrylate (EDGA).

The rate of polymerization (R_p) was evaluated from the maximum slope of the kinetic curves that is usually reached for conversions between 20 and 40%. Values of R_p are typically in the range of 150 to 1300 mol $L^{-1}s^{-1}$, depending on the photoinitiator and oligomer used. The polyurethane was found to be slightly less reactive than the epoxy (Ebecryl 605) which in turn is less reactive than the polyester (Ebecryl 830). By taking into account the amount of light absorbed by the photoresist (I_a), it is then possible to evaluate the quantum yield of the polymerization (Φ_p), i.e., the number of acrylate groups which have polymerized for each photon absorbed by the coating:
$\Phi_p = R_p / I_a$.

The importance of the chemical amplification in those negative photoresists can be deduced from the values of

Figure 4—Dependence of the scanning speed on the diameter of the laser beam in the UV curing of a polyester-acrylate photoresist under 363.8 nm laser irradiation

Φ_p that happened to be all confined in a limited range: 560 to 800 mol E^{-1}. It thus appears that, despite the high rate of initiation provided by the laser beam, the curing proceeds extensively in those multifunctional systems since each photon absorbed can create up to 800 crosslinks. Furthermore, the relatively small variations of Φ_p values indicate that the various formulations studied have quite comparable intrinsic photoreactivities. Therefore, the large changes in rate of cure as illustrated by Figures 2 and 3 result essentially from the differences in the fraction of laser light absorbed by the coating, i.e., in the absorbance of the photoinitiator at 363.8 nm.

Focused Laser Beams

Much larger rates of cure can be reached if the laser beam is sharply focused by means of a microscope objective. With a $10\,\mu m$ laser spot for instance, the power density increases to 20 kW cm^{-2} and the incident light-intensity reaches 6×10^{-2} E $s^{-1}cm^{-2}$. Under those conditions, the exposure time drops into the microsecond range while the laser scanning speed (S) increases to a few meters per second. By using the most sensitive formulations that consist of polyester- or epoxy-acrylate oligomers and acetophenone-based photoinitiator systems, S was found to exceed 10 m s^{-1}. If an even faster curing is required for some specific applications, one can still act, first, on the power of the laser emission which can be increased from 10 to 80 mW and, secondly, by even more sharply focusing the laser beam down into the micrometer or submicrometer range. It is thus possible to obtain high resolution relief images by drawing the microcircuit directly with the laser beam onto the photoresist coated wafer.

Such a large increase of the scanning speed by focusing of the laser beam was actually unexpected since, if the polymerization rate were proportional to the square root of the light-intensity, as for conventional free-radical photopolymerizations, S should not depend on the diameter of the laser beam. Indeed, S is related to R_p by the equation:

$$S = \frac{d}{t_1} = \frac{2d \cdot R_p}{A_o}$$

where d is the diameter of the laser spot and t the exposure time. If $R_p = k_1 I_0^{0.5}$, then S should be proportional to $I_0^{0.5}$. Since the light-intensity is defined as the flux of photons that passes through a given surface per unit of time, it will vary as the reciprocal square of the beam diameter: $I_0 = k_2 / d^2$ for a given power output. Consequently, it follows that:

$$S = d\, k_1\, I_0^{0.5} / A_o = k_1\, k_2^{0.5} / A_o$$

and the scanning speed should thus be independent on d, i.e. on the sharpness of the focusing.

Experimentally, we found that the scanning speed increases steadily when the diameter of the laser beam was reduced, as shown by the log-log plot of Figure 4 and by Table 2. This result implies that the usual half-order kinetic law ($R_p \sim I_0^{0.5}$) is not valid for these crosslinking polymerizations. The observed dependence of S on the size of the laser spot, $S \sim d^{-0.7}$, together with the still large
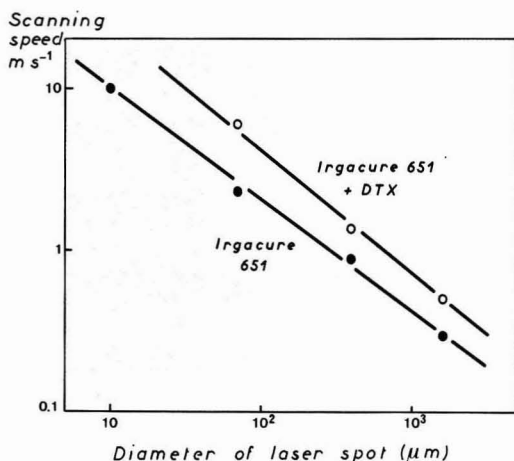
values of Φ_p (500 mol E^{-1}) despite the four orders of magnitude increase of the light-intensity, indicate a close to first-order kinetic law between R_p and I_o : $R_p \sim I_o^{0.5}$. Thus it is reasonable to believe that, in the polymerization of these multifunctional monomers, the termination of the growing polymer chains occurs by a unimolecular process rather than by the usual bimolecular reaction of polymer radicals. The most feasible pathways are now being investigated.

CURING WITH VISIBLE-LASER RADIATIONS

One of the limitations of lasers emitting in a continuous wave mode consists in the relatively low energy outputs available in the UV range. For the argon-ion laser, the most intense emission lines are located at 488 and 514.5 nm; the maximum power output of each of these lines was 5 W for the type of laser that we employed, compared to only 80 mW for the 363.8 nm emission line. Since the most efficient photoinitiators commonly used in the UV curing of coatings do not absorb in the visible range, a new type of photoinitiator had to be selected to take advantage of the intense laser emission at 488 nm for inducing the polymerization process. Benzoquinone was chosen because it absorbs in this wavelength region and is known to yield reactive quinone-olefin diradicals upon laser illumination.[11] Furthermore, Castle has recently shown that multiacrylate monomers polymerize effectively in the presence of benzoquinone when they are exposed to the 488 nm emission of an argon-ion laser.[12] These experiments were done in dilute CH_2Cl_2 solution under a dry nitrogen purge and lead ultimately to the formation of an insoluble gel. We carried out a similar work, on our epoxy-acrylate and polyester-acrylate photoresists, but in the condensed phase and in the presence of air.

In 5% benzoquinone, the $10 \mu m$ thick film absorbs only a few percent of the laser incident light. But because of the tremendously high power density, 3 MW cm^{-2} for the focused beam, it proved to be sufficient to initiate the crosslinking-polymerization of both photoresists; this visible-curing was completed within a few milliseconds and yielded an insoluble polymer. Interestingly, we observed that the addition of a few percent of Irgacure 651 in the formulation significantly increases the cure rate. Since Irgacure 651 alone was found to be totally
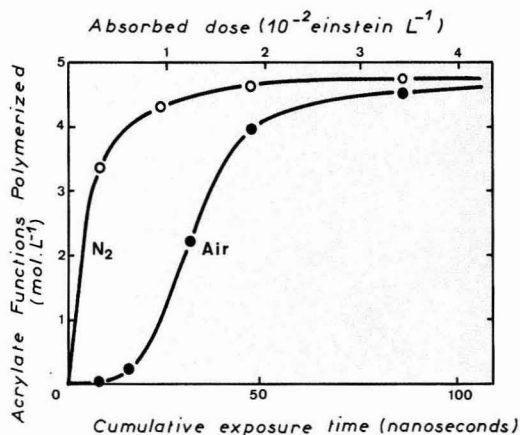
Figure 5—Kinetics of the polymerization of an epoxy-acrylate photoresist under pulsed laser irradiation at 337.1 nm in the presence of air (●) or pure nitrogen (○)

inefficient in promoting the polymerization under 488 nm radiation, this synergetic effect suggests that transfer reactions between benzoquinone and Irgacure 651 are taking place effectively under those conditions.

Quantum yield measurements reveal that the intrinsic photoreactivity of the benzoquinone-based photoresists is still three orders of magnitude lower than the acetophenone-based formulations cured with UV light. This dramatic deficiency is partly overcome by the large power output of the 488 nm emission of the argon-ion laser. Further progress in the curing of coatings by visible-laser radiations can be expected by using photoinitiators that would exhibit both an increased absorbance at 488 nm and an improved efficiency in producing initiating radicals. Current efforts are being directed to this end.

CURING WITH UV-LASER FLASHES

Since the UV curing of these multifunctional acrylates proceeds effectively, even at the extremely high initiation rates provided by sharply focused laser beams, it was tempting to see whether this would hold true when the light-intensity was further increased by several orders of

Table 2—Rates and Quantum Yields of Polymerization in the Laser Curing of Epoxy-Acrylate Photoresists

Argon-Ion Laser (γ = 363.8 nm)	Diameter of Laser Spot d (μm)	Absorbed Light-Intensity I_a (einstein $l^{-1}s^{-1}$)	Scanning Speed S (ms^{-1})	Exposure Time[a] t_i (s)	Rate of Polymerization[b] R_{p_i} (mol $l^{-1}s^{-1}$)	Polymerization Quantum Yield[c] ϕ_p (mol einstein^{-1})
Unfocused	1500	1	0.5	3.10^{-3}	13.10^3	1330
Focused	10	10^4	10	10^{-6}	4.10^6	400

(a) t_i: laser exposure time required for 50% conversion ($t_i = \dfrac{d}{s}$)

(b) $R_p = \dfrac{0.5[A]_o}{t_i}$ with $[A]_o$: initial concentration of acrylate groups

(c) $\phi_p = \dfrac{R_p}{I_a}$

DR. CHRISTIAN DECKER, Màitre de Recherches at the CNRS (France), obtained the Ph.D. Degree in Physical Sciences from the University of Strasbourg in 1967. After a post-doctorate at SRI International (Menlo Park, CA), he worked on radiation-induced reactions in polymer materials at the Centre de Recherches sur les Macromolécules in Strasbourg. Dr. Decker joined the University of Haute-Alsace as a senior Research Chemist in 1975 and has been head of a research group on photopolymers at the Lab. of General Photochemistry in Mulhouse since 1981.

magnitude or if some saturation effect would appear. A similar investigation was therefore carried out by using high-intensity pulses of a nitrogen laser to initiate the polymerization. The 337.1 nm emission line of this laser is particularly well suited to promote the UV curing of the photoresists since it fairly well corresponds to the absorption region of the photoinitiator that leads to radical formation ($n\pi^*$ transition). In addition, nitrogen lasers can deliver large power outputs, up to 1 MW cm^{-2} which may provide the required instantaneous cure. As shown by *Figure* 5, the amount of polymerized acrylate functionality increases steadily with the cumulative exposure time which is now in the nanosecond range. In the presence of air, typical S-shaped kinetic curves were obtained while, under a nitrogen purge, insoluble coatings were formed after only one single laser shot, 8 ns wide. The apparent rate of polymerization, determined from the maximum slope of these kinetic curves, reaches extremely high values, in the order of 10^8 mol L^{-1}s^{-1}. It should be mentioned that these values may be overestimates since our R_p calculations assume that the polymerization occurs only during the 8 ns duration of the laser pulse. Actually it is very likely that some post-polymerization also takes place during the short lapse of time between the laser shot and the infrared analysis. Further investigations are in progress to evaluate the importance of this post-effect.

A remarkable feature of the pulsed laser curing is that the values of the quantum yield of polymerization, inferred from R_p and I_a values, appear to be of the same order of magnitude (~ 400 mol E^{-1}) as when the 10^5 times less intense unfocused argon-ion laser beam was used. This means that the intrinsic reactivity of the multiacrylate photoresists studied is essentially the same, whatever the light-intensity, a result that again suggests a nearly first-order dependence of R_p on the rate of initiation and shows that no saturation effect has yet occurred. Consequently, it will be possible to carry out photopolymerizations at extremely high power densities, without substantial loss of the sensitivity, thus allowing ultra-fast cure of acrylate coatings to be achieved.[10]

To compare the sensitivity of the various photoresists to the pulsed laser emission at 337.1 nm, we measured the threshold energy density E_t, i.e., the amount of incident laser energy which is needed to react one-half of the acrylate double bonds. E_t values are relatively low and fall within the same range as for the 363.8 nm laser emission in the c.w. mode: 6.6 to 27 mJ cm^{-2}, depending on the formulation. For the most sensitive system that consists of Ebecryl 830, PETA, and Irgacure 651 associated to DTX, a thin polymer film appeared after the first laser shot, thus indicating that enough initiator radicals have been produced to overcome the O_2 inhibition effect. By focusing the laser beam down to a 1 mm wide line, all of the formulations studied could be cured in air by a single laser pulse.

SUMMARY

The curing of multiacrylate photoresists can be effectively induced by means of high-power lasers emitting in the near UV range in a continuous or pulsed wave mode. Even though there are extremely high rates of initiation, the crosslinking polymerization is extensively developed. This is apparent from the large values of the quantum yield: up to 800 acrylate double bonds polymerized per photon absorbed. Because the surface covered by the laser beam is relatively small, laser curing is expected to find important applications particularly in the field of microlithography. By using this technique, it is now possible to obtain instantaneously the high-resolution relief images needed for the fabrication of semiconductor microelectronic devices. While nitrogen lasers are likely to be used primarily as powerful UV light sources for projection systems, the potential applications of argon-ion lasers should concentrate on the direct drawing of microcircuits by highly focused laser beams, thus making maskless photoimaging feasible.

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Kinetics and Mechanism of Film Growth For the Cathodic Electrodeposition Process From Epoxy Resin-Curing Agent Latexes

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The kinetics of film growth by the cathodic electro-deposition process of a two component reactive latex mixture were investigated at constant voltage. The mass deposited increased linearly with deposition time suggesting an unimpeded film growth. Most of the deposition occurred in two stages: an initial fast growth stage in which the rate of film growth increased with the increase in applied voltage, followed by a much slower rate which represented consolidation of the deposited film. The initial fast growth stage became shorter as the applied voltage increased. The kinetic data can be explained by a concentration accumulation mechanism. According to this mechanism, the driving force for deposition is provided by the applied voltage and a two-layer deposit is formed at the cathode: an inner 'fixed' layer of coalesced latex particles and an outer 'fluid' layer of redispersible particles. The pressure required for initiation of flocculation of particles in the inner layer is determined by the coulombic electrical pressure in the redispersible layer.

INTRODUCTION

Cathodic electrodeposition is an electrochemical process employed in applying protective coatings on metal substrates. The cationic coating material migrates under

the influence of an external electric field and deposits on the cathode which is the metal object to be coated. Owing to the superior inherent corrosion protection qualities of the cathodically deposited coating over those deposited anoidically,[1] cathodic electrodeposition has recently assumed major commercial significance in the industrial and automotive areas. Most of the fundamental studies of cathodic electrodeposition were carried out on solubilized polymer resin systems.[2] In contrast, information on the kinetics of cathodic electrodeposition of polymer latexes is practically non-existent. Wessling, et al.[3] have reported on the cathodic electrodeposition of quaternary ammonium ion-stabilized latexes; however, the kinetics aspect of the process was not dealt with.

The electrodeposition of solubilized polymer resins differs from that of latexes in that the former coalesce easily upon electrodeposition to form a coherent film which is resistant to the passage of current whereas the latter may give rise to porous, conducting film. It should be noted, however, that one of the first technological applications of the electrodeposition process was from natural rubber latexes, which was reported by Shepard and Eberlin in 1925.[4] Other publications on electrodeposition of rubber from latex suspension can be found from the works of Lond,[5] Klein,[6] Turner and Coler,[7] Beal,[8] and Flint.[9] Early work also included electrodeposition of synthetic rubber latex.[10] These early works have led to the manufacture of rubber-coated articles, such as wires and perforated shaped articles, and rubber gloves by the dipping process.[11]

Recent work initiated in these laboratories has thrown some light on the cathodic electrodeposition behavior of an epoxy latex onto steel substrate.[12] Various factors
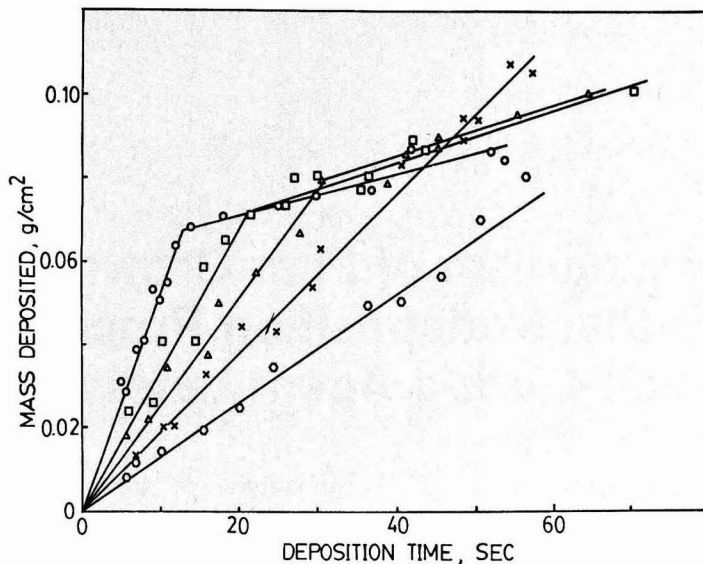
Figure 1—Mass deposited as a function of deposition time for stoichiometric latex mixtures of Epon 1001: Emerez 1511 aged 2¼ hours before deposition at 90 volts (○), 140 volts (X), 180 volts (△), 220 volts (□) and 280 volts (O)

influencing the kinetics of film growth of the above system were also investigated.[13] This paper reports the cathodic electrodeposition of a two-component system comprising mixtures of latexes of epoxy resin and curing-agent. From the kinetic data collected on the deposition and also from insights gained from the one-component

Figure 2—Effect of applied voltage on film growth rate at the initial stage

system, an explanation on the mechanism of film formation for the cathodic process is proposed.

MATERIAL AND EXPERIMENTAL

The epoxy resin used for this work was Epon® 1001 (epoxide equivalent 450–500; Shell Chemical Co.) and the curing agent was Emerez® 1511 (amine value 230–246, Emery Industries). Latexes were prepared from these resins by direct emulsification method.[14] The physical properties of these latexes have been described previously.[12] Stoichiometric mixtures of epoxy resin latex and curing agent latex were aged for 2¼ hours at room temperature before deposition. The resulting mixtures contained 10% solids and were at a pH of 9.4–9.7. Untreated cold-rolled steel plate was used as the cathode and two carbon rods as the anodes. The plates were electro-coated for various periods of time at a constant applied voltage. Details of the experimental set-up and the electrodeposition procedure were published elsewhere.[12] For some of the experiments, a thermocouple probe was positioned very close to the plate inside the deposition bath to monitor the temperature within the film as it was being formed. The response from the thermocouple was recorded as a function of time simultaneously with the current-time curve. After deposition the plate was removed immediately and dipwashed with deionized water, baked at 90°C and weighed to determine the amount of polymer deposited.

RESULTS AND DISCUSSION

Deposition Mass-Time Relationship

The deposition kinetics were followed by observing current flow and extent of film growth as a function of

deposition time at constant applied voltage. The results given in *Figure 1* show that the deposited mass of the films at different applied voltages (viz., 90, 140, 180, 220 and 280 volts) all gave straight line plots when treated as a linear function of deposition time. When the data were replotted against the square root and the logarithm functions of the deposition time, respectively, considerable scattering of data points was noted. In addition, no obvious trend was observed as the applied voltage was varied. Thus it would seem that the data were best described by a linear deposition time dependency. According to Uhlig,[15] a linear relationship indicates that the presence of the film does not affect continued film growth.

The deposition mass versus time plot gave only one growth rate for the entire deposition duration at the low deposition voltages of 90 and 140 volts. At higher applied voltages of 180, 220 and 280 volts, a change in the slope was observed at longer deposition times, indicating a transition to a slower film build-up after an initial steep rise. The film growth rate in the initial stage was strongly dependent upon the applied voltage; the higher the applied voltage, the faster the rate of deposition. This rate varied from 1.28×10^{-3} g/cm^2/sec at 90 volts to 5.30×10^{-3} g/cm^2/sec at 280 volts. This is shown in *Figure 2* which indicates that the relation between the growth rate and the applied voltage is an exponential one and can be expressed as growth rate (initial stage) = $0.65 \times 10^{-3} e^{0.0076V}$ g/cm^2/sec. This expression indicates non-ohmic current density-field strength relation. The second slower growth rate at longer deposition time, as exhibited by deposition at higher voltage, was found to vary within a narrow range of $4.2 \times 10^{-4} - 6.6 \times 10^{-4}$ g/cm^2/sec. The transition to a slower rate at longer deposition time could signify compaction of the coating film after a certain film mass was reached, thereby slowing down further deposition. Compaction only occurred at the higher applied voltages employed.

The initial linear portion of deposited mass versus time plot for each applied voltage was found to pass through the origin indicating that film growth was directly proportional to deposition time. This agrees with previous observations by other workers[16] on anodic deposition of polymer resins where film deposition starts almost instantaneously under constant voltage conditions. In contrast, an induction period has been observed for the deposition of the epoxy resin latex itself.[13] The coulombic efficiency for the present system was found to be independent of the applied voltage and a value of 98.3 mg/coulomb was obtained.

