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Basic Research

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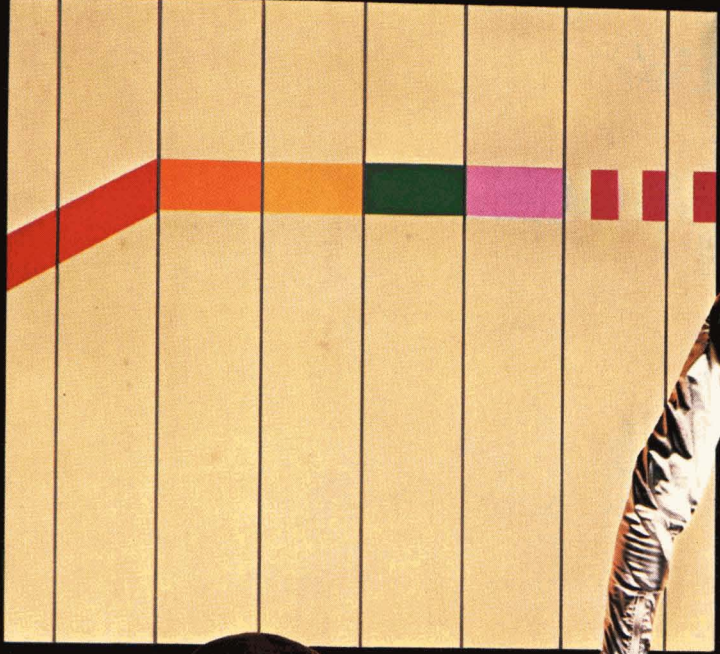
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In fact, we expect the coatings industry's demand for oxygenated solvents to remain in excess of 2,000,000,000 pounds a year through 1980. That's big business. And we're committed to it.

Today, these exempt solvents provide an economical and efficient answer to environmental controls. Coatings of the future —like High Solids and Water-borne—will continue to depend on these same oxygenated solvents.

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Our commitment to oxygenated solvents is a major factor in making us the leading supplier to the industry. And we intend to continue providing both our technical assistance and our broad line of products.

You see, we expect the commitments we make today to make very good history tomorrow.

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save money four ways!"

1. Saves on environmental expenditures — *SUP-R-CONC* pigments are *dustless,* and because of this critically important feature you may avoid many costly and troublesome occupational safety and health problems.

2. Saves on capital equipment — you don't have to invest in costly new capital equipment to expand your production since *SUP-R-CONC* pigments can be processed on your *existing* popularly-used dispersion machinery.

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4. Saves time — *SUP-R-CONC* pigments require less time to achieve higher tinctorial value; cleaner, more rapid color development and more uniform particle size . . . you produce tinctorially stronger finished products *faster.*

Stop using dry colors and save
If you aren't interested in saving money, you can continue to use old-fashioned dry colors . . . but you really owe it to yourself and your company to try uniquely different *SUP-R-CONC* pigments. Ask yourself why you should continue using hard-to-disperse dry colors that can cause dusting in your plant when *SUP-R-CONC* will help you avoid such problems. Your job is making a quality finished product at the lowest possible cost. Our job — and a way of life at Hilton-Davis — is to find innovative ways to provide you colorants that are easier, safe and more economical to use.

Complete coupon and mail today to get your free SUP-R-CONC pigment testing samples.

"SUP-R-CONC colorants are easier to use than dry colors. Let's switch!"

Conversations such as this are occurring in numerous companies throughout the country today. By now, well informed color technologists have thoroughly tested and evaluated *SUP-R-CONC*, the super concentrated, non-dusting, free flowing, water dispersible pigment from Hilton-Davis. And, because results have been consistently favorable, *SUP-R-CONC* pigments are being used extensively.

Economy is big factor
Saving money is unquestionably on everyone's mind in these highly inflationary times, and this is encouraging the changeover to easy-to-use, *SUP-R-CONC* pigments. This is one switch that *saves* rather than costs money . . . in *all* these different ways:

Welcome to Philadelphia

The Federation office joins the Philadelphia Convention and Visitors Bureau in inviting Federation members everywhere to the City of Brotherly Love during this Bicentennial Year.

The city is about ready for the anticipated 15 million visitors. The Liberty Bell has been moved 200 feet (from Independence Hall) where it will be more visible. Elfreth's Alley is sprucing up. Franklin Institute and other museums and art institutes will be chock full of American history. Chestnut Street has been made a "transitway" so that visitors will not have to contend with downtown traffic.

It is too bad that products of the paint industry are not sharing more in the celebration here. New paint jobs — based on what can be seen in center city — are not very evident. There are no patriotically-painted fireplugs and no "City Walls."

Food color and printing ink manufacturers, however, are faring pretty well because everything being sold in the shops, it seems, is either packaged in Bicentennial colors or is affixed with a "76" label.

It would not surprise anyone if the famous Philadelphia soft pretzel becomes red and white and is served with blue mustard. Someone is marketing scrapple-molds of Ben Franklin.

Even the City Fathers, not to be outdone, are planning special Bicentennial "treats" for tourists: increases in taxes on hotel rooms, meals, amusements, alcoholic beverages, and parking.

In spite of all this commercial and political hoopla, there is a lot of history to show you here, and the warm and wonderful people of "Delaware Valley U. S. A." welcome you with a promise that your visit will be a memorable one.

The Federation office is located at 1315 Walnut St. in the center of the city (about six blocks from the Liberty Bell and two blocks from the sky-high statue of Billy Penn atop City Hall). Come on in and say hello.—FJB

AMSCO *is doing* *great things* *with polymers . . .*

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Versatile AMSCO-RES® polymer emulsions are real economizers. They'll help you stretch your compounding capabilities and still hold the line on raw material costs. You can count on AMSCO-RES polymers to optimize the properties you want in any paint product—interior or exterior, flat or semi-gloss, standard paint or specialty coating. And you can hold a target price point and still maintain high product quality. For proof, take a look at some of the starter formulas developed by AMSCO and Union Oil Research. Their "bottom lines" show some very interesting RMC's.

We're in great shape to fill your orders; we have recently doubled the capacity of our polymer plants. And we're always ready to help with test samples, product data, and technical help if you need it.

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You're the director . . . tell us what you want!

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bead which is directly interchangeable with sand.
Same specific gravity, same size range.

We make no silly claims. It won't double your
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Chalk adhesion plus economy

Fewer manufacturing problems—Rhoplex AC-64 acrylic emulsion provides outstanding adhesion to weathered chalky substrates. With Rhoplex AC-64, you can formulate latex exterior paints without alkyd or oil modification . . . and thereby eliminate many manufacturing and performance problems caused by oleoresinous additives—stability, color acceptance, color drift, durability, mildew resistance. When used as the sole vehicle, Rhoplex AC-64 provides exceptional flow, leveling, and film build, plus the excellent weatherability typical of Rhoplex all-acrylic polymers.

Most for your money—Rhoplex AC-64 offers attractive cost/performance. It can be formulated into a broad range of paints . . . from quality-economy to the highest quality.

Makes exterior and interior paints—Consolidating with a multi-purpose vehicle offers savings through bulk purchasing plus simplified storage and handling. The high solids (60%) of Rhoplex AC-64 allows wide formulating latitude.

Write for a sample of Rhoplex AC-64 and technical literature.

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AC-64

Abstracts of Papers in This Issue

SELECTED APPLICATIONS OF ELECTRO-CHEMICAL ANALYSIS IN THE COATINGS INDUSTRY—D. R. Brezinski

Journal of Coatings Technology, 48, No. 613, 42 (Feb. 1976)

The application of electrochemical analysis to the coatings industry is discussed with particular emphasis given to polarography and modern voltammetric techniques. Because modern voltammetry is new in its application to the industry, the theory is briefly discussed and examples included for purposes of illustration. The techniques offer high sensitivity and versatility as they are applicable to both trace metal and organic functional group analysis.

COLOR AND APPEARANCE OF METALLIZED PAINT FILMS II. INITIAL APPLICATION OF TURBID-MEDIUM THEORY—F. W. Billmeyer, Jr. and E. C. Carter

Journal of Coatings Technology, 48, No. 613, 53 (Feb. 1976)

Despite the preliminary nature of this initial application of turbid-medium theory to metallized paint films, certain trends became apparent. This report presents guidelines and recommendations. Preferred conditions include collimated illumination along the normal to the sample and collimated viewing at two angles, one within and one far outside the specular envelope. (These conditions require use of equipment not commercially available in the U.S.) A many-flux calculation using approximately twelve fluxes is required. Preliminary results are encouraging, and ultimate extension to computer formulation in metallic systems should be straightforward though complex. Future theoretical research, as specified, should be centered on pigment and sample characterization and application of the many-flux theory.

RULE 66 — AFTER EIGHT YEARS—Los Angeles Society for Coatings Technology

Journal of Coatings Technology, 48, No. 613, 61 (Feb. 1976)

A review of Los Angeles County Air Pollution Control District's Rule 66 shows that it has grown through amendments and additions.

Predicted costs were measured against actual costs, which were found to be relatively close to the predictions. These costs were less than the cost of inflation. Surveys were made of emissions histories of some counties adjacent to Los Angeles County. These surveys showed that definite improvements have been made on the part of industry in the control of organic emissions. Conversely, there has been an increase of emissions from mobile sources, particularly gasoline-powered engines.

Papers to be Published in Future Issues

"Use of SEM/EDXA in Characterizing Water-Based Surface Treatments for Wood" — R. L. Desai and W. A. Cote, Jr., of College of Environmental Science and Forestry.

"Solvent Flash Points—Expected and Unexpected" — W. H. Ellis, of Chevron Research Co.

"Single Pigment Paints" — Philadelphia Society for Coatings Technology.

"Quick Method for Optimizing Protective Coatings"—J. Rybicky and J. P. Marton, of Welwyn Canada Ltd.

"New Class of Conductive Extenders in Zinc-Rich Coatings" — F. A. Simko, Jr. and U. P. Simpson, of Hooker Chemicals & Plastics Corp.

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Report of By-Laws Committee

The following amendment is to be acted upon at the Federation Council Meeting in Toronto, on May 14, 1976.

ARTICLE X
DUES

WHEREAS the Board of Directors has requested an increase in the member dues because of increasing costs of operation, be it

RESOLVED THAT Article X, A, which fixes annual dues at ten dollars ($10.00) per capita be amended to read:

"Each constituent Society shall pay to the Federation office annual dues of fifteen dollars ($15.00) per capita for each Active, Associate and Society Honorary Member of the Constituent Society."

The balance of Article X is to remain unchanged.

Comment of the By-Laws Committee

The following valid points have been raised by the Board of Directors:

(1) Dues were raised from $5.00 to $10.00 in 1971, and since that time the Federation's costs of operation have escalated.

(2) The operating budget of the Federation has gone from $538,000, in 1971 to $648,000, in 1976.

(3) Since 1971, JCT advertising rates have increased three times; paint show exhibit rates three times; and Year Book and Paint Show Program Book advertising twice.

(4) If the Federation is to continue its various services to members and the industry, then membership must share a part of the increasing costs of operation.

The By-Laws Committee endorses this resolution.

HOWARD JEROME, *Chairman*
By-Laws Committee

Book Review

POLYMER MOLECULAR WEIGHTS

Edited by Philip E. Slade, Jr.
Marcel Dekker, Inc.
270 Madison Ave.,
New York, N. Y. 10016
1975 (623 pages)

Reviewed by
John. L. Wuepper
Whirlpool Corp.
Benton Harbor, Mich.

This is the fourth volume (in two parts) of a four-volume series entitled, "Techniques and Methods of Polymer Evaluation." This text is a detailed practical survey of current methods used to determine molecular weights.

A brief preliminary discussion of the various molecular weight definitions and molecular weight distributions is followed by chapters on membrane osmometry, end group determinations, absolute colligative property methods, light scattering, gel permeation chromatography, viscometric methods and sedimentation techniques. Each chapter is nicely balanced between theory, definitions, instrument or equipment descriptions, data treatment, and applications. A valuable list of references follows each chapter, and a cumulative author index and subject index are included at the end of the second part. One definite advantage of the book is that it gives the reader a comprehensive and current discussion of the various molecular weight measurement techniques in one place. This makes it easy to study all the techniques together and encourages a better understanding of the meaning of molecular weight moment data as obtained by different methods. The presentation is one that should appeal to chemists in research and development, educators (good topics course text), and students in polymer and analytical-physical chemistry. The text is a practical one.

The chapter on gel permeation chromatography is typical. The first section on theory describes size separations, chromatographic efficiency, calibration and data reduction. This is followed by a detailed description of instrument construction from injection valves and column construction to detectors. Miscellaneous topics such as sample preparation, solvent choice, maintenance and preparative GPC, and others are covered briefly.

The lack of editorial and author comment on relationships between polymer end use and molecular weights and molecular weight distribution is somewhat disappointing. While the omission of this topic may have been intentional, it is the reason for which many careful molecular weight determinations are most often made. The editor hints at the importance of such relationships in his preface; however, little else is mentioned about the subject throughout the two volumes. This gap is bridged, to some extent, in the chapter on gel permeation by the inclusion of a represenative list of "applications" with corresponding references. This list contains approximately 130 applications and references for each.

In any case, the strong points of this work far outweigh any weaknesses, and these two volumes should find good use by many investigators in the field of polymer evaluation.

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that equals or better

40 PVC OIL ALKYD 1:1 PRIMER

NALZIN™ SC-1   Calcium boro-silicate

2 YRS. ATMOSPHERIC EXPOSURE
(45° South, Hightstown, N.J.)
Corrosion-Inhibitive Pigments:
    Equal weight (0.85 lbs./gal.)
Substrate: Hot rolled steel, sandblasted
Application: Brush
No. of Coats: 1 coat primer overall
    2nd coat over upper half
Total Film Thickness:
    Upper half—3.0 mils (dry)
    Lower half—1.5 mils (dry)

NALZIN™ SC-1   Calcium boro-silicate

2 YEARS MARINE EXPOSURE
(45° South, Ocean City, N.J.)
Corrosion-Inhibitive Pigments:
    Equal weight (0.85 lbs./gal.)
Substrate:
    Hot rolled steel, sandblasted
Application: Brush
No. of Coats: 2 self-primed
Total Film Thickness: 4 mils (dry)

NALZIN™ SC-1   Calcium boro-silicate

340 HOURS SALT FOG
(ASTM Test B117-64)
Corrosion-Inhibitive Pigments:
    Equal cost (formulated
    to constant PVC)
Substrate: Phosphated steel
Application: Brush
No. of Coats: 1
Total Film Thickness: 2 mils (dry)

30 PVC STYRENE ACRYLIC LATEX PRIMER

NALZIN™ SC-1   Zinc-calcium molybdate

9 MOS. ATMOSPHERIC EXPOSURE
(45° South, Hightstown, N.J.)
Corrosion-Inhibitive Pigments:
    Equal weight (1.0 lbs./gal.)
Substrate:
    Hot rolled steel, sandblasted
Application: Brush
No. of Coats: 2 self-primed
Total Film Thickness: 3.0 mils (dry)

NALZIN™ SC-1   Zinc-calcium molybdate

44 DAYS MARINE EXPOSURE
(45° South, Ocean City, N.J.)
Corrosion-Inhibitive Pigments:
    Equal weight (1.0 lbs./gal.)
Substrate:
    Hot rolled steel, sandblasted
Application: Brush
No. of Coats: 2 self-primed
Total Film Thickness: 3.0 mils (dry)

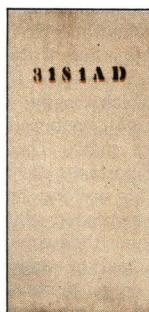NALZIN™ SC-1   Zinc-calcium molybdate

350 HOURS SALT FOG
(ASTM Test B117-64)
Corrosion-Inhibitive Pigments:
    Equal cost (formulat+
    to constant PVC)
Substrate: Phosphated steel
Application: Brush
No. of Coats: 2
Total Film Thickness: 2 mils (dry)

News from Washington

HM-102 Compliance Became Mandatory on January 1

Docket HM-102, *Flammable, Combustible, and Pyrophoric Liquids, Definitions*, took effect on January 1, 1976, and involves some of the most sweeping changes in requirements for shipping hazardous materials that the industry has experienced.

Much confusion has been generated over the terms and applications of the new requirements, and the National Paint and Coatings Association has issued some general comments in an attempt to answer some frequently asked questions.

Basically, HM-102 includes three major changes: (1) Flammable Liquid category is expanded to include those materials flashing below 100°F; (2) New category of hazard, identified as Combustible Liquid, is created; (3) Closed-cup test method is required for testing for flash point.

NPCA's Legal Division says part of the confusion with HM-102 stems from the attempt to read this amendment in the abstract, without reference to the complete text of the Department of Transportation's Hazardous Materials Regulations (HMR). Reading the amendment out of context can be misleading. Docket HM-102 is significant to paint and coatings shippers for what it does *not* do. It does not alter the traditional exemption for Paints and Related Materials of containers with a capacity of five gallons and less in Section 173.128(c) of the HMR.

The exemption for Combustible Liquids should be mentioned first, in the interest of clarity. Section 173.118 (e) of HM-102 states, "The requirements for this subchapter do not apply to combustible liquids in packaging having capacities of 110 gallons or less."

This means there are no requirements imposed for shipping Combustible Liquids packaged in such quantities. There is no need to worry about specification packaging, marking, labeling, or bill of lading entries. When portable tanks containing Combustible Liquids with a capacity of over 110 gallons are shipped, the shipper must ensure that the container meets specifications, is properly marked, and the appropriate entry is made on the bill of lading.

However, the expanded Flammable Liquid category is more complicated. It is essential to remember that the Section 173.128, "Paint and Related Materials" exemption, traditionally available in the existing Hazardous Materials Regulations, *is still available*. The exemptions, mentioned in Section 173.118(a) of HM-102, are not particularly attractive to paint and coatings shippers, because the same exemptions have always been available through Section 173.128 of the HMR, regardless of the 73°F breakpoint.

HM-102's Section 173.118(b) does, nevertheless, contain a specification packaging exemption available at the shipper's option. Shippers in our industry are concerned with this section only when shipping in containers of over five gallons, since Section 173.128(c) of the HMR provides broader relief for shipment of containers with a capacity of five gallons or less.

Section 173.118(b) of HM-102 states that shippers do not need to use a DOT specification container (for example, a 55-gallon drum) if two conditions are met. First, the material going into the container must flash at 73°F or higher; second, the outside of the container must be marked "Flashes at 73°F or higher" (or similar wording). This exemption is limited to *packaging only*. Shippers must still label and mark, as well as enter the appropriate notation on the bill of lading.

The Seta Flash Test Method has been approved by DOT as an alternative to the Pensky-Martens Closed Cup Test Method of testing for flash point.

It bears repeating that an understanding of the Docket HM-102 is not possible unless the DOT Hazardous Materials Regulations are understood in their entirety. Accordingly, every shipper should have a full text of the Regulations for ready reference.

NPCA recommends *Graziano's Tariff No. 30*, available from Bureau of Explosives, Association of American Railroads, Washington, D. C. 20036. Price is $18 for the looseleaf copy; this is supplemented as the Regulations are amended.

NPCA Comments on OSHA Proposed Lead Standard

In recent comments to the Occupational Safety and Health Administration, the National Paint and Coatings Association stated that many of the requirements in the proposed standard for lead are "unnecessary and unduly restrictive" since they do not take into account employee exposures on a limited and infrequent scale.

NPCA submitted its comments on January 16, in response to an OSHA proposal to set new job health standards for worker exposure to lead. The standard reduces the permissible exposure from 200 micrograms to 100 micrograms of lead per cu m of air, averaged over an 8-hr period. Employers would be required to determine whether employee exposures exceed an "action level" of 50 micrograms per cu m of air. Exposures above that level would require employers to measure lead exposures regularly and to notify workers of the results. The lead standard was proposed in the October 3, 1975 *Federal Register*, along with standards for toluene and asbestos, and 11 other chemicals.

NPCA explained that a worker in the paint and coatings industry most likely to be exposed to airborne concentrations of lead will handle many different materials in one day. The possibility of exposure to lead materials would not exist on a continuous 8-hr day, 40-hr week basis. "Exposure would exist only during the brief period when the lead pigment is being added to the batch (of paint)," NPCA said.

The Association added that these varied, short periods of exposure should not be lumped into the general industrial uses of lead and its compounds. "Regulations issued by OSHA must be responsive to these uses and should not impose unnecessary and inappropriate restrictions."

In other areas, NPCA stated that the establishment of one standard for lead does not take into account the many and varied lead compounds used in the paint and coatings industry. "There appears to be no valid reason to lump short term exposure to relatively unsoluble paint pigments of lead . . . with fumes from molten lead and other hazardous lead sources," NPCA said.

The action level concept of arbitrarily halving the known exposure limit value was again objected to by the Association, who also commented on: the proposed requirements to maintain airborne lead concentrations for a year and to conduct air monitoring in certain occupations, the proposed restrictions on respirator usage, and the training and information requirements.

Federal Trade Commission Issues Rules on Warranties

By unanimous vote, the Federal Trade Commission has issued three rules under the Magnuson-Moss Warranty Act.

Requirements are established for (1) Disclosure of written warranty terms; (2) Pre-sale availability of such warranties; (3) Minimum requirements for informal dispute settlement mechanisms. The first two rules will go into effect January 1, 1977; the third rule becomes effective on July 4, 1976.

Each of the rules were modified in various respects following public hearings and numerous written comments received on the proposed versions, published on July 16, 1975.

The original proposed rule on disclosure has been simplified in its final form. It applies to written warranties on consumer products actually costing the consumer more than $15 (increased from $5 in the proposed rule). The warrantor must disclose "in simple and readily understood language" the following items of information, among others: (1) What is covered by and, where necessary for clarification, is excluded from the warranty; (2) What the warrantor will do in the event of a defect, malfunction, or failure to conform with the written warranty, including a statement of what items or services will be paid for or provided by the warrantor and, where necessary for clarification, those that will not be; (3) Step-by-step explanation of what the purchaser should do to get the warranty honored.

Commenting on the disclosure rule, the FTC said, "A requirement of uniformity in warranty disclosures should enable consumers to make valid and informed comparisons of warranties for similar products, and insofar as their purchasing decisions are influenced by such comparisons, better able to make educated buying choices."

This rule, said the Commission, provides the seller with four alternative means by which warranties can be made available to prospective buyers prior to sale. The seller, at a minimum, must employ one of the means cited, but may use any additional means desired.

The rule governing informal dispute settlement mechanisms sets forth the duties of a warrantor who elects to incorporate such a mechanism in the terms of a warranty; and establishes the minimum operational requirements for, among other things, staffing, investigative procedures, time limits, record keeping, audit, and confidentiality.

Update on Toxic Substances Act

The on again-off again consideration by Congress of proposed legislation to control toxic substances is once again in the news. The National Paint and Coatings Association is monitoring progress of current bills in the House and Senate and has reported its assessment of proposed legislation.

The U.S. Congress is again actively considering proposed toxic substances control legislation which would empower the Environmental Protection Agency to regulate industrial use of chemicals and prevent dangerous substances from reaching the marketplace.

First introduced in 1971, bills have been passed in various forms by both the House of Representataives and the Senate. On both occasions, however, the House and Senate sponsors were unable to reach a compromise and the legislation died.

Once again, both Houses are considering versions of toxic substances control legislation. This time, however, the bills are closer on key points than previous versions. The stronger Senate version, S.776, is currently awaiting mark-up before the Senate Commerce Committee. The House version, H.R. 10318, recently reported out of the House Subcommittee on Consumer Protection & Finance, is awaiting action by the House Committee on Interstate and Foreign Commerce.

Testing

Under both versions, EPA could require manufacturers to test certain chemicals which are suspected of being hazardous to human health or environment. EPA would also be empowered to set general guidelines and requirements for such tests, and could publish the results. Both bills require EPA to develop a priority list of chemicals for testing and would allow the agency to require testing for others as well.

The Senate version directs EPA to require testing under certain circumstances, while the House bill says the agency "may" require testing.

Regulation

Both the House and Senate versions contain provisions which empower EPA to issue regulations in the event it is found that a chemical presents or is likely to present an unreasonable risk to health or environment. Under these provisions EPA could regulate the manufacture, distribution, labeling, use and disposal of the chemical in question. Where necessary, EPA could totally prohibit or limit the chemical's commerce.

Both proposals would apply to all chemicals regardless of whether or not they are new.

Screening

Both measures would require manufacturers to notify EPA three months before marketing a new chemical or an existing substance which would be marketed for a significant new use. If testing were required, the firm would submit the test results to EPA along with the three month notice. During the pre-market period, EPA could ban a substance, restrict its use, or publish regulations governing its labeling or disposal.

Reporting Information

Both bills would require manufacturers to provide EPA with information relative to the chemical products they produce, including chemical properties, quantities, uses, number of workers exposed and results of health and safety tests. Any company which discovered a hazard connected with any of its products would be required to report it to EPA immediately.

Chemical Substances

With a combination of substances, such as a coating or similar formulated product, if a chemical reaction takes place, the product would fall under the definition of "chemical substance" in both bills. Such products would thus be subject to the full impact of the legislation. If a chemical reaction does not take place, such products would be considered "mixtures". While mixtures are covered by both versions of the bill, the impact of the legislation is not as severe.

The forecast for passage of a Toxic Substances Control Act is good this year, if the House and the Senate can agree on a compromise version.

NPCA, through its Product Safety Task Force, is working to ensure that any legislation adopted is reasonable with respect to its application to the paint and coatings industry.

News from Washington

Chemical Coatings Conference to be Held At Cincinnati Convention Center, April 21-23

The pros and cons of the newest coatings systems for products will be discussed by 56 chemical coatings industry experts and product manufacturers using coatings at a conference being sponsored by the National Paint and Coatings Association at the Cincinnati Convention Center on April 21-23.

The Conference will cover emerging technologies such as Powder Coating, Electrocoating, Water-Borne Coatings, High-Solids Coatings, and Radiation-Cured Coatings. Manufacturers already using the new systems will discuss their experiences and such problems as emission and energy reduction, and installation and operation of the new systems.

In announcing the program, Howard J. Mather, Vice President, Industrial Products, PPG Industries, Inc. and Conference General Chairman, said, "This conference will be invaluable for product manufacturers seeking the latest finishing systems information." He said the program has been structured as a learning seminar with ample opportunities for audience questions and answers.

The Conference will open April 21 with Robert M. Cox, Sr., of The Gilbert Spruance Co. and Chairman of NPCA's Chemical Coatings Steering Committee, presiding. NPCA President Robert A. Roland will deliver the keynote address on "Government Interface with Business". "National Economic Trends" will be covered by Dr. Carl Madden, of the Chamber of Commerce of the United States. "A Challenge to the Coatings Industry" will be presented by Harry Holiday, Jr., President of Armco Steel Corp.

Concurrent programs on April 22 will cover Powder Coatings and High-Solids Coatings and Electrocoating.

"The Powder Coatings Market", with emphasis on its problem-solving abilities, its energy saving impact, its economies, quality control aspects, low temperature curing epoxies, polypropylene powders, water-borne powders, and a comparison of thermoset powders, will be discussed at this session. Other topics at this session will include: "Suppliers — New Powder Equipment", with presentations on new application, powder handling and recovery systems equipment; and "Powder Users", the experiences,

problems encountered and solved, values, economies, comparisons with conventional coatings, and future requirements.

In a concurrent morning program, speakers will discuss High-Solids Coatings. Topics will include: "Types, Economics, Energy & Environment Considerations"; "High-Solids/Low Energy — Is There Compatibility?"; "High-Solids Coatings — Where Can They Be Used?"; "Advances in Technology and Equipment for Two-Component Urethanes"; and "Experience with High-Solids Coatings in the Appliance Industry".

An afternoon concurrent session will cover Electrocoating. Topics include: "Electrocoat—Overview of the Past and State of the Art Today"; "Program Transfer System Concepts for Electro-Deposition"; "Major Appliance Electrocoat"; "Automotive Electrocoat"; "General Metals Electrocoat"; "Effects of Energy, Ecology and Economics on Electrocoating"; and "Summary of the Papers and the Future of Electrocoat".

Sessions on April 23 will focus on Water-Borne Coatings and Radiation-Cured Coatings.

The Water-Borne Coatings session will run all day and cover: "A User's Case History — Automotive, Appliance, Metal Packaging, Coil Coating, and Business Equipment"; "How to Convert to Water — Material Availability and Selection, Pretreatment Changes, Application Equipment, and Training"; "Water-Borne Coating Usage — Current and Future"; "Water As a Compliance Coating — EPA/OSHA/Waste Disposal"; "Future Water-Borne Coating"; "The Clock Is Running"; and "A Wrap-Up".

A concurrent morning session will be held on Radiation-Cured Coatings. Topics include: "Electron Beam Equipment"; "Ultraviolet Equipment"; "Radiation Curing/Wood"; "Radiation Curing/Metal"; and "Graphics-Metal Decorating".

Registration fee for the Conference is $50.00, up to March 31; thereafter, the fee is $60.00.

For further program information, copies of the Conference and hotel registration forms, contact Jerry Hall, Director, Chemical Coatings Div., National Paint and Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D. C. 20005.

MCA Calls for Corrections In Water Pollution Control Act

A spokesman for the Manufacturing Chemists Association told the National Commission on Water Quality that mid-course corrections are needed in the requirements of the Federal Water Pollution Control Act Amendments of 1972.

Union Carbide Corp. Chairman F. Perry Wilson made the comment at January 19 hearings on the commission's staff report. Speaking on behalf of MCA and its member companies, Mr. Wilson said that there will be a dramatic improvement in the nation's water quality by the time the 1977 requirements of the act are met, and better water quality will be produced than was anticipated at the time the requirements were enacted.

He noted that data from the commission staff show that during seasonal low flow conditions, 8% of the 4,600 river miles which have been studied do not now meet the minimum criterion of four milligrams dissolved oxygen per liter of water. By 1977, he added, technology in use by that time will have reduced this to 5%, and when all the 1977 requirements have been met, only eight-tenths of 1% will fail to meet the criterion. In turn, utilization of the presently mandated 1983 technology would only reduce this to five-tenths of 1%.

"The staff report's projections on investment and operating costs for the chemical industry to achieve these incremental improvements in water quality are at the crux of MCA's position," said Mr. Wilson. Estimates are for a $5.3 billion investment between now and 1977 with annual operating and maintenance costs at $861 million, he stressed, and installation of 1983 technology would add another $4.2 billion and increase annual operating costs by $2.6 billion — increases of 79 and 300% beyond the 1977 levels. Not included are an estimated $2.7 billion to provide control technology for new manufacturing facilities from 1975 to 1983. "Clearly, this is a classic case of diminishing returns and an unwise use of the nation's resources," he said.

