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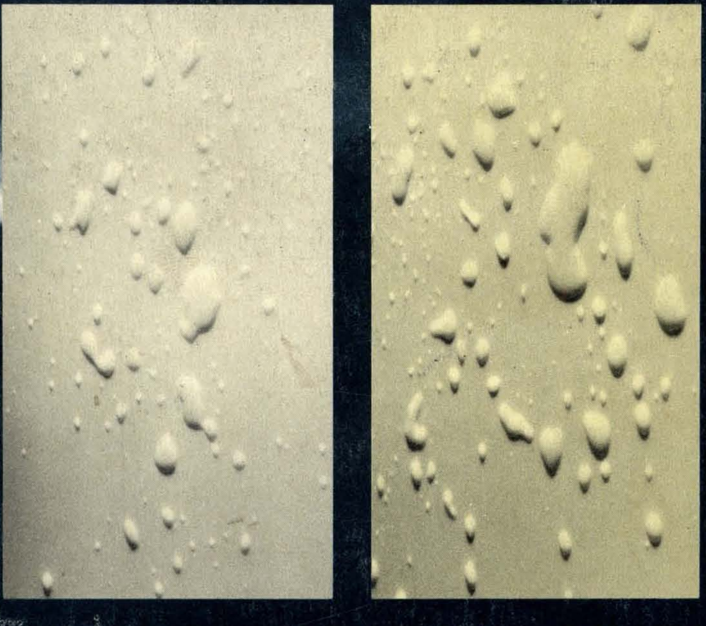

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*A water thinnable coating formulated by the Coatings Division of General Electric with Spencer Kellogg Kelsol 3902 resin.

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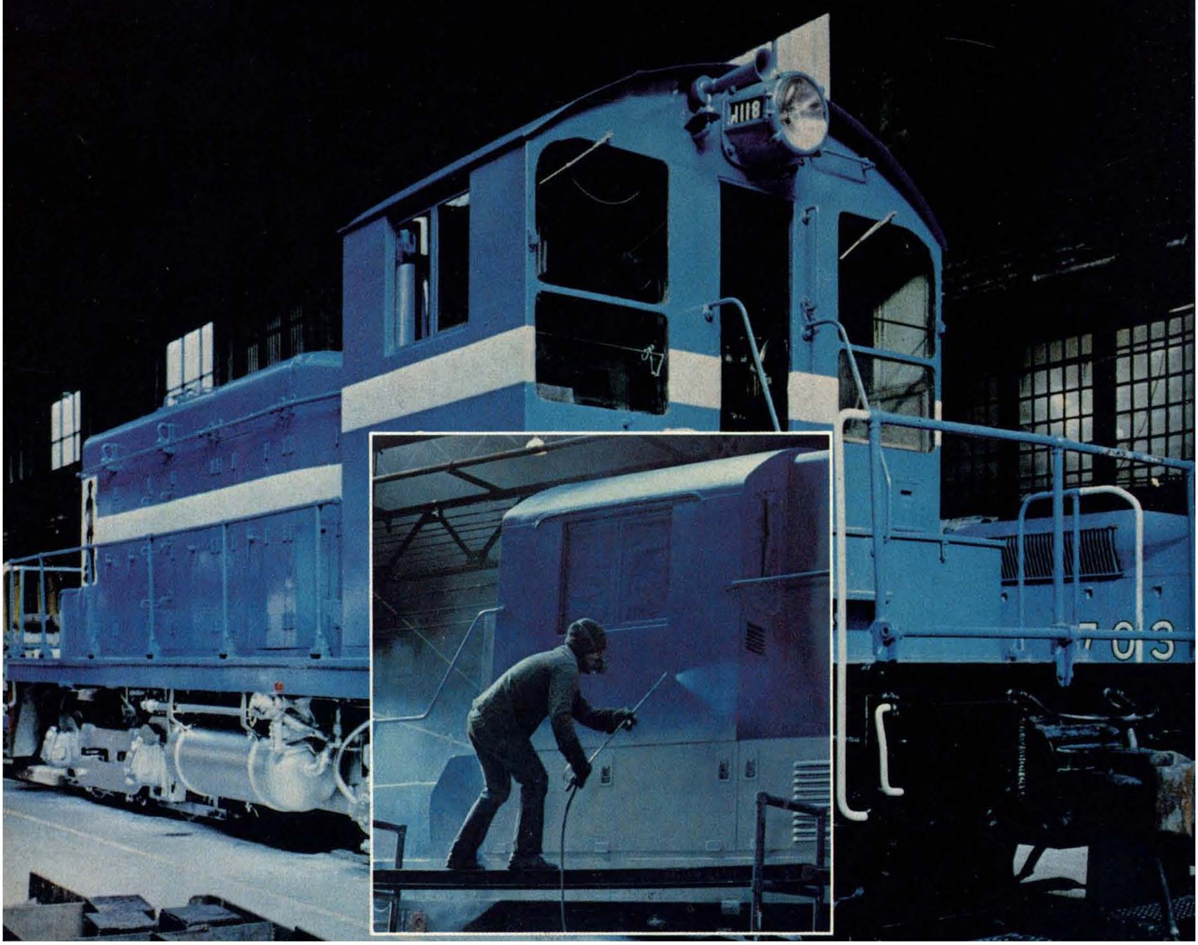

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Volume 51 Number 657

Features

Federation Activities

Departments

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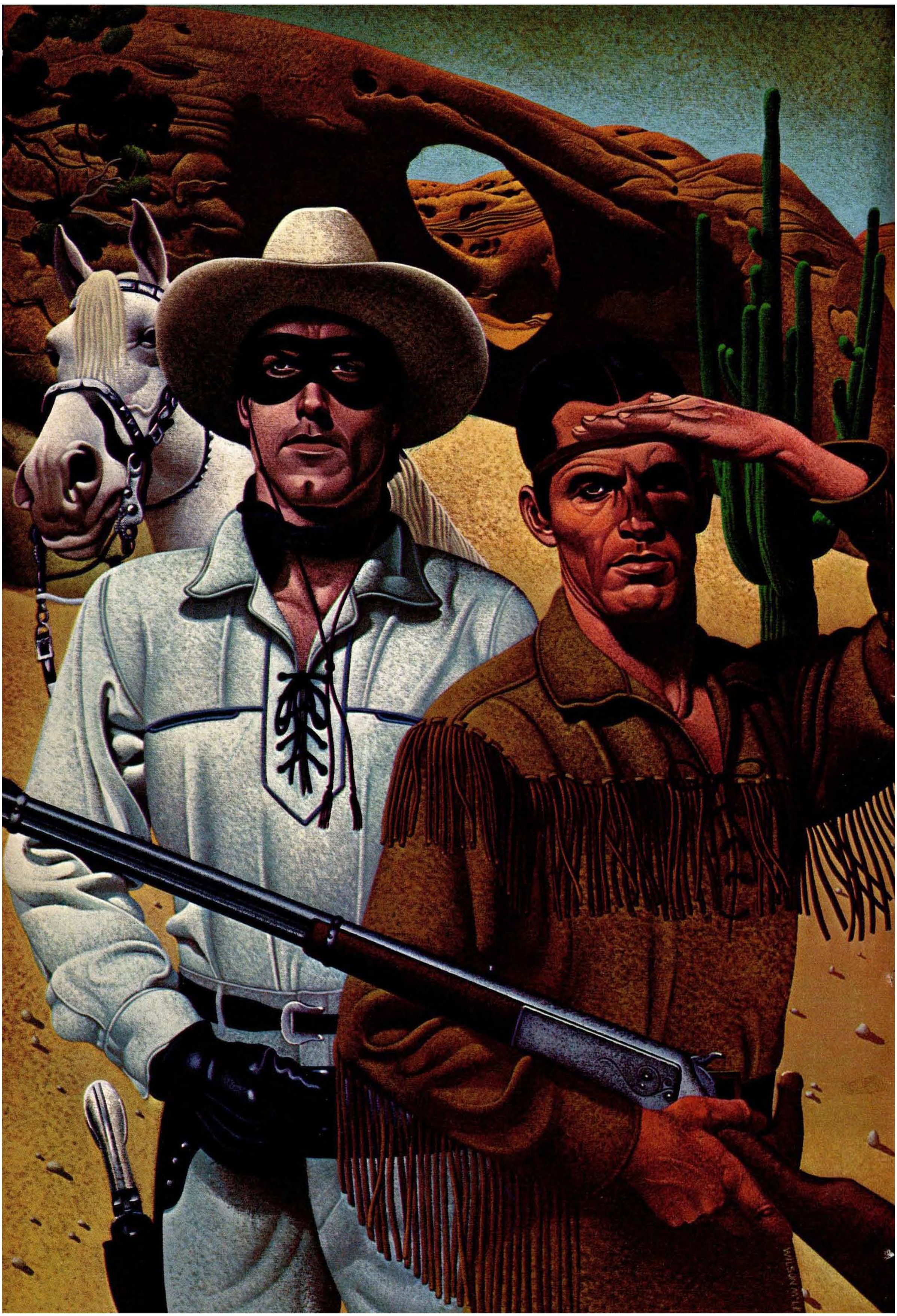

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Comment

Encouraging Numbers

At a recent meeting of the Joint Paint Industry Coordinating Committee (composed of the Federation, the National Paint and Coatings Association, the National Decorating Products Association, and the Painting and Decorating Contractors of America) the NDPA distributed some interesting and encouraging figures regarding sales of paint products in paint dealer stores, which NDPA correctly calls "Decorating Centers."

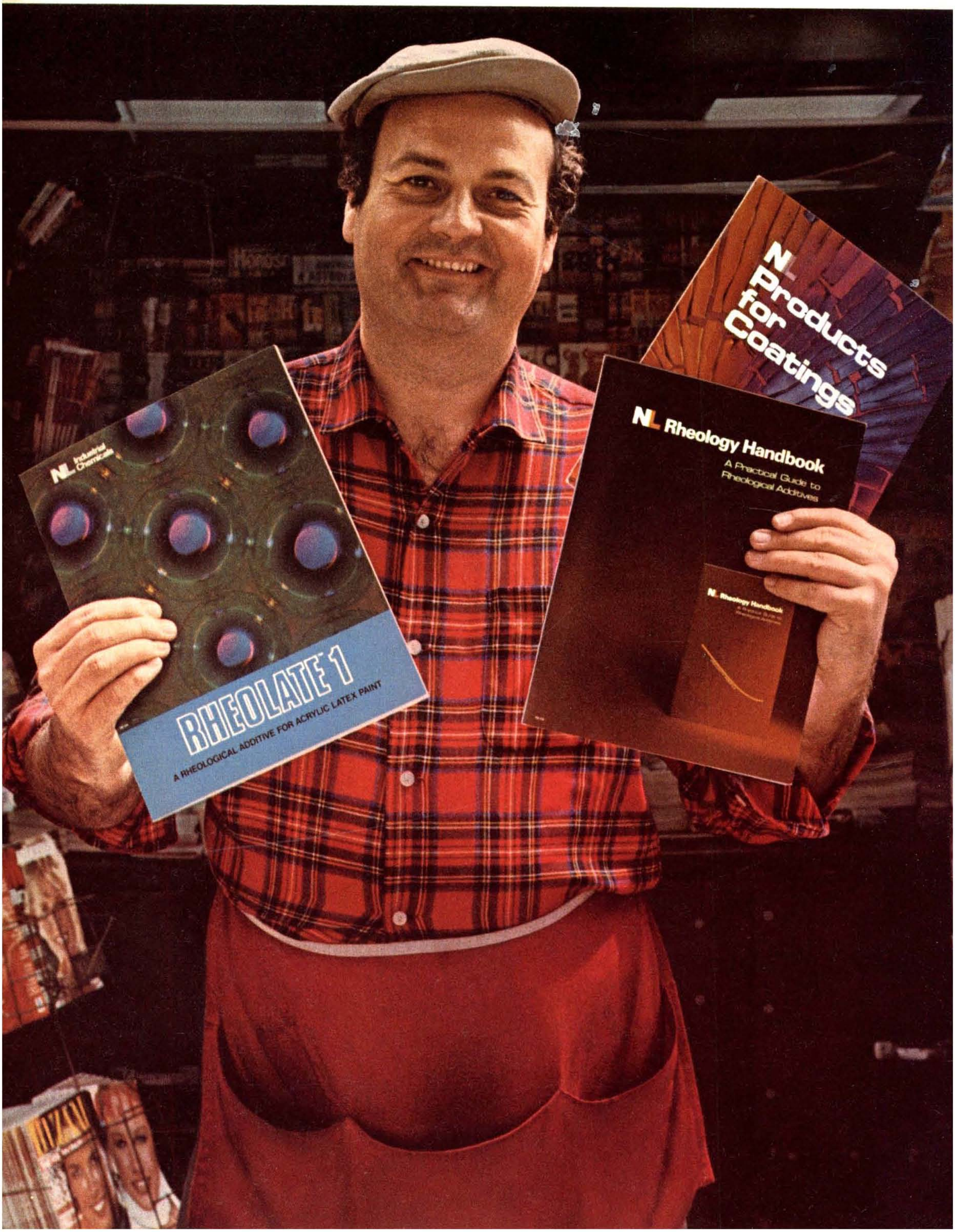
According to NDPA's Research Dept., the sales of paint products in 1978 amounted to $2,430,967,000, representing 46% of total sales. Wallcoverings were at $1,268,335,000 for 24%. Floorcoverings, sundries, art materials, and window treatments accounted for the remaining 30%.

In 1983, NDPA projects that paint sales will reach $5,020,308,000 (41%), wallcoverings 22%, and other 37%.

Although that looks like a fairly promising future, it is also a challenge to science & technology to develop new and better paint products in order to earn a bigger share of that other 51% of the consumer's dollar.

Another bit of information noted in Census of Business Reports from the U.S. Dept. of Commerce is that one of the seven types of retail outlets that has increased appreciably during the past five years is "Building Products," into which paint products fall. The leaders in this group are: Fuel (naturally), Sporting Goods, and Restaurants.

That's pretty solid company and a good indication that the coatings industry is in step with both trends and the times.—FJB.



NL Industrial Chemicals
RHEOLATE 1
A RHEOLOGICAL ADDITIVE FOR ACRYLIC LATEX PAINT
NL Products for Coatings
NL Rheology Handbook
A Practical Guide to Rheological Additives


NL Rheology Handbook
NL Products for Coatings
NL Industrial Chemicals
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RHEOLATE 1
A RHEOLOGICAL ADDITIVE FOR ACRYLIC LATEX PAINT

Abstracts of Papers in This Issue

POLYACRYLATE-MODIFIED WATER-BORNE ALKYDS—E. Levine and E.J. Kuzma

Journal of Coatings Technology, 51, No. 657, 35 (Oct. 1979)

A process for the improvement of color, drying rate, early water resistance and long-term flexibility of water-borne, air-drying alkyds is described. The process consists (a) of preparing a low molecular weight acrylic solution polymer with both hydroxyl and carboxyl functionality, and (b) of charging the reactive acrylic polymer to the alkyd reactor with the conventional alkyd components and processing as usual. Performance of polyacrylate-modified alkyds is compared to suitable controls and to one commercial standard. Use of polyacrylic resins high in ethyl acrylate or butyl acrylate as internal plasticizers for alkyds is discussed, as is the effect upon price of polyacrylate modification.

NEW SOLVENTLESS POLYMERIC PROTECTIVE COATINGS FROM FATTY ACID DERIVATIVES—F.L. Thomas and L.E. Gast

Journal of Coatings Technology, 51, No. 657, 51 (Oct. 1979)

Substituted amides of methyl azelaaldehydate dimethyl acetal enol ether (MAZDAEE), methyl azelaaldehydate dimethyl acetal (MAZDA), methyl 9(10)-methoxymethylene stearate (MMMS), and methyl 9,9(10,10)-bis(hydroxymethyl)octadecanoate acetone acetal (BHMOAA), alone or blended with commercial amino resins, were catalytically converted to solventless polymeric compounds. The polymeric compounds were drawn to films of 1 or 2 mil thickness on metal Q panels, baked, and then tested for hardness, color, impact and resistance to sodium hydroxide, hydrochloric acid, xylene, water, and a commercial detergent. Most films from MAZDA and its derivatives blended with hydroxyethyl-substituted amines showed high resistance to xylene and good hardness. In general, favorable impact and hardness results were dependent on the percent catalyst used as well as the millimole ratios when two or more compounds were blended together. Hydroxyethyl-substituted amides of MAZDA, MAZDAEE, and MMMS with commercial resins produced coatings with the best overall film properties: hardness values were from 8-83, alkali resistance ranged from one hour to greater than 120 hours; resistance was fair to xylene, water, and detergent solution, and poor to hydrochloric acid; impact resistance ranged from <10 in. lb to >160 in. lb.

TRIGLYCERIDE AND FREE FATTY ACID COMPOSITION OF LINSEED OIL IN WOOD—M.H. Schneider

Journal of Coatings Technology, 51, No. 657, 61 (Oct. 1979)

Linseed oil was allowed to move into wood and the free fatty acid content of the oil was measured at various distances of travel. The amount of free fatty acid in the oil increased as distance of travel increased. This may have implications for many oil-type coatings applied to wood.

STUDY OF LATEX CROSSLINKING BY THERMAL EVOLUTION TECHNIQUES—D.R. Bassett, M.S. Sherwin, and S.L. Hager

Journal of Coatings Technology, 51, No. 657, 65 (Oct. 1979)

Thermal evolution analysis and thermal gas chromatography were used to investigate the crosslinking characteristics of emulsion polymers containing N-(*iso*-butoxymethyl) acrylamide. Kinetic parameters, obtained by measuring isobutanol evolution as a function of temperature, were used to assess the relative importance of polymer design and formulation variables on reactivity. Crosslinking was promoted by the presence of copolymerized carboxyl groups, but was relatively unaffected by the presence of hydroxyls. Crosslinking in unneutralized latexes was accelerated by strong acid catalysts, but the catalytic effect was inhibited by neutralization.

STUDIES ON ADHESION OF ALKYD BASED TiO_2 PAINTS: ROLE OF ACID AND HYDROXYL VALUES OF THE MEDIUM—M.N. Sathyanarayana, P.S. Sampathkumaran, and M.A. Sivasamban

Journal of Coatings Technology, 51, No. 657, 73 (Oct. 1979)

Adhesion to the substrate is an important property of surface coatings. In the present work, the effect of acid and hydroxyl values of an alkyd on the adhesion properties of anatase titanium dioxide paints on a mild steel substrate has been studied. The bond strength of the paint film has been determined by the sandwich pull-off technique using a Hounsfield tensometer.

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Elder C. Larson, of Houston Society, Becomes Fifty-Eighth Federation President

Elder C. Larson, Senior Research Chemist at Shell Development Co., Houston, Tex., became the 58th President of the Federation of Societies for Coatings Technology on October 5 at the Federation's Annual Meeting in St. Louis, Mo.

William H. Ellis, of Chevron Research Co., El Segundo, Calif., was named President-Elect, and Howard Jerome, of Spatz/Vane-Calvert Paint Co., St. Louis, Mo., was elected Treasurer.

President Larson

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

He has been a member of the Federation's Board of Directors, and Finance Committee and has also served on the Editorial Review Board of the Federation's Publication Committee.

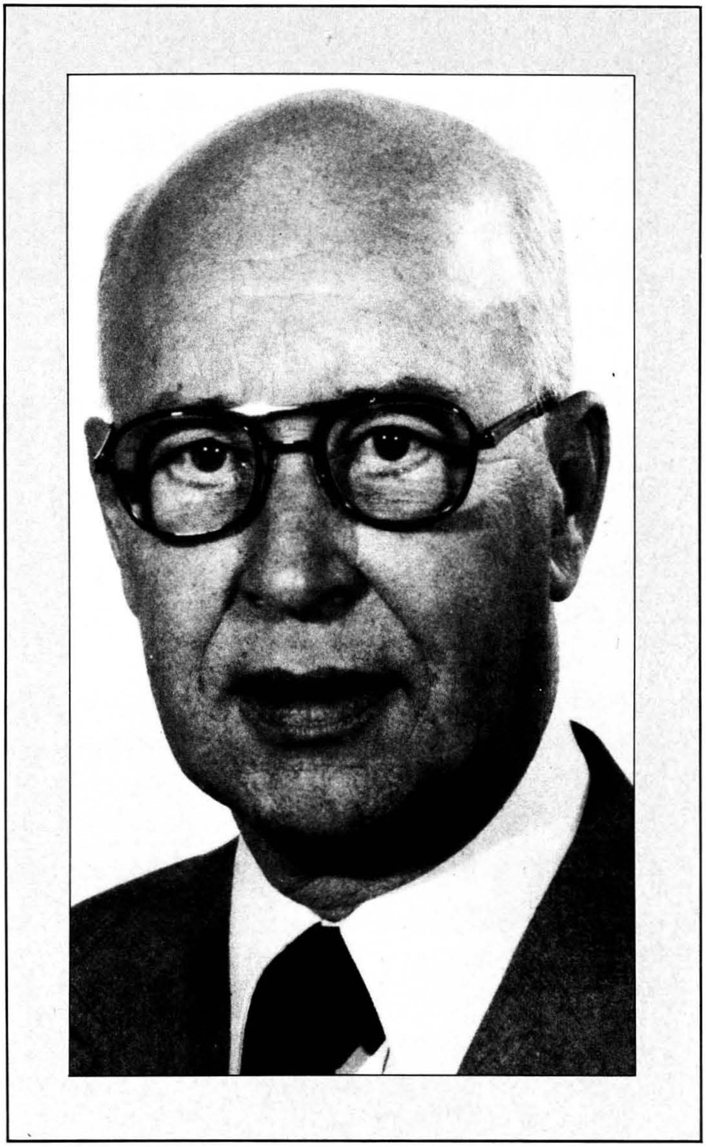
Mr. Larson, who has been with Shell for 45 years, is a graduate of Washington University, St. Louis, and is a member of the American Chemical Society. He and his wife, Margaret, reside in Houston.

President-Elect Ellis

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

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

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



W.H. Ellis

H. Jerome

Treasurer Jerome

Mr. Jerome is a Past-President and Honorary Member of the New England Society (where he also served as Federation Council Representative), and most recently served as the St. Louis Society's Representative to the Federation's Board of Directors.

He has also served as Chairman of the Federation's Technical Advisory Committee (1969-70) and the By-Laws Committee.

Mr. Jerome is a graduate of Northeastern University.

President Larson Announces Committee Chairmen for 1979-80

Chairmen of the 30 committees of the Federation of Societies for Coatings Technology for 1979-80 have been announced by President Elder C. Larson. A complete roster of all committees will be published in the 1980 Year Book.

An asterisk (*) indicates re-appointment for 1980.

A. F. Voss/American Paint & Coatings Journal Awards—Horace S. Philipp, of Sherwin-Williams Co., Montreal.*

Bruning Award—Ruth M. Johnston-Feller, of Pittsburgh, Pa.*

By-Laws—Fred Schwab, of Coatings Research Group, Cleveland, Ohio.

Corrosion—Saul Spindel, of D/L Labs, Inc., New York, N.Y.

Definitions—Stanley LeSota, of Rohm and Haas Co., Spring House, Pa.*

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

Environmental Control—S. Leonard Davidson, of N L Industries, Inc., Hightstown, N.J.*

Finance—James A. McCormick, of Inland Leidy, Baltimore, Md.

Heckel Award—Herbert L. Fenburr, of Columbus, Ohio.

Host (Annual Meeting)—Berger Justen, of Justen and Associates, Tampa, Fla.

Inter-Society Color Council—Robert T. Marcus, of PPG Industries, Inc., Springdale, Pa.*

Investment—Herbert L. Fenburr, of Columbus, Ohio.*

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

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

Mattiello Lecture—Thomas J. Miranda, of Whirlpool Corp., Benton Harbor, Mich.

MMA Awards—William T. Cochran, of Bruning Paint Co., Baltimore, Md.*

Membership—William F. Holmes, of DeSoto, Inc., Dallas, Tx.

Memorial—Carroll M. Scholle, of Chicago, Ill.*

Metric Systems—Ernest L. Humburger, of Schenectady Chemicals, Ltd., Scarborough, Ont.*

Nominating—James A. McCormick, of Inland Leidy, Baltimore, Md.

Paint Industries' Show—Deryk R. Pawsey, of Rohm and Haas Canada Ltd., Vancouver.*

Program—Hugh W. Lowrey, of Indurall Coatings, Inc., Birmingham, Ala.

Program Awards—Gordon Allison, of McCormick Paint Works, Rockville, Md.*

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

Public Relations—Harry Poth, of Dean & Barry Co., Columbus, Ohio.*

Roon Awards—Umberto Ancona, of McCloskey Varnish Co., Philadelphia, Pa.*

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

Technical Advisory—Colin Penny, of Hampton Paint Mfg. Co., Hampton, Va.*

Technical Info Systems—Helen Skowronska, of Cleveland, Ohio.*

Trigg Awards—Al Seneker, of Ameron Corporate Research, South Gate, Calif.

Delegates to Other Organizations

National Association of Corrosion Engineers—Tom Ginsberg, of Union Carbide Corp., Bound Brook, N.J.

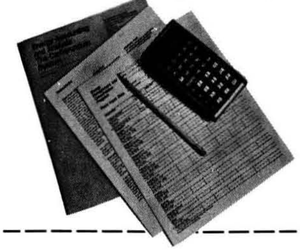
National Paint and Coatings Association, Scientific Committee—Ted Provder, of Glidden Coatings & Resins Div., Strongsville, Ohio.*

Steel Structures Painting Council—Sid Levinson, of D/L Labs, Inc., New York, N.Y.

National Fire Protection Association—Donald Fritz, of Superior Varnish & Drier Co., Merchantville, N.J.

National Paint and Coatings Association and Government Agencies (Environmental Control)—S. Leonard Davidson, of N L. Industries, Hightstown, N.J.*

International Union of Pure and Applied Chemistry—Milton A. Glaser, Consultant, Glencoe, Ill. and Percy Pierce, of PPG Industries, Inc., Allison Park, Pa.*



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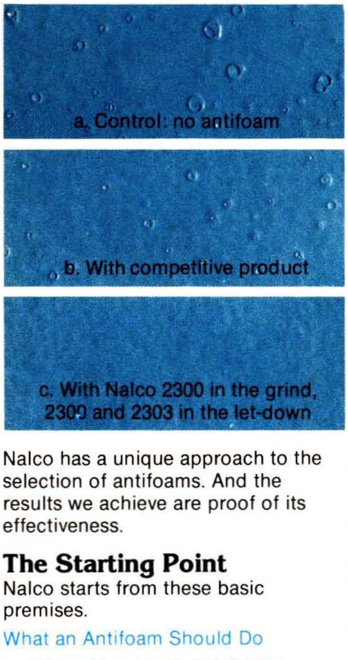

Nalco has a unique approach to the selection of antifoams. And the results we achieve are proof of its effectiveness.

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Nalco starts from these basic premises.

What an Antifoam Should Do

1. It should prevent and destroy foam.
2. It should be persistent.
3. It should not adversely affect color acceptance, gloss, water sensitivity, or intercoat adhesion.
4. It should not cause surface defects such as crawling, pinholes, or fisheyes.

Nalco is not satisfied with an antifoam selection until it meets all four requirements and achieves the results you are looking for.

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A Systematic Approach

Nalco uses a systematic screening procedure to determine antifoam performance. And before Nalco recommends an antifoam for your coating, we thoroughly analyze its effect in your total system. We:

Analyze Your Formulation The surfactants, co-solvents, flow control additives, pH, pigments, and resin type in your formula are studied since they affect foam stability and antifoam performance.

Analyze Your Manufacturing Procedures High sheer dispersion phases, transfer, and filling operations cause foam and may require several antifoams for effectiveness.

Analyze Your Application Procedures Techniques involving recirculation and high shear, such as spray and flow, can cause persistency problems and are considered when solving the foam problem.

Nalco's tests are designed to be as similar to actual usage as possible. Our recommendations may include products for the grind and others for the let-down. And to make sure the recommendation is right, Nalco checks results with the actual lab manufacture of your paint whenever possible.

A Bank of Knowledge

Nalco works directly with new resin technology and may have already screened the resin you are using. And there probably is not a foam problem in manufacturing or application we have not seen before. We are old hands at licking foam problems. You gain the advantage of our experience.

A Broad Line of Products

From a broad selection of non-silicone and silicone types, you can choose the right defoamer for use in the grind and the let-down, for your trade sales coatings or industrial finishes. When used properly, it will give you effective foam control and minimize risk to film quality, color acceptance, and persistency.

How to Get Started

If you are reformulating or developing a new water-based paint, give Nalco a call. Our paint experts will work with you from the start to develop the best foam control program possible. Just use our "hotline" number (312) 887-7500 ext. 1214. Or consult our literature. Write for bulletins K-8 and K-10.

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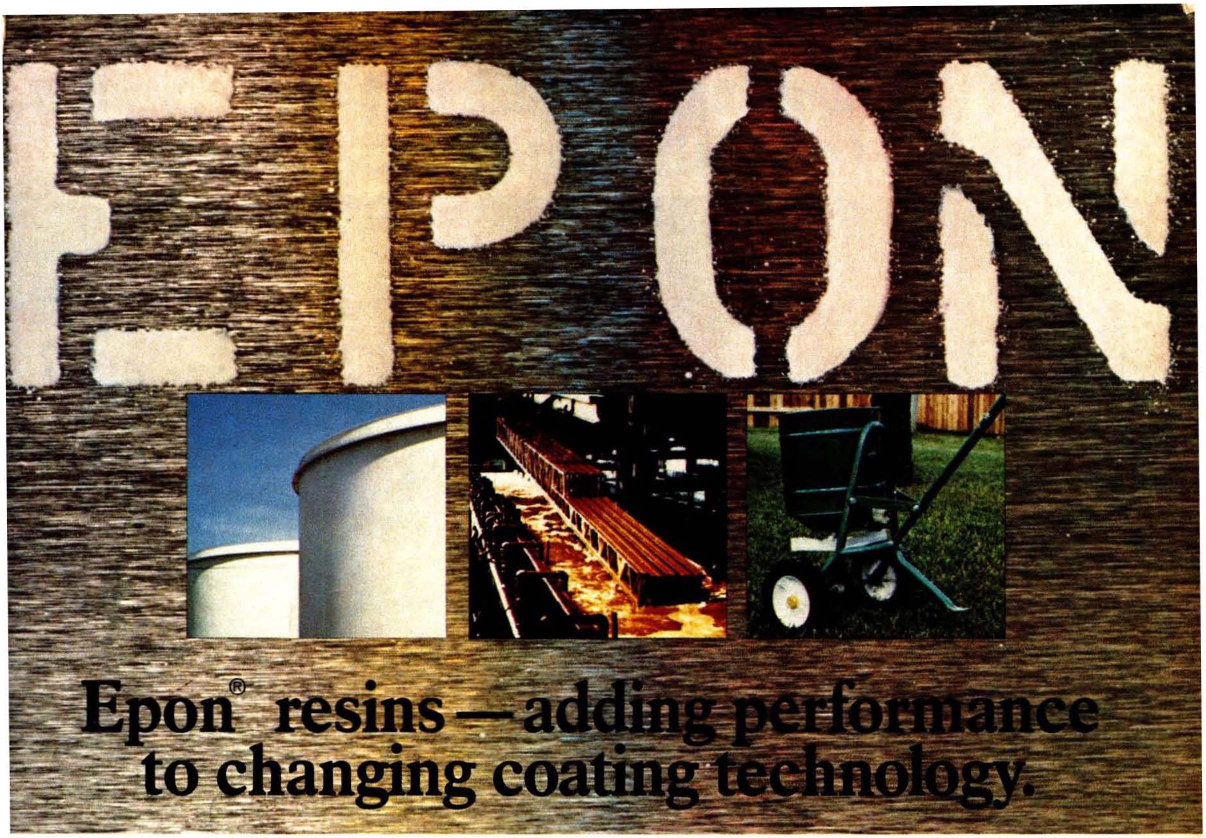

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Epon resins as modifiers

Epon resins continue to find use as modifiers for acrylic, alkyd, urethane and other coating systems. Whenever you need to incorporate the toughness and adhesion of epoxy, investigate the use of an Epon resins modifier to enhance the balance of properties of the finished coating.

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When you want traditional epoxy strengths plus enduring gloss, try Shell's new Eponex™ resins. Coatings formulated with Eponex resins, the latest development from Shell's coatings laboratory, resist chalking and yellowing in the sun.

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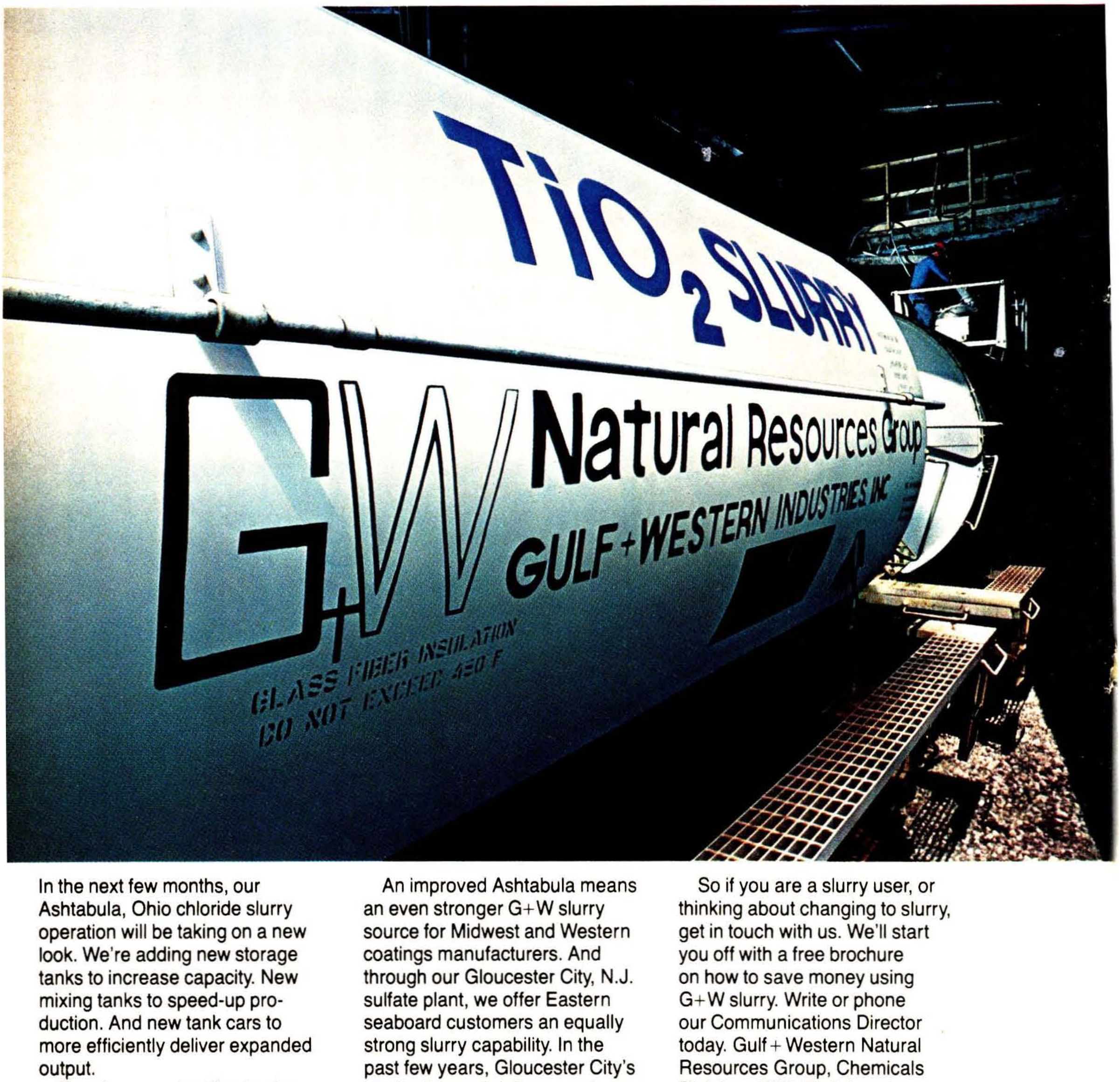
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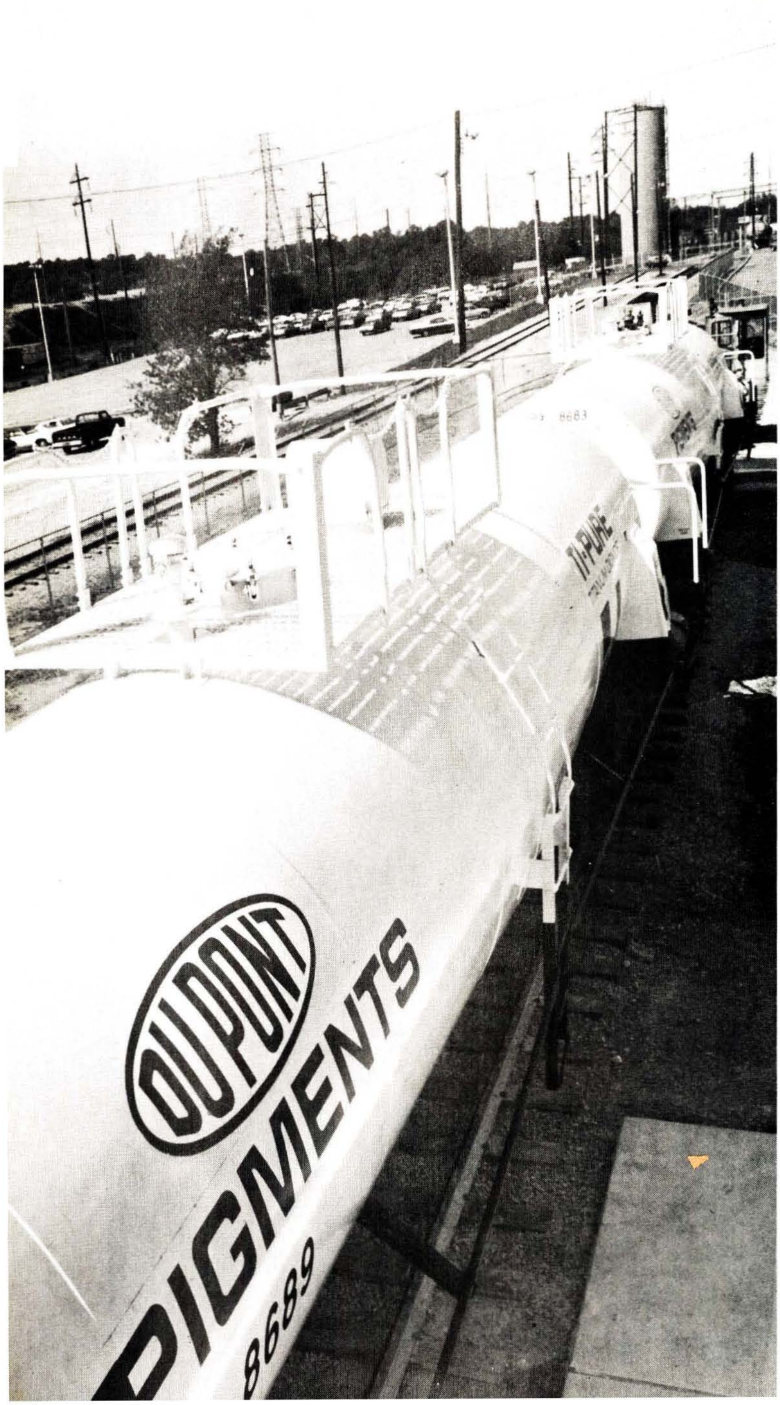
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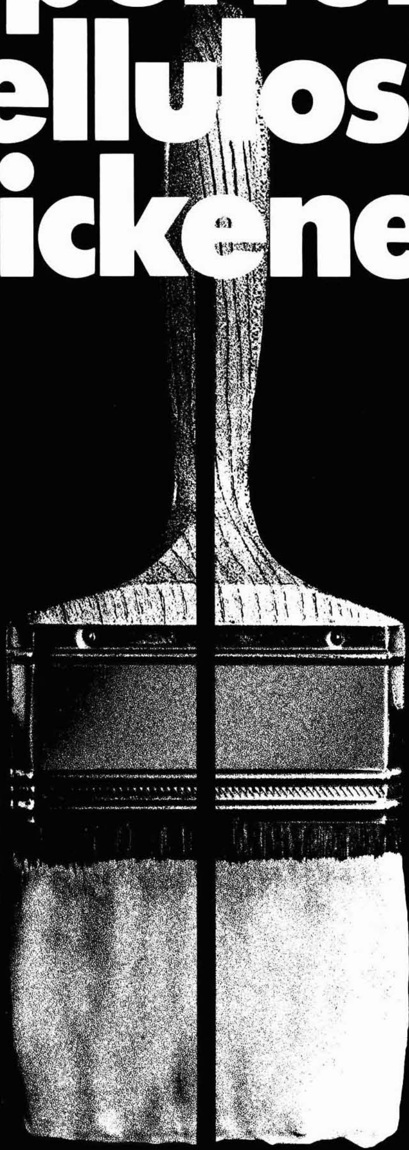


Committee Activities

LIAISON

Progress Report on IUPAC's Supported Polymer Films Group

The International Union of Pure and Applied Chemistry (IUPAC) is the only international organization that is involved with *all* branches of chemistry. Its purpose is the advancement of chemistry and the world-wide dissemination of such knowledge. Created after World War I, the IUPAC, in the United States, is an arm of the National Academy of Sciences—National Research Council. A total of about fifty national organizations are represented in IUPAC.

We in the organic coatings industry are fortunate to be represented by a Supported Polymer Films Group (SPF) which is part of the large Macromolecular Division of IUPAC. The official representatives to this group are Percy Pierce, of the Pittsburgh Society and Milton A. Glaser, of the Chicago Society.

The following is a progress report of the Group by its Chairman Mr. P. Fink-Jensen, of Denmark. Also included are the minutes of the Group's meeting in Brussels held in November 1978. It is felt that information on these activities would be of interest to all JCT readers.

MILTON A. GLASER, *Chairman*
Federation Liaison Committee

Within the Macromolecular Div., the working party is concerned with scientific and technical questions of importance to the efficient use of organic coatings for protection and decoration of surfaces.