Effect of Current and Applied Voltage

Plots of current density against deposition time at various applied voltages are presented in *Figure 3*. The current density for all the curves decayed towards a common residual current of approximately 7 mamp/cm^2, irrespective of the applied voltage. The drop in current density with time was the steepest for the highest voltage studied. The decrease was more gradual for lower voltages. Thus, deposition at higher voltage offered rapid
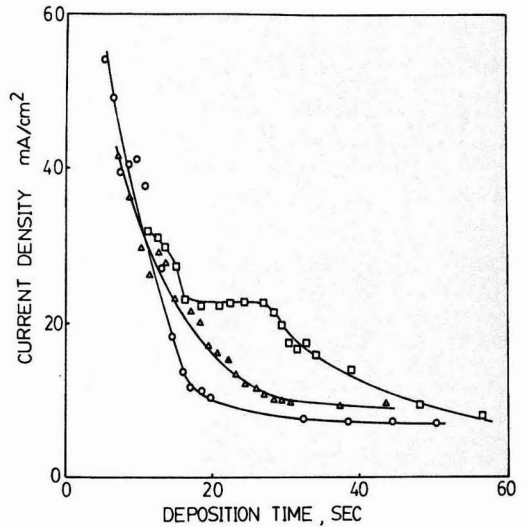
Figure 3—Variation of current density with deposition time for various applied voltages: 180 volts (□); 220 volts (△) and 280 volts (○)

current cut-off as the film became insulating. At an applied voltage of 180 volts or smaller, an initial rapid decrease was followed by a constant current density region before decreasing further, but gradually, towards the residual value. The inverse square of the current against deposition time gave a straight line plot for deposition at 280 volts (*Figure 4*). According to Finn and Hasnip[17] this would indicate a constant specific resistance
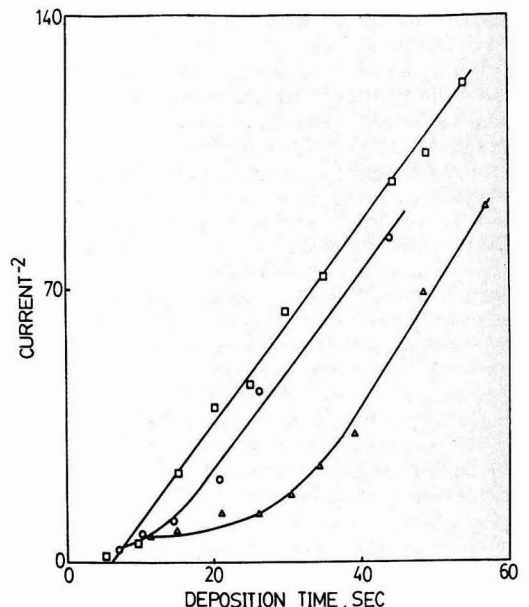
Figure 4—The inverse square of current as a function of deposition time at 180 volts (△); 220 volts (○) and 280 volts (□)
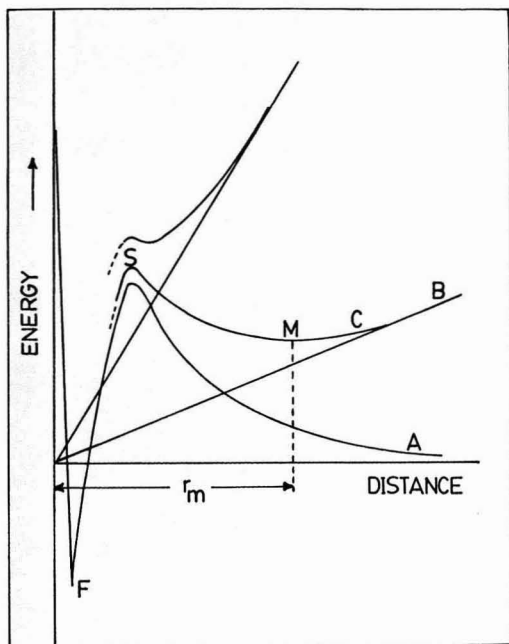
Figure 5—The shape of the potential energy curves during the process of deposit formation

for the film during the entire deposition period. Deviation from linearity became apparent again for the lower deposition voltages. The field strength within the film during deposition was typically ca. 5×10^3 volt/cm which is about two orders of magnitude smaller than those reported for solubilized polymer resins deposited anodically.[18] The current density-field strength relationship was however non-ohmic.

The deposition behavior is a reflection of the chemical and physical nature of the coating bath and the growing film. It is known[19] that partial heterogeneous coagulation would take place in the emulsion form, upon mixing, between the smaller size latex particles of the curing agent and the larger size epoxy latex particles to give even larger globules. Chemical reaction between the epoxide groups and the curing agent at the latex particle surface would begin immediately upon coalescence of the two components. Consequently, the deposition pattern would be determined by the following factors: (a) the relative mobilities of the various charged species present, i.e., epoxy particles, curing agent particles, and the aggregated globules of the two; (b) the degree of physical compaction at the cathode during and after deposition; (c) the extent of the occurrence of crosslinking between the reactive groups on the particle surface during aging and as well as during the course of deposition; and (d) the temperature build-up at the cathode and its effect on the rate of the curing reaction. It is envisaged that at the lower applied voltage a segregation occurred within the thickness of the deposited film as a result of the different rates of deposition of the various species depending upon electrophoretic mobility differences. This may result in

different degrees of physical compaction and non-uniformity in chemical composition across the film thickness. On the other hand, the very much faster rate of deposition under high applied voltage may help to obliterate the mobility differences and result in a more homogeneous film both chemically and physically and a high growth rate, as shown in *Figure* 2. Furthermore, the much higher temperature attained within the film deposited at higher applied voltages had the added effect of increasing the "flow" and fusion of the coalesced particles and the subsequent curing rate of the components. A maximum temperature of 100°C was recorded within the film deposited at 280 volts, whereas the maximum temperature was only 58°C at 180 volts. The maximum temperature was attained within 5–10 seconds from the beginning of the deposition process.

Mechanism of Cathodic Electrodeposition From Polymer Latexes

The latexes used for the present studies were stabilized with adsorbed molecules of hexadecyltrimethyl ammonium bromide, which is a strong basic emulsifier, fully ionized at wide range of pH. The latexes thus prepared were stable against coagulation. An ionic charge destruction mechanism upon deposition commonly encountered by protonated amine-based latexes is therefore not applicable here. Experimental evidence[20] also ruled out the possibility of destabilization of the latex particles at the cathode by electrolyte generated by the attendant electrolysis. Thus, it would seem that an explanation by way of concentration coagulation would be the most suitable at this juncture. This mechanism, also called "accumulation mechanism," was first proposed by Hamaker and Verway[21] for electrodeposition through a
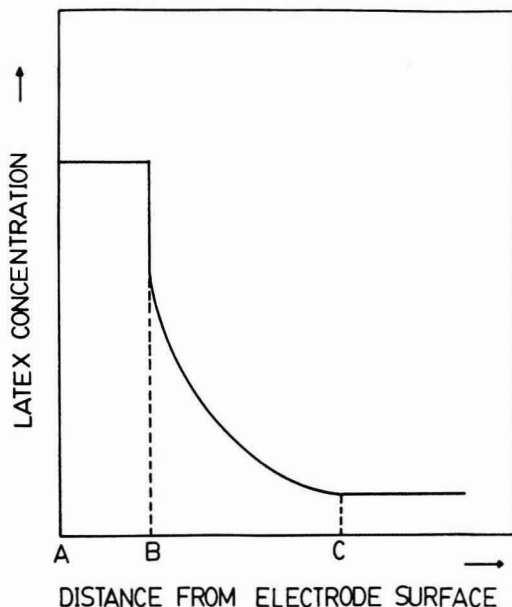
Figure 6—The concentration profile of the latex dispersion next to the electrode during electrodeposition

low-polarity liquid. It draws an analogy between the formation of an adherent layer on the bottom of a container by sedimentation and on an electrode by electrodeposition. The external electric field serves to move the charged particles towards the electrode and to provide a force which presses the particles together on the surface of the electrode in the same way as the force of gravity presses them on the bottom.

For a stable dispersion of latex particles, the electrical repulsion dominates over the attractive van der Waals forces giving rise to an energy barrier to aggregation as indicated by the familiar potential energy curve A in *Figure* 5. The effect of the gravitational force which presses the particles together can be represented by the straight line B through the origin. The energy of interaction of the settled particles would then be represented by the sum of the curves A and B, i.e., curve C. The average distance between the particles in a latex under these conditions is given by r_m at the minimum M of curve C. As more particles settle, the pressure on the lower layers increases as indicated by increasing the slope of the line B. However the difference between the minimum M and the maximum S decreases as the slope increases. Eventually, it may become so small that thermal agitation alone is sufficient to move the particles over S into the primary minimum F, i.e., the particles are withdrawn from the dispersion and deposited in the layer. The mechanism of electrodeposition is then explained by replacing the gravitational pressure by coulombic electrical "pressure".

The concentration gradient that may exist in the electrodeposition bath is illustrated schematically in *Figure* 6. Next to the electrode A is the layer already deposited, as indicated by a region of high but constant concentration. Surface B is where the actual formation of the deposit occurs and the concentration changes discontinuously corresponding to the transition from the deposited layer to the concentrated dispersion. The concentration decreases gradually from B to C and this represents the highly concentrated layer responsible for producing the "pressure" required for the formation of the deposit at B. At C, the concentration becomes equal to the normal concentration of the dispersion. Initially, the particles settling on the electrode are gradually pressed together under the influence of the applied potential. Then layer formation would take place in the discontinuous transition zone from a concentrated dispersion where the average distance between the particles has attained a critical value into a layer in which the particles are in contact. The outcome is a layer of very dense structure. The smaller the critical distance between the particles, the more regular would be the structure of the deposit and the greater its mechanical strength. The mechanical strength of the layer would continue to exist over a long period of time even after the electrical driving force on the particles is stopped. Thus, shaking the deposited layer would only redisperse the outermost layer of particles.

The above mechanism was substantiated by the following experiments. An electrodeposition series was designed for deposition to occur for a fixed duration and to allow the electrocoated plates to remain in the coating
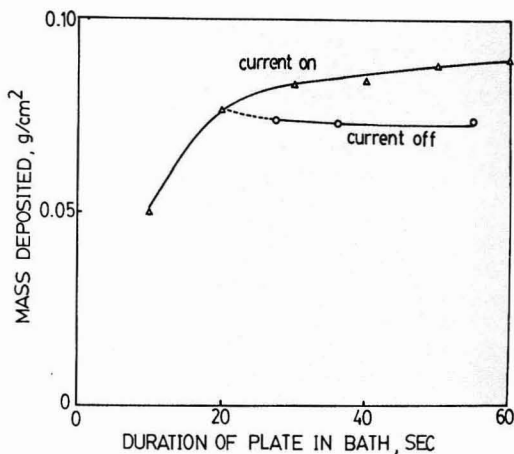
Figure 7—Mass deposited versus duration of plate in the deposition bath

bath (with the current switched off) for further time periods before they were removed, washed, dried, and weighed. It is noted from *Figure* 7 that the mass deposited was higher with increased duration in the case where the electrodeposition was carried out in the usual manner where the plate was removed immediately after deposition without switching off the current. In contrast, the deposited mass decreased with duration when the plates were allowed to stay in the bath after the current had been switched off. The decrease was marked in the first few seconds after the current was switched off but became very slow later. This clearly indicated a partial redispersion of the accumulated latex particles at the plate while it remained in the bath with the power turned off.

The accumulation mechanism also necessarily evoked a desorption followed by a redistribution of the emulsifier molecules originally associated with the latex particles that were deposited. This was borne out by further experiments[20] on the electrodeposition of the epoxy latex which indicated an increase in emulsifier concentration in the serum as latex particles were depleted upon deposition.

These observations together demonstrated that the electrodeposit, in fact, consisted of two parts as outlined above, i.e., an inner "fixed" layer and an outer "fluid" layer, represented by layers AB and BC, respectively, in *Figure* 6. Electrodeposition commenced with an initial deposition of a layer which remained totally fluid until sufficient electrical pressure was exerted to initiate coalescence of the innermost latex particles next to the electrode. Beyond this time, additional particles deposited upon the fluid layer resulted in further coalescence between particles causing the continued build-up of a "fixed" layer adjacent to the deposition electrode.

CONCLUSION

A general feature of cathodic electrodeposition from polymer latexes under constant voltage conditions is that relatively thicker coatings were obtained. These systems

exhibited an initially fast unimpeded film growth followed by a slower consolidation and compaction stage. The growth rate and the extent of the compaction of the resultant film were strongly dependent upon the applied voltage. This is manifested in two seemingly different deposition patterns operative at low and at high applied voltage. Deposition at high voltage produced rapid current cut-off and an insulating film. However the deposition behavior was non-ohmic.

Even though differences between the single component latex system and the two-component reactive latex system were discernible, the overall general trend of the two systems was similar. This is not altogether unexpected, since deposition from a reactive latex mixture is complicated by concurrent heterogeneous flocculation of the mixed latex particles and chemical reaction of the epoxide groups with the amide groups. The rate of agglomeration of the smaller Emerez 1511 particles with the larger Epon 1001 depends on the reactivity of the particles. Chemical reaction begins at the interface of the reactive particles in the agglomerates. Both these factors strongly influence the surface properties of the migrating latex particles and hence the electrodeposition behavior.

The kinetic data are consistent with a non-ionic, concentration accumulation mechanism of film formation. According to this mechanism the latex particles moved towards the cathode under the influence of the applied voltage and formed a two-layer electrodeposit there. The inner "fixed" layer consisted of coalesced particles whereas the outer "fluid" layer redispersed if allowed to remain in the bath after the electrical driving force was removed. The pressure required for initiation of coalescence of particles in the inner layer was determined by the coulombic electrical pressure in the redispersible layer. These observations indicate that film formation from polymer latexes by the cathodic electrodeposition process follows a different mechanism from those operative for the anodic process.

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1,000 X

3,500 X

10,000 X

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Internal Stress
Of Cured Epoxide Resin Coatings
Having Different Network Chains

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Epoxide resin coatings were cured with tertiary amine catalyst, and with aliphatic diamines with and without salicylic acid as an accelerator. The coatings formed a network structure composed of ether, amine, and both amine and ether linkages, respectively. The mechanism for the development of internal stress was investigated in detail for these coatings. For all cured systems, the internal stress was found to increase linearly with increasing shrinkage in the glassy region. Furthermore, both the internal stress and the shrinkage in the glassy region depended on the temperature difference between the glass transition temperature and room temperature. From these results, shrinkage is apparently converted directly to internal stress because the motion of the network segments is restricted in this region. The measured internal stress was in good agreement with the calculated value based on the magnitude of the shrinkage and the modulus of coatings.

INTRODUCTION

Polymeric coatings are widely utilized for decoration and protection in various industrial fields. However, the coatings usually shrink with evaporation of solvents or with curing reaction, and thus internal stress is generated in the coatings. The shrinkage and internal stress causes cracks and other coatings defects. For epoxide resin coatings, many investigators have tried to reduce the internal stress, and have evaluated its magnitude by the bimetallic[1-3] or cantilever[4-6] methods. In most of these investigations, the epoxide resin coatings were cured at room temperature, so that the curing reactions did not

reach an equilibrium state. As a result, the internal stress showed large differences for each investigation, ranging from 5.06 MPa[22] to 0.324MPa[26] for epoxide resin coatings cured with ethylenediamine. Thus, it was important to study the exact shrinkage and internal stress of epoxide resin coatings.

In the previous studies, we measured the shrinkage and internal stress of the bulk epoxide resin by the photoelastic[7] and strain-gauge[8-13] methods. Determined from these studies was the mechanism for the occurrence of internal stress in the bulk epoxide resins cured aliphatic[7,9,13] and aromatic diamines[10,12] or diacids,[8,13] and modified with various fillers[11,12] and liquid rubbers.[10] For the internal stress in the coatings, it is necessary to consider the effect of solvents, reactive diluents, and plasticizers. We have studied the internal stress in solvent-free epoxide resin coatings[14] and in coatings modified with reactive diluents.[15]

On the other hand, we have found from studies on the acceleration mechanism of epoxide resins that some accelerators catalyze selectively the reaction between the specific active groups.[16,18] Consequently, we could form the pure network structures composed of only ester[16-19] or amine[13,20] linkages.

In the present work, the three epoxide resin coating systems composed of amine, ether, and both amine and ether linkages, were prepared by using the selective acceleration technique. The relationship between the internal stress and the chemical structure of these coatings and the mechanism for occurrence of internal stress in the coatings are investigated in detail.

EXPERIMENTAL

Materials

The epoxide resin used was liquid bisphenol-A-type epoxide resin (Epikote® 828, epoxide eq.:190 ± 5, $\overline{M}n$:380).
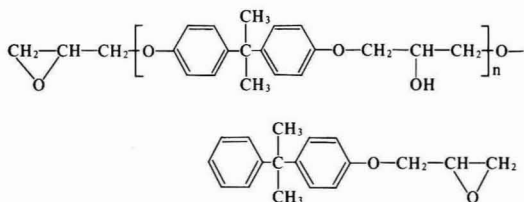
Four aliphatic α,ω-diamines, $H_2N\text{-}(CH_2)_{m'}\text{-}NH_2$, were used as curing agents: ethylenediamine (EDA, $m'=2$); tetramethylenediamine (TMDA, $m'=4$); hexamethylene-diamine (HMDA, $m'=6$); and dodecamethylenediamine (DDMDA, $m'=12$). Tertiary amine, i.e., 2,4,6-tris(di-methylaminomethyl)phenol (TDAMP), was also used as curing catalyst. The accelerator was salicylic acid. The curing agent, catalyst, and accelerator were E.P. grade materials and were used without further purification.

Curing of Epoxide Resin

Resin and curing agents were compounded stoichio-metrically, and in the accelerated systems, 1 phr of salicylic acid was added to the resin. These mixtures were cured at 80°C for four hours and then 180°C for four hours. In the system for which tertiary amine was used as the curing catalyst, 10 phr of amine was mixed with the resin. This system was cured at 80°C for two hours and then 180°C for six hours. It was confirmed for all cured systems that the conversion of epoxide groups could not be changed by further curing.

Measurement

The shapes and the dimensions of specimens for measuring the internal stress of the coatings are shown in *Figure 1*. Aluminum foil (thickness: 200 μm) was used as the substrate. Substrates were cleaned with trichloro-etylene and air-dried. Epoxide resin was applied to one
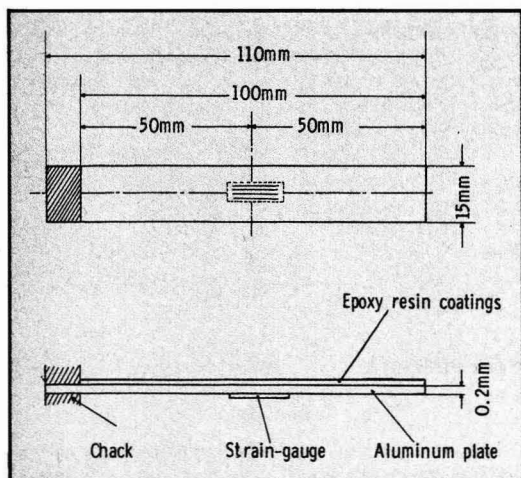
Figure 1—Specimen for internal stress measurement

side of the cleaned substrate, and a strain-gauge (KFC-10-C-11, Kyowa Electric Co. Ltd.) was bonded with adhesives to the other side of the substrate.

As the epoxide resins are cured, the aluminum substrate is subjected to stress, resulting in strain.[4,6,21] The strain of substrate was measured and reduced to the internal stress by using the equation.[22,23]

$$P = \frac{E.h_1^3}{12.bh_2} \cdot \frac{2}{\rho(h_1 + h_2)}\left[1 + \frac{1}{3}(\frac{h_1}{h_1 + h_2})^2\right] \quad (1)$$

$$\rho = \frac{(1 + \epsilon) \cdot h_1}{2\epsilon}$$

Where P is the internal stress and E, ρ, h_1, b, and ϵ are the modulus, the radius of curvature, the thickness, the width, and the strain of the substrate, respectively; h_2 is the thickness of the coating.

The gel content was determined by soaking for 21 days in THF at 25°C.[24] The contents of epoxide and primary amino groups were measured by the method of Bell;[25] the former was determined by applying the pyridine-HCl method for sample powder in the refluxing solvent. The latter was measured by titration of the thiocarbamic acid with 0.2N-NaOH, which results from the reaction of the primary amine group and CS_2. The tertiary amino groups were determined by direct titration with perchloric acid after a preliminary acetylation of the primary and secondary amino groups with acetic anhydride.[26]

Dynamic mechanical properties were measured at 0.3–3.0Hz with a torsion pendulum according to ASTM D 2236-64T.[25] Samples were heated at 1°C/min *in vacuo.*

The concentration of the network chains (ν) was calculated from the equation of rubber elasticity.[27,28]

$$G = \phi\nu RT \quad (2)$$

where G is the shear modulus at the rubbery region (40°C above Tg), ϕ is the front factor, which is unity for ideal rubbers, R is the gas constant, and T is the absolute temperature.

Linear expansion coefficients were calculated from the slope of the plots of sample length versus temperature.

$$\alpha_r = \frac{(l_0 - l_{Tg})}{l_0} \times \frac{1}{180 - Tg} \times 100$$

$$\alpha_g = \frac{(l_{Tg} - l_{25})}{l_{Tg}} \times \frac{1}{Tg - 25} \times 100 \quad (3)$$

Where α_r and α_g are the linear expansion coefficient in the rubbery and glassy regions, l_0, l_{Tg}, and l_{25} are the sample length at curing temperature (180°C), glass transition temperature (Tg), and room temperature, respectively.

RESULTS AND DISCUSSION

Network Structure
Of Cured Epoxide Resin Systems

The gel content and the chemical conversion of epoxide resins cured with the four aliphatic diamines in the presence or absence of salicylic acid as an accelerator and with a tertiary amine are summarized in *Table 1*.

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Table 1—Chemical Composition of Cured Epoxide Resins

Curing Agents or Catalyst		Gel Content (%)	Conversion of Epoxide Group (%)			Total Amine Linkages (%)	Ether Linkage (%)	Tg (C)
			Total	Reaction with Primary Amine	Reaction with Secondary Amine			
Amine linkages[a] .... Ethylenediamine	(m′ = 2)	99	91	47	38	85	6	130
Tetramethylenediamine	(m′ = 4)	99	90	43	42	85	5	125
Hexamethylenediamine	(m′ = 6)	99	90	42	42	84	6	119
Dodecamethylenediamine	(m′ = 12)	99	87	44	38	82	5	105
Amine-and-ether linkages .... Ethylenediamine	(m′ = 2)	98	95	49	23	72	23	145
Tetramethylenediamine	(m′ = 4)	98	93	49	15	64	27	126
Hexamethylenediamine	(m′ = 6)	99	93	49	13	62	31	114
Dodecamethylenediamine	(m′ = 12)	99	91	49	11	60	33	102
Ether linkage .... TDAMP[b]		99	99	—	—	—	99	124

(a) Accelerated with salicylic acid.
(b) Catalytically cured with TDAMP (2,4,6-tris(dimethylaminomethyl)phenol)

In the cured systems containing accelerator, the gel content is 99% and the conversion of epoxide groups is 91-87%. The epoxide group is mainly reacted with the primary and secondary amines, and ether formation is very slight (5-6%). Therefore, we may regard these cured systems as the amine-crosslinked network.

It is well known that the network structure of epoxide resin cured with tertiary amine such as TDAMP is composed of ether linkages,[29-31] and this fact was also supported by our work.[32-34] In this system, we can consider that the sample is completely cured, because both the gel content and the conversion of epoxide groups of this system are 99% (Table 1). We denote this system the ether-crosslinked networks.

In the epoxide resin system cured with diamines without accelerator, 49 and 23-11% of epoxide groups reacted with primary and secondary amines, respectively. Consequently, these systems contain significant amounts of ether linkages (33-23%). We denote these systems the amine-and-ether crosslinked networks.

The structural schemes of these reaction processes and their products are shown in Figure 2. We have discussed these schemes in the other papers.[13]

Dynamic Mechanical Properties Of the Cured Epoxide Resins

Dynamic mechanical properties of the amine-and-ether systems are shown in Figure 3 (A). Since the measurements were carried out in the range 0.3-3.0Hz, the temperature where the elastic modulus decreased drastically and the damping showed the maximum value was regarded as the glass transition temperature (Tg).