Mr. Wilson emphasized that MCA believes it is in the nation's best interest to amend the Water Pollution Control Act by making the interim water quality goal the principal goal and by eliminating the mandatory requirements of best available technology.

VAP 2573

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News from PRI

Study Group Reports on Survey

At a meeting on November 6, 1974 the Board of Trustees passed a resolution as recorded in the following transcribed minutes:

"P. 497 Report by Gerhart

Gerhart will contact heads of laboratories to get their ideas and comments on the objectives and methods of PRI. He emphasized the importance of interesting younger people in our industry. In Europe, there are paint research institutes, generally affiliated with a university. The paint research institute conducts some teaching activity and some contract research. Active participation of science advisors from industry is prevalent. The question was raised whether PRI should have a center or facility to work on industry-wide problems. Tomecko moved that Trustees approve the formulation of a special study group to develop a model incorporating the objectives and operations of a research institute for the paint industry. Teas seconded the motion, which was passed. Tess appointed Gerhart as chairman. Seiner raised the possibility of partial government financing. Glaser raised the point that a considerable number of new problems have beset the paint industry due to social changes, ecological factors, raw material changes, etc. It was agreed that the basic function of PRI to promote basic research in our industry will be maintained. A suggestion was made that some additional functions of an industry-wide research institute could be toxological studies and advanced analytical procedures. A motion was made by Dunn to appropriate $2000 to defray the expenses of the study group. Seconded by Estrada and the motion was carried."

Eleven Study Group members were appointed on December 5, 1974 with suggestions to obtain a consensus specifically regarding "—develop a model incorporating the objectives and operations of a research institute for the paint industry," and separately "—get (their) ideas and comments on the objectives and methods of PRI."

Two communications were employed: (a) letters to individuals active in Federation committees and in the 25 societies; (b) a questionnaire prepared with the suggestion and hope that individual revisions be made by each offeror. During the period January to May 1975, each Society announced the fact of the study and many distributed questionnaires at monthly meetings, sometimes accompanied by discussions. Several hundred answers were received, along with many letters expanding opinions upon PRI objectives and operations.

Letters from individuals closely associated with research (in contrast to development functions) were, by their individual responses, overwhelmingly in favor of planning for an institute at a specific locus. This subject was however closed on May 16 by the Board declaring to the Federation Council Representatives that an institute system of operation is unnecessary, undesirable and impractical.

On June 12, nine members of the Study Group summarized the statistics and opinions concerning PRI objectives and operations as presented in the questionnaires. One obvious conclusion is that the extent of the activities is underrated by the belief that the expenditures are a mere fraction of actual. There is an indication that the published reports of sponsored work are not widely read or comprehended. Some respondents were satisfied or at least partially so and offered no narrative amplification. One secure conclusion is the desire for more support to research projects which can presently or predictably, in the reasonable future, benefit the formulation and manufacture of paint. Answers to the questionnaire cannot be further analyzed by statistical methods. The individual replies have been made available to the Trustees who also thank the Study Group members for the survey.

At a meeting on October 30, 1975 the above report was authorized for publication in the Journal.

H. L. GERHART, *Honorary Trustee*

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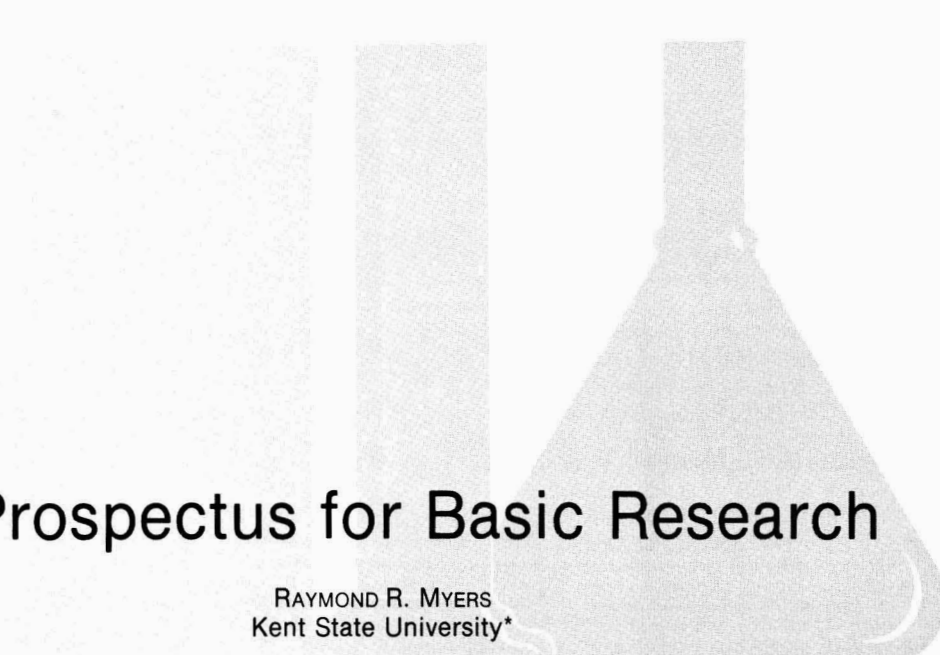
A Prospectus for Basic Research

RAYMOND R. MYERS
Kent State University*

INTRODUCTION

I shot an arrow into the air;
It fell to earth I knew not where . . .

Research has been described by metaphors to an extent greater than any other endeavor of man, with the possible exception of falling in love. As a result, those who look to research for answers to real-life problems are inclined to regard this highest level of scientific activity as something tangible, like game for a marksman, as if Longfellow's metaphor had come to life. An arrow is something which has to be targeted in order to be effective, they argue; therefore should not research also be conducted according to the same primordial rule?

Any prescription for conducting research on an industry-wide basis must address this question. We shall refer to the concept that research objectives can be delineated in advance as the *targeted model.*

In working out the logistics of the marksman's model there exists the incidental expectation that the missile be aimed correctly in order not to be downright hazardous; or perhaps targets should be selected so broadly and indiscriminately that a shot at random is bound to reach one of them. Success in archery depends largely on the skill and common sense of the person wielding the bow.

I breathed a song into the air;
It fell to earth I knew not where . . .

An alternative philosophy of research recognizes that targets can be elusive. Research can either be directed or it may take a more subtle approach, recognizing that targets sometimes lie beyond the line of sight. In these cases one's aim must cover a broader azimuth or perhaps involve a homing device which elicits some cooperation on the part of the target, in which case the technique has some of the characteristics of seduction. Whether one would employ a minstrel to lure game into range can be debated, but the concept of building a fundamental re-

Raymond R. Myers

A specialist in rheology and inorganic chemistry, Dr. Myers is a 1941 Phi Beta Kappa graduate of Lehigh University (A.B. Degree). He received his Master's Degree in 1942 from the University of Tennessee, and his Ph.D. from Lehigh in 1952.

He served as a Graduate Assistant at the University of Tennessee while earning his Master's, then joined Monsanto Co. in 1942 as a Research Chemist. While there he also served as a part-time instructor at the University of Dayton. In 1946 he left Monsanto to work with Jefferson Chemical Co. as a Research Chemist.

He joined Lehigh University in 1950 as a Research Associate while working on his doctorate. During his Lehigh tenure, Dr. Myers served as a teacher and a director of contract research, mostly in rheology. He was Research Assistant Professor from 1953-57, and Research Associate Professor from 1957 until 1961, when he was appointed Research Professor of Chemistry. In 1960 he was awarded a PRI grant for a dynamic study of film drying and the means of catalyzing the conversion.

In January 1964, Dr. Myers was appointed Director of the Paint Research Institute, succeeding Dr. J. S. Long. The following year he joined Kent State University as Professor and Chairman of the Department of Chemistry.

His PRI responsibilities have focused on assessing and disseminating the results of basic research projects being conducted under PRI sponsorship at various colleges and universities. He has been instrumental in improving the returns from inter-disciplinary research, including the use of encounter techniques in invading new research areas such as mildew defacement and corrosion control, and also extending to the making of projections into the deep future (which he maintains is easier than forecasting short-term events).

For his outstanding contributions to the Federation and to the advancement of science and research through the Paint Research Institute, he was awarded the Federation's 1973 George Baugh Heckel Award.

A Fellow of the New York Academy of Science, he was the recipient of its A. Cressy Morrison Award in Natural Science in 1958 for a theoretical development in catalysis, supplementing an earlier concept in 1953 which was featured in *Chemical Week* magazine. In 1971 he was awarded the American Chemical Society Award in the Chemistry of Coatings and Plastics, sponsored by the Borden Foundation. He was honored for his pioneering research on the chemical drying of coatings, the flow characteristics of solutions and dispersions, and the development of equipment and measuring techniques used in coatings and related research.
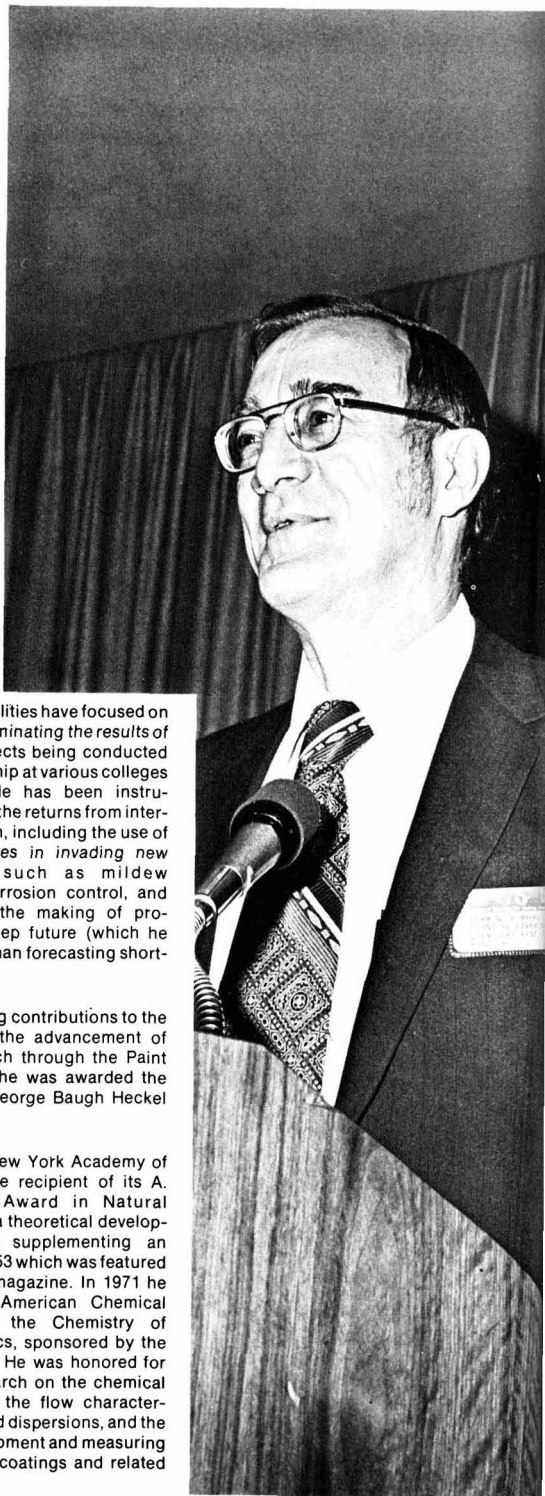
search effort around what we refer to as a *broad-casting format* is well established.

Are the two philosophies compatible?

One of the problems facing basic researchers over many decades is that the goals they seek lie well over the horizon. Their instincts tell them that *something* exists worth discovering; yet they know not what it is. They possess the skill and the common sense that justifies equipping them with heavy ordnance, yet they must know why they are so equipped. Their motivation derives from curiosity about some aspect of the physical world, yet they derive support from institutions that operate with budgets. As a consequence, the hallmark of basic research is the question mark, overlaid by the dollar sign. The overlay is especially prominent when the research support is provided by a given segment of society, as in the case of an industry-sponsored research institute. As a consequence, although this Mattiello Lecture is an account of research conducted by the coatings industry, it is cast in a framework familiar to the economist: *a prospectus for basic research.*

DEFINITIONS AND A RESTRICTION

A prospectus is a preliminary statement describing an enterprise intended for distribution to prospective participants. The Paint Research Institute seeks participation by Federation members in such a variety of capacities that any coatings scientist may participate in at least one of them. Let us count the ways:

(1) Grant monitors

(2) Proposal evaluators

(3) Symposium participants

(4) Encounter group participants, and

(5) Trustees.

There are other ways to be presented later.

Basic research always stops short of carrying the application of research results to the solution of practical problems; and even if this limitation were not implied in the general understanding of what constitutes basic research, PRI's tax-exempt status prevents us from engaging directly in applications. Therefore, *the technical competence of our supporters offers the best opportunity for interfacing with the Federation's research effort.* We view the PRI role as spotters for those in the academic sector who are aiming at targets over the horizon and who need an occasional correction in their aim. This correction, competently applied, is the responsibility of the industrial community. Coordination between the marksman and the spotter is one of the objectives of this prospectus; the other objective is coordination between the spotter and those who direct the fire, especially during these times of shifting priorities.

NEED FOR COATINGS RESEARCH

PROTECTIVE AND DECORATIVE VALUES

Sixteen thousand years ago coatings were made and applied by hand; natural earth pigments were suspended in natural binders whose main function was to transport the pigment to rock substrates in the shelter of prehistoric caves. The only function of the coating, which had virtually no film integrity by modern standards, was decorative; there was no need to protect anything. The contoured paintings of bison in Altamira and etched designs of game in Lascaux are prime examples (see *Figures* 1 and 2).

Coatings which were both artistic and protective have been known for 5000 years, but the high-technology coatings industry that has developed since the industrial revolution stands as far apart from these ancient lacquer developments as they do from the drawings of prehistory. The emergence of the supportive science capable of extending the utility of coatings is responsible for the contrast.

In the 1920's houses were painted with lethal material, for federal legislation prohibited the use of extenders for lead pigments then in vogue. This paint blistered and lost gloss so that repainting had to be done at intervals. Many of these houses lay in paths of expanding ghettos with the result that the captivating taste of the lead compounds provided some of the best treats afforded the ghetto children. Although EPA was unknown at the time, long-range research conducted according to the broadcast format, at least without regard to the then unknown toxicology problem, was responsible for uncovering superior pigments which today are neither toxic nor prohibitively expensive. Improvements have resulted in the dispersion of these and other pigments, in the flow properties of the dispersions, and in optical properties of the dried films, all stemming from basic research designed to learn more about the phenomena associated with pigment/vehicle interactions.

Now that research has become an integral part of the overall effort in producing coatings for the future, one can expect an accelerated movement into the next level of sophistication which will be increasingly more directed or targeted. Today's research on coatings will deliver systems capable of curing in seconds, resisting the attack of chemical and biological agents, adhering to imperfect substrates, offering unusual optical effects, and presenting an impermeable barrier to corrodents. All of these achievements will have to be accomplished in an economical fashion, using materials in reasonable supply, and offering minimal hazard to the consumer.

The Paint Research Institute has supported much of the work which undergirds the expected
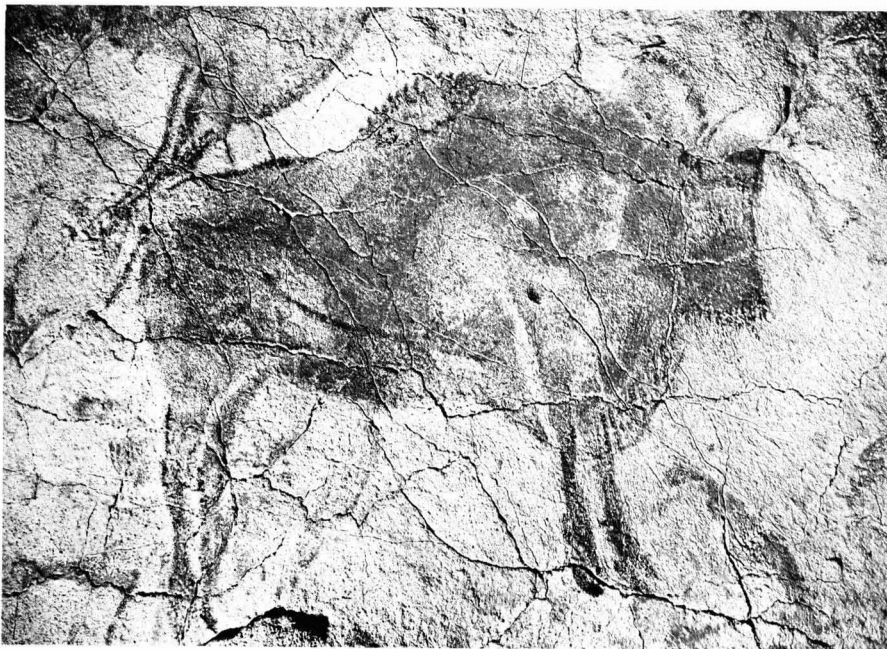
Figure 1—Altamira Bison. Applied from aqueous suspension, this coating amounts to nothing more (technologically) than a rust stain on a rock substrate

new developments. The extent to which PRI may be judged successful will depend on events in this second decade of our existence. Below, we attempt to show that our principal investigators have been addressing relevant questions. That we have enjoyed the benefits of excellent supporting talent among industry personnel will become evident in what follows.

SCIENTIFIC BASIS OF COATINGS RESEARCH

Applied as a fluid, a coating undergoes some remarkable transitions in order to become an effective protective and decorative barrier. It must wet the substrate; it must have prescribed flow characteristics in order to produce an even, adherent film; it must maintain adhesion and integrity (cohesion) on drying, even though shrinkage stresses are bound to set in; it must develop desired optical properties such as controlled gloss and color; it must develop hardness without becoming brittle; and it must resist such external elements as radiation, oxidants, and diffusants.

Subdisciplines of science which govern these properties are interfacial chemistry, rheology, chemical kinetics, optics, thermodynamics, and transport phenomena. These subdisciplines can be mastered only by experts; the knowledge of the experts, in turn, can be put to use only by development per-

sonnel who are prepared to assimilate what the experts communicate. The coatings industry has thousands of scientists on its collective payroll who are professionals in one or more of these subdisciplines and who can perceive an application of a new concept. Most of these scientists are of the marksman variety who have a built-in skepticism concerning the balladeers in their midst; they need a coupling mechanism between the concept and the application. Like Odysseus' crew,[1] they turn a deaf ear to those whom they suspect are offering up siren songs that could divert them from their primary task. The objective of research by prospectus is to ensure that the sirens are tuned out before they play havoc with the industry by obscuring real signals and preventing one from responding to legitimate blandishments.

PRI PORTFOLIO

Present operation of the Paint Research Institute minimizes the diversions from relevance that are bound to creep into any basic research program. False starts are characteristic of pioneering efforts, and are to be expected; and just as a seasoned military commander will send out a scouting party to reconnoiter strange territory, a well-run corporation will probe unfamiliar areas with the same hesitant

Figure 2—Lascaux Horse. Etching prior to painting and application of dry manganese dioxide pigment by blowpipe (at nostril and mane) and by "chalk" crayon (for the outline) required several technologies

degree of commitment. Indeed, the commitment often takes the form of cooperative research with costs shared by other corporations.

BROADCAST FORMAT

In the PRI portfolio there exist many examples of high-risk explorations. In our first decade of operation we sent parties in search of concepts that underlay: (1) the dispersion of pigments in vehicles;[2,3] (2) the preparation of latexes with controlled particle size;[4,5] (3) the oxidative polymerization of unsaturated oils;[6,7] (4) the compatibility of resins with vehicles;[8,9] (5) the diffusion of penetrants into films;[10,11] (6) the imaginative use of molecularly bound metals;[12,13] and (7) the rheology of film formation. Incidental to these findings were developments that were arrived at by serendipity—small bonuses that one can rely upon when alert investigators are at work:

(1) Dispersion studies paved the way for energy economies 15 years later.

(2) Uniformly sized latexes appear destined to provide hiding in addition to the sought opalescence.

(3) Success with complexed metals other than cobalt promises to figure prominently in today's search for heavy metal replacement, activated by Project Cope.

(4) Compatibility has been placed on a kinetic basis and has explained certain delayed effects as blushing and sweating out of plasticizer.

(5) Penetrant diffusion has been judged to figure prominently in corrosion, one of our new targeted areas.

(6) Metal binding has also extended beyond its original confines and now represents one of the attacks on the corrosion problem.

(7) Film formation has moved into an arena in which rapidly curing and low-energy curing systems are being developed.

In addition to these unexpected findings there were some more or less mundane accomplishments: characterization procedures on which the industry can rely[14] and which become standard test methods in due course; penetrating insights into compatibility that permit one to take advantage of phase separations;[15] mastery of sophisticated instruments that probe the molecular structure and morphology of film formers;[16] possible exploitation of unanticipated optical effects;[17] and ways to detect incipient adhesive failure.[18]
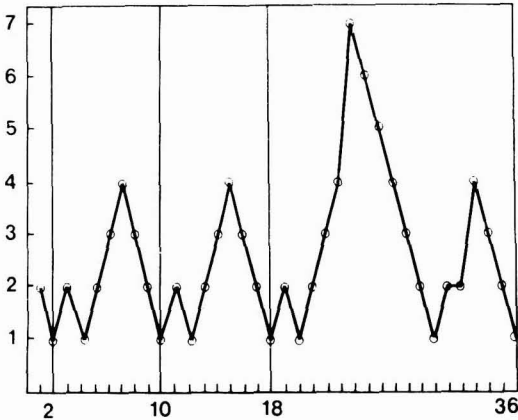
Figure 3—Sawtooth periodicity. Certain properties of the elements reach sharp maxima in the middle of the period. Multiplicity of the arc spectrum, shown here, is the easiest to quantify; magnetic susceptibility and catalytic activity behave similarly; so does color, inevitably

Clearly, these achievements required prepared minds, operating in a free and not excessively structured environment, and primed to make whatever use of a concept would serve the fundamental problem at hand. For example, the simple concept of the 3d orbital activity of the transition metals underlies an impressive array of principles which are involved in one or more of the PRI studies: in our work on catalysis, where the concept began; in the molecular design experiments initiated by J. S. Long and brought into focus on silicon by Shelby Thames; in the discovery of metal participation in ferrocenes by Jack Richards, exploited in the making of polymers by Charles Pittman; and in the use of direct metal bonding as a means of securing a polymer to a surface so tightly that corrodents cannot gain a foothold even if they do diffuse to the interface.

With such a variety of unanticipated findings it should not be difficult to persuade even the most skeptical reader that a variety of research lifestyles is needed in order to accommodate the individuals on both sides of the industry-academic interface. In addition, it is across this interface that the dissemination of knowledge (and of the industry's needs) must take place, so one might embrace education in the general category of research and consider how the combination of education and research can operate synergistically. For example, in squaring off against the heavy metal problem a research chemist would start with the periodic table and attempt to replicate the desired property of one metal without retaining such properties as toxicity. In so doing, the theoretical development represented by *Figure 3* which has not yet been published may serve a useful purpose in avoiding or minimizing false starts.

Table 1—Transition Metal Properties

(A) Dependent on 3d Electrons in Ions

   Catalytic activity (oxidation and radical formation)
   Magnetic susceptibility
   Color (with an important exception)

(B) Dependent on Metal-Metal Bonding

   Hardness
   Density

The sawtooth trend represents what I call Type 2 periodicity in the unpublished manuscript (reserving Type 1 for the overriding trend based on electronegativity). Maxima in the property (multiplicity of the atom's spectrum in this case) appear in the middle of the transition, right where cobalt and manganese are found; and the same maxima will appear in later transition series. Unfortunately the later series contain expensive metals, but this should not deter one from uncovering the principles involved and thereby set the stage for the prepared minds in the industry to apply them.

Reference was made to the ubiquitous nature of 3d electrons in metals of interest to the coatings industry, particularly in the transition metals. One result of developing a thorough understanding of how these electrons govern certain periodic properties is to conclude where tradeoffs must be tolerated. *Table 1* lists some transition metal properties and shows that color also peaks at the middle of a period, precisely where the other valuable properties reach their maximum.

RESEARCH LIFESTYLES

The earliest philosophers, particularly those with an inclination to be scientists or explorers of unseen lands, relied on a patron from the ranks of royalty for their support. As natural philosophy gave way to a more rigorous form of natural science the new breed of intellectuals turned to a less charismatic way of earning their sustenance and began writing unsolicited research proposals which were subjected to peer review. The industrial counterpart of these individuals had to be content with the clandestine research that management allowed, generally up to 20% of the scheduled time in the laboratory. With the departure of the salad days and the onset of environmental concerns, both the academic and industrial scientist turned increasingly to research by predetermined objective. Hence, the concept of a prospectus. The effect of limited resources has been to shift the selection of objectives toward those who pay the bills, so that research targets are now roughed out in advance and the PRI "spotter" is called in to direct the aim of the academic "marksman." From our vantage point we should also be able to improve the aim of the amorphous group

Table 2—Research Lifestyles

Period	Style of Support	Examples
World discovery	Patronage	Columbus' voyages da Vinci's inventions
Industrial revolution	Clandestine research	Early chemical industry Electronics industry
	Unsolicited proposal	Academic institutions Research institutes
Counter culture	Monitored research	Coatings rheology* Interfacial chemistry Alternate routes to hiding
	Research by prospectus	Mildew defacement* Corrosion control

* Examples used in this presentation.

of "field commanders" represented by the industrial R & D personnel.

The historical trend in styles of research support and examples of each are listed in *Table 2*.

Mildew defacement affords a textbook example of targeted research. A discussion of PRI's venture into that particular arena constitutes the initial offering of the prospectus, followed by a description of a more mature effort in rheology which was conducted under the broadcast format.

MILDEW DEFACEMENT OF COATINGS

Long, long afterward in an oak
I found the arrow still unbroke ...

The PRI portfolio now has equity in the basic mycology of mold growth, having discovered a new *modus operandi* in which the scouting of new terrain is conducted by an encounter group. Basic research has been conducted for decades in classifying bacteria and fungi, in observing their modes of growth and reproduction, in identifying the enzymes and other metabolites that they produce, and in seeking natural and synthetic agents to combat the disfigurement. But no directed effort was made to bring the community of coatings scientists to research level in the field of mycology until 1971 when a new era of PRI effort was started. This era has been referred to as the "Counter Culture" in *Table 2*, for it has ushered in a radical approach to research, which traditionally has been dominated by conservative directives.

No field of science was further removed from the expertise of the average paint chemist than was the microbiological basis of mildew defacement at the time the first encounter session was held four years ago;[19] and it is with some gratification that one could observe a general increase in the rapport of the participants during the second session held in

1975.[20] These encounters have been referred to as MIDOC (mildew-induced defacement of coatings) and MIDOS (of surfaces), respectively.

The encounter session brings together two groups of widely diverse backgrounds: coatings scientists and professionals in the field to be invaded. Such heterogeneity and the likelihood that one participating group will not have met the other beforehand requires a medium for exchange of thoughts before the encounter. This exchange is provided in the form of a questionnaire based partly on the well-known Delphi method of technological forecasting. The "oracles" in this case are the coatings scientists and the outside experts, of which there are six each. Their returned questionnaires are fashioned into an agenda for the initial confrontation; this agenda is sharpened by the group director during the encounter, typed during the lunch break, and resubmitted to the participants for the afternoon session. By the time the 12 participants sit with the director in a final session to finalize the wording of the questions, the agenda has undergone a complete metamorphosis and has emerged as a research prospectus. It states what problems are in need of solution and invites professionals in the field to submit bids to do the research that will supply the answers.

The prospectus also serves as documentation supporting requests to other agencies for support of the program. In the case of the mildew study, support by the National Paint and Coatings Association marked a return to the fold by that key organization.

MICROECOLOGY OF MOLD GROWTH

The type of question which found its way into the MIDOC prospectus[19] is exemplified by the microecology of mold growth, the first category selected by the combined group at the conclusion of the encounter session. By common agreement all of the participants thought that information on microorganism population trends was the first question to ask, followed by queries into the enzymology and metabolism of the organisms. Four years later[20] the MIDOS experts made a mid-course correction in the objectives; they relegated the enzyme study to a position under the general category of micrecology, and significant changes were made in the originally proposed metabolic study. Comparison of *Tables* 3A and 3B shows the effectiveness of the technique.

Unexpected findings soon emerged from attempts to grow cultures on a standard coating made from a vinyl acrylic latex containing no inhibitors. No growth of the prevalent fungal species could be maintained unless certain bacteria were present in addition to the mold culture. This finding was reported as mildew-bacteria symbiosis[21] and later it was supplemented by the discovery that the prevalent species suffers a delay in its appearance, possibly awaiting the development of nutrient from enzymat-

Table 3A—MIDOC

Mildew Ecology

(a) Isolate strains of fungi and bacteria from mildewed panels (acrylics) at monthly intervals. Attempt to identify the first invaders and the climax vegetation.

(b) Formulate an acrylic with known surfactant and examine films on exposure and under laboratory conditions.

(c) Conduct a similar study using *A. pullulans* with and without isolated bacteria from the first invaders.

(d) Attempt to delineate the succession of organisms, hoping to trace the population from first invaders to climax vegetation.

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ic attack by early species. This conclusion is not yet firm enough to report in our favorite primary journal (the JCT) and is being checked; but the overall accumulation of knowledge is an excellent example of how the aim of the researcher has been improved with minimal commitment of industrial manpower via the use of an industry-sponsored research organization.

It is contended that PRI developed research-level capability in a new and uncharted area within the span of four years. The nature of mycology research is such that widespread acceptance of reported results will require replications of the findings and the establishment of suitable controls; as a consequence it will be necessary to wait several years longer for definitive answers to the question of succession, and still longer for the enzyme studies to be completed. But it will be necessary for the struggle against mildew defacement to return to basics time after time in order to renew its strength and gain new orientations, just as the legendary Greek wrestler, Antaeus, gained renewed strength every time he was thrown to the ground, for his mother was Goddess of the Earth.*

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* This particular metaphor should not be carried too far, because Hercules finally killed Antaeus by holding him in the air while choking him.[22]

Table 3B—MIDOS

Succession of Organisms

(a) Expose panels at susceptible areas. Include the high-mold season. Identify the first invaders, intermediates, and climax microflora. Quantify the resident population at the time of sampling. Identify the source of *A. pullulans*.

(b) Attempt to duplicate a growth pattern obtained outdoors by a sequence of laboratory inoculations on uncoated unglazed ceramic surfaces, using controlled nutrient. Inoculate with the several species seen outdoors and also a climax population.