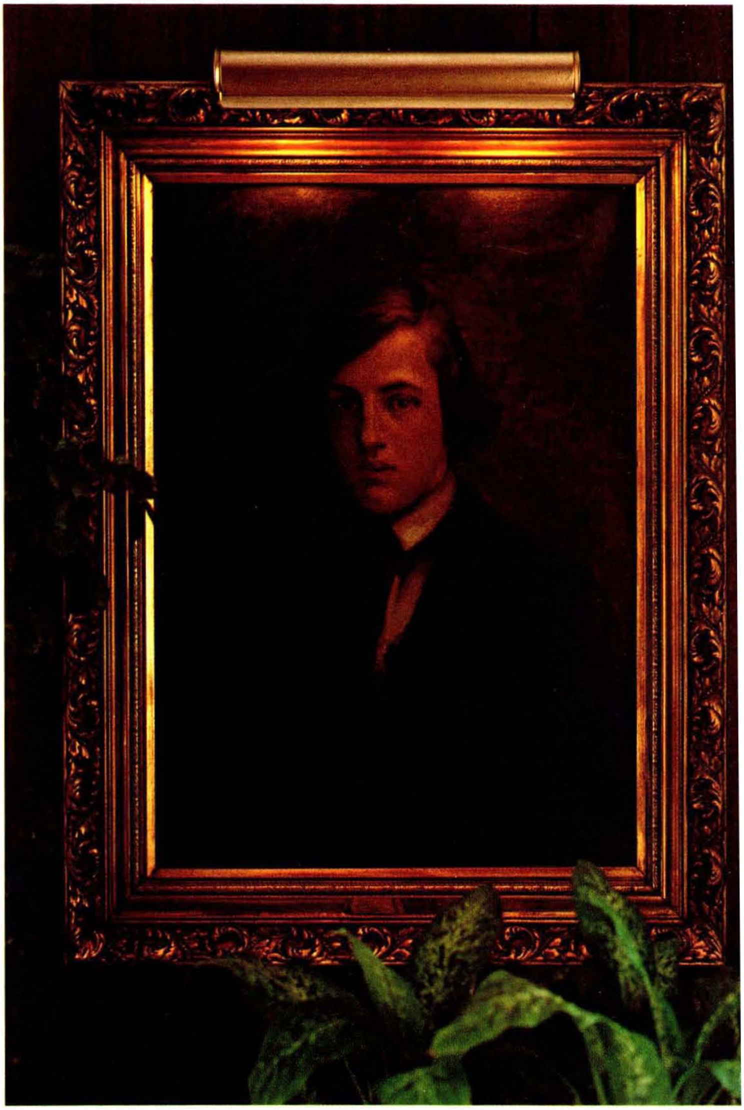
The group consists of about 25 members who regularly take part in the activities and about 15 associated members, i.e., prospective and past members and other particularly interested persons. The Chairman is P. Fink-Jensen; L. Dulog is Chairman-Elect. The Secretary was U. Zorll until the end of 1978; this function is now held by J. Sickfeld.

The working party provides meetings, usually once a year. The last two were at Eastbourne (June 15-16, 1977) and in Brussels (November 15-16, 1978). The next meeting is scheduled for October 10-11, 1979 in Berlin.

Current Projects

ANALYSIS OF FUNCTIONAL GROUPS IN AMINO RESINS (G. Christensen, Group Leader): Besides its relevance to the analytical field, this study is a prerequisite to planned work on the polymerization and copolymerization reactions of amino resins as one component of coating compositions. A literature study with the title of the project was prepared and published in *Progress in Organic Coatings,* May 1978.

Four methods of analysis have been worked out (solvent removal, ^{1}H NMR-spectroscopy, transetherification + GLC, and Zeisel/Merz cleavage + GLC). They have now been applied to four synthesized model compounds and three commercial products distributed to 10 participants (four institutes, three raw material suppliers, and three paint companies). In this interlaboratory exercise, two laboratories have applied ^{13}C-NMR spectroscopy. The prelimi-



nary results were discussed at the Brussels meeting and several improvements of the methods were obtained. Some analyses were rerun by a few laboratories to verify the improvements. The final results are presently being compiled by the project leader, who will present a report at the Berlin meeting. This report will have the four recommended analytical methods as attachments. The final report should be ready for publication shortly after the Berlin meeting.

A paper on the solvent removal procedure (% NV determination) is being prepared by Dr. Kambanis.

ADHESION GROUP (U. Zorll, Group Leader): Inadequate adhesion to the substrate is probably the most frequent cause of severe failure of coatings. The practical "adhesion" depends on the rheological properties of the film, the stresses and inhomogeneity set up by polymerization, aging, and external forces, besides the state of the boundary surface. By means of a questionnaire (1978) it has been established in which application areas "adhesion" is of prime importance (corrosion protection headed the list) and which methods of characterization are appropriate in each area.

Fundamentals of the widely used tear-off test method and the blister method have been studied. In this context two papers (by J. Sickfeld) were published: "Experimental Aspects of Adhesion Testing" (1978); and "Adhesion Testing with the Tear-off Method" (1979). A paper on the blister method is being considered for publication.

LITERATURE RETRIEVAL GROUP (H. K. Raaschou Nielsen, Group Leader): After repeated attempts to contact 73 research institutes and information centers (in 33 countries) assumed to have literature services within the organic coatings and printing ink field, a total of 52 completed questionnaires were returned. In 30 of the organizations returning questionnaires, some kind of literature service was provided. It is to be regretted that response from Eastern Europe is deficient although various lines of attack (including Division members) have been attempted in the last year.

A draft report will be discussed at the Berlin meeting.

ISO: Comments to ISO Draft proposals on epoxy resins have been submitted. Further, a member (Zorll) has represented IUPAC during ISO meetings.

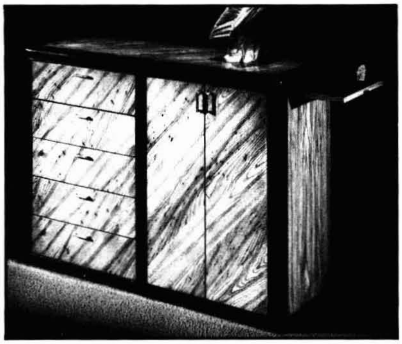
New Projects

A number of new activities suggested in Brussels (see minutes) will be discussed in Berlin. Tentative schemes have been made regarding the items: solvent polymer interaction, stability of solutions of amino resin-alkyd compositions, and differences between polymer in bulk and as supported film. Under particular consideration are also analysis of coating compositions dispersed in water and rheological properties of high-solids paints.

P. FINK-JENSEN

(Continued on page 100)

Who says CAB finishes are just as beautiful as nitrocellulose?



633 out of 635 people at the 1978/79 Paint Shows.

You don't have to sacrifice an attractive finish to get superior physical properties.

To prove it, we finished some of these server drawers with a Cellulose Acetate Butyrate lacquer and others with a conventional nitrocellulose lacquer. Then, we asked 635 people at the 1978 Paint Industries' Show and the 1979 Western Coatings Show to try to tell the difference. Only 2 people out of 635 selected correctly.

Furniture finishes from coast to coast are resisting staining and yellowing with CAB.

Its clear lacquer finish protects against moisture and sunlight.

It also resists the tacky feeling caused by extended contact with plastic and vinyl. And because the CAB lacquers are formulated with economical hydrocarbon and alcohol solvents, these lacquers can be less expensive to use than nitrocellulose lacquers.

For more information, call your lacquer supplier or write Jack Frye at Eastman Chemical Products, Inc., a subsidiary of Eastman Kodak Company, Coatings Chemicals Division, Kingsport, Tennessee 37662.

EASTMAN CAB
Cellulose Acetate Butyrate

1880 Kodak *1980*

HALOX REPORT:TR9

Inhibiting steel corrosion with calcium boro silicates

Let's review the three principal classes of anti-corrosive metal primers:

Barrier primers protect simply by raising the electrical resistance across the anodic and cathodic areas of local galvanic corrosion cells on the steel surface.

Zinc-metal containing films act as the anode and the steel itself is the cathode. The films override all local cell action on the steel surface, and initially, at least, sacrifice themselves to maintain the metal substrate intact.

Inhibitive primers, the most widely used, protect by slowly releasing inhibitive ions from pigments—or reaction products of pigments and vehicles from the film—which are carried by diffusing water to the steel surface. There, they modify the degrees of anodic and/or cathodic polarization—or increase the thickness of the air-formed layer. This increases the electrical resistance of the total coating system.

Direct and indirect

This third class can be divided into direct and indirect inhibitors. Direct inhibitors use pigments that release inhibitive ions; indirect inhibitors use pigments that, not necessarily inhibitive themselves, produce soluble inhibitive species when reacted with chemically modifying constituents from the vehicle.

Historically, the most effective inhibitive pigments have been those containing chromates (direct) or lead (indirect). But because both are under increasing criticism and regulatory constraints, the paint industry is testing alternatives.

HALOX shows promise

Halox composite pigments show considerable promise. These are silicate composites of basic phosphates or borates of calcium, barium, magnesium, or zinc.

Synergistic performance

Calcium phosphate and calcium borate are known as corrosion inhibitors, of course, but we find them to be more efficient as a composite or complex with silica or silicate minerals. We believe that the change from a crystalline to an amorphous state during manufacture improves effectiveness.

Mechanism of inhibition

Early tests in oleoresinous systems, comparing performance with that of red lead and chromated pigments, led us to the assumption that boro silicates are indirect inhibitors like lead-base products. Tests by Abou-Khalil of Cambridge University, who worked with Halox CW-221, supported this. However, our similar experiments with both CW-221 and CW-2230 (higher B_2O_3 pigments) indicated a direct as well as indirect contribution.

Mayne-Appelby tests

Results of our Mayne-Appelby tests using liquor extracts of pigments and paints on sandblasted steel appear in Table 1. The times to first corrosion for red lead pigment and its paint show red lead to be an indirect inhibitor. Similar comparisons for CW-221 and CW-2230 show them to be both direct and indirect. The results of the same experiment with cold-rolled steel and aged liquors (Table 2) seem more definitive.

Tests of Halox pigments in both latex paints and the relatively nonreactive vinyl toluene lacquers support the assumption of a direct contribution.

Table I

Corrosion of Sandblasted Steel in Aqueous Extracts of Pigments and Paints

Extract	Time to First Corrosion Hrs.	Propagation at Six Weeks	Weight Loss in Coupon % of Original Weight
Red Lead Pigment	0.29/0.14	Complete/ Complete	0.66% Loss/ 0.89% Loss
Red Lead/ Linseed Oil Primer	4.69/2.40	Moderate/ None	0.80% Loss/ 0.08% Gain
Halox CW-2230	3.36/2.70	Very Light/ None	0.56% Loss/ 0.12% Loss
Halox CW-2230/ Linseed Oil Primer	1.00/0.64	Moderate/ Moderate	0.77% Loss/ 0.64% Loss
Halox CW-221	2.32	Moderate	0.45% Loss
Halox CW-221/ Linseed Oil Primer	41.0/17.0	None/None	0.22% Gain/ 0.26% Gain

All coupons were blasted steel stored in air for 24 hours prior to testing

Table II

Corrosion of Cold Rolled Steel in Aqueous Extracts of Pigments and Paints
Clean Ground Q-Panels in Aged Extract Liquors

Extract	Time to First Corrosion Hrs.	Propagation at Six Weeks
Red Lead Pigment	0.9/1.9	Complete/Complete
Red Lead/Linseed Oil Primer	1000+/1000+	None/None
Halox CW-2230	1000+/1000+	None/None
Halox CW-2230/ Linseed Oil Primer	1000+/1000+	None/None
Halox CW-221	1000+	None
Halox CW-221/ Linseed Oil Primer	24/32	Moderate/Moderate

All coupons were clean Q-Panels Ground on One Side, stored in air for several days before testing.

Effective substitute

In our opinion, the calcium boro silicates, in properly formulated primer systems, are likely candidates for the nontoxic replacement of lead and hexavalent chromium-based inhibitors.

We invite your inquiry for more details on Halox pigments and specific applications where corrosion resistance is a consideration.

HALOX®

HALOX PIGMENTS
425 Manor Oak One, 1910 Cochran Road
Pittsburgh, Pa. 15220 (412) 344-5811

A DIVISION OF HAMMOND LEAD PRODUCTS, INC.

NPCA Scientific Committee Establishes State Legislative Awareness Network, Seeks Monitors

NPCA's Scientific Committee has undertaken the task of providing early information on state legislative activities to Association headquarters in Washington. The committee has begun the organization of an "Awareness Network" based on the cooperation of member companies and responsible individuals within these companies.

Purpose of the Network is to ensure that proposed state laws are brought to the attention of the NPCA headquarters staff routinely and promptly. Effective action can then be taken when deemed necessary and in the best interests of the industry.

To date the committee has identified 20 individuals representing 19 states. Most of these volunteers are from the Scientific Committee membership. The individual monitors are asked to read all laws proposed for adoption in their state which may have an impact on the paint and coatings industry — either adverse or favorable. This information is available from state legislative reporting services and many companies subscribe to such services in the states in which they operate.

NPCA has prepared one-page forms which are to be used in reporting legislative information to its Government Relations Division staff, which needs concise information abstracted from the proposed bill and an opinion from the monitor on how the law will impact the industry. It is not necessary to send copies of the bills.

The Scientific Committee hopes to get at least one monitor in each of the 50 states. Currently, volunteers are serving from the following states: California, Connecticut, Delaware, Georgia, Indiana, Illinois, Kentucky, Maryland, Massachusetts, Michigan, Minnesota, Missouri, New Jersey, New York, Ohio, Oklahoma, Pennsylvania, Texas, and West Virginia.

The Scientific Committee is continuing its efforts to enlist monitors in those states in which there are none, as well as to recruit others who will assist in the states where there is representation.

For more information, or to volunteer, contact Royal A. Brown, Vice President — Technical, NPCA, 1500 Rhode Island Ave., N.W., Washington, D.C. 20005.

Calif. Architectural Coatings Regs Now in Effect Throughout Most Areas of the State

California's Architectural Coatings Regulations, which drastically reduce the allowable solvent content of most consumer products, became effective in most areas of the state on September 2.

Regulations restricting the amount of volatile organic material allowable in architectural coatings apply in at least 21 of the state's Air Pollution Control Districts. Included are the three major districts: South Coast Air Quality Management District (Rule 1113); San Diego Air Pollution Control District (Rule 67); and the Bay Area Air Quality Management District (Regulation 9). In four other districts, the regulations will become effective on the following dates: Kings County on May 29, 1980; Monterey Bay Unified on July 1, 1980; Placer County on January 1, 1980; and Stanislaus County on March 1, 1980.

The various regulations impose identical restrictions, although the language may differ slightly from that of the California Air Resources Board (CARB) proposal. They all state that no person may sell, offer for sale or apply any architectural coatings manufactured after the effective date which contain more than 250 grams of volatile organic material per liter of coating as applied excluding water. The rule applies to any coating used on stationary structures and their appurtenances, mobile homes, pavements, or curbs.

Architectural coatings recommended solely for use on interior surfaces will be allowed to contain 350 grams of volatile organic material per liter of coating until September 2, 1980. Small businesses, as defined in the California Administrative Code are not subject to the restrictions of the regulation until September 2, 1980.

The 250 gram per liter restriction does not apply to the following coatings manufactured prior to September 2, 1982: architectural coatings supplied in containers having capacities of one liter or less; traffic coatings applied to public streets and highways; varnishes, lacquers or shellacs; semi-transparent stains; opaque stains on bare redwood cedar, mahogany, or douglas fir; primers, sealers, or undercoaters; wood preservatives; fire retardant coatings; tile-like glaze coatings; waterproofing coatings — except bituminous pavement sealers; industrial maintenance finishes; metallic pigmented coatings; swimming pool coatings, graphic art coatings; mastic coatings; and multi-colored coatings. The exempt products are specifically defined in each of the local regulations.

Containers for all coatings subject to the 250 gram per liter limitation must display the manufacture date of the contents or a code indicating the date.

SSPC Surveying Low-Solvent Maintenance Coatings for DOT

Information on low-solvent maintenance coatings is being sought by the Steel Structures Painting Council in behalf of the Federal Highway Administration of the U.S. Department of Transportation.

The FHwA is the major source of information for all 50 state highway departments, and it is vitally concerned with the kinds of coatings which will be available within the next few years, particularly those developed to meet anticipated governmental regulations. They have, therefore, selected SSPC to help identify current research, development, effectiveness, and regulatory aspects of low-solvent coatings for use on steel bridges and other structures. Products in commercial use, in field testing, ready for field testing, or still under development are of interest. These coatings may be either water-based or high-solids. Confidentiality of proprietary information will, of course, be strictly respected. Results may be useful both in industry planning and in avoiding unrealistic regulations.

Anyone wishing to cooperate and to obtain advance copies of the reports resulting from this investigation should contact John D. Keane, Director of Research, Steel Structures Painting Council, 4400 Fifth Ave., Pittsburgh, Pa. 15213.

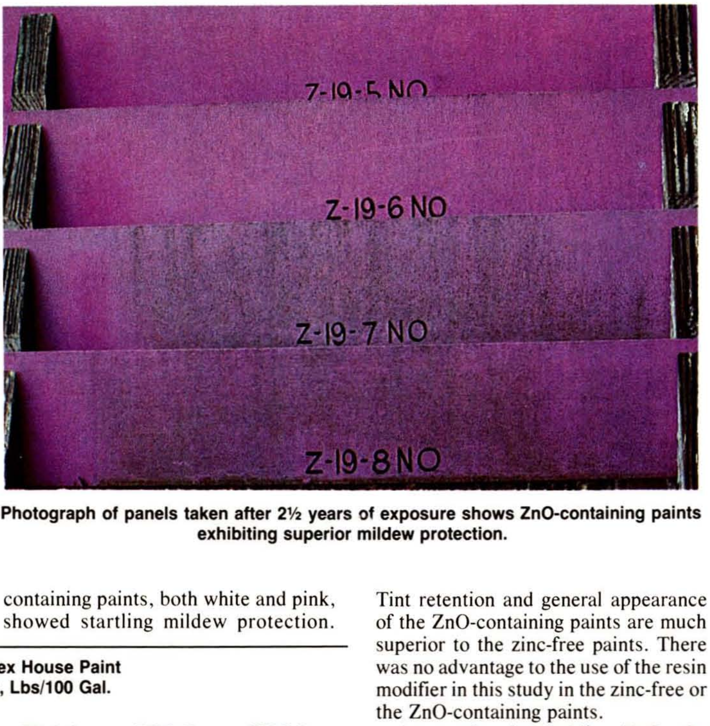
Zinc Institute House Paint Study Designed for High Gloss Shows Superior Mildew Protection and Excellent Tint Retention

In 1975 the Paint Evaluation Group of the Zinc Institute initiated Z 1-19 program to develop an exterior gloss latex house paint with ZnO and a special resin modifier. The paints as formulated contained 50 lbs. of ZnO per 100 gallons with and without the special resin modifier designed to improve gloss.

Zinc-free paints were also made with and without the resin modifier.

One set of paints was tinted pink and the other set was left white. The paints were applied to cedar panels which had been primed with a zinc-free alkyd primer applied at the rate of 450 sq. ft. per lb.

The special topcoats were applied at the rate of 400 sq. ft. per lb. Exposures were conducted at Ashtabula, Ohio, and New Orleans, La. Within a matter of months, the 60° gloss values which were originally 41 to 40 on the paints containing ZnO and the resin modifier, and 44 to 57 on the zinc-free paints, had all dropped to the range of 15 to 20. It was decided to continue the exposure series for mildew and tint retention.



Photograph of panels taken after 2½ years of exposure shows ZnO-containing paints exhibiting superior mildew protection.

After 2½ years' exposure the ZnO-containing paints, both white and pink, showed startling mildew protection. Tint retention and general appearance of the ZnO-containing paints are much superior to the zinc-free paints. There was no advantage to the use of the resin modifier in this study in the zinc-free or the ZnO-containing paints.

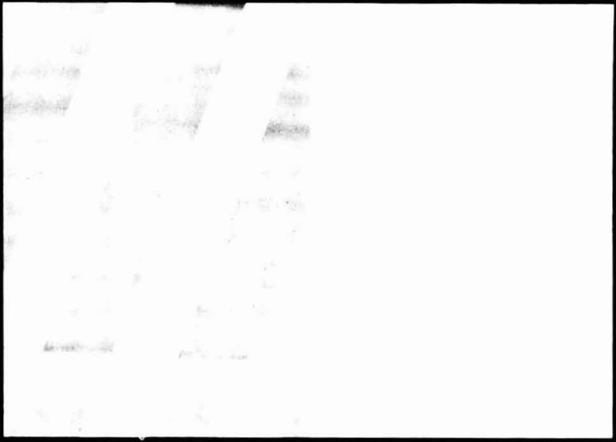
As usual, when adding ZnO, the non-mercurial fungicide was added at 10% of the recommended level and TiO_2 was reduced by 25 lbs. per 100 gals.

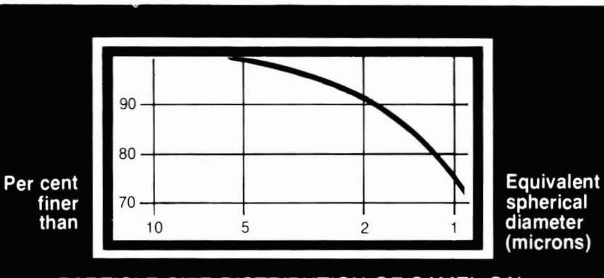
Gloss Exterior Latex House Paint
Formulation Data, Lbs/100 Gal.

Materials	Z19-1, 5 Pounds	Z19-2, 6 Pounds	Z19-3, 7 Pounds	Z19-4, 8 Pounds
Propylene glycol	70.00	70.00	70.00	70.00
Dow's HG-90®	0.70	0.70	0.70	0.70
Water	50.00	60.00	60.00	50.00
Tamol® 850 (30%)	6.00	6.00	6.00	6.00
Foamaster® B	2.00	2.00	2.00	2.00
R&H stabilizer #612	3.00	3.00	3.00	3.00
Amical® #48	0.50	0.50	5.00	5.00
TiO_2 R-900	225.00	240.00	250.00	250.00
Zinc oxide	50.00	50.00	none	none
Igepal® CO-710	4.00	4.00	4.00	4.00
R&H latex resin-AC-507® (46.5%)	590.00	430.00	408.60	590.00
6% Cobalt drier	none	1.33	1.33	none
6% Manganese drier	none	1.33	1.33	none
24% Lead drier	none	0.33	0.33	none
Foamaster B	2.00	2.00	2.00	2.00
Monsanto resin-RF-8057	none	81.66	76.00	none
Texanol®	24.00	18.00	18.00	24.00
Propylene glycol	30.00	30.00	30.00	30.00
Water	5.60	68.06	98.00	5.60
Totals	1062.80	1068.90	1036.29	1042.30
PVC	20.8	20.82	20.01	20.06
Lbs/Gal.	10.62	10.68	10.36	10.42
KU	80	80	80	80

Alkyd Primer
(No Zinc Oxide)
Formulation Data, Lbs/100 Gal.

Ti-Pure® R-902	250.0 Lbs.
Nytal® 300	250.0
No. 1 White	116.5
Bentone 38	4.3
Vancide® PA	1.5
Aroplaz® 1271	89.8
Aroplaz 1266M-70	299.3
#140 Mineral Spirits	169.9
8% Zn Naphthenate	4.1
4% Ca Naphthenate	9.2
6% Co Naphthenate	1.7
Anti-Skinning Agent	1.7
	1198.0 Lbs.
PV =	40.7%
(Initial KU)	82




90
80
70
10
5
2
1
Per cent finer than
Equivalent spherical diameter (microns)


PAINT/COATINGS DICTIONARY
FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY
Additives
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Cementitious Products Color Corrosion
Coil Coating
Decorating
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Finishing Techniques Lacquers Monomers
Naval Stores Oils Pigments, Dyes Plastics
Plasticizers Polymers (Synthetic Resins)
Printing Inks Resins (Natural) Rheology
Sealants, Caulks Sealers, Fillers Shellac
Solvents, Solvency, Thinners Surfactants
Varnishes Water-Soluble Resins,
Gums Waxes Methods of
Application

PAINT/COATINGS DICTIONARY

An invaluable reference source containing definitions for more than 4500 coatings-related terms. . . . Classification section listing all terms in total of 73 categories. . . . Extensive bibliography (over 600 references). . . . 632 pages (6 x 9 in.), case-bound.

Approximately 4500 terms of the coatings industry and its interfacing technologies are defined in this comprehensive volume, which has been compiled by the Definitions Committee of the Federation of Societies for Coatings Technology. Unique feature is classification of these definitions into one or more of 73 categories (color, pigments, additives, methods of application, etc.). These categories have been number coded and appear as superscripts at the end of each definition. Conversely, all terms defined under each category are listed in back of the book and serve as a thesaurus for key words, research papers, and literature searches. Pigments have also been classified into their Color Index numbers, and pigment synonyms have been extensively cross-indexed to a commonly accepted name.

- -

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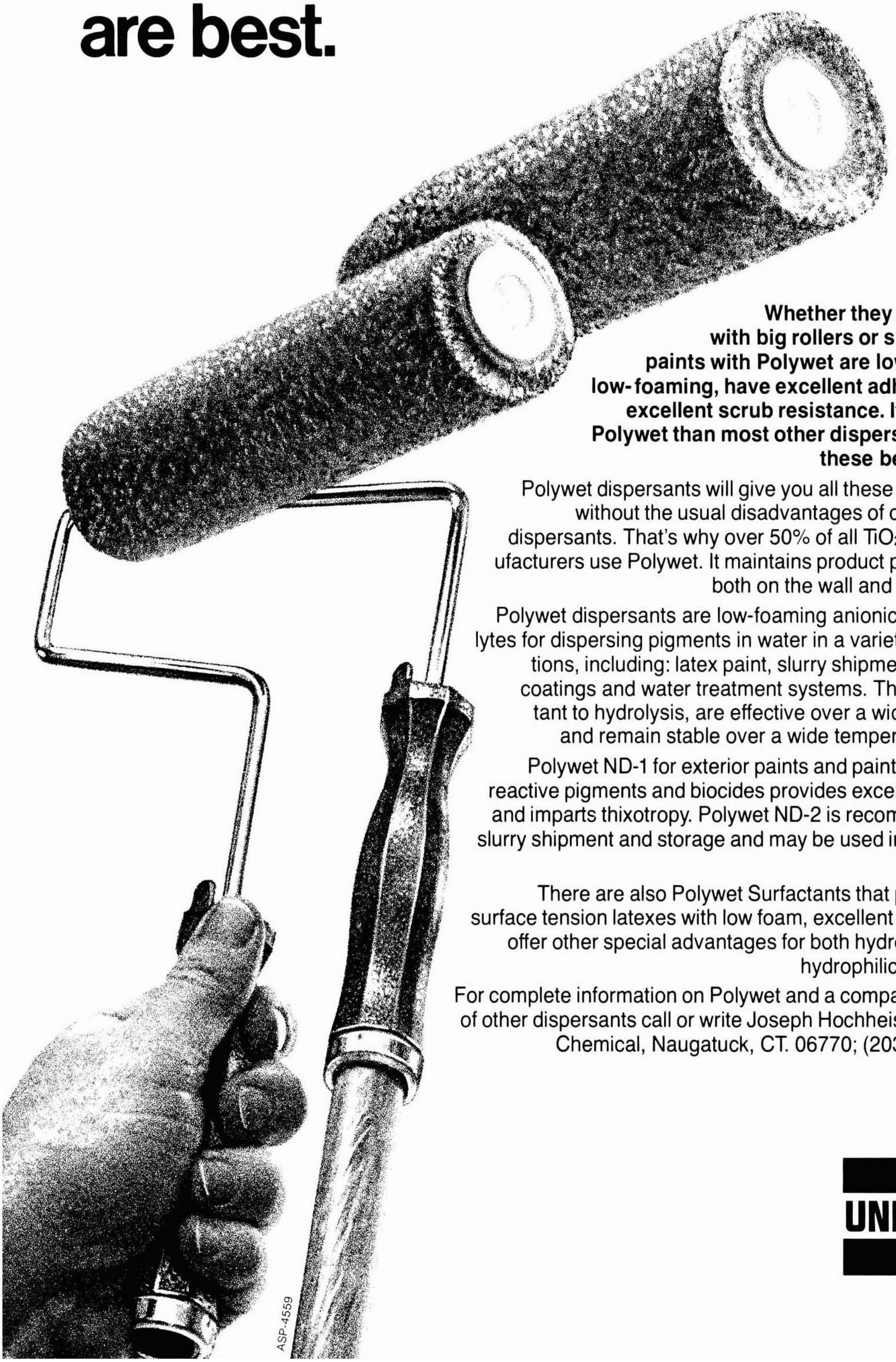
Low cratering is just one reason why Polywet® dispersants are best.



Whether they are applied with big rollers or small rollers, paints with Polywet are low cratering, low-foaming, have excellent adhesion, and excellent scrub resistance. It takes less Polywet than most other dispersants to get these benefits, too.

Polywet dispersants will give you all these advantages without the usual disadvantages of conventional dispersants. That's why over 50% of all TiO_2 slurry manufacturers use Polywet. It maintains product performance both on the wall and on the shelf.

Polywet dispersants are low-foaming anionic polyelectrolytes for dispersing pigments in water in a variety of applications, including: latex paint, slurry shipment, specialty coatings and water treatment systems. They are resistant to hydrolysis, are effective over a wide pH range, and remain stable over a wide temperature range.

Polywet ND-1 for exterior paints and paints containing reactive pigments and biocides provides excellent stability and imparts thixotropy. Polywet ND-2 is recommended for slurry shipment and storage and may be used in all types of latex paints.

There are also Polywet Surfactants that provide high surface tension latexes with low foam, excellent stability and offer other special advantages for both hydrophobic and hydrophilic monomers.

For complete information on Polywet and a comparative study of other dispersants call or write Joseph Hochheiser, Uniroyal Chemical, Naugatuck, CT. 06770; (203) 723-3445.

UNIROYAL

Polyacrylate-Modified Water-Borne Alkyds

Eli Levine and Edward J. Kuzma
Celanese Chemical Company, Incorporated*

A process for the improvement of color, drying rate, early water resistance and long-term flexibility of water-borne, air-drying alkyds is described. The process consists (a) of preparing a low molecular weight acrylic solution polymer with both hydroxyl and carboxyl functionality, and (b) of charging the reactive acrylic polymer to the alkyd reactor with the conventional alkyd components and processing as usual. Performance of polyacrylate-modified alkyds is compared to suitable controls and to one commercial standard. Use of polyacrylic resins high in ethyl acrylate or butyl acrylate as internal plasticizers for alkyds is discussed, as is the effect upon price of polyacrylate modification.

INTRODUCTION

Although the use of water-based architectural and general industrial finishes continues to show steady growth, the rate of increase has been reported to be less than the rates predicted by many industry experts.[1] A major cause for the gap between promise and fulfillment has been ascribed to product or performance deficiencies.[2] Thus, it was recently noted that currently available water-borne alkyds suffer from the following deficiencies:[3] (1) odors due to amines and coupling solvents; (2) slow rate of drying; and (3) yellowing tendencies.

Water Solubilization Techniques

In order to see why these deficiencies exist, a brief and very basic review of the techniques of water solubilization is in order.

Alkyd resins which have been processed to low acid values are inherently insoluble in water. In order to make useful water "solutions" of alkyds, several techniques are employed, usually in combination.

The first is to prepare alkyds in which the acid values are normally 40 or higher. Interruption of processing at acid values as high as these ensures that molecular weight remains relatively low. In addition, neutralization of the free carboxyl groups with ammonia, or other volatile amine compounds, in an aqueous medium causes a high degree of hydration and swelling to occur. These changes are essential if a useful degree of solubilization is to occur. However, low molecular weight alkyd resins remain soft and possess minimal protective properties for extended periods following application. Thus, these two essential concessions to solubilization (low molecular weight plus neutralization) cause "slow drying" and amine odors.

An additional solubilizing procedure calls for the use of such coupling solvents as ether alcohols, often in admixture with lower aliphatic alcohols. The use of water miscible solvents is required because, despite the solubilizing measures just described, resin chemists have found it necessary to increase the dissolving power of the aqueous phase in order to effect a commercially acceptable level of solubilization.[4] Unfortunately, solvents of these types have odors which are sufficiently distinctive to have become sources of complaint.

The yellowing tendencies[3] also flow largely from the use of ammonia as a neutralizing agent. Resin chemists have attempted unsuccessfully for years to arrest formation of the chromophoric groups which appear, inevitably, when alkyd resins are neutralized with ammonia.

Use of such materials as styrene or methyl methacrylate to modify water-borne alkyds is one way in which polymer chemists have attempted to overcome these deficiencies. A widely used method of preparing monomer-modified alkyds and polymers is, as follows:[5]

(a) Prepare an alkyd resin, or its precursor, containing centers of unsaturation.

(b) Add monomers and initiators and promote polymerization by suitable heat and agitation.

(c) If an alkyd precursor has been used as the sub-

Presented at the Water-Borne and Higher Solids Coatings Symposium in New Orleans, La., February 12-14, 1979, this paper won the First Annual Interstab Prize.

*P.O. Box 1000, Summit, N.J. 07901.

Table 1 — Process for the Preparation Of a Typical Reactive Acrylic Polymer

Reactive Polymer #1	Parts by Weight	
SOLUTION A		
Methyl methacrylate (50 ppm MEHQ) (duPont)	200.0	
Ethyl acrylate (15 ppm MEHQ) (Celanese)	160.7	
Hydroxyethyl methacrylate (Rohm and Haas)	24.0	
Methacrylic acid (100 ppm MEHQ) (Rohm and Haas)	12.0	
n-Dodecyl mercaptan (Pennwalt Corp.)	1.3	
Sub-Total "A"		398.0
SOLUTION B		
Di Cup R (Hercules)	12.0	
Xylol	590.0	
Sub-Total "B"		602.0
Total		1000.0

PROCEDURE

Prepare solutions A and B as indicated. Charge 133 pbw of solution B to reactor. Hold out 35 pbw of solution B for post-addition. Blend balance of B (434 pbw) with solution A and set up solution blend for delayed addition. Heat reactor plus contents to 120°C, under inert atmosphere, and start adding solution blend over 3½ hour period. Maintain polymerization temperature of 125-130°C. Following polymerization, add 35 parts of solution B over 15 minute period. Maintain batch temperature of 125-130°C during addition of scavenger solution, and for an additional period of 45 minutes. Cool to 60°C or less and pour off to storage.

strate, complete the resin by the addition of the remaining ingredients.

Resins of these types have several advantages. They are substantially lighter in color than their monomer-free analogs. This is true not only because of the dilution effect of the polystyrene or polymethyl methacrylate, but also because of the reduction of drying oil fatty acid unsaturation which occurs by virtue of polymer grafting. In addition, these resins dry rapidly to form films of great hardness and high gloss.

However, they also suffer from substantial disadvantages. In general, they are characterized by poor adhesion and a tendency to fail through embrittlement when used for exterior applications. Further, they frequently exhibit poor shelf stability because of the presence of unreacted monomer. In addition, it is generally acknowledged that a mixture of unmodified alkyd, unmodified homopolymer, and monomer-modified alkyd are formed in the process. Resulting tendencies toward limited solubility or compatibility may cause poor shelf life, poor pigment wetting properties, and inadequate flow and leveling characteristics.

In 1958, Dr. D. H. Solomon[6] was granted a patent for a process of "forming a vinyl copolymer containing carboxyl groups and reacting this copolymer with a fatty acid partial ester of a polyfunctional alcohol, either before, during, or after the condensation of the partial ester with a polybasic carboxylic acid."

An attempt to implement Dr. Solomon's process in the preparation of an (essentially solvent-free) polymer-modified long oil alkyd for use as a latex paint additive was only partially successful.[7] However, his work provided the basis for a process which was successfully applied in the preparation of polymer-modified long oil alkyds as latex paint modifiers.[8]

The process which was finally developed called for the preparation of a reactive acrylic polymer which contained both hydroxyl-bearing and carboxyl-bearing monomers. Reactive acrylic polymers of this type were then charged to the alkyd kettle along with drying oil fatty acids, aromatic dibasic acids, and polyol. These polyacrylics, reactive with every component of fatty acid-based alkyd resins, contributed to the preparation of alkyd resins of excellent color, stability, clarity, and weather resistance.

In order to be able to incorporate the maximum level of reactive polymeric material into the alkyd, polymer molecular weight had to be kept as low as possible. Accordingly, the polymerization process was carried out at relatively high temperatures, and with an excess of initiator. A chain transfer agent could also be included.

The present report describes this polymerization process, as it evolved, to the preparation of improved water-borne alkyds.

RELEVANCE OF POLYMERIC MODIFICATION

In considering the likelihood of product improvement by means of polymeric modification, several possibilities came immediately to mind. Two of the most important and advantageous properties of polymethyl methacrylate polymers and copolymers are an absence of color and a strong resistance to yellowing. It seemed to follow, then, that the use of such polymers as mod-

Table 2 — Reactive Acrylic Polymers Prepared and Evaluated as Water-Borne Alkyd Components

	Composition					Tg Cal'd.	Unreacted Monomer		
Polymer #	% MMA	% EA	% BA	% HEMA	% MAA	°C	% MMA	% EA	% BA
RAP-1	50	41	—	6	3	39	0.44%	0.37%	—
RAP-2	65	26	—	6	3	59	0.23%	N.D.	—
RAP-3	75	16	—	6	3	74	1.18%	N.D.	—
RAP-4	65	22	—	10	3	64	0.43%	N.D.	—
RAP-5	—	—	91	6	3	−38	—	—	*
RAP-6	—	87	—	10	3	−11	—	0.37	—

N.D. = not detectable.
*Could not be determined because of interference from solvent.

ifiers of water-borne alkyds might be expected to reduce resin color and to enhance long-term color stability.

Likewise, incorporation of reactive polymeric material could be expected to result in earlier film formation and increased early hardness. This is of critical importance because it is during the early stages of film formation that a newly applied paint is most vulnerable to dust, careless handling, and moisture.

On the other hand, as long as solubilization is achieved through the use of salt formation and of water miscible solvents, use of polymeric modifiers should not be expected to have any significant effect on the odor due to amines and solvents.

However, in view of the potential of polymeric modification to provide improvement in at least two key areas, evaluation of the modified Solomon method of incorporating polymeric material in water-borne air-drying alkyds seemed appropriate.

Importance of Plasticizing Monomers

Obviously, copolymers of methyl methacrylate, hydroxyethyl methacrylate, and methacrylic acid could be prepared and incorporated into water-borne alkyds. Resins of this type could be expected to have some advantageous properties. In the authors' view, however, this approach leaves a great deal to be desired. Application of a polymethyl methacrylate-modified water-borne alkyd at relatively low temperatures could result in poor film properties. In addition, embrittlement is a frequent cause of alkyd failure and inclusion within the polymeric matrix of blocks of crosslinked polymethyl methacrylate can only act to make excessive brittleness and adhesion failure even more likely.

For these reasons, plasticizing monomers were included in every reactive polymer evaluated during this program, to give reactive acrylic polymers with widely differing glass transition temperatures.

The effects of variations in hardness of the various reactive acrylic polymers upon the rate of hardness development of the modified alkyds was perceived as one of the more important goals of this study.

Table 3 — Reactive Acrylic Polymer Molecular Weights

Polymer No.	M_n	M_w	M_w/M_n
RAP-1	2670	9220	3.5
RAP-5	1280	5540	4.3
RAP-6	1340	5740	4.3

PREPARATION OF REACTIVE ACRYLIC POLYMERS

The formulation and procedure used in the preparation of a typical reactive acrylic polymer is shown in *Table* 1.

The combination of dicumyl peroxide (3% on weight of monomer) as initiator, and xylol as reaction medium, at temperatures close to its boiling point, had, in previous work, resulted in high conversion and low molecular weight.[8] For these reasons, the combination was used in the present investigation as well. To help ensure the development of low molecular weight polymer, 0.33% of n-dodecyl mercaptan, on weight of monomer, was also included in the formulation.

In the present investigation, reactive acrylic polymers ranging in composition from 75% methyl methacrylate/16% ethyl acrylate/6% hydroxyethyl methacrylate/3% methacrylic acid to 91% butyl acrylate/6% hydroxyethyl methacrylate/3% methacrylic acid were made and evaluated.

For illustrative purposes, six reactive acrylic polymers were prepared and evaluated. Their compositions are noted in *Table* 2. All were formulated to give 40% solutions, by weight, in xylol; all contained the same ratios of initiator and chain transfer agent to monomer, and all were processed as indicated in *Table* 1.

It has been noted that acrylic polymers of low

Table 4 — Composition of Low Isophthalic Acid Alkyds

Component	L (Control)	L1A	L1B	L1C	L1D	L2
Reactive acrylic polymer	—	7.9	15.9	22.9	23.9	7.9
Pamolyn 200	49.0	42.2	34.8	27.0	26.8	42.2
Isophthalic acid	22.1	22.4	22.6	22.5	22.7	22.4
Trimethylolpropane	24.0	23.7	23.2	23.6	23.1	23.7
Trimellitic anhydride[a]	4.9	3.8	3.5	4.0	3.5	3.8
	100.0	100.0	100.0	100.0	100.0	100.0
Composition of Reactive Acrylic Polymer						
Methyl methacrylate	—	3.95	7.95	11.45	11.95	—
Ethyl acrylate	—	3.24	6.52	9.39	9.80	—
Hydroxyethyl methacrylate	—	0.47	0.95	1.37	1.43	0.47
Methacrylic acid	—	0.24	0.48	0.69	0.72	0.24
Butyl acrylate	—	—	—	—	—	7.19
		7.90	15.90	22.90	23.90	7.90

(a) Amoco Chemical Company, *Chelated Modified Improved Water Soluble Implement Enamels*, bulletin TMA 117, Nov., 1974.

Table 5 — Properties of Low Isophthalic Acid Alkyds

	Control	L1A	L1B	L1C	L1D	L2
% Excess hydroxyl	3.8	10%	15%	22.5%	21.8%	10%
Resin viscosity @ 70% n.v., cps*	400	1720	7400	7200	—	1300
Acid value, 100% n.v. basis	38	36	37	46	45	39
Gardner Holdt color @ 70% n.v.	4	2-1/2	2	2	2	3
Dispersibility in ammoniacal water @ 40% n.v. (pH = 8.5)	o.k.	o.k.	o.k.	o.k.	n.g.	o.k.

*Solvent fraction consists of 50% Propasol P/50% sec-butanol.

molecular weight are desirable for the present application. The reasons for this become apparent when it is remembered that the solvent system used in coatings based upon water-borne alkyds is a poor one, and that if acrylic polymer molecular weights are not kept as low as possible, viscosity considerations will make it difficult to include more than minimal quantities of reactive acrylic material as co-reactants in the alkyd formulation.