In the amine linked systems, the Tg of the cured systems and the elastic modulus (G) in the glassy (<Tg) and rubbery (>Tg) regions decreased with increase in m′ of the curing agents.

The β and γ relaxations, which are due to the motion of hydroxy-ether groups[20] and six or more methylene units, were observed at -50 and $-140°$C, respectively.

Table 2—Calculation of Internal Stresses in Epoxide Resin Coatings from Thermal Expansion

Curing Agents or Catalyst	m′	Linear Shrinkage (%)	G × 10⁹ (MPa)	ν (×10⁻³ mol/cm³)	E × 10³ᶜ (MPa)	Internal Stress (MPa) (obsd.)	σᵈ (MPa) (calcd.)	σ Int. Stress
Amine linkages[a] .... Ethylenediamine	2	0.64	1.196	3.79	3.24	5.08	5.90	
Tetramethylenediamine	4	0.58	1.025	3.46	2.78	4.33	4.55	
Hexamethylenediamine	6	0.53	0.925	3.15	2.51	3.66	4.01	
Dodecamethylenediamine	12	0.46	0.643	2.55	1.74	3.02	2.54ˡ	
Amine-and-ether linkages .... Ethylenediamine	2	0.66	1.045	4.18	2.84	5.60	4.67	0.95 ± 0.2
Tetramethylenediamine	4	0.54	0.943	3.08	2.56	4.36	3.79	
Hexamethylenediamine	6	0.49	0.888	2.73	2.41	3.48	3.12	
Dodecamethylenediamine	12	0.41	0.694	2.35	1.88	2.75	2.23	
Ether linkage[b] .... TDAMP[b]	—	0.57	1.043	3.50	2.83	4.22	4.29	

(a) Accelerated with salicylic acid.
(b) Catalytically cured with TDAMP. (2,4,6-tris(dimethylaminomethyl)phenol).
(c) Calcd. from E = 2.66G, Poisson's ratio = 0.33.
(d) Calcd. from $\sigma = \int_{30}^{Tg} (\alpha_c - \alpha_s)$ Edt, α_c and α_s Coefficient of thermal expansion of coatings: and substrate, respectively.
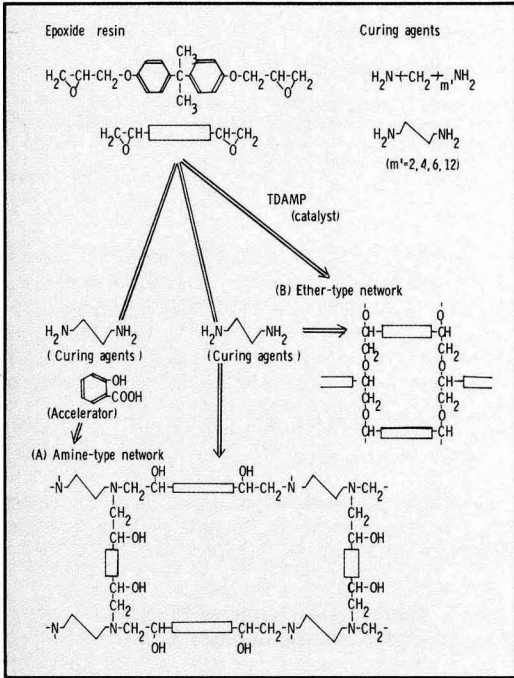
Figure 2—Structural schemes for cured epoxide resins

In the all ether linked system, the G in the rubbery (>Tg) region is higher than those of the amine systems. In addition, the β relaxation, which is due to the motion of the segment including ether linkages,[20] was observed at −80°C.

Dynamic mechanical properties of the amine-and-ether linked systems are shown in *Figure* 3 (B). The Tg and G of these systems as well as above systems increased with decrease in m' of the curing agents.

The β relaxation of these systems increased in peak height and shifted to lower temperature with increase in m' of the curing agents; this relaxation approximates that of the ether system. This result is explained by the increase in ether linkages with increase in m' (*Table* 1). In addition, the γ relaxation was observed at −140°C.

Internal Stress in the Cured Epoxide Resin

Plots of the internal stress in the amine linked, ether linked, and amine-and-ether linked systems vs. ambient temperature are shown in *Figure* 4. Internal stresses in all the systems were almost absent in the rubbery (>Tg) region, and increased greatly with decreasing ambient temperature in the glassy (<Tg) region [*Figure* 4(A)(B)].

Since the deflection points of the internal stress-temperature curves correspond to the Tg of each system, these curves were replotted by considering the Tg of each system as an original point [*Figure* 4 (C)]. This figure shows that the relationship between the internal stress of the all-cured systems and the temperature difference from Tg (t-Tg) can be expressed by a straight line, even if the network structure (*Table* 1, *Figure* 2) and concentration of network chains (*Table* 2) are different in each system. We concluded from this result that the internal stress in cured epoxide resins is not generated in the rubbery region and increases at a constant ratio with decreasing ambient temperature in the glassy region, regardless of the network structure. Thus, the internal stress at room temperature depends only on the temperature difference
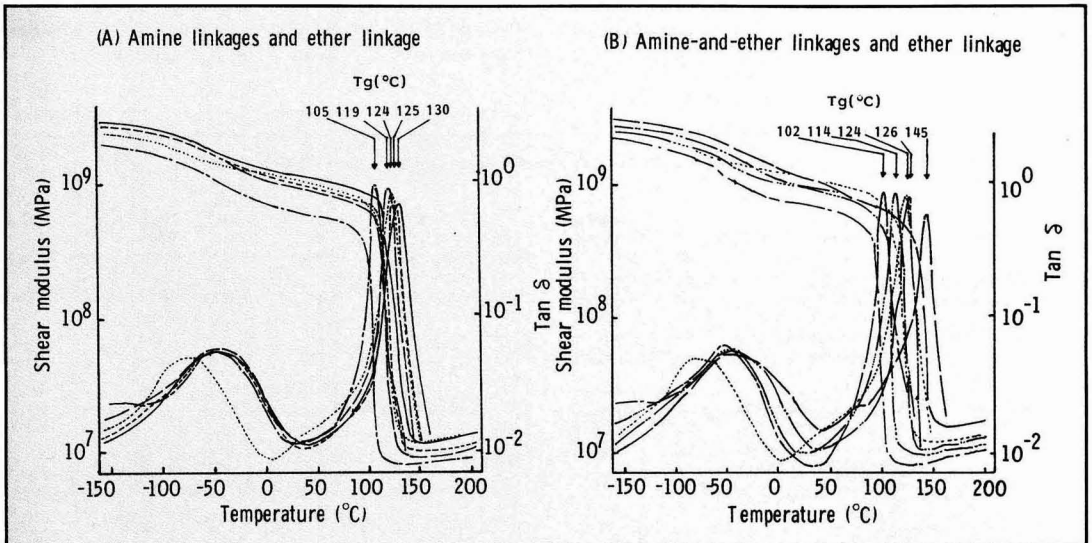
Figure 3—Dynamic mechanical properties of cured epoxide resins. (A) Amine linkages: _____ (EDA); -----(TMDA); _ _ _ (HMDA); _._ _ (DDMDA). (B) Amine-and-ether linkages: ___ (EDA); _··_ (TMDA); _····_ (HMDA); _·_ (DDMDA). (A&B): Ether linkages:........ (TDAMP)

between Tg and room temperature, as shown in *Figure* 5 (A).

The concentration (ν) of network chains in the cured systems is calculated from the G at rubbery region (40°C above Tg) by using the equation of rubber elasticity.[27,28] The plots of the internal stress at room temperature vs. ν of the cured epoxy resins are shown in *Figure* 5 (B). An approximately linear relationship exists between ν and the internal stress. This result is reasonable, because the Tg of cured systems increase with increasing the concentration of network chains.

Shrinkage in the Cured Epoxide Resin and Mechanism for the Occurrence of Internal Stress

We have reported that the internal stress in the bulk epoxide resin is mainly induced by shrinkage in the glassy region.[7-10] In this work, the relationship between the internal stress and shrinkage in the coatings is studied.

Plots of linear shrinkage in the glassy region vs. temperature are shown in *Figure* 6. The linear shrinkage in the amine, ether, and amine-and-ether linked systems increased linearly with decreasing ambient temperature. The magnitude of the linear shrinkage at room temperature increased with decrease in m' of the curing agents.

To compare the behavior of shrinkage in these systems, the linear shrinkage-temperature plots constructed by regarding Tg as the origin are shown in *Figure* 6 (C).
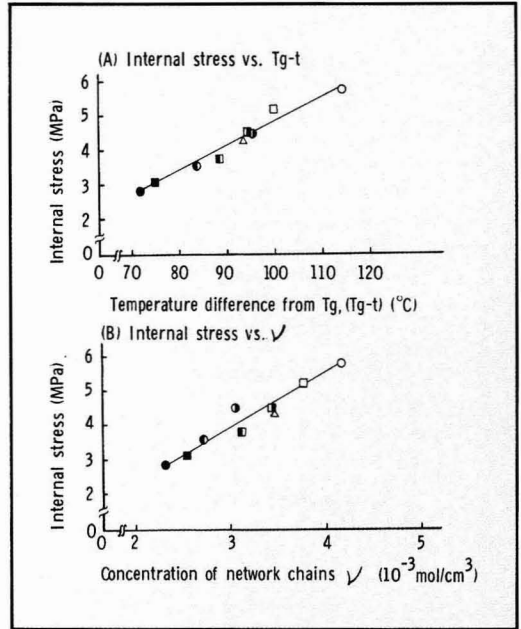
Figure 5—Internal stress vs Tg-t (A) and v (B) of cured epoxide resins. Legend same as *Figure 4*
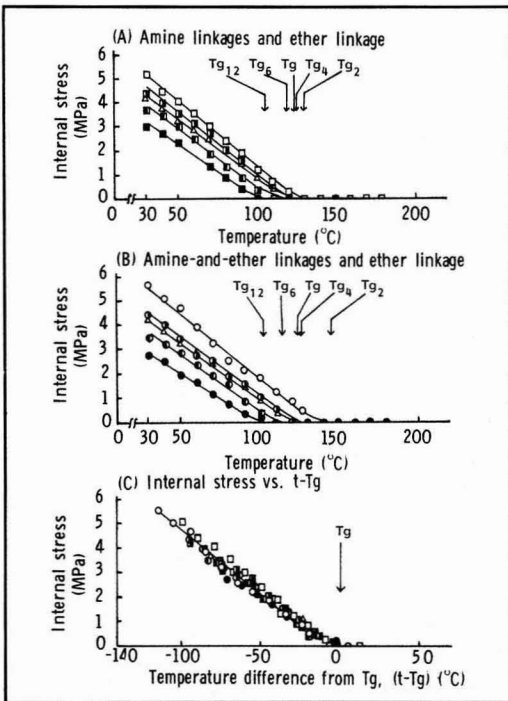
Figure 4—Internal stress of cured epoxide resins. Legend: (A) Amine linkages: (□) EDA; (▨) TMDA; (▧) HMDA; (■) DDMDA. (B) Amine-and-ether linkages: (○) EDA; (◐) TMDA; (◑) HMDA; (●) DDMDA. (C) Ether linkages: (△) TDAMP
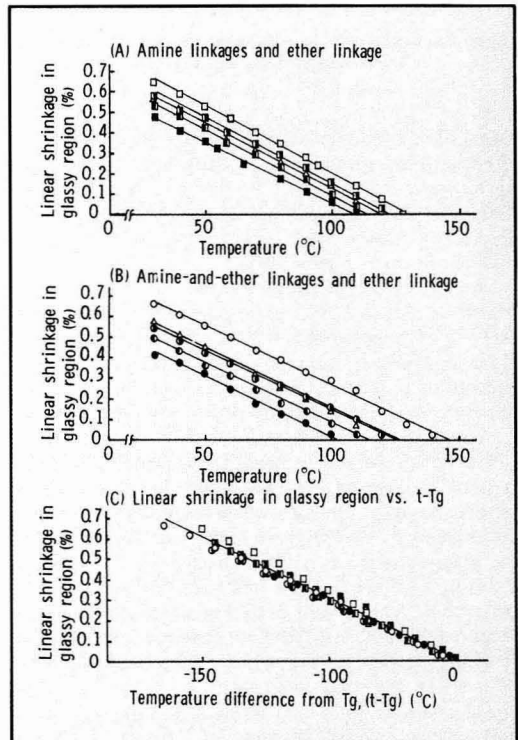
Figure 6—Linear shrinkage in glassy region of cured epoxide resins. Legend same as *Figure 4*
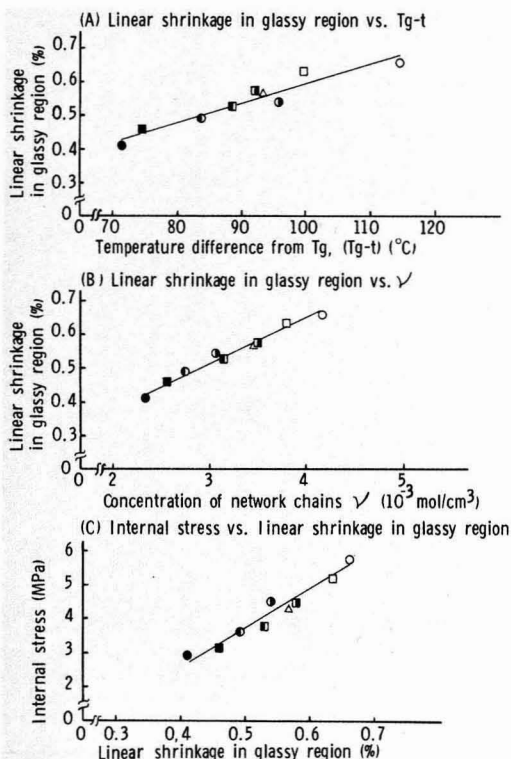
Figure 7—Linear shrinkage and internal stress of cured epoxide resins. Legend same as *Figure* 4

From these plots, the changes in the linear shrinkage appeared to be represented by a straight line, even though the network structure and ν are different in each system. The linear shrinkage at room temperature is dependent on the temperature difference from Tg to room temperature, as shown in *Figure* 7 (A).

Plots of linear shrinkage vs. ν of cured systems are shown in *Figure* 7 (B). An approximately linear relationship exists between ν and the linear shrinkage. This result is expected, since the Tg of the cured systems depends on the concentration of network chains and the linear shrinkage in the glassy region is governed by the temperature difference from Tg to room temperature.

The linear thermal expansion coefficient α of these systems is shown in *Figure* 8. The value of α changed remarkably in the Tg region, while it remained unchanged in the glassy (<Tg) and in the rubbery (>Tg) regions. In the glassy region, α is little affected by the network structure of these systems, and is on the order of 10^{-5} cm/cm/°C. This is the reason why the linear shrinkage [*Figure* 6 (C) and 7 (A)] did not depend on the network structure, but depends only on the temperature difference between Tg and room temperature.

The relationship of internal stress to shrinkage in the glassy region is plotted in *Figure* 7 (C). An approximately linear relationship existed between the internal stress and the shrinkage in the glassy region for all cured systems

having a different network structure and concentration of network chains. From this result, we conclude that the shrinkage in the glassy region was converted directly to internal stress, because the motion of the network segments was restricted in this region. On the other hand, internal stress could not be generated in the rubbery region, as shown in *Figure* 4, because the motion of the network segments was facile and the cured system could relax in this region.

Estimation of the Internal Stress

Estimation of internal stress induced in the epoxide resin coatings is shown in *Table* 2. The internal stress is directly proportional to the linear shrinkage in the glassy region [*Figure* 7 (C)]. Thus, it should be possible to calculate this stress, based on the temperature coefficient of expansion. If α_c is the linear expansion coefficient of the epoxide resin coatings, α_s that of the substrate, E the tensile modulus, and t the temperature, the internal stress σ is calculated from the following equation:

$$\sigma = \int_{30}^{Tg} (\alpha_c - \alpha_c)\, E dt \qquad (4)$$

The shear modulus, G, rather than the tensile modulus, E, of the cured systems was measured in this work [*Figure* 3 (A) (B)]. The value of E in the equation was calculated
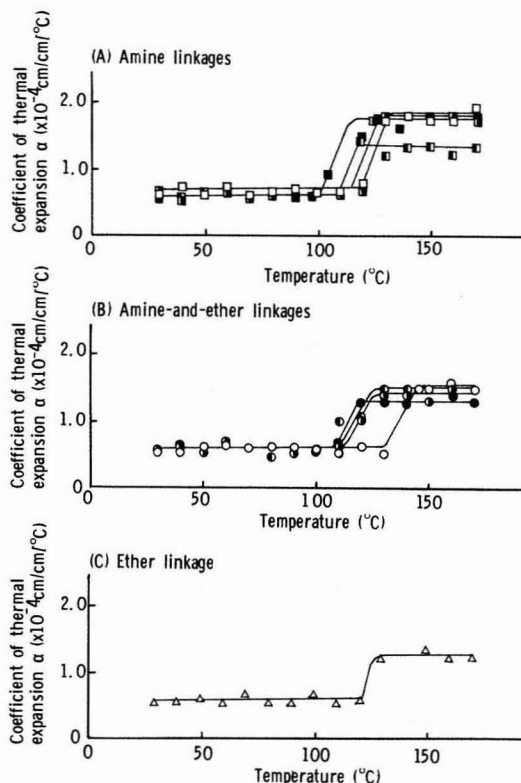
Figure 8—Coefficient of thermal expansion of cured epoxide resins. Legend same as *Figure* 4

from G by using an assumed value of 0.33 for Poisson's ratio. (*Table* 2). The value of α calculated from the above equation are also shown in this table. The ratio of the calculated internal stresses with the experimental values is 0.95 ± 0.21 for all cured systems. Since the experimental values of internal stress agreed with the calculated values, it is clear that the internal stress in the coatings is due to the shrinkage in the glassy region.

CONCLUSIONS

The bisphenol-A-type epoxide resin was cured with four aliphatic α, ω-diamines in the presence or absence of salicylic acid as an accelerator, and with a tertiary amine as a curing catalyst. The magnitudes of the internal stress and the shrinkage were related to the chemical structure of these cured systems, and the mechanism for the occurrence of the internal stress was investigated in detail.

The following conclusions were obtained:

(1) The tertiary amine catalytically cured system and the diamine-crosslinked system with or without an accelerator formed network structures composed of the ether, the amine, and both the ether and amine linkages, respectively.

(2) For all cured systems, the internal stress is almost absent in the rubbery region and is mainly induced by shrinkage in the glassy region. This means that though the internal stress is easily relaxed in the rubbery region by the motion of the network segments, in the glassy region the shrinkage is directly converted to internal stress because the motion of the network segments is restricted in this region.

(3) The internal stress and the shrinkage in the glassy region linearly increase with increase in the concentration of network chains and the temperature difference from Tg to room temperature, because the Tg of these cured systems is governed with the concentration of network chains.

(4) Increasing the length of the methylene sequence in the amine curing agents or decreasing the glass transition temperature and the concentration of network chains reduces the internal stress generated in the epoxide resin coatings.

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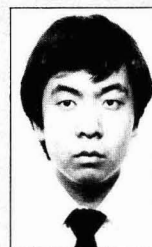
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The Simplex Mixture Screening Design In Coatings Research

K.K. Hesler, J.R. Lofstrom, and J.A. Greenwald
DeSoto, Incorporated*

The mixture screening design permits quick and efficient investigation of the effects of a large number of components. Determination of the co-efficients of a linear equation model allows the calculation of component effects. With consideration of the component effects, the number of candidate components can be reduced to a reasonable number of essential components. Graphical analysis of the results of a mixture screening design can supplement or obviate the need for the mathematical determination of model coefficients and component effects. The simplex mixture screening design can result in the immediate application of a number of the particular components evaluated, or to the design of more comprehensive mixture studies.

INTRODUCTION

Many coating formulas contain a number of ingredients known as additives. These additives, while comprising only a small percentage of the total composition, play a vital role in the performance of the coating. Dispersing and stabilizing surfactants are additives which control the dispersion of the pigment, the viscosity, and shading paste stability of the coating system. Traditional methods of stabilizing a formulary involve the preparation of many individual batches of the coating, in an attempt to evaluate all the possible combinations of all surfactants under consideration. Utilizing a simplex mixture screening design that treats the surfactants as components of a mixture enables efficient evaluation.

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This paper outlines the use of a 12-component mixture screening study to evaluate the effects of 12 dispersing and stabilizing surfactants. The experimental methodologies presented here are applicable to studies involving fewer or more components.

THEORY

In a previous paper[1] we discussed the use of simplex lattice design experimentation when dealing with relatively few mixture components. In the normal course of experimental investigation, however, the researcher would begin with a relatively large number of variables, in this case, mixture components. The first step in good experimental strategy is to study all of the potentially important variables in a screening study. After it has been determined which have the largest or smallest (depending on the particular situation) effects, then those components (normally three to five) are studied in greater detail in a full simplex lattice design.

The techniques[2-6] for the design of simplex lattice mixture studies apply to simplex screening studies. The simplex mixture screening design is a subset of the full simplex lattice design. The composition of the blends in the simplex screening design is achieved by the use of a $(3q + 1)$ design, which contains the q "vertices," or pure components; the q "interior" blends; the overall "centroid"; and the q "end effect" blends, where q is the number of components.