Then, after the succession of organisms is better understood:

(c) Grow *A. pullulans* on unexposed and exposed surfaces using the succession approach. Isolate the enzymes therefrom. Relate extracellular enzymology to the reproduction cycle. Repeat on inhibited films at sublethal levels.

(d) Ascertain what components of the standard coating may supply nutrients for the organisms on new and on exposed leached panels. What are the features of an assimilable nutrient?

(e) Ascertain the alkali sensitivity of *A. pullulans* and its possible symbionts such as *Alternaria* sp. and *Aspergillus* sp.

PAINT RHEOLOGY

The life history of a polymer coating is predestined by its mechanical properties; therefore, rheology provides the rationale for perennial research activity. PRI support of rheology extends over a decade, during which advances have been made in every facet of the coatings industry, from formulation to drying behavior to performance. The consciousness raising which resulted in the shift to research by prospectus rather than by research proposal reduced the PRI portfolio to three grants of the conventional type, two of which are in rheology. These grants come under an umbrella category recognized by the Trustees as meeting certain basic needs of the industry.

Rheology is the study of the deformation and flow of matter. The terminology stems from 1929 when Bingham coined the word from the Greek $\rho\epsilon\omega$, to flow. No other branch of science has undergirded paint technology more extensively than has rheology, for in its wider application it embraces plastic flow and elastic deformation, both of which characterize the responses expected of coatings.

MECHANICAL PROPERTIES OF COATINGS

Let us examine in depth the enormity of the rheological properties which must be controlled in making, applying, and using a protective coating. A coating experiences a variation of demands during its birth, life, and death so that mechanical properties often must be measured while the coating is in a transition between states.

Spraying, rolling, or brushing require great mobility on the part of the material; then comes a series of transitions which lead to such a remarkable change in physical properties that the experimenter can take advantage of them in establishing sensitive criteria for film formers. A liquid, for example, has virtually no rigidity; the solid film to which it converts is rigid. Instruments developed by the PRI can measure this conversion in quantitative terms, thereby reflecting the true magnitude of the structure development and providing a laboratory characterization of this most important aspect of a coating.

The mechanical behavior of a coating is established in the beginning, when resin selection is made and the pigment is prepared for incorporation therein. The key property at this juncture is flow. The first reference to flow appears in a song by the prophetess Deborah[23] who celebrated a crucial victory of the Israelites over the Philistines by claiming that the mountains flowed unto the Lord. Marcus Reiner,[24] the great white father of rheology, claims that Deborah was a better rheologist than the translators of the King James version of the Bible, who

misinterpreted the true meaning and wrote that the mountains *melted* before the Lord. The key to understanding the behavior of both mountains and surface coatings consists on applying stress over a span of time that brings the Deborah Number, D, where

$$D = \tau/t, \tag{1}$$

as close to unity as practical. In equation (1), t is the time of observation and τ is the relaxation time of the material. For rocks, τ is of the order of eons; and as a consequence, for mountains under the kind of stresses that plate tectonics impart, t approaches eternity and geologists rather than laboratory scientists perform the study.

Coatings, on the other hand, start out with τ's on the opposite end of the mechanical spectrum. A typical low molecuar weight polymer will display a relaxation time around 10^{-6} to 10^{-9} seconds. It is possible to measure the viscosity of such a material under conditions of shear, relying on virtually complete relaxation to occur. But some methods of film application (particularly in industrial coatings) apply shear at such high rates over such a short time span that complete relaxation does not occur in practice; the system is elastic under these conditions; it presents the rheologist with the problem of measuring the rigidity of a material that does not have a fully developed structure. It is PRI's mission to show formulators and applicators how to measure and contend with this important factor.

Under the PRI basic research grants program several devices were developed to measure viscous and elastic properties simultaneously during the life cycle of a film. The program started with the measurement of viscosity at *extremely low shear rates* to solve problems involving pigment/vehicle interactions[25] in formulations, relying on low shear to disrupt the bonds as little as possible. Fragile structures created by the interaction of pigment particles with each other, in preference to vehicle, created just sufficient rigidity to prevent sagging without interfering with brushing or rolling. These structures were broken by shear, and the viscosity of the dispersion at high shear approached the value of the more readily dispersed systems.

Viscometric studies, even at extremely low shear rates, are both disruptive of structure and time-consuming by virtue of requiring readings over a span of shear rates. Transitions of the type involved in film formation require more sophisticated techniques.

KINETIC RHEOLOGY

The simple approach based on viscosity would not serve the purpose of studying either high-speed applications[26] or the conversions involved in drying cycles,[27] despite the demonstrated success of vis-
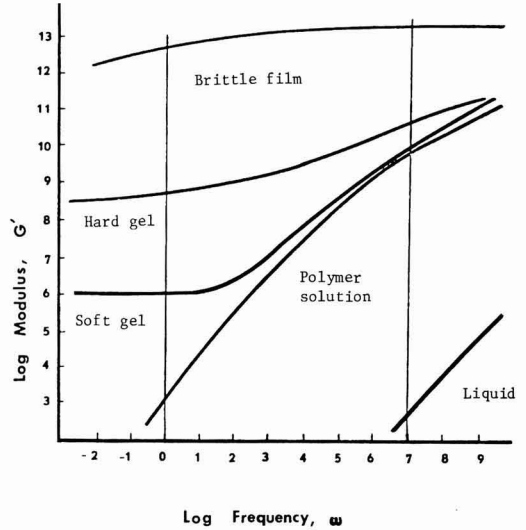
Figure 4—Frequency dependence of rigidity. Liquids display rigidity only when the time of the measurement is exceedingly short (ω is high). Sols and gels display intermediate behavior; crystals and glasses require eons (ω approaches zero). The vertical line at unit frequency represents TBA frequency; the one at 10^7 Hz represents ultrasonic frequency. Although the scan along the TBA line offers wider latitude, the one at 10^7 Hz is more suitable for kinetic rheometry of rapidly curing systems

cometric studies in the study of structures. In their place it was necessary to measure both viscosity and elasticity of a system in transition. The secret to measuring these quantities simultaneously consists of applying a cyclic shear stress, rather than continual shear as in a viscometer, and measuring the delayed response of the coating. Structures are not broken under these conditions.

Whenever an alternating force is applied to a system, whether it results from house current flowing in an appliance or corrugated roads impacting on the front-end suspension of an automobile, the experimenter has two measurements at his disposal; one is the amplitude of the oscillation and the other is the phase relationship between the applied force and the response of the system. By evaluating two important parameters at the same time (dynamic viscosity η' and dynamic rigidity G') over a range of frequencies and temperatures, rheologists offer a complete picture of how a practical system responds under any conceivable conditions of applied stress, such as impact resistance, crazing on drying, or thermal changes.

A significant dependence of G' on frequency characterizes liquids and soft solids; on the opposite end of the scale, crystalline and glassy films display little dependence, as shown in *Figure* 4. Diagrams of this nature reveal more about a formulation than do flow curves,[25] the customary way of displaying viscometry data. Moreover, for every *storage* modulus G' there is a *loss* modulus that relates to η'; the bal-

ance between these two material constants determines the resiliency of the polymer.

The feature of *Figure* 4 which makes it useful in portraying film drying is the two vertical scans shown at frequencies of 1 hertz and 10 megahertz.[28] If a cyclic stress of 1 hertz frequency (log f = 0) is applied to a polymer solution, hardly any rigidity can be detected (log G' < 0); as solvent is released, the molecules of the neat polymer become entangled and the polymer displays a perceptible modulus; if the entanglements then crosslink, the modulus becomes essentially independent of frequency in the range of low frequency. The extent of crosslinking determines the G' level, so that a condition of such short-range order can be achieved on curing that no frequency dependence of modulus is noted. By this time the film will be crystalline or glassy.

TORSIONAL BRAID ANALYSIS

Figure 4 is oversimplified in the sense that the horizontal placement of each of the systems on the graph is adjusted to provide optimum superposition. Despite this adjustment, it is clear that the differential between liquid and solid behavior is most pronounced at low frequencies, so that a frequency at which D = 1.0 is spanned during drying is the range of choice in characterizing this important transition from liquid to solid. One of the early achievements of the PRI was the discovery of a means to study coatings at low frequency with minimal interference by the substrate. The problem was to provide a support for the wet film without overriding its feeble display of a modulus by the rigidity of the support. This objective was achieved by modifying a torsional pendulum in such a manner that the coating was applied to the suspension thread which, in turn, was adapted to the occasion by being made in the form of a braid. This refinement, called TBA (torsional braid analyzer), permitted the suspension to retain significant loadings of coating without sagging and it also provided a suspension of negligible restoring force in torsion, thereby permitting the coating to bear the full brunt of the twisting force. The two moduli emerged from the oscillation frequency and rate of damping, and calculations were made of their ratios.

One of the earliest curing systems to be reported by the TBA was an epoxy;[29] in this case G' was reported relative to its value in the dried film. Other systems were selected so as to represent the full range of drying mechanisms with the following general results: an appreciable loss modulus G'' developed at about the same time as rigidity G' came into measurable range; at first the increase in loss modulus (G'') outpaced that in storage modulus (G'), so that a characteristic profile of a transition is rep-

resented by a peak in the G''/G' quotient. The material in transition is said to be "lossy."

In a practical sense one would prefer a lossy film during the critical gelation stage of film drying, avoiding rigidity as long as appreciable shrinkage of the film can take place. This requirement is particularly acute in the case of latexes, resulting in the failure of latexes to dry to a continuous film if the temperature of drying falls below a critical value. G' increases sharply as temperature is decreased below the glass transition temperature; consequently, latexes will not dry to a continuum below a certain film-forming temperature.

HIGH-FREQUENCY KINETIC STUDIES

Inspection of the right-hand side of *Figure* 4 reveals that the drying of a film can be monitored, at least in the early stages, by frequencies in the range of 10^7 Hz. Actual locations of the four curves have been shifted by an arbitrary factor, but even after this artifact is compensated for it is evident that differences between liquids and solids ultimately disappear at high frequencies. The very short wavelengths and short durations of stress cycles at ultrasonic frequencies are desired, however, because they permit a coating to be studied without interference from the substrate. Application of stress from the substrate and into the colloidal dimension of the coating requires short wavelengths. Since short wavelengths are attained at high frequencies the time required for a measurement is short and rapid drying processes can be monitored.

To accomplish these objectives PRI adapted an ultrasonic impedance device[30] for kinetic studies as a means of studying reactions leading to rigidity.[31] In the course of this work discoveries were made of incidental occurrences such as loss of adhesion[32] during drying and the attack of dried films by water and solvents.[33] The insight gained from these phenomena led to formulation breakthroughs which provide unusual optical effects in addition to paving the way for the casting of tough coatings.

FORMULATING BY RHEOLOGY

It was observed above that latex drying involves a transition in which the relaxation (G'') component outpaces that leading to rigidity. There must be some provision during film drying for the relaxation of stresses,[34] for all conversions known to date (except for a few speculative reaction paths) result in volume shrinkage leading to shear stresses of magnitudes which depend on G'. A PRI suggestion that resin emulsions be made from particles sheathed with material of low G' has been responsible for the development of latexes which minimize residual stresses and provide toughness as well as opacity. This contribution to coatings formulation grew from
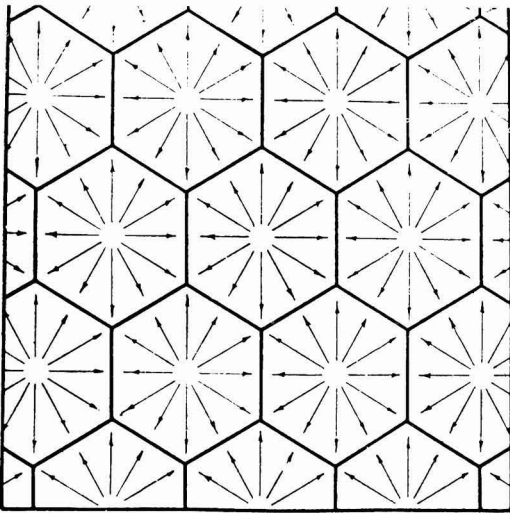
Figure 5—Residual stresses in deformed particles. Idealized conception of the ultimate deformation of close-packed uniform spheres shows the residual stresses which extend laterally from the center of each particle. These stresses are responsible for an inherent tendency for the coating to fail; their magnitude is in the proportion to the modulus of rigidity

Figure 6—Stresses in sheathed particles. The use of low-modulus sheaths permits most of the deformation to take place in the sheath and effects a reduction in residual stresses. Resulting film is a composite and may actually be tougher than a homogeneous film

a symbiotic relation involving the two PRI rheology grants and the industry monitor of a third grant in an unrelated subject.

The chronology is illustrative of how extensive a basic study can be. The failure of films was recognized early as a rheological problem due to the development of stresses in the film on drying. Since the substrate cannot shrink, the coating takes the brunt of the stress. Latexes offer hope for mastery of the shrinkage problem for the simple reason that the polymer is preformed and distributed in water as tiny spheres, about the size of individual colloidal droplets in milk. Drying of this latex is accompanied by a flattening out of the spheres onto the surface so that the stress is confined to miniature domains, as shown in *Figure* 5. Now if a sizable reduction in rigidity modulus is built into such a formulation the resulting stress will fall within the tolerable limits; i.e., the product of modulus and deformation will lie well below the energy of bond rupture; but for practical purposes this reduction may not be achieved at the expense of film hardness, and so according to the new concept the major part of the deformation is confined to the sheath of the particle, as shown in *Figure* 6.

A well-known consequence of embedding soft particles in a rigid continuum is impact resistance and toughness. Glassy polystyrene kernels sheathed in a soft polymer such as ethyl acrylate result in rigid particles in a soft continuum, as shown in *Figure* 6, and the composite displays the unusual

optical characterstics, in addition, for the isolated particles have higher refractive index than the matrix, thereby contributing to hiding. Moreover, if the particles are monodisperse they tend to line up in domains in each of which light is refracted according to the orientation of the domain.[35] The result is an iridescence which suggests that some day our customers will have painted surfaces that look like opal.

An additional possibility which is ready to move from the laboratory curiosity stage is to build in an intentional deficiency of the soft sheath, preventing it from filling all of the interstitial space.[36] This idea was suggested by Jerome Seiner who recognized that one result could be enhanced hiding by the well-
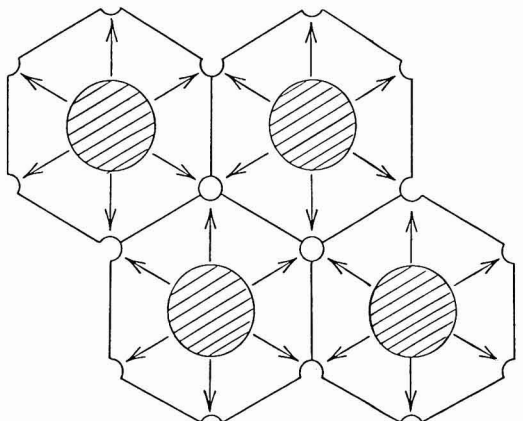
Figure 7—Stress reduction by microvoids. Additional alleviation of stresses wrought by drying can be achieved by incorporating microvoids in the interstices. Sharp corners are avoided and cavities remain in which pigment may be dispersed. The potential for increased or drastically reduced hiding exists in the pigmented model

spaced microvoids and improved film hardness by virtue of tolerating either a higher modulus or smaller sheath, as shown in *Figure* 7. Films made in this manner should tend to be free of residual stress; moreover, if pigment particles are present in the interstices as the last traces of water leave the film, they should be particularly effective opacifiers, relying on dry hiding[17] for enhancement of their scattering ability.*

Rheology has led or accompanied the coatings industry on a long path of steady development. Measuring from the early days of paint science pivoted on Joe Mattiello, one surveys a territory which encompasses other giants, such as Eugene Bingham and Marcus Reiner, and observes a steady development of applications: the understanding of sagging and its control without disturbing brushability, the identification of an elastic component in high-speed roll coating, and exploitation of the synergism found in properly formulated composites. The next step in the development of true insight of coatings behavior will be taken in the realm of kinetic rheology. Devices are on the drawing board and, as the electronics experts say, are being breadboarded to follow the course of polymerization reactions in bulk as well as in coatings. The many orders of magnitude through which G' mounts during polymerization, drying, or curing establishes kinetic rheology as a remarkably sensitive probe.

INDUSTRY INVOLVEMENT

COMMUNICATION, A TEMPORAL PROBLEM

There are seven ways in which industry-wide participation in academic research can be achieved. These ways were listed in the Research Director's 1974 annual report to the PRI Trustees[36] as devices to bring university professors onto the coatings scene in the following order of increasing involvement:

(1) *Ad hoc* consultantship

(2) Retaining consultantship

(3) Summer or temporary appointment

(4) Supplementary appointment

(5) Shared appointment

(6) Subsidized appointment

(7) Establishment of an institute

The costs of such participation need not be unreasonably high. Depending on the returns expected, an *ad hoc* consultantship can solve a particular

problem where the target is in view but special ordnance is needed, such as an analysis of the surface area of a pigment. Longer term consultantships and limited appointments of faculty usually are negotiated on a retainer basis in a manner which preserves the distinction between the academic activity and that which is done on the "outside." Only in cases where the industrial support reaches into the university setting can one gain satisfactory control over the activity, as it has in the supplementary appointment of the PRI Research Director.

In short, present PRI operation fits squarely in the middle of the possible degrees of university involvement. Therefore, a prescription for what ails basic research with regard to its relevance must start at level four of the above listing. Consultantships are adequate for the solution of problems facing a particular manufacturer, but for wider dissemination of the results on a noncompetitive basis it is necessary to accumulate some equity on the academic front. Heretofore the only equity which has been gained has resulted from the ability of the industry to hire graduates with prepared minds who can be productive during their first year of employment, and PRI's record has been excellent in that regard (64 PRI fellows supported in the years 1960-1974 have entered the industry or are committed academics.) But there are other ways, as suggested by the listed categories of support, which involve a long-term commitment, such as a shared or subsidized appointment.

We have just weathered a year-long analysis of the PRI format which resulted in the conclusion that we should not take the institute route with its concomitant acquisition of permanent staff. The increased involvement suggested by this prospectus heeds the exhortations of three charismatic speakers at recent Federation meetings: John Weaver,[37] who has pressed for Federation specialist committees; Howard Gerhart,[38] who has reached out for the uncommitted paint scientist to solve problems of significance; and Shelby Thames,[39] who proposes a parallel coatings educational institute. My stand has been that research *is* education and that the two cannot be divorced. Concepts that were research-level chemistry a decade ago are now part of the undergraduate curriculum; obsolescence of scientific knowledge has long been recognized as an occupational hazard of technical people; communication has always been recognized as the weak link between what is tucked away in peoples' minds and what is available to others *when they need the information.* The temporal aspects of scientific knowledge are especially important. What the industry needs is a coupling mechanism to link research findings to the industry problems at the time the problems surface.

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* The present state of the science is exactly the opposite: certain size relationships involving pigments and microvoids produce transparency rather than enhanced hiding.

THE COUPLER

Having faulted our present practice for lacking a coupling mechanism, we turn now to a solution to that chronic problem. Keynote speakers have argued that both the industry and our academic institutions have talent that often remains unexploited; these people are resources that should not be wasted. A recent questionnaire circulated by the PRI elicited the repeated suggestion that research not be sown like grain in a desert without follow-up attempts to nourish the sprouts. We have not taken due cognizance of the fact that the institutions at which basic research is taking place are also centers of higher education. They are equipped to play the role of coupler between research and its ultimate application, not by engaging in development activity of their own but by serving as the focal point for educating the development people in the industry.

The coupling mechanism would involve the grant principal and his monitors as instructors in a series of tandem or parallel workshops held at a central location. Each PRI grant would be covered at a two-day session constructed around lectures by the principal investigator and coatings scientists knowledgeable in the subject. Encounter sessions would be held between defenders of the research and the Federation committee of specialists in the cognizant discipline. Between sessions the participants would meet informally and at the end of the workshop a prospectus would emerge from the group.

The research workshop would become recognized as an annual affair. As regular as the seasons, as soon as classes end in the spring the PRI would schedule a two-week series open to participants on a subject-by-subject basis. The principals and their monitors would arrive the evening before their scheduled two days of presentation; they would have arranged beforehand a schedule of presentations that would work as follows: a tutorial lecture would open the meeting; a research paper would serve as a prime disseminator of knowledge in the selected area; then a carefully planned adversarial discussion session would be held to: (a) assess the finding; (b) establish its relevance; (c) chart the course for subsequent research; and (d) provide a work assignment for each member of the cognizant specialist committee. Finally, a non-adversarial group meeting would arrive at common objectives for the ensuing year, thereby producing a prospectus for attracting new talent and funds.

The academic setting would have a salutary effect on all concerned, for it would emphasize the long-range aspects of the material being covered and
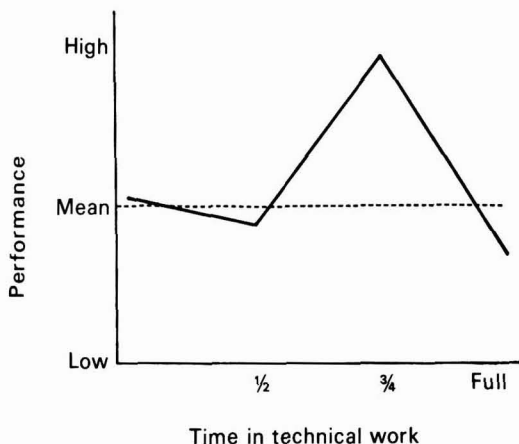

Figure 8—Performance improvement by participation. Pelz and Andrews data gathered from individuals within companies are extrapolated to the situation involving an activity in behalf of an industry-wide effort. Research managers are encouraged to offer up to 25% of each professional employee's time for participation in the PRI program and related activities

yet be a change of pace for both the principal investigator and the industry scientists. Studies reported by Pelz and Andrews[40] have revealed that the scientific contribution of a laboratory scientist reaches a peak when 25% of his work schedule takes him from the laboratory, and an activity such as monitoring grants and participating in job-related workshops should be viewed by employers as a rewarding effort from management's viewpoint. See *Figure 8*.

This proposal assigns a meaning to the ampersand in the inseparable R & D. Whether the coupler is viewed as a broker of research ideas or as a spotter helping the academic-industrial artillery zero in on a distant target is immaterial; the style of operation would depend on the problem to be solved. In the case of well-focused objectives such as the tracing of populations of microorganisms so that one can tamper with the succession, the encounter session has been demonstrated to be effective. On the opposite end of the spectrum, as exemplified by the search for rheological principles in modern curing methods, the pendulum may swing more toward the tutorial aspects of communication. In view of the inseparability of education and research we offer this prospectus to elicit participation by those who wish to be on the receiving end of both endeavors.

> . . . and the song from beginning to end
> I found again in the heart of a friend.

References

(1) Homer, "The Odyssey," Translated by E. V. Rieu, London: Methuen (1952).

(2) Schiesser, R. H., Lui, Y. K., Schaeffer, W. D., and Zettlemoyer, A. C., "Pigment Dispersion in High Speed Impeller Mixers," Official DIGEST, *34*, No. 446, 265 (1962).

(3) Schaeffer, W. D., "A Supplementary Analysis of Adsorbed Alkyd Films," Official DIGEST, *37*, No. 490, 1305 (1965).

(4) Serafini, T. T. and Bobalek, E. G., "Lithium Soap Recipes for Particle Size Control in Emulsion Copolymerization of Styrene and Butadiene," Official DIGEST, *32*, No. 429, 1259 (1960).

(5) Woods, M. E., Dodge, J. S., Krieger, I. M., and Pierce, P. E., "Monodisperse Latices: I," JOURNAL OF PAINT TECHNOLOGY, *40*, No. 527, 541 (1968).

(6) Myers, R. R., "The Rheology of the Drying Process," Official DIGEST, *33*, No. 439, 940 (1961).

(7) Myers, R. R., "Catalysis of Film Formation and Degradation," Official DIGEST, *34*, No. 449, 575 (1962).

(8) Noel, R. and Patterson, D. D., "Polymers in Mixed Solvents," Official DIGEST, *32*, No. 423, 443 (1960); Delmas, G. and Patterson, D. D., "New Aspects of Polymer Solution Thermodynamics," ibid. *34*. No. 450, 677 (1962).

(9) Burrell, H., "Solubility Parameters for Film Formers," Official DIGEST, *27*, No. 369, 726 (1955). "The Challenge of the Solubility of Parameter Concept," JOURNAL OF PAINT TECHNOLOGY, *40*, No. 520, 197 (1968).

(10) Spencer, H. G., "Effects of Chemical Composition on the Diffusion and Permeability of Water Vapor in Polymer Films," Official DIGEST, *37*, No. 486, 757 (1965).

(11) Brown, W. R. and Park, G. S., "Diffusion of Solvents and Swellers in Polymers," JOURNAL OF PAINT TECHNOLOGY, *42*, No. 540, 16 (1970).

(12) Richards, J. H., "Reactions of Metallocenes," Official DIGEST, *36*, No. 479, 1433 (1964); "Ferrocene Photochemistry," JOURNAL OF PAINT TECHNOLOGY, *39*, No. 513, 569; "Metallocene Photochemistry," JOURNAL OF PAINT TECHNOLOGY, *41*, No. 533, 363 (1969).

(13) Pittman, C. U., Jr., "Preparation of Organometallic Polymers of Transition Metals," JOURNAL OF PAINT TECHNOLOGY, *43*, No. 561, 29 (1971); "Preparation of Linseed Oil Films Containing Chemically Bound Ferrocene," JOURNAL OF PAINT TECHNOLOGY, *45*, No. 582, 78 (1973); "Incorporation of Ferrocene and Other Organometallic Compounds Into Polymers and Films," JOURNAL OF PAINT TECHNOLOGY, *46*, No. 597, 35 (1974).

(14) Myers, R. R., Knauss, C. J., and Shroff, R. N., "Thermal Profiles by Torsional Braid Analysis," Intern. Congr. Rheology, Fifth Congr. Kyoto, Oct. 7-11, 1968, Proceedings *1*, 473 (1969).

(15) Seiner, J. A. and Gerhart, H. L., "Light Scattering from Microvoids: a Formulation Technique for Polymer Coatings," FATIPEC (Fed. Assoc. Techniciens Ind. Peintures, Vernis, Emaus Encres Europe Continental), 11th Congress, Florence, Italy, 127 (1972).

(16) Low, M. J. D., and Mark, H., "Infrared Fourier Transform Spectroscopy in the Coatings Industry" JOURNAL OF PAINT TECHNOLOGY, *42*, No. 544, 265 (1970); *43* No. 553, 31 (1971); *43*, No. 562, 49 (1971).

(17) Kerker, M., Cooke, D. D., and Ross, W. D., "Pigmented Microvoid Coatings: Theoretical Study of Three Models," JOURNAL OF PAINT TECHNOLOGY, *47*, No. 603, 33 (1975).

(18) Myers, R. R. and Schultz, R. K., "Acrylic Latex Film Formation in the Critical Temperature Range," J. Appl. Polymer Sci., *8*, 755 (1964).

(19) Myers, R. R., "Mildew Defacement of Organic Coatings," JOURNAL OF PAINT TECHNOLOGY, *43*, No. 558, 47 (1971).

(20) Myers, R. R., "Mildew Induced Defacement of Surfaces," JOURNAL OF PAINT TECHNOLOGY, *47*, No. 608, 62 (1975).

(21) Schmitt, J. A. and Padgett, D., "Mildew-Bacteria Symbiosis," JOURNAL OF PAINT TECHNOLOGY, *45*, No. 581, 32 (1973).

(22) Bennett, W. F., "Scientists or Citizens: The Goals Are the Same," Official DIGEST, *35*, No. 467, 1264 (1963).

(23) Judges 5:5.

(24) Reiner, M., "The Deborah Number," Physics Today, *17*, No. 62 (1964).

(25) Myers, R. R., Miller, J. C., and Zettlemoyer, A. C., "Viscometric Analysis of Dispersions at Small Shear Stresses," J. Appl. Phys., *27*, 468 (1956).

(26) Miller, J. C. and Myers, R. R., "A Photographic Study of Liquid Flow in a Roll Nip," Trans. Soc. Rheol. II, 77, (1959).

(27) Myers, R. R. and Schultz, R. K., "A Kinetic Study of Film Drying via Changes in Mechanical Properties," Official DIGEST, *34*, No. 451, 801 (1962).

(28) Myers, R. R., "Physical Characteristics of Film Formation," Chapter 22 in "Applied Polymer Science," J. K. Graver and R. W. Tess, Editors, Organic Coatings & Plastics Div. of American Chemical Society, 1975.

(29) Lewis, A. F. and Gillham, J. K., "Novel Technique for Following the Rigidity Changes Accompanying the Curing of Polymers," J. Appl. Polymer Sci. VI, 422 (1962).

(30) Mason, W. P., Baker, W. O., McSkimin, H. J., and Heiss, J. H., "Measurement of Shear Elasticity and Viscosity of Liquids at Ultrasonic Frequencies," Phys. Rev., *75*, 936 (1949).

(31) Myers, R. R. and Schultz, R. K., "Acrylic Latex Film Formation in the Critical Temperature Range," J. Appl. Polymer Sci., *8*, 755 (1964).

(32) Myers, R. R. and Knauss, C. J., "Drying Behavior and Adhesion of Acrylic Latexes," JOURNAL OF PAINT TECHNOLOGY, *40*, No. 523, 315 (1968).

(33) Myers, R. R., Klimek, J., and Knauss, C. J., "Continuous Monitoring of Changes in Mechanical Properties During Film Formation," JOURNAL OF PAINT TECHNOLOGY, *38*, No. 500, 479 (1966).

(34) Myers, R. R., "Relaxations During the Formation of Films," J. Polymer Sci., Part C, *35*, 3 (1971).

(35) Dodge, J. S., Woods, M. E., and Krieger I. M., "Monodisperse Latices II: Seed Polymerization Techniques Using Mixtures of Anionic and Nonionic Surfactants," JOURNAL OF PAINT TECHNOLOGY, *42*, No. 541, 71 (1970); Papir, Y. S., Woods, M. E., and Krieger, I. M., "Monodisperse Latices III: Cross-Linked Polystyrene Latices," JOURNAL OF PAINT TECHNOLOGY, *42*, No. 550, 571 (1970).

(36) Myers, R. R., "Report of the Research Director," JOURNAL OF PAINT TECHNOLOGY, *47*, No. 604, 25 (1975).