Table 2 also contains the calculated glass transition temperatures of the six reactive acrylic polymers.

Table 6 — Test Paint Formulation

I. Prepare 50% resin solution as follows:	
70% resin solution	116.1
28% ammonia	9.1
Mix until uniform. Add:	
Water	37.3
	162.6 p.b.w.
II. Prepare pigment dispersion as follows:	
50% resin solution	50.0
TiO_2, R-960 (duPont)	75.0
	125.0 p.b.w.
Mix until pigment is thoroughly wet with resin solution. Mill until desired degree of dispersion is obtained.	
III. Prepare drier mixture as follows:	
6% zirconium Ten-Cem (Mooney)	2.50
6% cobalt (octoate) (Tenneco)	2.25
Activ-8 (R.T. Vanderbilt Co.)	0.25
	5.00 p.b.w.
IV. Prepare paint as follows:	
50% resin solution	112.8
pigment dispersion	125.0
drier mixture	5.0
water	114.2
	357.0 p.b.w.
Paint Data	
Non-volatile content	43.8%
Resin/pigment	52/48
Zirconium (metal)/resin solids	0.18%
Cobalt (metal)/resin solids	0.16%
Activ-8 solution/resin solids	0.30%

Table 3 lists the molecular weights of three of the reactive acrylics included in the present study. Molecular weight determinations were made by gel permeation chromatography of THF solutions of dried films.

In determining these molecular weights, RAP5 (91% butyl acrylate) was compared to a standard polybutyl acrylate of known molecular weight, RAP6 (87% ethyl acrylate) and RAP1 (41% ethyl acrylate) were compared to a standard polyethyl acrylate of known molecular weight. Since there was significant deviation in composition between experimental resins and standards, the results given in *Table* 3 should be considered only as approximate values. However, they may be considered as confirmation that the polymerization process is indeed producing low molecular weight polymer.

FORMULATING ALKYDS WITH REACTIVE ACRYLIC POLYMERS

In attempting to determine how best to use reactive acrylics in the formulation of improved alkyds, it is important to remember that alkyd resins dry faster and give harder, tougher films than their corresponding drying oils because of the high crosslink density imparted to the film by the aromatic dibasic acid component. Since this is so, it would be a step backward to replace any portion of the aromatic dibasic acid in the formulation with the lightly crosslinked acrylic polymer.*

For the same reason, the polyol cannot be replaced, even to a slight extent, by a reactive acrylic polymer without some reduction in desirable properties.

The one component in water-borne alkyds which contributes a roughly similar crosslink density to that imparted by reactive acrylic polymers is the fatty acid component. Both may be considered linear and neither is highly crosslinked during the early life of the film. It is true that the difference in molecular weight weakens the analogy somewhat. However, in this work, it was found that partial replacement of the fatty acid component by reactive acrylic polymer, essentially on an equal weight basis, gives the most desirable results. The level of

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*This hypothesis has been confirmed experimentally by the authors. It was observed that the hardness of the reactive polymer did not compensate for the properties imparted by the portion of aromatic dibasic acid which was removed. A resin in which such a partial replacement of isophthalic acid by a hard acrylic polymer was made dried more slowly than the control resin and resulted in a mechanically inferior film.

Table 7 — Low Isophthalic Acid Resin-Based Paint Data

Resin	Set-to-Touch (min)	Tack-Free (hr)	60° Gloss After One Week	Early Water* Resistance Rating
L	13	10-1/2	85.0	2-3
L1A	12	5-1/2	89.2	2-3
L1B	15	7-1/2	87.0	1
L1C	14	8-1/2	86.6	1-2
L2	14	8	87.4	1-2

*Effect of a drop of water in contact with the coating film for 5 min, determined 1 hr after film was applied. 1 = no effect; 2 = trace etch; 3 = etch; 4 = severe etch; 5 = denuded.

excess hydroxyl in the polyacrylate-modified alkyd, however, must be increased to permit inclusion of the higher molecular weight polyacrylic material. In all of the work being presently reported, partial replacement of fatty acids by polyacrylic resin was made on this basis.

MODIFICATION OF LOW ISOPHTHALIC ACID ALKYDS

A series of six low isophthalic acid resins was prepared and evaluated. Of the six, one was a control resin, four contained varying quantities of a single moderately hard reactive acrylic polymer, and one contained a very soft reactive acrylic polymer. *Table* 4 shows the compositions of the resins.

Drying Properties

The control resin, L, was a relatively slow-drying resin, which, however, exhibited good protective properties upon drying. A sub-series within this group, L1A, L1B, L1C, and L1D contained increasing percentages of reactive polymer #1 (see *Table* 1).

Table 4 indicates that the control resin, L, has a slightly higher trimellitic anhydride content than do the modified resins. During the course of this work, there were indications that polyacrylic modification improved the dispersibility of an alkyd in weakly ammoniacal water. For this reason, slight reductions in the trimellitic anhydride level, relative to the control, were made in the modified resins. The first three resins in the sub-group retained their dispersibility in weakly ammoniacal water at a non-volatile content of 40%. Resin L1D did not. Apparently, too great a burden, both in terms of polymer molecular weight and degree of branching, was imposed upon the 3.5% of trimellitic anhydride used in L1D.

It is likely that there is an optimal trimellitic anhydride level for each level of polyacrylic modifier, and determining this ratio will assist greatly in achieving a desirable balance of properties.

Another characteristic is the lighter color of the modified resins (*Table* 5). This stems from the fact that the polyacrylic modifier is being used in partial replacement of drying oil fatty acids, and because fatty acids are the principal sources of color, polyacrylate-modified resins will be lighter. Where resin color is critical in a water-borne alkyd, it will be advantageous to modify the alkyd to the greatest extent possible.

The six resins in the low isophthalic acid series were compounded into enamels (*Table* 6) and compared for several key properties. *Table* 7 contains this data.

That all of the modified resins became tack-free in significantly shorter periods than did the control was not surprising. Inclusion of substantial percentages of polyacrylic material in place of drying oil fatty acids cannot help but superimpose a lacquer-like drying mechanism upon the oxidative drying mechanism associated with fatty acid-containing resins. That L1B and L1C took longer to become tack-free than did L1A, which had only 7.9% of polyacrylic modifier, is somewhat unexpected. Increased solvent retention with increasing polyacrylic modification is one possible explanation. Drier absorption by the polyacrylic material at higher levels of modification is another. Formulators interested in developing the work presently being reported should consider both possibilities. It may be that different solvents are required for modified alkyds. It may also be that a more efficient drier system is needed for modified alkyds. It is clear, however, that the polyacrylate-modified low isophthalic acid resins, as a class, dried much faster than the control, justifying further development of resins of this type.

Water-Resistance

The same considerations apply to the development of early water resistance. The fact that three out of four modified resins exhibited better early water resistance than did the control is of primary significance, and indicates that those formulators interested in developing low phthalic or isophthalic acid-based resins with improved early water resistance now have the means with which to accomplish this. The fact that L1B, with 15.9% of polyacrylic material, was better than either L1A or L1C may mean nothing more than that solvent or drier optimization is needed.

Film Hardness

In the course of this study, film hardness measurements were taken periodically, following application of the paint, for a period of up to 28 days. Measurements relative to the low isophthalic acid resin-based coatings are shown in *Figures* 1 and 2.

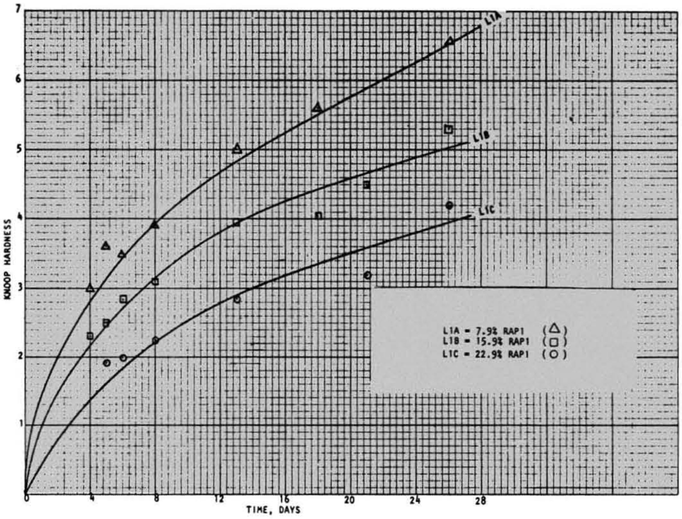

Figure 1—Rates of hardness development of coatings based on modified low isophthalic acid resins as a function of reactive polyacrylic resin content

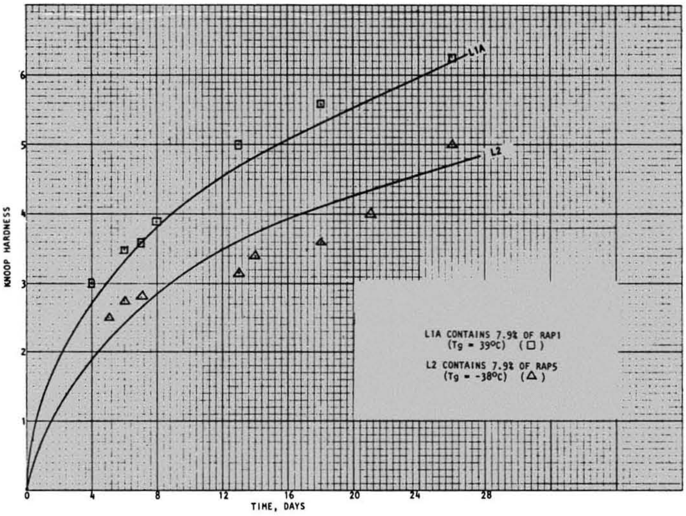

Figure 2—Rates of hardness development of coatings based on low isophthalic acid resins as a function of monomer composition of polyacrylate modifier

It should be pointed out that the reproducibility of Tukon hardness measurements increases significantly as film hardness increases. (Table 8).

Accordingly, in drawing the hardness profiles of the various coatings tested, least weight was placed on those data points gathered when the film was relatively fresh.

Figure 1 presents hardness profiles of coatings based upon L1A, L1B, and L1C. It will be recalled that resins L1A, L1B, and L1C contained, respectively, 7.9%, 15.9%, and 22.9% of a reactive acrylic polymer of intermediate hardness (RAP1, Tg = 39°C).

Figure 1 shows that the rate of hardness development decreased as the level of modifier RAP1 increased, over the period tested. (For reference, coatings with hardnesses of 4 or higher are, in general, resistant to fingernail scratch tests.)

A reasonable attempt at explaining this observed phenomenon is as follows: as post-film formation oxidative crosslinking continued, the Tg of the increasingly crosslinked alkyd-rich areas soon exceeded that of the polyacrylic-rich areas, at which point the polyacrylate modifier assumed the functions of a nonextractable plasticizer. The presence of this plasticizing material acted as a brake on the development of further hardness while oxidative crosslinking continued.

(Where the Tg of the modifying polymer is relatively high, as would be the case in a styrenated alkyd, the

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Note: All paint film hardness measurements presented in this report were measured by Tukon Tester, rather than the commonly used pencil hardness test, for greatest possible sensitivity and reproducibility. The painted panels were stored in a constant temperature, constant humidity room (70°F/50% R.H.), and measurements were taken in the same environment. Hardnesses measured by Tukon Tester were expressed in Knoop Hardness Units.

modifying polymer may become a source of hardness. An example of this is in the next section.)

It cannot be assumed that these differences in the rates of post-film formation hardening will persist throughout the life of the coating, although, of course, they may be long-lived. But to the extent that they do persist, they should prolong the useful life of outdoor coatings in which they are used. Many alkyd-based exterior coatings, as a result of continued post-film formation crosslinking, ultimately reach a point at which they are no longer able to expand or contract in response to seasonal or diurnal temperature changes. When this occurs, cracking is the result, and the film's protective functions have been lost.

Exterior Durability

The presence of any component which tends to diminish the rate of post-film formation hardening can be expected to prolong the useful life of the film provided that this component itself does not detract from the coating's exterior durability. Because it is generally recognized that acrylic polymers exhibit excellent exterior durability, use of properly designed polyacrylic modifiers in water-borne alkyds should result in exterior vehicles of very high quality.

The types and ratios of monomers which will provide the maximum improvement in exterior durability cannot be determined without extensive exposure tests. Unfortunately, tests of this kind were beyond the scope of the present program. *Figure* 2, however, provides some idea of the effect of monomer composition of the modifier upon post film formation hardness development.

Resin L1A has already been described. Resin L2 also contained 7.9% of polyacrylic modifier, but 91% of the modifier was butyl acrylate. Coatings based upon these two modifier alkyds should be expected to exhibit different rates of post-film formation hardening, and *Figure* 2 confirms that this is so.

It is apparent that proper choice of the monomer components of polyacrylic modifiers is at least as important as the level of polyacrylic modifier used in the design of polyacrylated alkyds for exterior use, and that the proper use of plasticizing monomers is an area that merits thorough exploration.

Table 8 — Film Hardness Measurements

Age of Film	Knoop Hardness Number	Arithmetic Mean	Average Deviation
48 hours	2.15	—	—
	3.50	—	—
	1.90	—	—
	1.65	—	—
	2.32	—	—
	2.81	—	—
		2.39	0.51
26 days	8.47	—	—
	7.90	—	—
	7.65	—	—
	8.05	—	—
	7.72	—	—
	8.12	—	—
		7.99	0.23

Table 9 — Low Isophthalic Acid Resin Viscosities As a Function of Non-Volatile Content, in Centipoise

Resin No.	70% n.v.	60% n.v.	50% n.v.	40% n.v.
L	400	370	450	700
L1A	1720	1200	1540	2120
L1B	7400	3400	4050	5050
L1C	7200	2640	2200	2640
L2	1300	1240	1100	1570

Viscosities

The last characteristics of the low isophthalic acid resin group to be discussed are their viscosities as a function of their non-volatile contents as they are diluted with ammonia and distilled water from a solids content of 70% (nonaqueous) to one of 40%.

Inspection of the viscosities (shown in *Table* 9) of this group leads to two principal conclusions: (1) The control resin should have been slightly shorter in oil length in order to give it a higher viscosity; and (2) None of the polymer-modified resins are excessively viscous, indicating that modification of the low isophthalic acid resins produces acceptable application properties.

MODIFICATION OF MEDIUM ISOPHTHALIC ACID ALKYDS

Normally, alkyds with lower fatty acid contents and higher dibasic aromatic acid levels are used when more rapid drying rates and improved early protective properties are desired. *Figure* 3 illustrates the rates of hardness development of the low, medium, and high isophthalic acid control resins prepared and used during this program.*

For purposes of clarity, the medium isophthalic acid resin modifications will be discussed as three sub-series. The first sub-series consists of resins M (control), M1, M3, and M4. *Table* 10 contains the compositions of the four resins, and *Table* 11 shows relevant resin data.

As before, approximately one part by weight of polyacrylic resin solids was used per part by weight of fatty acids taken from the control resin, and, as before, the tendency towards higher viscosity was largely offset by an increase in the level of excess hydroxyl in the alkyd. With respect to the resin viscosities obtained, it is apparent, once again, that the viscosity of the control alkyd was slightly low. The polyacrylate-modified alkyds were once again substantially more viscous, but had viscosities which permitted convenient handling.

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*Note: The designations of low, medium, and high isophthalic acid resins for polymers containing approximately 22%, 28%, and 35% isophthalic acid were our own and were purely arbitrary.

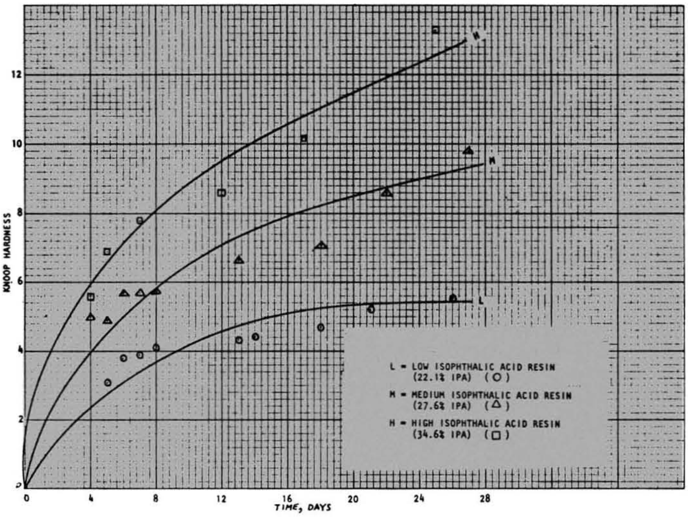


Figure 3—Rates of hardness development of coatings based on the three control resins: L, M, and H

(Note: In terms of Gardner-Holdt viscosity measurements, viscosities of all medium isophthalic acid resins, M1—M6, inclusive, ranged from Z5 to Z6+, at 70% n.v.)

The objectives of this particular sub-series (M, M1, M3, and M4) were to determine how RAP2 would affect the drying rate, whether increasing levels of RAP2 would affect the rate of hardness development and whether, as the level of excess hydroxyl donated by the trimethylolpropane component was increased, a point would be reached at which the early water resistance of the coating would begin to suffer.

The resins were compounded into enamels, as before, and the coatings were tested for drying rates and early water resistance. Results are shown in *Figure* 4 and *Table* 12.

It can be seen in *Table* 12 that all three modifications of M dried to a tack-free state much more rapidly than did the control. It is apparent that polyacrylic modification of medium isophthalic acid resins, as in the case of the lower isophthalic acid series, is a viable way of reducing the vulnerability of a freshly painted surface by moisture, dust, or poor handling.

With respect to the rates of hardness development (*Figure* 4), modification of M with either 11.4% or 15.9% of RAP2 seems not to have had a significant effect. A reasonable explanation is that the hardness of the control resin M and that of RAP2 (Tg 59°C) are relatively close, at least for the period over which hardness measurements were made. As post-film formation oxidation of the four resins proceeds, it is probable that the coating based upon M ultimately will develop hardness at a somewhat greater rate than the coatings based upon the three modified vehicles because of its higher unsaturated fatty acid content, but, plainly, a polyacrylic component with a Tg of 59°C is a relatively inefficient plasticizer. Reactive polyacrylics richer in plasticizing monomers almost certainly would provide a better balance of properties as components of exterior paint vehicles.

Table 10 — Composition of Medium Isophthalic Acid Alkyds M, M1, M3, M4

Components	Resin Composition M	M1	M3	M4
RAP2 (Tg 59°C)	—	11.4	11.4	15.9
Pamolyn 200	41.3	30.8	31.0	27.0
Isophthalic acid	27.6	27.5	27.6	26.9
Trimethylolpropane	26.2	26.0	26.1	26.0
Trimellitic anhydride	4.9	4.3	3.9	4.2
	100.0	100.0	100.0	100.0

Table 11 — Resin Data

Property	M	M1	M3	M4
% Excess hydroxyl	5%	14%	15.6%	20%
Viscosity, 70% n.v., cps	2,520	14,000	19,500	9,200
Acid value	44.6	43.9	40.3	42.5

With respect to early water resistance, it appears that at a level of modification of 11.4%, the presence of the reactive acrylic polymer added more than was taken away by the increase in excess hydroxyl (from 5% to 15%). However, at the higher level of polyacrylic modification, 15.9%, results indicate that the unreacted hydroxyl may have detracted as much from the early water resistance of the coating as had been contributed by the polyacrylic modifier.

It may be concluded that, for maximum early water resistance properties, there is an optimum balance of excess hydroxyl and level of polyacrylic modification, and that this balance should be determined experimentally.

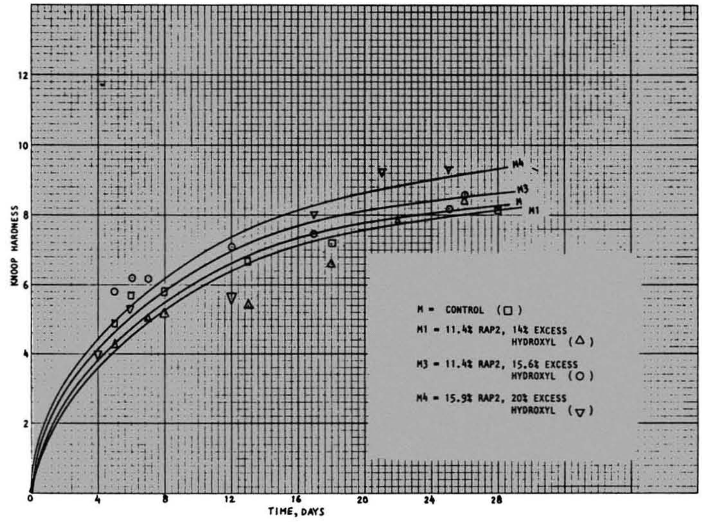


Figure 4—Rates of hardness development of coatings based on modified medium isophthalic acid resins as a function of excess hydroxyl level

For several reasons, and in spite of the foregoing discussion, the presence of relatively high levels of unreacted hydroxyl groups might be a highly desirable attribute in a water-borne alkyd. In the first place, high levels of hydroxyl could be expected to enhance dispersibility in the ether alcohol/alcohol/water solvent blends in current use, thus enhancing package stability. It is also possible that vehicles of this type might permit still further reduction in trimellitic anhydride levels, with the attendant advantage of a reduced amine requirement. Improved solubility in lower alcohols, or other polar solvents, for ink applications, is yet another possibility.

It is obvious that a second source of excess hydroxyl in a polyacrylate-modified alkyd is the hydroxyethyl methacrylate component of the reactive acrylic polymer. Resin M5 was prepared in order to determine the effects upon performance of a reactive acrylic polymer with a relatively high hydroxyethyl methacrylate content. It was compared to a resin with a lower level of hydroxyethyl methacrylate, as well as to the control.

Table 13 contains the formulations of the resins of this sub-series and *Table* 14 contains the relevant resin data.

The three resins were compounded into enamels, as before, and the drying characteristics of the coatings were compared.

As shown in *Table* 15, coatings based upon both modified resins dried more rapidly than the coating based upon the control. The substantial difference in tack-free times between the coatings based upon M3 (lower hydroxyethyl methacrylate) and M5 (higher hydroxyethyl methacrylate) is probably due to increased solvent retention of the enamel based upon M5. However, despite this demonstration of increased solvent retention, early water resistance of the coating based upon M5 was unimpaired.

Table 12 — Paint Data

Resin	Set to Touch, Minutes	Tack-free, Hours	60° Gloss	Early Water Resistance
M..........	11	5-1/4	85.8	1-2
M1.........	12	3/4	84.4	1
M3.........	12	1-1/4	85.8	1
M4.........	12	3/4	82.2	1-2

Table 13 — Comparison of Hydroxyethyl Methacrylate Levels

Component	M	M3	M5
RAP 3 (6% hydroxyethyl methacrylate)........................	—	11.4	—
RAP4 (10% Hydroxyethyl methacrylate)	—	—	11.4
Pamolyn 200..........................	41.3	31.0	31.0
Isophthalic Acid	27.6	27.6	27.6
Trimethylolpropane	26.2	26.1	26.1
Trimellitic Anhydride..................	4.9	3.9	3.9
	100.0	100.0	100.0

Table 14 — Resin Data

Property	M	M3	M5
% Excess hydroxyl (excluding RAP	5%	15.6%	15.6%
Viscosity @ 70% n.v., cps.....................	2,520	19,500	8,000
Acid value.....................	44.6	40.3	44.6

Table 15 — Paint Data

Resin	Set-to-Touch, Minutes	Tack-free, Hours	60° Gloss	Early Water Resistance
M	11	5-1/4	85.8	1-2
M3	12	1-1/4	85.8	1
M5	13	3-1/2	86.0	1

Table 16 — Reduction in Level of Trimellitic Anhydride

Component	M	M6	M3	M2
RAP3 (Tg 74°C)	—	11.4	11.4	11.4
Pamolyn 200	41.3	30.8	31.0	31.2
Isophthalic acid	27.6	27.5	27.6	27.7
Trimethylolpropane	26.2	26.0	26.1	26.2
Trimellitic anhydride	4.9	4.3	3.9	3.5
	100.0	100.0	100.0	100.0

Table 17 — Resin Data

Property	M	M6	M3	M2
% Excess hydroxyl	5%	15.6%	15.6%	15.6%
Viscosity @ 70% n.v., cps	2,520	20,500	19,500	13,500
Acid value	44.6	42.0	40.3	39.3

Table 18 — Paint Data

Resin	Set-to-Touch, Minutes	Tack-free, Hours	60° Gloss	Early Water Resistance
M	11	5-1/4	85.8	1-2
M6	12	3/4	85.8	1
M3	12	1-1/4	85.8	1
M2	13	1-1/4	86.0	1

These results suggest that reactive acrylic polymers with hydroxyethyl methacrylate contents well in excess of 6% deserve serious consideration for the reasons previously suggested.

An additional aspect of resin solubilization which was briefly examined involved the use of RAP3 (6% hydroxyethyl methacrylate), at a constant level, while decreasing the level of trimellitic anhydride. The aim of this particular experiment was to determine whether a series of reductions in the level of trimellitic anhydride, in the presence of polyacrylate modification, would have an effect upon resin dispersibility.

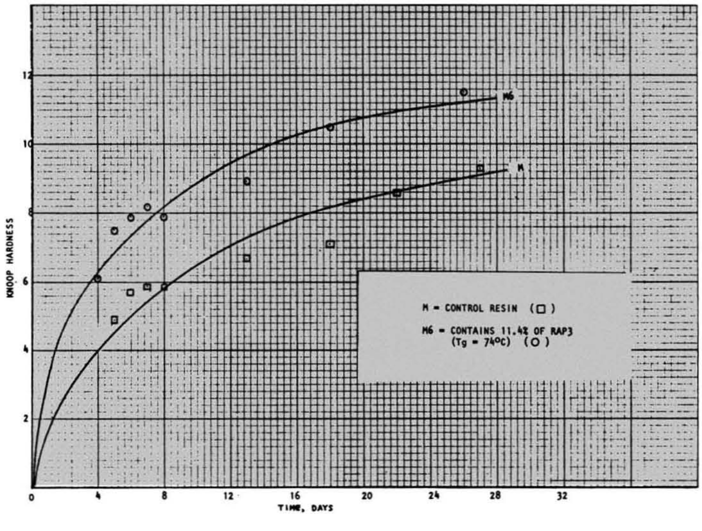
Resin formulations for this sub-series are shown in *Table* 16 and appropriate resin data are shown in *Table* 17.

All resins shown in these tables were dispersible in weakly ammoniacal water, at a level of 40% n.v., and all resins were easily compounded into enamels. Paint data is shown in *Table* 18.

Within the context of this sub-series of resins, the most significant results shown in *Table* 18 are the gloss measurements. Had the resins containing the lowest levels of trimellitic anhydride exhibited any degree of impaired dispersibility, the effects would have been seen in reduced gloss measurements of the corresponding enamels. The fact that pigment flocculation did not occur is of significance because the state of the pigment dispersion is a sensitive indicator of vehicle instability.

Obviously, many factors are involved in determining the optimum level of trimellitic anhydride, whether the resin is polyacrylate-modified or not. This brief comparison is intended only as a further suggestion that the polyacrylate modifier may exhibit a stabilizing influ-

Figure 5—Rates of hardness development of coatings based on M and M6



ence, as well as the trimellitic anhydride component.

A final word about the medium isophthalic acid resin series is in order. *Figure* 2 illustrated the plasticizing effect of a reactive acrylic polymer with a low glass transition temperature. *Figure* 5 illustrates the opposite condition, in which the rates of hardness development of M6, modified with a hard reactive acrylic polymer, and M, unmodified, are compared.

The comparison clearly demonstrates the hardening effect of the high methyl methacrylate copolymer. A resin similar to M6 might be considered for use where a high degree of early hardness is desired, and it offers the additional potential advantages of somewhat improved low temperature film formation as well as improved adhesion (as opposed to styrenated or methacrylated vehicles).

MODIFICATION OF HIGH ISOPHTHALIC ACID ALKYDS

Attempts to modify a high isophthalic acid alkyd presented a difficult problem. Resins of this type are heavily branched, highly viscous materials. In order to successfully modify the control resin, H, it was necessary that an inordinately high level of excess hydroxyl be retained in the finished alkyd (*Tables* 19 and 20), and even when this was done, only 5.1% of polyacrylic material was successfully incorporated.

The result of having this high level of excess hydroxyl, as can be seen in *Table* 21, appears to have been a substantial reduction in the early water resistance of the coating based upon the modified alkyd, H1. It should also be noted that the drying rate of the control alkyd was so rapid that it could scarcely have been increased by the low level of modification achieved.

It is true that the ethyl acrylate (4.4% on total weight) in H1 appears to be functioning very effectively as a plasticizer (*Figure* 6). (In this connection, reverse im-

Table 19 — Composition of High Isophthalic Acid Resins

Component	Resin Composition H	Resin Composition H1
Reactive acrylic polymer (RAP6)	—	5.1
Pamolyn 200	28.6	22.3
Isophthalic acid	34.6	34.0
Trimethylolpropane	31.6	33.5
Trimellitic anhydride	5.2	5.1
	100.0	100.0
Monomer Content		
Ethyl acrylate	—	4.44
Hydroxyethyl methacrylate	—	0.51
Methacrylic acid	—	0.15
		5.10

Table 20 — Properties of High Isophthalic Acid Resins

	H	H1
% Excess hydroxyl	18	31.6
Resin viscosity @ 70%, cps*	34,400	17,600
Acid value, 100% n.v. basis	47.2	33.1
Gardner Holdt color at 70% n.v.	2-1/2	2-1/2
Dispersibility in ammoniacal water at 40% n.v. (pH = 8.6)	o.k.	o.k.

*Solvent fraction consists of 50% Propasol P/50% secondary butanol.

Table 21 — High Isophthalic Acid Resin-Based Paint Data

Resin No.	Set-to-Touch, minutes	Tack-Free, minutes	60° Gloss After 1 week	Early Water Resistance Rating*
H	6	22	79.2	1
H1	5	23	86.4	3
Commercial Standard #1	5	60	80.2	1

*Effect of a drop of water in contact with coating film for 5 minutes, determined one hour after film was applied. 1 = no effect; 2 = trace etch; 3 = etch; 4 = severe etch; 5 = denuded.

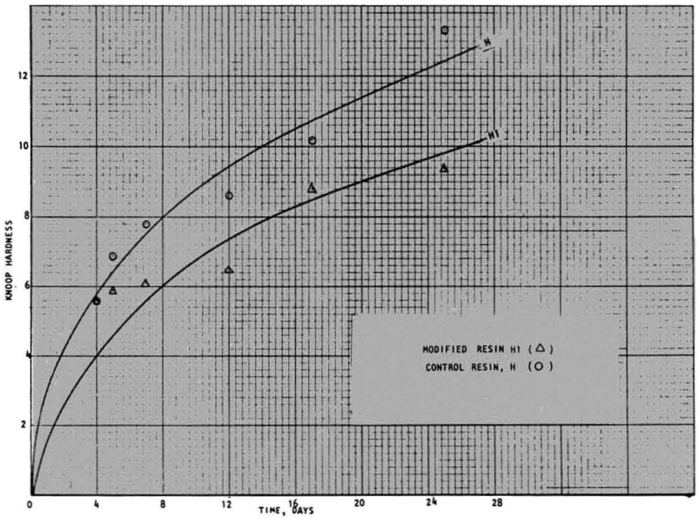


Figure 6—Rates of hardness development of coatings based on modified high isophthalic acid resin, H1, and the high isophthalic acid control resin, H

Table 22 — Comparison of Resin Data for Resins H, M6 and Commercial Standard #1

Resin	Viscosity @ 70% n.v., cps	Acid Value	Gardner-Holdt Color @ 70% n.v.
H	34,400	47.2	1-1/2
M6	20,500	42.0	2
Commercial Standard #1	12,000	41.0	5-1/2

Table 23 — Comparison of Paint Data for Coatings Based Upon Resins H, M6, and Commercial Standard #1

	Coating Properties			
Alkyd	Set-to-Touch, minutes	Tack-Free, minutes	60° Gloss	Early Water Resistance*
H	6	22	79.2	1
M6	12	45	82.2	1
Commercial Standard #1	5	60	80.2	1

*Effect of a drop of water in contact with the coating film for 5 minutes, determined one hour after film was applied. 1 = no effect; 2 = trace etch; 3 = etch; 4 = severe etch; 5 = denuded.

pact tests performed upon the two films showed that the control coating failed at 128 in. lbs. while the coating based upon the modified alkyd passed 160 in. lbs.). However, the substantial decrease in early water resistance warns us that we have probably exceeded the permissible limit of free alkyd hydroxyl for a useful coating.

Polyacrylate modification of alkyds with isophthalic acid levels of approximately 35% conceivably might be justified for some unusually specialized applications, but, in general, modification of alkyds of this type is probably of limited value.

Table 24 — Estimated Selling Prices Of Low Isophthalic Acid Resin Series Modified With RAP1

Resin	% RAP1	Estimated Selling Price, ¢/lb. (70% n.v. by weight)
L	—	65.5
L1A	7.9%	68.4
L1B	15.9%	70.9
L1C	22.9%	73.6

A further word remains to be said about water-borne, air-drying alkyds which develop high degrees of hardness rapidly. Commercial standard #1 is a resin of excellent overall quality, used where fast drying, excellent early water resistance, and high degrees of hardness are desired. It is a widely used product and resins of this type are gaining rapidly in popularity. The data presented to this point strongly suggest that the modified medium isophthalic acid resin M6, and H, strongly resemble the commercial product. *Table* 22 lists relevant data for the three resins, and *Table* 23 is a comparison of paint data based upon the three resins.

Figure 7 presents hardness profiles for the three coatings for the period of four weeks following application. So closely do the profiles resemble each other that the single line which was drawn in could describe the rates of hardness development of the three coatings.

It will be seen that the three coatings are remarkably similar in their drying rates, development of early water resistance, and in their rates of hardness development.

This particular comparison has been made for two reasons. The first is to demonstrate that a suitably modified medium level isophthalic acid level can come very close to duplicating many of the key properties of a conventional high dibasic acid alkyd. The second is to point out that the same excellence of performance exhibited by commercial standard #1 may be obtained from a conventional alkyd containing only trimethylol-

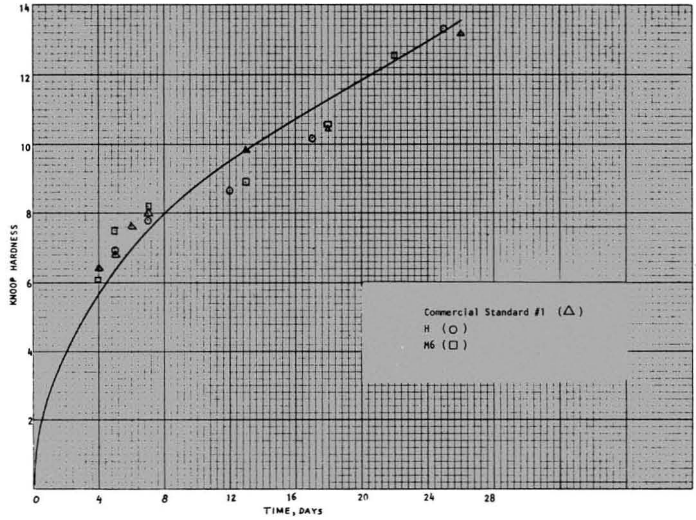


Figure 7—Rates of hardness development of coatings based on resins H, M6, and commercial standard #1

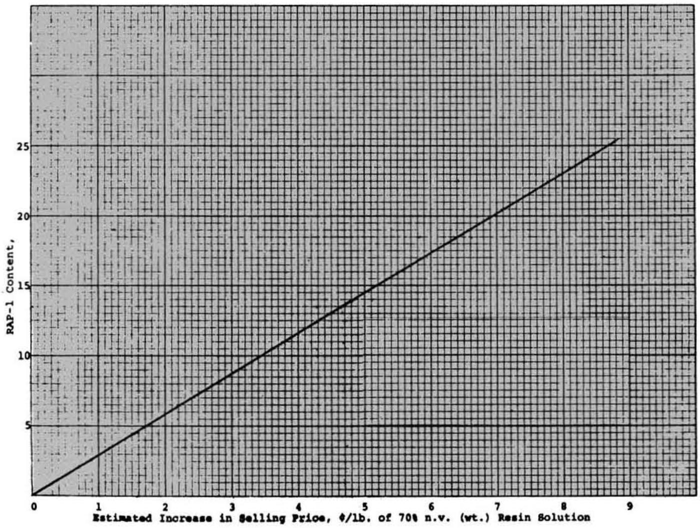


Figure 8—Estimated increase in selling price of low isophthalic acid alkyd, L, as a function of RAP-1 level

propane, isophthalic acid, Pamolyn 200®, and trimellitic anhydride.

COST CONSIDERATIONS

Inevitably, when a concept of this kind is discussed, there is the question of its effect upon raw material costs and, more importantly, upon the cost of the resin to the user.

It is quite apparent that: (1) In going from a one-stage to a two-stage process, direct labor costs and fixed costs will increase; and (2) Replacement of first quality drying oil fatty acids by polymers consisting largely of such relatively inexpensive materials as acrylate monomers and methyl methacrylate should limit the cost increase to a relatively modest level.

Precise determination of the effects of polyacrylate modification upon price will vary, of course, from company to company and even, probably, from plant to plant within one company. However, if we avail ourselves of the rule of thumb that RMC multiplied by 1.5 gives a figure which, for discussion purposes, is acceptably close to selling price, both of the above perceptions appear reasonable.

Consider first, the family of resins consisting of the low isophthalic acid resins L, L1A, L1B, and L1C (*Table* 4). This series, it will be recalled, consists of a control resin and three modified resins, containing respectively, 7.9%, 15.9%, and 22.9% of a reactive acrylic material (Tg 39°C) which reasonably might be used to modify an alkyd of this type.*

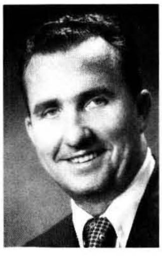
In determining the effects of the various levels of modification upon price, the following additional assumptions were made:

(1) That the alkyd processor purchased the reactive acrylic polymer for a price equal to 1.5 times its RMC.

(2) That the solvent charged to the alkyd kettle with the reactive acrylic material was recovered, fit for reuse, with the exception of sufficient xylol, retained in the alkyd, such that 4% of the final resin solution, by weight, is xylol.

Estimated costs (based on raw material prices prevailing in late 1978) are shown in *Table* 24, and a graphical representation of the results is shown in *Figure* 8. It will be observed that the price of a low isophthalic acid alkyd resin, 70% n.v., by weight, showed an estimated price increase of 3.5¢ per 10% level of modification with RAP1. In light of the performance improvements obtained, this increase in price, for most applications, at least, appears to be modest indeed.

ELI LEVINE received the B. S. Degree from Polytechnic Institute of Brooklyn and the M. S. Degree from Newark College of Engineering. He has been associated with Celanese Chemical Company, Inc. since 1963. He has been awarded eight patents and has written several articles on water-borne resins.



EDWARD J. KUZMA attended Union College and Rutgers University. He has been associated with Celanese Chemical Company, Inc. since 1954. Mr. Kuzma has been awarded several patents pertaining to protective coatings and has also co-authored several papers on alkyd resins.

Pamolyn is a registered trademark of Hercules Incorporated.

*Note: All alkyds in the series were reduced from 96% n.v. to 70% n.v. by weight, with a 50/50 blend of Propasol® P and secondary butanol.

Propasol is a registered trademark of Union Carbide Corp.

the reactive acrylic component will also affect the price of modified resins, as the following comparison demonstrates.

The estimated selling price of M, the medium isophthalic acid resin control, at 70% n.v., was 64.3¢ per pound. Inclusion of 11.4% of RAP3 (containing 75% methyl methacrylate) raised the estimated selling price to 69.2¢ per pound, an increase of 4.9¢ per pound. However, if all the methyl methacrylate in RAP3 were replaced by ethyl acrylate, the new estimated price is 67.8¢ per pound, and the estimated increase is limited to 3.5¢ per pound. Clearly, acrylate monomers may be used, not only to improve coating performance, but for economic advantage as well.

SUMMARY

The use of reactive acrylic polymers of low molecular weight to improve alkyd performance, first made public in 1969, has been extended to include water-borne alkyds.

Typical reactive acrylic polymers include a hardening monomer, a plasticizing monomer, a hydroxyl-bearing monomer, and a carboxylic monomer.

Reactive acrylic polymers are charged to the alkyd kettle along with drying oil fatty acids, aromatic dibasic acid (preferably isophthalic acid) and polyol (preferably trimethylolpropane). The preferred formulating technique is to replace a portion of the drying oil fatty acids with reactive acrylic polymer, essentially on a pound for pound basis.

Three classes of alkyds were studied: low, medium, and high isophthalic acid types. Greatest benefits were conferred upon low and medium isophthalic acid alkyds. These benefits include superior color, faster drying times, and improved early waster resistance. Modification of high isophthalic acid resins (approximately 36% isophthalic acid) yielded minimal benefit. Study of hardness profiles of test paint films during the first four weeks after application confirmed that reactive acrylic polymers with high glass transition temperatures act as hardening agents, but that reactive acrylic polymers with low glass transition temperatures act as internally bound plasticizers. It is believed that alkyds of the latter type may exhibit superior exterior durability.

For discussion purposes, an average increase in the selling price of 3.5¢ per pound of 70% n.v. (weight) alkyd solution may be assumed for every 10% of polyacrylic co-reactant solids included in the formulation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the technical assistance of their colleagues in the Marketing and Technical Development Laboratory of Celanese Chemical Company, Inc.

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New Solventless Polymeric Protective Coatings From Fatty Acid Derivatives

Freddie L. Thomas and Lyle E. Gast
United States Department of Agriculture*

Substituted amides of methyl azelaaldehydate dimethyl acetal enol ether (MAZDAEE), methyl azelaaldehydate dimethyl acetal (MAZDA), methyl 9(10)-methoxymethylene stearate (MMMS), and methyl 9,9(10,10)-bis(hydroxymethyl)octadecanoate acetone acetal (BHMOAA), alone or blended with commercial amino resins, were catalytically converted to solventless polymeric compounds. The polymeric compounds were drawn to films of 1 or 2 mil thickness on metal Q panels, baked, and then tested for hardness, color, impact and resistance to sodium hydroxide, hydrochloric acid, xylene, water, and a commercial detergent. Most films from MAZDA and its derivatives blended with hydroxyethyl-substituted amines showed high resistance to xylene and good hardness. In general, favorable impact and hardness results were dependent on the percent catalyst used as well as the millimole ratios when two or more compounds were blended together. Hydroxyethyl-substituted amides of MAZDA, MAZDAEE, and MMMS with commercial resins produced coatings with the best overall film properties: hardness values were from 8-83, alkali resistance ranged from one hour to greater than 120 hours; resistance was fair to xylene, water, and detergent solution, and poor to hydrochloric acid; impact resistance ranged from <10 in. lb to >160 in. lb.