The analysis of the simplex mixture screening design study is divided into two parts: graphical and mathematical. The graphical analysis consists of plotting responses along the component axes and drawing lines between each response associated with each component. This creates a continuum of response as the fraction of each component in the mixture is increased from 0–100%. The mathematical analysis of mixture screening designs

Table 1—Simplex Screening Design Points

Design Point		Composition				
Class	No.	X_1	X_2	X_3	. .	X_q
Vertices	1	1	0	0	. .	0
	2	0	1	0	. .	0
	3	0	0	1	. .	0
	.	.	.	.	. .	.
	q	0	0	0	. .	1
Interior	1	$(q+1)/2q$	$1/2q$	$1/2q$	. .	$1/2q$
	2	$1/2q$	$(q+1)/2q$	$1/2q$	. .	$1/2q$
	3	$1/2q$	$1/2q$	$(q+1)/2q$	. .	$1/2q$
	.	.	.	.	. .	.
	q	$1/2q$	$1/2q$	$1/2q$	. .	$(q+1)/2q$
Centroid	1	$1/q$	$1/q$	$1/q$	. .	$1/q$
End Effects	1	0	$1/(q-1)$	$1/(q-1)$	. .	$1/(q-1)$
	2	$1/(q-1)$	0	$1/(q-1)$	. .	$1/(q-1)$
	3	$1/(q-1)$	$1/(q-1)$	0	. .	$1/(q-1)$
	.	.	.	.	. .	.
	q	$1/(q-1)$	$1/(q-1)$	$1/(q-1)$	. .	0

involves four sets of calculations: the component mixture model coefficients (b_i's), the component effects (E_i's), the confidence limits for the coefficients, and the confidence limits for the effects. The coefficients are associated with a linear model. The model is of the form:

$$Y = b_1X_1 + b_2X_2 + \cdots + b_qX_q \tag{1}$$

where X_1, X_2, etc., represent the mixture components coded 1, 2, etc., and their associated concentrations, X, expressed as a decimal; b_1, b_2, etc., represent the coefficients associated with each component, and describe the linear effects of changes in the component levels; and q represents the total number of components in the mixture. The component effects are given by:

$$E_i = (1/q - 1)(qb_i - B_{total}) \tag{2}$$

where q is the number of components in the screening study; the b_i's are the individual coefficients, and the B_{total} is the sum of all the coefficients ($b_1 + b_2 + \cdots + b_q$). The coefficient and component effect confidence limits are given by:

$$b_i +/- tS(VB)^{1/2} \tag{3}$$

$$E_i +/- tS(VE)^{1/2} \tag{4}$$

respectively, where S is the standard deviation of experimental error; $S(Vb)^{1/2}$ is the coefficient standard

Table 2—Twelve-Component Simplex Screening Design

Design Point		Composition											
Class	No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}
Vertices	1	1	0	0	0	0	0	0	0	0	0	0	0
	2	0	1	0	0	0	0	0	0	0	0	0	0
	3	0	0	1	0	0	0	0	0	0	0	0	0
	4	0	0	0	1	0	0	0	0	0	0	0	0
	5	0	0	0	0	1	0	0	0	0	0	0	0
	6	0	0	0	0	0	1	0	0	0	0	0	0
	7	0	0	0	0	0	0	1	0	0	0	0	0
	8	0	0	0	0	0	0	0	1	0	0	0	0
	9	0	0	0	0	0	0	0	0	1	0	0	0
	10	0	0	0	0	0	0	0	0	0	1	0	0
	11	0	0	0	0	0	0	0	0	0	0	1	0
	12	0	0	0	0	0	0	0	0	0	0	0	1
Interior	13	13/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
	14	1/24	13/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
	15	1/24	1/24	13/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
	16	1/24	1/24	1/24	13/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
	17	1/24	1/24	1/24	1/24	13/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
	18	1/24	1/24	1/24	1/24	1/24	13/24	1/24	1/24	1/24	1/24	1/24	1/24
	19	1/24	1/24	1/24	1/24	1/24	1/24	13/24	1/24	1/24	1/24	1/24	1/24
	20	1/24	1/24	1/24	1/24	1/24	1/24	1/24	13/24	1/24	1/24	1/24	1/24
	21	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	13/24	1/24	1/24	1/24
	22	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	13/24	1/24	1/24
	23	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	13/24	1/24
	24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	13/24
Centroid	25	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12
End Effects	26	0	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11
	27	1/11	0	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11
	28	1/11	1/11	0	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11
	29	1/11	1/11	1/11	0	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11
	30	1/11	1/11	1/11	1/11	0	1/11	1/11	1/11	1/11	1/11	1/11	1/11
	31	1/11	1/11	1/11	1/11	1/11	0	1/11	1/11	1/11	1/11	1/11	1/11
	32	1/11	1/11	1/11	1/11	1/11	1/11	0	1/11	1/11	1/11	1/11	1/11
	33	1/11	1/11	1/11	1/11	1/11	1/11	1/11	0	1/11	1/11	1/11	1/11
	34	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	0	1/11	1/11	1/11
	35	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	0	1/11	1/11
	36	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	0	1/11
	37	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	1/11	0

error; $S(VE)^{1/2}$ is the component effect standard error; and t is the student's t-statistic for the assigned probability level and degrees of freedom associated with S.

These confidence limits are used to establish the uncertainty associated with model equations and component effects. The calculation of the linear model coefficients and component effects was accomplished using a computer and a general purpose regression analysis program. There is a hand-calculation procedure which can be used in lieu of a computer program.[2]

EXPERIMENTAL

The screening design involved selecting a group of dispersing and stabilizing surfactants. Candidate selection was based upon a number of considerations, including general classification type (ionic, nonionic), HLB range for the nonionics, and prior experience. A total surfactant level was chosen. Since this level represented the entire simplex region, no pseudocomponent transformations were necessary.

Individual paint systems were prepared based on a (3q + 1) or ABCD design as shown in *Table* 1. The design was composed of 12 "vertex" paints (q = 12 for our experiment), each containing a single separate surfactant;

12 "interior" paints, each of the composition $(q + 1)/2q$ in one surfactant, and $1/2q$ in the remaining surfactants; one "centroid" paint containing $1/q$ of each of the surfactants, and 12 "end effect" paints, each void of one of the surfactants, and containing $1/(q - 1)$ of each of the remaining surfactants. Each of the 37 paints were prepared individually. *Table* 2 shows the complete 37 blend 12-component simplex mixture design. The 12 surfactant components are coded A through L, and represent X_1 through X_{12}. Each of the 37 blends system paints were tinted with a standard quantity of shading paste prior to the start of the testing.

Evaluation involved testing each system quantitatively as follows: (a) initial viscosity; (b) two and five week viscosity after aging at room temperature (70°F); (c) two and five week viscosity after aging at high temperature (130°F); and (d) viscosity after 10 day mechanical jar roller aging. Qualitative evaluation involved assessing the degree of color float resistance after the aforementioned aging periods. Color float refers to an uneven distribution of pigment between the surface and bulk of the liquid coating. A color float resistance rating of 10 represents complete homogeneous color distribution which is desirable, while a rating of 0 represents an undesirable complete heterogeneous distribution.

Table 3—Viscosity Stability/Color Float Resistance

Design Point			Viscosity (KU)		Viscosity Change (KU)					Color Float Resistance			
Class	No.	Surfactant	Preadjustment	Initial	2wk.RT	2wk.HT	5wk.RT	5wk.HT	10dy.MS	2wk.RT	2wk.HT	5wk.RT	5wk.HT
Vertices	1	A	90	117	4	0	6	3	1	6	2	8	2
	2	B	102	102	4	−1	5	−6	−6	4	6	4	4
	3	C	102	95	9	−2	9	−5	−4	7	0	3	0
	4	D	97	92	10	−4	10	−6	−4	7	0	8	0
	5	E	94	86	5	−6	7	−19	−3	10	0	6	0
	6	F	91	93	5	−26	3	−25	−10	7	1	6	1
	7	G	95	88	3	−10	3	−14	−11	4	0	4	0
	8	H	97	91	2	−10	2	−13	−6	3	0	3	0
	9	I	69	94	5	−3	5	−1	−7	5	8	6	5
	10	J	63	94	11	6	12	6	−5	5	9	8	9
	11	K	76	94	−2	8	−3	−8	−16	5	5	6	4
	12	L	53	102	5	−7	4	−6	2	10	9	10	5
Interior	13	A	90	81	7	4	9	3	−2	7	7	9	3
	14	B	83	88	5	−4	7	1	0	7	5	6	4
	15	C	88	83	7	4	8	2	0	4	4	8	5
	16	D	86	86	4	1	7	1	−2	6	6	8	3
	17	E	74	102	2	−14	3	−9	−2	8	6	9	7
	18	F	87	89	−2	−26	−3	−26	−10	7	7	7	2
	19	G	104	88	4	−1	8	−6	−7	8	5	7	3
	20	H	102	91	1	−8	3	0	−4	6	7	7	3
	21	I	68	102	5	3	7	6	1	6	5	6	5
	22	J	67	93	7	8	9	11	1	6	9	6	5
	23	K	69	102	−4	2	7	4	1	8	9	7	5
	24	L	60	113	5	−2	9	−3	0	10	9	9	5
Centroid	25	All	79	97	−1	−10	−4	−10	−4	10	9	8	7
End Effect	26	A	79	97	−1	−9	−4	−11	−4	10	9	8	8
	27	B	81	94	−1	−9	−3	−11	−6	10	9	8	8
	28	C	79	98	−1	−10	−3	−12	−5	9	9	8	8
	29	D	78	98	−1	−11	−3	−11	−5	10	9	8	8
	30	E	78	98	−1	−5	−3	−23	−4	9	7	8	6
	31	F	88	84	2	−2	1	−7	−5	7	6	8	6
	32	G	71	102	−2	−12	−5	−12	−6	8	8	7	6
	33	H	70	102	1	−8	−2	−12	−3	8	8	7	6
	34	I	81	89	−1	−13	9	−12	−5	7	6	6	2
	35	J	85	86	−2	−11	−3	−12	0	8	4	9	6
	36	K	82	90	−3	−15	−4	−15	−7	7	7	6	3
	37	L	89	86	−8	−19	−10	−21	−12	6	4	5	2
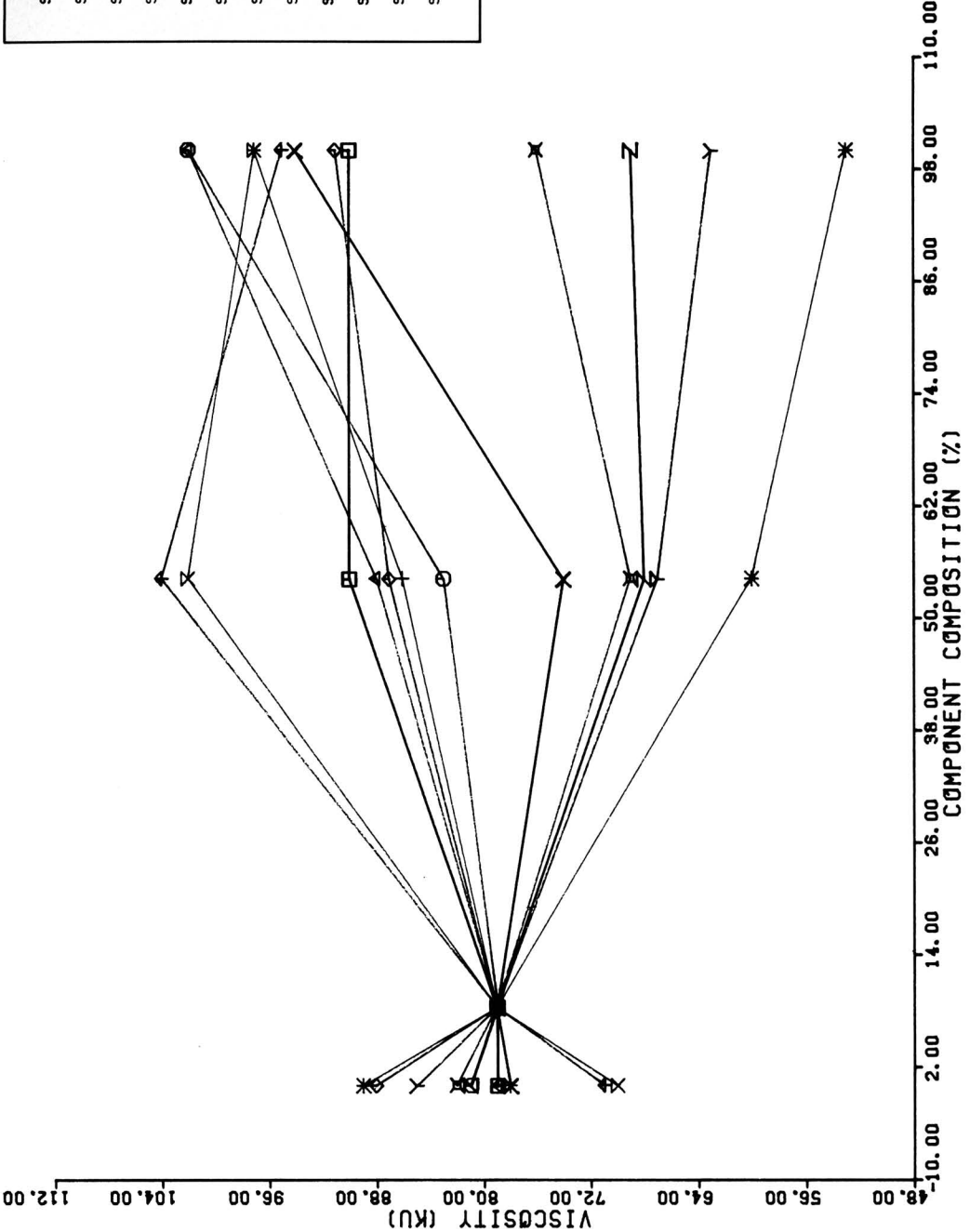
Figure 1—Preadjustment viscosities

Legend (surfactant symbols):

- SURFACTANT A ⊟
- SURFACTANT B ⊝
- SURFACTANT C ◁
- SURFACTANT D +
- SURFACTANT E ✕
- SURFACTANT F ◇
- SURFACTANT G ⟊
- SURFACTANT H ⋈
- SURFACTANT I Ｚ
- SURFACTANT J Ｙ
- SURFACTANT K ⋈
- SURFACTANT L ✳

X-axis: COMPONENT COMPOSITION (%) — -10.00, 2.00, 14.00, 26.00, 38.00, 50.00, 62.00, 74.00, 86.00, 98.00, 110.00

Y-axis: VISCOSITY (KU) — 48.00, 56.00, 64.00, 72.00, 80.00, 88.00, 96.00, 104.00, 112.00

Table 4—Linear Coefficients (b_i)/Component Effects (E_i) for Viscosity Stability

| | Stability Regimen | | | | | | | | | |
| | 2 wk.RT | | 2wk.HT | | 5wk.RT | | 5wk.HT | | 10dy.MS | |
Surfactant	b_i	E_i	b_i	E_i	b_i	E_i	b_i	E_i	b_i	E_i
A	2.78	0.57	0.22	6.75	4.64	1.99	2.64	11.11	0.86	5.74
B	1.99	−0.30	−3.74	2.42	2.98	0.18	−5.31	2.43	−3.78	0.69
C	6.76	4.91	−1.30	5.09	6.56	4.09	−4.05	3.80	−2.26	2.35
D	6.37	4.48	−4.01	2.13	6.96	4.52	−5.31	2.43	−3.05	1.48
E	1.60	−0.72	−11.98	−6.56	2.98	0.19	−18.79	−12.25	−2.33	2.27
F	−0.20	−2.69	−32.87	−29.36	−2.87	−6.19	−31.43	−26.07	−11.00	−7.19
G	0.87	−1.52	−9.50	−3.87	1.92	−0.97	−14.39	−7.47	−10.54	−6.68
H	−1.33	−8.51	−2.78	−6.41	−1.07	−4.23	−11.21	−4.01	−5.58	−1.28
I	2.79	0.57	−5.80	0.18	2.12	−0.76	−0.72	9.01	−4.25	0.17
J	8.43	6.73	6.73	13.84	9.34	7.13	8.27	17.25	−2.73	1.83
K	−6.21	−9.24	6.23	−13.13	−3.32	−6.69	−5.43	2.30	−11.28	−7.49
L	3.29	1.12	−7.01	−1.15	3.48	0.73	−6.18	1.48	3.02	8.10

After accumulation of the viscosity changes and color float resistance ratings, these responses were plotted graphically, as shown in the *Figures* 1–10. The responses (Y values) are plotted versus the individual component composition (X values). The centroid is common to all of the components, and all of the systems have a common response at that composition.

The linear model coefficients and the component effects were calculated using a general purpose regression analysis program, and the results appear in *Tables* 4 and 5. For reasons of expediency, no replication of any of the blend systems was made. Therefore, the confidence limits for the model coefficients and component effects were not determined.

RESULTS AND DISCUSSION

Table 3 enumerates the complete data accumulation for the experiment. The graphical analysis of the mixture screening study results consists of consideration of *Figures* 1–10, which were plotted from the data in *Table* 3. *Figure* I shows the effect of each surfactant on the initial viscosity of the systems. Four of the surfactants, I,J,K,

and L, produced depressing effects on the initial preadjustment viscosities of the systems. The remaining surfactants, A–H, produced increasing effects on the initial preadjustment viscosities. The effect of each surfactant component can be traced by following the response line from the end effect composition (0% of the particular component), to the centroid composition (8.33%), to the interior point composition (54.17%), to the vertex (100%).

Figures 2–6 show the change in viscosity versus composition after each phase of stability testing. Most of the stability testing resulted in viscosity decreases. In general, we were looking for those surfactants which produced the least viscosity increase or decrease (a viscosity change centered around zero). These surfactants were I, A and C and B and L, and J and K, respectively (after five week 130°F aging). *Figures* 7–10 show the qualitative response of color float resistance rating versus component composition after each phase of stability testing.

Two surfactants, L and J, stand out as affecting the highest color float resistance ratings after all phases of stability. At this stage in the analysis of the simplex

Table 5—Linear Coefficients (b_i)/Component Effects (E_i) for Color Float Resistance

| | Stability Regimen | | | | | | | |
| | 2wk.RT | | 2wk.HT | | 5wk.RT | | 5wk.HT | |
Surfactant	b_i	E_i	b_i	E_i	b_i	E_i	b_i	E_i
A	7.10	−0.03	4.77	−1.12	9.13	2.37	3.20	−1.11
B	5.50	−1.76	7.16	1.49	4.76	−2.40	5.19	1.06
C	6.78	−0.38	1.98	−4.16	4.76	−2.40	2.40	−1.99
D	7.50	0.41	2.78	−3.29	8.74	1.94	1.61	−2.85
E	10.75	3.96	2.92	−3.13	7.54	0.63	3.34	−0.96
F	8.11	1.08	4.19	−1.76	6.75	−0.23	2.15	−2.26
G	6.04	−1.18	2.45	−3.64	5.23	−1.89	1.75	−2.70
H	4.46	−2.91	3.25	−2.78	4.43	−2.76	1.75	−2.70
I	6.12	−1.10	8.97	3.46	6.50	−0.51	6.81	2.82
J	6.05	−1.17	11.49	6.21	7.87	0.99	9.71	5.99
K	5.32	−1.97	8.09	2.51	6.89	−0.08	5.94	1.88
L	11.76	5.06	11.49	6.21	10.94	4.34	6.81	2.82
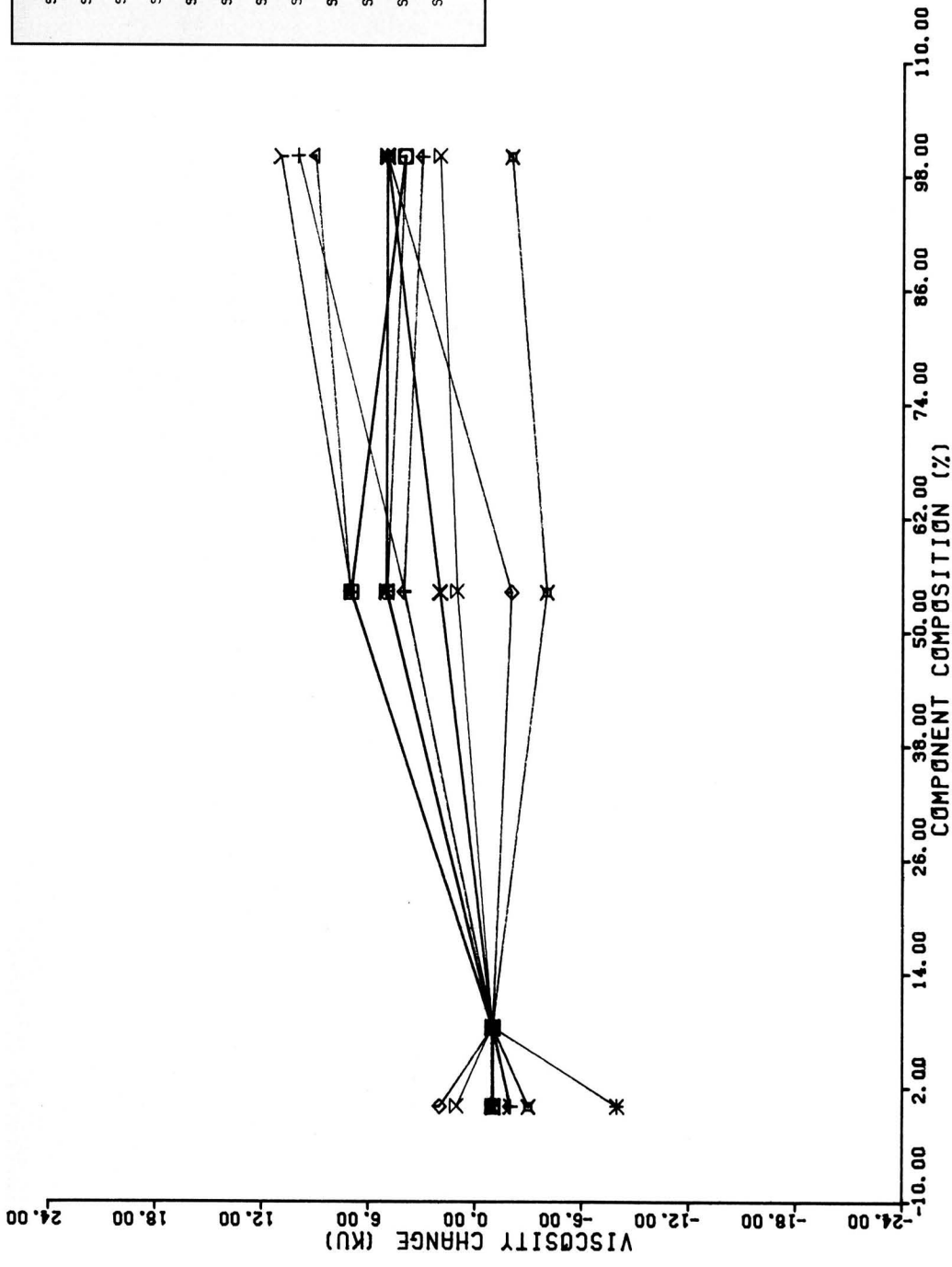
Figure 2—Two week room temperature stability

Legend:
- □ SURFACTANT A
- ⊖ SURFACTANT B
- △ SURFACTANT C
- + SURFACTANT D
- ✕ SURFACTANT E
- ◇ SURFACTANT F
- ⟡ SURFACTANT G
- ⋈ SURFACTANT H
- ℤ SURFACTANT I
- Υ SURFACTANT J
- ⋈ SURFACTANT K
- ✳ SURFACTANT L

VISCOSITY CHANGE (KU)