(37) Weaver, J. C., "People, Politics, & Publications," JOURNAL OF PAINT TECHNOLOGY, *46*, No. 589, 64 (1974).

(38) Gerhart, H. L., "Making Coatings Science Useful," JOURNAL OF PAINT TECHNOLOGY, *46*, No. 593, 38 (1974).

(39) Thames, S. F., "Coatings 1975-1985," JOURNAL OF PAINT TECHNOLOGY, *47*, No. 603, 19 (1975).

(40) Pelz, D. C. and Andrews, F. M., "Scientists in Organizations," John Wiley & Sons, 1966.

POSTSCRIPT

In 1965 the author reprinted in the *Transactions of the Society of Rheology,* 9 (1) 1 (1965) the following apocryphal story created by Dr. W. J. Wiswesser. The intent was to explain to TSOR referees why an occasional manuscript will appear in print over their objections.

Now, ten years later, the parable carries as much significance in connection with my message regarding faith in basic research. Having shared this gem with certain coatings scientists and having secured Dr. Wiswesser's permission, I submit it with a subheading appropriate to the occasion to the wider readership of the JCT as a suitable epilog to the lecture.

RAYMOND R. MYERS

The Empty Column

A Parable About an Idea and Its Encounter With an Unprepared Mind

Many years ago a Roman civil engineer, who was a high official in Alexandria, was approached by a young Arabian mathematician with an idea which the Easterner believed would be of much value to the Roman government in their road-building, navigating, tax-collecting, and census-taking activities. As the Arabian explained in his manuscript, he had discovered a new type of notation for number writing, which was inspired from some Hindu inscriptions.

The Roman official presumably studied this manuscript very carefully for several hours, then wrote the following reply:

"Your courier brought your proposal at a time when my duties were light, so fortunately I have had the opportunity to study it carefully, and am glad to be able to submit these detailed comments.

"Your new notation may have a number of merits, as you claim, but it is doubtful whether it ever would be of any practical value to the Roman Empire. Even if authorized by the Emperor himself, as a proposal of this magnitude would have to be, it would be vigorously opposed by the populace, principally because those who had to use it would not sympathize with your radical ideas. Our scribes complain loudly that they have too many letters in the Roman alphabet as it is, and now you propose these ten additional symbols of your number system, namely,

1, 2, 3, 4, 5, 6, 7, 8, 9, and your 0.

"It is clear that your 1-mark has the same meaning as our mark-I, but since this mark-I already is a well-established character, why is there any need for yours?

"Then you explain that last circle-mark, like our letter O, as representing "an empty column," or meaning nothing. If it means nothing, what is the purpose of writing it? I cannot see that it is serving any useful purpose; but to make sure, I asked my assistant to read this section, and he drew the same conclusion.

"You say that the number 01 means the same as just 1. This is an intolerable ambiguity and could not be permitted in any legal Roman documents. Your notation has other ambiguities which seem even worse: You explain that the Mark-1 means ONE, yet on the very same page you show it to mean TEN in 10, and one HUNDRED in your 100. If my official duties had not been light while reading this, I would have stopped here; you must realize that examiners will not pay much attention to material containing such obvious errors."

Further on, you claim that your system of enumeration is much simpler than with Roman numerals. I regret to advise that I have examined this point very carefully and must conclude otherwise. For example, counting up to FIVE, you require *five* new symbols whereas we Romans accomplish this with just two old ones, the mark-I and the mark-V. At first sight the combination IV (meaning ONE before FIVE) for four may seem less direct than the old IIII, but note that this alert representation involves LESS EFFORT, and that gain is the conquering principle of the Empire.

Counting up to twenty (the commonest counting range among the populace), you require *ten* symbols whereas we now need but three: the I, V, and X. Note particularly the pictorial suggestiveness of the V as *half* of the X. Moreover, it is pictorially evident that XX means ten-and-ten, and this seems much preferred over your 20. These pictorial associations are very important to the lower classes, for as the African says, "Picture tells thousand words."

You claim that your numbers as a whole are briefer than the Roman numerals, but this is not made evident in your proofs. Even if true, it is doubtful that this would mean much to the welfare of the Empire, since numbers account for only a small fraction of the written records; and in any case, there are plenty of slaves with plenty of time to do this work.

When you attempt to show that you can manipulate these numbers much more readily than Roman numerals, your explanations are particularly bad and obscure. For example, you show in one addition that 2 and 3 equal 5, yet in the case which you write as:

$$\begin{array}{r} 79 \\ \&\ 16 \\ \hline 95 \end{array}$$

this indicates that 9 and 6 also equal 5. How can this be? While that is not clear, it is evident that the other part is in error, for we know that 7 and 1 equal 8, not 9.

Your so-called "repeating and dividing" tables also require much more explanation, and possibly correction of errors. I can see that your "Nine Times" Table gives sets which add up to nine, namely

18 27 36 45 54 63 72 81 and 90,

but I see no such useful correlation in the "Seven Times" Table, for example. Since we have SEVEN, not nine, days in the Roman week, it seems far more important to have a system that gives more sensible combinations in this "Seven Times" Table.

All in all, I would advise you to forget this overly ambitious proposal, return to your sand piles, and leave the number reckoning to the official Census Takers and Tax Collectors. I am sure that they give these matters a great deal more thought than you or I can.

Selected Applications
Of Electrochemical Analysis
In the Coatings Industry

DARLENE R. BREZINSKI
DeSoto, Incorporated*

The application of electrochemical analysis to the coatings industry is discussed with particular emphasis given to polarography and modern voltammetric techniques. Because modern voltammetry is new in its application to the industry, the theory is briefly discussed and examples included for purposes of illustration. The techniques offer high sensitivity and versatility as they are applicable to both trace metal and organic functional group analysis.

KEY WORDS: Electrochemical analysis; Polarography; Voltammetry; Trace metal analysis; Organic functional group analysis.

INTRODUCTION

Within the last decade, a great deal of stress has been placed on the detection of heavy metals, especially those metals of toxilogical concern. In addition to metal analyses, recently organic materials have become the object of perhaps an even closer scrutiny. Governmental agencies have applied increasing regulatory pressure in the past few years and months on all industries in terms of toxic substances in their plants, their products and their waste materials. For many toxic substances, parts-per-million analyses no longer suffice, and parts-per-billion and sub part-per-billion detection levels are becoming routine requirements.

In order to meet new standards and requirements, a variety of sensitive techniques have been developed. For this reason many industries have looked to voltammetry and recent polarographic developments to meet new low level sensitivity standards. The versatility of polarography is ideal because it can be used to analyze trace metals as well as

organic functional groups, indeed virtually all compounds capable of being oxidized or reduced, hence its multifunctional capabilities.

The following discussion is not intended to be a review, however it is intended to present a new technique available to the paint and coatings industry — a technique which offers high sensitivity and versatility. Because this is a new technique to the industry, some discussion concerning the nature of polarography is needed, in addition to related examples.

Electroanalytical techniques fall into three major categories: potentiometry, coulometry and voltammetry. Voltammetry deals with the current-potential behavior of a system; the potential of an electrode is controlled and the resulting current measured. Voltammetry at a dropping mercury electrode (DME) has conventionally been called polarography.

The development of polarography began in 1922 with the work of Heyrovsky and marked a significant advance in electrochemical methodology. The fundamental dc, or classical, polarographic techniques were acceptable for analysis on the order of 10^{-5}M, but suffered from a lack of sensitivity when atomic absorption, atomic fluorescence and other micro techniques were developed. The electronic difficulties hindering the classical polarographic technique were overcome in the early 1960's, and the last decade has witnessed sophisticated techniques such as stripping analysis, ac polarography, square-wave and pulsed wave forms of polarography. Today, inexpensive multipurpose instrumentation provides sensitivity to the parts-per-billion level for many electroactive species.

$E_{1/2} \rightarrow$

-0.2   -0.4   -0.6   -0.8
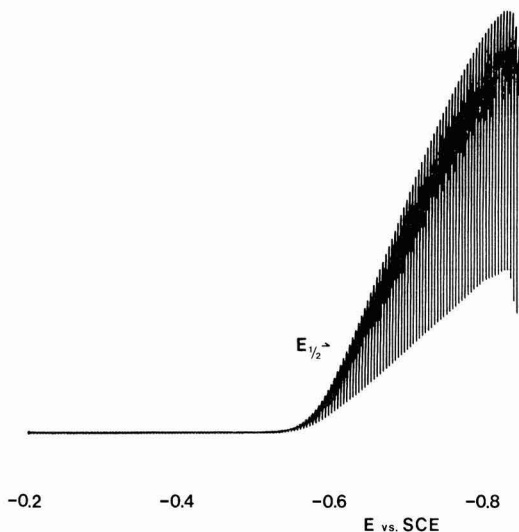
E vs. SCE

Figure 1—DC polarogram of cadmium (II). 10^2 M Cd (II) in 1 N NaOH. Scan rate of 2 mV/sec; drop time of 2 sec; current range of 0.1 mA

CLASSICAL OR CONVENTIONAL DC POLAROGRAPHY

DC polarography is a technique in which the current at a DME is measured as a function of potential. The technique involves applying a linearly varying dc potential between two electrodes, normally a DME and a suitable reference electrode such as the saturated calomel electrode (SCE). The current between these electrodes is recorded as a function of the applied potential.

Initially, very little faradaic current is observed until a potential is reached at which the metal ion(s) in solution undergoes reduction at the DME. Then the current increases very rapidly until it becomes diffusion limited. For each electroactive species a characteristic step like current-voltage wave is obtained. A typical dc polarogram is shown in *Figure 1*.

From the current-voltage curve, two important pieces of information may be obtained. First, the potential at the midpoint of the rising portion of the wave is known as the half-wave potential, $E_{1/2}$. The $E_{1/2}$ is characteristic for every electroactive species but is also a function of the solution conditions, i.e., electrolyte, pH, temperature, etc. Tables of $E_{1/2}$ values for various inorganic and organic substances in a variety of supporting electrolyte-solvent systems are available.[1,2]

In addition to a qualitative analysis of the species on the basis of its $E_{1/2}$ value, one may also measure the diffusion current, i_d, which is the difference in current between the baseline and the plateau of the wave. This difference in current is proportional to the concentration of the species in solution.

From observation of the polarographic wave (*Figure* 1) it becomes obvious why the classical method is lacking in sensitivity. The current oscillates between a near-zero value just after a drop is dislodged to a maximum value before the next drop falls. Because the electrode surface is repeatedly growing to a maximum as the drop grows and to zero as the drop dislodges, the current flowing in the system fluctuates in the same fashion.

The total observable current is a result of two different phenomena. The first contribution to the total current is the faradaic current arising as a result of the transfer of electrons across the electrode-solution interface. The second phenomenon is the capacitance current resulting because the electrode-solution interface exhibits capacitive characteristics. The capacitance current in dc polarography is a direct result of the change in electrode area. This is the main source of noise in a classical dc polarogram and, consequently, does not allow a high degree of sensitivity. All improved instrumentation for voltammetry is aimed at discriminating against the capacitance current.

PULSE POLAROGRAPHY

Frequently, the term 'pulse polarography' is used loosely without distinguishing between normal pulse polarography and differential pulse polarography. In pulsed techniques advantage is taken of the fact that following a sudden surge in applied potential, the capacitance current decays much more rapidly than the faradaic current.

In normal pulse polarography, potential pulses of successively increasing amplitude are applied to the DME at a fixed time during the drop life. Usually the pulse is applied toward the end of the drop life when dA/dt is small and the electrode may be considered a stationary electrode. The pulses are usually of about 50 mS in duration and the current is measured at some fixed time (about 40 mS) after the pulse application. The noise or capacitance current decays exponentially so the recorded signal is mainly faradaic and, therefore, sensitivity is improved about two orders of magnitude (10^{-7}M).

DIFFERENTIAL PULSE POLAROGRAPHY

In differential pulse polarography (DPP) a slowly varying potential ramp is applied to the electrode and superimposed are constant amplitude pulses of short duration occuring at the end of the drop life. DPP makes use of two equal length current samplings during the life of the drop. A sampling is taken before the pulse is applied and again after the pulse has been applied and the capacitance current has decayed. The difference in current is displayed on a recorder. Current differences only occur in the region of the half-wave potential, $E_{1/2}$, where the current is changing rapidly with potential. The
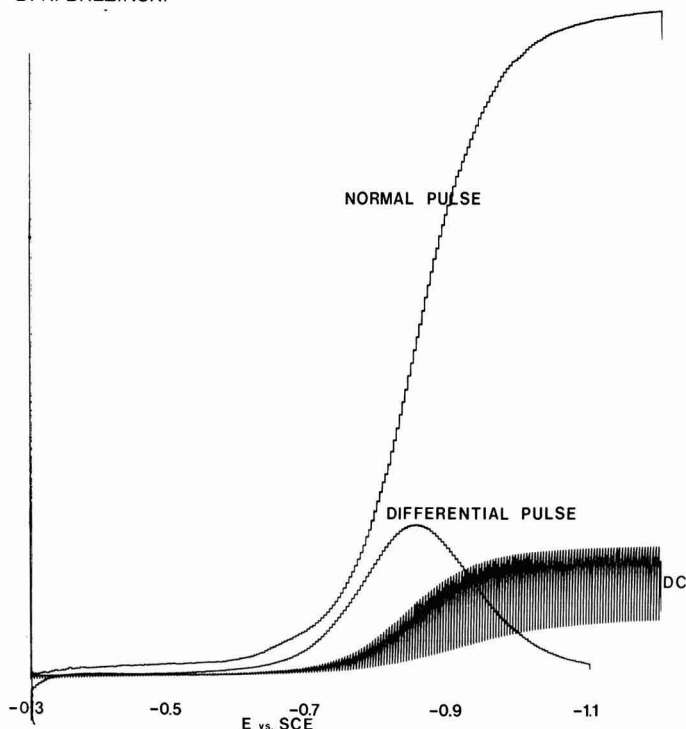
polarogram recorded is a peak shaped first derivative of a conventional dc polarogram. *Figure* 2 illustrates a comparison of dc and pulsed polarography for the reduction of Cr(VI) in 1N NaOH. From the polarogram, one can observe that the pulsed polarographic forms offer increased sensitivity over the conventional dc wave.

ANODIC STRIPPING VOLTAMMETRY (ASV)

Stripping voltammetry is a trace analysis technique whose sensitivity has improved considerably due to instrumentation advances. Comprehensive discussions of pulsed and stripping voltammetry are available,[3-8] and much current analytical work in the ppb or sub-ppb region is accomplished using various forms of stripping analysis.

The most widely applied version of stripping voltammetry is anodic stripping voltammetry (ASV). The technique may be characterized by three discrete steps: (1) the analytical species is deposited onto or into the working electrode; (2) a short period of equilibrium is attained; and (3) the species is oxidized or 'stripped' back into the solution.

The working electrode most widely used for ASV is the hanging mercury drop electrode (HMDE). This electrode is commercially available and consists of a capillary with a mercury reservoir and a micrometer syringe. The mercury drop is renewed between runs by 'dialing out' the size of drop required using the micrometer.

The technique involves a preconcentration step in which a metal ion(s) in solution is reduced by a controlled potential more negative than the reduction potential of the species being determined. The reduced metal forms an amalgam with the mercury electrode. The concentration step must be long enough to produce the required sensitivity; most analyses require 90-120 sec. The metals which are being deposited arrive at the electrode at rates determined by the concentration of the metal, the area of the electrode and the diffusion properties of the electrolyte.

Most stripping analysis work makes use of the sensitivity attained by the differential pulse technique. The differential pulse anodic stripping voltammetry (DPASV) technique combines the differential pulse technique with the preconcentration step of stripping analysis and permits sub-ppb analysis. Following the concentration step, the potential is scanned anodically thus stripping (oxidizing) the metal from the electrode. The faradaic current produced by the oxidation of each species is measured and a peak is recorded in the scan. The peak recorded is stripping current as a function of potential; the peak potential is a qualitative indication of the identity of the species, and the peak height a quantitative measure of concentration.

Figure 3 illustrates the DPASV analysis of an aqueous solution containing 500 ppb each of zinc (II), cadmium (II), lead (II) and copper (II). The
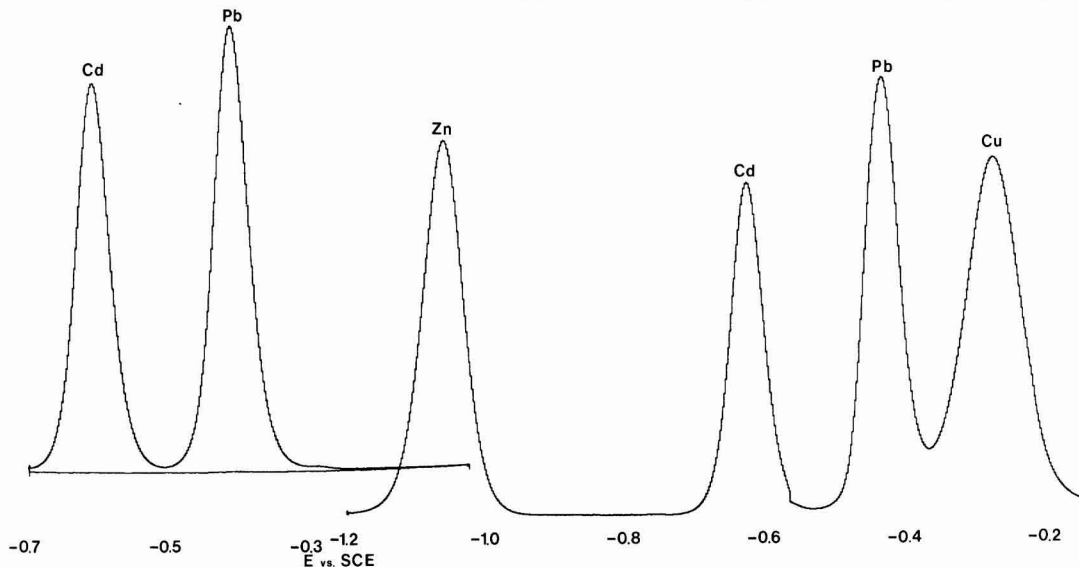
Figure 3—DPAS voltammetry of an aqueous solution containing 500 ppb each of Zn, Pb, Cd, and Cu. Scan rate of 2 mV/sec; deposition time of 60 sec; equilibration time of 30 sec; modulation amplitude of 25 mV; current range of 10-20μ A

solution is acidified with HNO_3 and the potential range scanned for cadmium and lead. A few drops of ammonia buffer are added to the cell to raise the pH and the sample is again scanned for zinc and copper. The concentration of each species, although known, was determined by comparison to standard calibration curves using the same deposition parameters. Recovery was 99% for all cations. This analysis has been run successfully on plant effluent samples with no prior treatment of the sample other than a simple filtration. For paint matrices, sample treatment (digestion) is necessary.

DPASV is certainly comparable to other sensitive techniques such as atomic absorption, atomic emission and atomic fluorescence. DPASV also has some very decided advantages: (1) qualitative and quantitative analysis; (2) simultaneous analysis of more than one species in a single scan; (3) very small sample size (5-100 nanograms); (4) nondestructive analysis; and (5) detection limits of 10^{-8}M (1 ppb) and below. One very obvious disadvantage of the technique is the contamination present in many electrolytes; ultra trace analysis requires high purity reagents and solvents, however this is also true for many trace techniques.

INSTRUMENTATION

All voltammetry in the present paper was done using a Princeton Applied Research polarographic analyzer Model 174, a Model 315 Automated Electroanalysis Controller, and a Houston omnigraphic x-y recorder. For most forms of voltammetry the following is necessary:

(1) a three electrode potentiostat
(2) a voltage ramp generator
(3) current measuring circuitry
(4) cell with working, reference and counter electrodes
(5) recorder or appropriate readout.

Characteristic of modern polarographic analyzers is potentiostatic control of the working electrode potential. In conventional forms of polarography, i.e., a two electrode system, the potential is applied across the entire cell and not just the solution-working electrode interface. If the cell contains a solution of high resistance, the current flowing through the cell will cause an appreciable voltage drop which will result in a shift in the peak potential, $E_{1/2}$, and reduce the total current thereby introducing errors into the results. To overcome this difficulty a third electrode, a reference counter electrode of constant potential, is introduced into the cell.
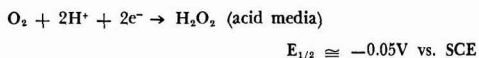
The potentiostatic system operates by first measuring the potential between the cell's working electrode and the reference electrode. This value is compared to the desired controlled potential and the difference adjusted to zero by circuitry, resistors and the cell's working and auxiliary electrodes. There is no current flow through the reference electrode circuit; for readout purposes the current measured is that flowing through the auxiliary and working electrodes.[5]

The electronic system must be capable of a minimum potential range from + 1.0 volts to −2.0 volts vs. the SCE. The current measuring circuitry
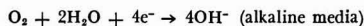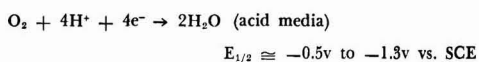
DR. DARLENE BREZINSKI is Technical Manager of the Instrumental Analysis Group in the Research Services Department of DeSoto, Inc. She received her M.S. and Ph.D. Degrees from Iowa State University in 1967 and 1969, respectively. Prior to joining DeSoto, she served as Assistant Professor and Chairman of the Chemistry Department of Mundelein College, Chicago, Ill.

must be sensitive to fractions of a microamp or nanoamp for ultra trace work.

The cell system contains the solution to be analyzed, the three electrodes and a nitrogen port for removing oxygen from the system. Before analysis, the solution should be purged with nitrogen to remove all dissolved oxygen from the solution. Solutions exposed to the atmosphere contain about 1 mM of dissolved oxygen. Oxygen interferes because it is reduced polarographically to water and hydrogen peroxide. Initially oxygen is reduced to hydrogen peroxide and/or hydroxide.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (acid media)}$$
$$E_{1/2} \cong -0.05V \text{ vs. SCE}$$
$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \text{ (alkaline media)}$$

Oxygen may be further reduced to water and hydroxide.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (acid media)}$$
$$E_{1/2} \cong -0.5v \text{ to } -1.3v \text{ vs. SCE}$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (alkaline media)}$$

In addition, the hydrogen peroxide produced can also affect other species in solution because it functions either as an oxidizing or reducing agent dependent on solution conditions. During analysis, the solution is also blanketed with nitrogen, to prevent dissolution of oxygen.

ELECTRODES
Working Electrodes

DME — The DME is the most commonly used type of microelectrode. This small polarized electrode is formed from a very fine bore glass capillary (0.05 – 0.08 mm id) which is connected to an elevated mercury reservoir on one end with the other end immersed in the solution. The pressure of the mercury column forces mercury through the capillary, a drop forms at the tip, grows, dislodges and a new drop forms. Stirring of the solution is caused by the falling drop.

The DME is useful over a potential range of + 0.3v to −2.8v vs. the SCE. At potentials more positive than +0.3v mercury is oxidized and gives an anodic wave. More positive potentials may be obtained by using non-complexing anions such as nitrate that form soluble mercury(I) and (II) salts. In 1 M HCl,

hydrogen evolution will occur at potentials more negative than −1.2v; supporting electrolytes of alkali salts are reduced at potentials approaching −2.0 volts.

The obvious advantages of using the DME are:

(1) a constantly renewable electrode surface is available

(2) surface area is reproducible with any given capillary

(3) hydrogen overpotential is high.

HMDE—The HMDE is used for stripping analysis. Its applicable potential range is limited on the anodic side by the oxidation of mercury. This occurs at approximately +0.3v vs. the SCE. On the cathodic side it is limited by H_2 evolution at approximately 1.8v vs. the SCE. This potential is pH dependent.

Both the DME and the HMDE are used mainly for reduction processes, but they can also be used for oxidation processes as in stripping voltammetry (Cu, Zn, Pb, Cd, Sb, Sn, etc.), the oxidation of various metal ions (Fe(II), Cr(II), etc.) and the oxidation of many organic compounds.

CARBON ELECTRODES—Carbon electrodes are very valuable in studying oxidative processes at potentials where mercury would be oxidized. Carbon electrodes are frequently used for studying amines and phenols. Of the many types of electrodes available, the glassy carbon electrode would be considered the optimum electrode of choice. It is an exceptionally hard electrode, has a high resistance to chemical attack and is the easiest to maintain.

REFERENCE ELECTRODES — The most commonly used reference electrode in polarographic or voltammetric work is the saturated calomel electrode (SCE). Also used with frequency is the silver-silver chloride electrode. For many non-aqueous solvents (pyridine, acetonitrile, acetic acid, dimethyl formamide, etc.) other reference electrodes may perform much better. The choice of reference electrodes in a non-aqueous solution is discussed thoroughly by Mann.[9]

COUNTER ELECTRODES—Any inert conductive material will serve as a counter electrode. The only requirement of the electrode is that it does not contribute any reducible species to the solution. A platinum wire dipping into the cell suffices nicely as a counter electrode.

SAMPLE PREPARATION

Electrochemical analysis is a solution technique. It therefore becomes essential that the species be in solution in a well characterized form whether it be as a metal cation, anion or an organic functional group. As with many other analytical techniques, sample dissolution and treatment is often the most

difficult and the most important step. If the material is water soluble, as in a plant effluent, there usually is no problem. Filtration, or centrifugation, may suffice and the sample may be run directly with only the addition of an appropriate acid or base. If the matrix is not water soluble, an organic cosolvent such as alcohol, dioxane, acetonitrile and dimethylsulfoxide may work well. Most samples in the coatings industry however require some type of prior treatment.

All metals analyzed in paint matrices were prepared by digesting the sample, (whole paint basis), in a Teflon lined bomb, using a 5:3 mixture of sulfuric and nitric acids. Sample size was on the order of 0.3 to 0.6 g. Following digestion, samples were carefully evaporated to near dryness and diluted to volume with distilled water.

For some samples, the Schöniger oxygen flask was used. The paint matrix (solids bases) was combusted, collected in a slightly acidic or basic medium and analyzed directly. Two difficulties need to be considered with the oxygen flask method. First, some metals tend to amalgamate with the platinum carrier in the flask,[10] and secondly, a given species may be oxidized to a higher oxidation state than desired.

The supporting electrolytes used are acids, bases or buffers. The purpose of the supporting electrolyte is to provide a conductive but electroinactive medium to 'carry' the current. In organic functional group analysis, pH is most important because hydrogen participates in most reductions, consequently buffer solutions are often used.

$$O = \langle \; \rangle = O \; + \; 2e^- \; + \; 2H^+ \longrightarrow \; HO - \langle \; \rangle - OH$$
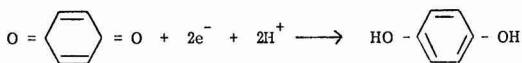
The field of organic polarography is currently as broad as that of metal analysis and is rapidly growing. The number of applications in the literature has mushroomed in the past two years. Excellent discussions of organic polarography are available.[11-13]

APPLICATIONS

The following discussion is concerned with applications of polarographic analysis for the paint and coatings industries, and includes some illustrative examples. Trace metal analysis is exceedingly important today with the ever-growing stress being placed on toxic materials and environmental haz-
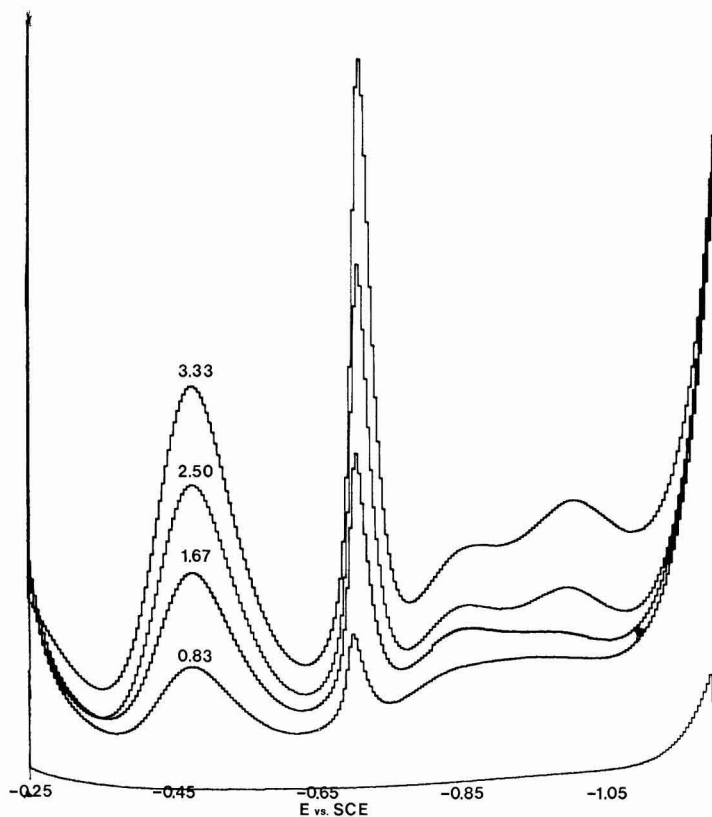

Figure 4—Differential pulse polarogram of arsenic (0.8-3.3 ppm). Arsenic (III) in 1 M HCl. Scan rate of 2 mV/sec; drop time of 2 sec; modulation amplitude of 50 mV; current range of 2 μA
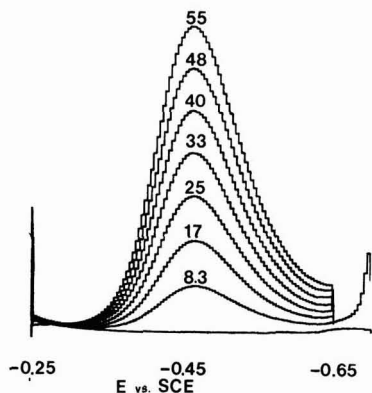
Figure 5—Differential pulse polarogram of arsenic (8-55 ppm). Arsenic (UI) in 1 M HCl. Scan rate of 2 mV/sec; drop time of 2 sec; modulation amplitude of 50 mV; current range of 0.05 mA
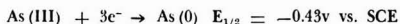
ards. Polarography is ideal for virtually all metal analyses, particularly because of its high sensitivity. It needs to be stressed, however, that the metal being analyzed must be present in a form suitable for analysis, hence the extreme importance of proper sample preparation. For purposes of illustration, arsenic, selenium and lead were determined in paint matrices. Sample preparation involved digestion in a Teflon lined bomb, evaporation to near dryness and dilution to volume. The bomb combustion technique appears to be suitable for all metals thus far examined that, due to matrix effects, cannot be analyzed directly.