INTRODUCTION

Vegetable oil fatty acid derivatives are well known as components in protective coatings. Many of these coatings generally need improvement in their durability, hardness, rate of drying, and ease of application. The preparation of polyesteramides from linseed and soybean oils in this laboratory has already been reported.[1,2] Films from these polymers have a wide range of properties related to their composition. The polymers were shown to dry rapidly to hard, chemical-resistant films. A later report[3] elucidated the film properties of urethane-polyesteramides from hydroxyl-terminated polyesteramides of soybean and linseed oils modified with diisocyanate. Depending on chemical composition, structure, and curing conditions, films from these polymers had a wide range of drying characteristics, hardness, and chemical resistance. All these films were deposited from petrochemical solvents.

This paper describes the preparation of solventless coatings obtained from derivatives of methyl azelaaldehydate dimethyl acetal (MAZDA), methyl azelaaldehydate dimethyl acetal enol ether (MAZDAEE), methyl 9(10)-methyoxymethylene stearate (MMMS), and methyl 9,9(10,10)-bis(hydroxymethyl)octadecanoate acetone acetal (BHMOAA). The subsequent films, made from blends of various commercial amino resins with hydroxyethyl-substituted amides and an acid catalyst, were tested for hardness, impact, and solvent resistance. These compounds apparently have not been evaluated as coatings before and may have a unique potential as inexpensive solventless protective industrial films.

EXPERIMENTAL

Materials

Crude MAZDA obtained from ozonized methyl soyate[4] was prepared by Archer-Daniels-Midland Co. Gas liquid chromatography (GLC) of this material showed it contained 4.4% pelargonaldehyde, 16.9% MAZDAEE, 20.9% methyl azelaaldehydate (MAZ), 32.2% MAZDA, 21.4% dimethyl azelate, and 7.8% palmitate. MMMS was prepared as previously reported.[5] GLC of MMMS gave 3.8% formylstearic acid, 12.3% formylstearate, and 83.9% MMMS. An attempt to purify (remove the formylstearic acid) the MMMS by dissolving it in petroleum ether and eluting through an alumina column was unsuccessful. BHMOAA was prepared as described elsewhere.[6] This material contained 93.3% BHMOAA, 1.7% methyl 9,9(10,10)-bis(hydroxymethyl)octadecanoate (BHMO), 2.6% methyl

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*Northern Regional Research Center, Agricultural Research, 1815 N. University St., Peoria, Ill. 61604.

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Table 1—Film Properties of Polymeric Diethanolamides

Film Designation	Polymers[a]	Catalyst[b]	%	Baked Time & Temp. hr	Baked Time & Temp. °C	Hardness	Gardner Color	Impact[c] D in lb	Impact[c] R in lb	Chemical Resistance: 5% NaOH, Time Exposed min	5% HCl hr	Xylene hr	Water hr	1% S&S[d] hr
A	MAZDA	PTSA	1.0	1/2	150	8	3	120	30	25	1-2/3	>120	24	1
B	MAZDA	PTSA	5.0	1/2	150	6	3	>160	>160	1	2/3	>120	22	3/4
C	MAZDAEE	PTSA	8.5	1/2	150	6	4	>160	>160	3	1/6	>120	2	1/6
D	MAZDAEE	PTSA	7.7	1/6	190	23	8	>160	>160	2	1-1/2	>120	8-1/2	8-1/2
E	MMMS	Pb Naph	1.3	3	150	61	17	60	120	10	19	>120	66	86
F	MMMS	PTSA	2.1	1	150	43	15	>160	120	10	5	>120	24	24
G	MMMS	SC	6.3	1	190	9	16	>160	150	10	19	1	18	18

(a) Methyl azelaaldehydate dimethyl acetal (MAZDA); methyl azelaaldehydate dimethyl acetal enol ether (MAZDAEE); methyl 9(10)-methoxy methylene stearate (MMMS); thickness of all samples was 2 mil.

(b) p-Toluenesulfonic acid (PTSA); stannous chloride (SC); lead naphthenate (Pb Naph).

(c) Direct (D); reverse (R).

(d) Spic and Span (S&S).

hydroxymethylstearate, 1.4% methyl carboxystearate, and 1.0% unknown as analyzed by GLC. N,N-bis(2-hydroxyethyl)linseed amide/monoglyceride mixture [(HELA-MONO), M.W. -365] was prepared as described by Schneider and Gast.[7] Hexamethoxymethylmelamine (Cymel® 303, M.W. 390), methylated urea-formaldehyde resin (Beetle 65®, M.W. 236) and acid catalyst CYZAC 4040 (40% active catalyst, 60% isopropyl alcohol) were obtained from the American Cyanamid Co., Wayne, N.J. Diethanolamine (DEA) and ethanolamine (EA), of Fisher Scientific Co., were fractionally distilled, and potassium hydrogen sulfate ($KHSO_4$) was fused and ground. Sodium methoxide was prepared by reacting sodium metal with dry methanol.[7] Glycerine, stannous chloride, and formic acid were purchased from Fisher Scientific Co. Lead acetate, stannic chloride, and potassium bisulfate were obtained from Baker Chemical Co. Trichloroacetic acid came from Eastman Kodak Co., and p-toluenesulfonic acid (PTSA) from Matheson Coleman & Bell. The Q-Panels®, 4 in. × 8 in. were supplied by the Q-Panel Co., Industrial Parkway, Cleveland, Ohio 44135. Spic and Span® (S&S) is product of Procter and Gamble Co., and shall be referred to as detergent.

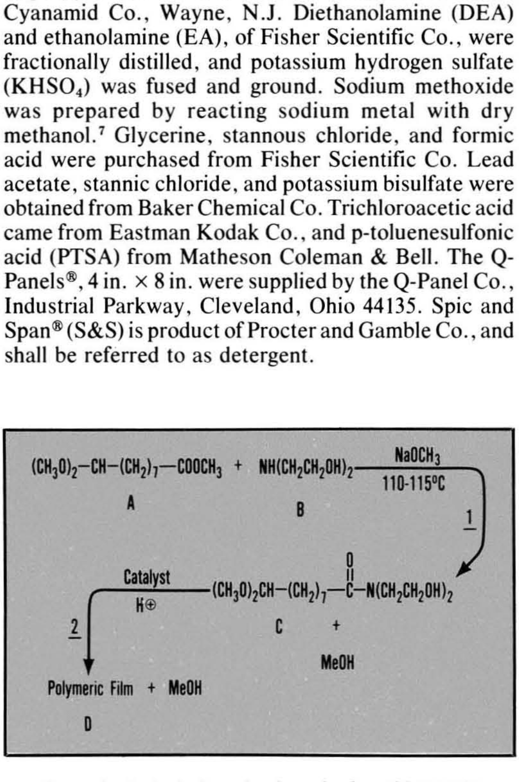

Figure 1—Aminolysis and polymerization of fatty acid derivatives

Methods

Acid values were determined by the Official AOCS Method CD-63. Thin-layer chromatography (TLC) with commercially precoated plates (Brinkmann, Silica Gel F-254) was carried out as described elsewhere.[1] GLC of the esters was analyzed on an OD stainless-steel column 8 ft × ⅛ in., packed with 10% SP-1000 on Gas Chrom P, 100/120 mesh (Supelco, Inc., Bellafonte, Pa.) in a model 1625C Varian gas chromatograph. The column was held at 190°C with helium flow of 35 ml/min. Infrared (IR) spectra were recorded with a Beckman IR8 spectrophotometer. Films were tested for hardness by the Sward Rocker technique. Impact tests were conducted on a Gardner impact tester (cat. #IG-1120). Methods for chemical solvent tests and film casting have been reported previously.[1] Thickness of the films was determined by an electronic thickness tester, Permascope, type ES. Gardner colors were obtained by comparing the panels in a lighted area with standard colored Gardner tubes. The film on the panel that closely matched the color of the tube was given that number.

PREPARATION OF METHYL AZELAALDEHYDATE (MAZ): MAZDA (125 g) and 3 N HCl (500 ml) were stirred at room temperature under nitrogen for one hour. The mixture was placed in an ice bath to prevent foaming when neutralized with sodium bicarbonate and then washed three times with ethyl ether and water. The two layers were separated, and the aqueous layer was also extracted three times with ethyl ether. The ethyl ether extracts were then combined and dried over anhydrous sodium sulfate. The ethyl ether solution was filtered and evaporated to leave a colorless oil (104.2 g) of 65% purity by GLC analysis.

MAZ (99.5 g, 65% purity) was purified further by sodium bisulfite (150 g) addition as described by Miller, et al.[8] to yield 51.0 g of colorless oil, which was analyzed by GLC as 92.4% pure. IR analysis showed presence of aldehyde.

PREPARATION OF METHYL AZELAALDEHYDATE DIMETHYL ACETAL (MAZDA): MAZ (50.6 g, 92.4% pure)

Table 2—Film Properties of Polymers from MAZDA[a] And MAZDA Derivatives Mixed with Hydroxyethyl-Substituted Amines

Film Designation	Polymers[b] + mMoles Ratios	Film Thickness (mil)	Catalyst[c], %		Baked Time & Temp.		Hardness	Gardner Color	Impact[d]		Chemical Resistance				
											5% NaOH	5% HCl	Xylene	Water	1% S&S[e]
											Time Exposed				
					hr	°C			D	R	min	hr	hr	hr	hr
									in lb						
A	MAZ/DEA 6/10	1	Pb(OAc)	1.5	3/4	150	13	6	>160	>160	1	4/15	>120	16	16
B	MAZ/DEA 6/5	1	Pb(OAc)	1.9	1/2	190	18	7	>160	>160	1	1-2/3	>120	16	16
C	MAZ/DEA 6/5	1	None		1/2	190	13	11	>160	>160	1	1-2/3	>120	16	16
D	MAZ/HELA-MONO 6/1.2	1	Pb(OAc)	1.9	1	190	11	11	>160	>160	1	16-1/2	>120	16	16
E	MAZ/Glycerine 6/10	1	Pb(OAc)	2.3	1	150	12	11	>160	>160	1	1/12	>120	25-1/2	1
F	MAZDA/DEA 6/15	2	Pb(OAc)	2.2	3	190	34	10	>160	>160	10	1/6	>120	34	22
G	MAZDA/DEA 6/15	1	PTSA	2.6	3/4	190	18	14	>160	>160	2	1/30	>120	1/10	3
H	MAZDA/DEA 6/5	1	Tri Chl acid	1.7	1/2	190	52	11	>160	>160	5	1/12	>120	19	2-3/4
I	MAZDA/HELA-MONO 6/3	1	PTSA	2.0	1	190	28	15	>160	>160	4	24	>120	48	24
J	MAZDA/HELA-MONO 6/3	2	PTSA	2.0	1/2	190	6	10	>160	>160	2	2	>120	48	16
K	MAZDA/HELA-Mono 6/3	2	Pb Naph	1.3	1	190	50	13	>160	>160	5	16	>120	56	64
L	MAZDA/HELA-Mono 6/6	2	Pb Naph	1.3	3	150	24	14	120	80	5	16	>120	48	16
M	MAZDA/Glycerine 6/10	2	Pb(OAc)	4.8	1/2	190	16	10	>160	>160	1	1-1/4	>120	1/4	1/4
N	MAZDA/EA 6/25	2	PTSA	3.9	1/6	190	13	7	>160	>160	1770	1/30	>120	6	20-1/2
O	MAZDAEE/DEA 6/15	2	PTSA	2.1	1/6	190	28	10	>160	>160	8	1/30	>120	16	25
P	MAZDAEE/DEA 6/15	1	PTSA	3.1	3/4	190	39	10	>160	>160	30	2	>120	48	22
Q	MAZDAEE/HELA-Mono 6/3	2	Pb(OAc)	2.0	1/2	190	24	9	>160	>160	3	48	>120	75	48
R	MAZDAEE/Glycerine 6/15	2	Pb(OAc)	2.2	1/6	190	14	2	>160	>160	60	3	>120	8	1
S	MAZDAEE/EA 6/75	2	PTSA	2.2	1/2	190	37	13	>160	80	5	1/12	>120	1-1/2	18

(a) Methyl azelaaldehydate dimethyl acetal (MAZDA).

(b) Methyl azelaaldehydate (MAZ); diethanolamine (DEA); N,N-bis(2-hydroxyethyl)linseed amide monoglyceride (HELA-MONO); ethanolamine (EA); methyl azelaaldehydate dimethyl acetal enol ether (MAZDAEE).

(c) Lead acetate (Pb OAc); p-toluenesulfonic acid (PTSA); lead naphthenate (Pb Naph); trichloroacetic acid (Tri Chl acid).

(d) Direct (D); reverse (R).

(e) Spic and Span (S&S).

Table 3—Film Properties of Polymers from Amides Crosslinked with Commercial Amino Resins Baked at 190°C

Film Designation	Polymers[a] + mMoles Ratios	Film Thickness (mil)	Catalyst[b], %		Baked Time hr	Hardness	Gardner Color	Impact[c]		Chemical Resistance Time Exposed				
								D in lb	R	5% NaOH hr	5% HCl hr	Xylene hr	Water hr	1% S&S[d] hr
A	MAZDADEA/ Cymel 303 6/3	2	4040	5.2	1/6	61	2	20	<10	64	1/6	>120	24	16
B	MAZDADEA/ Beetle 65 6/6	2	4040	6.0	1/6	44	3	20	<10	52	1/4	>120	24	40
C	MAZDA/ Beetle 65 6/6	2	4040	6.0	1/6	19	5	<10	<10	1	1	>120	19	19
D	MAZDAEEDEA/ Cymel 303 6/1.5	2	4040	4.1	1/6	48	2	20	<10	24	2-1/2	>120	55	80
E	MAZDAEEDEA/ Cymel 303 6/1.5	2	4040	6.0	1/6	56	4	<10	<10	>120	3-1/2	>120	>120	>120
F	MAZDAEEDEA/ Cymel 303 6/1.5	2	PTSA	5.3	1/6	72	4	10	<10	>120	1-1/2	>120	8-1/2	8-1/2
G	MAZDAEEDEA/ Beetle 65 6/3	2	PTSA	3.7	1/6	83	5	30	<10	26-1/2	1-1/2	>120	8-1/2	32
H	MMMSDEA/ Cymel 303 6/6	2	4040	3.9	1/4	7	2	20	<10	>120	7	>120	6	6
I	MMMSDEA/ Cymel 303 6/3	2	4040	5.9	1/6	37	2	20	<10	43	2-1/2	2-1/4	6	6
J	MMMSDEA/ Cymel 303 6/3	1	4040	6.0	1/6	43	2	20	<10	>120	2	2	17	4
K	MMMSEA/ Cymel 303 6/2	2	4040	4.0	1/6	19	2	>160	>160	28	1	>120	28	25
L	MMMSDEA/ Beetle 65 6/12	2	4040	3.5	1/6	21	2	>160	>160	20	1/12	3	6	6
M	MMMSDEA/ Beetle 65 6/24	2	4040	2.8	1/2	37	2	20	20	45	2	>120	16	5
N	MMMSDEA/ Beetle 65 6/1.5	2	4040	6.0	1/3	8	5	>160	>160	22	1/4	16	3	2
O	MMMSDEA/ Beetle 65 6/12	2	4040	6.3	1/6	45	2	20	<10	>120	2	>120	6	6

P	MMMSDEA/ Beetle 65 6/3	2	4040	6.0	1/2	21	5	>160	>160	8	18	2/3	24	24
Q	MMMSDEA/ Beetle 65 6/3	1	4040	6.0	1/6	16	4	>160	>160	22	1/4	16	3	4-1/2
R	MMMSDEA/ Beetle 65 6/6	2	4040	6.0	1/6	40	2	40	<10	24	2	2	17	17
S	MMMSEA/ Beetle 65 6/3	2	4040	6.9	1/6	10	4	>160	>160	22	6-1/2	30-1/2	30	26
T	MMMSEA/ Beetle 65 6/3	2	4040	5.2	1/6	8	5	>160	>160	1	4	1	18	26

(a) Methyl azelaaldehydate dimethyl acetal (MAZDA); diethanolamine (DEA); hexamethoxymethylmelamine (Cymel 303); methyl-urea formaldehyde resin (Beetle 65); methyl 9(10)-methoxy methylene stearate (MMMS); ethanolamine (EA).

(b) 4040 acid catalyst (40% active catalyst, 60% isopropanol); p-toluenesulfonic acid (PTSA).

(c) Direct (D); reverse (R).

(d) Spic and Span (S&S).

was stirred with methanol (500 ml) and conc. HCl (2 ml) for 24 hr at room temperature. The mixture was neutralized with sodium bicarbonate and the methanol was removed by a rotary evaporator. The mixture was dissolved in ethyl ether dried over anhydrous sodium sulfate, filtered, and stripped to dryness. The colorless oil obtained was distilled to yield a product (54.7 g) of 88% purity by GLC.

PREPARATION OF METHYL AZELAALDEHYDATE DIMETHYL ACETAL ENOL ETHER (MAZDAEE): MAZDA (14.3 g, 92% purity) and fused $KHSO_4$ were heated at 150°C for 6 hr, during which the methanol formed was removed by vacuum.[9] The solution was cooled, dissolved in ethyl ether, washed several times with water, dried over anhydrous sodium sulfate, filtered, and evaporated to give a reddish oil that was analyzed (GLC) as 87% pure.

PREPARATION OF 9,9(10,10)-BIS(HYDROXYMETHYL) OCTADECANOATE (BHMO): BHMOAA (10 g, 93% purity) was heated with water (150 ml) and conc. H_2SO_4 acid (5 drops) to boiling for 15 min as detailed by Miller and Pryde.[6] The mixture was cooled, dissolved in ethyl ether, washed with water, and dried with anhydrous sodium sulfate. Filtration and evaporation left 8.5 g of light yellow oil of 100% purity by GLC. IR showed presence of strong hydroxyl absorbance at 3.0 microns and strong C-O ester absorbance at 5.8 microns.

PREPARATION OF 9,9(10,10)-BIS(HYDROXYMETHYL) OCTADECANOIC ACID (BHMOA): BHMO (19.9 g) was reacted with 20% KOH-ETOH (20 ml) and refluxed for 30 min and then isolated as described by Miller and Pryde.[6] Acid value of the light yellow oil (18.1 g) was 159.8 (theoretical 162.8).

PARTIAL POLYMERIZATION OF BHMOA: (A) BHMOA [neutral equivalent (N.E. = 344.52)] was heated for 31 hr at 100°C in a silicone oil bath. Samples were taken periodically and monitored by IR for the reduction of the hydroxyl absorbance at 3.0 microns. N.E. of the very viscous yellow product was 640 (dimer, N.E. = 689.04).

(B) BHMOA was heated for 3 hr at 100°C in a silicone oil bath. The N.E. of the slightly viscous yellow oil was 399.

AMINOLYSIS OF FATTY ACID DERIVATIVES: Distilled diethanolamine (DEA) (6.41 g, 0.10 mole plus 5% excess) was placed in a round-bottomed flask fitted with stirrer, thermometer, nitrogen tube, and dropping funnel as outlined by Gast, et al.[1] Sodium methoxide catalyst (0.07 g, 0.0013 mole) was added, and the flask was heated to 110-115°C. MMMS (34.05 g, 0.10 mole) was added dropwise over a period of 15 min. After the addition of ester, the dropping funnel was replaced by a vacuum take-off and the reaction was continued for one hour under pressure of 20 mm to facilitate removal of methanol formed during the reaction. After cooling, the reaction mixture was dissolved in ethyl ether, washed with 15% aqueous sodium chloride, and dried. The ethyl ether solution was filtered and ethyl ether was removed to yield 33.3 g of yellow oil (97% yield). TLC

Table 4—Film Properties of BHMO[a] and BHMO Derivatives Crosslinked with Commercial Resins Baked at 190° C

Film Designation	Polymers[b] + mMoles Ratios	Film Thickness (mil)	Catalyst[c]	%	Baked Time hr	Hardness	Gardner Color	Impact[d] D in lb	Impact[d] R in lb	Chemical Resistance Time Exposed: 5% NaOH hr	5% HCl hr	Xylene hr	Water hr	1% S&S[e] hr
A	BHMO/ Cymel 303 6/2	2	4040	6.4	1/2	14	5	10	<10	4-3/4	22.5	1/60	32.5	8.5
B	BHMO/ Cymel 303 6/3	2	4040	6.0	1/6	20	1	40	10	21	21	1/60	96	8
C	BHMO/ Cymel 303 6/6	2	4040	5.1	1/6	51	1	<10	<10	1.75	1.5	18	5.5	8.5
D	BHMO/ Beetle 65 6/4	2	4040	6.1	1/6	6	4	<10	<10	23	2	1/60	18	21
E	BHMODEA/ Cymel 303 6/6	2	4040	3.7	1/6	40	1	<10	<10	>120	6.25	6	8.5	85
F	BHMOEA/ Cymel 303 6/3	2	4040	6.0	1/6	12	2	<10	60	30	44	1/60	17	85
G	BHMOEA/ Cymel 303 6/6	2	4040	6.2	1/6	61	1	<10	<10	48	29	1.5	2	35
H	BHMOEA/ Beetle 65 6/3	2	4040	6.1	1	6	2	>160	>160	1 >120	20 26.5	0.25 2-1/6	2.5 26	20 >120
I	BHMOA/ Cymel 303 6/3	2	4040	6.9	1/6	42	2	<10	<10	23	2	0.25	24	20
J	BHMOA/ Cymel 303 6/1.5	2	4040	5.9	1/2	4	2	>160	>160	29	21	0.25	18	27
K	BHMOA(PP31)	2	4040	1.9	1/2	8	7	150	>160					
L	BHMOA(PP31)/ Cymel 303 6/6	2	4040	6.2	1/6	71	1	<10	<10	1/6	20.5	1/12	19	1/6
M	BHMOA(PP31)/ Cymel 303 6/3	2	4040	1.4	1/6	55	1	10	<10	19 24	2 20	1 22.5	20 2	43 3
N	BHMOA(PP31)/ Beetle 65 6/6	2	4040	6.5	1/6	33	4	60	40	>120	22.5	>120	>120	>120
O	BHMOA(PP31)/ Beetle 65 6/3	2	4040	0.9	1/6	4	1	120	>160	19	2-1/6	>120	>120	>120

P	BHMOA(PP3)	2	4040	5.3	1/2	7	5	100	>160	1	20	0.25	2.5	20
Q	BHMOA(PP3)/ Cymel 303 6/2.4	2	4040	2.0	1/6	61	1	<10	<10	>120	26.5	2-1/6	26	>120
R	BHMOA(PP3)/ Cymel 303 6/2.4	2	4040	1.7	1/6	39	1	10	<10	4.5	21	3	>120	>120
S	BHMOA(PP3)/ Beetle 65 6/4.8	2	4040	2.8	1/6	5	2	>160	>160	1/6	4.5	>120	1	4
T	BHMOA(PP3)/ Beetle 65 6/4.8	2	4040	1.4	1/6	6	1	>160	>160	5/6	3	>120	1	2-2/3

(a) 9,9(10,10)-Bis(hydroxymethyl)octadecanoate (BHMO).

(b) 9,9(10,10)Bis(hydroxymethyl)octadecanoate diethanolamide (BHMODEA); 9,9(10,10)-bis(hydroxymethyl)octadecanoate ethanolamide (BHMOEA); 9,9(10,10)-bis(hydroxymethyl)octadecanoic acid partial polymerized 3 hr [BHMOA(PP3)]; 9,9(10,10)-Bis(hydroxymethyl)octadecanoic acid partial polymerized 31 hr [BHMOA(PP31)]; hexamethoxymethylmelamine (Cymel 303); methyl-urea formaldehyde resin (Beetle 65); film thickness was 2 mil.

(c) 4040 acid catalyst (40% active catalyst, 60% isopropyl alcohol, American Cyanamid Co.).

(d) Direct (D); reverse (R).

(e) Spic and Span (S&S).

of the product on a silicic acid plate with a solvent system of 70 ml hexane, 30 ml EE, 1.0 ml acetic acid showed it to be essentially MMMS amide, except for traces of methyl 9(10)-formylstearic acid. This procedure was used for all aminolyses using DEA or EA.

FILM FORMATION: Dihydroxyethylamides of MAZDA, MAZDAEE, and MMMS were mixed with a strong acid catalyst (solid catalysts and samples were heated together in hot tap water, a heated sand bed or a heated oil bath, until catalyst dissolved) and films were drawn down on Q panels to 1 or 2 mil thickness with a machined drawdown bar. The films then were baked at 150 or 190°C.

MAZDA and MAZDA derivatives were mixed, each with varying amounts of glycerine, ethanolamine (EA), diethanolamine (DEA), HELA-MONO, and appropriate catalyst, and the resulting mixture was spread on metal panels and baked.

Commercial amino resins, Cymel 303 and Beetle 65, each blended with mono- and dihydroxyethylamides of MAZDA, MAZDAEE, and MMMS, were catalyzed with commercial catalyst 4040 or PTSA and their films were baked at 190°C until film was dry.

BHMO and BHMO derivatives were blended with Cymel 303 and Beetle 65 and catalyzed by acid 4040. The mixtures were spread on a metal substrate (Q panels) and baked at 190°C.

CHEMICAL RESISTANCE: Chemical and solvent resistance was measured by placing a 1.5-in. diameter watch glass, convex side down, on the surface of the film and introducing the reagent or solvent (0.25 ml) between the watch glass and film surface. Periodic examination was conducted until the film showed evidence of softening or other forms of deterioration.[1]

RESULTS AND DISCUSSION

The reaction sequence shown in *Figure* 1 illustrates the apparent pathway by which solid films are obtained from solventless coating materials. As can be seen in *Figure* 1, aminolysis of sample A with sample B results in what can be considered the solventless vehicle, product C. Product C then is mixed with an appropriate catalyst and applied to a metal panel, and the coated metal panel is baked until a hard polymeric film (D) is formed. We believe the curing mechanism is a transacetalization involving the primary hydroxyl groups of the diethanolamide. *Figure* 2 shows the structural formulas of the compounds used in the film preparations. The film properties of the diethanolamide polymers of MAZDA, MAZDAEE, and MMMS catalyzed with various quantities of PTSA, stannous chloride, or lead naphthenate are shown in *Table* 1. Polymerization of MAZDA with 1.0% PTSA produces a soft film with relatively poor reverse impact but high alkali resistance. MAZDAEE with PTSA at 7.7% concentration gave a film of 23 hardness and an increased impact resistance. Good film hardness occurred with MMMS when catalyzed with 1.3% lead naphthenate or 2.1% PTSA baked at three or 1 hour, respectively. However, Gardner color was poor in each instance. Each film shown in *Table* 1 with the exception of the one catalyzed with stannous chloride gave excellent resistance to xylene. Stannic chloride and formic acid prove to be unsuccessful catalytic agents when used with the compounds shown in *Table* 1.

In another experiment designed to simplify the film-making process, the aminolysis (Step 1, *Figure* 1) procedure as described above under Methods was eliminated. Compounds A and B were mixed with an acid catalyst and baked to form product D. The film properties of polymers from MAZDA and MAZDA

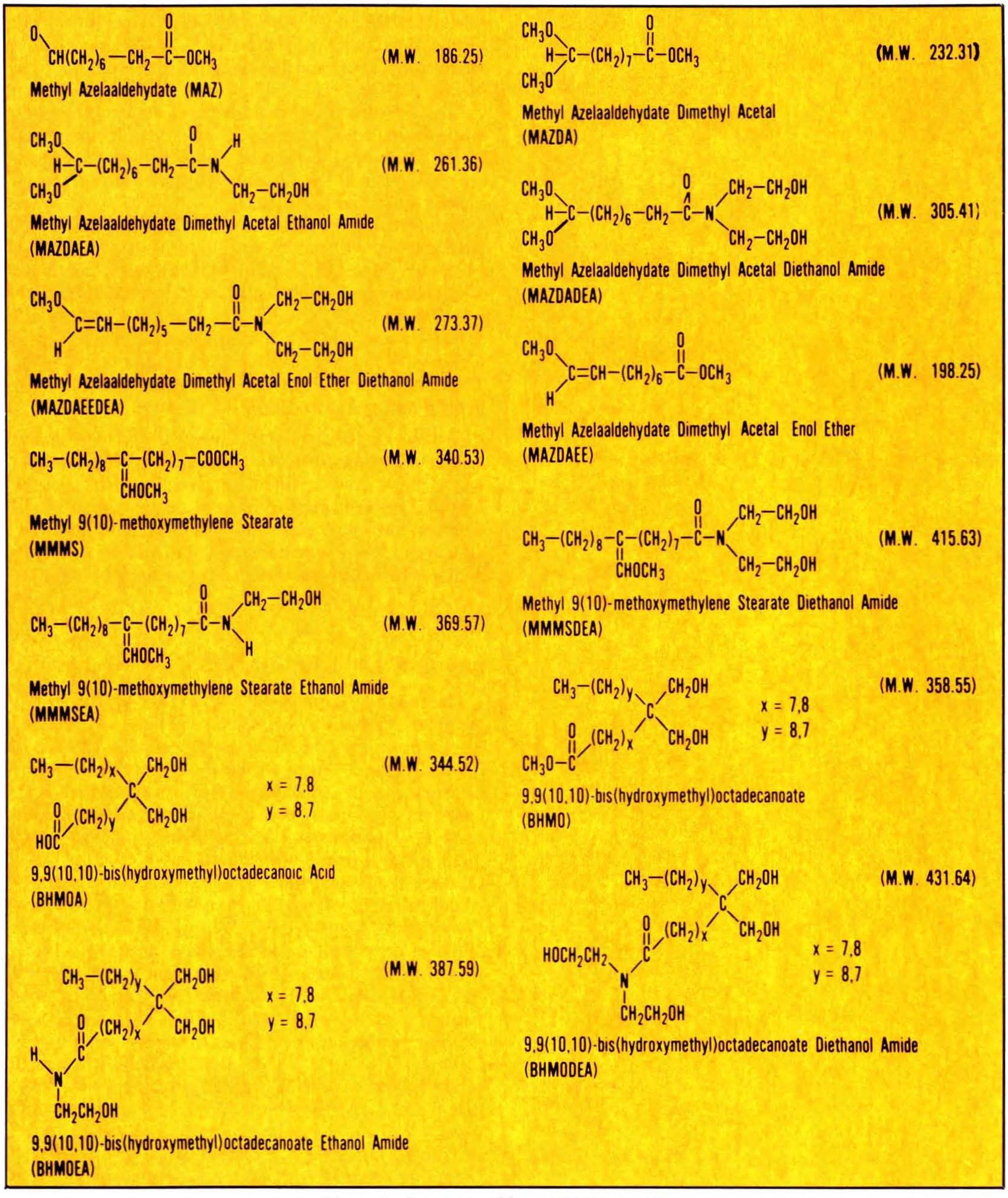

Figure 2—Structures of fatty acid compounds

derivatives blended with various hydroxyethyl-substituted amines are shown in *Table* 2. As can be seen, each film showed good hardness and impact resistance. Relatively superior characteristics were exhibited with films F, H, and P. Again, all films were resistant to xylene. All of the films showed poor resistance to acid and all but one, film N, showed poor resistance to alkali. Gardner color was excellent for only one film, film R. Attempts to polymerize MMMS with the hydroxyethyl-substituted amines (shown in *Table* 2) failed.

In an attempt to increase their chemical resistance, the mono- and disubstituted amides from MAZDA, MAZDAEE, and MMMS were blended with two commercial amino compounds, Beetle 65 and Cymel 303. These amino compounds have been reported [10-13] to be very reactive to pendant hydroxyl groups and also to show some reactivity to carboxyl and amide groups. Polymers made with these amino compounds were reported to exhibit excellent stability and film properties.[10-13] When the mono- and disubstituted amides were blended with these two amino compounds, the resulting films exhibited improved hardness, lighter Gardner color, an improved resistance to alkali, and excellent resistance to xylene (*Table* 3). However, the acid resistance was lowered slightly. Several films failed the impact test, as can be expected with an increase of film hardness. The ratios of polymers to amino resins and the percent catalyst used has a significant effect on the overall quality of the film. For example, when four mMoles of MAZDAEEDEA and one mMole of Cymel 303 are mixed with 6% 4040 catalyst (film E), the film resistance to alkali, xylene, water, and detergent solution is good; comparing the same mixture, but with the addition of only 4% 4040 catalyst (film D), shows a relative reduction of film resistance to all chemicals tested except xylene (*Table* 3). To ensure that the test results of the films produced by the blending of the amino compounds and the mono- and disubstituted amides were not the sole result of self-condensation of the amino compounds, films were also made from the amino compounds alone. The films cracked and peeled away from the metal panel upon cooling.

The two commercial amino compounds were also blended with BHMO and its amide derivatives, and the results of such a film are shown in *Table* 4. BHMODEA was too viscous for spreading; therefore, only one film blended with Cymel 303 was produced. These amino compounds also show reactivity towards carboxyl.[10-13] BHMO was converted to BHMOA and blended mainly with Cymel 303. Blends with Beetle 65 and BHMOA were unsuccessful because the Beetle 65 is reactive to hydroxyl only.[10] However, after BHMOA was partially polymerized, Beetle 65 became reactive (*Table* 4). Polymerizing BHMOA for 31 hr produced a product that was very viscous and made spreading very difficult. To reduce the viscosity, the polymerization was reduced to 3 hr. These partially polymerized samples blended with Beetle 65 and Cymel 303 gave the best chemically resistant films (*Table* 4). Overall, none of these films were as consistently hard or as alkali resistant as those produced from the blended hydroxyethyl-substituted amide polymers (*Table* 3).

CONCLUSION

There is much yet to be learned about solventless polymeric protective coatings of this type. The obvious advantage to such films is the speed and ease with which they are produced. In this stage of preliminary investigation, it is believed that further research is indeed warranted. The data suggest that improvements can be made on the films by researching new catalysts and by incorporating various compounds known to impart improved impact and chemical resistance.

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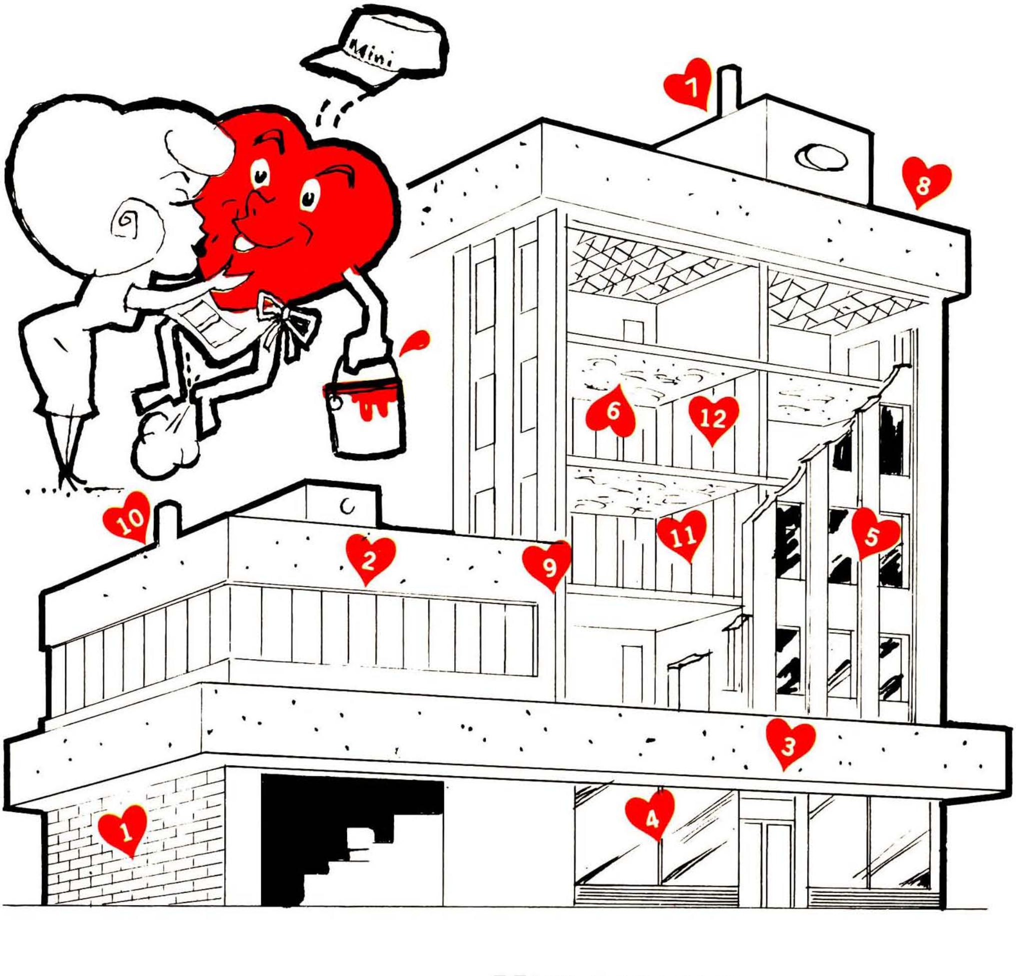
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Triglyceride And Free Fatty Acid Composition Of Linseed Oil in Wood

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Linseed oil was allowed to move into wood and the free fatty acid content of the oil was measured at various distances of travel. The amount of free fatty acid in the oil increased as distance of travel increased. This may have implications for many oil-type coatings applied to wood.

INTRODUCTION

Most coatings are mixtures and combinations of a great many chemical entities. Wood is a porous, polar solid. It is reasonable to expect that various coatings chemicals may move differently into wood during the time when they are fluid. This would deplete the coating film of some components. It also might cause these same components to have an important effect upon those aspects of performance, such as adhesion and water resistance, determined by the wood-coating interfacial region.

Linseed oil is an important part of many wood coatings and is itself a mixture of two major component classes—triglycerides of C_{18} fatty acids and the free C_{18} fatty acids themselves. The triglycerides have molecular weights of approximately 890, while the FFA molecular weights are about 280. The molecular weights and structures of linseed oil components are such that they can be readily studied using standard analytical procedures. The oil, if in the raw form, cures slowly enough that useful measurements can be made before solidification. For these reasons, linseed oil was chosen as a model substance for the study of differential migration into wood. The work reported here is a condensed version of part of the work reported in the author's doctoral dissertation.[1]

EXPERIMENTAL PROCEDURE

Bulk Oil FFA Determination

The FFA content of the batch of raw linseed oil used in this work was determined by the method developed by Baker,[2] modified slightly to give more data points in the range of FFA content useful in this study. Briefly, cupric acetate is reacted with known amounts of FFA to form green salts, the absorbance of which is measured at 640 nm to give a calibration. The FFA contents of unknowns are then determined from the same salt reaction using the calibration.

The Wood

The wood used in the study was a white spruce (*Picea glauca* Moench. (Voss)) block 15 cm along the grain and 4 × 4 cm in cross section. It was extracted in a soxhlet using 95% ethyl alcohol-benzene (1:2) in order to remove resin acids which would confuse analysis of FFA content.

Exposure to Oil

The wood block was set, one square cross-sectional surface down, in a pan containing 4 mm of the linseed oil, and left for about four hours with oil added to the pan periodically to maintain the head at 4 mm. The block was then split along the grain into four pieces 15 × 1 × 1 cm. These pieces were sliced at measured intervals using a precision saw. The 1 cm square sections thus produced were split in two, and each of the two pieces subdivided to fit in one dram stoppered vials where extraction of the linseed oil took place.

Oil Extraction

Spectroscopic grade chloroform and acetone were used for extracting the oil from the wood. Chloroform

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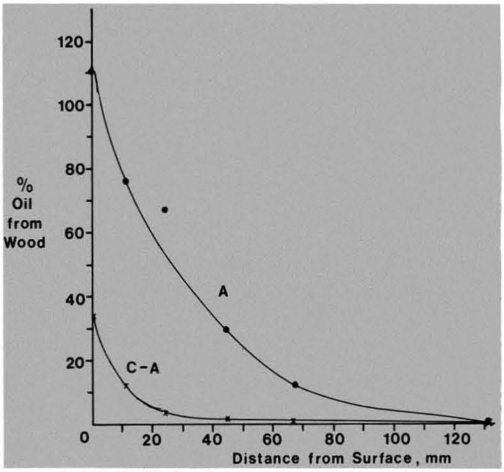

Figure 1—Oil distribution in spruce block where oil entered via one cross-sectional surface. Curve A is oil extracted using acetone and C-A represents oil extracted by acetone after some was first removed by chloroform in this same sample

does not swell wood, and therefore would probably remove oil molecules in cell cavities more efficiently than those which are adsorbed on cell walls. Acetone, on the other hand, does swell wood and should be more efficient in removing adsorbed oil molecules from cell walls. Successive extractions with these solvents thus might reveal something about FFA gradients within cells.

One half of each slice from the block in which oil had travelled was immersed in chloroform for six hours, and the extract discarded. The wood was dried and then aspirated in acetone and allowed to stand for 10 days. This acetone was poured off, fresh was added and was left for one more day. The two acetone extracts were combined and the acetone evaporated under reduced pressure. This yielded extracted oil which presumably was closely associated with wood cell walls before extraction. This series was called C-A.

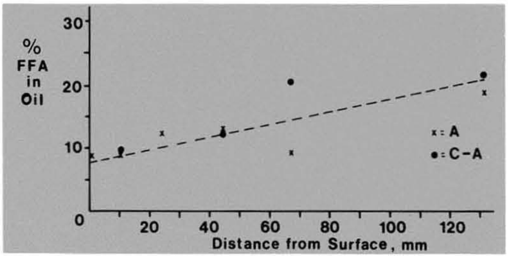

Figure 3—Percent of free fatty acid in oil *versus* distance from wood cross-sectional exposure surface. The line was fitted by least squares regression, and was highly significant

The other half of each slice was aspirated in acetone and left for five days. This was replaced with fresh solvent and allowed to stand for an additional day. The extracts were combined and the acetone evaporated under vacuum. This series should be more representative of the whole extracted oil—that from both cell cavities and walls. This was the A series. Quantities of oil removed were measured as the various extraction procedures progressed. Both dried wood and dried extractives quantities were monitored as a check on each other.