COMPONENT COMPOSITION (%)
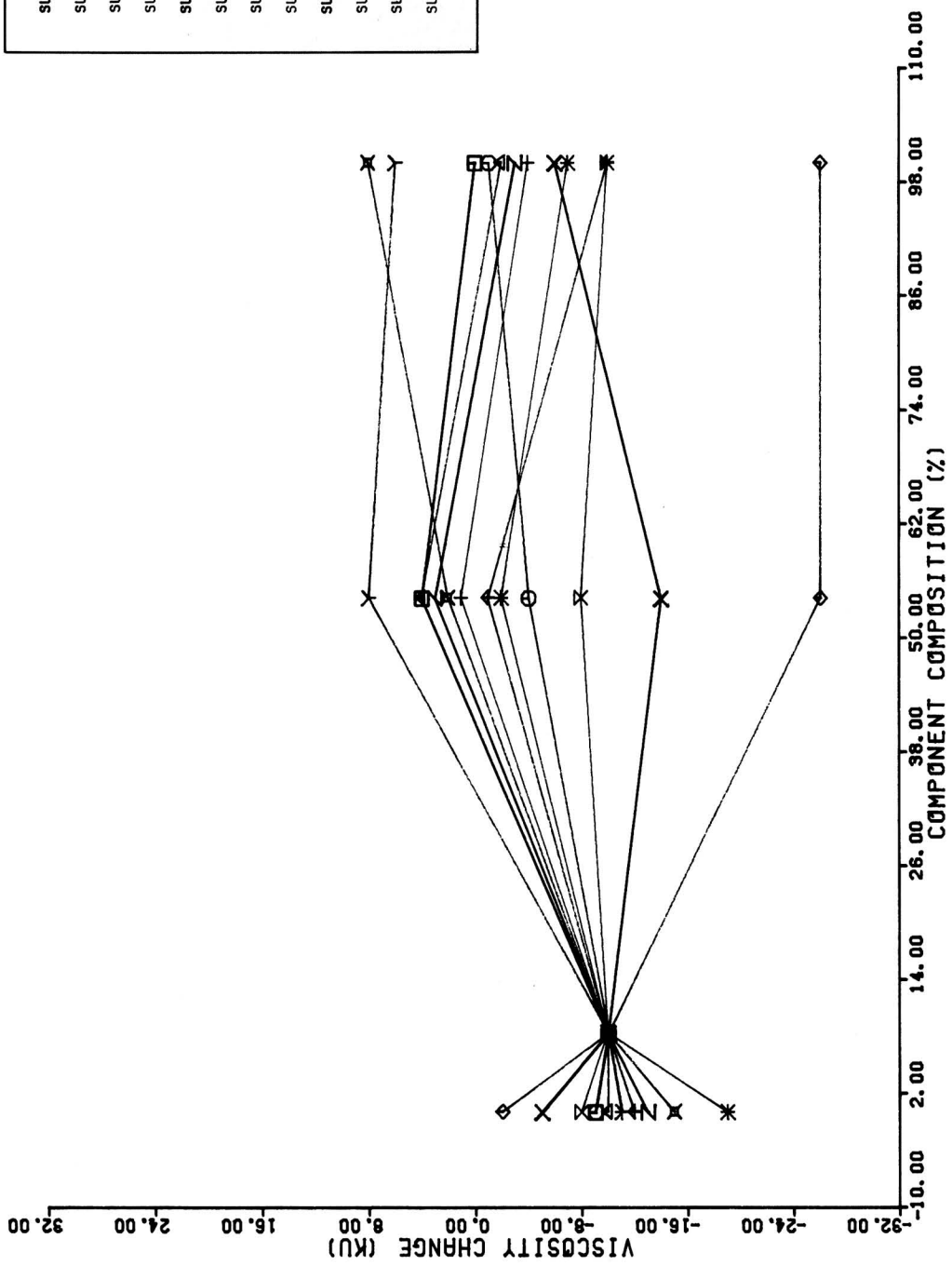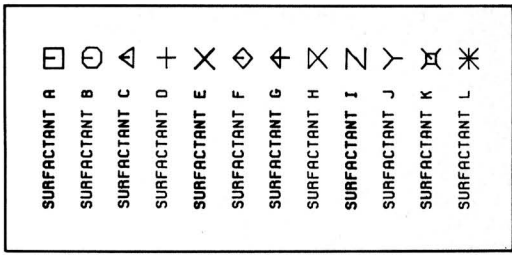
Figure 3—Two week high temperature stability

Legend:

Symbol	Surfactant
⊟	SURFACTANT A
⊖	SURFACTANT B
◁	SURFACTANT C
+	SURFACTANT D
✕	SURFACTANT E
◇	SURFACTANT F
⟋	SURFACTANT G
⋉	SURFACTANT H
N	SURFACTANT I
Y	SURFACTANT J
⋈	SURFACTANT K
✳	SURFACTANT L

Axis labels:

COMPONENT COMPOSITION (%): -10.00, 2.00, 14.00, 26.00, 38.00, 50.00, 62.00, 74.00, 86.00, 98.00, 110.00

VISCOSITY CHANGE (KU): -32.00, -24.00, -16.00, -8.00, 0.00, 8.00, 16.00, 24.00, 32.00
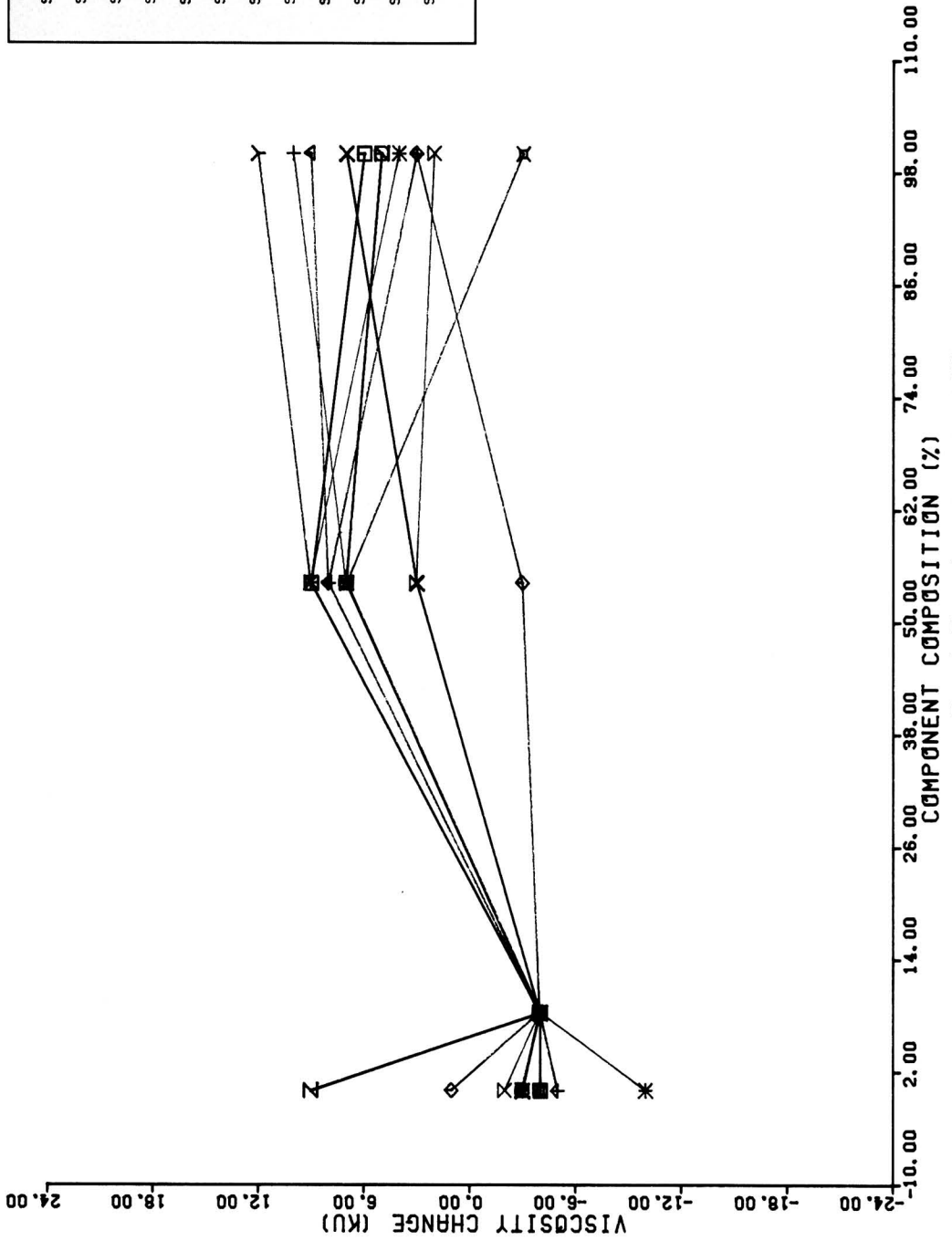
Figure 4—Five week room temperature stability

Legend:
- SURFACTANT A
- SURFACTANT B
- SURFACTANT C
- SURFACTANT D
- SURFACTANT E
- SURFACTANT F
- SURFACTANT G
- SURFACTANT H
- SURFACTANT I
- SURFACTANT J
- SURFACTANT K
- SURFACTANT L

Figure 5—Five week high temperature stability

SURFACTANT A
SURFACTANT B
SURFACTANT C
SURFACTANT D
SURFACTANT E
SURFACTANT F
SURFACTANT G
SURFACTANT H
SURFACTANT I
SURFACTANT J
SURFACTANT K
SURFACTANT L

COMPONENT COMPOSITION (%)

VISCOSITY CHANGE (KU)
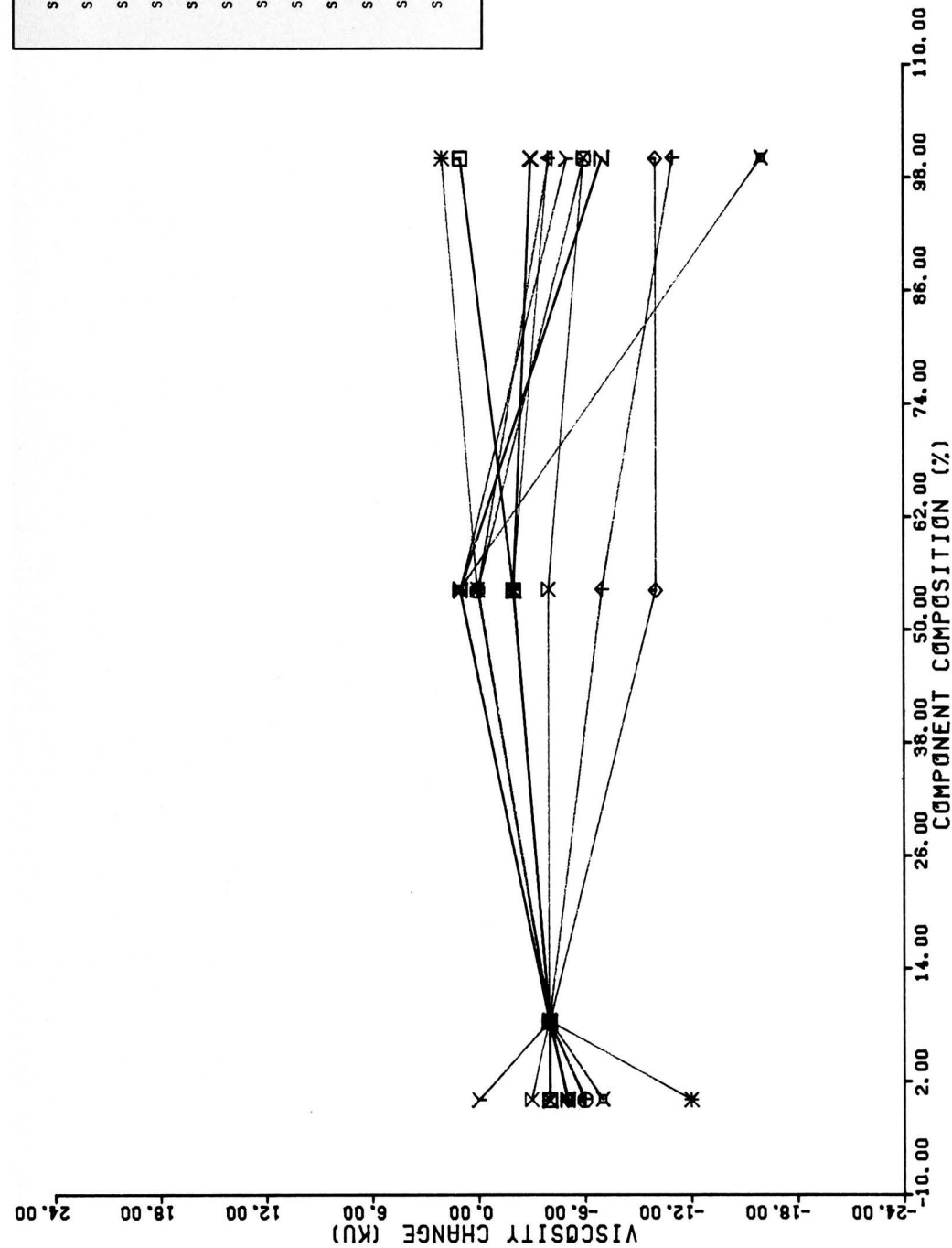
Figure 6—Ten day mechanical stability

SURFACTANT A
SURFACTANT B
SURFACTANT C
SURFACTANT D
SURFACTANT E
SURFACTANT F
SURFACTANT G
SURFACTANT H
SURFACTANT I
SURFACTANT J
SURFACTANT K
SURFACTANT L

COMPONENT COMPOSITION (%)

VISCOSITY CHANGE (KU)
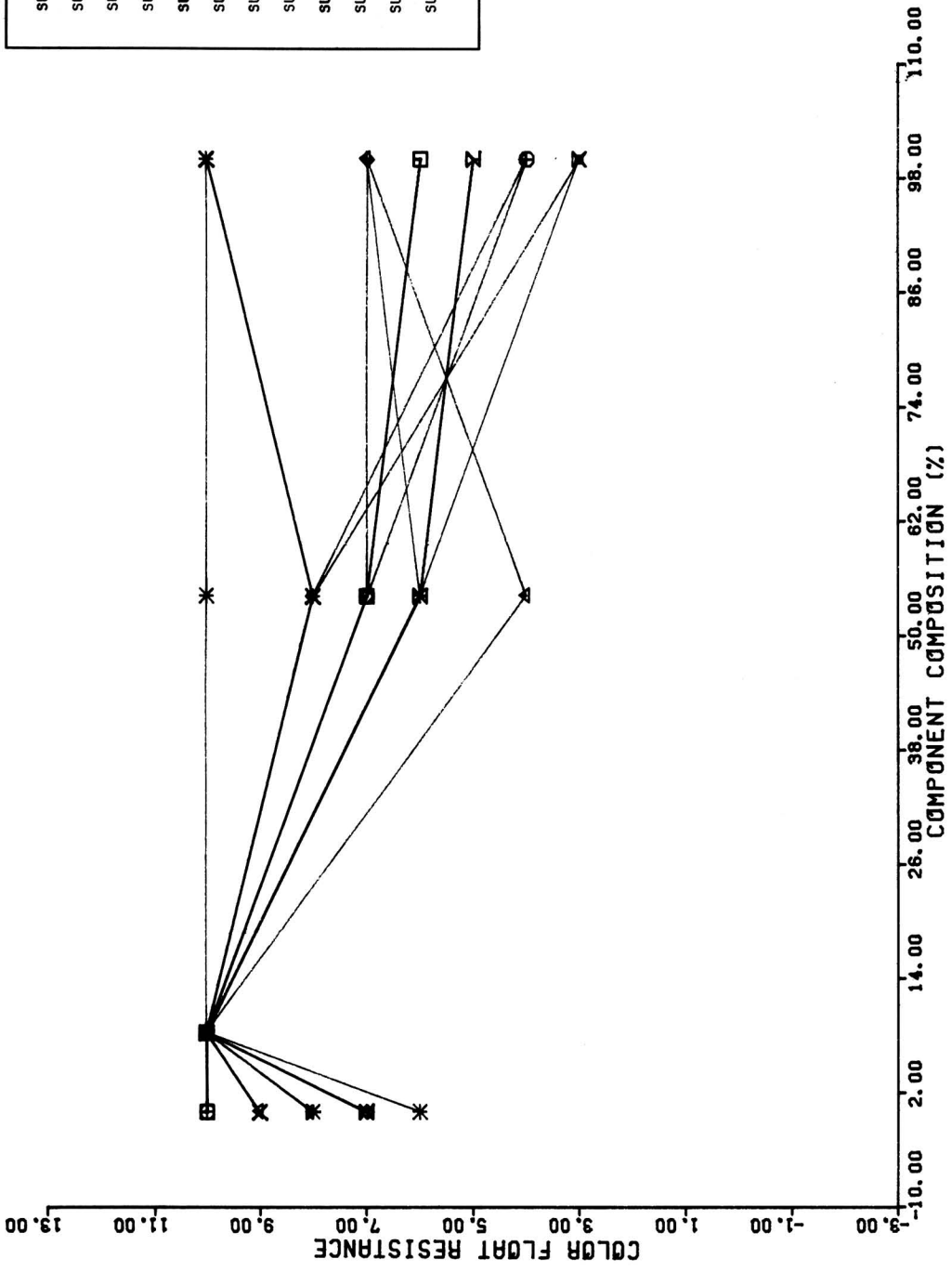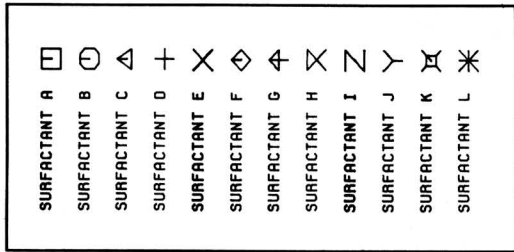
Figure 7—Two week room temperature color float resistance

Figure 8—Five week room temperature color float resistance

Legend:
- SURFACTANT A
- SURFACTANT B
- SURFACTANT C
- SURFACTANT D
- SURFACTANT E
- SURFACTANT F
- SURFACTANT G
- SURFACTANT H
- SURFACTANT I
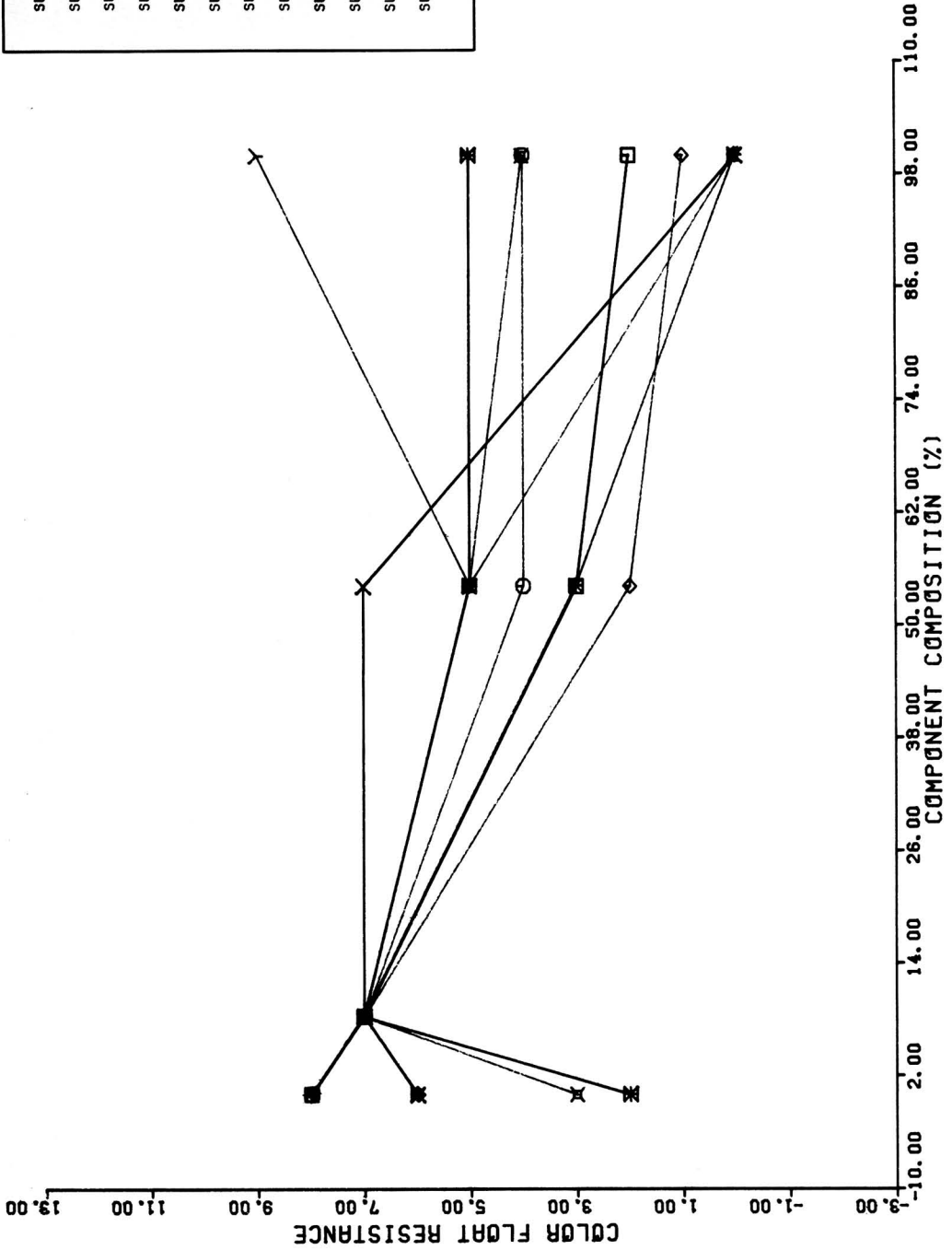- SURFACTANT J
- SURFACTANT K
- SURFACTANT L

COMPONENT COMPOSITION (%)