ARSENIC

Arsenic is frequently found as a trace contaminant particularly in many pigments. Its accurate determination becomes increasingly important as governmental regulatory agencies become more stringent. Most sensitive arsenic analyses involve its reduction to arsine which is both time-consuming and often not reproducible.

The polarographic behavior of arsenic in various media has been reviewed by Arnold and Johnson.[14] In an acidic medium, the stepwise reduction of arsenic shows two waves. The first represents the reduction of arsenic (III) to arsenic (0), the second wave is due to further reduction to arsine.

$$As\,(III) + 3e^- \rightarrow As\,(0) \quad E_{1/2} = -0.43v \text{ vs. SCE}$$

$$As\,(0) + 3e^- + 3H^+ \rightarrow AsH_3 \quad E_{1/2} = -0.84v \text{ vs. SCE}$$

A current spike, or polarographic maximum, appears in the polarogram at −0.64 volts; this maximum disappears at arsenic concentrations below ~300 ppb. By measuring the first arsenic wave, arsenite concentrations ranging from 0.6 to 60 ppm can be determined accurately. The detection limit for arsenic is 0.22 ppb at the 95% confidence level.[15]

Figure 4 illustrates polarograms of arsenic at various concentrations (0.8 − 3.3 ppm) in 1M HCl; the blank scan may also be seen. Microliter spikes of arsenic were added from a standard arsenic stock solution prepared from As_2O_3 in a NaOH/HOH solution. A second set of arsenic polarograms (*Figure* 5) were run covering the range from 8 to 55 ppm. Only the first arsenic peak (−0.43v) was scanned.

Oxygen flask combustion was attempted on paint samples which had been spiked to contain 50 and 100 ppm of arsenic. Samples, weighing approximately 50 mg on a solids basis, were burned and collected in 0.1M HCl. For 10 samples analyzed, arsenic recovery averaged 65%. It was believed that this may be due to partial oxidation of arsenic (III) to arsenic (V) which is polarographically inactive in 0.1M or 1M HCl. Arsenic (V) can be reduced to arsenic (III) with copper (II) in concentrated HCl or by hydrazine sulfate.
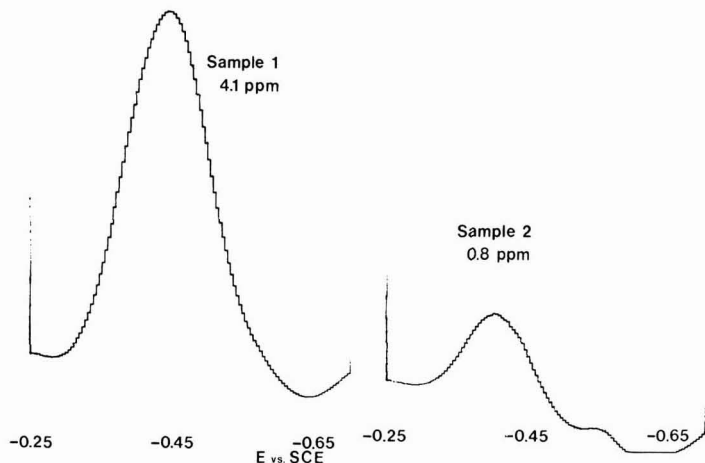

Figure 6—Differential pulse polarogram of arsenic in paint

Sample	Arsenic Added ppm	Arsenic Determined ppm	% Recovery
1	4.2	4.1	97.6
2	0.8	0.8	100.0
3	2.6	2.4	92.3
4	1.3	1.5	115.4
5	3.4	3.1	91.2

Lead Added ppm	Average Lead Determined ppm	Number of Analysis	Average % Recovery
0.30	0.29	5	96.7
0.50	0.48	4	96.0
1.0	1.0	5	100.0
1.5	1.45	6	96.7

The relatively poor arsenic recovery using the oxygen flask prompted the use of the bomb method previously described. Five separate samples were taken from a 100 ppm arsenic spiked paint, and subsequent aliquots analyzed. *Figure* 6 shows the actual polarograms obtained from two of the paint samples. The concentration of arsenic in each sample was calculated by comparison to standard calibration curves for arsenic using the same experimental parameters. *Table* 1 indicates the results of the five samples analyzed. Recovery for the five bomb digested samples averaged 99.3%, however individual recoveries varied ± 15%.

Lead (II), tin (II), and tin (IV) are known interferences in the arsenic determination. If they are known to be present in the solution, one may record the polarogram, add a small amount of cerium (IV) which oxidizes all arsenic (III) to arsenic (V) and rerecord to get the proper baseline. The excess cerium (IV) is reduced by the mercury metal present in the cell.

Micro quantities of selenium can be determined fluorometrically with great accuracy, however the procedures are time-consuming and require a number of extractions. Selenium (IV) in the presence of halide ions forms a complex which is absorbed on the surface of a hanging mercury drop electrode. This compound can be cathodically stripped from the HMDE and, since the stripping peak current is linear with concentration, can be used to quantitatively determine selenium. A comprehensive work concerning the polarographic behavior of selenium (IV) in various electrolytes is by Bock and Kau.[16]

Selenium is oxidized to the (IV) oxidation state using a sulfuric-nitric acid digestion in a Teflon lined bomb. Two selenium cathodic stripping peaks appear (*Figure* 7), one at −0.07v and one at −0.54v vs. a SCE. Both peaks may be used for quantitative work; however, the second peak is useful over a much wider concentration range. *Table* 2 shows the results of samples spiked to contain 25 ppb selenium.

Figure 7 is the polarogram of sample number one; the selenium concentration in the cell corresponds to 24 ppb (calculated from a standard calibration curve); theoretical selenium content was 25 ppb.

Paint chips containing lead as lead octoate were weighed, burned in the oxygen flask and collected in dilute nitric acid. The lead content as determined by atomic absorption spectroscopy was 212 ppb; lead determined by DPASV was 203 ppb (average of five determinations). The lead detection limit is known to be between 5-10 ppb with deposition times ranging from one to five min.

Lead was also spiked into wet paint samples and digested in the bomb. *Figure* 8 depicts four separate paint samples each containing different aliquots of lead, ranging from 0.3 to 1.5 ppm, final concentration. *Table* 3 indicates typical results obtained.

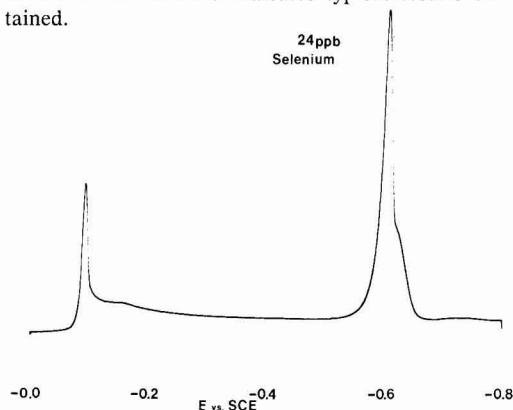| Sample	Selenium Added ppb	Selenium Determined ppb	% Recovery
1	25	24	96
2	25	24	96
3	25	25	100
4	25	26	104
5	25	25	100
		X = 24.8 St.Dev. = 0.8 RSD = 3.3	Avg. = 99.2

Figure 7—Cathodic stripping polarogram—paint spiked with selenium (100 ppm). Selenium (IV) in 0.2 M HCl. Scan rate of 20 mV/sec; deposition time of 60 sec; equilibration time of 30 sec; current range of - 0.5 μA
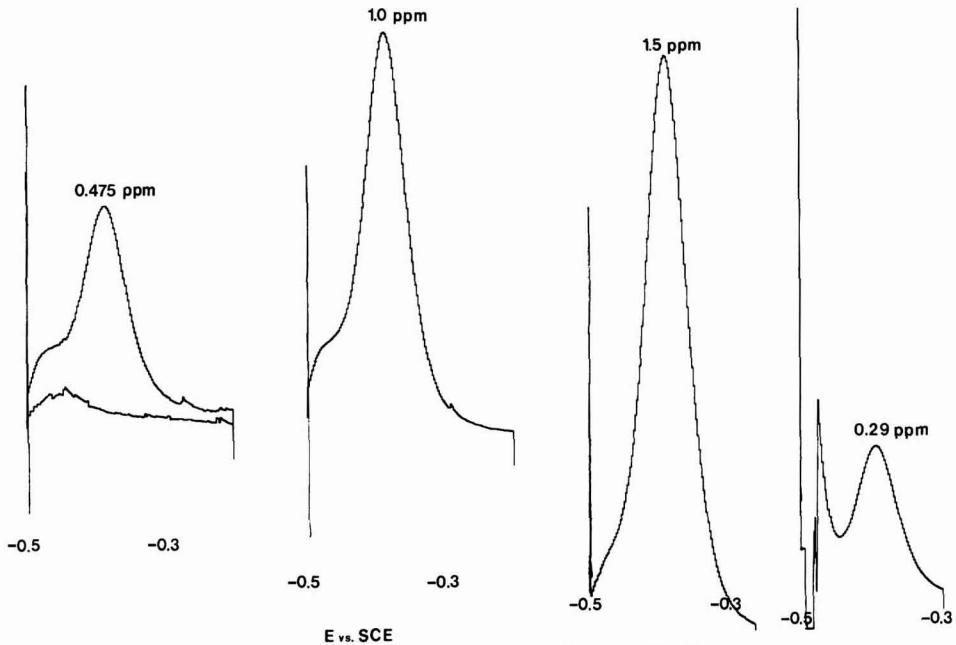
Figure 8—Differential pulse anodic stripping of lead in paint. Scan rate of 2 mV/sec; deposition time of 90 sec; equilibration time of 30 sec; modulation amplitude of 25 mV

It is often desirable to determine lead at low pH conditions (~1.5). At this pH, hydrogen reduction may interfere with the simultaneous reduction and determination of zinc, but it also insures that no lead is lost due to the presence of electroinactive lead-hydroxy complexes.

It is not redundant to again point out that one must choose the electrolyte that will give well-defined polarographic waves separated from interfering reactions. Typically one wants good separation between the metal ion(s) of interest and any other electroactive species known to be present in solution. The selection of proper electrolyte comes from consulting tables of half-wave potentials, the literature and experimentally accumulated information.

OTHER APPLICATIONS

The ability to determine most metals is limited primarily by the potential range of the electrodes of choice. Graphite electrodes are available and often desirable because the discharge-ionization reactions of hydrogen and oxygen occur with a high overvoltage. Methods are also available for the noble metals, thus expanding the versatility of voltammetry. In addition to the metals previously discussed, methods are available for gold, silver, mercury, bismuth, antimony, tin, nickel, cobalt, thallium, indium, and iron. The determination of the various oxidation states of iron is particularly attractive for corrosion studies. Metallic crosslinking

agents are often used in the industry and their determination necessary.

Figure 9 shows the polarographic waves of ammonia in an aqueous medium. Ammonia reacts with formaldehyde in an acetate buffer to yield hexamethylene triamine which can be determined by DPP. The applicable concentration range varies from 50 ppb to 600 ppb; the peak potential is at −0.9v vs. the SCE. Note should be taken of the level of ammonia present in the blank even though deionized distilled water was used. This high level of ammonia was detected in all samples analyzed. This method should be applicable to the determination of ammonia in emulsions.

Formaldehyde, which is used for the analysis of ammonia, can also be determined quantitatively in a lithium hydroxide-lithium chloride electrolyte. The peak potential appears at −1.7 volts with the detection limit at 20-30 ppb.

Figure 10 is a polarogram for 1 ppm maleic acid in the presence of 0.5 ppm fumaric acid. This analysis was done in an ammoniacal phosphate buffer which should allow simultaneous analysis of both acids. The shoulder of the fumaric acid can be seen at −1.6v, but in the electrolyte of choice (pH 7.2) the peak could not be separated. However, the sum of both acids may be determined in an acid medium, the maleic determined in a phosphate buffer and the fumaric determined by difference. Both acids are of interest because of their use in poly-
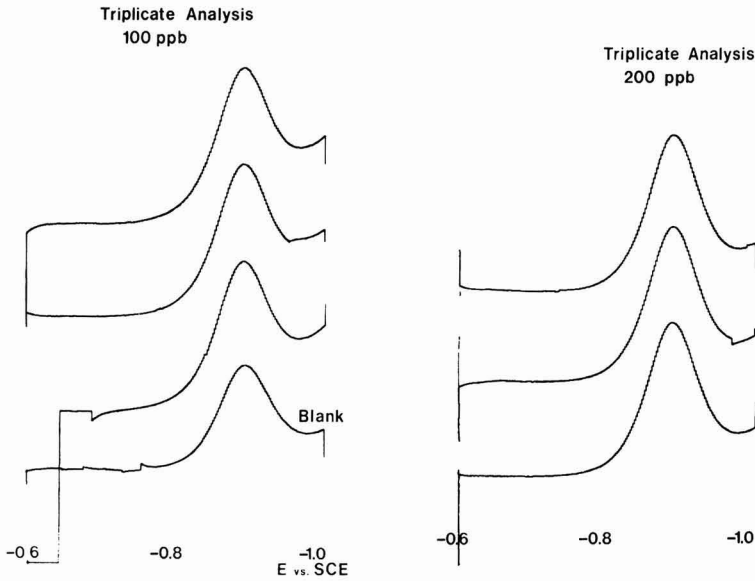
Triplicate Analysis
100 ppb

Triplicate Analysis
200 ppb

Blank

-0.6   -0.8   -1.0
E vs. SCE

Figure 9—Differential pulse polarogram of ammonia. Ammonia in acetate buffer with formalde-
hyde. Scan rate of 2 mV/sec; drop time of 1 sec; modulation amplitude of 25 mV; current range
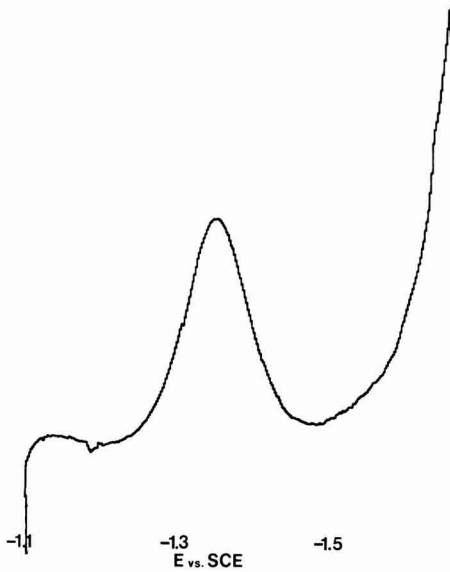of 1 µA, 2 µA

Maleic
Acid

Fumaric
Acid

-1.1   -1.3   -1.5
E vs. SCE

-1.0   -1.2   -1.4   -1.6
E vs. SCE

Figure 10—Differential pulse polarogram of maleic acid.
Phosphate-ammonia buffer. Scan rate of 2 mV/sec; drop time
of 2 sec; modulation amplitude of 25 mV; current range of 0.5 µA
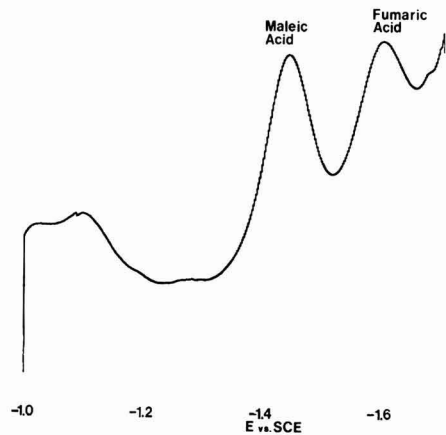
Figure 11—Differential pulse polarogram of maleic and fumaric
acids. Phosphate-ammonia buffer (pH 8.2). Scan rate of 2 mV/
sec; drop time of 1 sec; modulation amplitude of 25 mV; current
range of 1 µ A

Table 4—Reducible Organic Functional Groups

Acids	—RCOOH	Disulfide	—S—S—
Aldehyde	—CHO	Hydroxylamine	—NHOH
Alkene	>C=C<	Nitrile	—C≡N—
Anhydrides	(R—CO)$_2$O	Nitrate	—ONO$_2$—
Alcohols	—C—OH	Nitrite	—ONO—
Azo	—N=N—	Nitro	—NO$_2$
Azomethine	>C=N—	Nitroso	—NÓ
Azoxy	—NO=N—		

ester and alkyd resins. For fumaric and maleic acids it is the activated double bond that is reduced.

To illustrate the importance of the buffer and pH for organic functional group analysis, the above fumaric and maleic mixture (0.5 ppm: 1 ppm) was reanalyzed in a new ammoniacal phosphate buffer, pH 8.2. *Figure* 11 shows the polarogram of the two acids with the fumaric acid peak resolved.

Many organic functional groups lend themselves to polarographic analysis quite nicely. *Table* 4 enumerates some of these reducible functional groups.

The presence of the above functional group is not always sufficient to bring the wave of interest within an easily accessible potential range. The presence of another activating group is often necessary. Generally double bonds activated by the presence of a β-carbonyl group or conjugated with other double bonds are easily reduced. Many monomers and polymers contain double bonds that are amenable to polarographic analysis. Functional groups such as amines, phenols and mercaptans are oxidizable functional groups and as such can also be analyzed polarographically.

Particularly applicable to polymer analysis is the polarographic determination of acrylonitrile, alkyl methacrylates, styrene, vinyl acetate, phthalate esters and anhydrides. Antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tocopherols can be analyzed by DPP. Also easily analyzed by DPP are the photosensitizers, i.e., the benzophenones and quinones. The applications to the paint and coatings industry are many: residual monomers, functional end group analysis, catalyst residue (oxidizing agents, reducing agents, peroxides) etc., however the experimental parameters for most of the applicable areas need to be determined.

SUMMARY

As can be seen from the above discussion, polarography and modern voltammetric techniques have many applications in the field of chemical analysis, ranging from trace metals to organic functional groups.

The inherent sensitivity of pulsed and strip-ping techniques place polarography on a par with other atomic techniques commonly used. Polarography can complement other trace methods such as atomic absorption spectroscopy, fluorescence spectroscopy, etc., for those applications common to both. Perhaps of far greater importance is its utility and versatility for trace organic analysis. Polarographic techniques offer some distinct advantages, particularly where simultaneous analyses can be performed, and in terms of an extremely small sample size. Polarography can also distinguish between various species in solution, i.e., it is specific for chromium (VI) not total chrome in solution, iron (II), not total iron, etc. This type of information is frequently desired. The instrumentation is relatively inexpensive and quite easy to operate.

There are difficulties however, and those difficulties are concerned with sample preparation. This is particularly true when the matrix is complex as is often the case in the coatings industry. For trace metal analysis, sample digestion with precautions to ensure the correct oxidation state of the metal desired and minimal loss due to volatilization appears to be simple, rapid, reproducible and accurate. For organic analysis however, much more experimental work in the field is necessary. □

References

(1) Meites, L., "Polarographic Techniques," 2nd ed., Interscience, New York, 1965.

(2) Meites, L., ed., "Handbook of Analytical Chemistry," McGraw-Hill, New York, 1963.

(3) Brainina, Kh. Z., "Stripping Voltammetry in Chemical Analysis," John Wiley and Sons, New York, 1974.

(4) Barendrecht, E., "Stripping Voltammetry," Chapter in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, ed., Marcel Dekker, New York, 1967.

(5) Ellis, W. D., *J. Chem. Ed.*, 50, No. 3, A131 (1973).

(6) Copeland, T. R. and Skogerboe, R. K., *Anal. Chem.*, 46, 1257A (1974).

(7) Parry, E. P. and Osteryoung, R. A., *Anal. Chem.*, 37, 1634 (1965).

(8) Siegerman, H. and O'Dom, G., *Amer. Lab.*, 4(6), 59 (1972).

(9) Mann, C. K., "Electroanalytical Chemistry," Vol. 3, A. J. Bard, ed., Marcel Dekker, New York, 1969.

(10) Bishara, S. W., Gawargious, Y. A., and Faltaoos, B. N., *Anal. Chem.*, 46, 1103 (1974).

(12) Zuman, P., "Topics in Organic Polarography," Plenum Press, Oxford, England, 1964.

(12) Auman, P., "Topics in Organic Polarography," Plenum Press, New York, 1970.

(13) Zuman, P., "Substituent Effects in Organic Polarography," Plenum Press, New York, 1967.

(14) Arnold, J. P. and Johnson, R. M., *Talanta*, 16, 1191 (1969).

(15) Myers, D. J. and Osteryoung, J., *Anal. Chem.*, 45, 267 (1973).

(16) Bock, R. and Kau, H., *Z. Anal. Chem.*, 188, 28 (1962).

Color and Appearance
Of Metallized Paint Films

II. Initial Application of Turbid-Medium Theory

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Despite the preliminary nature of this initial application of turbid-medium theory to metallized paint films, certain trends became apparent. This report presents guidelines and recommendations. Preferred conditions include collimated illumination along the normal to the sample and collimated viewing at two angles, one within and one far outside the specular envelope. (These conditions require use of equipment not commercially available in the U.S.) A many-flux calculation using approximately twelve fluxes is required. Preliminary results are encouraging, and ultimate extension to computer formulation in metallic systems should be straightforward though complex. Future theoretical research, as specified, should be centered on pigment and sample characterization and application of the many-flux theory.

KEY WORDS: Color, Metallized paint films; Turbid-medium theory, Computer formulation.

INTRODUCTION

The difficulties of color matching in metallized paint films, by which we mean paints containing flake aluminum or the like as a pigment, are well known. Even the quantitative instrumental characterization of these materials is difficult and, as described in our preceding papers on this subject,[1-3] requires special instrumentation not widely available.

In addition to the characterization of materials in terms of numerical data, the objective approach to color matching in metallized paint films requires appropriate theory. To date such theory has not been fully developed, to our knowledge. It is the purpose of this paper to describe our own research in this direction, even though it has not yet led to a complete solution to the color-matching problem,

and to outline the features we think should be incorporated in such a solution.

The metallic effect which makes color matching in the paint films under consideration both important and difficult consists in the change in color and appearance of the film with change in illuminating and viewing conditions. As described in Paper I[3] of this series, this change is attributed to the presence of the aluminum flakes, oriented nearly parallel to the surface of the film. For any angle of illumination, there exists a range of viewing angles, which we call the specular envelope, within which light is reflected from the flakes; this component of the reflected light contributes strongly to the lightness and color of the sample. At viewing angles outside the specular envelope, this effect is absent; the sample usually appears darker and possibly different in color.

The flakes of aluminum responsible for this effect are much larger in lateral dimensions than most pigments, being typically 1-60 μm in diameter, but only about 1/1000 as thick. They are opaque, and because of their size are often described as reflecting rather than scattering light. The relations among physical properties such as size and surface area of aluminum flake pigments, and their optical properties including reflectivity are described elsewhere,[4,5] as is the variety of visual effects obtained by combining them with various sorts of conventional colorants.[6]

PREVIOUS ATTEMPTS TO COLOR MATCH METALLIZED PAINT FILMS INSTRUMENTALLY

None of the previous efforts to apply instrumental measurement and computation to color matching in metallized paint films has taken into account both the specialized nature of the measure-

ments and the special theory required. On the whole, all must be considered empirical modifications of more or less conventional techniques. That some have met with at least partial success must be attributed, in our opinion, more to the power of the iterative approach to a computer color match than to the proper application of measurement techniques and theory. As a recent review[7] points out, it often seems that even the crudest theory, applied repetitively, can yield useful results in computer color matching.

The earliest description of which we are aware of computer color matching of metallized paint films was H. R. Davidson's application[8] of the "COMIC I" colorant mixture computer to this problem. Only one measurement, typically using integrating-sphere geometry, was made, and the COMIC-I approximation to Kubelka-Munk two-flux theory was used. The only recommended change from conventional techniques was to obtain basic calibration data from mixtures of colored pigment and aluminum rather than colored pigment and white. The attempts were not sufficiently successful to warrant further development.

A more recent attempt[9] to utilize conventional measuring instruments, not yet described in the literature, is stated to use two sets of integrating-sphere measurements, with the specular component included and excluded, to get some information related to the appearance of the sample including and excluding at least a part of the specular envelope. Presumably, conventional Kubelka-Munk turbid-medium theory is used, and the computation is such as to match the two sets of tristimulus values. The method is said to be under test, with no results yet available.

A recent patent[10] describes a similar approach, except that the two measurements are derived from biconical reflectance factors (see the Appendix to Paper I[3] for definitions of this and other terms) obtained with illuminating and viewing angles 45° apart, preferably −45°/0° and 25°/70° for illuminating/viewing, respectively.

Another approach[11] of this type, but better in that a wider selection of angles is available, employs the Leres "Trilac" (Kollmorgen KCS-15) goniospectrophotometer. Here, at least, it would be possible to select illuminating and viewing angles not constrained to a fixed angular separation, so that measurements within and outside the specular envelope could be obtained. Not described in the literature, the approach is said to be under test, but no results are available. The goniospectrophotometer is no longer commercially available in the U.S.

Only one paper is known to us in which an attempt was made to derive special theory to cover the case of metallized paint films. Grösswang[12] modified the conventional derivation of Kubelka-

Munk two-flux theory by including a variable ratio of forward to backward scattering. The case of a metallized film was considered to result in a much greater backward than forward scattering, due to reflection from the aluminum flakes. A simple result was obtained for opaque samples: Instead of the usual Kubelka-Munk function $K/S = (1-R)^2/2R$, Grösswang derived $K/S = (1-R)/2R$ for the metallic case. In his only reported test of the relation, conventional (but unspecified) measurements were used. We are not aware that his theory has been further applied.

EXPERIMENTAL
Instrumentation

SPECTROPHOTOMETRY AND COMPUTATIONS—Conventional spectrophotometric measurements were made on a Kollmorgen[13] KCS-40 abridged spectrophotometer,[14] utilizing diffuse illumination and viewing 6° from the normal with an integrating sphere. Various numbers of narrow-band interference filters, up to 38 spaced at 10-nm intervals from 380 to 750 nm, were used to obtain spectral reflectance factors with pressed $BaSO_4$ as the white reflectance standard. The specularly reflected component could be included or excluded as desired. The instrument is interfaced to a PDP-8 digital computer, on which CIE tristimulus values for illuminant C and the 1931 2° standard observer, and FMC-2 color differences could be calculated. Other calculations were made on an IBM 360-50 computer.

SPECTROGONIOPHOTOMETRY — Measurements as a function of wavelength at various illuminating and viewing angles were made on a research spectrogoniophotometer.[2] One of the main limitations of this instrument in its original form was that the physical size of the components required at least a 23° angular separation between the illuminating and viewing beams. To reduce this separation, a set of
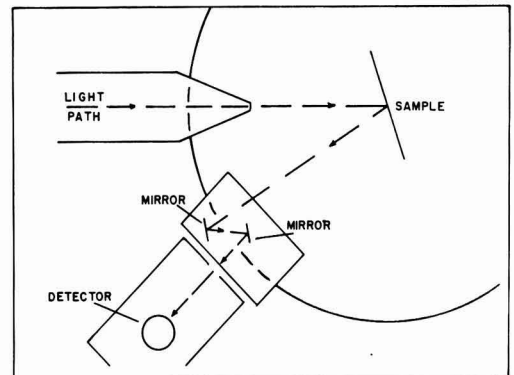

Figure 1—Light path in the modified research spectrogoniophotometer, allowing the illuminating and viewing beams to be within 5° angular separation

mirrors was mounted in the viewing beam, as indicated in *Figure* 1, in such a way as to allow sample measurement with the two beams separated by as little as 5°.

The white standard used in this apparatus was pressed $BaSO_4$ measured with −45/0 geometry. Relative biconical reflectance factors measured in this way were occasionally arbitrarily but consistently multiplied by 0.5 to reduce numerical values below 100 for convenience in color-difference calculation. Radiometric calibration in terms of radiances or reflectances (see Appendix of Paper I[3]) was not made.

PHASE FUNCTIONS—Measurement of the phase function was made on conventional light-scattering photometers.[15,16] By phase function we mean the angular distribution of the light scattering by a colorant when measured in a sufficiently dilute suspension that the once-scattered light is observed directly, without being rescattered.

Samples and Measurements

Three series of samples, described in *Table* 1, were used in this work.[17,18] They consisted of alkyd melamine resin paints sprayed on metal plates. The pigments used were quinacridone violet (Quindo Violet RV6902, Harmon Colors, Allied Chemical Corp.), and phthalocyanine green (exact pigment unknown). The aluminum was either Alcoa Tinting Paste 222 (coarse grade) or 1595 (fine grade) (Alcoa). Series M was the same set of samples used in Paper I.[3]

Each sample was measured three times at each of three geometries: diffuse/6° on the KCS-40, and 0/8° and 0/75° on the research spectrogoniophotometer. The latter geometries were selected to be inside and well outside the specular envelope, respectively. The geometry inside the specular envelope was far enough from the specular angle to
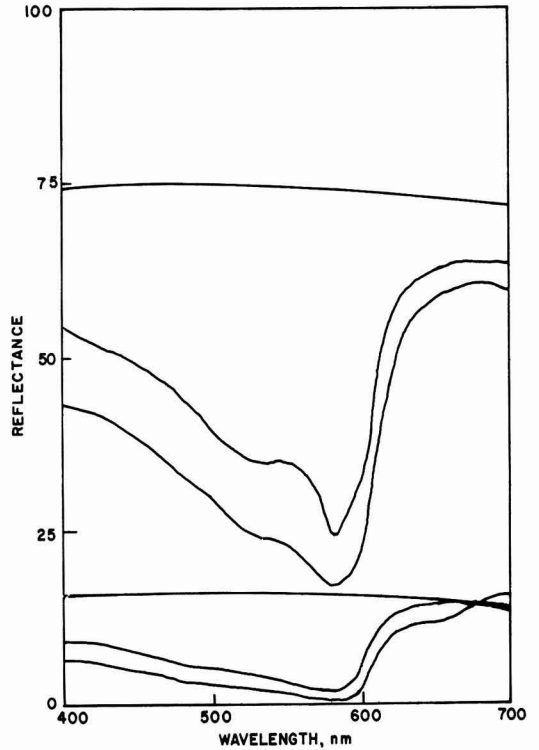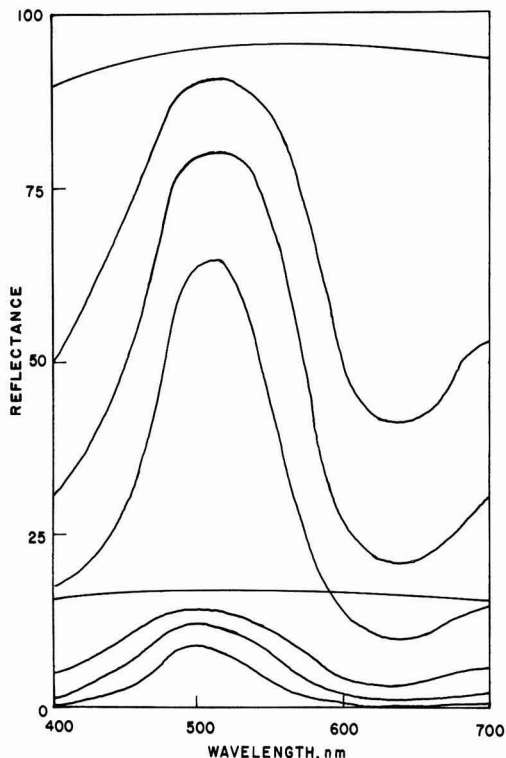

Figure 2—Spectrogoniophotometric curves of the samples of Series M at two illuminating-viewing geometries. The ordinate is relative biconical reflectance factor. Top to bottom, the geometries and samples are: 0/8°, M-54, M-57, M-60; 0/75°, M-54, M-57, M-60

avoid the sample's first surface reflection. The measurements were made at 16 wavelengths at 20-nm intervals from 400 to 700 nm. The average of the three measurements at each wavelength and geometry was calculated. These averages are plotted as spectrophotometric curves in *Figures* 2 and 3 for Series M and K, respectively; results for Series J were quite similar to those for Series K.