FFA in Extracted Oil

FFA content of oil extracted from wood was determined from the infrared carbonyl stretching band. The intensity of the FFA acid carbonyl (1712 cm^{-1}) was compared to the ester carbonyl (1748 cm^{-1}) intensity originating from the triglycerides. Spectra from known FFA concentrations in oil were used to obtain a calibration equation. Spectra were obtained by placing neat extract on a KBr disc and adjusting sample thickness to get the ester carbonyl peak to an absorbance of approximately 0.4. The acid carbonyl was never less than 0.05 absorbance at such thickness. Three scans of the 1600 cm^{-1} to 1900 cm^{-1} region were run for each sample on a Beckman IR-12 instrument using 3.2% gain and 80 cm^{-1} scan speed.

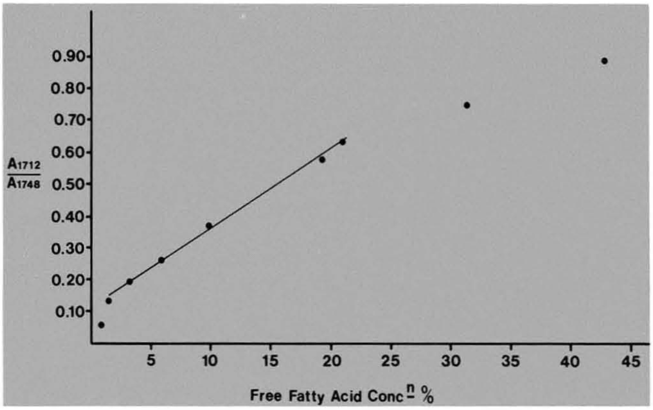

Figure 2—Ratio of acid to ester carbonyl IR absorbance related to free fatty acid concentration (ratio of weight of acids to weight of triglycerides times 100). The curve was constructed using known amounts of FFA in oil, and was used as the basis for determining FFA contents of oil samples removed from wood. Least squares regression was used to fit the linear portion of the curve

RESULTS AND DISCUSSION

The relationship of the amount of oil extracted to the distance from the sample surface can be seen in *Figure* 1. The difference in oil content between the whole extract (A) curve and the previously chloroform extracted curve (C-A) at various distances into the wood represents the amount of oil extracted by the chloroform in the C-A series.

The calibration curve for the infrared absorbance ratio method of determining FFA content is given in *Figure* 2. FFA contents of oil extracted from wood fell within the linear region. The bulk oil had an FFA content of 0.64%.

Figure 3 shows that contact with wood has the effect of increasing FFA content of linseed oil. Over the distance of travel in the wood sample used in this experiment, FFA concentration in oil approximately doubled. Results for the whole extract (A) and the second extract (C-A) are similar, suggesting that FFA concentration was fairly uniform throughout the oil, regardless of its location in wood cells.

The FFA concentration based on wood rather than on oil is shown in *Figure* 4. As oil migrated further into wood, the amount of FFA in the wood decreased. The decrease in concentration over distance of travel is much less than for the whole oil (*Figure* 1). This, and the analysis shown in *Figure* 3, indicates that the FFA fraction is moving more easily into the wood than the triglyceride fraction. It also suggests that a coating film containing linseed oil would become depleted in FFA when applied on wood.

CONCLUSIONS

As linseed oil moves into white spruce wood, its free fatty acid concentration increases markedly, This indicates that a linseed oil coating film will have a lower FFA content than it had before it was applied to wood. It also suggests that the FFA part of the oil interacts differently with wood than the triglyceride fraction.

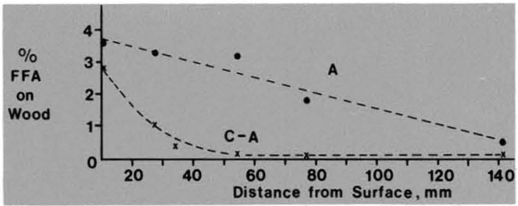

Figure 4—Free fatty acid as percent of dry wood *versus* distance from exposure surface

If the selective migration observed for this model system occurs widely in wood-coatings systems, the compositions of wood coatings films may not be the same as they are in bulk. Also, certain components of wood coatings, even if present in only small quantities, may be important to the interactions which occur between coating and wood.

ACKNOWLEDGMENTS

Advice from Drs. J. Findlay and Z. Valenta, UNB Chemistry Department; Dr. G. M. Strunz, Maritimes Forest Research Centre, Canadian Forestry Service; and Dr. C. J. Wiesner, New Brunswick Research and Productivity Council was helpful during the planning, execution, and reporting of this work. The work could not have been accomplished without access to equipment in UNB's Departments of Chemistry and Physics.

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Study of Latex Crosslinking By Thermal Evolution Techniques

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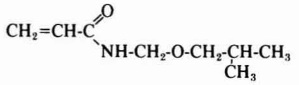
Thermal evolution analysis and thermal gas chromatography were used to investigate the crosslinking characteristics of emulsion polymers containing N-(*iso*-butoxymethyl) acrylamide. Kinetic parameters, obtained by measuring isobutanol evolution as a function of temperature, were used to assess the relative importance of polymer design and formulation variables on reactivity. Crosslinking was promoted by the presence of copolymerized carboxyl groups, but was relatively unaffected by the presence of hydroxyls. Crosslinking in unneutralized latexes was accelerated by strong acid catalysts, but the catalytic effect was inhibited by neutralization.

INTRODUCTION

Coatings designed for industrial applications generally contain functional groups capable of undergoing crosslinking reactions. These thermosetting reactions can involve self-crosslinking, in which bridging occurs directly between functional groups attached to different polymer molecules, or external crosslinking, in which a separate functional additive is employed to bond the polymer chains. Of the two possibilities, self-crosslinking is less common in practical systems due to the lack of appropriate functional monomers, especially ones suitable for emulsion polymerization. The advantages of self-crosslinking include ease of formulation and better control over film properties by polymer design. Perhaps the most common functional monomer used in emulsion polymerization that is capable of self-crosslinking is N-methylol-acrylamide (NMA). Unfortunately, NMA is not soluble in common monomers and is susceptible to premature crosslinking.

Recently, another substituted amide monomer, N-(*iso*-butoxymethyl) acrylamide (IBMA), became commercially available:[1]



$$CH_2{=}CH{-}C(=O){-}NH{-}CH_2{-}O{-}CH_2{-}CH(CH_3){-}CH_3$$

Although first prepared as a monomer in 1962,[2] the IBMA functionality has been more commonly prepared *in situ* by alcohol substitution on polymers containing acrylamide or NMA.[3] In addition to the self-crosslinking capability of IBMA copolymers, another attractive feature is the FDA approval for thermosetting interior can coatings which employ the chemistry associated with the monomer.[4]

Unlike the N-methylol derivative, IBMA is insoluble in water, soluble in common monomers, and resistant to premature crosslinking in aqueous systems. In addition to self-condensation, IBMA moieties can react with amide, hydroxyl, and carboxyl groups, thus allowing a wide range of design combinations.

In this investigation, model emulsion polymers were prepared in order to study the kinetics of the crosslinking reactions which occur in latexes containing IBMA and carboxyl and hydroxyl functionality. To accomplish this goal, two evolved gas analysis techniques, thermal evolution analysis (TEA) and thermal gas chromatography (TGC), were used to measure byproduct evolution from the crosslinking reactions which occurred when these copolymers were subjected to various temperatures. The objective of the study was to determine the temperature range over which the reaction takes place and to assess the relative importance of process and polymer design variables on the rate of reaction. In addition, an attempt was made to correlate these findings with the physical properties of paints made with selected latexes containing IBMA.

Portions of this paper were presented at the Fourth Water-Borne and Higher-Solids Symposium, New Orleans, Feb. 14-16, 1977.

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Table 1—Emulsion Polymer Compositions with IBMA

Sample	Reference	Polymer Composition STY/EA/MAA/HEA/IBMA[a]	BuMc[b]
A	24B108	45/45/—/—/10	0.125
B	24B37	45/40/—/ 5/10	0.125
C	24B31	40/40/ 5/ 5/10	0.125
D	24B30	← ←[c] → 40/40/ 5/ 5/10	0.125
E	24B29	→[d] 45/40/ 5/—/10	0.125
F	24B25	→ 45/40/ 5/—/10	—
G	32B2	→ ← 45/40/ 5/—/10	0.125
H	26B29	35/35/10/10/10	1.0
I	30B69	35/35/10/10/10	—
J	30B70	40/40/10/—/10	—
K	32B113	40/40/10/—/10	0.125

(a) STY = styrene, EA = ethyl acrylate, MAA = methacrylic acid, HEA = 2-hydroxyethyl acrylate, IBMA = (N-*iso*-butoxymethyl) acrylamide,
(b) BuMc = butyl mercaptan.
(c) ← = introduced in first half of monomer feed.
(d) → = introduced in second half of monomer feed.

EXPERIMENTAL

Latex Preparation

One problem encountered in emulsion polymerization of IBMA copolymers was that of latex stability. While it was possible to carry out polymerizations in the presence of a single anionic surfactant, the use of an anionic/nonionic surfactant combination in the present study was found to produce consistently stable latexes. For this purpose, mixtures of Aerosol® 102 (nonionic/anionic) and Aerosol OT or Aerosol 22 (anionic) were used.

Emulsion polymerizations were carried out in the following manner. The surfactants were added to distilled water in a three-liter glass reaction flask fitted with stirrer, baffles, and monomer dip tube. The contents of the reactor were brought to 80°C, and the initiator was added. The monomer mix was then fed into the reactor at a rate of 1% per minute. At the end of the monomer feed, the resultant latex was heated for an additional hour at 80°C to ensure complete reaction. The monomer mix consisted of approximately equal weights of styrene and ethyl acrylate, plus various amounts of methacrylic acid, 2-hydroxyethyl acrylate, and IMBA. Monomers were used as received. IBMA monomer is 85% active with the residual impurities being approximately equal fractions of acrylamide, N-methylol acrylamide, and isobutanol. Butyl mercaptan was employed as a chain transfer agent to control the polymer molecular weight. Latexes were produced in this manner at approximately 42% solids with a particle size of about 0.15 μ.

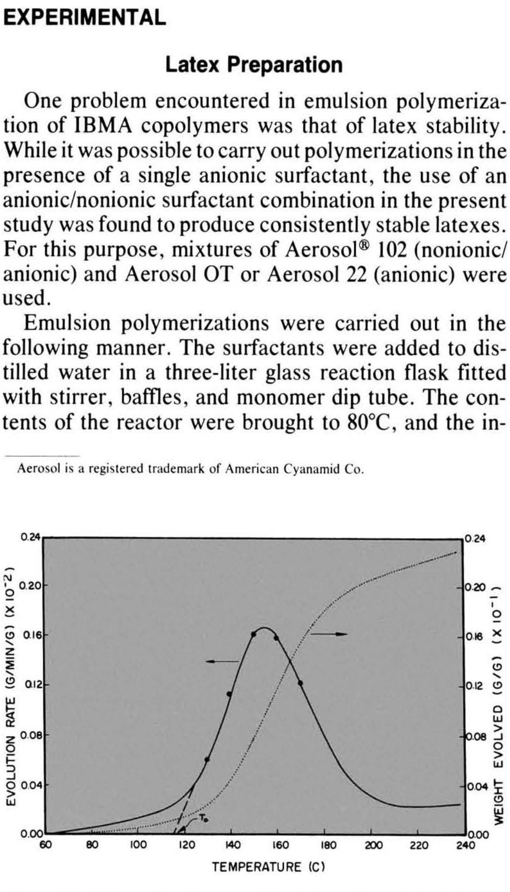

Figure 1—Schematic diagram of equipment used for thermal evolution analysis and thermal gas chromatography

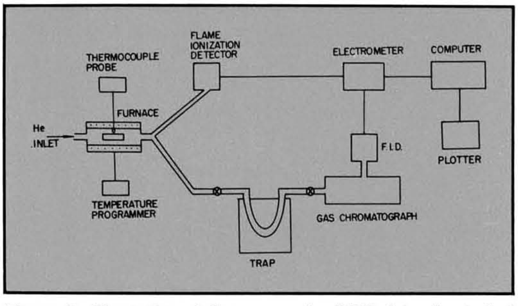

Figure 2—Thermal evolution curve for IBMA latex heated at 4°C/minute. T_o indicates approximate onset temperature; solid points are calculated evolution rates using equation (2) with values of A_p and E_a given in Table 3 for n = 2

In an effort to vary the functional group location in the particles, the monomer feed was sometimes divided into two equal portions, the functional monomers being included in either the first half or the second half of the monomer feed. Otherwise, the functional monomers were uniformly present in the feed. The particular compositions and modes of functional monomer addition are listed in *Table* 1.

Thermal Evolution Analysis

A duPont Thermal Evolution Analyzer (Model 916) and a Chromalytics Thermal Gas Chromatograph (Model MP-3) were used to study the crosslinking reactions. The instruments, shown schematically in *Figure* 1, were interfaced with a PDP 1147 computer, which performed direct data acquisitions, and plotting.[5]

In thermal evolution analysis (TEA), the rate of evolution of organic species from a sample is measured, either during programmed heating or under isothermal conditions. A nitrogen or helium purge carries the evolved products through a flame ionization detector (FID) which continuously measures the organic concentration in the stream. With proper manipulation, a plot of evolution rate as a function of temperature can be obtained. TEA is thus an excellent tool for studying crosslinking reactions from which volatile by-products are evolved. Since the FID does not respond to noncombustible materials, measurements on water-borne systems are simplified.

Aerosol is a registered trademark of American Cyanamid Co.

Table 2—Onset and Peak Temperatures for Unneutralized IBMA Latexes by Thermal Evolution Analysis

Sample	Composition STY/EA/MAA/HEA/IBMA	Reaction Temperature,°C Onset	Reaction Temperature,°C Peak
K	40/40/10/—/10	60	145
K(PTSA)	40/40/10/—/10	<60	130
H	35/35/10/10/10	90	145
C	40/40/ 5/ 5/10	90	150
	→ ←		
G	45/40/ 5/—/10	110	160
	← ← →		
D	40/40/ 5/ 5/10	115	160
	← ← →		
D(PTSA)[a]	40/40/ 5/ 5/10	50	142
A	45/45/—/—/10	115	164
A(PTSA)	45/45/—/—/10	60	140
	→		
E	45/40/ 5/—/10	80	165

(a) PTSA = para-toluene sulfonic acid (1 PHR).

Thermal gas chromatography (TGC) is similar to TEA in that the evolution of organic reaction products is monitored as a function of temperature or, in the case of isothermal studies, as a function of time. However, with TGC, the volatiles are trapped in a column packed with absorbent material (Poropak Q). After evolution is complete at a given temperature, the trap is rapidly heated and the volatiles are backflushed into a chromatographic column. The column resolves individual components which are then measured by an FID. In this work, a Dexsil column (6 ft. × ⅛ in. with 8% Dexsil 300 on $^{80}/_{100}$ Chromosorb, supplied with the instrument) was used to separate the components using a helium flow rate of 20 cc/min. The detector was calibrated with standard solutions of the evolution products.

RESULTS AND DISCUSSION

The organic evolution vs temperature curve (*Figure* 2) measured by TEA can provide a quick indication of the temperature range where crosslinking occurs when a volatile organic by-product is produced during the reaction. Two quantities, the threshold or onset temperature, and the peak evolution temperature, can serve to assess a given crosslinking reaction within an arbitrary framework of reaction energy demand, and should be useful in ranking the relative effectiveness of various polymer design approaches for promoting crosslinking.

With this aim in mind, latex samples containing IBMA were heated at 4°C per minute from 60 to 300°C while measuring the evolution rate of organic components including isobutanol, a by-product of the crosslinking reaction. Results of a typical TEA curve are shown in *Figure* 2. The onset temperature, T_o, was obtained by extrapolating a line from the peak through the point of maximum slope to the base line. Onset and peak reaction temperatures for a series of unneutralized latexes are given in *Table* 2. Subsequent chromatographic results indicated that volatile components of the latexes, other than isobutanol, can evolve in the vicinity of T_o leading to uncertainity in the use of onset temperatures as a means of comparing crosslinking rates. Peak temperatures are relatively well defined, however, and the examples in *Table* 2 are ranked in order of increasing peak temperature.

Several general conclusions can be made from this ranking: strong acid catalysis effectively increases the reaction rate (lower peak reaction temperature); copolymerized acid also promotes crosslinking, but hydroxyls seem to have little effect. Although the peak temperature is a quick and useful means of comparing reactivity, it does not give quantitative information about cure times as a function of temperature or about reaction kinetics.

Reaction Kinetics From TEA

Kinetic parameters in the Arrhenius expression can be estimated from the overall TEA curve. This is done by using the evolution rate curve and its integral (*Figure* 2) to determine the fractional reaction rate and the fraction of reactants remaining over a temperature range encompassing the reaction peak. In the present study, values of the pre-exponential factor, A_p, and activation energy, E_a, that gave the best fit to the reaction data were obtained by multi-variable function optimization using a flexible simplex method.[6] The function to be optimized was obtained by substituting the Arrhenius expression for k in the rate equation as follows:

$$\frac{-d[x]}{dt} = k\,[x]^n \qquad (1)$$

Substituting:

$$k = A_p e^{-E_a/RT}, \quad \text{and} \quad \alpha = \frac{[x]}{[x_o]}$$

$$\frac{d\alpha}{dt} = \alpha^n [x_o]^{n-1} A_p e^{-E_a/RT} \qquad (2)$$

where $-d\alpha/dt$ = fractional reaction rate, α is the fraction tion unreacted, X_o is the initial concentration, x is the concentration remaining at time t, and n the reaction order.

The values of A_p and E_a which minimize the sum of squares of the difference between the log of the predicted reaction rate and the measured rate were obtained for reaction orders of 0.5, 1.0, 1.5, 2.0, and 3.0. Second-order kinetics (n=2) consistently gave the low-

Table 3—Selection of Reaction Order, n, to Give Best Fit To Data in *Figure* 2 Using Optimum Values of E_a and A_p In Equation (2)

n[a]	A_p[b]	E_a[c]	Sum of Squares of Deviations
0.5	2.0×10^4	10.8	0.035
1.0	9.8×10^6	15.6	0.018
1.5	5.0×10^9	20.5	0.0071
2.0	2.6×10^{12}	25.3	0.0013
3.0	6.6×10^{17}	35.0	0.0055

(a) n = Reaction order.
(b) A_p = Arrhenius pre-exponential factor.
(c) E_a = Activation energy.

Table 4—Kinetic Results for IBMA Crosslinking In Unneutralized Latexes

Sample	STY/EA/MAA/ HEA/IBMA	A_p[a]X10^{-8}	E_a[b]	k[c] (143°C)	$t_{1/2}$[d] (143°C)
K	40/40/10/—/10	23.4	18.6	0.46	3.4
K (PTSA)[e]	40/40/10/—/10	reaction during drying			
H	35/35/10/10/10	4.8	17.8	0.25	6.3
C	40/40/ 5/ 5/10	1.9	17.3	0.18	8.6
E	→ 45/40/ 5/—/10	13.2	18.9	0.18	8.6
D	← ← → 40/40/ 5/ 5/10	15,600	25.3	0.10	
D (PTSA)	← ← → 40/40/ 5/ 5/10	30	21.8	0.76	2.1
G	→ ← 45/40/ 5/—/10	4,500	24.3	0.094	16.6
A	45/45/—/—/10	60	20.8	0.084	18.6
A (PTSA)	45/45/—/—/10	0.06	13.7	0.43	3.6

(a) A_p = Arrhenius pre-exponential factor (M^{-1} min^{-1}).
(b) E_a = Activation energy (kcal/mole).
(c) k = Reaction rate constant (M^{-1} min^{-1}).
(d) $t_{1/2}$ = Reaction half-life (min).
(e) (PTSA) = Catalyzed with 1 PHR para-toluene sulfonic acid.

Table 5—Effect of Catalyst and pH On Crosslinking Rates in IBMA Latexes

Sample	Condition	A_pX10^{-8}	E_a	k (153°C)	$t_{1/2}$ (143°C)
A	Unneutralized	60	20.8	0.084	18.6
A	pH=8.8(NH_4OH)	1240	25.4	0.066	23.7
A	Unneutralized + 1% PTSA	0.06	13.7	0.43	3.6[a]
A	NH_4OH + 1% PTSA	3.6×10^3	24.4	0.064	10.4[b]
C	Unneutralized	1.92	17.3	0.18	8.7
C	pH=8.5(NH_4OH)	1.4×10^4	25.1	0.11	14.2
C	Unneutralized + 1% PTSA	7×10^6	27.6	2.7	0.6[a]
C	NH_4OH + 1% PTSA	9.3	19.6	0.055	12.5[b]
C	NH_4OH + 2% $MgSiF_6$	1.2×10^7	30.5	0.15	10.4

A_p, E_a, k, and $t_{1/2}$ as in *Table* 4.
(a) Significant uncertainty in data caused by reaction during drying.
(b) These two systems gave optimum fit with first-order kinetics in which the units of A_p and k are min^{-1}. The remaining examples were best fit with second-order kinetics as in *Table* 4.

est sum of squares for unneutralized samples with and without catalyst as demonstrated in *Table* 3 for the reaction profile shown in *Figure* 2. Additional support for second-order kinetics was obtained by using TEA to monitor isobutanol formation rate as a function of time at 84°C for sample D. Plotting log fraction reaction rate vs log fraction remaining revealed a slope of 2.0 ± 0.2 to greater than 50% reacted for catalyzed and uncatalyzed specimens.

Table 4 lists the optimum values of E_a and A_p obtained under the assumption of second-order kinetics for unneutralized latexes of varying polymer composition. Because of the assumptions involved in fitting the TEA data to equation (2) (e.g., no change in reaction mechanism with degree of reaction, and n=2) and uncertainty in the measurements, the values of E_a and A_p should only be taken as fitting parameters for predicting reaction rates and not as proven Arrhenius parameters for the crosslinking reaction. For unneutralized and uncatalyzed formulations, the reaction rates predicted with these values match the measured rates to within ± 12% (95% confidence level) over the bulk of the reaction (see *Figure* 2). Catalyzed formulations gave slightly larger deviations, while neutralized systems generally did not fit second-order kinetics (discussed later). Rate constants and half-lives predicted from the optimum fitting parameters for duplicate runs were reproducible to about the same confidence interval as the measured and predicted rates except very early (<10% reacted) and late (>75% reacted) in the reaction. The rate constants predicted at 143°C, a typical industrial cure temperature, are used in this work to show the relative reactivity of IBMA in the different formulations.

The reactivities of the samples described in *Table* 4 are listed in decreasing order according to rate constants at 143°C. With the exception of Sample E, the ranking is approximately the same as that in *Table* 2. The effect of added catalyst is plainly evident, as is the accelerating effect of copolymerized acid. It is interesting to note that the addition of PTSA to Sample A (containing IBMA only) increased its reactivity almost to that of uncatalyzed Sample K (containing IBMA and methacrylic acid). In the presence of PTSA, Sample K showed evidence of crosslinking well before the sample was dry. A comparison of Samples D and G suggests that the location of IBMA segments near the particle surface facilitated crosslinking.

The effect of acid catalysis on IBMA crosslinking is illustrated more fully in *Table* 5 in which two compositions are compared under various pH conditions: Sample A, containing only IBMA, and Sample C, containing IBMA, carboxyl and hydroxyl functions. Neutralization of Sample A with ammonium hydroxide retarded the reaction at 143°C, whereas the addition of a strong acid catalysis (PTSA) to the unneutralized latex increased the reaction rate five times. Addition of PTSA to the already neutralized latex almost doubled the rate.

Neutralization of Sample C resulted in a more pronounced decrease in the crosslinking rate. The addition of PTSA to the unneutralized latex resulted, as expected, in substantial reactivity during drying with evolution beginning at approximately 60°C. The addition of PTSA to the neutralized latex increased the rate of crosslinking only slightly.

These results indicate that acid salts, both carboxylate and sulfonate, are considerably less effective in promoting crosslinking than the free acids. The salts are apparently quite stable and resist reversion to the free acid form until relatively high temperatures are reached. Even the use of such a volatile base as ammonium hydroxide does not avoid this problem. A Lewis acid catalyst, $MgSiF_6$, was employed in an effort to avoid the salt inhibition in neutralized samples. This attempt was somewhat successful; as the results in *Table* 4 show. The reaction rate was higher than in the

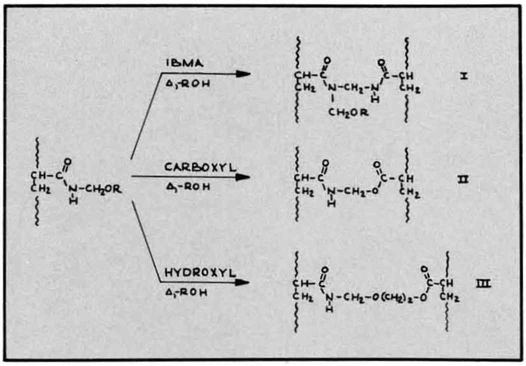

Figure 3—Possible crosslink structures in thermally cured copolymers containing IBMA alone and with copolymerized carboxyl and hydroxyl groups. R = isobutyl group

case of PTSA but still lower than that of the unneutralized example.

Evidence that the evolution of isobutanol did indeed indicate that crosslinking was taking place within the polymer films was obtained by measurement of glass transition temperatures as a function of cure temperature. For instance, in the case of Sample D, the onset of the glass transition, as measured by differential scanning calorimetry, increased by approximately 12°C as the cure temperature was raised from 125°C to 200°C.

Crosslinking Mechanisms

Kinetic information and the quantitative analysis of evolved components provide the basis for a discussion of the probable mechanisms involved in IBMA crosslinking. Several possible crosslink structures are shown in *Figure* 3 for the reaction of IBMA moieties with each other and with copolymerized carboxyl and hydroxyl groups at moderate temperature (150°C). Studies by Hübner and Kollinsky[8] of N-(*iso*-butoxymethyl) methacrylamide crosslinking in nonaqueous systems indicate that the crosslink structure is a substituted methylene-bis-acrylamide linkage. Their results suggest that, in the absence of acid catalysis, the linkage contains an N-*iso*-butoxymethyl pendant group (Structure 1, *Figure* 3). In the present study, thermal gas chromatography indicated a high degree of removal of isobutanol from emulsion polymers containing only IBMA functional groups, probably a result of hydrolysis and additional crosslinking through the side chain during thermal treatment. Even at high temperature (255°C), no formaldehyde evolution was observed in this case. With acid catalysis (1% PTSA), however, formaldehyde evolution was observed at 255°C after most of the isobutanol had already evolved. In this case, the methylene-bis-acrylamide linkage is probably formed exclusively.

Table 6—IBMA Crosslinking at 122°C in Sample E

Time at 122°C (min)	Isobutanol Evolved (% of Sample Wt.)	IBMA Remaining (%)
10	0.22	98.7
30	0.40	81.3
70	0.63	70.6
130	0.94	56.1
310	1.28	31.8
330	1.53	28.5
1250	1.98	7.5
∞	2.14	—

Structures II and III in *Figure* 3 are the result of IBMA crosslinking with copolymerized carboxyl or hydroxyl groups, respectively, at temperatures below approximately 200°C. Above this temperature, formaldehyde evolution was observed in both cases, suggesting a further contraction of the crosslink structure (see *Figure* 5). The evolution of isobutanol in all three cases illustrated in *Figure* 3 is consistent with the second-order kinetics derived from the thermal evolution measurements previously described.

Crosslinking in Neutralized Latexes

The fact that a substantial retardation in reaction rate was observed on neutralization of IBMA latexes containing copolymerized carboxyl groups (*Table* 5) suggested that the volatility of the base (and the stability of the salt formed) is an important factor in determining crosslinking rates. Since amines are commonly used in commercial industrial coatings formulations, additional studies of amine-neutralized latexes were carried out. The thermal evolution technique previously utilized was not applicable in this endeavor because amines generally evolved in the same temperature range as the expected reaction products thus causing interference with the measurement. For this reason, thermal gas chromatography was employed so that the evolved components could be resolved and measured quantitatively.

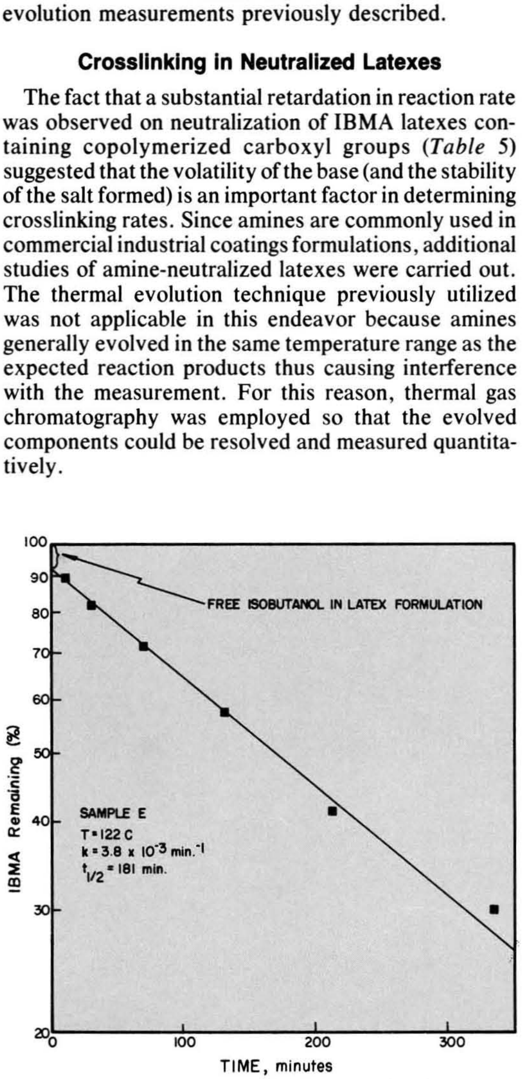

Figure 4—First-order plot of isobutanol evolution from a neutralized IBMA latex at 122°C

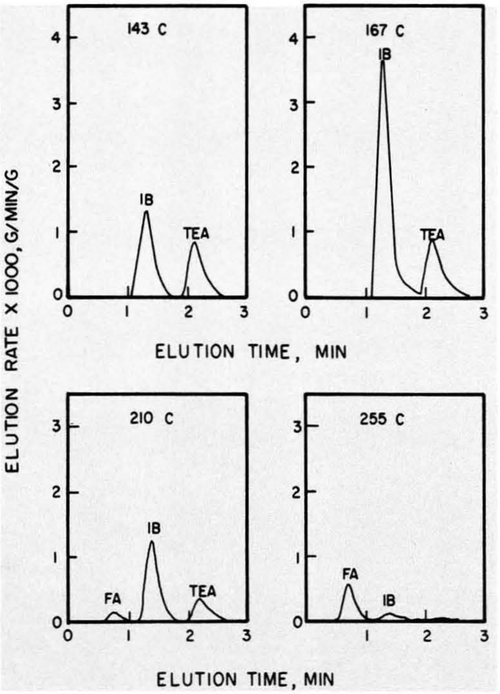

Figure 5—Thermal gas chromatography curves showing the components evolved from Sample D held for 10 minutes at the indicated temperatures. IB = isobutanol, TEA = triethylamine, FA = formaldehyde

Table 8—Kinetic Results for IBMA Crosslinking in Latexes Neutralized with Triethylamine

Sample	STY/EA/MAA/ HEA/IBMA	k, (min^{-1}) 143°C	167°C	E_a (kcal/ mole)	$t_{1/2}$ (min) 143°C
H	35/35/10/10/10 (L)[b]	0.043	0.114	14.8	16.1
	→				
E (PTSA)[a]	45/40/ 5/—/10	0.036	0.128	19.2	19.2
J	40/40/10/—/10 (H)[c]	0.033	0.150	23.0	21.0
	→				
E	45/40/ 5/—/10	0.030	0.088	16.3	23.1
	→				
F	45/40/ 5/—/10 (H)[e]	0.029	0.102	19.1	23.9
I	35/35/10/10/10 (H)[c]	0.029	0.150	24.9	23.9
C	40/40/ 5/ 5/10	0.025	0.116	23.3	27.7
	← ← →				
D (PTSA)[a]	40/40/ 5/ 5/10	0.024	0.133	26.0	28.9
	← ← →				
D	40/40/ 5/ 5/10	0.022	0.098	22.6	31.5
A	45/45/—/—/10	0.018	0.066	19.7	38.5
B	45/40/—/ 5/10	0.017	0.099	26.7	40.8

(a) PTSA = para-toluene sulfonic acid (1 PHR).
(b) (L) = low molecular weight (% butyl mercaptan).
(c) (H) = high molecular weight (no chain transfer agent employed).

Thermal gas chromatography permits the determination of reaction rates by monitoring the evolution of isobutanol as a function of temperature. The assumption made is that the crosslinking rate is proportional to the evolution rate of a selected reaction by-product. In the case of IBMA, this by-product is isobutanol. Several procedures may be used for determining reaction rates from evolution data. One involves the measurement of the amount of isobutanol evolved at a given temperature over progressively longer hold periods. For example, Sample E was heated at 122°C for various lengths of time, and the amount of isobutanol was determined by TGC, as given in *Table* 6. Assuming the IBMA molecule contains 47.1% isobutanol, the total possible evolution of isobutanol from this sample was approximately 2.1% which agreed very well with the measured value of 2.14%. A semi-log plot of the fraction of IBMA remaining in the sample as a function of time (*Figure* 4) indicated a first-order rate equation could fit the reaction data to greater than 60% reacted. The rate constant can be obtained from the slope of this line according to:

Table 7—Isobutanol Formation as a Function of Temperature

Sample	% of Total Isobutanol Formed 122°C	143°C	167°C	210°C	255°C
A	9	14	37	39	1
B	10	10	47	28	0
C	5	21	51	23	1
D	4	19	48	28	1
D (PTSA)	9	19	53	18	1
E	8	24	40	26	3
E (PTSA)	10	27	45	17	1
F	9	23	43	23	2
H	9	19	49	21	2
I	8	23	54	13	1
J	12	28	45	14	1

$$f = e^{-kt}, \text{ or } k = \frac{-\ln f}{t} \qquad (3)$$

where f is the fraction of IBMA unreacted, t is the time, and k is the rate constant. The reaction proceeds with a first-order (or pseudo first-order) rate constant of 0.00383 min^{-1} and a half-life of 181 min.

The shift from second-order kinetics for unneutralized systems to apparent first-order kinetics for neutralized systems may be a result of reaction control by the rate of catalyst formation through decomposition of salts formed with PTSA and with the copolymerized acid. However, more work is required to accurately identify the mechanisms involved.

Since the reaction was found to fit first-order kinetics to a relatively high degree of conversion, an alternate, and faster, procedure was adopted to measure kinetic parameters. This procedure involved measurements of the fraction of isobutanol evolved during constant hold periods at progressively higher temperatures. In the present study, hold periods of 10 minutes were employed at five temperatures from 122°C to 255°C, above which no isobutanol was evolved (*Table* 7).

The TGC elution curves for Sample D, shown in *Figure* 5, are typical of the results obtained in this study. Computer integration of the isobutanol peaks gave the evolved amount at each temperature. Good

Table 9—Cure Response of Sample C in Pigmented Coating[a]

Catalyst	Cure Cycle	Pencil Hardness	Acetone Rubs	2 Hr. Water Soak (22°C)[b] Adhesion	Blush	Hardness
None	Air Dry	2B	4	0	6	5B+
	20′ @ 71°C	B	3	0	9	5B+
	20′ @ 93°C	HB	14	0	8	5B+
	20′ @ 107°C	HB	100+	10	10	B
	20′ @ 121°C	HB	100+	10	9	HB
1 PHR PTSA	20′ @ 71°C	HB	2	0	0	4B
	20′ @ 93°C	F	3	4	4	5B
	20′ @ 107°C	HB	10	6	6	3B
	20′ @ 121°C	F	68	10	9	2B
1 PHR $MgSiF_6$	20′ @ 80°C	HB	6	0	2	5B+
	20′ @ 93°C	HB	8	0	2	5B+
	20′ @ 107°C	HB	100+	0	8	4B
	20′ @ 121°C	H	100+	10	10	HB

(a) Lead Chromate-phthalo green (0.3 P/B) on iron phosphate treated steel.
(b) Adhesion and blush ratings from 0 (complete failure) to 10 (no change).

separation was obtained between isobutanol, formaldehyde, and triethylamine. Note that triethylamine was still present at 210°C, even though its boiling point is 90°C.

The isobutanol evolution data given in *Table* 8 were obtained from a series of curves similar to those in *Figure* 5. Assuming first-order kinetics, the multitemperature results can be used to calculate activation energies using the expression

$$E_a = \frac{R\,T_1T_2}{(T_2-T_1)} \ln \frac{k_2}{k_1}, \quad (4)$$

where k_1 and k_2 are rate constants at two different temperatures, T_1 and T_2, and R is the gas constant. The rate constants calculated [equation (3)] from the amounts of isobutanol evolved at 143°C and 167°C gave the activation energies shown in *Table* 8. The major uncertainty in the rate constants and activation energies is from the temperature variation (± 1°C maximum). The estimated 95% confidence limits were ±9% for the rate constants and ±14% for the activation energies.

The latexes listed in *Table* 8 are given in order of decreasing reactivity as indicated by the decreasing rate constants at 143°C (or the increasing half-lives). This temperature was selected for comparison because it is near the temperature employed in curing conventional external crosslinker melamines. With the exception of Sample C, the latexes common to *Tables* 4 and 8 were ranked in the same order. Note, however, that the reaction half-lives were considerably higher for the latexes neutralized with triethylamine. As expected, the addition of PTSA (with latexes D and E) increased the reaction rates only slightly. A comparison of Sample H (low molecular weight) and I (high molecular weight) indicated that the low molecular weight version reacted approximately 50% faster. This enhanced reactivity may be due to increased polymer chain mobility which would allow the functional groups to come into more favorable positions for crosslinking.

The importance of copolymerized methacrylic acid on reaction rate was again demonstrated as in the unneutralized example previously discussed. The presence of hydroxyl groups in the polymer had little or no effect on the rate of IBMA crosslinking in these exam-

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ples. Although not a strong effect, the addition of IBMA during the latter stages of polymerization appeared to promote crosslinking (Sample E).

It is likely that the crosslinking kinetics in these systems were determined to a great extent by the evolution of the amine. The first-order kinetics observed with neutralized latexes, as compared with the second-order kinetics in the case of unneutralized samples, were most probably a result of the salt formation already discussed. In amine-neutralized latex formulations IBMA crosslinking cannot be considered a low temperature process. However, when compared with conventional thermosetting systems employing, for example, melamine crosslinking resins, equivalent crosslinking with IBMA polymers should start at a somewhat lower temperature.

IBMA LATEX COATINGS

Evidence of crosslinking alone is not sufficient to ensure useful coatings properties. In an effort to relate the kinetic data regarding the cure response of IBMA latexes, summarized in *Tables* 4, 5, and 8, to practical curing conditions, Sample C (see *Table* 1) was formulated into a thermosetting coating. The pH of the paint was adjusted to approximately 8.5 with triethylamine, and the paint was spray-applied onto iron phosphated cold-rolled steel test panels to obtain a dry film thickness of approximately one mil. The coatings were baked as noted and aged three days before testing. The pencil hardness and acetone resistance of the dry films were determined. The coatings were soaked in distilled water for two hours at room temperature and the wet films immediately tested for adhesive tape adhesion on a crosshatched area, blush, and pencil hardness.

The performance results given in *Table* 9 are consistent with the kinetic results previously discussed. No appreciable crosslinking was detected below 107°C. The cure rate with the protonic acid catalyst, PTSA, was actually retarded compared to the uncatalyzed example, indicating that the rate was controlled by the thermal dissociation of the triethylamine salt which was slower than the volatilization of the free amine. The Lewis acid catalyst, $MgSiF_6$, did not show a similar retardation and its rate was very similar to the uncatalyzed example. At 121°C, $MgSiF_6$ provided the best overall properties, indicating some catalytic effect once the triethylamine had volatilized. These results indicate that the low temperature crosslinking potential of IBMA latexes would be greatly limited in practical coatings formulations due to the presence of base. Even so, the evidence in *Table* 9 indicates that crosslinking occurs at lower temperatures than normally expected in conventional melamine-cured latexes.

CONCLUSIONS

In this investigation, the utility of thermal evolution analysis and thermal gas chromatography was demonstrated in studies of IBMA crosslinking in which a volatile reaction by-product (isobutanol) was produced. TEA allowed a rough determination of the temperature at which the reaction began and the temperature at which the crosslinking rate was a maximum. Thermal evolution curves were used to derive kinetic parameters such as activation energies, rate constants, and reaction half-lives by which the effects of polymer design and formulation variables were assessed. In the presence of other organic components, such as amines, these kinetic parameters were determined using TGC to resolve and identify the various evolving species.

IBMA crosslinking in emulsion polymers was strongly promoted by the presence of copolymerized carboxyl groups, but relatively unaffected by the presence of hydroxyls. Some kinetic results indicated that IBMA moieties located near the latex particle surface facilitated crosslinking. Acid catalysis strongly accelerated crosslinking in unneutralized latexes, but salt formation minimized the effect in neutralized systems, even when normally volatile bases were used. Although some triethylamine was shown to remain in latex films heated in excess of 200°C, IBMA latex paints containing triethylamine began to show thermosetting characteristics at about 120°C.

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Studies on Adhesion Of Alkyd Based TiO_2 Paints: Role of Acid and Hydroxyl Values of the Medium

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Adhesion to the substrate is an important property of surface coatings. In the present work, the effect of acid value and hydroxyl value of an alkyd on the adhesion properties of anatase titanium dioxide paints on a mild steel substrate has been studied. The bond strength of the paint film has been determined by the sandwich pull-off technique using a Hounsfield tensometer.

INTRODUCTION

One of the main functions of a surface coating is protection of the substrate against harmful environmental factors like moisture, soluble salts, and corrosive gases. It is evident that however excellent the other properties of the coating may be, this prime function cannot be fulfilled if adhesion to the substrate is unsatisfactory. Many factors are known to contribute to the adhesion of a paint, e.g., nature of the substrate, composition of the medium, etc. The correlation between many of these factors and adhesion has not yet been fully established. It is the purpose of this paper to present a study of the effect of some characteristics of the medium on the adhesion of the paint, formulated from the medium, to metal substrates. The medium chosen was a long oil length linseed glycerol-phthalate alkyd, and the characteristics studied were its acid and hydroxyl values, with reference to their effect on the adhesion of the paint to a mild steel substrate. In order to study the effect of each of these characteristics without interference by the other, two sets of alkyds were prepared by suitable techniques: Set I, varying in acid value and having negligible hydroxyl value; and Set II, varying in hydroxyl value and having negligible acid value. To minimize the effect of variable factors on the adhesion properties, the following steps were taken. The same solvent system was used for all the alkyd paints and, as substrate, discs punched out from the same mild steel (M.S.) plate and cleaned by identical procedures were used. The drying of the paint films was carried out under closely controlled temperature and humidity conditions and discs, coated to similar dry film thicknesses, were selected for the adhesion tests. A number of methods available for measurement of adhesion have been reviewed in recent years;[1-6] in the present study the direct pull-off technique based on the use of the Hounsfield tensometer was selected, for reasons examined by Bullet and Prosser.[4]

EXPERIMENTAL

Materials

MEDIUM: Conventional alkyd resins (66% oil length) were prepared by the standard monoglyceride process using linseed oil, glycerin, and phthalic anhydride. These conventional alkyds had acid values of about 10 units or less and hydroxyl values in the range of 36 to 41. One of these alkyds, having acid value 6.5 mg of KOH per gram of the material, hydroxyl value of 37.7 mg of KOH equivalent to the hydroxyl content of one gram of the material, molecular weight 1987, and viscosity 5.30 poise (30°C), was selected for the present study.