COLOR FLOAT RESISTANCE
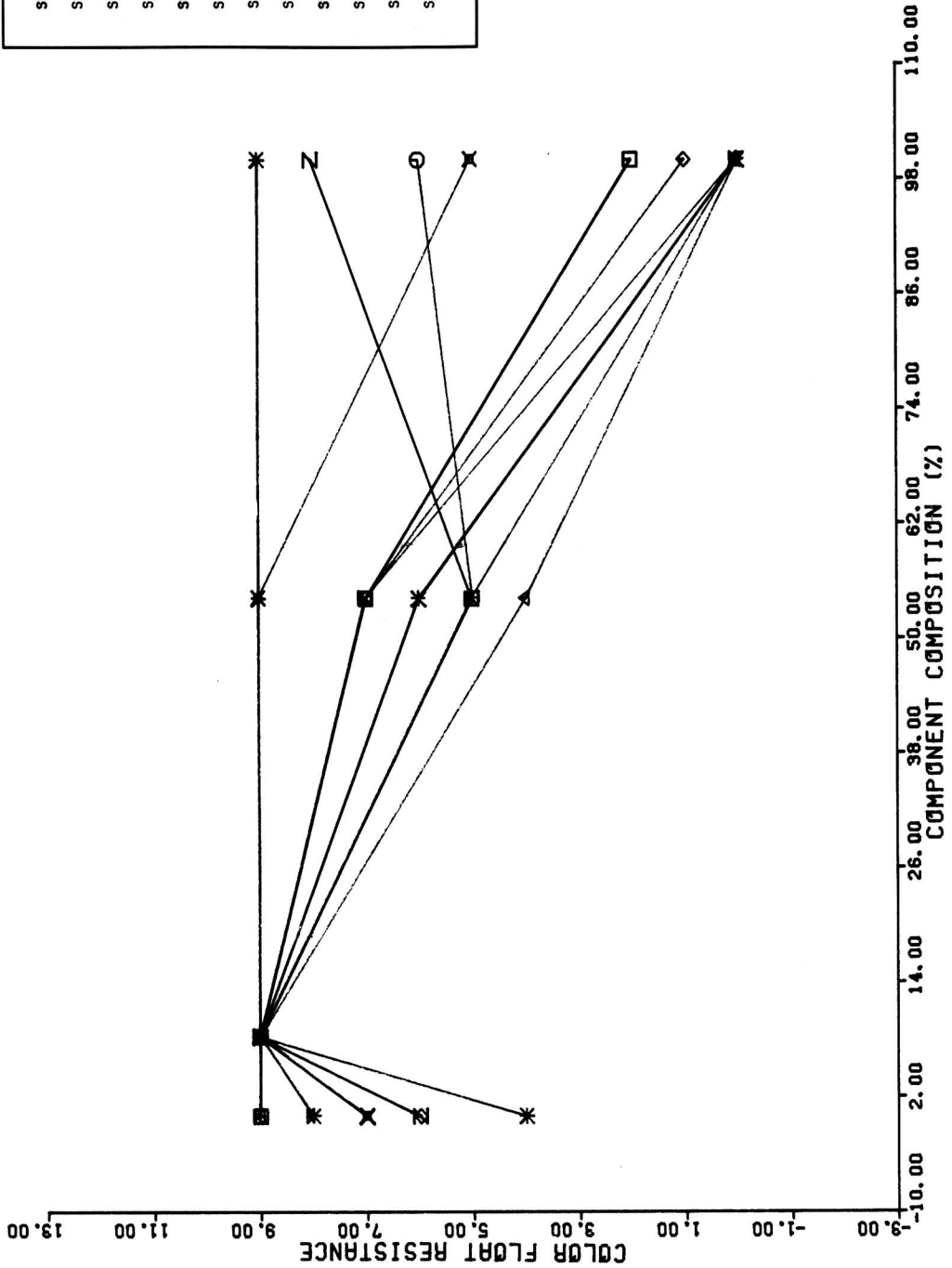
Figure 9—Two week high temperature color float resistance

Figure 10—Five week high temperature color float resistance

Legend:
SURFACTANT A
SURFACTANT B
SURFACTANT C
SURFACTANT D
SURFACTANT E
SURFACTANT F
SURFACTANT G
SURFACTANT H
SURFACTANT I
SURFACTANT J
SURFACTANT K
SURFACTANT L

X-axis: COMPONENT COMPOSITION (%)
Y-axis: COLOR FLOAT RESISTANCE

mixture screening study, the graphical interpretations have given enough information about the effects of the 12 surfactants to discontinue any further investigations. The three to five surfactants resulting in the best combination of viscosity stability and color float resistance could be chosen for a more comprehensive full simplex mixture study, or the best two to three surfactants could be used without additional experimental investigation.

The mathematical analyses of the screening mixture study responses are found in *Tables* 4 and 5. The coefficients (b_i's) in *Table* 4 are for the linear model of average viscosity change (Y), as a function of the composition of each of the 12 surfactants, expressed as a decimal (see equation (1)). The larger the absolute value of each coefficient, the greater the effect of each surfactant. The component effects (E_i's) (see equation (2)) associated with each coefficient found in *Table* 5 are the most important mathematical consequences of the screening mixture study. These component effects are the linear effects of the components over the full range of the screening study, in this case from 0-100%. A listing of the averaged values of the combined viscosity stability and the combined color float resistance rating component effects (*Table* 6), offers a complete summary of the screening experiment, and shows that surfactants B, I, and L are best for viscosity stability, and surfactants L and J are best for color float resistance. Since in screening experiments we are interested in detecting large effects, perhaps five to six times larger than the experimental error, precise estimates of model coefficients and component effects are less important than in full simplex design studies. Therefore, we did not compute confidence limits for either the model coefficients or the component effects. To this end, we did not replicate any of the blends in the screening study (five to ten are recommended) to estimate the experimental error, nor did we use an estimate of experimental error based upon previous experience, or use the regression analysis mean square to estimate experimental error.

SUMMARY

The use of a simplex mixture screening study has enabled us to characterize the effects of 12 separate components, and to reduce this candidate number to four

KENNETH K. HESLER is a Research Associate for DeSoto, Inc. He received the Bachelor Degree in Chemistry from Elmhurst College in 1966 and performed graduate work at Roosevelt University from 1967-69. His work includes the design of coatings formulation development experiments, and the statistical and graphical analysis of the experimental data. Mr. Hesler is a member of the Chicago Society for Coatings Technology, the American Chemical Society and the American Society for Testing and Materials.

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components. These four components could be used immediately to formulate an acceptable coating system, or they could be experimented with more intensely in a full simplex mixture study to further optimize their use levels.

ACKNOWLEDGMENTS

Table 6—$\overline{E}_i$ for Viscosity Stability/Color Float Resistance

Surfactant	$\overline{E}_i$ Viscosity Stability	$\overline{E}_i$ Color Float Resistance
A	5.23	0.03
B	1.08	−0.40
C	4.05	−2.23
D	3.01	−0.95
E	−3.41	0.12
F	−14.3	−0.79
G	−4.10	−2.35
H	−4.89	−2.79
I	1.83	1.17
J	9.36	3.00
K	−6.85	0.58
L	2.06	4.61

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Corrosion resistance *and* cost effectiveness with HALOX rust preventive pigments

In the more than one decade since their introduction, HALOX non-toxic rust inhibitive pigments have proved themselves effective and reliable alternatives to lead- and chrome-based pigments. Not only are they non-toxic, they are versatile—able to perform effectively in both water- and solvent-based systems. An expanding history of successful use has emerged and an increasingly large body of formulation technology, which we are ready to share, is available.

But, the paint chemist may ask, just how cost-effective are HALOX pigments? The answer is that HALOX pigments can confer major advantages without exacting a cost or performance penalty.

HALOX pigments are attractively low priced

Compared with lead or chromate and even with other non-toxic pigments, HALOX pigments are reasonable in price. They are priced favorably with pigments such as zinc phosphate, red lead, zinc chromate, zinc molybdate and others. We invite you to make your own comparisons.

Must larger amounts of HALOX pigments be used to get good results? The answer is usually no. But if larger amounts are required to provide comparable levels of service life, the increases are not usually great enough to offset the economic advantage.

HALOX minimizes formulating problems

Use of HALOX pigments does not run development or formulating costs out of sight. In general, HALOX pigments demand no major changes in proportion, technology or practice. They are compatible with other pigments and virtually every common paint vehicle, modifier and additive. And there's a wealth of technical information available. HALOX Pigments is willing to share formulating guidelines and starting formulae for paints and primers to handle a wide range of service assignments.

Non-toxicity can also cut costs

Because HALOX pigments are non-toxic, they automatically reduce costly provisions for safe handling required for problem materials in plants or in the field. This can actually cut costs in storage, handling, mixing, packaging and paint application.

HALOX pigments are cost-effective for customers, too

Abbreviated formulas for four typical coatings are given below. They show how much HALOX pigment is typically used to achieve accepted levels of salt fog performance and cost-effective field service life.

For more information

Detailed information is available on any HALOX pigment product in the form of product data sheets, formulations, application information and research reports. Your letterhead request will bring an immediate response.

Expected performance of coatings and primers formulated with HALOX rust inhibiting pigments

	Typical Alkyd Shop Primer	Two-part Epoxy Bridge Primer	Typical 3-Coat Alkyd Bridge System	Typical Latex Primer
Vehicle	Medium Oil Alkyd	Epoxy-Polyamide	Long Oil Alkyd	Acrylic or Styrenated Acrylic
Pigments	HALOX CW-221	HALOX BW-111	HALOX CW-2230	HALOX BW-191
HALOX composition, lb/gal	1.0-1.5	1.0	3.5	0.75-1.50
Expected salt fog performance, hr.	350	1000-1500	3000-4000	1000-1500
Expected field service life, yr	1-3	10-12	8-12	7-10

HALOX

HALOX PIGMENTS

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Pittsburgh, Pa. 15220, (412) 344-5811
A DIVISION OF HAMMOND LEAD PRODUCTS, INC.

Influence of Co-Solvents
On the Film Properties
Of Water-Soluble Alkyds

A. Jones and L. Campey
Toronto Society for Coatings Technology
Technical Committee

The dry retention and pH stability of a water-soluble alkyd resin carried in butyl cellosolve and water was studied for nine months utilizing a variety of driers and methods of addition. Though some loss in tack-free time and film hardness was observed, the most significant observation was that the loss in pH was not a continuous phenomenon. It followed a two stage process, falling rapidly over the first three months, stabilizing for three months, and then continuing to fall from six to nine months.

Solutions of various glycol ethers in water demonstrate a loss in pH both in the presence or absence of amines in under three months suggesting an explanation for the observed discontinuity in pH loss behavior.

INTRODUCTION

Alkyd resin solutions designed for water-reducible coatings are characteristically resins with a high acid value and are dissolved in a co-solvent or coupling solvent which is mutually miscible with water. An amine is added to form a salt with available carboxyl groups built into the resin which subsequently will accept water to form a water/coupler/resin solution. Since the alkyd is an ester it is subject to hydrolysis in the presence of a basic medium. It has been generally believed that such a solution will, after preparation, fall in pH until it reaches a pH where it becomes unstable. Loss of drying and film forming properties which may be associated with this process, assuming that degradation of the resin occurs, could reduce its capability to polymerize and form useful films.

The present work was undertaken to determine the rate at which dry would deteriorate and pH would fall when the driers were varied and the manner of addition was modified. Further to this, we were interested whether there was a clear relationship between change in pH and dry performance.

A literature survey revealed no pertinent information on this subject.

EXPERIMENTAL—PART 1

Procedures

The following variables were selected to study the effect of drier selection:

(1) Driers added as naphthenates prior to solubilization: (0.1% Cobalt + 0.1 Manganese); (0.2% Cobalt); (0.2% Manganese).

(2) Driers added as synthetic acid derivatives prior to solubilization: (0.1% Cobalt + 0.1% Manganese); (0.2% Cobalt); (0.2% Manganese).

(3) Driers added as water dispersible naphthenates after solubilization: (0.1% Cobalt + 0.1% Manganese); (0.2% Cobalt); (0.2% Manganese).

(4) Driers added as synthetic acid derivatives to presolubilized resin solution which had been stored until time of test: (0.1% Cobalt + 0.1% Manganese); (0.2% Cobalt); (0.2% Manganese).

(5) Driers added as synthetic acid derivatives to a xylol solution of the resin plus the common level of triethylamine used in other systems: (0.1% Cobalt + 0.1% Manganese); (0.2% Cobalt); (0.2% Manganese).

(6) Driers added as synthetic derivatives to the resin in xylol with no amine: (0.1% Cobalt + 0.1% Manganese); (0.2% Cobalt); (0.2% Manganese).

All drier additions were calculated as percent metal on resin solids. The resin used in these studies was based on isophthalic acid, trimellitic anhydride and conjugated fatty acids. This was a commercial product with an acid value of 40 and supplied at 75% solids in butyl cellosolve.

The test solutions were prepared as follows:

Samples 1–4: Water plus triethylamine plus resin, to a pH of 9.0–9.5.

Sample 5: Xylol plus triethylamine plus resin. The TEA was added at the level used to achieve pH 9.0–9.5 in the water solutions.

Sample 6: Xylol plus resin.

All samples were reduced to 30% solids. Films were applied to glass using a 3 mil gap applicator.

Test Methods

Tests were conducted at 24 hours, and 3, 6, 7½, and 9 months. Tests conducted were: (1) Finger tack free time in minutes; (2) Sward hardness at 24 and 96 hours; (3) pH using a Beckman digital pH meter; (4) Visual stability (recorded as liquid or gelled).

Temperature and humidity were recorded at the time of testing.

Results and Discussion

With reference to the results listed in *Table* 1, the following observations can be made:

Table 1—Aging Data on Alkyd Resin Solutions

Drier Addition[a]	% Metal[b]	Finger Tack Free (mins)					Sward Hardness at 24 hr/96 hr					pH				
		Init.	3m	6m	7½m	9m	Init.	3m	6m	7½m	9m	Init.	3m	6m	7½m	9m
1	A	114	458	Gel	Gel 125c	95c	8.4/15	6/11.3	4/7	−/8	6/7	9.0	7.7	7.6	6.7/6.6c	−/6.4c
	B	117	450	Gel	Gel 123c	119c	10.6/14	8/10.6	5/7	−/9	8/9	9.0	7.8	7.6	−/6.5c	−/6.4c
	C	119	457	646	Gel 179c	130c	7.2/12	8/11.3	4/7	−/10	7/9	9.0	7.8	7.9	6.8/6.8c	6.7/6.7c
2	A	118	461	Gel	Gel 145c	105c	9.4/16	10/12.6	5/8	−/8	6/7	9.0	7.8	7.8	6.7/6.6	6.7/6.8c
	B	124	445	Gel	Gel 126c	120c	9.6/14	8/12	6/9	−/12	7/9	9.0	7.6	7.4	−/6.5c	−/6.4c
	C	121	467	688	173	145	6.2/14	8/10.6	6/9	−/12	8/11	9.0	7.7	7.7	6.8	6.8
3	A	149	469	824	169	140	6.2/12	8/10	4/7	−/12	7/10	9.0	7.9	7.9	7.1	6.8
	B	162	451	601	165	135	7.8/16	6/8.6	5/8	−/−12	9/10	9.0	7.9	8.0	7.1	6.8
	C	142	478	851	332	285c	7.8/12	8/9.3	5/7	−/8	6/10	9.0	7.9	7.9	7.0	6.9
4	A	155	468	797	174	146	9.6/17	7/11.3	6/10	−/10	6/8	9.0	7.8	7.9	7.1	6.9
	B	160	427	482	189	178	6.8/12	7/10.6	6/12	−/14	9/12	9.0	7.7	7.8	7.1	6.8
	C	153	461	668	185	269c	6.8/14	7/10.6	6/10.6	−/10	8/11	9.0	7.7	7.9	7.1	7.0
5	A	97	422	530	339	275c	7/14	10/12	7/13	−/13	9/11	—	—	—	—	—
	B	101	421	532	316	271	10.2/18	10/13.3	4/9	−/12	8/10	—	—	—	—	—
	C	104	423	665	323	268	6.2/12	10/14.6	8/13	−/12	9/10	—	—	—	—	—
6	A	149d	300	450	125c/94	174/175c	10.8/18	14/17.3	11/14	−/15	8/13	—	—	—	—	—
	B	147	240	271	125c/113	178/155c	8.6/16	16/18	12/18	−/18	12/16	—	—	—	—	—
	C	146	311	477	−/925c	−/172c	12/18	13/18	10/15	−/19	13/17	—	—	—	—	—

	Initial	3m	6m	7½m	9m
Temperature at time of test	74	76	73	70	70
Relative humidity at time of test	65/50	74	77	63	48

(a) 1 Naphthenate prior to solubilization
    2 Synthetic acid type prior to solubilization
    3 Emulsified type after solubilization
    4 Synthetic acid type to varnish at time of test
    5 Synthetic acid type to xylol solution + T.E.A.
    6 Synthetic acid type to xylol solution
(b) A 0.1% Co + 0.1% Mn.
    B 0.2% Co
    C 0.2% Mn.
(c) Sample reconstituted with 10% Butanol
(d) Fresh sample of 6A made up at 7½ months to see if original resin was found—tack free 90 mins.
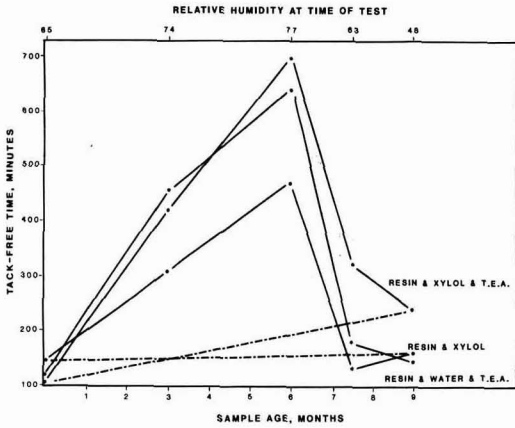(e) After 7½ months aging fresh drier was added to these samples using the same amount as originally added

Figure 1—Tack free time of alkyd resin solutions on aging. (Data for manganese drier at 0.2%)
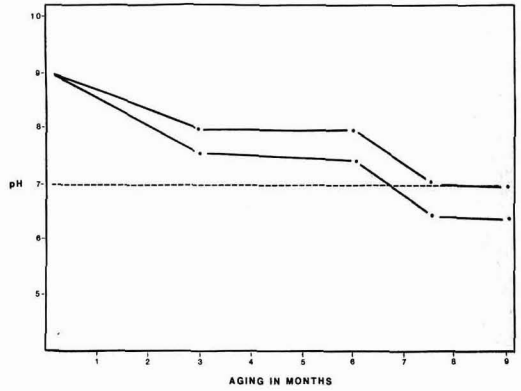

Figure 3—Effect on pH of aging alkyd solutions. (Maximum and minimum pH of all samples under test)

(1) After aging for nine months, all 18 samples displayed modest increases in tack free time or no increase in tack free time.

(2) Within the framework of tack free time, cobalt and manganese are equal initially, with cobalt displaying slightly superior dry retention.

(3) The acid used to manufacture the driers, whether naphthenic or synthetic, does not confer substantial differences in dry rate with aging.

(4) Water dispersible driers do not perform better than conventional driers.

(5) Though not quite as effective as adding driers to the resin prior to solubilization in water, the addition of driers after water addition promotes reasonable dry time.

(6) In the samples where solvent was employed, rather than water, the presence of TEA accelerated initial dry but showed poorer dry retention on aging.

(7) The most significant variable in all the dry tests is humidity. This is illustrated in *Figure* 1 which displays the

data for manganese at 0.2% over the range of the experiment.

The results which were determined initially and at nine months and which were run at similar humidities indicate minimal loss of dry. The results at three and six months demonstrate the dramatic effect of high relative humidity.

(8) The water reduced system showed a significant loss in hardness as measured by Sward Rocker over the nine month period. This is illustrated in *Figure* 2 using the data for manganese at 0.2%. The resin in xylol is relatively unaffected where no T.E.A. is used but behaves similarly to the water reduced version in the presence of T.E.A.

(9) *Figure* 3 represents the range of pH change with time of all samples under test. A clear plateau exists in the fall of pH at approximately three to six months. The rate of pH loss prior to three months is unknown since readings were not taken during this period. The pH loss
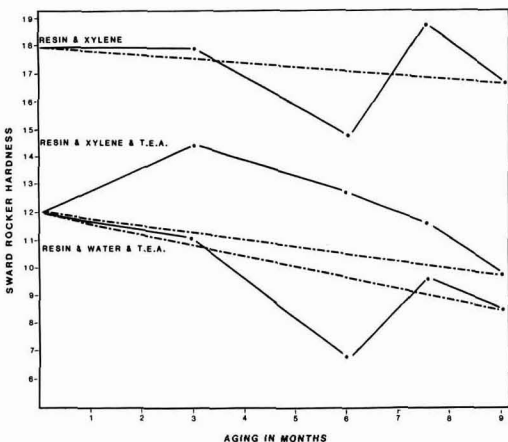
Figure 2—Hardness of alkyd resin films as solutions are aged. (Data for manganese drier at 0.2%)

Table 2—pH Stability of Aqueous Coalescing Solvents

	Initial	pH Four Weeks at R.T.	Four Weeks at 130°F
Ethylene glycol monobutyl ether	8.7	7.2	4.0
Ethylene glycol monoethyl ether	9.1	7.8	5.5
Diethylene glycol monoethyl ether	9.7	7.8	3.8
Ethylene glycol monomethyl ether	10.0	8.3	8.9
Propylene glycol monopropyl ether	9.8	9.4	9.0
Isopropanol	10.0	9.4	9.3
Ethylene glycol monoethyl ether acetate	9.1	4.9	2.8
Diethylene glycol monobutyl ether	9.0	5.2	3.5
4-Methoxy 4-Methyl 2-Pentanone	8.7	6.0	5.0
Propanol	10.0	8.6	8.8

Table 3—pH Stability of Aqueous Glycol Ethers in Distilled Water

Solvent 20: Distilled water 80

		pH	
	Initial	17 Days R.T.	17 Days 130°F
Ethylene glycol monomethyl ether 7.3		4.8	3.2
Ethylene glycol ethyl ether 7.0		5.1	4.7
Ethylene glycol propyl ether 3.4		3.4	3.3
Ethylene glycol butyl ether 3.2		3.5	3.3

Table 4—pH Stability of Aqueous Glycol Ethers in Tap Water

Solvent 20: Tapwater 80

		pH	
	Initial	17 Days R.T.	17 Days 130°F
Ethylene glycol monomethyl ether 7.1		7.0	3.0
Ethylene glycol ethyl ether 7.0		7.0	6.7
Ethylene glycol propyl ether 7.4		4.6	3.6
Ethylene glycol butyl ether 6.5		4.7	3.5

Table 5—pH Stability of Aqueous Glycol Ethers in Distilled Water with 2 AMP

Solvent 20: Distilled water 80
2-AMP: 1 Drop to 100 grams

		pH	
	Initial	17 Days R.T.	17 Days 130°F
Ethylene glycol monomethyl ether 10.6		10.2	3.4
Ethylene glycol ethyl ether 10.3		9.8	6.6
Ethylene glycol propyl ether 8.5		4.7	3.9
Ethylene glycol butyl ether 7.5		3.2	4.0

Table 6—pH Stability of Aqueous Glycol Ethers in Tap Water with 2 AMP

Solvent 20: Tapwater 80
2-Amp: 1 drop to 100 grams

		pH	
	Initial	17 Days R.T.	17 Days 130°F
Ethylene glycol monomethyl ether 9.7		9.2	5.3
Ethylene glycol ethyl ether 9.8		8.5	7.8
Ethylene glycol propyl ether 9.3		5.6	4.5
Ethylene glycol butyl ether 8.7		6.2	4.3

between 6 and 7.5 months suggests two separate mechanisms generating pH change.