The variability in the spectrogoniophotometric measurements is substantially greater than in the conventional spectrophotometric measurements (mean color difference among measurements 1.3 and 0.35 units, respectively). We attribute this difference in part to the greater stability of the KCS-40, typical of double-beam vs. single-beam instrumentation, and in part to the fact that diffuse illumination minimizes the variations in reflection due to irregular orientation of the aluminum flakes.

Determination of Constants

SCATTERING AND ABSORPTION COEFFICIENTS — For the quinacridone violet, a spectral reflectance factor curve of the pigment in TiO_2 at complete hiding, provided by Harmon Colors, was used for the cal-

Table 1—Samples and Their Components

| Sample Number | Aluminum | | Pigment | |
	Type	Concentration*	Name	Concentration[a]
M-54	222	0.03	——	——
M-57	222	0.03	Quinacridone violet	0.03
M-60	222	0.03	Quinacridone violet	0.06
J-2	222	1.00	——	——
J-3	222	0.75	Phthalocyanine green	0.25
J-4	222	0.50	Phthalocyanine green	0.50
J-5	222	0.25	Phthalocyanine green	0.75
K-2	1595	1.00	——	——
K-3	1595	0.75	Phthalocyanine green	0.25
K-4	1595	0.50	Phthalocyanine green	0.50
K-5	1595	0.25	Phthalocyanine green	0.75

(a) Concentration is given in percent by weight.

Figure 3—Spectrogoniophotometric curves of the samples of Series K at two illuminating-viewing geometries. The ordinate is relative biconical reflectance factor. Top to bottom, the geometries and samples are: 0/8°, K-2, K-3, K-4, K-5; 0/75°, K-2, K-3, K-4, K-5. The curves for the samples of Series J are quite similar, and are not shown

culation of the ratio of Kubelka-Munk absorption and scattering coefficients using the function.

$$K/S = (1 - R\infty)^2/2R\infty, \qquad (1)$$

where $R\infty$ is reflectance factor at complete hiding.

A film at incomplete hiding, of known thickness and pigment concentration, was available[18] for the phthalocyanine green. Separate values of K and S were calculated in several ways: (1) from reflectance factor R_0 over black and diffuse transmittance T, both measured on a General Electric (Hardy) spectrophotometer using illumination at 6° from the normal and diffuse viewing; (2) R_0 and reflectance factor R over a background (nominally white) with reflectance factor R_g measured on the KCS-40; and (3) from R_0, R, and R_g determined with biconical geometry on the spectrogoniophotometer. For case (1) the relations used were

$$
\begin{aligned}
a &= (1 + R_o{}^2 - T^2)/2R_o \\
b &= (a^2 - 1)^{1/2} \\
S &= (1/bX) [sinh^{-1} (b/T) - sinh^{-1} b] \\
K &= aS - S
\end{aligned}
\qquad (2)
$$

where X is the sample thickness. For cases (2) and (3), they were

$$
\begin{aligned}
a &= \frac{1}{2}[R + (R_o - R + R_g)/R_oR_g] \\
b &= (a^2 - 1)^{1/2} \\
S &= (1/bX) coth^{-1} [(1 - aR_o)/bR_o] \\
\text{or} \quad S &= (1/bX) [coth^{-1} \frac{a-R}{b} - coth^{-1} \frac{a-R_g}{b}] \\
K &= aS - S
\end{aligned}
\qquad (3)
$$

The values of K and S determined were quite different for the three cases, but the subsequent predictions using these constants appeared to be largely independent of the method so long as predictions made with one set of constants are compared to reflectance factors measured with the same geometry.

PHASE FUNCTION—The phase function for flake aluminum was determined by spectrogoniophotometric measurement of a paint sample containing flake aluminum only at normal incidence. The result is shown in *Figure* 4, curve (a). In the figure, the convention for enumerating angle is such that 180° is the normal to the film and 90° is parallel to the surface of the film. Corrections were made to the data for first-surface reflections and internal scattering angle; in terms of the latter and the scale plotted, measurements were available between about 176° and 135°. Beyond these limits the data were
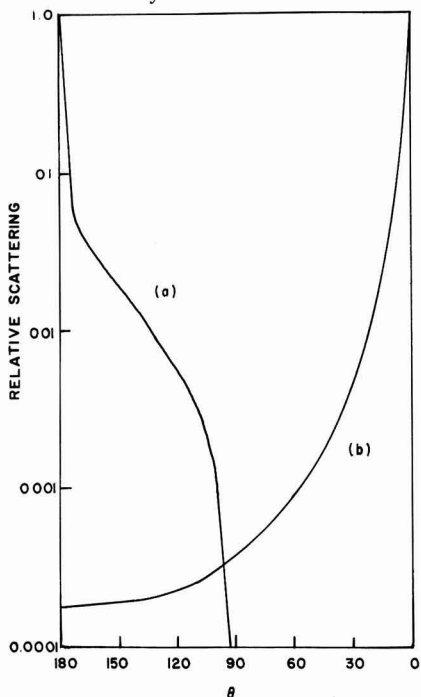
Figure 4—Phase functions for (a) aluminum flakes and (b) quinacridone magenta. Note that zero angle represents the direction of regular transmission through the sample, as is customary in scattering measurements

extrapolated smoothly to 180° and to zero at 90°, on the assumption that the relatively large, opaque, flakes do not scatter significantly in the forward direction (angles less than 90° as plotted). Although the latter extrapolation appears extreme, the way in which the phase function is used in the many-flux theory makes the data in this region less important.

The phase function for quinacridone violet, shown in *Figure 4*, curve (b), was assumed to be in the same as that for quinacridone magenta, and the phase function for this pigment was measured on a dilute suspension of the pigment in benzene (which has the same refractive index as the dry alkyd melamine resin system). The measurements were made at $\lambda = 436$ nm on conventional light-scattering photometers over the angular range 0-150° (measured from the transmitted beam direction) and extrapolated graphically from 150° to 180°.

APPLICATION OF TURBID-MEDIUM THEORY
Model

In review of Paper I,[3] the minimum model for a metallized paint film used in this research consists of a film of finite thickness, large in lateral dimensions compared to its thickness. It is illuminated by any desired combination of diffuse and collimated light, and the angle of illumination for the collimated portion can be varied from normal to grazing. There is a change in refractive index at the sample boundaries, described by the usual reflection coefficients.

Inside the sample, collimated and diffuse light beams are scattered and absorbed by pigment particles (if present). Light is absorbed and reflected, but not scattered, by the metallic flakes, which are oriented approximately parallel to the surface of the film. Light reflected from the flakes is observed outside the film over a range of angles around the specular reflection angle, forming what we call a specular envelope.

Reflections at the back surface of the film, which may or may not be in optical contact with a background, must be taken into account. The flux leaving the front surface of the film may be observed at any angle, or diffusely as with an integrating sphere.

Kubelka-Munk Approach

THEORY — It is well known that the Kubelka-Munk (K-M) and other two-flux turbid-medium theories[19] require a single measurement of all the reflected light; they cannot account for the metallic effects in detail. Nevertheless it was considered instructive to introduce terms corresponding to the effect of the metallic flakes into the K-M theory be-

cause of its simplicity. This was done by defining the following two terms:

"C" is defined as the effective fraction of the illuminated area of the film which is filled or covered with aluminum flakes; it is a function of the concentration of aluminum in the film.

"A'" is the reflectivity or reflection coefficient of the aluminum; it is a function of the orientation of the flakes.

The derivation of the K-M theory proceeds from a consideration of what happens to a diffuse light flux on passing through a layer inside the film. In the conventional case it is decreased by absorption and scattering in amounts proportional to K and S, respectively; in the metallic case it is also decreased by reflection from the aluminum, proportional to C. The flux is also increased by light coming from a second flux traveling in the opposite direction. In the conventional theory, this increase is proportional to S; in the metallic case we add a further increase proportional to CA. The net effect of these changes is to substitute [S + CA] for S wherever it occurs in the K-M equations, and [K + C(1−A)] for K wherever it occurs. These changes lead, for example, to what we call the metallic K-M function.

$$\frac{K + C(1-A)}{S + CA} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{4}$$

replacing equation (1).

APPROACH — When there is no scattering pigment in the film (aluminum only present), equation (4) reduces to

$$\frac{1 - A}{A} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{5}$$

which can be used to evaluate A. Then C may be evaluated from measurements on a film containing both aluminum and a scattering pigment for which K and S have been determined. Equation (4) is solved for C to do this:

$$C = \frac{(1 - R_\infty)^2 S + 2R_\infty K}{2R_\infty - A(1 + R_\infty)^2} \tag{4a}$$

Even though it is well known to be inappropriate, we tested these equations using spectrogoniophotometric data for the samples of series J and K, utilizing the following steps:

(1) Measure all samples, including those with aluminum only and those with pigment only, at 0/8° and 0/75° geometries, for each of 16 wavelengths.

(2) Correct all relative reflectance factors for surface reflections following Saunderson,[20] and using the theoretical[21] value for the diffuse internal reflection coefficient.

(3) Calculate A from equation (5) for the samples containing aluminum only.

(4) Calculate K and S at unit concentration for

the pigment from the samples containing phthalocyanine green only (case (3) of the preceding section).

(5) Calculate C at unit concentration from the above constants and data for one of the samples of the series.

(6) Calculate the metallic K-M function from the above optical constants and the concentrations corresponding to the remaining samples of the series. Assume that K and S are proportional to the concentration of the phthalocyanine green, and C is proportional to the concentration of the aluminum.

(7) Calculate relative reflectance factors, correct them for surface reflection by applying Saunderson in reverse, calculate tristimulus values, and calculate FMC-2 color differences between these predicted tristimulus values and those derived from measurement of the samples.

RESULTS — Values of the reflectivity A of the aluminum appeared quite reasonable, being near 0.95-1.0 for the 0/8° geometry and near 0.3 for the 0/75° geometry, and essentially independent of wavelength in both cases. No significance is attributed to a non-zero value of A outside the specular envelope since it is well recognized that the K-M approach fails to account properly for the physical behavior of the system.

Values of the effective surface area of the aluminum, C, appeared to be less satisfactory. Their wavelength dependence strongly resembled the reflectance curve of the phthalocyanine green, and for the 0/8° geometry there was a strong dependence on pigment and aluminum concentrations (which were varied simultaneously; see *Table* 1). Neither of these features was expected, since C should enter only into a description of the effect of the flake aluminum in reflecting light, completely independent of the presence or characteristics of other pigments in the film.

Despite the problems with C, the predicted relative reflectance factors and tristimulus values for 0/75° geometry were remarkably close to those measured, the color differences averaging 1.3 units. It should be pointed out that these were single, not iterative, calculations. For the 0/8° geometry, however, where the effect of the aluminum was much greater, lightness was very poorly predicted, and the color differences (virtually entirely lightness differences) averaged about 53 units.

Within the limits of error of the experiments, the metallic K-M function was a linear function of concentration, as the theory predicts.

B-A-B Approach

Similar studies were made using the four-flux theory of Beasley, Atkins and Billmeyer,[1,22] but the additional complexity of this theory led to no improvement in results. This is also not unexpected, since the four-flux theory for the metallic effect has the same shortcomings as the Kubelka-Munk theory.

Many-Flux Approach

THEORY — The many-flux approach developed by Richards,[23,24] offers the opportunity of accounting for the metallic effect angle by angle, provided that appropriate geometries of illumination and viewing are selected. As the method is formulated, the channels in which the flux is evaluated are symmetrical about the normal to the surface of the sample. It is necessary to employ illumination along the normal (0° illuminating angle) to preserve this symmetry. Viewing angles may then be selected to be inside and outside of the specular envelope, as desired; in this work, they were selected to be 8° and 75° for these two conditions, respectively.

In the many-flux approach, the metallic flake and the scattering pigment are treated alike as far as optical constants are concerned: Each is characterized by an absorption coefficient for collimated flux, k (not the Kubelka-Munk K; in general,[25] $K \cong 2k$), and the phase function which describes its scattering as a function of angle. The equivalent of a statement that the aluminum reflects rather than scatters is contained in the phase function, which goes to zero at angles in the forward direction as *Figure* 4 shows.

APPROACH — Many-flux calculations were carried out using a computer program obtained from L. W. Richards.[26] In preparing to perform these calculations, it is convenient first to determine the refractive index of the medium (the paint film without pigments), n, and calculate the critical angle for total reflection θ_c from the relation $\sin \theta_c = 1/n$ (assuming the film to be in air, n = 1). In our case n = 1.50 and $\theta_c = 41°49'$.

The choice of the number of fluxes or channels and their definition must next be made. Many factors influence this choice, and our work does not lead to clear-cut recommendations. It is convenient to isolate the incident beam and the two alternative viewing beams in relatively narrow channels, and to place an additional channel boundary at or near the critical angle. For the choice of geometries we made, the critical angle was close to the angle inside the film (40°5′) corresponding to the 75° viewing angle, so that one boundary of that viewing channel could be placed near the critical angle. Thus, in one study we used 12 channels with the following angular ranges inside the film: 0–1° (illuminating), 1°−4.5°, 4.5°−6.5° (around the 8° viewing angle which is 5°19′ inside the film), 6.5°−39°, 39°−41° (around the 75° viewing angle and ending near the critical angle), 41°−90°, and for computational convenience the six

symmetrical to these between 90° and 180°.* This appears to be the minimum number of channels required to describe the model; we are uncertain whether more channels are needed or desirable.

The channels are defined by: (1) the mean cosine of the angle for each one, which is simply the arithmetic average of the cosines of the two boundary angles θ_1 and θ_2; and (2) the solid angle in each channel, ω

$$\omega = 2\pi \, (\cos \theta_2 - \cos \theta_1) \qquad (6)$$

Ultimately, one is interested in the flux passing through unit area parallel to the surface of the film rather than through the area corresponding to ω. This is calculated by

$$\omega' = \pi \, (\sin^2 \theta_2 - \sin^2 \theta_1) \qquad (7)$$

The Fresnel reflection coefficients averaged over each channel must also be calculated, and this can most easily be done using equations published by Allen.[27]

The absorption coefficients for the pigments and flake aluminum must be those for collimated light, taken preferably from measurements of regular transmittance in an instrument which excludes all scattered light. For pigments with low scattering power (such as those normally used in metallized paint films and those used in this study) the measurements are not difficult, but the measurement of the collimated-light absorption coefficient in the presence of large amounts of scattering can be a serious problem whose treatment is beyond the scope of this research. The absorption coefficient of the aluminum flake is closely akin to the effective surface area discussed in relation to the Kubelka-Munk approach; it is measured as for the pigments.

It is necessary to express the data for the phase function as an algebraic expression. Richards[24] suggests the use of Legendre polynominals, and we fit the phase function of *Figure* 4 by ten-term Legendre series using IBM Scientific Subroutine QSF. The practical aspects of achieving the proper representation of typical phase functions require, in our opinion, considerably more study.

Finally, the many-flux calculation requires the definition of such boundary conditions as the optical thickness of the sample, the diffuse and collimated reflectance of the background, and whether the sample is in optical contact with the background or not.

RESULTS — Many-flux calculations were carried out for the samples of Series M using four fluxes (simulating the BAB approach), 12 fluxes, and 22
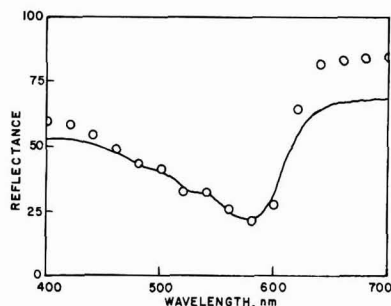
Figure 5—Comparison of measured (—) and calcuated (0) relative reflectance factors for sample M-57 at 0/8° geometry. Calculations were carried out using four fluxes in the many-flux approach

fluxes. Results for the 0/8° geometry were considered satisfactory; a typical comparison between measured and calculated relative reflectance factors is shown in *Figure* 5. Color differences between the measured and calculated results averaged about 12 units. For the 0/75° geometry, however, the predicted relative reflectance factors were roughly an order of magnitude too high, leading to color differences averaging over 700 units. These data were obtained using four fluxes; results with 12 and 22 fluxes were not significantly improved. We suspect, from examination of intermediate results, that the phase functions were not properly represented by the Legendre polynominals used.

CONCLUSIONS

Although the present research has not led to a complete demonstration of the successful application of turbid-medium theory to metallized paint films, we believe the following conclusions are both valid and encouraging. We anticipate that they set forth the proper routes for further research, and that consideration of work in other directions should be carefully evaluated against these conclusions before implementation.

(1) As Paper I[3] showed, the characterization of metallized paint films requires measurement at two different illuminating and viewing geometries, with one viewing angle within and the other outside the specular envelope. This requires special instrumentation, not currently commercially available in the U.S. However, care should be taken to avoid specular reflection from the surface of the sample, while including the highlights from the metallic flakes.

(2) For an accurate theoretical approach, the use of a corresponding turbid-medium theory is essential. This requires utilization of a many-flux theory or the equivalent, so that the fluxes in the illuminating and two viewing directions can be explored independently and specifically.

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* It should be noted that here we number angles from zero at the normal, whereas in describing phase functions we take zero to be the direction of the transmitted beam, and 180° corresponds to the normal on the illuminated side of the film.

(3) Considerations of symmetry require, for application of presently developed many-flux theory, that the illumination be along the normal to the sample. This puts a further restriction on the illuminating-viewing geometry, since the viewing angle within the specular envelope must also be quite close to the normal so that only a few degrees separate the two.

(4) More research is needed with respect to measurement conditions, in particular to insure proper radiometric calibration of the bidirectional reflectances (not reflectance factors) required in the turbid-medium theory.

(5) More research is needed with respect to sample characterization, in particular to obtain appropriate absorption coefficients and phase functions for the metallic pigments.

(6) More research is required with respect to application of the many-flux theory, in particular to develop better methods for finding algebraic expressions for the phase functions.

(7) Despite these unfulfilled requirements, the preliminary application of turbid-medium theory to metallized paint films is encouraging. As long as optical constants obtained under one set of conditions are used to make predictions for the same conditions, reasonable success can be obtained. For example, even a simple Kubelka-Munk approach is useful for viewing angles outside the specular envelope, and the present crude application of the many-flux theory has worked well for viewing angles within the specular envelope.

(8) Once the proper application of turbid-medium theory has been achieved, extension to computer formulation of metallized paint films should be straightforward.

ACKNOWLEDGMENTS

References

(1) Billmeyer, F. W., Jr., Abrams, R. L., and Davidson, J. G., JOURNAL OF PAINT TECHNOLOGY, 40, No. 519, 143 (1968).

(2) Billmeyer, F. W., Jr., and Davidson, J. G., JOURNAL OF PAINT TECHNOLOGY, 41, No. 539, 647 (1969).

(3) Billmeyer, F. W., Jr., and Davidson, J. G., JOURNAL OF PAINT TECHNOLOGY, 46, No. 593, 31 (1974).

(4) Rolls, R., and Luyk, K. E., JOURNAL OF PAINT TECHNOLOGY, 40, No. 517, 85 (1968).

(5) Sopp, A. L., Jr., and Brandt, J. L., "Reflectivity and Emissivity of Bare and Coated Aluminum", Finishes Div., Alcoa Research Laboratories.

(6) Felsher, H.-C., and Hanau, W. J., in Proceedings, 1st AIC Congress "Color 69", Musterschmidt-Verlag, Göttingen, Germany, 1970, Vol. 2, 92.

(7) Gall, L., "Colour 73", Halsted Press, Div. John Wiley & Sons, New York, 1973, 153.

(8) Davidson, H. R., Color Eng., 5, (1), 22 (1965).

(9) Stanziola, R., private communication, 1973.

(10) Armstrong, W. S., Jr., Edwards, W. H., Laird, J. P., and Vining, R. H. (to du Pont de Nemours and Co., Inc.), U. S. Patent 3,690,771 (1972).

(11) Johnston, R. M., private communication, 1973.

(12) Grösswang, H., Deutsche Farben-Zts., 4, 169 (1971).

(13) Kollmorgen Corp., P. O. Drawer 950, Newburgh, N. Y. 12550.

(14) Bentley, G. P., paper presented at the Society of Plastics Engineers Regional Technical Conference "Coloring of Plastics V," Cleveland, Ohio, January, 1971, 13.

(15) Baum, F. J., and Billmeyer, F. W., Jr., J. Opt. Soc. Am., 51, 452 (1961).

(16) Livesey, P. J., and Billmeyer, F. W., Jr., J. Colloid Interface Sci., 30, 447 (1969).

(17) We thank Ruth M. Johnston, then of the Kollmorgen Corp., for supplying the samples of Series M.

(18) We thank Rolf Rolles of Alcoa for supplying the samples of Series J and K.

(19) For a review, see Billmeyer, F. W., Jr., and Richards, L. W., J. Color and Appearance, 2, (2), 4 (1973).

(20) Saunderson, J. L., J. Opt. Soc. Am., 32, 727 (1942).

(21) Campbell, E. D., and Billmeyer, F. W., Jr., J. Color and Appearance, 1, (2), 39 (1971); Billmeyer, F. W., and Alman, D. H., ibid., 2 (1), 36 (1973).

(22) Beasley, J. K., Atkins, J. T., and Billmeyer, F. W., Jr., in Rowell, R. L., and Stein R. S., "Electromagnetic Scattering," Gordon and Breach Science Publishers, New York, 1967, 765.

(23) Richards, L. W., JOURNAL OF PAINT TECHNOLOGY, 42, No. 544, 276 (1970).

(24) Mudgett, P. S. and Richards, L. W., Applied Optics, 10, 1485 (1971).

(25) Mudgett, P. S., and Richards, L. W., JOURNAL OF PAINT TECHNOLOGY, 45, No. 586, 44 (1973).

(26) We thank L. W. Richards, then of the Cabot Corp., for the use of the many-flux computer program.

(27) Allen, W., J. Opt. Soc. Am., 63, 664 (1973).

Rule 66 — After Eight Years

LOS ANGELES SOCIETY FOR COATINGS TECHNOLOGY
Technical Subcommittee

A review of Los Angeles County Air Pollution Control District's Rule 66 shows that it has grown through amendments and additions.

Predicted costs were measured against actual costs, which were found to be relatively close to the predictions. These costs were less than the cost of inflation. Surveys were made of emissions histories of some counties adjacent to Los Angeles County. These surveys showed that definite improvements have been made on the part of industry in the control of organic emissions. Conversely, there has been an increase of emissions from mobile sources, particularly gasoline-powered engines.

KEY WORDS: Rule 66; Solvents; Extraction; Hydrogenation; Pollution; Environmental controls; Costs.

INTRODUCTION

The Los Angeles County Board of Supervisors adopted the Los Angeles County Air Pollution Control District's Rule 66 on July 28, 1966. It took effect one year later—July 1, 1967. The purpose of the rule was to control organic solvent emissions from stationary sources in Los Angeles County. It had been determined by the Los Angeles APCD in January, 1962 that emissions from solvent usage in Los Angeles County amounted to 445 tons per calendar day, or approximately 22% of a total of 2,050 tons/day from all sources except shipping from refineries.[1] It was, therefore, considered one of the major sources of organic emissions in Los Angeles County.

Rule 66 was probably the most talked-about single piece of air pollution legislation enacted to that time. The legislation actually consisted of three rules — Rule 66, Rule 66.1, and Rule 66.2.

Rule 66 applied principally to processes and equipment used by industry and commerce and the definition of reactive and nonreactive solvents. Rule 66.1 applied specifically to architectural coatings such as are used by the general public. Rule 66.2 applied to the disposal of solvents or materials containing solvents.[2] Timetables were attached for compliance.

Changes in Rule 66

Since that time, Rule 66 has been amended and added to as follows:

8/31/71—Amended:

66 (a & b)—Hourly limits were placed upon emissions.

66 (c)—Hourly and daily limits were placed on nonreactive solvent emissions.

66 (i)—Aqueous systems containing no more than 20% of nonphotochemically reactive solvent classed as exempt.

66 (j)—Boiling and evaporation rates of solvents defined.

11/2/72—Amended:

66 (i)—To classify as exempt high solids coatings with no more than 5% of nonreactive organic solvent. To limit exemptions of aqueous and high solids vehicles—prohibiting contact with flame.

66 (j)—Materials with a boiling point higher than 220°F at 0.5 mm mercury absolute pressure or having an equivalent vapor pressure shall not be considered to be solvents unless exposed to temperatures exceeding 220°F.

11/21/74—Rules 66.3, 66.4, and 66.5 adopted and added:

66.3—Applies to use and composition of dry cleaning solvents.

66.4—Applies to the use and/or dilution of metal surface coatings.

66.5—Applies to the use of photochemically reactive solvents in surface cleaning and degreasing.

From the above, it is readily apparent that Rule 66 is a viable instrument for improvement of the environment. To us, "viable" means not only alive, but also capable of growth—as shown.

It should not be thought that Rule 66 was born without "labor pains." Industry did not ask for the Rule; in fact, it objected. In the end, however, it realized that something had to be done.

Even though Rule 66 was adopted in public hearing without dissension, it should be noted that,

as a Los Angeles APCD member stated,[3] "Industry recognized that organic solvent control was inevitable for Los Angeles County, and industry actively participated for more than a year in the performance of tests and the drafting of the legislation. Their participation during this drafting period secured several changes which resulted in Rules less detrimental in their effect upon industry. At the same time, the side-effects of these changes offered the promise of greater benefits to the community in the decrease of air pollution from solvent usage." Rule 66, as finally adopted, was not only better, but was actually less expensive than that which had been first proposed. This was due to the cooperation of industry and government.

Geographic Growth

Rule 66 was designed for Los Angeles County, but it spread to other parts of the country as far away as New York City,[4] as well as to the counties contiguous to Los Angeles County. As a result, the neighboring counties also adopted rules similar to the Los Angeles County Rule 66, and are now in the process of discussing a "South Coast Air Basin." Rule 66 has also been used by the Federal Environmental Protection Agency as a guide for legislation throughout the United States. It has been adopted in all or part by 21 states.

Scope of Paper

As the title suggests, it has been thought fitting to review the development of the rule and its effect upon: the solvent supplier; the manufacturer; the consumer; and the environment.

PROBLEMS OF THE SUPPLIER

The supplier of solvents to the manufacturer of coatings materials had to supply solvents (exempt under Rule 66) for the coatings formulator to use. These solvents fall into three classes: (1) Polar or Oxygenated; (2) Aromatics; and (3) Aliphatic.

Polar or oxygenated solvents such as alcohols, ketones, and esters are chemical compounds and are also well-known and available to a degree. Their characteristics were known and they had been in use for some time—to provide specific properties of solvency. However, the sudden demand for many of these items surpassed the supply. Existing facilities had to be expanded and newer facilities built.

The aromatic solvents are, in general, pure compounds, and while they are derived from several sources, their characteristics are well-known. Because of their greater photochemical reactivity, they are, to a degree, "the bad guys"—particularly xylol—they are and had been readily available to formulators of protective coatings.

Aliphatic Petroleum Thinners

The aliphatic solvents, on the other hand, were homogeneous mixtures of compounds of which an important part were the aromatic components such as toluol and xylol, as mentioned above. The petroleum solvents depended upon their aromatic content for much of their solvency. So, suppliers of petroleum solvents generally faced a more complicated and difficult job than did the suppliers of chemical compounds such as ketones, esters, etc. Petroleum industry suppliers had to reduce the aromatic content to meet Rule 66 limitations and, hopefully, still supply a product which had sufficient solvent power to be useful in the manufacture of protective coatings.

The advent of Rule 66 necessitated a change in the approach to solvency. Previously, solvents had been monitored by physical properties such as specific gravity, kauri-butanol value, aniline point, and distillation range. Now it became necessary to look at composition. In mineral spirits, for example, it became necessary to reduce the C_8+ aromatic hydrocarbon content below 8%. The usual aromatic content of a conventional distillation fraction of the proper boiling range is 10-25%. Obviously, the aromatic content had to be reduced.

TYPES OF HYDROCARBON SOLVENTS

There were three major types of compounds to be considered: aromatics, naphthenes, and paraffins.

Aromatics are good solvents with strong odor. Naphthenes have fair solvency and moderate odor. Paraffins have low solvency and low odor.

The petroleum industry is a primary supplier of solvents, and changing a refinery process cannot be done cheaply or quickly. Therefore, the total picture had to be reviewed.

Three options were available, and each of them required a low aromatic blending stock.

The first option was to blend odorless mineral spirits (no aromatics) with regular mineral spirits to achieve the desired level of aromatic content. This could be done immediately, and many exempt mineral spirits were so made. However, such blends had lower kauri-butanol values and solvency; e.g., if the regular mineral spirits had a KB value of 41, the above blend would have a KB value of 31. In addition, the price of odorless mineral spirits was 40% higher than the price of regular mineral spirits, and the price of the blend reflected the proportion of the volume of each component.

A second option was to blend aromatics with odorless mineral spirits. But, when such a blend was

made, the resulting KB value was only 28—somewhat less than that offered by Option No. 1. And, with the higher cost of odorless mineral spirits, this option was not desirable from an economic standpoint. Comparatively, the price of Option No. 2 was 40% higher than Option No. 1. Obviously, this was no bargain.