Set I and Set II alkyds were prepared by modification with calculated amounts of benzoic acid (based on the OH value of the conventional alkyd) or n-octanol (based on the acid value of the conventional alkyd), respectively.

In the case of Set I alkyds, the benzoic acid was added about ½ hr after the addition of phthalic anhydride, the temperature being maintained at about 100°C during the addition of phthalic anhydride and benzoic acid.

After completing the addition of benzoic acid, the temperature was raised to, and maintained at, 220-240°C to bring about the esterification reaction. The acid value of the reaction product was determined at

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Table 1—Characterization of the Alkyds

Alkyd No.	Acid[a] Value	Hydroxyl[b] Value	Viscosity (poises, 30°C)	Molecular weight (number average)
Conventional	6.5	37.7	5.30	1987
Set I				
1.	7.4	2.4	2.65	1605
2.	12.5	2.7	—	—
3.	16.2	3.6	2.60	1595
4.	20.0	5.0	—	—
5.	25.5	nil	2.10	1520
Set II				
6.	5.1	12.2	4.80	1900
7.	2.3	23.4	3.00	1666
8.	5.2	29.0	3.45	1736
9.	4.6	41.2	3.10	1680
10.	3.2	48.1	4.30	1860
11.	5.3	54.8	4.50	1892

(a) Acid value = mg KOH/g of alkyd.
(b) Hydroxyl value = mg KOH equivalent to the hydroxyl content of 1 g of alkyd.

half-hourly intervals during the reaction until an acid value four to five units more than that required was obtained. At this stage, the temperature was raised to 270°C, and bodying (thermal polymerization) was carried out at 270 ± 5°C until the reaction product attained a string of 12 to 18 in., after which any unreacted phthalic anhydride still remaining was blown off by a stream of carbon dioxide. The string formation was tested by placing a drop of the reaction product (resin) on a clean glass plate, cooling it, drawing the string with a finger tip, and determining the length to which a continuous string could be drawn. The product was finally cooled and stored in bottles. The characteristics of these alkyds are listed in *Table* 1.

In the case of Set II alkyds, the calculated amount of n-octanol was added two hours after the addition of phthalic anhydride, the temperature being maintained at about 180°C during the addition of phthalic anhydride and n-octanol. After the addition of n-octanol was completed, the alkyd was processed further, similar to Set I alkyd, except that, in this case, the per cent excess glycerin added was varied to obtain a series of alkyds having negligible acid values but varying in hydroxyl values. From these alkyds a selection was made for the present study. The characteristics of the selected alkyd resins are given in *Table* 1.

Table 2—Typical Formulation for the Preparation Of Paints with Different PVCs Using Any One Alkyd

Calculations for formulating a paint of 10% PVC

Density of TiO_2 (anatase):	3.84
Vehicle (alkyd) density:	1.00
Titanium dioxide (for 10% PVC):	10 × 3.84 = 38.40 g
Vehicle (remainder 90%):	90 × 1.00 = 90.00 g
Total weight of pigment (for 10% PVC):	$\frac{100 \times 38.40}{128.4} = 29.90$ g
Total weight of alkyd:	$\frac{100 \times 90.00}{128.4} = 70.09$ g
(Total amount of paint: 100 g).	

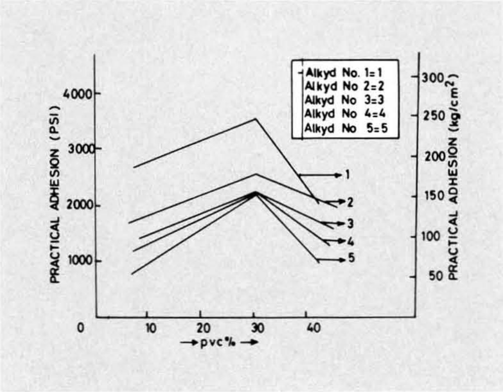

Figure 1—Alkyd paints—Set I: bond strength vs PVC%.

PIGMENTS: A pigment grade titanium dioxide commonly used in India (anatase, Travancore Titanium Products, India), specific gravity 3.84, main oxide content 97.9%, water solubles 0.04%, moisture content 0.22%, pH 6.2, and identified as TiO_2 (anatase) by X-ray diffraction pattern was used.

SOLVENTS: Rectified xylene (BDH), bp 138°C; white spirit (Burmah Shell), bp 150-200°C; and methyl ethyl ketone (extra pure E. Merck) bp 79.6°C, were employed.

DRIERS: Cobalt naphthenate (6% Co) and lead naphthenate (24% Pb) were used.

EMERY PAPER: Emery papers of grade numbers 180, 220, 320, and 400, silicon carbide water proof paper of Carborundum Universal Ltd., India, were used.

MILD STEEL DISCS AND PANELS: Mild steel discs of 32 mm in diameter, were punched out of a plate of gauge 20 (0.9 mm), abraded with emery papers of increasing fineness in white spirits medium, swabbed successively with xylene, and finally, degreased in a soxhlet extractor with methyl ethyl ketone for two hours. The residual solvent from the degreased specimens was removed in a vacuum desiccator and paints were applied immediately afterwards.

The mild steel panels of 152 × 102 mm also were punched out of a plate of gauge 20 (0.9 mm), abraded with emery papers of increasing fineness in white spirits medium, and swabbed successively with xylene.

TIN PANELS: Panels of 150 × 150 mm cut out from electrolytic tinned mild steel (0.315 mm thick) were used. The tin panels were lightly abraded with a fine emery paper and swabbed successively with xylene.

TIN FOILS: Tin foils, 204 × 102 mm and 0.025 mm thick, were used.

PAINTS: A set of paints with pigment volume concentration (PVC) varying between 10 to 40% was prepared, using each of the alkyds of Set I and Set II and conventional alkyd, and by grinding the TiO_2 in the

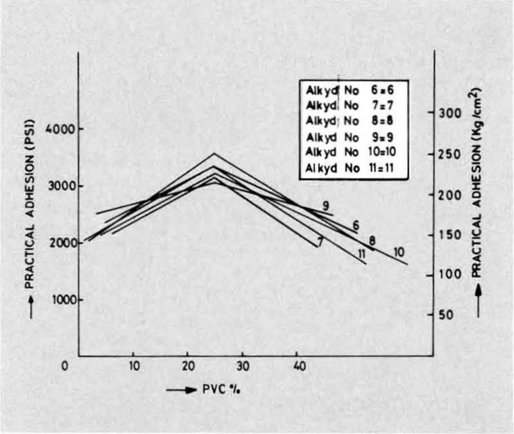

Figure 2—Alkyd paints—Set II: bond strength vs PVC%.

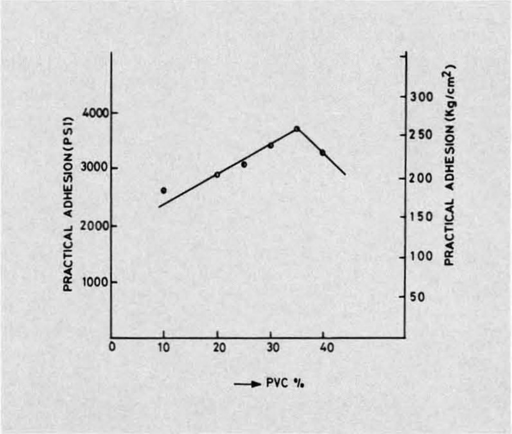

Figure 3—Conventional alkyd paints: bond strength vs PVC% (mainly adhesive failure)

medium to the Hegman gauge 7-8 in a laboratory ball mill. The calculations involved in formulating the paints to a desired PVC are illustrated and the pigments and resin quantities used at each PVC chosen are indicated in *Table* 2. After grinding, the paints were filtered through a fine muslin cloth and thinned to brushable consistency (60 secs, Ford cup No. 4), or spin coating consistency (40-50 secs, Ford cup No. 4) as required, by diluting with a suitable quantity of xylene-white spirit mixture (1:1 v/v). Driers were added (0.05% cobalt and 0.5% lead as metals on the weight of the binder) and mixed into the paint formulation and the paints were stored in closed bottles for a period of 24 hours for maturing.

METHODS

Determination of Alkyds Characteristics

MOLECULAR WEIGHT: The molecular weights[7] of the alkyds were determined by cryoscopic method using crystallizable benzene (BDH grade).

VISCOSITY: The viscosities of the alkyds were determined using Emila rotary viscometer which is based on the torque principle. The measurements were done with 66.6% solutions prepared in white spirit and xylene (1:1 v/v) mixture.

PIGMENT-ALKYD ABSORPTION: The procedure employed was similar to the method used to determine oil absorption,[8,9] except that, in the place of linseed oil, the alkyd resin (100% solids) was used. The object was to arrive at a measure of the interaction between the pigment and the different type of alkyds. The usual procedure was modified by taking a known weight of the alkyd on the glazed tile (2-3 g) and adding small portions from the weighed pigment to the alkyd. The mixture was pressed, rubbed, and rolled with the help of a palette knife until a putty was formed. The amount of alkyd needed for 100 g of pigment was calculated. This value was taken as a pigment-alkyd absorption value (*Table* 4).

Adhesion By "Sandwich Pull-off" Technique

The bond strength was determined by the sandwich pull-off technique, using a Hounsfield tensometer.[3-4,10-11]

The test specimens were prepared by applying paints to the mild steel discs of suitable size by an ICI spin coater to a dry film thickness of about 1-1.5 mils (25-37.5/μm). The paints were dried for seven days at room temperature. The test doublets were prepared by gluing the painted disc between two stainless steel cylindrical test pieces two inches long (50.8 mm) and one inch in diameter (25.4 mm). The test piece attached to the painted face was turned down to ¾ inch diameter (19 mm), so that higher forces could be applied, thus eliminating the possibility of a break between the coupling test piece and the unpainted side of the disc. For the bonding, an adhesive of suitably high bond strength for use on the substrate and on the paint surface was chosen so that failure could occur only at the paint-substrate interface or in the body of the paint film during the test. The adhesive used for bonding was Araldite® AW 106 and Hardener® HV 953U. The bond strength

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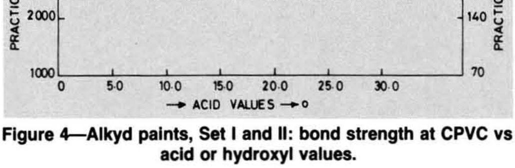

Figure 4—Alkyd paints, Set I and II: bond strength at CPVC vs acid or hydroxyl values.

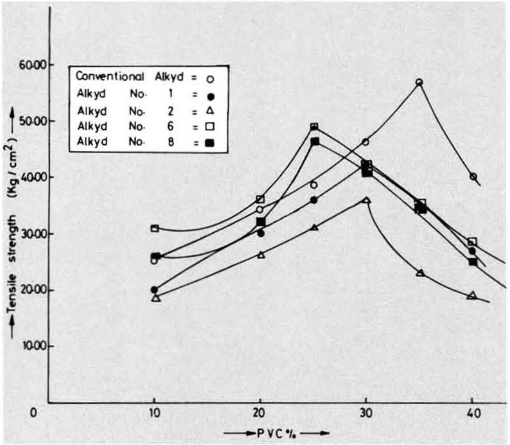

Figure 5—Alkyd paints: Set I, II, and Conventional: Tensile strength vs PVC%.

on mild steel of the Araldite and Hardener was found to be about 4000 psi (280 kg/sq cm).

During the curing of the adhesive, the doublets were kept aligned on parallel rod jigs of the same diameter as the cylinders, with enough pressure being applied to squeeze out the excess adhesive without starving the joints. Great care was exercised in laying the test doublets securely on the alignment block for proper alignment of the test specimens. The test doublets were kept under pressure for 48 hr, to allow the adhesive to cure, the bowing effect of the doublets in the assembly being removed by suitable clamping arrangements.

When curing of the adhesive was complete, these were taken out of the alignment blocks. Curing continued by keeping these doublets in a vertical position for a further period of 12 hr. The doublets were pulled apart by subjecting them to progressively increasing stresses at a constant rate, until failure of the adhesive joint took place. Sagging of the doublet in the tensometer was prevented by suitable holders.

Based on the area of the bonded paint surface and the load indicated by the Hounsfield Tensometer at the time of bond failure, adhesion was expressed as practical adhesion.[12] Cohesive failure refers to any break in the body of the paint film and adhesive failure describes the break between the paint and the substrate. Classification of the nature of the failure is estimated in the case of ferrous metals by applying copper sulphate solution to the painted surface of the disc after the test and by counting the squares of the brown deposit by superimposing a transparent plastic sheet on which squares are engraved. The average practical adhesion value is calculated from the results of 15 to 20 test specimens. *Figures* 1, 2, and 3 give the practical adhesion values of the alkyd paints; *Figure* 4 gives the relation between the maximum practical adhesion values and acid values (Set I) and hydroxyl values (Set II) of alkyd paints.

Other Properties of the Paints

TENSILE STRENGTH OF THE PAINT FILMS: The electrically operated Gardner tensile strength and elongation apparatus was used[13] for determining the tensile strength of the paint films which were obtained by the amalgamation technique. The tensile strength values (kg/cm^2) are plotted against the PVC (per cent) for the alkyds in *Figure* 5.

GLOSS OF PAINTS: Gloss of the paint films was determined using Gardner Multiangle Gloss meter.[14]

SCRATCH HARDNESS: Scratch hardness was determined on an automatic power operated test unit[15] (Research Equipment London, Ltd.).

IMPACT RESISTANCE: Impact resistance was measured by a falling weight type instrument using 10.5 lbs (4.7 kg) weight, from a fixed height of 23 in. (58.4 cms).[16]

These properties for a few alkyd systems are listed in *Table* 3.

DISCUSSION

Experiments carried out to determine the effect of variation of acid and hydroxyl values of alkyd resins on the adhesion of the paints to mild steel substrates have led to some interesting conclusions. An examination of the results given in *Figures* 1, 2, and 3 shows that, in the case of paints based on conventional alkyd and Set II alkyds, the failure of the bonding is predominantly in-

Table 3—Gloss, Scratch Hardness, Impact Resistance and Resistance to Solvents Of Alkyd-Titanium Dioxide Paints at Different Pigment Volume Concentrations

%	% Gloss at 45° (Gardner Scale)					Scratch Hardness (g)					Resistance to 1% NaOH (failed in minutes)					Xylene (failed in minutes)				
PVC	a	b	c	d	e	a	b	c	d	e	a	b	c	d	e	a	b	c	d	e
10	98	98	98	98	98	700	500	550	700	750	15	8	6	14	15	3	3	4	3	3
20	90	95	90	94	94	750	650	600	850	850	20	10	8	18	17	3	3	4	3	3
25	86	90	82	90	90	850	750	700	950	1050	22	12	10	22	18	4	4	5	4	4
30	82	84	78	85	85	1000	950	850	800	950	24	15	11	24	18	6	4	5	4	4
35	76	76	72	79	81	1150	850	750	750	900	25	16	12	24	18	8	5	6	4	4
40	66	68	66	73	75	900	700	600	700	850	25	16	12	24	19	7	5	6	5	5

Distilled water (24 hr), 5% Na_2CO_3 (4 hr), 5% H_2SO_4 (4 hr), and White spirit (4 hr) were found to have no effect at all the Pigment Volume Concentrations.
All the paints passed in the impact resistance test.
a = Conventional alkyd; b = Alkyd 1; c = Alkyd 4; d = Alkyd 6; e = Alkyd 8.

Table 4—Pigment-Alkyd Absorption of Few Alkyds
(Set-I, Set-II and Conventional Alkyds)

Alkyd No.	Acid[a] Value	Hydroxyl[b] Value	Weight of Pigment (TiO_2), g	Weight of Alkyd Absorbed, g
Conventional	6.5	37.7	100.00	39.30
1	7.4	2.4	100.00	42.00
4	20.0	5.0	100.00	40.50
6	5.1	12.2	100.00	51.40
8	5.2	29.0	100.00	48.60

(a) Acid value = mg KOH/g of alkyd.
(b) Hydroxyl value = mg KOH equivalent to the hydroxyl content of 1 g of alkyd.

terfacial. For paints based on Set I alkyds, however, the failure is predominantly cohesive. In order to arrive at an understanding of this difference in behavior, the tensile strengths of free films of these alkyds were determined (*Figure* 5), since tensile and cohesive strengths are interrelated. The results show that the paints based on conventional and Set II alkyds have higher tensile strength than those from Set I alkyd, at pigment volume concentrations (PVC) up to critical pigment volume concentration (CPVC), indicating that Set I alkyd paints have poorer cohesive strength than the other paints. This provides an explanation of the predominantly cohesive failure of the Set I alkyd paints in the adhesion test.

The results of the adhesion experiments at different pigment volume concentrations for the paints based on the conventional alkyd as well as Set I and Set II alkyds show that, in all cases, the practical adhesion value attains a maximum at a particular PVC, which is seen to be the critical pigment volume concentration (CPVC), confirmed by determining the CPVC values through measurement of the tensile strength of the free films of the paints. This is in accordance with earlier work carried out in this laboratory.[17] It is seen, however, that the CPVC value at which the maximum practical adhesion value is attained is different for each set of paints: viz., 35% for paints from conventional alkyd; 30% for paints from Set I alkyds; and 25% for paints from Set II alkyds.

In order to understand the variation in the CPVC values of the three sets of paints, it is useful to refer to earlier work on the effect of the nature of the vehicle on oil absorption of pigments, since CPVC and oil absorption are interrelated characteristics pertaining to a paint. According to Remington,[9] as the acid value of the linseed oil used in the oil absorption test increases, the amount of oil used also increases. This may be due to either greater particle dispersion or to thickening caused by the formation of metallic soaps. If the oil absorption tests are made with other oils, then the results will be related to the dispersing effect of the liquid used and its viscosity.

Based on the above observations, alkyd absorption tests were carried out on the anatase TiO_2 using conventional alkyd, Set I alkyds and Set II alkyds as the liquid, instead of linseed oil. An examination of the alkyd absorption results (*Table* 4) shows that, of the three types of alkyds under study, Set II alkyds have the highest dispersing power, followed by Set I alkyds and the conventional alkyd. Set II alkyds, with their higher OH value, are likely to be adsorbed more strongly than the Set I alkyds on the anatase TiO_2, which is slightly acidic in nature, leading to the higher alkyd absorption value. The stronger adsorption of Set II alkyds on the TiO_2 would also lead to the higher tensile strength of the films of the paints made from them and help to explain why these paints fail interfacially in the adhesion test; whereas the Set I alkyd paints with their lower tensile strength fail cohesively. In the case of conventional alkyd, however, although it has a slightly less alkyd absorption value than the Set I alkyds, the tensile strength is considerably higher. This perhaps could be explained on the basis that no monofunctional reactants which are likely to have a negative effect on film strength, have been used in its formulation.

An explanation for the difference in the CPVC values of the three sets of alkyd paints is thus possible on the basis of their comparative dispersing power (wetting power): the alkyd with the highest dispersing power gives the lowest CPVC. In this context, the changes in the alkyd structure arising from the treatment with benzoic acid or n-octanol used to prepare the Set I and Set II alkyds also need to be considered. The modification with such monofunctional materials can be expected to lead to a comparatively less complex molecular structure for the alkyd. This, combined with the presence of the monoester formed in both cases, can be expected to increase the dispersing power of the resin, which would lead to lower CPVC values in the paint. By this token, it would appear that the OH groups increase the dispersing power of the resin more than the COOH groups.

With the present data, it is not possible to explain why the CPVC within the same set of alkyds has an identical value, except to infer that, with regard to CPVC, apart from the relative wetting power of the different sets of alkyds as measured by the alkyd absorption values, the chemical configuration of each set of alkyds, whether conventional, modified with benzoic acid (Set I), or modified with n-octanol (Set II), has an important role to play. This aspect of the work requires further study for elucidation.

A study of the relationship between the practical adhesion value at CPVC and the characteristics of the alkyd resin (i.e., OH value or acid value) based on the results with Set I and Set II alkyds has led to the following conclusions:

(1) In the case of Set II (OH value variation) alkyd paints, it is seen that an increase in the OH value up to 55 has no significant effect on the practical adhesion value (*Figure* 4).

(2) In the case of Set I (acid value variation) alkyd paints, it is seen that an increase in acid value brings about a rapid decrease in the practical adhesion value (*Figure* 4) up to an acid value of 15, after which there is a leveling off.

This difference in behavior of the paints based on Set I and Set II alkyds can be understood by referring to the data obtained on tensile strength of their free films (*Figure* 5). It is seen that an increase in OH value of the alkyd has no significant effect on the tensile strength; whereas increase in acid value has brought about a lowering of tensile strength. Since the bond failure in the adhesion test is related to the tensile strength of the film, this explains why an increase in OH value has practically no effect on the practical adhesion value, while an increase in acid value brings about a decrease in this value.

Variations in the acid and hydroxyl values of the alkyd resins were seen to have an effect on the drying time of the paints formulated from these resins. While the paint based on conventional alkyd dried in 5-6 hr, paints from alkyds of Set II (OH value variation) took longer time to dry, i.e., 6-10 hr. The paints from alkyds of Set I (acid value variation) required considerably longer time for drying, the ones based on the alkyds of higher acid values (ca. 15 onwards) taking as long as 7-10 days.

Taking into consideration the overall properties of the paints prepared from the alkyds, such as drying time, film strength, and adhesion, it is seen that these properties are best if the alkyd has a combination of low acid value of about 7 and OH value in the range 30-40. Hence, we find that the conventional alkyd having acid value of 7 and OH value of 37 is found to have good properties.

CONCLUSION

The aim of the work described in this paper was to arrive at a relationship between the acid and hydroxyl value of an alkyd resin and the adhesion of paints formulated using the alkyd. It is seen that, for practical adhesion of the paint to be high, the acid value of the alkyd has to be quite low, in the region of 7. As far as the hydroxyl value is concerned, however, there is little effect on the practical adhesion by its variation over a wide range. The combination of acid and hydroxyl values usually found in conventionally prepared alkyd resins of less than 10 and 30-40 respectively are seen to be the best in terms of practical adhesion, as well as other properties of the alkyd.

An interesting observation arising from the results is that the practical adhesion value, in the case of all the paints, increases with PVC and attains a maximum at a PVC value which is shown to be the CPVC value of the paint. It is further seen that the methods used to modify the alkyd resin bring about a change in the CPVC value of the paints based on them. This can be related to their comparative dispersing and wetting power and also their chemical configuration. Thus, while the conventional alkyd paint has a CPVC value of 35, in the case of acid value alkyds, the CPVC of the paint is decreased to 30 and with OH value alkyds a further shift downwards to a CPVC value of 25 takes place.

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Assessment of Dispersion

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Various methods for measuring the dispersion state of pigments in liquid media are described. The rheological properties of dispersion system and the sedimentation behavior of pigments in the media are discussed in relation to the dispersion state of pigments. The interaction between particles is discussed in terms of the potential energy curves.

Dispersion Process

The terms dispersion, dispersibility, and dispersion stability should be defined prior to discussion on the dispersion process. According to Parfitt,[1] dispersion refers to a complete process of incorporating an aggregated powder into fine particles in liquid medium. Dispersibility is defined as the ease with which a dry powder is dispersed in a liquid. The stability of dispersion is the resistance to flocculation. In this context, however, the term dispersion is occasionally used to express dispersed system.

Most particles, such as pigments in the dry state, contain agglomerates (or aggregates). In order to disperse the agglomerates in liquid medium, they should be subjected to three stages of dispersion processes: deagglomeration (or disaggregation), wetting, and stabilization. The initial stage of the process is breaking down of the agglomerates into fine particles by mechanical means, such as grinding or milling. In the incorporation of dry powder into a liquid medium, the air adsorbed on the particle surface must be displaced by the liquid. This phenomenon of the displacement is defined as wetting and the degree of ease with which the air is displaced by liquid is defined as wettability. The deagglomeration process and the wetting process usually occur simultaneously. Dispersibility is determined by the bonding strength between the particles and the wettability. The wettability depends on the affinity of particle surface with the liquid or the interfacial tension at the solid/liquid interface. When the particle surface has a low energy (or low polarity), the particle is easily wetted and dispersed in non-polar or weakly polar liquids. In such a case, the particle is classified as lyophilic (or hydrophobic). When the particle surface has high energy (or high polarity), the particle is easily wetted and dispersed in highly polar liquids. In such a case, the particle is classified as a hydrophilic.

If the surface is not wetted by liquid, the particles cannot be dispersed in the liquid even if the agglomerates are broken up by high mechanical shear. The chemical properties of the surface must be altered to obtain stable dispersion. Surface active agents are widely used to improve the wettability in many industries. Good wetting can be obtained by proper selection of these surface active agents.

If the agglomerates are broken down and the surfaces are wetted, the final stage of dispersion process is the stabilization of the dispersion. The dispersion stability will be discussed in detail in the following chapters.

Dispersion States

Particles in liquid media are present in various forms, e.g., primary particles, agglomerates, aggregates, and flocculates. These must be distinguished in order to understand the dispersion state. According to Bell and Crowl,[2] an aggregate is a cluster in which primary particles are joined together at crystal faces. An agglomerate is one in which the particles are joined only at edges or corners forming a looser, more open structure than aggregates. The aggregates and agglomerates are present in dry powders prior to mixing into liquid medium. The aggregates or agglomerates in liquid medium are, therefore, in most cases, the ones which have not been broken down in the initial stage of dispersion process as described above. Therefore, the aggregates or agglomerates in the dispersed system should be reduced by improving the mechanical breaking-down process and wettability.

Flocculates are different from aggregates or agglomerates in that they are formed in the liquid medium at the final stage of the dispersion process. There are two types of flocculates: a strong flocculate and a weak flocculate. The former is the one in which the particles are firmly bound together in the medium and the latter is the one in which the particles are very loosely bound together. (See *Figure* 1.)

The difference in structure of these flocculates are interpreted in terms of potential energy curves. The stability of dispersion can be quantitatively expressed in terms of potential energy change between two approaching particles. The potential energy between two particles consists of two terms: attraction and repulsion. The attraction is due to the Van der Waals attractive forces and repulsion is due to either electrical repulsive force or sterical repulsive force due to absorbed layer of polymer on the particles. The mechanism of attraction and repulsion has been extensively discussed elsewhere.[3-6]

The potential energy curves for attractive energy V_A, repulsive energy V_R, and total potential energy $V_T = V_A + V_R$ between two particles are illustrated in *Figure* 2. The attractive energy, V_A, increases rapidly as the particles approach each other while the repulsive energy V_R changes somewhat more slowly. The sharp increase of repulsive energy at very close approach is the repulsion between the electron clouds of atoms of the particles and is referred to as Born repulsive energy, V_R^{Born}. In general, the total potential energy curve has a maximum peak,

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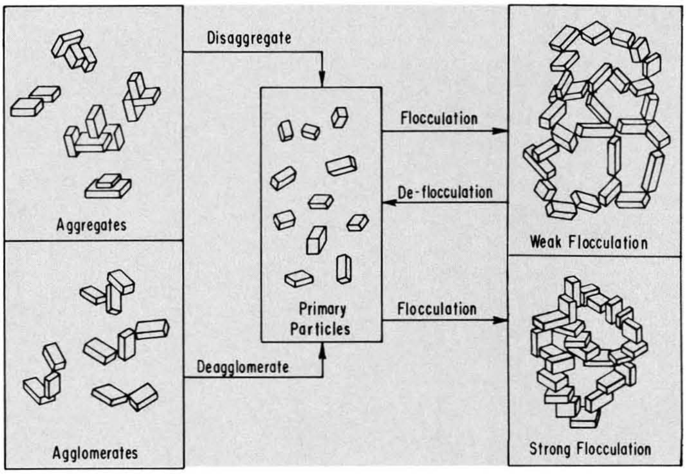

Figure 1—Schematic illustration of dispersion process and dispersion state

V_{max}, which constitutes an energy barrier against the adherence of the particles. As the particles approach one another, they may overcome the repulsive barrier, V_{max}, after which the particles are attracted strongly and the potential energy falls rapidly into the primary minimum. The particles joined together at this primary minimum are bound firmly together and form strong flocculates.

In some cases, the total potential energy curve may develop a secondary minimum at an appreciable distance of separation, as shown in *Figure* 2. The depth of the potential energy at the secondary minimum is much smaller than that at the primary minimum. If this secondary minimum is several times kT deep, it may overcome the effect of Brownian motion and give rise to weak flocculation at the secondary minimum. The character of this type of flocculation is quite different from that in the primary minimum. The binding energy between particles is much smaller and the separation distance is much greater than that at the primary minimum. This type of weak flocculates is usually formed in open network structure (as shown in *Figure* 7). The weak flocculation is completely reversible and easily redispersed by light stirring. This kind

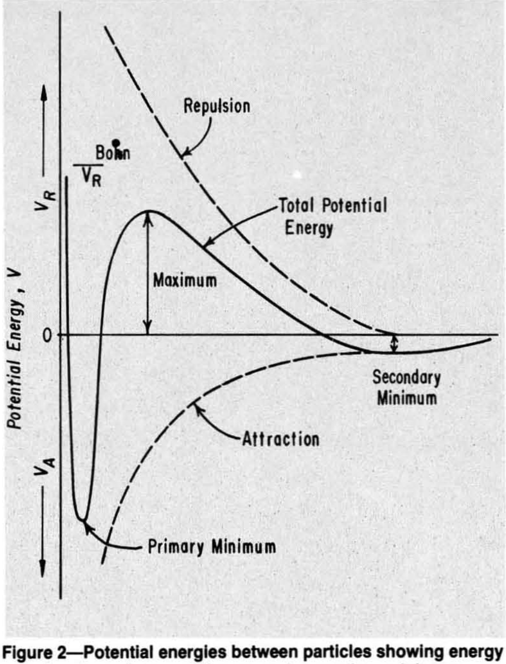

Figure 2—Potential energies between particles showing energy barrier, primary minimum, and secondary minimum

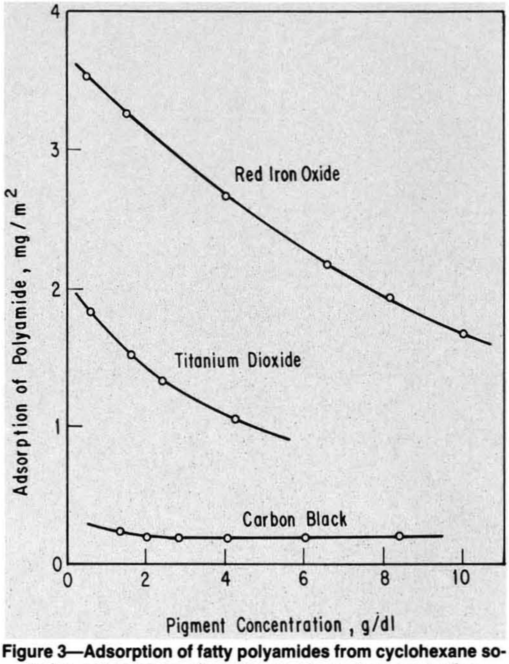

Figure 3—Adsorption of fatty polyamides from cyclohexane solution onto various pigments vs. pigment concentration

of flocculation is usually not a serious problem in actual disperse systems such as paint, while the strong flocculation at the primary minimum is essentially irreversible and high mechanical shear is required to break this type of flocculate.

Assessment of Dispersion

Dispersion state can be determined by various methods as reviewed by Carr.[7] Among these methods, rheological measurements and sedimentation methods are most widely used to assess the dispersion state.

RHEOLOGICAL MEASUREMENTS: Rheological methods have many attractions, since these methods are easy, quick, and the sample does not need to be diluted. But the weakness of these methods is that they are indirect observations of the dispersion state and that the dispersion state depends on interpretation of the result. Therefore, the relationship between the rheological properties and dispersion state must be clearly understood. In many systems, however, rheological properties of the dispersed system depend on various factors and the analysis of the dispersion state is difficult.

In general, the rheological properties of dispersed systems depend on the following factors:[8] (1) the viscosity of the fluid medium; (2) the concentration of the particles; (3) the size and shape of the particles; and (4) the interaction between the particles, that is, the degree of stability of dispersion. The applicable methods of rheological measurement depend on whether the particle concentration is low or high. When the particle concentration is so low that the particle - particle interaction can be ignored, the dispersion state can be determined by measuring the particle size by applying the Einstein equation. On the other hand, when the particle content is high, the particle - particle interaction must be taken into account.

Dilute dispersed system—The dispersion state in dilute systems can be determined by measuring the particle size in the medium. If the particles are flocculated, the particle size in the medium is much greater than the size of the primary particles. The basic equation for the system where the particle - particle (or the flocculate - flocculate) interaction is negligible, is the Einstein equation,

$$\eta = \eta_s (1 + 2.5\phi) \qquad (1)$$

where ϕ is the volume fraction of spherical particles, and η_s are the viscosities of the disperse system and its medium, respectively. Smith[9] reviewed the application of the Einstein equation to an infinitely diluted dispersion which contains immobilized liquid in its structure. Assuming that liquid absorbed on the surface (solvation layer) and liquid entrapped physically in the net work structure behave like a part of the flocculate, the hydrodynamic volume of flocculate is considerably greater than the actual volume of the solid particles. Let ϕ_f be the hydrodynamic volume fraction of flocculate (particle plus immobilized liquid), ϕ_p the volume fraction of deflocculated particles, ϕ_s the volume fraction of solid material, and $\phi\ell$ the volume fraction of immobilized liquid. Then

$$\phi_f + \phi_p = \phi_s + \phi\ell$$

Smith[9] assumes that the Einstein equation can be written as:

$$\eta = \eta_s \{ 1 + 2.5 (\phi_s + \phi\ell) \}$$

As flocculation proceeds, $\phi\ell/\phi_s$ increases since the immobilized liquid increases with flocculation. $\phi\ell/\phi_s$ is determined by measuring η, and $\eta_s \cdot \phi\ell$ depends on the shear rate when measuring η and η_s. As the shear rate increases, loosely bound flocculates are broken down and the immobilized liquid in the flocculate becomes free. Sato[10] determined the hydrodynamic volume fraction of partially flocculated spherical zinc dust (diameter 3.2μ) in an aqueous solution of polysaccharides (0.1%) by measuring η and η_s with a Brookfield viscometer. ϕ was calculated by the Guth-Gold-Simha equation which was derived by considering the hydrodynamic interaction between particles [equation (2)]. The $\phi\ell$ decreased as shear rate increased, as seen in *Table* 1.

Table 1—Volume Fraction of Immobilized Liquid in Zinc Dust Flocculate In Polysaccharide Solution (0.1%)

		Zinc Dust Content	
		60 g/ℓ	120 g/ℓ
Volume fraction of zinc dust, ϕ_s		0.009	0.018
Hydrodynamic volume fraction, $\phi_s + \phi\ell$	3 rpm	0.039	0.061
	6 rpm	0.033	0.052
	30 rpm	0.032	0.044
Volume fraction of immobilized, liquid, $\phi\ell$	3 rpm	0.030	0.043
	6 rpm	0.024	0.034
	30 rpm	0.023	0.026
$\phi\ell / \phi_s$	3 rpm	3.33	2.39
	6 rpm	2.67	1.89
	30 rpm	2.56	1.44

$$\eta = \eta_s (1 + 2.5\phi + 14.1\phi^2) \qquad (2)$$

It is interesting to note that the $\phi\ell/\phi_s$ depends on the zinc dust concentration. It is important to know that the amount of immobilized liquid or the amount of adsorbed polymer on a unit surface area of particle is dependent on the particle concentration. Sato[11-13] measured the amount of polymer adsorption on various pigments as a function of the pigment concentration. It was found[13] that the adsorption of fatty polyamides from cyclohexanone solution onto the unit surface of metallic oxides decreases markedly with the pigment concentration, while that onto carbon black does not, as shown in *Figure* 3. This phenomenon occurs since, in the case of metallic oxides, the available surface area for the adsorption per unit amount of pigment decreases as the pigment concentration increases since the particle - particle contact increases. On the other hand, in the case of the adsorption on the carbon black, the available surface area per unit amount of pigment is independent of the pigment concentration since the pigments are deflocculated. Therefore, the slopes of the curves in *Figure* 3 are indicative of the degree of flocculation. The steeper the slope, the higher the flocculation degree. This agrees with the results obtained by the sedimentation method.

Concentrated system—For the interpretation of rheological data of a concentrated dispersed system, the Mooney equation (3) is widely used,[14] which is given by

$$\frac{\phi}{\ell n \eta_r} = \frac{1}{k_e} - \frac{S}{k_e} \phi \qquad (3)$$

where k_e is the Einstein coefficient (usually 2.5), S is a crowding factor (= $1/\phi_{max}$, and ϕ_{max} is a maximum volumetric packing fraction). As ϕ approaches zero, the equation approaches the Einstein equation. The volume fraction of the densest packing uniform

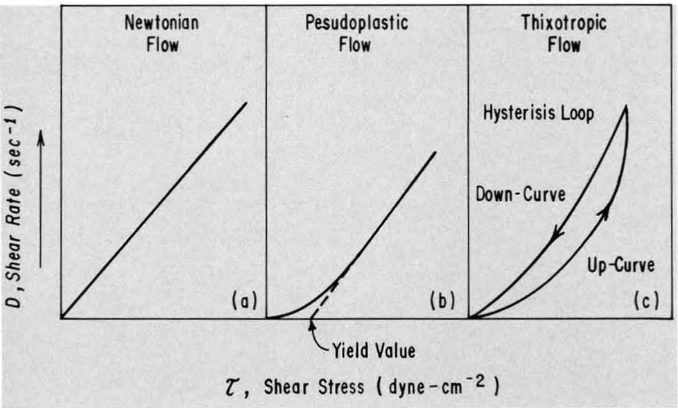

Figure 4—Flow curves of Newtonian and non-Newtonian system

sphere is 0.74 for a face centered cubic lattice and $\pi/6 = 0.524$ for a simple cubic lattice. Hence, it is expected that S lies between $1.35 \leq S \leq 1.91$.[15] The applicability of the Mooney equation has been examined by many investigators.[15-17] According to the Mooney equation, $\phi/\ell n\ \eta_r$ is a linear function of ϕ. Therefore, S/k_e can be determined from the slope of the straight line. Lewis and Nielsen[15] studied the dispersion state of spherical glass in chlorinated biphenyl (Aroclor)®. They found that this system fits the Mooney equation in the range from zero to as high as $\phi = 0.5$, if k_e is increased for the flocculated system. They derived the Einstein coefficient k_e as a function of immobilized liquid.

If the volume packing fraction of the spheres forming the flocculates ϕ_a is given by

$$\phi_a = \frac{\phi_s}{\phi_s + \phi\ell}$$

Then Einstein's coefficient can be expressed as

$$k_e = \frac{2.5}{\phi_a} = \frac{2.5\ (\phi_s + \phi\ell)}{\phi_s} \qquad (4)$$

The equation indicates that k_e increases as $\phi\ell$ increases. For the spherical particles, the value of k_e starts at 2.5 for single spheres and approaches a maximum value of 4.9 for large flocculates.[15]

Very concentrated system—In very concentrated dispersion systems, the particles may link to build a network matrix which extends through the whole system. In such a case, measurement of hydrodynamic volume of dispersed phase is no longer valid. The dispersion state in such a system is usually studied by measuring the change in the flow properties by varying the shear rate. It is necessary to apply sufficient stress to break this network structure for the system to flow. The minimum shear stress required for the system to commence to flow is designated as the yield value (or yield stress). The magnitude of the yield stress is a measure for the strength and the number of the links.

The system of this type becomes thinner on stirring because the network structure is broken, and becomes thicker again on standing because the network structure is reestablished. The structure broken by stirring, however, usually does not reform immediately. Therefore, the structure of particles in this system is dependent upon the shear history. This characteristic of flow is designated thixotropy.

The concentrated dispersion is characterized by the yield value and the thixotropy. The dispersion state of particles in this system can be studied indirectly from the measurement of these properties. These flow properties are usually determined by measuring the relationship between the shear rate and the shear stress. The typical shapes of the plots of shear rate D vs. shear stress τ (flow curve) are illustrated in *Figure* 4. The reciprocal of the slope of the line through the origin (τ/D) is the coefficient of viscosity.

A Newtonian system flows under any applied force, as shown in *Figure* 4 (a), and the slope is a constant, indicating that the viscosity is independent of shear rate.

If the particles are forming network structure, the flow curve shows the yield value, as shown in *Figure* 4 (b). When the system is thixotropic, the flow curve shows a hysterisis loop, as shown in *Figure* 4 (c). The structure is being broken on the up-curve and reforming on the down-curve. The area of the loop between two curves represents the degree of thixotropy. The relationship between the shear rate D and the shear stress τ is commonly expressed by the empirical equation,[18]

$$D = \kappa\tau^n \qquad (5)$$

where κ is the consistency index and n is a flow index which is a measure of the degree of deviation from Newtonian behavior. If n = 1, the solution is Newtonian. This equation fits most of experimental data[19] although lacking theoretical significance. An alternate expression of wide applicability was proposed by Casson.[20]

$$\tau^{1/2} = \tau_0^{1/2} + \eta_\infty^{1/2}\ D^{1/2} \qquad (6)$$

where τ_0 is the yield value and η_∞ is the viscosity at infinite shear rate.