EXPERIMENTAL—PART II

The data shown in *Table* 2 shows the pH stability of several solvents which might be employed as coupling solvents in water soluble alkyd resins.

The samples were prepared as follows: Solvent—20 grams; Water—80 grams; 2-amino, 1-methyl propanol one drop. The alkyd used in the drier studies contained ethylene glycol monobutyl ether. Since the rate of pH fall was of a similar order to that displayed by data in *Table* 2, the work carried out by Donlin was repeated using glycol ethers, under varying conditions.

Results and Discussion

The results are listed in *Tables* 3, 4, 5, and 6. Regardless of whether distilled or tap water is used and whether or not amine is added, the following general observations can be made:

(1) The initial pH of 80/20 water/glycol mixtures (this ratio being typical of those encountered in water reducible alkyd systems) tends to decrease as the molecular weight of the glycol ether increases.

(2) The pH decreases rapidly on aging.

(3) The rate of pH drop is accelerated by elevated temperature.

CONCLUSIONS

The water reduced alkyd solutions used in the drier study show a drop of pH over the first three months of storage.

The glycol ether/water solutions, particularly the ethylene glycol monobutyl ether solutions, display a similar drop in pH within the same time frame.

The above suggests that loss of pH in water soluble systems containing glycol ethers may be due to properties of the glycol ether used. This possibility is currently being investigated by the Toronto Society for Coatings Technology Technical Committee.

Society Meetings

BIRMINGHAM .... **MAR.**

"Powder Coating Manufacturing Methods"

Society President Harry Griffiths presented Distinguished Service Awards to George Hind, Hal Clarke, and George Tennant.

President of the Society in 1957, Mr. Hind served on the Program, Publicity and Executive Committees. Mr. Clarke was President in 1961 and has actively served as a member of the Executive Committee and as a member and chairman of the Membership Committee. In addition to his contribution to the preparation of the audio visuals on the Setaflash and the Paint Industry, Mr. Tennant served as Society Secretary in 1974–76 and for part of 1977. He has also served on the Program, Publicity, and Executive Committees.

Mr. E.E. Byerley, of Byerley Machinery Sales, spoke on "POWDER COATING MANUFACTURING METHODS."

Mr. Byerley noted that, despite considerable diversification of powder type in the last eight years, machinery has remained basically unchanged from 1970-84. He showed slides of stirrer, bin, and ribbon blenders, listing space saving and process speed as the principal advantages of the former two, and ease of cleaning as the main benefit of the latter. He then described various feeders and the methods used to protect against foreign objects reaching the extruder. Particularly stressed was the need for accurate feed rates.

Continuing his presentation with an examination of the various extruders on the market, he showed different cooler, kibbler, milling and classification machinery. He concluded with a discussion of changes and development in this field.

DONALD H. CLEMENT, *Secretary*

CLEVELAND .... **MAR.**

Graphic Arts Operation Tour

James N. Apotsos and Beverly A. Damko, of the Sherwin-Williams Graphic Arts Operation, presented a slide demonstration detailing the plant and its operations. Society members were then led on a guided tour of the plant. Among the operations shown was computer-controlled color matching using an Applied

Color Systems Color Control System computer.

SCOTT E. RICKERT, *Secretary*

LOS ANGELES .... **MAR.**

Past-President's Night

In honor of Past-President's Night, President Lloyd Haanstra recognized the following Past-Presidents in attendance: Romer Johnson (1982–83); Don Jordan (1980–81); Al Seneker (1979–80); Fred Croad (1978–79); Bob Koperek (1977–78); Gerry West (1976–77); Ken O'Morrow (1975–76); Bill Ellis (1971–72); Duke Cromwell (1970–71); Trev Whittington (1969–70); Al Aronow (1964–65); Walt Barber (1963–64); Al Hershey (1961–62); Fred Oberlin (1960–61); Leonard Feldman (1959–60); Dan Heisler (1955–56); Clyde Smith (1946–47); John Warner (1945–46) and Bert Martin (1943–44).

Lloyd Haanstra reported on the Architectural Task Force meeting. During the meeting, the evaluation results of six paints (three interior, three exterior; two oil based, four latex based) were discussed. According to Mr. Haanstra, the results showed that the oil paints were superior to the latex products in all cases. Therefore, he moved to extend the 380 VOC rule to September of 1989. Also discussed by Mr. Haanstra were alternate approaches to regulating architectural products, the CARB 1113 hearing, and a Hazardous Materials Management Conference and Exhibition held in April.

SOCIETY PRESIDENT Lloyd Haanstra (left) presents Mike Gildon with the Trigg Award certificate at the L.A. Society meeting.

Mr. Haanstra reminded members of the scholarship funds available for eligible students.

Mike Gildon was presented with the Trigg Award certificate for his excellence in recording the Society minutes during 1982-83. The APJ/A.F. Voss Award was presented to the Technical Committee for their work on the paper, "Water-Based Aerosols."

Robert N. Price, of Spencer-Kellogg, spoke on "WATER, HIGH SOLIDS, OR BOTH."

According to Mr. Price, increasing implementation of VOC regulations, coupled with continued high solvent costs are accelerating the pace towards compliant coatings in particular and

PAST-PRESIDENTS of the L.A. Society were honored at the March meeting of the Society. Those in attendance included (top row, left to right): Al Seneker, Don Jordan, Romer Johnson, Fred Croad, Bob Koperek. (bottom, left to right): Duke Cromwell, Bill Ellis, Ken O'Morrow, and Gerry West.

lower solvent coatings in general. Water thinned and high solids are both viable approaches to this demand for low solvent coatings, he stated. The decision of which approach is to be used becomes a matter of personal preference based on comparative performance data, he concluded.

Q. How does the shelf stability of water-based versus high solids compare?

A. It is difficult to generalize, however, high solids products have an overall tendency to be more stable than water-based systems. Bear in mind that water-based systems are continually being improved.

HARRY J. KIRSCH, *Secretary*

LOUISVILLE . . . . MAR.

"Computer Software for the Coatings Industry"

Don Erwin, of Erwin, Schafer Assoc. Computer Software, spoke on "COMPUTER SOFTWARE FOR THE COATINGS INDUSTRY."

Mr. Erwin discussed the many uses for computers in the coatings industry. Uses for laboratory orientation include raw material management, formula management, production management, and purchase order management. Some of the benefits of computerization he described were the reduction of raw material cost, improved laboratory efficiency, increased production efficiency; improved customer services; and reduction of purchasing costs.

M. JOYCE SPECHT, *Secretary*

WESTERN NEW YORK . . . NOV.

"Formulating Parameters For Gloss Latex Paints"

Twenty-five year pins were presented to Dick Hong, John Kowalski (retired), Robert Price, and Mark Markoff, all of Spencer-Kellogg Div., Textron, Inc.

"FORMULATING PARAMETERS FOR GLOSS LATEX PAINTS" was presented by A. Clarke Boyce, of Nacan Products Ltd.

The parameters discussed by Mr. Boyce were: polymer, pigments, dispersants, surfactants, glycol levels, thickener levels, other additives. Mr. Boyce explained how each one of these parameters could affect properties such as gloss, hiding, durability, stability, color retention, wet edge, lap time, flow, etc. He also emphasized how molecular weights of the polymer can be a key property—dictating reactivity, hardness, strength, and degree of cure.

Next, Mr. Boyce discussed how the glass transition temperatures of the emulsion are important, from the standpoint of paint application, where the emulsion must be above Tg, while being applied to the surface, or adhesion will be lost.

CHARLES TABBI, *Secretary*

Elections

BIRMINGHAM

Active

GRAHAM, CHARLES MILES—International Paint, Birmingham, England.

CHICAGO

Active

ANGELOS, EVANS—Kraft Chemical Co., Melrose Park, IL.
FRANICEVIC, GEORGE J.—DeSoto, Inc., Marengo, IL.
LEEP, RICHARD H.—Zummach-Peerless Chem., Milwaukee, WI.
NONWEJLER, MARK A.—A P Nonwejler Co., Inc., Oshkosh, WI.
VOLK, VINCE—The Meyercord Co., Carol Stream, IL.

Associate

FAASSEN, E. JOHN—Henley & Co., Inc., Lake Bluff, IL.
HUNT, JAMES G.—Polyvinyl Chemicals, Naperville, IL.
LENOBLE, AUDREY—Carl Lechner, Inc., Northbrook, IL.
RAHMAN, M.S.—McCook Paint Co., Inc., McCook, IL.

CLEVELAND

Active

AHLUWALIA, SURINDER S.—Premier Industrial Corp., Cleveland, OH.
ANTHONY, ROBERT D.—Glidden Coatings, Westlake, OH.
BARR, THOMAS F.—Consultant, Parma Heights, OH.
BURDT, DALE M.—Master Builders, Cleveland.
CARLOZZO, BEN J.—Sherwin-Williams Co., Cleveland.
GROSS, MELVIN A.—Sherwin-Williams Co., Cleveland.
HORIGUCHI, TAKUYA TED—Shinto Paint Co., Ltd., Cleveland.
KLEMBARA, DEBORAH—SCM Corporation, Strongsville, OH.
LOBERGER, ANDREW C.—Glidden C&R Div. SCM., Strongsville.
LOZA, ROSEMARY B.—Standard Oil (Ohio), Cleveland.
MCALLISTER, RAYMOND P.—Beaver Paint Co., Girard, PA.
NEMUNAITIS, DANIEL P.—Sherwin-Williams Co., Cleveland.
OGURCHAK, ANDREW—Sherwin-Williams Co., Cleveland.
PANT, BIPIN CHANDRA—Polycarb-Inc., Solon, OH.
RADKE, DAVID J.—Glidden Coatings & Resins, Strongsville.
SOBEK, SUSAN M.—Glidden Coatings & Resins, Strongsville.

TAGGART, JOHN S.—Acconoplast, Inc., Cleveland.
TISEVICH, JOHN A.—Glidden Coatings & Res., Strongsville.
TOKAR, VALERY—Euclid Chemical Co., Cleveland.
WEBER, AL—Pratt & Lambert Inc., Pepper Pike, OH.
WHITE, JOHN EDWARD—Glidden Coatings & Resins, Westlake.

Associate

BRUNING, ROBERT A.—Lucidol Div. - Pennwalt, Buffalo, NY.
SIMONTIS, ALFRED—Byk-Mallinckrodt USA, Lakewood, OH.

Retired

LEVY, MORTON L.—Shaker Hts., OH.
MCCLURE, EARL F.—Cuyahoga Falls, OH.
WANDERSLEBEN, A.J.—Alliance, OH.

DETROIT

Active

CEDERNA, JOANNE C.—Inmont Corp., Southfield, MI.
GRIFFIS, WADE B.—Inmont Corp., Whitehouse, OH.
NIEMI, CAROL—Dow Chemical Co., Midland, MI.
SAUTURAL, DANIEL—Inmont Corporation, Detroit, MI.
STEWARD, GARY R.—Inmont Corporation, Detroit.
WYATT, MAXWELL—Seibert Oxidermo, Romulus, MI.

Associate

SANDERSON, TERRI—Dow Corning Corporation, Midland, MI.

GOLDEN GATE

Active

ATHEY, JR., R.D.—Athey Technologies, El Cerrito, CA.

BALESTRIERI, STEVEN G.—BAAQMD, San Francisco, CA.
BENEDETTI, RAYMOND J.—Triangle Coatings, Inc., Berkeley, CA.
BOSARGE, ROY—Bechtel Group, Inc., San Francisco.
BURKE, JAMES M.—Jasco Chemical Corp., Mountain View, CA.
BURTON, CURTIS—Masonite Corp., Ukiah, CA.
CHOW, JOSEPH—Versatec, Santa Clara, CA.
CONNELLY, FRED—Flecto Co., Inc., Oakland, CA.
DAVIS, JOHN J.—Aervoe Pacific Co., Inc., San Leandro, CA.
ENG, RICHARD Y.W.—Hi-Line Paint Co., Campbell, CA.
FILSON, DAVID—Clorox, Pleasanton, CA.
FREDERICK, MICHAEL—Glidden Ctgs. & Resins, San Francisco.
GOODSON, KEITH—Tandy Magnetic Media, San Jose, CA.
ISZAK, DAISY—Flecto Co., Inc., Oakland.
KELLY, JOHN—International Paint Co., Calif., S. San Francisco, CA.
LA MAR, GEORGIA—Orcon Corp., Union City, CA.
LEE, YU CHEUN—Dysan Corp., Newark, CA.
LIM, JULIETTE—International Paint Co., Calif., S. San Francisco, CA.
OWEN, DENNIS R.—Technical Coatings Co., Santa Clara, CA.
PHILLIPS, JOHN E.—BAAQMD, San Francisco.
SPECHT, TIMOTHY G.—Flecto Co., Inc., Oakland.
URIOSTE, SANDRA D.—Ashland Chemical Co., Newark, CA.

Associate

BARTON, JOE B.—Allied Corp., Half Moon Bay, CA.
CONOVER, JR., HOLLIS M.—Buckman Labs Inc., Novato, CA.
HAULIK, THOMAS J.—Union Carbide Corp., San Francisco, CA.
HUTCHINS, WADE—P.T. Hutchins Co., Emeryville, CA.
YURTIS, PHIL—Polyvinyl Chemical Ind., Vallejo, CA.

FSCT MEMBERSHIP ANNIVERSARIES

50-YEAR MEMBERS

Los Angeles

Bernard Friedland, Seaside Paint & Lacquer Co.

Rocky Mountain

Lyman P. Hunter, Retired.

25-YEAR MEMBERS

Southern

C. "Bud" Rystrom, Rystrom Laboratory.
Robert F. Woolard, Quality Coatings, Inc.

Meetings/Education

Houston and Dallas Host 250 at Southwestern Paint Convention in April

Eight papers, under the general theme of "Productivity and Opportunities in the 80's," were presented at the 41st Southwestern Paint Convention of the Houston and Dallas Societies for Coatings Technology, April 12–14, in Houston.

General Chairman of the event was John Pennington, of Cron Chemical Corp. Mike Winters, of Ribelin Distributors, was Vice-Chairman. Dick Batchelor, of Valspar Corp., was Program Chairman. Registered attendance was about 250.

The papers were:

"The Effects of Surface Defects in Coatings"—Clifford K. Schoff, of PPG Industries, Inc.

"Colloidal Silica—a Unique Pigment for the Coatings Industry"—Richard Thornton, of Nalco Chemical Co.

"High Speed Paint Filling"—Jill Ley, of Consolidated Packaging Machinery.

"Role of Acetylenic Glycols in Water-Borne Coatings"—Don Dennison, of Air Products & Chemicals, Inc.

"Dispersion of Carbon Blacks in Coatings Systems"—James Joudrey, of Columbian Chemicals Co.

"Management Information Systems"—John Stevenson, of Valspar Corp.

"Computer Color Matching"—David Atkinson, of Macbeth Div.

"Inerting for Safety in Coatings Plants"—Kevin Donahue, of Neutronics, Inc.

Officers of the Houston Society this year are: President—Don Montgomery, of The O'Brien Corp.; Vice-President—Mr. Batchelor; Secretary—Arthur McDermott, of Nalco Chemical Co.; Treasurer—Rudy Buri, of Champion Coatings, Inc.; and Society Representative—Willy C.P. Busch, of PPG Industries, Inc.

The 1985 Southwestern Paint Convention will be held in Dallas, April 12–15.

In a joint "Picture It Painted" venture of the Portland section of the Pacific Northwest Society and the Portland Paint and Coatings Association, nearly $5000 of paint and other materials were donated towards the renovation of the Portland, Oregon Ronald McDonald House. At ceremonies on March 5, 1984, a symbolic bucket of paint was presented by Society Secretary Jerry McKnight (left) and PCA President, Bill Tuor. This community service donation was accepted on behalf of the Ronald McDonald House Board of Directors by Mrs. Dolores Atiyeh, wife of the Oregon governor. Ronald McDonald himself was on hand to support their efforts

People

Dr. John C. Weaver has been elected Chairman of Committee D-1 on Paint and Related Coatings and Related Materials for the American Society for Testing and Materials (ASTM). A lecturer and consultant for the Dept. of Macromolecular Science at Case Western Reserve University, Dr. Weaver will serve a two-year term.

An active member of ASTM for many years, Dr. Weaver received honorary membership in 1976. He served on the board of directors from 1977–81. He is a member of the Cleveland Society and has served as Chairman for many Federation committees.

Frederick W. Armstrong, Jr. has been promoted to Vice-President/Technical Director of Chemray Coatings Corp., Middlesex, NJ. Active in the paint industry for over 25 years, Mr. Armstrong is a member of the New York Society.

Enterprise Chemical Coatings Co. has named Richard A. Elsner, Jr. as President. Involved in the paint industry for nearly 30 years, Mr. Elsner formerly served as Vice-President/General Manager for the firm.

Malcolm Penman has been appointed Manager of Process Development for Sartomer Co., a subsidiary of Atlantic Richfield Co. He will be responsible for all pilot plant development activities for the firm.

Jerome Frankel has been named Manager of International Operations for Interstab Chemicals, New Brunswick, NJ. Prior to this appointment, he served as Export Sales Manager. Mr. Frankel is a member of the New York Society.

Pierce & Stevens Chemical Corp., Buffalo, NY, appointed George E. Wickett to the position of Plant Manager. Mr. Wickett formerly held the position of Plant Supervisor.

CasChem, Inc., Bayonne, NJ, has appointed Steve C. Kondracki Customer Service Manager. He most recently held the position of Purchasing Agent.

J.C. Weaver F.W. Armstrong, Jr. E.M. Mattes T. Fitzgerald, Jr.

Union Carbide Corp., Danbury, CT, has appointed Eileen M. Mattes Marketing Research Programs Manager for the Silicones and Urethane Intermediates Div. Most recently, she served as Market Manager for organo-functional silanes, with responsibility for thermoset markets and glass fibers, coatings, and electronic applications.

Eastman Chemical Products, Inc., has named Lee H. Davis as Senior Marketing Representative in charge of special coatings accounts and distributors in the metropolitan Chicago area.

The O'Brien Corp., S. San Francisco, CA, has announced the following appointments for its Container Coatings Laboratory in South Bend, IN: Al Hatkevich—Senior Group Leader; and John Grubesic—Group Leader. Mr. Hatkevich is a member of the Chicago Society.

In addition, the company has named James R. Shirley National Sales Manager for the Container Coatings Div.

Sun Chemical Corp., Pigments Div., Cincinnati, OH, has announced the promotion of Jeff Hamilton to District Manager, West Coast. Joining Sun Chemical are: John Ignatius as Flush Research Manager; Jeffrey Randolph as Group Leader/Technical Service; Thomas Ashe and Robert Jancewicz to the Sales Department.

Dr. H. David Medley has rejoined Celanese Chemical Company, Inc., Dallas, TX, as Vice-President—Marketing. He is responsible for sales and marketing of the company's products in both domestic and overseas markets.

Thomas Fitzgerald, Jr. was appointed to the position of Technical Director of Negley Paint Co., San Antonio, TX. He was formerly Production Manager of the Devoe & Raynolds plant. Mr. Fitzgerald is a member of the Houston Society.

John E. Haddock was appointed Vice-President and General Manager for Manchem, Inc., Princeton, NJ. Mr. Haddock is a member of the New York Society.

The company has named Roger W. Cash Vice-President, Rubber Chemicals. He will be based in Hudson, OH.

Volstatic, Inc., Florence, KY, has announced the promotions of two new managers for their electrostatic powder coating equipment. G. Bruce Bryan, Jr. will manage the central region and Paul J. Lesniewski will assume responsibility for the eastern region.

Three members of the Birmingham Paint, Varnish and Lacquer Club were honored with Distinguished Service Awards at the meeting of March 1. George Hind joined the Club in 1946. He was President in 1959 and Social Officer from 1972–81. Since 1973, he has been Toastmaster at the Ladies Night Dinner Dance. Hal J. Clarke has been a member since 1954. He was elected to the Presidency in 1961 and served continuously on the Membership Committee from 1962–82. George H. Tennant served as Secretary from 1974–77 and was elected President in 1978. All three gentlemen are retired.

Ruth Johnston-Feller was presented with the Macbeth Award at the recent annual meeting of the Inter-Society Color Council. The award was in recognition of her many contributions to the field of color science. Mrs. Johnston-Feller was one of the first to introduce instrumental color-control in a major paint manufacturer in the United States.

Presently a consultant and research associate in color science at the Research Center on the Materials of the Artist and Conservator at Mellon Institute, Carnegie-Mellon University, Pittsburgh, Mrs. Johnston-Feller directs the color-science laboratory and research on fading of paints and textiles.

Previously, she was Manager of the Coatings and Colorimetry Laboratories of the Pigment Dept. of CIBA-GEIGY Corp. in Ardsley, NY, Director of Application Services of the Color Systems Div. of Kollmorgen Corp., and Project Leader for Color Research at the Coatings and Resins Div. of PPG Industries.

Mrs. Johnston-Feller is currently chairman of the Federation's Bruning Award Committee and served for many years as chairman of the Inter-Society Color Council Committee. She was a member of the Publications Committee and Editorial Review Board of the JOURNAL OF COATINGS TECHNOLOGY. She also served the Federation as a member of the Board of Directors and as a Trustee of the Paint Research Institute.

Mrs. Johnston-Feller is a previous winner of the Armin J. Bruning Award, and (with co-author Dennis Osmer, of CIBA-GEIGY) the Dry Color Manufacturer's Award.

Joyce Davenport, of DeSoto, Inc., Des Plaines, IL., was elected President of the Inter-Society Color Council at its recent annual meeting.

Ms. Davenport, a native of the United Kingdom, is Supervisor of Color Development with DeSoto, whom she joined in 1970 as Supervisor of Industrial Color.

Receiving her chemical education at the University of Nottingham, she was previously associated with the plastics industry in the United States.

Sam K. Mitchell has been appointed Technical Sales Representative for Sandoz Colors & Chemicals, Charlotte, NC. Mr. Mitchell will specialize in the sales and service of Sandoz colorants and specialty chemicals to the coatings, plastics, leather, cosmetic and household products industries on the West Coast. Mr. Mitchell is a member of the Los Angeles Society.

Obituary

Howard S. McCullough, Sr., a member of the Southern Society, died on March 21, 1984. Mr. McCullough served as President of McCullough & Benton, Inc., Atlanta, GA. He was 62 years old.

Martin J. Monahan, a former Vice-President of Research and Development of Acorn Chemical Co., died on February 26, 1984. He was 79 years old.