A third option was available to producers because, especially in California, regular mineral spirits has a high naphthene content. Odorless mineral spirits is predominantly paraffinic and has low solvency. Aromatic solvents such as xylene are the strongest of all, but the C_8 and heavier aromatics (except ethylbenzene) are now limited by Rule 66 to a volume of 8%. Naphthenes fall between paraffins and aromatics in solvent power. Therefore, it is highly desirable to have as high a naphthene content as possible.

Again, there was more than one alternative available.

First, by extraction, the aromatic content could be reduced to approximately 2%. This would allow blending of regular mineral spirits to achieve a level of less than 8% aromatics. In such an example, if the regular West Coast mineral spirits had a KB value of 41, the extracted product would be at approximately 36 KB, and a blend containing 8% total aromatics would have a KB value of approximately 39. Obviously, this approach or solution was not only better than the KB of 31 that could be obtained in Option No. 1, but was also better than the KB value of most solvents from other parts of the country. Therefore, Rule 66 was more tolerable, quality-wise, in California than it would have been east of the Rockies. The problem with extraction was that costly facilities had to be installed before manufacture could begin. This was done quickly, and the market price of mineral spirits rose only 2-4¢/gal (approximately 15%). Much of the actual cost was absorbed by the manufacturer or supplier.

Another and more desirable way to reduce the aromatic content of mineral spirits is to hydrogenate. This converts the aromatics to naphthenes, thus preserving as much permissible solvency as possible. This procedure is now used by several companies, but was not generally available in the beginning of the search for the optimum solution.

In summary, the solutions of the suppliers of mineral spirits meeting Rule 66 standards were, in order:

(1) Blending of regular mineral spirits and odorless mineral spirits.

(2) Extraction of aromatics from regular mineral spirits and blending of the resulting base with regular mineral spirits (particularly suitable for use with West Coast crudes).

(3) Hydrogenation of the aromatic components

of mineral spirits to naphthenes—which is applicable to all crudes, including those from areas other than the West Coast.

Solvents and thinners boiling below 250°F, such as lacquer diluents, did not present many problems because the aromatic contents of such distillates were low and because they contained only toluene. The legal maximum for toluene was a more liberal 20%.

Aromatic Replacements

Complicated as the above may have appeared, it was relatively simple compared to the problems encountered in replacing pure aromatics for use in industrial coatings. In the area of trade sales, the solvent supplier provided the solvent which could be used by the formulator across a broad spectrum. In industrial coatings, this was not so. The problem was not only more complex and difficult, but it was also more expensive. No other hydrocarbon solvents had as much solvency as aromatics. Therefore, the aromatics had to be replaced by blends of oxygenated solvents plus exempt aliphatics. Typically, 30% of the oxygenated solvent and 70% of the aliphatic solvent were required to duplicate the solvency of aromatics. Prices of these blends were 100-300% higher than the prices of the aromatics being replaced. Obviously this was a financial shock, due not only to initial cost, but also to the additional tankage and inventory required for these other solvents.

There was more to come. It quickly became apparent that there was no single blend that would replace a particular aromatic in all of its uses. For example, alcohols were good for alkyd resins but were not tolerated by acrylics. Thus, the number of different blends required grew by leaps and bounds. So complex did the situation become that it was difficult for some solvent suppliers to furnish all of the blends required by a manufacturer of coatings. Also, it became impossible for the coatings manufacturer to store all the blends required. Therefore, instead of buying a usable product, as in the case for trade sales, coatings manufacturers found it more convenient to store base components and make their own blends for various end products as needed. The applicator, on the other hand, used fewer different blends and found it more convenient to buy a pre-blended product.

Thus, in summary, the solvent supplier had to restructure his philosophy of solvency to include composition as well as physical characteristics such as KB value, aniline point, specific gravity, etc. In addition, the petroleum supplier had to restructure his operations to accommodate the requirements of Rule 66 in the most reasonable way. Suppliers of polar or oxygenated solvents had to increase their

manufacturing capacity in order to meet the demand.

These changes cost money, and although the supplier may have absorbed some of the cost in some cases, the ultimate cost was paid by the consumer. So, the impact of Rule 66 to the solvent supplier was an economic one—higher costs.

PROBLEMS OF THE COATINGS MANUFACTURER

Let us now consider the problems of the manufacturer who used the solvents which were regulated under Rule 66. It is true that the suppliers of solvents did a tremendous amount of work in providing products, blends, and back-up information for their customers.[5-12,17] However, it is also true that the coatings manufacturer—the user of such solvents—also had a lot of work to do to solve his problems.

In the protective coatings industry, for example, there are two types of manufacturers and users: manufacturers of the resin vehicles; and manufacturers of the final protective coatings.

Vehicle Manufacturing and Costs

For the vehicle manufacturer, there was a minimum of trouble in furnishing materials suitable for use in trade sales. Both low-odor and odorless mineral spirits had been available for some time, and Rule 66 mineral spirits soon became available. Where solvent processing (using xylol) had been used, it was necessary to carefully control the amount of xylol used for this purpose. Ethylbenzene was available, but its use could result in higher cost due to more frequent cleaning of process equipment. In some instances, any additional cost was absorbed by the manufacturer.

In the manufacture of vehicles of shorter oil length, where xylene had been used, it became necessary to change the solvent formulation. For ex-

ample, a mixture of VM&P naphtha and isobutanol was commonly used.

Before continuing, it should be pointed out that the cost comparisons which follow were based on prices in effect at any one time. In other words, cost comparisons were not made using prices in effect in 1966 vs. 1974 or 1975, except where specifically stated. One example is shown in *Table 1*.

Another problem encountered by the vehicle manufacturer was the difficult solubility of styrenated alkyds. One solution was to substitute the more soluble vinyl toluene copolymer for the styrenated alkyds.

The vehicle manufacturer had to increase his inventory and storage capacity to accommodate the requirements of Rule 66. In addition, he may well have had to modify his processing equipment to bring it into compliance. All of these things added to his costs. But, as shown in *Table 1*, that cost was minimal compared to the cost of inflation.

The vehicle manufacturer, in general, continued his long-term programs for the preparation of tougher and more effective films in spite of the crash programs caused by Rule 66. In addition, he became increasingly aware of the upcoming importance of water-based coatings.

Coatings Manufacture

The manufacturer of protective coatings also had several problems:

(1) He, too, had to restructure his philosophy of solvency to include composition and suitability.

(2) He had to invest manpower in re-examining his formulations under the new concept.

(3) He had to reformulate, in many instances.

(4) He had to test and re-test his reformulations to be sure he had a suitable, quality product.

(5) He, too, had to invest in more inventory and storage to meet the requirements of his new formulas.

Trade Sales Reformulation

In the field of trade sales, the coatings manufacturer was able to take advantage of the work done by the solvent supplier, with very few problems. As a matter of fact, some manufacturers, prodded by Rule 66 into examining their formulas more closely, were able to reduce costs by discovering areas of higher-than-necessary solvency.

Also in the field of trade sales, one manufacturer made a study of some areas other than raw material costs:

Production—Time cycles were essentially the same.

Pigment suspending properties—Slightly better for non-Rule 66 formulas, but the difference was not very apparent.

Table 1—Effects of Rule 66 and Inflation On Cost of an Alkyd Vehicle

	Old 1966	Rule 66 1967	Old 1974	Rule 66 1974
Solids %	60.0	60.0	60.0	60.0
Xylol %	40.0	—	40.0	—
VM&P naphtha %	—	28.0	—	28.0
Isobutanol %	—	12.0	—	12.0
Cost—cents/lb[a]	11.47	12.15	26.52	26.96
Difference in cents/lb	—	0.68	—	0.44

(a) The original difference between exempt and non-exempt solvents was approximately 0.7 cents/lb while the difference between the 1966 and 1967 costs and the 1974 costs was approximately 15 cents/lb or more than double the original Rule 66 cost.

Table 2—Cost Increases of Various Coatings Due to Rule 66

Coating Type	Average Increase, %
Catalyzed epoxy coating	6.0
Sanding sealer	4.0
Amine-modified enamel	14.0
Baking enamel	13.0
Chlorinated rubber coating	11.0
Industrial quick-dry alkyd finish	15.0
Acrylic O. D. coating	17.0
Epoxy—polyamide primer	9.0
Epoxy—polyamide finish coat[a]	— 3.5
Inorganic zinc-rich primer	2.0
Unweighted arithmetic average[b]	9.1

(a) Note that here is one case where, as previously noted, laboratory work refined a formula to result in cost savings.
(b) The method of obtaining this average is not strictly valid due to the absence of weighting, but it does give an indication, which is probably on the low side.

Straining properties—No apparent difference in straining.

Can stability—No customer complaints received. Laboratory retains did not show any marked difference in can stability.

Industrial Reformulation and Costs

As would be expected, the major impact was in the field of industrial and specialized coatings—with one exception. That exception was in the field of aerosols containing xylol and/or toluol, where package size (less than 32 fluid oz) made them exempt. Otherwise, just as in the case of the vehicle manufacturer, reformulation with more expensive components was necessary to obtain suitable exempt solvent mixtures.

When Rule 66 was first discussed in the protective coatings field, it was recognized that there would be an increase in cost. This increase was projected to be in the order of 10-20%. Let us see how close these estimates were. See *Table 2*. Actual cost increases were close but on the low side of estimates.

Now, for our own amazement, let us look again at a comparison of some 1966 costs and some 1974

Table 3—Comparison of Some Rule 66 Cost Increases Vs. the Cost of Inflation

Product	1966 % Increase	1974 % Increase
Chlorinated rubber coating	11	50
Industrial quick-dry alkyd finish	15	80
Acrylic O. D. coating	17	65
Unweighted average increase	14	65

This illustrates what a good job the coatings industry did in controlling the cost of Rule 66, compared to increases which were out of their control. Both columns are increased costs of exempt products.

costs of coatings. See *Table 3*. Inflation has made the Rule 66 cost impact relatively insignificant.

Roof Coatings

We have also obtained some information on the impact of Rule 66 with respect to roof coatings. This information, while it certainly concerns protective coatings, was separated for clarity.

Obviously, reformulation and testing and retesting had to be done with the burden of the ensuing costs. Such costs were absorbed by the manufacturer in solving problems such as can stability, application characteristics, etc. As expected, some of these reformulations required the use of more expensive oxygenated solvents.

Some problems also occurred in lack of leafing in the aluminum coatings due to the reduction of aromatics but, otherwise, the quality of the products did not suffer.

Some manufacturing techniques were changed, but no new equipment was required. Additional storage was needed.

Raw material costs increased by 5-15%, which is similar to values reported above.

In general, the same effect was noticed—an increase in cost without appreciable loss of quality. Increased costs of about 10% were passed on to the customer.

Baked Coatings

Emphasis has been placed on the formulation of coatings and vehicles that are exempt from Rule 66. This has been due to the desire of the user of industrial finishes to eliminate the necessity of installing expensive equipment for the incineration or adsorption of the non-exempt exhausts from such a system. Not only would the original cost be an important factor, but the continued maintenance of the system also had to be considered. No wonder that, wherever possible, the user of such coatings preferred the exempt solvent system.

Nevertheless, even exempt solvents are limited to the same extent as non-exempt solvents when the coating containing the solvent comes into contact with flame or is baked, heat-cured, or heat-polymerized in the presence of oxygen.

CONSUMER IMPACT

What was the impact of Rule 66 on the consumer? Exactly what one would expect. Although some costs were absorbed, the majority were passed on, and the consumer paid, as usual. It would have been a happy circumstance if all the costs had risen no more than an average of 10%.

Table 4—Los Angeles County APCD Estimated Solvent Emissions[13]

	Year								
	1966	1967	1968	1969	1970	1971	1972	1973	1974
Reactive, tons/day	345	430	300	100	—	100	40	40	45
Nonreactive, tons/day	205	90	160	400	—	400	355	315	315
Total	550	520	460	500	—	500	395	355	360

ENVIRONMENTAL IMPACT

What did the consumer get in addition to a product of equivalent quality at a higher price? The purpose of Rule 66 was to improve the environment. Through the cooperation of the Air Pollution Control Districts of Los Angeles, Riverside, and San Bernardino Counties, and the California Air Resources Board, information was available to provide at least a partial answer to that question. Since all counties have not as yet reported their data in exactly the same way, the data will be reported separately. See *Table* 4.[13]

Each year some potential organic emissions are being prevented from entering the atmosphere by collection, incineration, etc. This accounts for the lower totals of reactives and nonreactives.

For example, in 1973 without Rule 66, a total of 625 tons of emissions would have been introduced to the atmosphere had not 270 tons been prevented (355 plus 270 equals 625). Of the 355 actually emitted, only 40 were considered reactive, as compared to 430 listed as reactive in 1967.

The 1973 total emissions of 355 tons was down from 550 in 1966. The reactive solvent emitted was reduced from 345 tons in 1966 to 40 tons in 1973. Although limited in scope, this is a good range-finder approach to the effect of Rule 66 on stationary solvent-emission sources. These data are shown graphically in *Figure* 1.

The Los Angeles APCD also lists a detailed estimate of the emissions prevented from entering the atmosphere for all sources. A 1973 summary for organic solvents is shown in *Table* 5.[13]

These data show the success of Rule 66 in re-

Table 5—Los Angeles County APCD Estimated Organic Solvent Emissions[13]

	Actual Emissions (Tons/Day)			
Year	Total HC	Reactive HC	NO$_x$	Particulates
1973	355	40	—	15
1974	360	45	—	5

	Emissions Prevented (Tons/Day)			
Year	Total HC	Reactive HC	NO$_x$	Particulates
1973	270	350	—	5
1974	270	350	—	15

Table 6

Riverside County Organic Solvents, as of January 1971

Current emissions (tons/day)	7.00 (36% of ind. emissions)
Emissions prevented (tons/day)	6.67
Total possible emissions	13.67

Riverside County Hydrocarbon Emissions, as of January 1971

Current hydrocarbon stationary emissions (tons/day)	32.7
Stationary hydrocarbon emissions prevented (tons/day)	31.0
Total possible hydocarbon stationary emissions	63.7

	Average Tons per Day (Inventory Date—January 1)		
Emission Source	1969	1971	1973
Industrial	38.8(4%)	19.4(2%)	18.3(1.4%)
Incineration	104.5	55.8	18.2
Fuel combustion	12.8	6.5	6.3
Agriculture	22.6	11.5	12.3
Motor vehicles	733.7(76%)	767.2(83%)	1185.0(92%) *
Railroads	—	7.8	4.3
Aircraft	52.2	51.4	51.4
Total	964.6	919.6	1295.8

Figure 1—Los Angeles APCD estimated organic solvent emissions

(a) Method of test procedure changed by EPA and ARB.
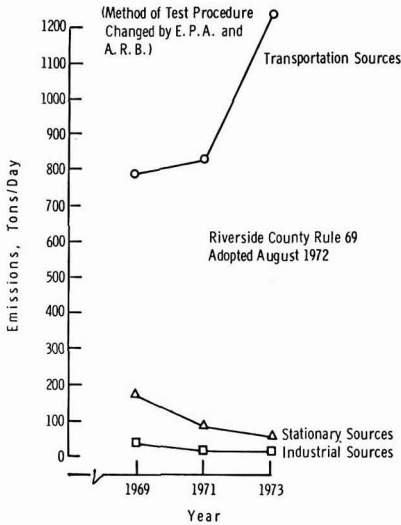
Figure 2—Relative emissions in Riverside County

Table 7—Available Data on Effect of Rule 66 — San Bernardino County

	Year				
	1969	1970	1971	1972	1973
Emissions[a]	10.8	10.5	8.8	5.4	4.8
Preventions	14.7	15.1	15.4	18.9	19.4
Total	25.5	25.6	24.2	24.3	24.2

(a) Reported as tons/day of hydrocarbons.

The emission inventories are of value as an indication of the trend of control.

It is of interest to note that all sources of emissions showed appreciable decreases, except for motor vehicles and aircraft. Aircraft remained relatively constant, whereas motor vehicle emissions showed an increase. In 1971 (the only complete and unchanged data available), the data showed that transportation accounted for 89.8% of the air pollution emissions — equal to 826 TPD out of a total of 920 TPD. Of this amount, motor vehicles accounted for the lion's share, i.e., 767 TPD (83% of the total). While no glaring comparisons are being attempted, the question remains — Are we (as individuals) as amenable to control as are the industrial enterprises?

San Bernardino County's Rule 66 (counterpart to the Los Angeles County Rule 66) was adopted August 18, 1970, to be effective December 31, 1971, on organic solvents. However, figures on emissions and preventions were available beginning in 1969. In addition, the Control District had been able to obtain the cooperation of a large share of industry prior to 1969, which resulted in the actual application or utilization of controls in years prior to the effective date of the regulations.[15] See Table 7 and Figure 3.

ducing the total volume of organic solvents emitted, as well as a significant reduction in reactives emitted.

Riverside County Rule 69 (counterpart to Los Angeles APCD Rule 66) was adopted August 1972. It was revised in January 1973.[14]

Figures on emissions were available as of January 1, 1969, January 1, 1971, and January 1, 1973 by source as industrial, incineration, etc. Organic solvent emissions as such are available only as of January 1, 1971 and are shown in Table 6. Also shown are the stationary hydrocarbon emissions, preventions, and totals for 1971, as well as the total emission inventories for 1969, 1971, 1973. (See Figure 2).

Figure 3—Relative emissions and preventions in San Bernardino County

Table 8—Average Emissions of Organic Compounds In Orange County[16]

	Organic Compounds (Tons/Day) (1973 Emissions Inventory)			
	Reactivity			
Emission Sources	High	Low	Subtotal	Total
Stationary				
Petroleum	10.5	10.5	21.0	
Organic solvent users	4.5	27.5	32.0	
Combustion of fuels	0.6	0.7	1.4	
Total stationary	15.6	38.7	54.4	(12%) 54.4
Mobile				
Gasoline motor vehicles	271	116	387	
Diesel powered	—	3	3	
Aircraft	0.9	0.2	1.1	
Total transportation	272	119	391	(88%) 391.0
				445.4
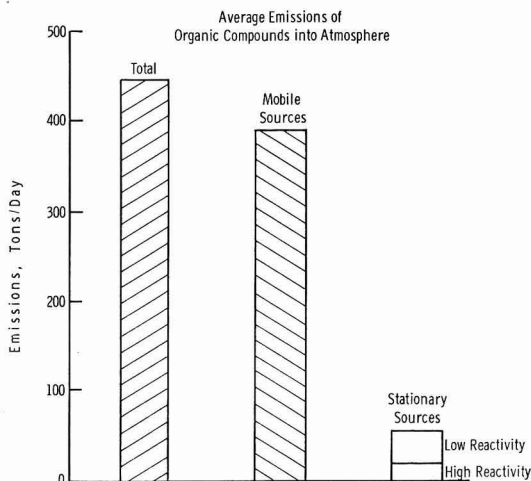
Figure 4—Orange County 1973 emissions inventory

The total figures are of interest in that they show that the industry concentration or density in San Bernardino County has remained relatively constant and, therefore, any reductions have been as a result of the controls under Rule 66, and not as a result of a decrease in business activity. Some of us can remember that, in the early days of activity on Rule 66, there were dire threats of the removal of industry from those areas affected by Rule 66.

The San Bernardino County Air Pollution Control District feels that there has been a definite impact and improvement in the environment, due to the application of controls under its Rule 66.

Some information was available for Orange County,[16] as shown in *Table* 8 and *Figure* 4.

While the information from Orange County consists of only one year's inventory, it is of interest to note that the mobile sources (notably gasoline powered) accounted for 88% of the emissions of organic compounds.

SUMMARY

The origin and growth of Los Angeles County APCD Rule 66, 66.1, 66.2 have been reviewed. It is capable of growth, and had been expanded by the additions of Rules 66.3, 66.4, 66.5. These new rules treat the composition of dry cleaning solvents, the use and/or dilution of metal surface coatings, and the use of photochemically reactive solvents in surface cleaning and degreasing.

The simultaneous concepts of solvent composition and suitability are discussed as being further requirements, in addition to the normal physical characteristics such as specific gravity, etc.

Techniques for producing exempt mineral spirits blends by extraction of aromatics and/or hydrogenation of aromatics to naphthenes are discussed.

The excellence of the job done by the protective coatings industry is borne out by the fact that the cost to the consumer was 5-15% (attributed to Rule 66), compared to an average increase of 50-85% due to inflation.

The effect of the Los Angeles Rule 66 and its benefit to the environment is evident from the reductions in organic emissions in Los Angeles, Riverside, and San Bernardino Counties. An inventory of emissions in Orange County is also included.

However, it is apparent that control by individual effort is less effective than control by industry.

ACKNOWLEDGMENT

References

(1) Chass, R. L., Kanter, C. V., and Elliott, J. H., 55th Annual Meeting, Air Pollution Control Association, Chicago, Ill., 1962.
(2) Lunche, R. G., 4th Technical Meeting, APCA — WCS, San Diego, Calif., 1967.
(3) Lunche, R. G., *Specification Forum*, 6 (1967).
(4) Higgons, R. H., *Am. Paint J.*, 56, No. 32, 7 (1967).
(5) Ellis, W. H. and Saary, Z., 79th Annual Meeting, National Paint, Varnish and Lacquer Association, Washington, D.C., Nov. 1, 1966.
(6) Ellis, W. H., Saary, Z., and Lesnini, D. G., JOURNAL OF PAINT TECHNOLOGY, 42, No. 531, 249 (1969).
(7) Commercial Solvents Corp., Technical Bulletins TB-No. 21 (Dec. 1966) and TB-No. 3 (May 1967).
(8) Hartman, L. M., *Specification Forum*, 6 (1967).
(9) Sipple, H. E., *Specification Forum*, 6 (1967).
(10) Dettenreider, F., *Specification Forum*, 6 (1967).
(11) Duzy, R. H., *Specification Forum*, 6 (1967).
(12) Caney, N. L., *Specification Forum*, 6 (1967).
(13) Krenz, W. B., private communications.
(14) Kennealy, M. J., Air Pollution Control District, Riverside County Air Pollution Emission Inventory Report.
(15) Hilovsky, R. J., Air Pollution Control District, San Bernardino County Air Pollution Reports.
(16) Tate, R., California Air Resources Board, Orange County 1973 Emissions Inventory.
(17) Seminar on Air Pollution sponsored by California Manufacturers Association and Los Angeles County Air Pollution Control District, November 4, 1965.

Society Meetings

Birmingham
December 4

T. R. Bullett, of the Paint Research Station, spoke on "WET COLOR CORRECTION."

Drawing on the 40 years' experience of the Paint Research Station in instrumental color measurement, Mr. Bullett discussed the optics of the human eye, the Kubelka-Munk theory of absorbing and scattering of light, and the mathematics involved for single pigments and mixtures. An example of the PRS computer color-matching program was shown, using X,Y, and Z values, which gave a match for one illuminant and one observer, with further programs giving a match over the entire spectral curve.

Traditionally, matching is carried out on a dry film. It was observed that changes in the color of a paint on drying were remarkably consistent for the same type of paint, so the theory was postulated that correction in the color of the wet paint should correspond to the dry film. Experimental results confirmed this theory. The problem of measuring the color of the wet paint due to the surface changing continuously on drying was overcome by using a continuously reforming surface technique and transmitting the color measured along fibre optics — filaments of glass pipes along which light travels by a series of internal reflections along its length.

The prototype PRS colorimeter was illustrated, as was a commercially manufactured instrument which is in use by a leading U.K.

Officers of the New England Society for Coatings Technology for 1975-76. Left to right: Secretary — Martin L. Davis, of Sterling-Clark-Lurton Corp.; Vice-President — Thomas J. Manning, of Samuel Cabot Inc.; President — James F. Craffey, of New England Resins & Pigments Corp.; and Treasurer — Paul J. Mueller, of D. H. Litter Co.

paint maker on air-drying decorative glass paints. Other uses of the fibre optics colorimeter include the control of colored anodizing and the accurate measurement of the color of a dry flake of paint 1 mm in diameter for forensic purposes.

The suggestion was made for the future of a series of base paints being used in the automatic titration of the paint to the color standard using a fibre optics colorimeter linked to a process control computer.

Q. How can we relate the computer to visual assessment, as it is this latter which decides what is acceptable?

A. There is a tendency of com-

panies towards instrumental colorimetric specification.

Q. You have evaded the question of deep colors. Do tristimulus values, etc., still apply?

A. For deep colors one must consider more factors. The fibre optics system is particularly good for dark colors as there is a low possibility of stray light interference.

Q. Is there any possibility of matching metallics this way?

A. We believe there is a possibility of matching, but another factor has to be introduced to account for the spectral reflection of the metallic particles.

Q. What allowance has to be made for batch-to-batch variation in tinter strength?

A. One way is to standardize the strength and dilute each batch to this strength. Another way is to determine a strength factor for each batch of tinter and apply this to the calculations.

Q. Is there any problem with aeration of the wet paint, particularly emulsions?

A. Yes, there are problems which require further work to overcome.

Q. We are not likely to make color matchers obsolete yet, then?

A. No, the fibre optics technique can be used to assist him in a visual technique. The colorimeter is five times more sensitive than the human eye in detecting color differences.

BRIAN F. GILLIAM, *Publicity Officer*

Executive Committee of the Birmingham Paint, Varnish & Lacquer Club for 1976. Left to right: (standing) Technical Committee Chairman—J. N. Hitchin; J. R. Jukes; R. A. J. Allan; and C. W. Gilbert; (seated) Secretary — G. H. Tennant; President — R. E. Arnold; President-Elect — B. J. Addenbrooke; and Treasurer — D. M. Heath

Merle D. Held, of Cyprus Industrial Minerals Co., spoke on "TALC—THAT CRAZY WHITE POWDER."

He began by listing the various places where talc is mined, which include the states of New York, Vermont, California, Montana, Texas, Alabama, and Georgia.

The interesting point about all the talcs is that none of them are exactly alike. Since talc is a secondary rock, there is no such thing as a primary talc. Talcs are formed by the alteration of some other rock. This alteration is brought about through the effect of heat and steam. Unlike granite and other hard rocks, talc is formed by a substitution in the crystalline lattice. When this reaction takes place, some of the base rock from which the talc is formed is left behind. That is why New York talcs are fibrous and Montana talcs are platty. California talc is a mixture of the above two.

Talcs occur in nature in many different colors. However, when talcs are calcined, they all become a beautiful white.

Mr. Held then presented a series of slides showing the locations of several open-pit mines and the character of natural occurring talc. Talc is generally quarried like any other rock.

Then the talk progressed into the grinding, sorting, and milling operations which produce the talc as it is used in the manufacture of paint. A series of photomicrographs then showed the differences in the crystalline structure of various talcs.

The purity of talc varies widely depending upon the area where it is produced. New York talc is the least pure, Montana talc is the purest, and California talc is in between. Chemically pure talc should be about one part magnesium oxide to two parts silica oxide. Montana talc most nearly approaches this ratio.

Q. Since you said you were working on the possibility of shipping talc in slurry form, what concentration of talc are you referring to?
A. We do not have it all worked out yet, but we are looking for 60% to 65% talc in the slurry. We have been able to make the slurry in small amounts, and we are now working on large amounts.

Q. What is the price of the talc?
A. $100 per ton, FOB the mine.

Q. Does your company make the fibrous talc?
A. No. We closed down our mine where we found Tremolite.

Q. Is there Tremolite in the Montana talc?
A. No, there is none in the Montana, Texas, Alabama, or Georgia talcs.

Q. Are you saying that the plattier the talc the less chance of Tremolite being present?
A. Yes.

Ed Born, of Cal/Ink Division of Tenneco, spoke on "DESIGNING TINT BASE COLOR SYSTEMS." A successful tint base system is dependent upon: (1) a series of tint bases designed to accept colorant; (2) a series of colorants compatible with the tint bases; (3) equipment for insuring proper color dispensing and proper dispersing; and (4) sales aids—a master color file with accurate color information.

RAY SCHOMAKER, *Secretary*

Detroit
December 9

Dr. George Brewer, Consultant, discussed his work for the Environmental Protection Agency on waste disposal from paint systems.

Dr. Brewer was consulted by EPA to do a waste load study, the purpose of which was to aid EPA in a position as to the effects of the source, the amount, and the types of systems of application.
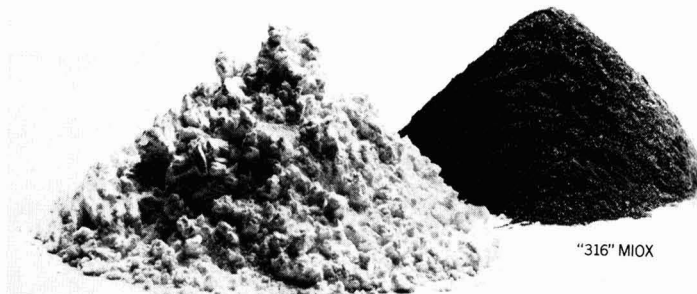
Wastes are caused by four factors: (1) organic solvents in the paint; (2) loss of paint from equipment; (3) paint curing operations; and (4) accidental paint losses.

Paint systems are normally classified by the type of film-former. However, if the waste of a paint by spray is greater than by roller, it is better to classify paints by application. Dr. Brewer therefore classified all paints into seven major categories:

(1) Spray paints
(2) Dip, flow, and curtain coating
(3) Coil coating and roller coating
(4) Electro coating
(5) Powder coating
(6) Radiation-cured coatings
(7) Newly developed coatings not

in general use (high solids, low solvent aqueous, and aqueous powder slurries)

Within each classification, he also sub-classified paints according to air-dry or bake and solvent or aqueous.

If particular painting equipment has a 100% transfer efficiency, there is 0% wasted NV (nonvolatile). On the other hand, if the transfer efficiency is only 50% (e.g., spray painting) and the % NV is 50%, then the wasted NV is 50% and the OV (organic volatile) is double (or 2 lb of OV per lb of paint actually used).

According to literature survey, the following are typical transfer efficiencies:

Spray — 30-60%

Electrostatic — 68-87%
Ransburg Disc. — 85-95%
Airless — 65-70%
Airless Electrostatic — 85-90%
Dip/Flow — 85-90%
Coil Coating — 90-93%
Electrocoat — 90-96%
Powder Coat — 50-99%

If the amount of OV is plotted against transfer efficiencies, the relationship is directly proportional. However, as the % NV is decreased in the paint, the amount of OV rises very sharply.

Q. How did you calculate the coreactants in the resins, for example, alcohols from aminoplast resins?

A. I was not always given the information, but the coreactants should definitely be treated as OV. This can be very difficult at times to calculate.