Asbeck[21] has subsequently applied this equation to coatings with success. In Asbeck's notation, the Casson equation is given by

$$\eta^{1/2} = \eta_\infty^{1/2} + \tau_0^{1/2}\ D^{-1/2} \qquad (7)$$

This equation suggests that $\eta^{1/2}$ vs. $D^{-1/2}$ gives a straight line with intercept equal to $\eta_\infty^{1/2}$ and slope $\tau_0^{1/2}$. τ_0 and η_∞ are related to practical coating characteristics of paint. η_∞ may be used as a measure of ease of application at high shear rate and τ_0 may be used as a measure of the sag resistance.[22] The Casson equation was derived under the assumption that the medium is a Newtonian liquid and that the non-Newtonian behavior of the system is solely due to the particle - particle interaction. Therefore, this equation does not hold in the case where the medium behaves as a shear-sensitive liquid. Onogi, et al.[23] modified the Casson equation by taking the non-Newtonian behavior of the medium into account. The modified equation is expressed as

$$\tau^{1/2} = \kappa_0 + \kappa_1 \left(\frac{\eta_a\ D}{\eta_0} \right)^{1/2} \qquad (8)$$

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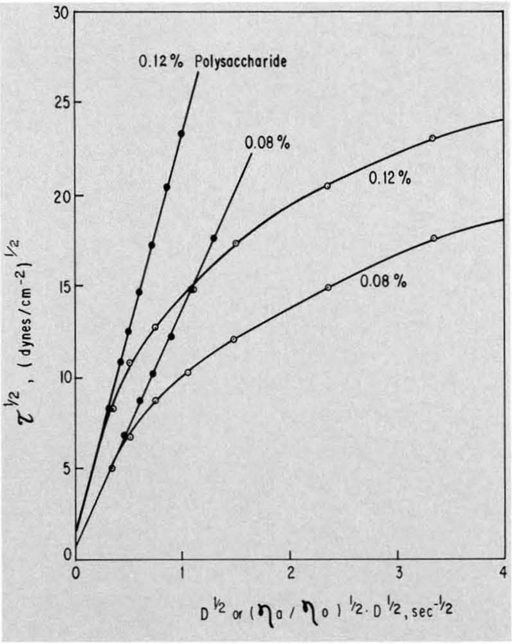
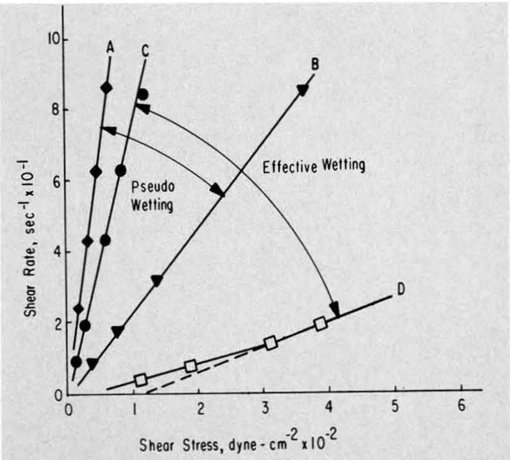


Figure 5—Casson plots (○) and modified Casson plots (•) of zinc dust dispersion in polysaccharide solution (zinc dust concentration = 12g/100 ml)



Component	Component weights and curve A	B	C	D
Nonreactive 60% alkyd	147	147	0	0
Reactive alkyd	0	0	147	147
Rutile and syloid	0	272	0	273
Solvent	73.5	73.5	73.5	73.5

Figure 6—SRL curves to illustrate the degree of pigment-polymer interaction Curves C—D represent strong interaction and good wetting of the pigment and high acid value medium. Curves A—B have similar values of the SRL rheologic parameters except η. The compositions of the systems are given in the above table

where η_a is the apparent viscosity of the dispersion medium and η_o is the zero shear viscosity. This equation predicts that a plot of $\tau^{1/2}$ against $(\eta_a D/\eta_o)^{1/2}$ should give a straight line over the entire range of shear. Sato[24] found that this equation fits the system where zinc dust is dispersed in aqueous solution of polysaccharide, while the Casson equation does not, as shown in *Figure* 5. The flow behavior of this system deviates from the Casson plots because its medium is extremely thixotropic.

To sum up, the assessment of dispersion state by means of the measurement of rheological properties is dependent upon the interpretation of the results. The relationship between rheological behavior and the dispersion state should be clearly understood in its application. The rheological properties of dispersed system, however, depend not only on dispersion state of particles, but also on the other parameters, such as the properties of medium, the shape, and the size of particles. If a system like a paint contains polymer, the interpretation becomes more difficult. Therefore, it is recommended that the rheological method be used in combination with the other more direct means, such as sedimentation methods, dielectric methods,[7] optical method,[25] or measurement of particle size methods.[26]

SEDIMENTATION METHODS: *Sedimentation rate methods*—The sedimentation rate of an isolated single spherical particle in a liquid is governed by Stokes Law.[27]

$$v = \frac{2r^2 (\rho - \rho_o) g}{9 \eta}$$

Where v = the sedimentation rate, cm/sec.
r = the radius of particle, cm
ρ = the specific gravity of the solid
ρ_o = the specific gravity of the liquid

Therefore, the sedimentation rate is proportional to the square of the particle diameter.

The Stokes equation is based on the assumption that sedimentation is free and not hindered by neighboring particles. The equation is considered to be applicable to the system where the particle volume content is less than 0.1%.

Where flocculation has occurred, the flocculates may behave as single large particles. The sedimentation rate of the flocculates depends on the size and the effective density of the flocculates. The density of the flocculates is lower than that of the solid phase since the liquid is entrapped in the structure. The liquid entrapped in the flocculates is immobilized and behaves as a part of the solid phase in the settling process. But the effect of entrapped liquid on the sedimentation is usually smaller than that attributable to only the increase in size. Consequently, the flocculates settle at a considerably higher rate than deflocculated particles.

Assuming that the flocculates are spherical, the size of the flocculate can

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be determined if the density of flocculates is known. Koglin[28] determined the density (porosity) of the flocculates of quartz in water by measuring the specific extinction cross-sectional area of the flocculates by means of a sedimentation balance. According to his results, as flocculation proceeds, the density of flocculates decreases.

In concentrated dispersions, the Stokes Law is not applicable since the effect of neighboring particles (or flocculates) is no longer negligible. In a concentrated system, a phenomenon termed hindered settling[29-32] is observed instead of the free settling of individual particles. In this type of settling, the liquid flow around the particles is mutually hindered by the other particles in the system. This hindrance becomes significant when the volume fraction of particle reaches about 0.01. Above this concentration of particles, the particles settle at a reduced rate due to the hindrance. In an ideal hindered settling system, all particles settle at the same rate irrespective of their size. This phenomenon is termed mass subsidence.[29] A mass subsidence occurs because the whole assembly moves as a cloud. The rate of settlement of this cloud is affected by its porosity (total volume of cloud - total volume of solid), which is equal to the total volume fraction of immobilized liquid in the cloud. Since hindered settling is directly related to dispersion stability, its measurement provides useful information on the dispersion. As yet few papers have appeared that describe such phenomena. Davies and Dollimore[31] studied the dispersion state of various carbonates in various liquids by measuring the rate of hindered settling. They found that the relationship between the degree of hindrance and flocculation depends on the dielectric constant of the medium. In a low dielectric medium, the hindrance increases as flocculation increases, while in high dielectric medium, the hindrance decreases as flocculation increases. This type of flocculation can be considered to be weak flocculation since the degree of flocculation changed reversibly with the dielectric constant of the medium.

Oesterle[33] studied the dispersion state by developing a concept of "equilibrium" flow curve. As mentioned above, the normal flow curve is time-dependent. If one repeats the measurement of the histerisis loop on the same system, one may obtain a different shape of the loop every time, depending on the shear history of the system. The hysterisis loop, if measured before the full network structure is rebuilt from the first measurement, is usually smaller than the first loop. With continuing cycling on the same system, the loop area approaches zero. This final curve is considered to be the flow curve at "equilibrium". Since the equilibrium curve is a limited curve for the system, its use in rheology is termed the Shear Rate Limit (SRL) method, by Oesterle.

The SRL measurement is very reproducible since it is independent of the shear history of the system. Oesterle[34,35] studied the pigment-polymer interaction by measuring the SRL curve by using highly wettable polymer and non-wettable polymer for the pigment. The results are illustrated in *Figure* 6 and the compositions of the systems are given. As mentioned above, there is no hysterisis loop in these flow curves. The curve C—D indicates strong interaction and good wetting between the pigment and the reactive resin and the curve A—B represents weak interaction between the pigment and non-reactive resin. The larger shift of the curve C to D by the addition of the pigment indicates that the pigment increases the viscosity and the yield value more remarkably than the other system. The greater change in the rheological properties by the addition of pigment is due to the formation of network structure of the pigments in system D. Application of the SRL methods for the study of dispersion state has been reviewed by Oesterle.[33]

Sedimentation volume methods—Measurement of sedimentation volume is probably the easiest method to measure the dispersion state. This test is easily carried out and does not require any sophisticated equipment. The sedimentation volume can be measured together with the sedimentation rate. The state of flocculation can be evaluated indirectly from the sedimentation rate and the sedimentation volume.

The flocculates settle considerably more rapidly than the deflocculated particles if the sedimentation is not hindered. In addition to the difference in the rate of sedimentation, the nature of the flocculated sediment also appreciably differs from that of the deflocculated one. The flocculated particles form soft and loosely packed sediment. Thus, the volume is considerably greater than a deflocculated one, as shown in *Figure* 7. This is true regardless of whether the flocculate is weak or strong, as shown in *Figure* 1. The sediment of flocculates is easily redispersed by light stirring. When the sediment consists of weak flocculates, it is redispersed to primary particles as previously mentioned. However, when the sediment consists of strong flocculates, it is redispersed to small flocs (but not to primary particles) due to breaking of the network structure. On the other hand, the deflocculated system forms closely packed sediment (hard cake) of considerably smaller volume than the flocculated one. The sediment of this type is not easily redispersed and requires high mechanical shear. The relationship for the two extreme types of systems is expressed in *Table* 2.

In a partly flocculated dispersion, the system may be separated into three phases if it stands without shaking for a certain period. The top layer is a clear layer in which no particle exists. The bottom layer is a loosely packed sediment of flocculates. Between these two

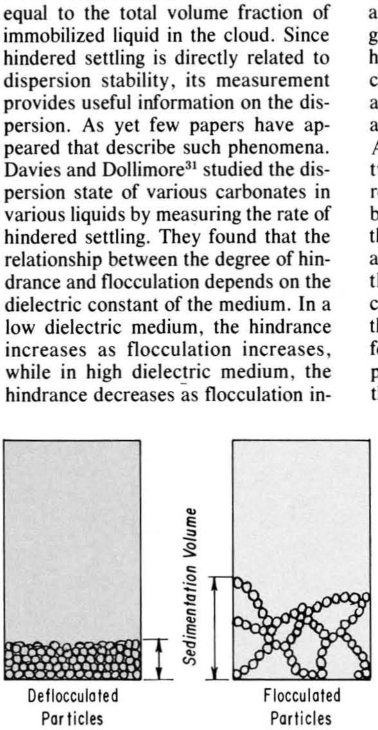

Figure 7—Sedimentation volume of flocculated and deflocculated dispersion

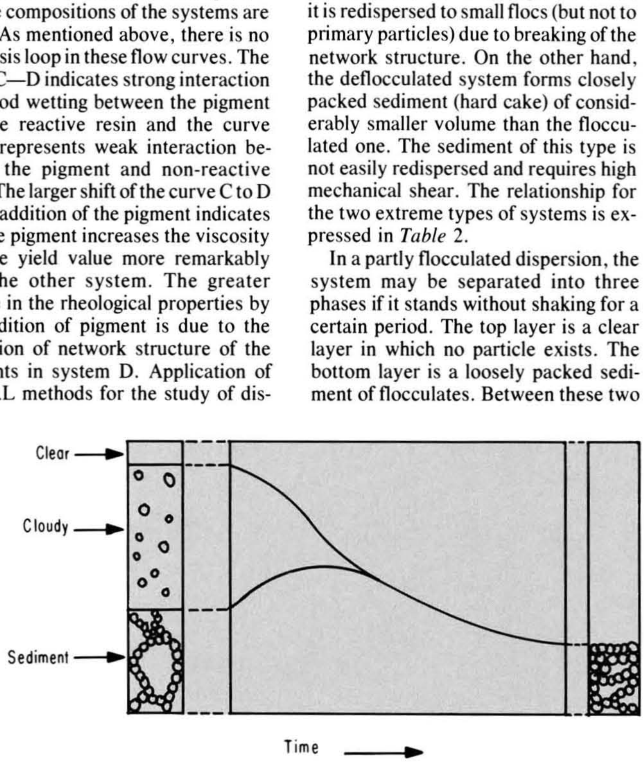

Figure 8—Change in sedimentation volume with time

Table 2—Sedimentation Properties of Dispersion

Dispersion State	Sedimentation Rate	Sedimentation Volume	Nature of Sediment	Redispersibility
Deflocculated	Slow	Low	Hard	Difficult
Flocculated	Rapid	High	Soft	Easy

layers, there may be a cloudy layer in which deflocculated particles are present. As the sedimentation proceeds, the sediment volume increases initially until all flocculates settle, then it decreases very slowly because the gravitational force compacts the loosely packed layer. The cloudy layer disappears when all deflocculated particles settle on the surface of flocculate layer. Therefore, the layer formed on the top of the sediment is a closely packed layer of fine particles.

Sedimentation may take a considerable time to reach equilibrium. For the practical assessment of the degree of dispersion, measurements of the change in sedimentation behavior should be taken for about a week. If one wants to obtain the data for final sedimentation, one can extrapolate the data to infinite time. In some cases, attempts are made to accelerate the sedimentation to expedite experimentation and to simulate long-term natural settling. The most common methods are the dilution of dispersion to reduce the viscosity, and the application of a centrifugal force. Considerable care should be taken in the application of these methods to insure the results obtained are meaningful since the dispersion state determined by those techniques may not be the dispersion state *in situ*. The dilution of the dispersion may cause dilution shock which degrades the dispersion. Carr[7] emphasized the importance of this phenomenon. Patton postulated that the centrifugal technique should be virtually excluded because the weak structural network of the flocculate is almost certain to be disrupted and particles which might remain suspended indefinitely under gravitational influence alone will rapidly pack at the bottom under centrifuging condition. Therefore, in assessment of the dispersion state, one must be very careful to choose a method which gives meaningful results to the objective.[26]

List of Symbols

D — shear rate, sec^{-1}
ke — Einstein coefficient
r — radius of particle
S — crowding factor = $1/\phi_{max}$
V_A — attractive energy, kT
V_R — repulsive energy, kT
V_T — total potential energy, kT
V_{max} — maximum potential energy, kT
ν — sedimentation rate, cm. sec^{-1}
ϕ — volume fraction of dispersed phase
ϕ_f — hydrodynamic volume fraction of flocculate
ϕ_ℓ — volume fraction of immobilized liquid
ϕ_p — volume fraction of deflocculated liquid
ϕ_s — volume fraction of solid phase
ϕ_a — volume packing fraction of spheres forming flocculate
Φ_{max} — maximum volumetric packing fraction
η — viscosity of dispersed phase, dyne • sec • cm^{-2}
η_m — viscosity of medium, dyne • sec • cm^{-2}
η_α — apparent viscosity, dyne • sec • cm^{-2}
η_o — zero shear viscosity, dyne • sec • cm^{-2}
η_∞ — infinite shear rate viscosity, dyne • sec • cm^{-2}
η_r — relative viscosity
τ — shear stress, dyne, cm^{-2}
τ_o — yield value, dyne cm^{-2}
ρ — specific gravity of solid, g. cm^{-3}
ρ_o — specific gravity of liquid, g. cm^{-3}

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TECHNOLOGY REVIEW

New Developments in Anti-Fouling: A Review of the Present State Of the Art

D. Atherton, J. Verborgt, and M.A.M. Winkeler
Sigma Coatings B.V.*

Composition of soluble matrix and insoluble matrix anti-fouling are discussed briefly and their inadequate performance in modern ship trading conditions described. Advantages of the recently developed hydrolizable organometallic copolymer binder anti-fouling are outlined. Toxin release by hydrolysis can be controlled and influence of composition of copolymer on the rate of hydrolysis is described with relationship to a variety of new copolymers. Stability of such organometallic copolymers during manufacture and storage is also discussed.

Introduction

For many years, it has been standard practice to test anti-fouling compositions by panel exposure on static rafts. When ships traded in the traditional pattern and experienced long periods at moorings or in anchorages during protracted loading and discharge of cargo, fouling by shell and algae was similar to that found on such rafts. Work during the period from about 1940 to 1960 was aimed at the control of this type of fouling and resulted in the development of soluble matrix (reinforced rosin) types pigmented essentially with cuprous oxide. It also led to the development of insoluble matrix "contact" type anti-foulings with very high loading of cuprous oxide in a vinyl copolymer vehicle. These tended to be replaced by binders containing major proportions of rosin, since the insoluble binder tended to allow premature fouling due to clogging of the denuded surface matrix with slime and debris.

As the pattern of ship operation changed to the now commonplace, quick turnaround, fast container ships and tankers, shell fouling ceased to be a major problem and was replaced by algal settlement between the deep and light load lines. This fouling was not killed during the rather short periods when this area was exposed to sun and air between cargo and ballast passages.

Raft exposure does not accurately reproduce this class of algal fouling, although techniques involving alternating lab rotor or spinner exposure in sea water with exposure on a raft close to the water line, or even in the horizontal plane, did give some degree of correlation. Ship experience and these modified raft trials proved that traditional cuprous oxide rosin combinations did not have adequate resistance to algae. During the 1960s to the 1970s, the problem was subjected to intensive investigation. During this period, the value of organo-metallic toxins was demonstrated; tributyltinoxide, tributyltin-fluoride, triphenyltinfluoride, and triphenylleadacetate were all found effective, particularly in vinyl copolymer and chlorinated rubber vehicles. These vehicles were sometimes modified with minor or even major proportions of rosin compounds. Mixtures of organic toxin and cuprous oxide and/or zinc oxide were also used. A variety of effective commercial products was developed, and control of shell and algal settlement for 18 to 24 months on these fast, quick turnaround ships was achieved.

It was recognized and has been emphasized by Christie[1] that all these traditional anti-foulings consisting of toxins dispersed in soluble, and even insoluble, matrix binders must suffer from exponential leaching. In practice, therefore, it is necessary to use high toxin loads in order to sustain adequate toxin release at the end of the designed sea water exposure period. Such high toxin loadings result in excessive leaching rates in the earlier stages of the life of the anti-foulings.

Several palliatives have been suggested to overcome this problem. One of these involved reversion to essentially insoluble matrix vehicles and periodic mechanical abrasion of the denuded surface matrix by scrub boat or a diver operated rotary brush in order to expose the fresh toxin layer. This type of process is perfectly feasible and, in fact, has been used with hard racing anti-foulings on easily slipped sailing yachts. It is not easy to visualize how this could be accurately controlled on very large ships, particularly in poor visibility conditions.

Another proposal involves the use of a two layer system in which the outer layer controls the rate of migration and, therefore, the leaching of toxin. Clearly, this is most likely to be effective with organic toxins which can diffuse through an organic membrane. It is possible to use a system in which the lower layer contains a high proportion of organic toxin and the outer layer a lower proportion of the same or perhaps a different organic toxin and, perhaps, cuprous oxide. A variant of this type proposes the use of a hydrocolloidal acrylic polymer as the outer layer, but this proposal has been criticized by Christie[1] with regard to claims for reduced frictional drag and also for possible problems when recoating at later dockings. It also seems probable that such polymers would be adversely affected by sunlight exposure of the area above

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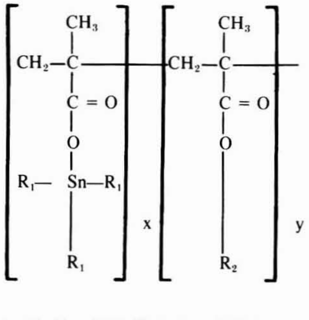
the light load line. This exposure is inevitable during ballast passages and also during any long or even short lay up periods. Of course it might be possible to use UV stabilizers in such polymers.

It has been recognized that some organometallic compounds and, in particular tributyltinoxide, can react with acidic polymers and even rosin acids. This principle has been exploited in the development of a wide variety of biologicially active organometallic modified resinous binders. Organotin modified polymers were described in literature in 1958 when J. C. Montermoso, et al.[2] investigated synthesis and physical properties of trialkyltinacrylates. This investigation was aimed at the production of polymers with improved thermal stability; possible use as filmforming biocides was not described. In 1963, Leebriek[3] described the synthesis and properties of a variety of organotin polymers and copolymers and proposed their use as anti-fouling fiber treatments (e.g., fish nets). Their use as bioactive filmforming compositions including anti-fouling paint was also suggested. In 1964, James[4] patented the use of organotin copolymers, including copolymers of tributyltinmethacrylate and methylmethacrylate, in anti-fouling paints containing major proportions of water soluble pigments, such as zinc oxide and cuprous oxide. Milne and Hailes, in 1974,[5] claimed advantage in the use of copolymers containing higher proportions of trialkyltin than was proposed by James. They also stated that retarders should be incorporated to reduce the rate of hydrolysis and the consequent erosion of the sea water soluble acidic polymer residue. It was claimed that, by use of sea water soluble pigments, a planing or smoothing effect was obtained during passage of the ship through the water.

Biologically Active Organometallic Polymers and Copolymers

Trialkyl modified acrylic copolymers have the general structure shown below:

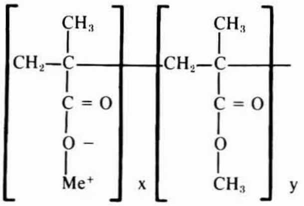


$$\left[-CH_2-C(CH_3)(C{=}O-O-SnR_1R_1R_1)-\right]_x\left[-CH_2-C(CH_3)(C{=}O-O-R_2)-\right]_y$$

R_1 in the trialkyltin moiety is preferably butyl or propyl, lower and higher alkyl tin oxides being less effective toxins. R_2 is usually a lower alkyl group, e.g. methyl, since higher alkyl groups tend to give soft films. Homopolymers of tripropyl or tributyltinmethacrylate, for example, can be prepared but give soft films. The trialkyltin radical is readily split off by hydrolysis in alkaline sea water to tributyltinoxide, for instance, which is an effective biocide. This would leave a residual polymer which is very water sensitive or even soluble in alkaline sea water. To illustrate, a copolymer prepared from 30/70 wt/wt ratio of methylmethacrylate and tributyltinmethacrylate when hydrolized will yield a residual polymer backbone containing about 68/32 wt/wt ratio of methylmethacrylate and methacrylic acid.

When immersed in sea water, unpigmented films prepared from such tributyltin copolymers do not develop milkiness or turbidity in the depth of the film. This indicates that hydrolysis progresses from the surface down and there is no evidence of significant hydrolysis in the lower part of the film. Currently, work using advanced analytical techniques including X-ray scanning is designed to examine this aspect in detail.

Although, as stated above, residual water sensitive backbone polymer remaining after hydrolysis may dissolve to some extent in alkaline sea water, it is believed that this may also be greatly influenced by the presence of sea water soluble or reactive pigments. It seems probable that the highly swollen ionomeric structure of the type shown below, then formed on the surface will be eroded readily, due to its low film strength, from the surface during ship passages together with these water sensitive pigments. It is not necessary to argue that this erosion is due entirely to water solubility of the polymer residue.



$$\left[-CH_2-C(CH_3)(C{=}O-O^-\,Me^+)-\right]_x\left[-CH_2-C(CH_3)(C{=}O-O-CH_3)-\right]_y$$

Effect of Composition of Copolymer On Hydrolysis and Film Erosion

Milne[5] has described the effect of the composition of the copolymer on the hydrolysis and erosion rate and the case is argued for use of a retarder to reduce this rate with copolymers containing high proportions of organotin comonomers. The use of very high ratios (120% on weight of organotin moiety) of materials such as DDT is suggested in lower layers of a multiple coat system.

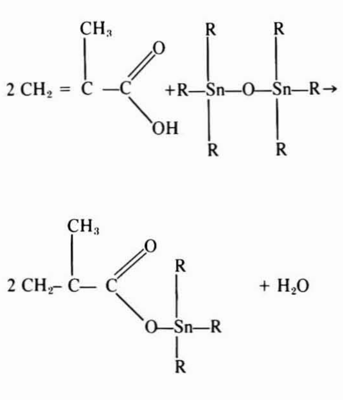
During our own investigations, a very wide range of copolymers was synthesized and examined for the rate of hydrolysis and film erosion as clear films and zinc oxide pigmented paints, by prolonged exposure in a seawater rotor apparatus. A few typical results are given in *Table* 1. The type of rotor test referred to in *Table* 1 is a valid lab control test when compared with ship performance of a control standard. In this case, copolymer 1 is known to give excessive erosion. Its comparison with copolymers 2 and 3 indicates the dramatic reduction in erosion which results from change of composition. It is obvious that any desired rate can be achieved, in theory, by the correct choice of constituents. Copolymer 2 represents one useful compromise and rotor/raft and ship trials confirm that the rate of toxin release and rate of erosion are within acceptable limits.

Further modification is possible using comonomers with hydrophylic properties and these will increase erosion rate of copolymers containing relatively low TBTMA ratios. This development promises a route to lower cost surface erosion copolymers with a lower rate of organotin toxin release.

It is possible, however, that dispersion of other organic or inorganic toxins may be required in practical anti-fouling paints but such materials are also proposed under pseudonyms in Milne's patent.[5]

Copolymerization Mechanisms And Viscosity Control During Manufacture and Storage

The acrylic monomer is generally prepared according to the following process:



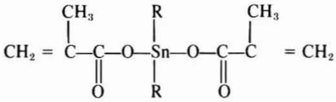
$$2\,CH_2=C(CH_3)-C({=}O)OH + R_3Sn-O-SnR_3 \rightarrow 2\,CH_2=C(CH_3)-C({=}O)-O-SnR_3 + H_2O$$

Table 1—Rate of Hydrolysis and Film Erosion By Prolonged Exposure in Seawater Rotor Apparatus

	Composition of Copolymer				Loss of Film Thickness (microns) in Rotor Test			
					2½ months		5 months	
No.	MMA	BA	Sty.	TBTMA	Clear	Pigmented	Clear	Pigmented
1	30	-	-	70	31	37	54	90
2	25	10	-	65	13	11	14	23
3	-	-	50	50	3	2	4	7

MMA = Methylmethacrylate
TBTMA = Tributyltinmethacrylate
BA = Butylacrylate
Sty = Styrene

Commercial TBTO, however, contains considerable proportions (up to 5%) of impurities such as dibutyltin oxide. These impurities, in turn, will give bifunctional monomers of the following structure:



$$CH_2=C(CH_3)-C(=O)-O-Sn(R)_2-O-C(=O)-C(CH_3)=CH_2$$

If formed in large amounts, such bifunctional monomers will give serious viscosity problems and even gelling during the polymerization. It was found to be difficult to reproduce product viscosities unless a good grade of fresh TBTO was used. The following results were obtained in two identical runs using the same grade of TBTO from the same supplier:

Run No. 1	Fresh TBTO	Copolymer viscosity 15,000 cps (Viscosity can be reproduced within ± 2,000 cps)
Run No. 2	2 year old TBTO	Copolymer viscosity >100,000 cps

Very high viscosity copolymers of the type produced in Run No. 2 give poor application properties. Methods for control of this side reaction were investigated. This work resulted in the development of coreactants which preferentially break down the bifunctional monomer and, consequently, avoid development of highly crosslinked and viscous copolymers.

Table 2—Rate of Viscosity After UV Exposure

Exposure Time (hrs)	Viscosity (cps)
0	14,200
2	18,500
4	21,800
8	25,700
11	59,000

Viscosity increase of pigmented organometallic copolymer anti-fouling compositions during storage can be due to the reaction between any residual free carboxylic groups in the copolymer and any reactive pigments, such as zinc oxide or cuprous oxide. It can also be caused by photochemical-induced oxidation of tributyltin moieties to dibutyltin moieties. This is demonstrated by viscosity change of copolymers stored in the laboratory in clear and brown bottles. In one experiment, a copolymer with initial viscosity 13,000 cps increased in viscosity to 16,000 cps when stored in a brown glass bottle, but to 58,000 cps when stored in a clear glass bottle. It has been found to be possible to prevent and even reverse this viscosity increase by the use of depolymerization agents, and this subject is still under intensive investigation.

Results of a typical experiment are given in *Table* 2. A sample of organotin copolymer was stored in a clear glass vessel and irradiated by a 50 watt UV lamp at 40 cm distance. One of the depolymerization agents was then added and found to reduce the viscosity as given in *Table* 3.

A further exposure of this sample to UV for 11 hrs raised the viscosity again to 10,000 cps, but this was lowered again by adding further depolymerization agent. It was demonstrated that the effect was not due simply to the dilution effect of the depolymerization agent by comparison with exposure when diluted with the same proportion of xylol or dimethylformamide (DMF). A copolymer with initial viscosity 70,000 cps was reduced in viscosity to 43,000 cps with 1%, and to 12,000 cps with 2% addition of depolymerization agent. Addition of 10% xylol reduced viscosity to 28,000 cps and 10% DMF reduced viscosity to 20,000 cps.

The photosensitivity of organotin copolymers and their related sensitivity to oxidation induced polymerization must be expected to affect the surface of a paint film exposed to light, e.g., on sides of a ship during light ship passages or lay up. The development of a significantly different composition on the surface may be one explanation for observed phenomena of the surface crazing or cracking of this class of material in sunlight exposure. Investigation of effect of UV stabilizers is in progress.

It is possible that swelling of the water sensitive hydrolized copolymer and its subsequent drying out when exposed to air and sun could also contribute to such cracking and crazing effects. Obviously, copolymers with very high ratios of hydrolizable organotin moieties will be more prone to this effect. Reduction in the proportion of organotin components by use of an internal plasticizing copolymer, such as butylacrylate, will alleviate the effect, but sufficient organotin component must be retained to provide adequate toxin release and erosion rates. Furthermore, the proportion of butylacrylate is limited by the need to produce tough non-tacky films.

The use of water sensitive pigments or fillers will increase hydrolysis in depth and will contribute to shorter service life and increased tendency to crazing or cracking in sunlight.

Biologically Active Copolymers Of Maleic Anhydride and Methylvinylether

Among the copolymers which could be used in biologically active antifouling paint binders are those which can be prepared from copolymers of maleic anhydride and methylvinylether. The anhydride group can be opened by alcohol or amine reaction and the resulting carboxyl reacted with tributyltinoxide. A series of experiments of this type is outlined in *Table* 4.

This type of organometallic co-

Table 3—Rate of Viscosity After Addition of Depolymerization Agent

% of Agent Added	Viscosity (cps)
0	59,000
1	13,000
2	4,500

Table 4—Organotin Copolymers Prepared from Maleic Anhydride/methylvinylether MA/MVE Resins

No.	MA/MVE Resin (gms)	Amine/Alcohol	(gms)	TBTO (gms)	Xylene (gms)	Film Properties
1	120	Butanol	44.6	278.4	443.0	Tacky
2	120	Cyclohexanol	60.0	278.4	458.4	Hard
3	120	Benzyl amine	64.3	278.4	565.5	Hard
4	120	Benzylalcohol	64.9	278.4	463.3	Sl. Tacky
5	120	Methanol	19.2	278.4	417.6	Sl. Tacky
6	120	Ethanol	27.6	278.4	520.8	Sl. Tacky
7	120	Aniline	55.9	278.4	454.3	Hard
8	120	nPropanol	36.1	278.4	434.5	Sl. Tacky

polymer is of particular interest, since it could be manufactured from performed MA/MVE copolymer in traditional alkyd resin making equipment. The work carried out so far indicates that a wide range of film hardness characteristics can be achieved and that some of the polymers hydrolize at acceptable rates. It must be stated, however, that this is only one example of a range of polyester, epoxy, vinyl, and other organometallic copolymers which may have value either in anti-fouling compositions or structural plastics with anti-fouling properties.

Conclusions

It is probable that a practical limit has been reached in efficacy of anti-fouling paints consisting of toxins dispersed in soluble or insoluble binders and only limited improvements will be achieved by use of multiple coat layers. The development of tributyltin modified copolymers and their exploitation in practical anti-fouling compositions has opened a new avenue of development which offers a promise of extended service life. The work is very likely to extend to the use of copolymers modified with other organometallic toxins and metal free organic toxins. It seems very probable that mixed biocides will often be required and, indeed, it would be unwise to assume that tributyltinoxide is, or will remain, the most effective marine biocide. There are already disquieting reports of settlement of goose barnacles on high performance tributyltinoxide-liberating class anti-foulings within their expected potency period and it must be stated that no normal rotor and raft test effectively tests potency against this deep water offshore marine animal. Quite possibly, an alternative hydrolizable toxin to tributyltin oxide and/or additional dispersed toxins will be required. Once again, the anti-fouling paint technologist is faced with the problem that the trusted rotor/raft test may not be providing the correct answers. It is difficult to predict how this new slant to an old problem is to be overcome, other than by the very time consuming and somewhat uncertain method of patch testing on ships operating within the specific trading conditions.

Summary

Anti-fouling compositions produced by dispersion of inorganic and/or organic toxins in soluble or insoluble binders suffer from excess leaching of toxin in early life, particularly when highly pigmented. In efforts to prolong effective life, some anti-foulings have been developed which can be regenerated by mechanical abrasion and others in which toxin release is controlled by use of a second layer of a different composition. The use of hydrolyzable organometallic copolymer binders allows incorporation of higher proportions of organometallic toxin and better control of rate of release of toxin is also possible.

DR. DONALD ATHERTON graduated with a degree in chemistry in 1937 and received the Ph.D. Degree from Liverpool University in 1940. His work in vegetable oil research while at the university led to his research on drying oils, alkyd resins, and general surface coating technology. He became Technical Director of Sigma Coatings Ltd. in 1971. Dr. Atherton now supervises the company's worldwide marine and offshore operations.

DR. JOZEF VERBORGT studied polymer chemistry at the University of Louvain in Belgium. After his Ph.D. work, he received a postdoctoral fellowship from the United States Air Force at the University of Arizona. He joined Petrofina laboratories in 1972 and became head of Sigma Coatings laboratories in 1976.

DR. M.A.M. WINKELER graduated from the Technical University at Delft in The Netherlands in 1968. He has been involved in the development of the first epoxy coatings in Europe. Recently, Dr. Winkeler has been appointed Technical Vice President of Sigma Coatings Inc., Harvey, La. His special interests are in heavy duty marine, offshore, construction, and anti-corrosive systems.

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Future Society Meetings

Chicago

(Nov. 5)—Panel Discussion on "WASTE MANAGEMENT"—R.A. Young, of Pollution Engineering and R.W. Eldridge, of Eldridge Engineering.

(Jan. 7)—Discussion of Society project on "INFRARED SPECTROSCOPY"—John Vandeberg, of DeSoto, Inc.; "MOTIVATION OF PRODUCTION PERSONNEL"—J. Richard Mathieson, of Dow Chemical.

(Feb. 4)—"EMULSION POLYMERIZATION TECHNIQUES"—speaker from Rohm and Haas Co.; "LATEX PAINT FORMULATION USING CPVC DETERMINATIONS"—Ken Hesler, of DeSoto, Inc.

(Mar. 3)—Society Manufacturing Committee Program; "INTERFACIAL CHEMISTRY IN CORROSION-INDUCED PAINT ADHESION LOSS"—Ray Dickie, of Ford Motor Co.

(April 7)—Society Technical Committee Program; "EVAPORATION BEHAVIOR OF ORGANIC CO-SOLVENTS IN WATER-BORNE COATINGS"—R. F. Eaton, of Union Carbide Corp.

C-D-I-C

(Nov. 12)—PLANT TOUR of Inland Manufacturing Div., General Motors.

(Dec. 10)—"AN OVERVIEW AND UPDATE OF MILDEW RESEARCH SPONSORED BY THE PAINT RESEARCH INSTITUTE"—Joan Schmitt, of The Ohio State University.

(Jan. 14)—"WHAT IS HAPPENING TO THE COATINGS INDUSTRY?"—Howard Ellerhorst, of Chemical Marketing Services, Inc.

(Mar. 10)—Society Technical Committee Program.

Louisville

(Nov. 19)—JOINT MEETING with Louisville Paint & Coatings Association.

(Jan. 16)—"AQUEOUS INDUSTRIAL COATINGS"—Nick Roman, of Rohm and Haas Co.

(Feb. 20)—"FOAM-RELATED ASPECTS OF WATER-REDUCIBLE ALKYDS"—Richard M. Thornton, of Nalco Chemical Co.

(Mar. 19)—"PLANT SAFETY"—Gil Kane, of Hercules Incorporated.

(Apr. 16)—FSCT SLIDE PRESENTATION—Federation Officers.

Montreal

(Nov. 7)—"CONVERSION COATING ENAMELS — ENERGY SAVERS"—Paul W. McCurdy, of Reichhold Chemicals, Inc.

(Dec. 5)—"ACCELERATED WEATHERING—YESTERDAY, TODAY AND TOMORROW—Roger Metzer, of Atlas Electric Devices Co.

(Jan. 9)—"TiO_2 GRADE RATIONALIZATION"—Joe Fiocco, of Canadian Titanium Pigments Ltd., and Robert Rauch, of Tioxide of Canada Ltd.

(Feb. 6)—"A SAFETY PROGRAM DESIGNED FOR THE PAINT PLANT"—Manufacturing Committee Presentation.

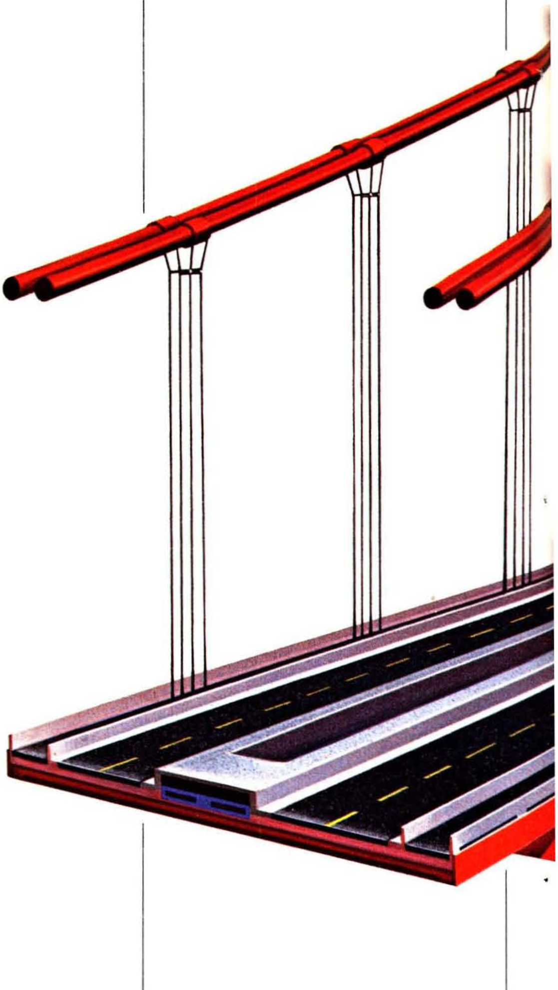
(Mar. 5)—JOINT MEETING with the Quebec Paint Industries Association.

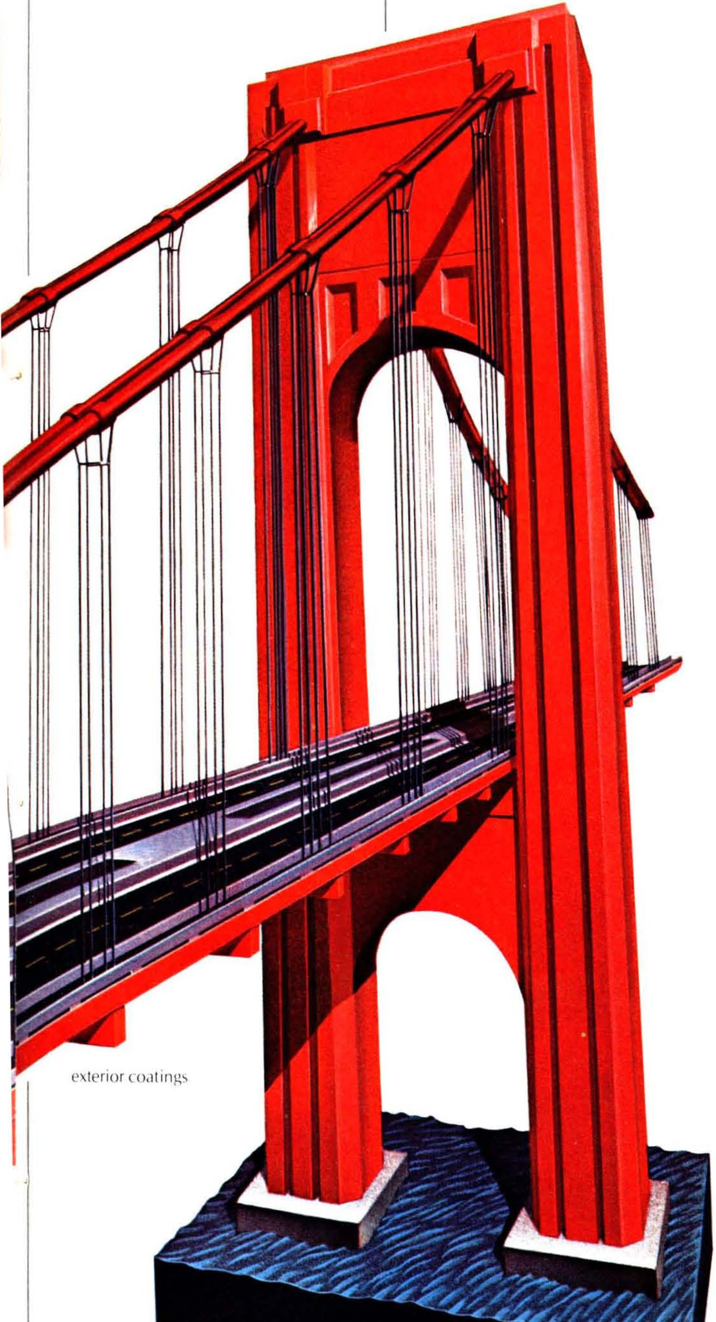
(Apr. 2)—Speaker to be announced.

(May 7)—"GOVERNMENT SPECIFICATIONS IN THE PAINT INDUSTRY"—Joe Roberge, of B.N.Q., and Frank Eadie, of C.G.S.B.

New York

(Nov. 13)—"FORMULATING ASPECTS OF WATER-REDUCIBLE COATINGS"—Al Heitkamp, of Cargill, Inc.