Mr. Monahan was associated with both the Chicago and the Cleveland Societies.

Paul A. O'Neill, formerly of Hercules, Incorporated, died on March 24 at the age of 71. Mr. O'Neill served as District Manager for the firm's Wilmington, DE sales office until his retirement in 1977.

Literature

Viscosity Loss Test

A three-page technical bulletin describing test procedures to determine the causes of viscosity loss in latex paint is now available. A four-step test procedure is outlined, followed by calculations that will identify the percent of viscosity loss. For a copy of Bulletin VC-492B, contact: Product Inquiry, Hercules, Incorporated, Hercules Plaza, Wilmington, DE 19894.

Color Control

Information is available on a new computer color system with remote communications capabilities. The system allows users to operate color control work stations in multiple locations, while accessing data from a central "host" system. For more information, contact Applied Color Systems, Inc., P.O. Box 5800, Princeton, NJ 08540.

Umbers

Recently released literature describes a new line of umbers with extra tinting strength, designed to reduce the amount of pigment necessary while improving "hide" in a given system. For further information, contact Reichard-Coulston, Inc., 1421 Mauch Chunk Rd., Bethlehem, PA 18018.

Resins

A bulletin discussing oil and alkyd modified polyurethane resins for wood finishing is now available. Included are suggested formulations for both clear and pigmented finishes and product specifications. The bulletin is available from Reichhold Chemicals, Inc., 525 North Broadway, White Plains, NY 10603.

Solvent Recovery

A series of two new solvent recovery stills is now available. These units are designed for salvaging valuable solvent from contaminated liquors typically found in inks, paint manufacture, and throughout the chemical industry. For additional information, contact Disti, Inc., 131 Prince St., New York, NY 10012.

Metallic Stearates

A new four-color brochure is available describing the properties and major applications of various groups of metallic stearates and allied soaps used in many different industries. The brochure discusses the key uses and functions of each family of stearates, including aluminum, calcium, lithium, sodium, magnesium and zinc stearates as well as special metalorganics. It also provides detailed typical property data on all grades of these products and describes applicable analytical procedures. The 18-page brochure can be obtained from Witco Chemical Corp., Organics Div., 400 North Michigan Ave., Chicago, IL 60611.

Diluent

Information is now available on a cycloaliphatic epoxide viscosity-reducing agent. The new reactive diluent is designed for use with cycloaliphatic epoxide resins to formulate photocurable coatings that exhibit low viscosity, rapid cure, and low toxicity. Further information on Cyracure® Diluent UVR-6200, including formulation suggestions, can be obtained from Union Carbide Corp., Specialty Polymers and Composites Div., Dept. M1553, Danbury, CT 06817.

Shipping and Storage Container

A container, for shipping and storage of improved bulk liquid, or flowable dry material, which has been developed to eliminate the 55 gallon drum and provide safety, space savings, sanitation, and cost efficiency, is the subject of new literature. Design features and use advantages are highlighted. For additional information, contact Clawson Tank Co., 4701 White Lake Rd., Clarkson, MI 48016.

Flow Agent

A versatile additive used in a variety of water-reducible finishes is the subject of a new technical bulletin. This flow agent is designed to promote better substrate wetting, resulting in smoother, more uniform films. Specifications, as well as ingredients for water baking and gray dipping enamels are provided. For more information, contact Reichhold Chemicals, Inc., 525 North Broadway, White Plains, NY 10603.

Urethane Solvent

Technical literature on a urethane grade solvent specifically designed to replace ethylene glycol ethel ether acetate in high solids industrial baked coatings systems can now be obtained. For a copy of the literature, contact Inquiry Services, Dow Chemical, USA, P.O. Box 1206, Midland, MI 48640.

Polymers

Information is now available which details new brand names and logos for polymer products. The new brand name will be used in conjunction with all polymer emulsions developed, manufactured and marketed by the polymer operation. For more information on 76 RES, contact Union Chemicals Div., Union Oil Co. of California, 1900 E. Golf Rd., Schaumburg, IL 60195.

Resins

A new color brochure that provides information on vinyl dispersion resins is now available. The literature discusses raw materials properties, rheology and fusion theory, preparation and testing of compounds, and processing methods. The text is illustrated with tables, figures, and application photos. For Bulletin G-74, "Geon® Vinyl Dispersion and Blending Resins," write BFGoodrich Co., Chemical Group, 6100 Oak Tree Blvd., Cleveland, OH 44131.

Flame Retardant System

A new brochure is available which gives comprehensive information on flame retardant systems for use in thermoplastic and engineering resins. The "Flame Retardant Systems" brochure may be obtained by writing PPG Industries, 8 North, One PPG Place, Pittsburgh, PA 15272.

Glycol Ethers

Literature detailing the use of propylene-based glycol ethers as high-quality direct replacement for ethylene-based glycol ethers in many coatings systems is now available. Contact Dow Chemical U.S.A., Inquiry Services, P.O. Box 1206, Midland, MI 48640 for a brochure.

Pump Catalog

A 16-page, condensed, fully illustrated pump catalog is now available. It includes revised pump features, specifications and drive arrangements. For more information on bulletin "S," contact Viking Pump Div., Houdaille Ind., Inc., Cedar Falls, IA 50613.

Incineration

Information is available which details the disposal of large volumes of full or empty waste aerosol cans by incineration. For copies of the literature, contact Ross Incineration Services, Inc., 394 Giles Rd., Grafton, OH 44044.

Color Matching System

Literature is available introducing a new DIANO color matching system which is 35% lower in cost than its predecessor yet features new color graphics capability and the flexibility of a personal computer. Discussed is DIANO Match-Mate™ 325 which features a personal computer selected specifically to satisfy extensive "number-crunching" applications associated with color matching and to provide broad functionality. Application advantages and available options of the system are highlighted. For information, write Bausch & Lomb, Inc., 1400 N. Goodman St., Rochester, NY 14625.

Attritor Systems

Literature has been published featuring two new attritor systems which have been developed for fine particle processing. Advantages of using the new systems are highlighted which include the elimination of metallic contamination since the grinding chambers are lined with polyethylene or ceramic materials and the other components are all made with non-metallic materials. For information, contact Jerry Malaga, Union Process, Inc., 1925 Akron-Peninsula Rd., Akron, OH 44313.

Diversified Products

A 36-page brochure that classifies a full range of diversified products into 10 major markets has been recently published. The products are based on 14 identified technologies that range from adhesives, abrasives, and coatings to films, fluorochemistry and information processing. For a copy of "3M Hears You," write 3M, Dept. 99/3M, P.O. Box 2202, Robbinsdale, MN 55422.

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HYDROUS AND ANHYDROUS ALUMINUM SILICATE PIGMENTS · KAOLIN CLAYS

Book Review

THE PRODUCTION AND APPLICATION OF FLUORESCENT BRIGHTENING AGENTS

Written by
Milos Zahradnik

Published by
John Wiley & Sons, Inc.
New York, NY
$29.95

Reviewed by
F. Louis Floyd
Glidden Ctgs. & Resins
Strongsville, OH

The author wrote the book in recognition of two facts: (1) there does not exist any textbook devoted exclusively to optical brighteners, and (2) optical brighteners are making major contributions to many branches of industry. From the tone of the introduction of the book, this reviewer was led to expect something on the order of a definitive textbook on the subject of optical brighteners. While the book certainly is a good introduction to the topical area, it does not serve the anticipated function.

The book reads as though it were written by an organic chemist for reading by other organic chemists. As a result, the organic chemistry is brushed over very quickly, while the physical chemistry is explained in considerable detail, lest the organicists fail to comprehend. Overall the book seems aimed at a novice chemist rather than an industrial practitioner. For example, the issue of structure/property relationships was covered in very general terms, without enough examples to allow the reader to develop a flavor for the nuances involved in the modification of the basic backbone of the brightener molecule.

Zahradnik provides a good overview of the production and use of optical brighteners worldwide, including a quite reasonable historical perspective. The organization of the descriptive organic chemistry is quite good, allowing the reader to systematically work through the various compositional types which form the basis of optical brighteners. The discussion of modifications of the backbone structures (primarily substitutions) was also quite reasonable. The style, unfortunately, was a bit stilted, reading much like a series of examples from patents around the world.

One major deficit existed in the book: no references were cited. Aside from the fact that normal attribution procedures require such referencing, this reviewer was particularly disturbed because the book failed to provide an introduction to the literature on the subject. The book, in fact, reads as if it were a rendering of the author's knowledge bank plus an exposition of selected examples from patent cases. The descriptions and assertions should be backed up with some hard data or at least hard references, so an interested reader can follow the information through to the original source.

Another deficiency was the absence of any discussion of economics of use. While it was acknowledged that fluorescing agents must be used in higher purity than most dyes, no discussion of use levels versus raw material cost was given in the text. This again prevents the reader from getting a good view of how this product fits into its end use marketplace as well as a feel for how fluorescent agents might fit into some other field not described in the book.

Overall, this was an average book of average content and clarity. It is a good introduction to the subject material, but the absence of references will prevent the reader from pursuing the knowledge bank beyond the text written. The value of this book will primarily be with the novice rather than with the experienced industrial practitioner. One final thought: who exactly is Milos Zahradnik? I searched through the book for some time without finding any references to the author or his background.

Coming Events

FEDERATION MEETINGS

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

1985

(May 14–17)—Federation "Spring Week." Seminar on 14th and 15th; Society Officers on 16th; and Board of Directors on 17th. Hilton Hotel, Baltimore, MD. (FSCT, 1315 Walnut St., Philadelphia, PA. 19107).

(Oct. 7–9)—63rd Annual Meeting and 50th Paint Industries' Show. Convention Center, St. Louis, MO. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

1986

(May 13–16)—Federation "Spring Week." Seminar on 13th and 14th; Society Officers on 15th; and Board of Directors on 16th. (FSCT. 1315 Walnut St., Philadelphia, PA 19107).

(Nov. 5–7)—64th Annual Meeting and 51st Paint Industries' Show. World Congress Center, Atlanta, GA. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

SPECIAL SOCIETY MEETINGS

(June 18)—Golden Gate Society for Coatings Technology's Manufacturing Committee Symposium on "Safety and Robotics." Sabella's, San Francisco, CA. (Louie Sanguinetti, Jasco Chemical Co., P.O. Drawer J. Mountain View, CA 94042).

1985

(Feb. 26–Mar. 1)—Western Coatings Societies Symposium and Show. Disneyland Hotel, Anaheim, CA.

(Mar. 26–28)—Southern Society. Annual Meeting. Atlanta Hilton Hotel, Atlanta, GA. (Salvatore G. Sanfilippo, Reichhold Chemicals, Inc., P.O. Box 1610, Tuscaloosa, AL 35403).

(Apr. 10–12)—Southwestern Paint Convention of Dallas and Houston Societies. Anatole Hotel, Dallas, TX. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

(Apr. 25–27)—Pacific Northwest Society for Coatings Technology Symposium. Empress Hotel, Victoria, B.C. (Ottwin Schmidt, Helzer Canada Ltd., 8531 Cullen Crescent, Richmond, B.C., V6Y 2W9 Canada).

1986

(Mar. 25–27)—Southern Society. Annual Meeting. Hilton Hotel, Savannah, GA. (Ronald R. Brown, Union Chemicals Div., P.O. Box 26845, Charlotte, NC 28213).

OTHER ORGANIZATIONS

(June 17–20)—Dry Color Manufacturers' Association's Annual Meeting. The Greenbrier, White Sulphur Springs, WV. (P.J. Lehr, DCMA, Suite 202, 206 N. Washington St., Alexandria, VA 22314).

(June 18–22)—"Principles of Color Technology" course. Rochester Institute of Technology, Rochester, NY. (Brenda Reimherr, T&E Center Seminar Coordinator, Rochester Institute of Technology, One Lomb Memorial Dr., P.O. Box 9887, Rochester, NY 14623).

(June 24–29)—"High Temperature and Coatings" Short Course. Stockholm, Sweden. (Continuing Education Institute—Europe, Rorstorpsvagen 5, S-612 00 Finspang, Sweden).

(June 25–29)—"Advances in Color Technology" course. Rochester Institute of Technology, Rochester, NY. (Brenda Reimherr, T&E Center Seminar Coordinator, Rochester Institute of Technology, One Lomb Memorial Dr., P.O. Box 9887, Rochester, NY 14623).

(June 25–29)—"High Solids Coatings" Short Course. North Dakota State University, Fargo, ND. (Dr. Frank N. Jones, Polymers & Coatings Dept., NDSU, Fargo, ND 58105).

(July 9–13)—10th International Conference on "Organic Coatings Science & Technology." Athens, Greece. (Prof. Angelos V. Patsis, Director, Materials Research Lab., CSB 209, State University of New York, New Paltz, NY 12561).

(July 31–Aug. 2)—"International Symposium on the Analysis and Identification of Polymers." Forensic Science Research and Training Center, Quantico, VA. (K.W. Nimmich, Symposium Coordinator, Forensic Science Research and Training Center, Bldg. 12, Rm. 212, FBI Academy, Quantico, VA 22135).

(Aug. 13-17)—Short Course on "Physics and Chemistry of Printing Inks." Davos, Switzerland. (Dr. M.S. El-Aasser, Dept. of Chemical Engineering, Sinclair Lab #7, Lehigh University, Bethlehem, PA 18015).

(Aug. 20-24)—Short Course on "Advances in Emulsion Polymerization and Latex Technology." Davos, Switzerland. (Dr. Gary Poehlein, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332).

(Aug. 20-24)—Short Course on "Nitride and Carbide Coatings: Deposition Processes and Applications." Soderkoping, Sweden. (Continuing Education Institute—Europe, Rorstorpsvagen 5, S-612 00 Finspang, Sweden).

(Sept. 10-13)—"Radcure '84" Conference on Radiation Curing sponsored by the Association for Finishing Processes of the Society of Manufacturing Engineers. Downtown Marriott, Atlanta, GA. (Donna Theisen, AFP/SME Administrator, Society of Manufacturing Engineers, One SME Drive, P.O. Box 930, Dearborn, MI 48128).

(Sept. 10-14)—"The Basic Composition of Coatings" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(Sept. 13-15)—Oil and Colour Chemists Association Australia. 26th Convention. Mandurah, Western Australia. (Grant McManus, P.O. Box 490, Cloverdale, Western Australia 6015).

(Sept. 17-20)—Steel Structures Painting Council Annual Meeting and Symposium on "Maintenance Painting of Industrial Plants." William Penn Hotel, Pittsburgh, PA (Harold Hower, Symposium Coordinator, Steel Structures Painting Council, 4400 Fifth Ave., Pittsburgh, PA 15213).

(Sept. 17-21)—"Physical Testing of Paints & Coatings" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(Sept. 22-25)—Canadian Paint and Coatings Association. Annual Convention. Westin Hotel, Winnipeg, Man., Canada. (CPCA, 515 St. Catherine St. W., Montreal, Que. H3B 1B4, Canada).

(Sept. 23-26)—American Oil Chemists' Society Short Course on Fatty Acids. Kings Island, OH. (AOCS, 508 S. Sixth St., Champaign, IL 61820).

(Sept. 23-28)—XVIIth Congress of FATIPEC (Federation of Associations of Technicians in the Paint, Varnish, Lacquer and Printing Ink Industries of Continental Europe). Lugano, Switzerland. (C. Bourgery, Secretary General, FATIPEC, Maison de la Chimie, 28 Rue St.-Dominque, 75 Paris (7), France).

(Oct. 1-5)—Short Course on "Physics and Chemistry of Printing Inks," Lehigh University, Bethlehem, PA (Dr. M.S. El-Aasser, Dept. of Chemical Engineering, Sinclair Lab #7, Lehigh University, Bethlehem, PA 18015).

(Oct. 8-12)—"Advanced Industrial Paint Formulation" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(Oct. 8-12)—Spray Painting Seminar. Binks Manufacturing Co., Atlanta, GA. (Binks Manufacturing Co., Training Div., 9201 W. Belmont Ave., Franklin Park, IL 60131).

(Oct. 21-26)—Interfinish '84. Jerusalem, Israel. (Interfinish '84 Secretariat, P.O. Box 29313, 61292 Tel Aviv, Israel).

(Oct. 22-24)—National Paint & Coatings Association 97th Annual Meeting. Palmer House, Chicago, IL. (Karen Bradley, NPCA, 1500 Rhode Island Ave., N.W., Washington, DC 20005).

(Oct. 23-24)—11th International Naval Stores Meeting. Fairmont Hotel, San Francisco, CA.

(Oct. 23-26)—Fall Technical Meeting of the National Coil Coaters Association. Hyatt Regency O'Hare Hotel, Chicago, IL. (NCCA, 1900 Arch St., Philadelphia, PA 19103).

(Nov. 7-8)—4th World Congress on "Coatings Systems for Bridges and Steel Structures." Breckenridge Concourse Hotel, St. Louis, MO. (Cindy Sonewald, University of Missouri-Rolla, Dept. of Chemistry, Rolla, MO 65401).

(Nov. 13-14)—"Innovations in Finishing and Machining for the Wood Industry" Conference, sponsored by the Association for Finishing Processes of the Society of Manufacturing Engineers. Greensboro-High Point Marriott Hotel, Greensboro, NC. (Donna Theisen, AFP/SME Administrator, Society of Manufacturing Engineers, One SME Drive, P.O. Box 930, Dearborn, MI 48128).

(Nov. 16-17)—37th National Decorating Products Show. McCormick Place, Chicago, IL. (NDPA, 1050 N. Lindbergh Blvd., St. Louis, MO 63132).

(Nov. 26-27)—"Job Estimating Workshop for Painting Contractors" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(Nov. 28-30)—FINSTRAT '84, Conference and Exposition on Finishing Strategies for the 80's. Marriott Hotel and Anaheim Convention Center, Anaheim, CA. (Association for Finishing Processes of SME, One SME Dr., P.O. Box 930, Dearborn, MI 48128).

(Nov. 28-30)—"Maintenance Painting" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(Dec. 3-7)—Spray Painting Seminar. Binks Manufacturing Co., Franklin Park, IL. (Binks Manufacturing Co., Training Div., 9201 W. Belmont Ave., Franklin Park, IL 60131).

(Dec. 4-6)—Plant Engineering and Maintenance Show and Conference/West. Moscone Convention Center, San Francisco, CA. (Show Manager, Plant Engineering & Maintenance Shows, 999 Summer St., Stamford, CT 06905).

(Dec. 16-21)—1984 International Chemical Congress of Pacific Basin Societies. Honolulu, Hawaii. (PAC CHEM '84, Meetings and Divisional Activities, American Chemical Society, 1155 Sixteenth St., N.W., Washington, DC 20036).

Advertisers Index

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Election Fever

Well, we're going to have to face it. No matter who gets nominated and who gets elected, this will be the year for crazy political and election stories. This month I shall endeavor to clear up my file on the subject and hope that it will help us laugh our way through some of the months to come.

Really, though, I think the candidates contribute enough of the ridiculous to keep us howling right through the elections. After that, it ain't funny any more. Two years from now we may mean it when we cry, "Where's the beef?"

• • •

Joe Boatwright and Frank Borrelle sent a couple of typical deliriums from the election fever. Abstracts from their somewhat long stories follow.

Joe's was found in *The Dispatch* of Lexington, N.C., where they claim that it is, "A Horse's Tale Worth Re-telling." You be the judge . . .

Mrs. George Wood had a mule who was named Horace. One night she called the doctor and said to him, "Doctor, Horace is sick, and I wish you would come and take a look at him."

The doctor said, "It's after 6 o'clock, and I'm eating supper. Give him a dose of mineral oil, and if he isn't all right in the morning, phone me, and I'll come and take a look at him."

"How will I give it to him?" she inquired.

"Through a funnel."

"But he might bite me," she protested.

"Oh,—You're a farm woman and you know about these things. Give it to him through the other end."

So she went out to the barn, and there stood Horace, with his head held down, moaning and groaning.

She looked around for the funnel but the only thing she could find was her Uncle Bill's hunting horn hanging on the wall. It was a beautiful gold plated instrument with gold tassels.

She took the horn and affixed it according to instructions. Horace paid no attention. Then she reached up to the shelf for the oil. But, instead of picking up the mineral oil, she grabbed a bottle of turpentine, and poured a liberal dose into the horn.

Horace raised his head with a sudden jerk and with a yell, reared up on his hind legs, knocked out the side of the barn and took off down the road at a mad gallop.

Now, Horace was in pain, so every few jumps he made, that horn would blow. All the dogs in the neighborhood knew that Uncle Bill was going fox hunting when that horn was blowing. So out on the highway they went, close behind Horace. And so, you had Horace going at top speed, hunting horn blowing, and the dogs barking loudly.

They passed the home of Old Man Hogan, who gazed in fascination at the wild sight in front of him. After many years of trusting his mind and body to the nourishment of local moonshine, he promptly broke every bottle in the house and swore to join Alcoholics Anonymous.

By this time it was dark and Horace and the dogs were approaching the river. The bridge tender heard the horn blowing and figured that a boat was approaching. So he hurried out and lifted the bridge. Horace went into the drink and was drowned. The dogs also went into the water, but they were able to swim out without too much trouble.

Now it so happened that the bridge tender was running for the office of Sheriff. At election he polled just seven votes with one hundred and eight going to his opponent. The voters figured that any man who didn't know the difference between a mule with a horn up his rear and a boat coming down the river wasn't fit to hold any public office.

• • •

Borrelle, who has a wide experience with bloopers came up with the following quotes which he didn't identify according to the source.

Politicians, whose lives and livelihoods depend on an endless output of words, are naturally more vulnerable than the rest of us to the occasional blooper. Indeed, a blooper once a day should be helpful in reducing the ego of the average politician, providing he recognizes a blooper when he hears it.

Attend a few city council or state legislative meetings and keep your pencil handy to jot down the more unusual pronouncements. You will soon have enough for a book.

From a sheriff addressing a city council:
"This common council is entirely too laxative about some matters."
"He was absolutely right to a certain extent."
"This will tie the hands of former common councils for the next thirty years."

From state assemblymen:
"When we get to that bridge we will jump."
"If we wait any longer it will be too late to lock the barn after the horse is stolen."

From an attorney:
"There is just one more thing I forgot to overlook."

And from a lobbyist:
"None of them facts are actual facts."

Some of the more startling quotes come from state legislatures, probably because of their diversity of membership:
"When I started talking I was for the bill, but the longer I talked the more I know I'm against it."
"I'm in favor of letting the status quo stay as it is."
"That's a horse of a different feather."
"That's one of the best maiden speeches he's made all year."
"Mentally this shakes me to my very foundations."
"I could go on and excite many other instances of immortality in this withholding."
"The banker's pockets are bulging with the sweat of the honest working man."

—*Herb Hillman*
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