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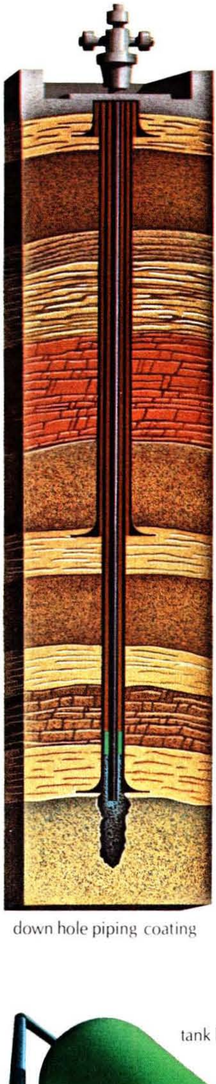

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BALTIMORE (Third Thursday — Eudowood Gardens, Towson). Mitchell Dudnikov, Harry T. Campell Sons, Executive Plaza IV, Hunt Valley, Md. 21031.

BIRMINGHAM (First Thursday—Calthorpe Suite, Edgbaston). B.J. Addenbrooke, Croda Paints Ltd, Bordesley Green Rd., Birmingham B9 4TE, England.

CHICAGO (First Monday — meeting sites in various suburban locations). John L. Petty, Sherwin-Williams Co. 10909 S. Cottage Grove, Chicago, Ill. 60628.

C-D-I-C (Second Monday — Sept., Nov., Jan., Mar., May in Columbus; Oct., Dec., Feb., Apr. in Cincinnati, Kings Island Inn). Robert D. Thomas, Perry & Derrick Co., P.O. Box 12049, Cincinnati, Ohio 45212.

CLEVELAND (Second Tuesday — meeting sites vary). Thomas Tuckerman, Coatings Research Group, Inc., 2340 Hamilton Ave., Cleveland, Ohio 44114.

DALLAS (Thursday following second Tuesday — Vic's Gallery Restaurant). Ray O. Marett, Western Specialty Ctgs., 4400 Singleton Blvd., Dallas, Tex. 75212.

DETROIT (Fourth Tuesday — meeting sites vary). John J. Gentilia, Union Carbide Corp., 26500 Northwestern Hwy., Southfield, Mich. 48037.

GOLDEN GATE (Monday before third Wednesday — Sabella's Restaurant, San Francisco). Don Mazzone, Fuller O'Brien Corp., 405 E. Grand Ave., S. San Francisco, Calif. 94080.

HOUSTON (Second Wednesday — Marriott Hotel, Astrodome). Duane Fields, Conchemco, Inc., 2503 W. 11th St., Houston, Tex. 77008.

KANSAS CITY (Second Thursday — Washington Street Station). Richard Warren, Cook Paint & Varnish Co., P.O. Box 389, Kansas City, Mo. 64141.

LOS ANGELES (Second Wednesday — Steven's Steak House). Romer E. Johnson, Dorsett & Jackson, Inc., 3800 Noakes St., Los Angeles, Calif. 90023.

LOUISVILLE (Third Wednesday — Essex House). J. Durham, Celanese Coatings Co., Technical Center, P.O. Box 8248, Louisville, Ky. 40208.

MEXICO (Fourth Thursday — meeting sites vary). Mauricio Esquivel, Pinturas Azteca, Av. De Las Torres 479, Mexico, D.F. Mexico.

MONTREAL (First Wednesday — Bill Wong's Restaurant). R. Kuhnen, Tioxide of Canada Ltd., P.O. Box 580, Sorel, Que., Canada J3P 5P8.

NEW ENGLAND (Third Thursday — Fantasia Restaurant, Cambridge). John E. Fitzwater, Jr., Polyvinyl Chemical Ind., 730 Main St., Wilmington, Mass. 01887.

NEW YORK (Second Tuesday — Landmark II, East Rutherford, N.J.). Donald E. Brody, Skeist Laboratories, Inc., 112 Naylon Ave., Livingston, N.J. 07039.

NORTHWESTERN (Tuesday after first Monday — Jax Cafe). G. Dale Ernst, Tennant Co., P.O. Box 1452, Minneapolis, Minn. 55440.

PACIFIC NORTHWEST (Portland Section — Tuesday following second Wednesday; Seattle Section — the day after Portland; British Columbia Section — the day after Seattle). Richard A. Stewart, Stainco, Box 67638, Stn. "O", Vancouver, B.C. V5W 3V1.

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PITTSBURGH (First Monday — Skibo Hall, Carnegie-Mellon University Campus). Richard Trudel, Mobil Chemical Co., 1000 Westhall St., Pittsburgh, Pa. 15233.

ROCKY MOUNTAIN (Monday prior to second Wednesday — Gusthaus Ridgeview, Wheatridge, Colo.). Steve Crouse, Kwal Paints, P.O. Box 5231, T.A. Denver, Colo. 80217.

ST. LOUIS (Third Tuesday — Salad Bowl Restaurant). John Kemper, Sinnett Lacquer Mfg. Co., 1378 Kingsland Ave., St. Louis, Mo. 63133.

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

TORONTO (Second Monday — Town and Country Restaurant). G.E. Abboud, Canadian Industries, Ltd., 1330 Castlefield Ave., Toronto, Ont., Canada, M6B 4B3.

WESTERN NEW YORK (Second Tuesday — Holiday Inn, Cheektowaga, N.Y.). Jay A. Robey, Spencer-Kellogg Div., P.O. Box 210, Buffalo, N.Y. 14225.

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Farbe und Lack
(in German)

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Wunsche, O. — "Expectation in Respect to Aggregates for Mixing and Milling at Achema 1979"; 445-447.

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Zorll, U. — "Results of Research for Practice. Balance of 12th Report of the Forschungsinstitut fur Pigmente und Lacke e.V. in Stuttgart"; 471-474.

German Standard Draft DIN 55 945 Part 13: Terms and Definitions for Paints, Varnishes and Similar Coating Materials; Supplement to DIN 55 945; 478.

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(in German)

Published by Elvira Moeller GmbH, Karl-Benz-Strasse 11,
Postfach 11 68, 7024 Filderstadt 1

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Plaste und Kautschuk
(in German)

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Double Liaison - Chimie Des Peintures
(in French)

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NPCA Hosts Annual Meeting in San Francisco

The National Paint and Coatings Association will hold its 92nd Annual Meeting at The San Francisco Hilton on October 29—31.

Keynote Address on Monday, October 29, by Senator S. I. Hayakawa (R-CA) will be on "The Economic & Energy Situation and Government Regulation of Business."

Monday afternoon's sessions will feature two concurrent forums. The Trade Sales Forum will focus on "Selling Your Value." The Manufacturing Management/Waste Management Forum will examine "Waste Management in a Coatings Manufacturing Plant."

Tuesday's program begins with a Small Paint Manufacturers Breakfast and will be followed by two concurrent sessions: the Chemical Coatings Forum, which will analyze "Strategic Planning for the Eighties," and the Management Information Forum, which will take a look at "Sources & Cost of Capital in the '80's.

Tuesday afternoon's session will be devoted to the Industry Suppliers Forum, "Raw Materials: Where Do We Stand?"

On Wednesday morning, a "Health and Environmental Regulatory Update" will be combined with a Continental Breakfast.

Later Wednesday morning, the General Session will feature Dr. Eugene Jennings' presentation on "The Arena of Life."

Wednesday's final luncheon will include a special audiovisual surprise followed by the musical group "Paradise." The Meeting will adjourn after lunch.

Complete member registration will be $120, for the three-day meeting, $80 for program sessions only, and $85 for the Spouse Program. Registration fees for non-members are double the above prices.

L. A. Society Offering Paint Technology Course

The Los Angeles Society for Coatings Technology has begun its two-year curriculum in Paint Manufacturing Technology, conducted in conjunction with Los Angeles Trade-Technical College. Instructor is Trev. Whittington.

The three-hour weekly evening classes began September 20.

The first semester focuses on Paint Fundamentals. Succeeding semesters will cover Paint Technical Preparation (specifications, tests, and calculations), Paint Raw Materials (film-formers, solvents, pigments, and additives), and Paint Formulation (principles and practices of paint formulation and paint manufacture of all types of paints). Students completing all four semesters earn a paint certificate.

Printing Inks is Subject of Lehigh Short Course

A one-week short course on the "Physics and Chemistry of Printing Inks," will be offered by Lehigh University, Bethlehem, Pa., on October 29 to November 2, 1979.

The course, designed for scientists, engineers, and chemists, will study the aspects of preparation, characterization, and application of printing inks, and the printing processes in which they are used. The course, comprising both lectures and lab demonstrations, will maintain a balance between the underlying theory and the practical application, as well as the physical and chemical problems in the preparation and application of printing inks.

Some subjects to be covered include: Principles of Surface Chemistry and Mechanism of Printing Processes; Compatibility of Polymer Vehicles and Solvents and Formulations using the Solubility Parameter Concept; Rheology of Printing Inks; Dispersion of Pigments; Compositions of Printing Inks; Principles of Color; and Printability. Lectures will be presented by both the faculty of Lehigh and staff members of the National Printing Ink Research Institute.

Fee for the course is $500 for the entire week or $115 per day for any part.

For further information, contact Dr. M.S. El-Aasser, Dept. of Chemical Engineering, Whitaker Laboratory, #5, Lehigh University, Bethlehem, Pa. 18015.

Past-President and Mrs. S. Leonard Davidson represented the Federation at the Biennial Conference of the Oil and Colour Chemists' Association, Stratford-on-Avon, England, June 20-23. In the photo, taken at the reception for overseas visitors, are (left to right): Mrs. Kooistra; Mart Kooistra, President of FATIPEC (European Federation); Borje Andersson, President of the Scandinavian Federation; Mrs. Isabel McLean; Angus McClean, President of OCCA; and Edythe and Leonard Davidson.

Minutes of SPF Meeting Held in Brussels, November 15-16, 1978

MEMBERSHIP

The various items of work within the SPF group have stimulated additional interest, so that support for the activities is provided now not only by formal SPF members but also by several associate members who can contribute experience from their specific fields and who also take part in current or prepared studies.

PROGRESS REPORTS

Analytical Group—The main topic for the group is "Analysis of Functional Groups in Amino Resins." According to the Group's leader, G. Christensen, four methods have been taken into consideration: Solvent removal, Proton-NMR-Spectroscopy, Transetherification and Zeisel cleavage, both combined with GLC. Various samples were tested in an interlaboratory exercise. The results obtained revealed that the methods provide sufficient possibilities for the analytical studies, but obviously need some additional modifications. The aim is to develop a series of recommendations as to the analysis of various functional groups in amino resins.

Adhesion Group—In order to find out the relationship between various practical situations in which adhesion phenomena play an important part, and to allow an assessment of the methods for measuring adhesion, a questionnaire action has been carried out to reveal the essential fields of interest. Generally, a great deal of methods are established in practice, with a dominance of those based on normal or shearing forces for the separation of the coating. The results are mostly evaluated in context with corrosion effects, as far as protective polymer films on metals are concerned. It is, however, difficult to derive fundamental data on the adhesion mechanism from results obtained by the methods mentioned. In many cases, a comprehensive view can only be obtained if marginal factors, such as temperature, surface roughness, and film thickness, are also taken into consideration. New aspects were presented by Sickfeld, who successfully studied the amount to which adhesion can be affected by geometrical factors, particularly form and size of of the studs in the tear-off test or film thickness and film elasticity. According to results obtained by van Laar, the blister method appears to be of special use for studies on filiform corrosion.

Information Retrieval Group—The compilation of data about literature sources is virtually finished and a publication of the results will be prepared in due course.

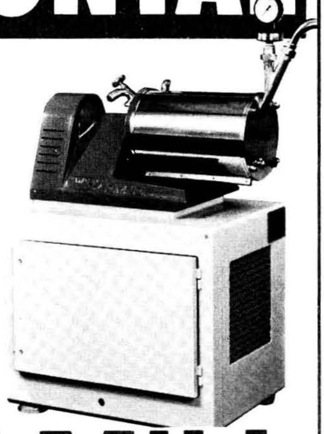
New Activities—The potential of applying sophisticated methods for surface characterization was demonstrated by Clark, who named IR- and ESCA-techniques together with surface energetical methods as the most important systems. Other new fields of interest, for which working programs are being prepared, comprise polymer-solvent interaction, homo- and copolymerization in alkyd-amino resins, stability of amino resins in binder systems, surface characterization by simple techniques, viscosity of high-solids paint materials, and properties of films and related bulk polymers.

Publications—Literature and methodical studies on amino resin analysis: *Progress in Organic Coatings*, Vol. 5, No. 3 (1978) p. 225; and Experimental aspects of adhesion testing: *Journal Oil & Colour Chemists Association*, Vol. 61 (1978) p. 292.

Present at the meeting were: J. H. Arendt, F. Bayersdorf, G. Christensen, D. T. Clark, L. Dulog, P. Fink-Jensen (Chairman), S. M. Kambanis, H. J. Kretschmar, H. J. Luthardt, J. A. W. van Laar, K. M. Oesterle, D. Pagani, J. Sickfeld, A. Toussaint, and U. Zorll (Secretary).

The preceding report was submitted by Milton A. Glaser, Chairman of the Federation's Liaison Committee.

For more information concerning the IUPAC's work in general, and the Supported Polymer Film Group in particular, contact Mr. Glaser at P.O. Box 7, Glencoe, Ill. 60022.



People

Richard W. Scott, Director of Analytical Research, Coatings, for the Sherwin-Williams Co., Chicago, Ill., was named the recipient of the 1979 Henry A. Gardner Award by the American Society for Testing and Materials (ASTM). Mr. Scott was cited for his competence in managing Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials, a unit of Committee D-1. A member of the Chicago Society, he is also coauthor of the soon-to-be-published book, *An Infrared Spectroscopy Atlas for the Coatings Industry* which contains a fundamental and comprehensive dissertation on the theory of IR, and qualitative and quantitative analysis.

William Grabowski has been appointed Division Vice-President of Materials Management for American Hoechst Corp. He will be in charge of the Corporate Distribution, Purchasing, Transportation, and Administrative Services departments of the firm, in Somerville, N.J.

Paul I. Prescott has been named Manager of Market Development of Freeport Kaolin Co., a division of Freeport Minerals Co., New York, N.Y. In his new position, he will be responsible for all marketing data including new product marketing research and development. Mr. Prescott is a member of the Southern Society for Coatings Technology.

The Chicago Society recently honored two of its Past-Presidents at their Annual Awards Night. **Thomas E. Nevins** and **Gus W. Leep** were both presented with Outstanding Service Awards. Included in the meeting was the introduction of seven members into the Society's 25-year club and three members into the 50-year club. In addition, **Wilbert B. Bartelt,** of Rust-Oleum Corp., succeeded **Walter J. Krason,** The Enterprise Co., as President of the Society.

The following were elected as 1980 Officers of the Division of Organic Coatings and Plastics Chemistry, American Chemical Society, at its recent meeting: Chairperson—**J.L. Gardon,** of M&T Chemicals, Inc.; Chairperson-Elect—**S.S. Labana,** of Ford Motor Co.; Vice-Chairperson—**R.H. Lalk,** of Dow Chemical; Treasurer—**Richard Mumma;** and Secretary—**M.J. Bowden.**

R.W. Scott

M.K. Yousuf

R.F. Jamrog

R.G. Boughton

M.K. Yousuf has been named Technical Manager, General Industrial Coatings, for Whittaker Corporation's Batavia Coatings and Chemicals Div., in Illinois. In his new position, Mr. Yousuf will be accountable for development in technical support of general industrial product coatings, including automotive, strippers, and wood finishes. He is a member of the Chicago Society for Coatings Technology.

The Automotive Group of Inmont Corp., New York, N.Y., has appointed **Robert F. Jamrog** Marketing Manager for General Motors finishes. He will be headquartered in Troy, Mich.

Two managerial appointments in the manufacturing and distribution areas at its automotive paint plant in Detroit have been announced by the Automotive Group of Inmont Corp. **Richard G. Simpson** has been named Manager of Manufacturing Services for the plant and **Edward J. Dzwonkowski, Jr.** has been appointed Superintendent of Distribution Services at the same location.

At the firm's automotive refinish paint plant at Grand Rapids, Mich., **Charles Magee** has been appointed Operations Manager. In his new position, he succeeds **Robert W. Jepson,** who is being transferred to another company management post at Akron, Ohio.

Inmont has also announced the appointments of **George B. Muir**—Market Manager of enamel products and **Ralph H. Zickefoose, Jr.**—Account Manager, Chrysler Corp. Both men are headquartered at the company's Troy, Mich. location.

Michael Bashir, of The Flecto Company, Inc., Oakland, Calif., has assumed the office of Executive Vice-President of the firm. Formerly with International Minerals Corp., Mr. Bashir is a member of the Chicago Society for Coatings Technology.

In a series of managerial appointments, the Petrochemicals Group, Union Chemicals Div., Union Oil Co. of Calif. has promoted **Frank M. Boka** to the position of Plant Manager, Kearny Industrial Plant; **Robert G. Boughton** to Senior Area Manager for the firm's South Chicago region; **Terrance M. Hanson** to the corresponding position of Senior Area Manager for Northern Chicago and; **Billy Morris** to Manager for the Michagen area.

Other regional managerial changes include the appointment of **Dennis E. Schendel** to Regional Commercial Development Manager and of **Ron A. Lawrence** to Account Supervisor for polymer emulsions, industrial polymer, and hot melt adhesives in the Chicago area.

The Freeman Chemical Corp., Port Washington, Wis., has named **R. Charles Ross** to the position of Vice-President and General Manager. In his new position, Mr. Ross will be responsible for the sales, production, technical, and purchasing divisions of the firm.

George E. Adams has been promoted to the position of Manager of Kerr-McGee Chemical Corporation's Hamilton, Miss. facilities. He will be responsible for operation of the company's pigment, parathion, and electrolytic plants at this site.

Also promoted was **B.J. Montgomery.** He will now serve as Manager of pigment and parathion plant services.

Dr. Arthur J. Yu has been appointed director of Development and Applications for Borden Chemical's Thermoplastic Div., Leominster, Mass. Dr. Yu is the author of several papers, technical book sections, and more than 70 U.S. and foreign patents dealing with plastics.

Hunter Associates Laboratory, Inc., Fairfax, Va., has named **William P. Burrows** West Coast Manager. Headquartered in Los Angeles, he will be working in close connection with Albright Associates, Hunterlab's Northwestern California representative.

Paul M. Dubanowitz will assume the responsibilities of Manager of the Reading, Mass. plant of GTR Coated Fabrics Co. His new duties will include all manufacturing and service operations at the plant.

Brian Garvey has been promoted to Manager of Sales and Marketing of industrial coatings for H.B. Fuller Co., St. Paul, Ill. In this capacity, he will be responsible for developing territories, hiring and training the sales force, and promoting the company's products.

Spencer-Kellogg Division of Textron, Inc. has promoted **James J. Rudnicki** to the position of Plant Manager at Buffalo, N.Y. and **William J. Dondarski** to Acting Plant Manager at Edgewater, N.J.

Jerome A. Seiner of PPG Industries, Inc. Allison Park, Pa., has been appointed Editor of *I & EC Product R/D,* a publication of the American Chemical Society. Associated with PPG Industries in various capacities since 1954, he was Associate Editor of the journal in 1978. Following the death of **Dr. Howard L. Gerhart,** Mr. Seiner assumed the duties of Editor. He is the third editor of the journal since its beginning in 1962.

A native of Pittsburgh, Seiner received the B.S. Degree in Chemical Engineering in 1954 and the B.S. in Industrial Management in 1960, both from Carnegie-Mellon University. Mr. Seiner presently serves as Manager of Consumer Products Research for PPG. He is a member of the Pittsburgh Society for Coatings Technology.

Also announced by the company was the promotion of **Dr. David T. McKeough** to the position of Research Associate in the Coatings and Resins Div. in Allison Park.

Phil Reitano has been named Technical Representative for Byk-Mallinckrodt, Melville, N.J. In this position, Mr. Reitano will serve the New York Metropolitan, New Jersey, and Eastern Pa. areas.

Obituary

Clarence H. Jocoy, Technical Manager of the Dixie Division of the O'Brien Corp. in Brunswick, Ga., died on August 21, following surgery for cancer. Employed in the paint industry all his adult life, Mr. Jocoy was a Past-President of the Southern Society for Coatings Technology. Prior to his association with the O'Brien Corp., he served as Technical Director for PPG Industries in East Point, Ga.; Springdale, Pa.; and Caracas, Venezuela.

Frank T. Schulte, 80, founder of Schulte Paint & Lacquer Co., died on Aug. 10 in St. Louis, Mo. Having served the coatings industry for over 50 years, he was active in the operation of the company until his death. Mr. Schulte was a member of the St. Louis Society for Coatings Technology.

George R. Somerville, Staff Research Chemist for Shell Development Co., died July 28 at his home in Houston, Texas. An active participant in various paint organizations, Mr. Somerville was a member of the Houston Society. He was 64 years old.

Literature

Computerized Spectrophotometer

Literature describing a computerized spectrophotometer with an advanced triple beam optical system has been recently published. For additional information, contact Diano Corp., 8 Commonwealth Ave., Woburn, Mass. 08101.

Multi-Angle Glossmeter

A new model multi-angle glossmeter, developed for standard laboratory measurements of gloss on surfaces at various gloss angles, is the subject of recently released literature. For additional information, contact Paul N. Gardner Co., P.O. Box 6633, Station 9, Fort Lauderdale, Fla. 33316.

Concentric Shaft Mixer

Information describing a new mixing lab is now available. Designed to perform complete laboratory evaluations, this unit produces a wide spectrum of mixing situations, including all types of high-speed dispersion, low-speed agitation, and homogenizing. To obtain a copy of the literature, contact James White, Hockmeyer Equipment Corp., 610 Worthington Ave., Harrison, N.J.

Thermal Analysis Application Study

A six-page application study describing the ASTM method for screening of potentially hazardous materials has been released. For a free copy of the Thermal Application Study, Order No. TAAS-28, write the Perkin-Elmer Corp., Instrument Div., Main Ave., Mail Station 12, Norwalk, Conn. 06856.

PVdC Emulsion

The advantages of polyvinylidene chloride (PVdC) high barrier coatings for packaging substrates are described in a new brochure. In addition to providing technical and marketing information, the brochure compares moisture, grease and oxygen barriers, heat sealability ranges, and the economics of various barrier packaging materials. For a copy of the brochure, or PVdC coating recommendations for any problem substrate, contact the Organics Chemicals Div., Industrial Chemicals Group, W.R. Grace & Co., 55 Hayden Ave., Lexington, Mass. 02173.

Signal Processor

Literature is now available which details the new features of a signal processor. Included in these is the permanent storage of 1000 product standards and tolerances, which eliminates the re-reading of the color standard each time differences are run. For additional information, contact HunterLab, Hunter Associates Laboratory, Inc., 9529 Lee Highway, Fairfax, Va. 22031.

Flocculating Agent

A new flocculating agent for latex paint waste water treatment is the subject of recently released literature. A polycationic polymer, this agent reportedly needs no extensive laboratory evaluation prior to use; it can be metered or pumped into the flocculating system, and does not require the use of sophisticated equipment. For detail sheet, contact George S. McTavey, VP-Sales, Cosan Chemical Corp., 400 Fourteenth St., Carlstadt, N.J. 07072.

"Today's Coatings and the Energy Supply"

Reprints of this National Paint and Coatings Association's (NPCA) brochure are now available. Designed to inform chemical coatings manufacturers' customers about the limited availability of petrochemicals and the impact this may have on coatings production, this bulletin may be obtained with a minimum order of 25 copies, for 35 cents. To order, write NPCA's Chemicals Coatings Div., 1500 Rhode Island Ave., Washington, D.C. 20005.

Color Cards

Information describing spectrophotometrically correct color cards is now available. These cards, the result of new technology combining a spectrophotometer and software, provide nonmetameric matches to all coatings products, in any gloss. For literature, write Sherwin-Williams Graphic Arts Div., 27254 Lorain Rd., North Olmsted, Ohio 44070.

Chemists and Chemical Engineer Register

The National Certification Commission in Chemistry and Chemical Engineering has issued its 1979 National Register of Certified Professional Chemists and Certified Chemical Engineers. It lists the names of 800 individuals who have been officially recognized for their participation in professional development and continuing education activities. Sample copies of the Register, provided free upon request to scientific and educational organizations, will be available for $5. For additional information, contact David A.H. Roethel, Executive Director, The American Institute of Chemists, 7315 Wisconsin Ave., Washington, D.C.

Phenoxy Resins for Adhesives

Phenoxy resins that can be used as adhesives without further chemical conversion, or used to modify other systems for enhanced properties, are discussed in a recently published 20-page booklet. Described as tough and ductile high molecular weight thermoplastics, these resins are thermally stable materials with a long shelf life. Solution viscosity, melt index ranges applications, physical properties, and compatibility of phenoxies with other resins are listed in the booklet in table form. "Bakelite Phenoxy Resins for Adhesives" is available from the Union Carbide Corp., Adhesives and Sealants Materials, Dept. JLS, 270 Park Ave., New York, N.Y. 10017.

Coating Thickness Gauges

A new range of portable "eddy-current" digital coating thickness gauges, now available in the U.S., is the subject of recently released literature. Additional information can be obtained by contacting Frank Rueter, Zormco Electronics Corp., 8520 Garfield Blvd., Dept H-8, Cleveland, Ohio 44125.

Scratch Hardness Tester

Literature is now available describing a new scratch hardness tester which established a standard repeatable procedure for determining the "scratch resistance" of a single or multi-layer coating. For more information, contact Frank Rueter, Zormco Electronics Corp., Dept. E-5, 8520 Garfield Blvd., Cleveland, Ohio 44125.

New Products Guide

A revised chemicals and resins product guide is now available. This booklet, which highlights special products such as bromine and brominated compounds, plasticizers, and aromatic chemicals derived from benzoic acid, can be obtained from Marketing Services, Chemicals and Resins, Velsicol Chemical Corp., 341 East Ohio St., Chicago, Ill. 60611.

Zinc Dust

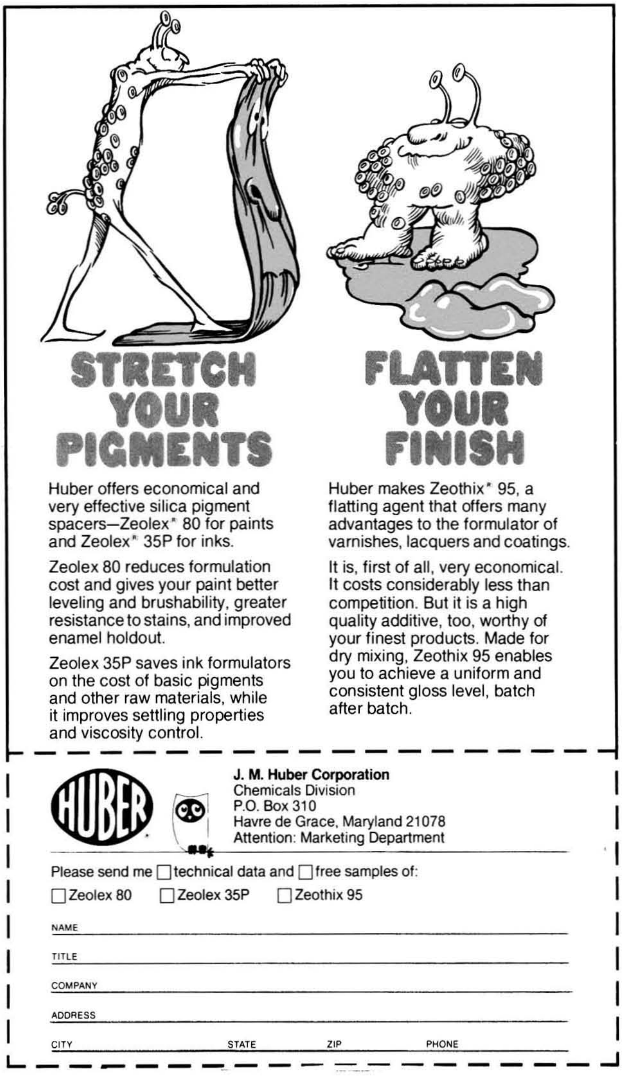
A new brochure describes the physical and chemical properties, as well as particle size distribution, for grades of zinc dust. Also provided are a flow sheet of the plant which produces zinc dust and illustrations of production and quality control facilities. Copies of the brochure are available from St. Joe Zinc Co., Chemical Sales, Two Oliver Plaza, Pittsburgh, Pa. 15222.

Computer Color Control System

Literature which describes a new color control system for computer color matching and correction is now available. This system is equipped with a video terminal, a disk drive system for increased mass storage capacity, and a high speed printer which can function as a back-up to the video terminal. For more information, contact Applied Color Systems, Inc., P.O. Box 5800, Princeton, N.J. 08540.

Flatting Agent

Information is now available which describes the expanded production capabilities of a flatting agent offering efficient flatting properties and high Hegman values for high quality finishes. For a copy of Data Sheet FF-384 write Carol Ebert, Filtration and Minerals Div., Johns-Manville, Ken-Caryl Ranch, Denver, Colo. 80217.



Letters to the Editor

Water Vapor Permeation Article Prompts Reinterpretation of Data

TO THE EDITOR:

The recent article by Messrs. Yaseen and Ashton (JCT October 1978, pp. 50–59) provided a most interesting and informative discussion on the effect of relative humidity and temperature on permeability and its relation to durability. They are certainly to be commended for their paper as not much work has been carried out on permeability of organic coatings and its change with temperature and relative humidity.

However, I would like to point out the shortcomings of their theoretical discussions. Most experimentalists like Yaseen and Ashton (concerned with permeation) have failed to distinguish between the permeation flux obtained in the laboratory and the diffusion flux. This has led them to misinterpret Fickian behaviour. To be more specific, the line, "Hence, water permeation through polymers *departs from* Fickian behaviour with changes in concentration of vapour pressure," which occurs in the last paragraph under the "Theoretical" sub-heading, is a misinterpretation of Fickean behaviour not only by Yaseen and Ashton but by most experimentalists in the past. Hence, the purpose of my clarification is to provide the right interpretation of permeation data through membranes.

Consider the transport equation:

$$N_t = -D \frac{dC_A}{dX} - \frac{D}{2C_M} \frac{dC_A^2}{dX} \qquad (1)$$

where N — Total flux (g mol/cm² sec)
D — Diffusivity (cm²/sec)
C — Concentration (g mol/cc)
X — Distance (cms)
$_t$ — total
$_A$ — Component A
$_M$ — Membrane

The above equation is developed for all types of membrane transport and provides the right correlation of permeation data. This is due to the fact that it takes into account bulk flow which previous experimentalists were neglecting.

The permeation flux N_t in equation (1) is the sum of the diffusion flux and the flux due to bulk flow (represented by the 2nd term).

Yaseen and Ashton have failed to recognize the bulk flow and hence interpreted the permeation flux N_t to be the diffusion flux J_A as in the equation below.

$$N_t = J_A = -D \frac{dC_A}{dX} \qquad (2)$$

In some systems, where the permeation flux is small, the above approximation could be considered but it is wrong in principle. Thus, in general, all experimentally obtained permeation data should be correlated by using equation (1) and not equation (2). The difference between equation (1) and equation (2) is the second term which is second order with respect to C_A. Hence, there is a non-linear relationship between the concentration gradient and the experimentally observed permeation flux. However, the system still obeys Fickean diffusion. Therefore, the correct transport equation should be equation (1) for all types of diffusion.

For further clarification, based on experimental evidences, the authors could refer to the book "Membranes in Separations," Vol. 7, by S.T. Hwang and K. Kammermeyer, and this writer's M.S. (Dept. of Materials & Chemical Engineering, U. of Iowa, 1977) dissertation thesis titled "Correct Calculation of Diffusivity from Membrane Permeation Data." The library services of the University of Iowa could be contacted for the above thesis.

I hope the authors will find the above clarification of use with respect to future experimentation.

M.A. MERCHANT
Bombay Paints
and Allied Products Ltd.
Bombay, India

Book Review

CONTROLLED RELEASE POLYMERIC FORMULATIONS

Edited by
D.R. Paul
and
F.W. Harris
American Chemical Society
Washington, D.C.
1976 (317 pages)
$20.00

Reviewed by
K.L. Mittal
International Business
Machines Corp.
Hopewell Junction, N.Y.

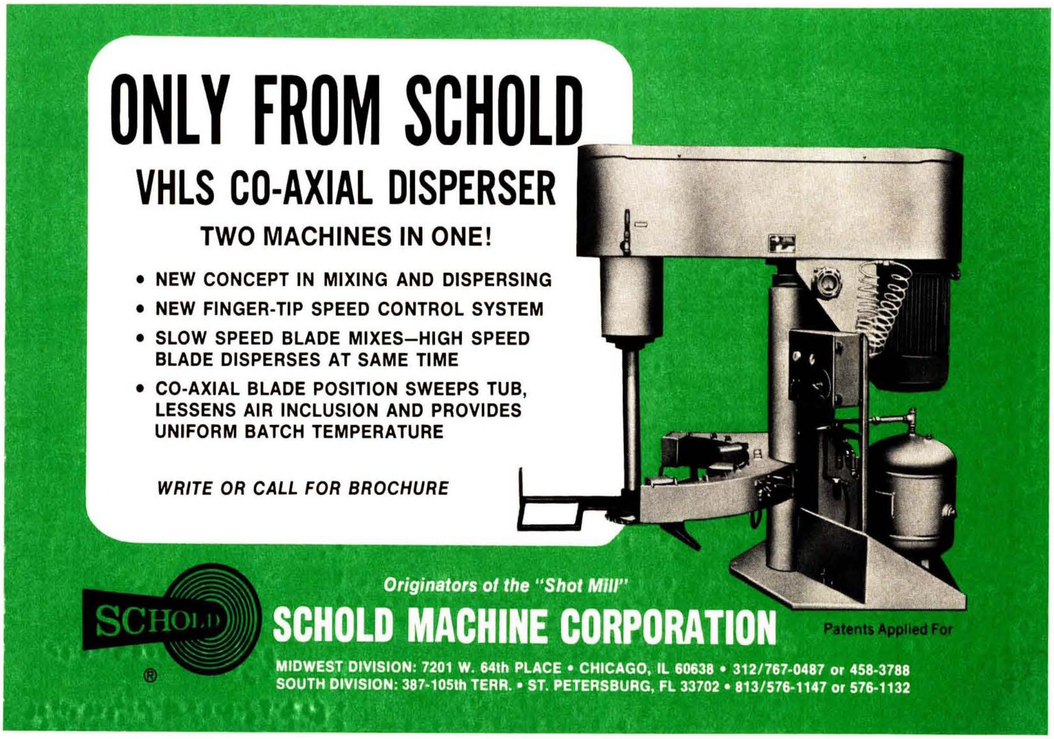
The contents of this book are based on 25 of the 28 papers presented at a symposium on controlled release, which was sponsored by the Division of Organic Coatings and Plastics Chemistry and the Division of Polymer Chemistry at the 171st Meeting of the American Chemical Society, New York, April 7-9, 1976.

There are many situations in which a controlled release of an active agent is preferred over the conventional method of administering it. Through the controlled release method, the active agent is administered at a rate which maintains its concentration within optimum limits and which directs the agent to the target area. The book emphasizes the role of the polymer as a rate controlling device, container, or carrier for the agent to be released. Selection of the appropriate polymer involves consideration of several elements and these are discussed.

A wide variety of applications and types of devices are considered in this volume. For example, medical applications which are discussed range from contraception to fluoride for dental purposes. A number of papers cover the control of pests through the release of toxicants or pheromones. The types of devices examined include devices that erode, membrane encapsulated reservoir devices, matrix devices, and reservoir devices without a membrane.

In addition to the 25 papers presented at the symposium, an additional opening paper by one of the editors (DRP) makes very interesting reading and it should be particularly valuable to those uninitiated in controlled release technology.

This book consists of a good collection of papers and it brings out, clearly, the latest activities in the field of controlled release technology and the importance of polymers in this technology. It is a valuable addition to the controlled release literature.



Coming Events

FEDERATION MEETINGS

1980

(May 15-17)—Federation Spring Meetings. Society Officers—15th; Executive Committee—16th; Board of Directors—16th and 17th. North Star Inn, Minneapolis, Minn. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, Pa. 19107).

(Oct. 28)—Federation Board of Directors Meeting. Atlanta Hilton Hotel, Atlanta, Ga. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, Pa. 19107).

(Oct. 29-31)—58th Annual Meeting and 45th Paint Industries' Show. Atlanta Civic Center, Atlanta, Ga. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, Pa. 19107).

SPECIAL SOCIETY MEETINGS

1980

(Mar. 10-12)—Seventh Annual Water-Borne and Higher-Solids Coatings Symposium. Hyatt Regency Hotel, New Orleans, La. Sponsored by Southern Society and University of Southern Mississippi. (Dr. George Bufkin, Dept. of Polymer Science, University of Southern Mississippi, Southern Station, Box 276, Hattiesburg, Miss. 39401).

(Mar. 12-14)—Southern Society. 44th Annual Meeting and Convention. Terrace Garden Inn, Atlanta, Ga.

(April 14-16)—Dallas and Houston Societies. Southwestern Paint Convention, Hilton Inn, Dallas, Tex.

(May 1-3)—Pacific Northwest Society Annual Symposium. Marriott Hotel, Portland, Ore.

1981

(Mar. 4-6)—Western Coatings Societies Symposium and Show. Disneyland Hotel, Anaheim, Ca.

OTHER ORGANIZATIONS

(Nov. 6-7)—Institute of Applied Technology, Mini Course, "The Specification Document: Key to Quality Coating Work." Dallas, Tex. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(Nov. 6-8)—Society of Plastics Engineers, National Technical Conference, "Plastics: The Answer to Transportation in the 80's." Detroit Plaza Hotel, Detroit, Mich. (Eugene E. Wilson, SPE, 656 W. Putnam Ave., Greenwich, Conn. 06830).

(Nov. 7-8)—2nd Resins and Pigments Exhibition. Royal Hotel, Copenhagen, Denmark. (Mike McIntyre, International Symposia & Exhibitions Ltd., Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS, England).

(Nov. 16-18)—Annual National Decorating Products Association Convention and Show. McCormick Place, Chicago, Ill. (NDPA, 9334 Dielman Industrial Dr., St. Louis, Mo. 63132).

(Nov. 20-21)—Institute of Applied Technology, Mini Course, "Estimating, Planning, and Scheduling Painting." Chicago, Ill. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(Dec. 3-7)—Institute of Applied Technology, Training Course, "Nuclear Quality-Assured Coating Work." Miami, Fla. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington D.C. 20006).

1980

(Feb. 4-6)—Inter-Society Color Council. Williamsburg Conference, Williamsburg, Va. (Dr. Fred W. Billmeyer, Secretary, ISCC, Rensselaer Polytechnic Institute, Troy, N.Y. 12181).

Coming Events (Continued)

(Mar. 3-7)—"CORROSION/80," sponsored by National Association of Corrosion Engineers. Palmer House, Chicago, Ill. (Membership Services Dept., NACE Headquarters, P.O. Box 986, Katy, Tex. 77450).

(Mar. 4-6)—National Association of Corrosion Engineers. Materials Performance and Corrosion Show. Palmer House, Chicago, Ill. (NACE, P.O. Box 986, Katy, Tex. 77450).

(Mar. 23-28)—Div. of Organic Coatings and Plastics Chemistry Symposiums and Spring Meeting of American Chemical Society. Houston, Texas. (American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036).

(April 20-22)—Inter-Society Color Council. Annual meeting. Downtown Holiday Inn, Rochester, N.Y. (Dr. Fred Billmeyer, Secretary, ISCC, Rensselaer Polytechnic Institute, Troy, N.Y. 12181).

(May 5-8)—Society of Plastics Engineers, 38th Annual Technical Conference (ANTEC). New York Hilton, N.Y. (Rod Ellis, SPE, 656 W. Putnam Ave., Greenwich, Conn. 06830).

(June 5-6)—The Metals Society, International Conference, "Production and Use of Coil-Coated Strip." Metropole Hotel/National Exhibtion Centre, Birmingham England. (T.L. Hughes, The Metals Society, 1 Carlton House Terrance, London SW1Y 5DB).

(June 8-13)—XVth Congress of FATIPEC. RAI Congress Centre, Amsterdam, Netherlands. "Activities of the Coatings Industry in the Framework of Ecology, Energy, and Economy Problems." (Congress Secretary is C. Kork, Oostenrijklaan 43, Haarlem, Nethlands).

(June 15-18)—Dry Color Manufacturers' Association Annual Meeting, The Greenbriar, White Sulpher Springs, W.Va. (J.L. Robinson, Dry Color Manufacturers' Association, Suite 100, 117 North 19th St., Arlington (Rosslyn) Va. 22209).

(Oct. 13-15)—Society of Plastics Engineers National Technical Conference, "Coloring of Plastics; Update of 'The Law and You'." RETEC sponsored by the Baltimore Section and Color and Appearance Div. Baltimore Hilton Hotel, Baltimore, Md. (Robert C. Foley, Society of Plastics Engineers, 656 W. Putnam Ave., Greenwich, Conn. 06830).

ATLANTA
1980

FSCT

58TH ANNUAL MEETING
AND 45TH PAINT
INDUSTRIES' SHOW
ATLANTA CIVIC CENTER

• OCTOBER 29, 30, 31 •

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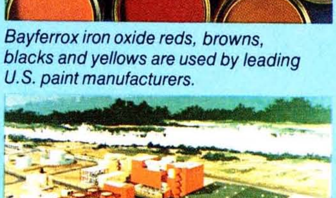

Free paint additives kit from Dow Corning helps you paint your world.

The proof is in the painting.

Dow Corning® silicone paint additives solve an exciting variety of paint problems. In a fantasy world. And in the real world. For example, problems such as foaming, nonwetting, orange peel, and pigment separation will disappear when you add silicone paint additives to your paint formulations. And the qualities your customers look for in paints—such as gloss, slip and adhesion—will improve with the help of silicone paint additives.

When you send for your free paint additives kit you'll see, for example, how a few drops of paint additive 3 prevent pigment separation. And help keep a castle or house evenly colored from top to bottom. Paint additives 11, 14, 56, and 57 improve flow-out and mar resistance. Which makes them great for train cars, automotive, and airplane finishes.

You'll see how paint additive 7 decreases foaming in solvent-based systems. And how paint additive 21 improves adhesion and salt-spray resistance of epoxy coatings—perfect for docks and boat hulls. In all, there are seven silicone additives to help you solve your paint problems.

Dow Corning silicone paint additives make it easy to solve problems in your world. The proof is in our free paint additives kit. Just write us on your letterhead and ask for a paint additives kit of your own. Send to:

Dow Corning Corporation, Dept. C-8580,
Midland, Mich. 48640.

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