Q. Was odor a consideration in your work?

A. No, this is usually reserved for OSHA and not EPA.

Q. What about formaldehyde?

A. No, this is usually handled by the health authorities.

Q. How about the use of asbestos?

A. Asbestos is now being considered a carcinogen, however, it was not considered in this study. Its use would be governed by OSHA.

Q. What does the EPA intend to do with these data?

A. It will be used by EPA representatives in estimating waste loads and in recommending alternate finishing systems.

Q. Did your study include any energy consumption rates?

A. No, this will probably be a new assignment by EPA and they will probably be looking for alternate paint curing systems.

MacKenzie K. Endo, *Secretary*

Kansas City
January 8

Honored guests in attendance were William Dunn, Federation President, and Thomas A. Kocis, Editor of the Journal of Coatings Technology.

Society President James Edwards presented a 25-Year pin to J. C. Leslie.

Sam Yankee, Chairman of the Environmental Control Committee, announced that the list of 300 chemicals now regulated by the oil spill law was published in the December 30 issue of the *Federal Register*.

Ray Wachala, of Nalco Corp., spoke on "Practical Use of Defoamers."

Ray D. Lawson, *Secretary*

Constituent Society Meetings and Secretaries

BALTIMORE (Third Thursday—Eudowood Gardens, Towson). C. HERBERT PUND, III, Conchemco, Inc., 1401 Severn St., Baltimore, Md. 21230.

BIRMINGHAM (First Thursday—Imperial Hotel). GEORGE H. TENNANT, Carr's Paints Ltd., Alvechurch Rd., Birmingham B31 3PG, England.

CHICAGO (First Monday—meeting sites in various suburban locations). RUDOLPH C. ALBRECHT, Standard T Chemicals, Inc., 10th & Washington Sts., Chicago, Ill. 60616.

C-D-I-C (Second Monday—Sept., Jan., Mar. in Columbus; Oct., Dec., Apr. in Cincinnati; Nov., Feb., May in Dayton). RAY SCHOMAKER, Foy-Johnston, Inc., 1176 Mentor Ave., Cincinnati, Ohio 45212.

CLEVELAND (Third Friday—meeting sites vary). Ms. HELEN SKOWRONSKA, Sherwin-Williams Co., P. O. Box 6027, Cleveland, Ohio 44101.

DALLAS (Thursday following second Tuesday—Vic's Gallery Restaurant). DONALD J. WEBB, Jones-Blair Co., P. O. Box 35286, Dallas, Tex. 75235.

DETROIT (Fourth Tuesday—Rackham Memorial Bldg.). MACKENZIE ENDO, Argo Paint & Chemical Co., 550 S. Edwin, Westland, Mich. 48185.

GOLDEN GATE (Monday before Third Wednesday—varies between Sabella's in San Francisco and His Lordship's Restaurant in Berkeley). KEN G. PROBST, San Jose Regional Vocational Center, 760 Hillsdale Ave., San Jose, Calif. 95123.

HOUSTON (Second Tuesday—Sonny Look's Sir-Loin Inn). GERRY J. GOLDBERG, San Jacinto Paint Co., P. O. Box 14312, Houston, Tex. 77021.

KANSAS CITY (Second Thursday—Fireside Inn). RAY LAWSON, Southwest Grease & Oil Co. (Kansas City), Inc., 1400 S. Harrison, Olathe, Kan. 66061.

LOS ANGELES (Second Wednesday—Home Furnishings Mart). FRED CROAD, Engard Coatings Corp., 15541 Commerce Ln., Huntington Beach, Calif. 92647.

LOUISVILLE (Third Wednesday—Essex House). NICK LANNING, Jelico Chemical Co., 829 S. 26th St., Louisville, Ky. 40211.

MONTREAL (First Wednesday—Bill Wong's Restaurant). J. W. A. MELSBACH, Sico, Inc., 2505 de la Metropole, Longueuil, Que., Canada.

NEW ENGLAND (Third Thursday—Fantasia Restaurant, Cambridge). MARTIN L. DAVIS, Sterling-Clark-Lurton Corp., P. O. Box J, Malden, Mass. 02148.

NEW YORK (Second Tuesday—varies between New York and New Jersey locations). GEORGE J. DIPPOLD, Whittaker, Clark & Daniels, Inc., 1000 Coolidge St., South Plainfield, N. J. 07080.

NORTHWESTERN (Tuesday after first Monday—Jax Cafe). JAMES E. FANSLOW, Farwell, Ozmun, Kirk & Co., 1200 Mendelssohn Ave. N., Golden Valley, Minn. 55427.

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

PHILADELPHIA (Second Thursday—Williamson's Restaurant, Presidential Apartments). WAYNE N. WOOD, Allentown Paint Mfg. Co., P. O. Box 597, Allentown, Pa. 18105.

PIEDMONT (Third Wednesday—Howard Johnson's, Greensboro, N. C.). JAMES A. MARTZ, The Lilly Co., P. O. Box 1821, High Point, N. C. 27261.

PITTSBURGH (First Monday—Skibo Hall, Carnegie-Mellon University Campus). GASPER CAJKA, Chase Chemical Corp., 3527 Smallman St., Pittsburgh, Pa. 15201.

ROCKY MOUNTAIN (Monday prior to second Wednesday—Gasthaus Ridgeview, Wheatridge, Colo.).

ST. LOUIS (Third Tuesday—Salad Bowl Restaurant). BERNARD M. BRILL, P. D. George Co., 5200 N. Second St., St. Louis, Mo. 63147.

SOUTHERN (Gulf Coast Section—Second Tuesday; Central Florida Section—Thursday after third Monday; Atlanta Section—Third Thursday). A ROY NEAL, Superior Lacquer Co., P. O. Box 849, Toccoa, Ga. 30577.

TORONTO (Second Monday—Town and Country Restaurant). PAUL D. F. COOPER, Chemetron of Canada Ltd., 137 Horner Ave., Toronto M82 4Y1, Ont., Canada.

WESTERN NEW YORK (Second Tuesday—Buffalo Trap and Field Club, Cheektowaga, N. Y.). PAUL R. GUEVIN, JR., Hughson Chemical Co., 2000 W. Grandview Blvd., Erie, Pa. 16512.

Montreal
December 3

Dr. D. Thieman, of Sherwin-Williams Co. of Canada Ltd., spoke on "POWDER COATINGS."

Dr. Thieman offered a list of the most common powders used today or under development which showed the trend of these relatively new coatings. The acrylics have several drawbacks, such as poor flexibility and poor detergent resistance; the polyesters and silicone polyesters show good over-all properties; the epoxies have found the best popularity because of versatility and cure rate, but they have poor weather resistance; the polyurethane powders supply the necessary outdoor resistance and good chemical and physical properties.

The major development is being conducted on the polyurethanes because of the tendency of the American market to use powders as topcoats, while in Europe and Japan they are used mainly as undercoats.

A review of the current methods of application was given, and the "Gema" system, with its complete recovery of wastes, was examined.

Peter A. Hiscocks, of Tioxide of Canada Ltd., spoke on "ADHESION OF LATEX PAINT," the Society paper presented at the Federation Annual Meeting in Los Angeles, and which was awarded first prize.

Coating failure through loss of intercoat adhesion is a frequent paint performance problem. A recent survey showed adhesion to be one of the most serious technical problems facing the gloss latex paint formulator. In this survey, adhesion to chalk was of concern in exterior systems, but wet adhesion and adhesion to aged gloss surfaces was of concern in all systems. With this as impetus, the MSCT is currently studying means of improving latex paint intercoat adhesion to surfaces.

The cross-hatch adhesion test method was evaluated for its ability to monitor changes in intercoat adhesion of latex paints to alkyd paints when pigment, polymer, PVC, and drying time of the latex systems were varied. It was found that the method has limitations at pigment volume concentrations much higher or lower than the critical pigment volume concentration of the latex test paints. Acicular and platy extenders imparted intercoat adhesion properties far superior to those of nodular and spherical types. Polymers varied widely in performance but intercoat adhesion was generally enhanced by fine particle types. Adhesion improvements on continued air drying varied with the polymer.

PAUL RUIZ, *Recording Secretary*

Northwestern
December 2

William J. Stewart, of Tenneco Chemicals, Inc., spoke on "Preventing Spoilage of Latex Paints."

Mr. Stewart prefaced his talk with a short statement on the use of mercury and EPA regulations. He stated that it now looks as though we may be able to continue to use mercury at the present levels.

Spoilage of latex can reveal itself through loss of viscosity, gas, odor, or discoloration. He pointed out that if the level of contamination is severe enough, it can overwhelm the agents used to protect against spoilage.

Primary sources of contamination are dust in the air, the water supply, uncovered raw materials, and aqueous dispersions. The most effective measures against spoilage are good "housekeeping" and proper use of protective agents, with mercury still being the best protective agent available.

Manufacturing Committee Chairman George Murphy announced that the society's symposium on "Low Energy Systems" will be held on March 9.

Membership voted to donate $500 to North Dakota State University.

James E. Fanslow, *Secretary*

Piedmont
November 19

Charles Murphy, of E. I. du Pont de Nemours & Co., Inc., spoke on "Elvacite EP-6500 — An Acrylic-Modified Resin for Nitrocellulose Lacquers."

Education Chairman Pete Teague reported that the Technician's Course being conducted at Guilford Technological Institute is scheduled to begin on January 6.

James A. Martz, *Secretary*

Western New York
December 9

Robert Vash, of Byk-Mallinckrodt Chemical Products GmbH, spoke on "New Concept of Hydrophobic Pigment Wetting in Aqueous Systems."

Mr. Vash defined wetting of the pigment as a displacement of air or moisture. These can be either cationic, anionic, or a combination of both. Some of the earlier wetting agents were surfactants which have a lower molecular weight than the current products.

He showed an idealized structure of one of these strong electrolyte salts which are water-soluble. He indicated that they usually result in flocculation when the coating dries. For this reason, poor salt spray re-

sistance is obtained, which prevents its use for industrial coatings and limits it to trade sales. He showed an idealized structure of its presence on a wetted pigment.

Some of his slides showed the idealized structure of his company's new product, Bykumen®. He indicated that this large molecular weight vehicle attaches to the pigment and "projects" the amine groups. He showed some idealized slides which illustrated how the wetted pigment is interspersed with latex vehicles, and how these surfactants wind up within the latex matrix. He also illustrated the effect of improved salt spray resistance using these products in primers.

Q. Can these new products be used in electrodeposition coatings?

A. Yes; in fact, this was its first use. These wetting agents attach to the pigment particle and facilitate transportation to the electrodes.

Q. Do they affect cure?

A. Not really; they are good for chromate and molybdate pigments used in primers.

Paul R. Guevin, *Secretary*
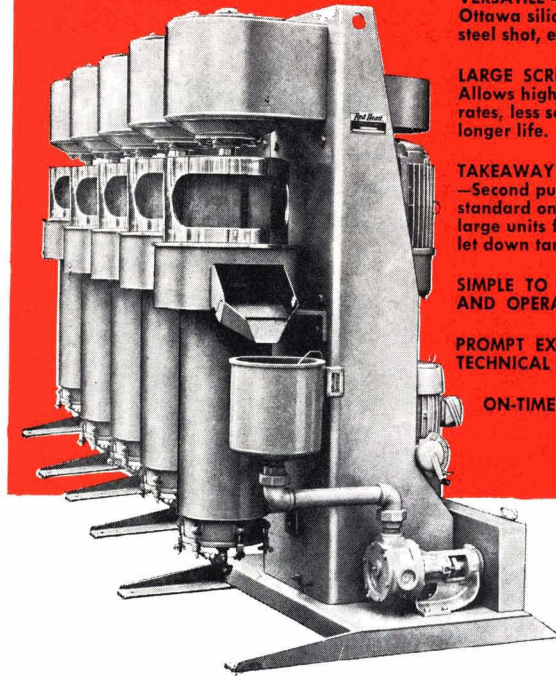
Elections

BALTIMORE

Active

CAHIR, THOMAS H. — O'Brien Corp., Baltimore, Md.
FALK, FREDERICK A. — Graphic/Supply, Inc., Hyattsville, Md.
PETTS, OMER F., JR. — Hanline Bros., Baltimore.
VANDERHOEK, ROBERT F. — Lenmar Lacquers, Inc., Baltimore.
YEGHIAZARIAN, VAHE — Lenmar Lacquers, Inc., Baltimore.

Associate

EDWARDS, JOSEPH C. — Textile Chemical Co., Inc., Baltimore.
HOLT, CLIFFORD L. — ICI United States, Inc., West Chester, Pa.
KASE, PAUL W. — Van Horn Metz & Co., Inc., Towson, Md.
MILLER, DONALD P. — Tenneco Chemicals, Columbia, Md.

Retired

PUND, C. HERBERT, JR. — Pasadena, Md.

BIRMINGHAM

Active

BRANT, M. — Mander Bros. Ltd., Wolverhampton, Staffordshire, England.
CALLAN, EUGENE G. — Batchelor Robinson Coatings Ltd., Aldridge, Staffordshire.

JONES, GRAHAM H. — Batchelor Robinson Coatings Ltd., Aldridge, Staffordshire.

CHICAGO

Active

BAGGIANI, JULIUS A. — Standard T Chemical Co., Inc., Chicago Heights, Ill.
BARTZ, CHARLES E. — General Paint & Chemical Co., Chicago, Ill.
CAVIN, EDWARD E. — James B. Day Co., Carpentersville, Ill.
FILIATRAULT, THOMAS M. — PPG Industries, Inc., Oak Creek, Wis.
FIZEL, DENISE — General Paint & Chemical Co., Chicago.
FOY, JAMES A. — Nalco Chemical Co., Chicago.
FREID, JAMES R. — PPG Industries, Inc., Oak Creek, Wis.
FULTON, ARTHUR M. — PPG Industries, Inc., Oak Creek.
GRACE, THOMAS W. — PPG Industries, Inc., Oak Creek.
HELMS, CLARK H. — Standard T Chemical Co., Inc., Chicago Heights.
KANNENBERG, WILLIAM E. — DeBeers Laboratories, Inc., Addison, Ill.
KOMIS, LEWIS E. — PPG Industries, Inc., Oak Creek.
MICHALSKI, RONALD E. — E-Z Paintr, Milwaukee, Wis.
PATEL, BABU R. — Remien & Kuhnert Co., Chicago.

PREGLOW, KENNETH — DeSoto, Inc., Chicago.
PRICE, JOHN F. — E-Z Paintr, Milwaukee.
ROBERTS, CURTIS C. — John L. Armitage Co., Elk Grove Vill., Ill.
TANNER, TERRY R. — Mobil Chemical Co., Kankakee, Ill.
WELKER, JACQUELINE K. — PPG Industries, Inc., Oak Creek.

Associate

BOLGER, ALBERT H. — Eagle Picher Ind. Inc., Naperville, Ill.
NOVY, GEORGE J. — American Cyanamid Co., Chicago.
SULLIVAN, RICHARD F. — Fisher-Calo Chemicals & Solvents Corp., Chicago.

Retired

ANDERSON, GILBERT R. — Western Springs, Ill.

CLEVELAND

Active

BRUENING, DAVID H. — Tremco Mfg. Co., Cleveland, Ohio.
BURTZLAFF, ROBERT A. — Potter Paint Co. of Ind., Inc., Cambridge City, Ind.
FARON, DARYL S. — Midland Div., Dexter Corp., Cleveland.
FRAUENHOFFER, NICHOLAS J., JR. — DeSoto, Inc., Columbus, Ohio.
GATES, RAYMOND D. — Morgan Adhesives Co., Stow, Ohio.
GEORGE, PHILLIP K. — Glidden-Durkee Div., SCM Corp., Cleveland.
NORBY, DAVID B. — Ashland Chemical Co., Dublin, Ohio.
SHAW, ROBERT M., JR. — Morgan Adhesives Co., Stow.
STOCKSTAD, RODNEY W. — Glidden-Durkee Div., SCM Corp., Cleveland.
THOMAS, ROBERT D. — Perry & Derrick Co., Cincinnati, Ohio.

Associate

ANDERSON, DOUGLAS R. — R. A. Mueller, Inc., Cincinnati.
LYKINS, JOSEPH D., III — Palmer Supplies of Cincinnati, Cincinnati.
WALKER, J. N. THOMAS — Sun Chemical Corp., Cincinnati.

Educator/Student

SCHILLER, ANDREW D. — Case Institute of Technology, Cleveland.

DALLAS

Active

HOLLIS, ROBERT L. — DeSoto, Inc., Garland, Tex.
HONEYCUTT, DEWITT W., JR. — Western Specialty Coatings Co., Dallas, Tex.
PARIKH, ASHWIN V. — Jennat, Union Carbide Corp., Garland.
REIMERS, GERDA C. — Standard T Chemical Co., Dallas.

Associate

NEWSOROFF, GEORGE P. — Southwestern Petroleum Corp., Ft. Worth, Tex.

DETROIT

Active

WOLPERT, STEPHEN M. — U. S. Army Tank/Automotive Command, Warren, Mich.

Committee Activities

Technical Articles in Other Publications

CHEMICAL REVIEWS

(Partial Contents)

Barton, A. F. M.—"Solubility Parameters;" 731-753 (review with 146 references).

DOUBLE LIAISON — CHIMIE DES PEINTURES
(in French)

Poisson, R., and Toussaint, A.—"Polymer Absorption Measurements on Solid Substrates by Means of Labelled Molecules. (Part II);" 21-26.
Layec, R.—"Ultra-Violet and Drying. (Part II);" 27-35.
Schwarz, H., Scimar, R., Seils, A., and Touissaint, A.—"Practical Recommendations Concerning the Protection by Paints of Hot-Dip Galvanized Steel;" 39-43.

FARBE und LACK
(in German)

Plum, G.—"Trade Report of the Paint and Varnish Industry for 1974;" 1095-1101.
Joppien, G. R.—"Characterization of Surfaces of Pigments and Fillers by Combined IR Spectroscopic and Gravimetric Adsorption and Desorption Measurements;" 1102-1108.
Novak, V., Dlaskova, M., Kase, J. and Franc, J.—"Electrochemical Oxidation of Acrylic Resins at Deposition on an Iron Anode;" 1109-1112.
Sickfield, J.—"Swelling Investigations on Technical Reaction Resins;" 1113-1125.
Stabryn, J.—"Contribution on Choosing Optimum Conditions for the Determination of the Brightening Power According to DIN 53 191;" 1126-1127.

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

Davidson, S. L.—"A New Versatile Lead Free Pigment;" 435-442.
Gay, P. J.—"Protection from Hypothesis to Principle;" 443-447.
Whiteley, P., and Rothwell, G. W.—"Paints for Buildings — the Potential and the Performance;" 448-455.

PIGMENT & RESIN TECHNOLOGY

Paladini, J. C.—"Some Recent Developments in Epoxy Systems for the Surface Coating Industry. Part II;" 3-38.
Americus—"Coatings Update: Alkyd Resin Technology;" 9-11.

PAINT MANUFACTURE

Hubble, L.—"Standardised Visual Assessment of Colour — a Progress Report;" 10-12.
Boxall, J., and von Fraunhofer, J. A.—"Permeability Considerations in Paint Films;" 14-15, 21.
Kuchenmeister, R.—"Water-Based Paint: An Answer to all Problems;" 17-21.
Ellinger, M.—"Anti-Corrosion and Marine Paints;" 22-24, 26.

Boxall, J., and Von Fraunhofer, J. A.—"Corrosion under Paint Films: Influence of the Electrolyte on the Protection Afforded by an Unpigmented Polymer;" 8-11.

SKANDINAVISK TIDSKRIFT for FARG och LACK

Nilsson, E.—"Internal Stresses in Paint Films;" 318-332. (in Swedish).

Khullar, M., and Pattyranie, C.—"Experience with Some Types of Zincrich Paints;" 359-375. (in Swedish).

Letters to the Editor

TO THE EDITOR:

It was with considerable interest that I read Fred Stieg's letter dealing with CPVC and latex paints in the December issue of JPT (pp. 36 and 37). As he mentioned, I had developed an early interest in the CPVC concept and its application to paint formulation. Of course, in those early days we dealt exclusively with oil-based paints. The reference he cited, however, is not correct, and I would like to supply the correct reference.

A few months ago I had occasion to review the literature dealing with the earliest history of the CPVC concept in connection with the preparation of a paper for presentation at the April 1976 meeting of the American Chemical Society in New York. It was in the early 1930s that my attention was attracted to a paper by Hans Wolf and collaborators in Germany which dealt with consistency as related to pigment concentration. What seemed especially interesting to me was the fact that what Wolf called "the critical point" coincided for all practical purposes with the pigment concentration that exposure tests had shown to yield optimum durability. Further exploration of this relationship demonstrated rather conclusively that it held for exterior linseed oil paints if the pigment concentration was expressed in volume percent of the paint solids [see "Fundamental Studies of Paints. Paint Durability as Affected by the Colloidal Properties of the Liquid Paint," by A. C. Elm, *Ind. Eng. Chem.*, 26, 1245 (1934)].

I had the opportunity to discuss the results of our tests with Hans Wolf during a visit to Germany in 1932. He was amazed that we had found a practical application of a concept which he had considered to be merely an interesting theoretical observation.

A. C. ELM
475 Lafayette Ave.
Palmerton, Pa. 18071

Stanford Research Plans Study Of Radiation-Curable Coatings

Stanford Research Institute is planning a study to analyze the technology and economics of radiation-curable coatings and inks.

Designed for sponsorship on a multi-client basis, the study is primarily experimental in scope. Researchers will assess model systems and practical compositions to seek solutions to specific problems, and will identify and pursue opportunities for development of new or improved systems or systems components.

Despite advanced technology of radiation-induced polymerization and cross-linking of polymers, problems still exist in applications to coatings and inks, such as low cure rates in systems cured by UV light, volatility and toxicity of system components, inadequate depth of cure in pigmented systems, and low efficiency and high-cost of sensitizers.

Kollmorgen's Macbeth Div. Offering Training Courses

An innovative one-week series of training courses on practical application of new color technologies is being offered by the Macbeth Div. of Kollmorgen Corp.

The course, "Color and the Behavior of Colorants," is designed to provide increased awareness of color technology to all levels of personnel, technicians, and management. The format will underscore practical application of colorant formulation theory. Included are discussions of methods to describe and measure color; color differences, specifications and tolerances; theories and how to apply them; and the application of instrumental techniques.

The basic information is presented in such a manner that each student can perform actual color matching experiments, with daily sessions scheduled to be segmented between lecture and lab work.

Previous knowledge of color or a formal advanced education are not prerequisites for anyone taking the course.

Courses are scheduled at both Newburgh, N. Y. and Tatamy, Pa. for the weeks of May 17, Sept. 20 and Dec. 6. Fee is $350 and includes textbooks, all necessary supplies, reference material, lunches, and a banquet.

For complete information, contact either Dr. J. G. Davidson, Macbeth Div., P. O. Drawer 950, Newburgh, N. Y. 12550, or H. R. Davidson, P. O. Box 157, Tatamy, Pa. 18055.
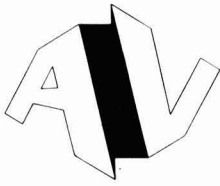
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J. E. Burrell, formerly Vice-President and General Manager of PPG Industries, Inc.'s Chemical Div., was elected Executive Vice-President, Operations, and **L. S. Williams**, who was previously Vice-President, Finance, was elected Executive Vice-President, Administration. Both men were also elected to the Board of Directors and named to the Executive Committee. At the same time, **V. A. Sarni** was elected Vice-President and General Manager of the Chemical Div., succeeding Mr. Burrell; **W. R. Harris**, formerly Vice-President, Organic Chemicals, succeeds Mr. Sarni as Vice-President and General Manager, Industrial Chemicals; and **R. E. Widing**, who had been Vice-President, Manufacturing—Industrial Chemicals, was named Vice-President, Operations of that unit.

Edward J. Reilly, previously Advertising Manager, Commercial Solvents Corp., recently acquired by International Minerals and Chemicals Corp., was appointed Marketing Coordinator in IMC's Marketing Services Div.

John Synol has been named General Manager of Bee Chemical Co.'s Western Chemical Div. He was previously Director of Operations for Bee's Industrial Coatings Div. at the firm's Lansing, Ill. headquarters.

Edgar L. Barrett has been named Vice-President, Assistant to the Chairman of the Board, Sherwin-Williams Co. He will continue to serve as Corporate Director of Development, a post he has held since 1970. **Wendell L. Gillund**, formerly Assistant to the Executive Vice-President, has been named Vice-President, Assistant to the President. **Geoffrey L. Tickner** was named Vice-President and General Manager of the Chemicals Div. He has served in the latter capacity since 1974.

William E. Steele was elected Group Vice-President, Ameron, Inc. He will serve as the corporate line officer responsible for those divisions which produce chemically based products. These include the Corrosion Control Div. which has headquarters in Brea, Calif., and

Enmar, a manufacturer of product finishes with operations in Little Rock, Ark. and Wichita, Kan.

James D. Parish has been appointed Sales Manager for The O'Brien Corp.'s Dixie-O'Brien Div. in Brunswick, Ga. He will be in charge of both consumer and industrial paint sales in 11 Southeastern states. Prior to joining O'Brien, Mr. Parish had served with Pratt & Lambert, Inc.

Donald Gels, formerly Vice-President—Sales of The Enterprise Co.'s Magicolor Paint Div., has been appointed Vice-President and General Manager of BPS Paint Co., a newly acquired Enterprise division.

The Color Marketing Group has announced newly elected members of its Board of Directors. They are: **Kenneth Charbonneau**, of Benjamin Moore & Co.; **Nadine Gross**, of Comark Plastics Div., United Merchants; and **Robert W. Miracle**, of Interpace Corp.

Dr. Bernard W. Greenwald has been appointed Director of Industrial and Agricultural Products for Merck & Co., Inc. He joined the firm in 1962 as a Chemist in the Product Development Section. His most recent position, which he had held since 1973, was Marketing Manager for Industrial and Agricultural Products. In 1974 he also assumed responsibility for magnesium products.

Dr. Shelby F. Thames, formerly Dean of the College of Science and Technology at the University of Southern Mississippi, has been named to the new position of Vice-President for Administration and

Regional Campuses. **Dr. Gary C. Wildman** succeeds Dr. Thames as Dean of the College of Science and Technology, and **Dr. B. George Bufkin** succeeds Dr. Wildman as Chairman of the Polymer Science Department.

William D. Mulliken has been elected Vice-President and Secretary of Central Solvents & Chemicals Co.

M. S. Birmingham, Jr. has joined the Chemical Specialties Group of Emery Industries, Inc. as a Sales Representative in the Group's Western Region. He was formerly with Westex Chemical Corp. **Bernard P. Olszowy** has joined Emery's Trylon Chemicals Group as a Sales Representative in the New York, New England, and northern New Jersey-New York metropolitan area. He was previously with Process Chemicals Div. of Diamond Shamrock Chemical Co.

John C. Dickman has been appointed Technical Director of Boysen Paint Co., a wholly owned subsidiary of Grow Chemical Corp. He previously held technical positions with Reichhold Chemicals, Royal Paint Co., Kelly Moore Paint Co., and Superior Coatings and Chemicals.

Andrew B. Chase, Jr. was named Industry Manager for Plastics Additives and Paints, Specialty Chemicals Div. of ICI United States Inc. He joined the company in 1974 as a Business Analyst for Specialty Chemicals Div.

Robert G. Wallace has been appointed Vice-President and General Manager of Conchemco Coatings' Western Div. He was formerly General Manager of the division.

R. Donald Griebel has been appointed Business Director, Polymers in the new Business Unit formed by AMSCO Div. of Union Oil Co. of California. The new group will be responsible for developing product and market strategies for polymer emulsions and hot melt adhesives manufactured by the division. Mr. Griebel, most recently Manager of Manufacturing, will be located at AMSCO headquarters in Palatine, Ill. The new Business Group will consist of **Dr. Ralph Bauer**, Technical Director; **James K. Merwin**, Product Manager, Polymers; and **Ben H. Flores**, Product Manager, Hot Melts.

Meanwhile, **Kenneth G. Oswald** has joined AMSCO as Manager of Manufacturing, succeeding Mr. Griebel. He was formerly Manager of Contract Coordination of the Union Oil Eastern Region Purchasing Department.

Albert R. Mersberg has joined BRINER Paint Manufacturing Co., Inc., Corpus Christi, Texas, as Technical Director.

Daniel J. Seeman has been named Sales Manager — Coatings for Kenrich Petrochemicals, Inc. He will be responsible for direct selling of the company's products in the epoxy and allied coatings market.

Dr. Suryya Das has been promoted to Senior Research Associate at PPG Industries, Inc. He joined the firm in 1963 and has been involved most recently in work on water-soluble polymers, latices, and other colloidal water-based systems.

J. E. Quinty has been named Sales Manager, Western Operations, for the Fatty & Dibasic Acids Group of Emery Industries, Inc. He will be responsible for all of the Group's field sales personnel west of the Rockies. He joined the firm in 1953, and most recently served in marketing management with Emery's Canadian subsidiary in Toronto.

R. Marshall Evans, Jr., formerly Vice-President of Sales, has been appointed Executive Vice-President for Thompson, Weinman and Co. He will continue to be responsible for the firm's sales and marketing, along with additional administrative responsibilities. He joined the company as a Salesman in 1963, and later served as Regional Sales Manager.

R. D. Griebel   K. G. Oswald   A. R. Mersberg   D. J. Seeman

The Dyes & Pigments Division of American Hoechst Corp. has announced personnel changes in two of its departments. In the Pigments and Specialty Chemicals Marketing Dept., **Peter A. Morris** has been promoted to District Manager, Cleveland, Ohio, where a new district has been established. In the Pigments and Specialty Chemicals Technical Dept., **Andrew C. Zamoyski** has been named a Printing Ink Technical Representative. Mr. Morris joined the firm's parent, Hoechst AG, in Germany in 1964, and transferred to American Hoechst in 1968. He most recently served as a Technical Sales Representative in the Chicago/Midwest territory. Mr. Zamoyski, who formerly served with Thiele-Engdahl and Tenneco, will be located in Coventry, R.I.

The Gibson-Homans Co., Cleveland, Ohio, has announced two personnel changes as part of its realignment plans. **Eric S. Wormser** has been named Chairman of the Board, succeeding **Wilbur F. Schmitt**, who retired on January 31. **S. Shaw Painter** has been named Vice-President, Research, also effective February 1. Mr. Wormser joined the firm in 1956 as Director of Research, and was formerly Vice-President, Research and Production, as well as a member of the Board of Directors. Mr. Painter joined the company in 1966, and currently serves as Chief Chemist.

Mautz Paint Co. has announced the following personnel changes: **Tony Braaksma** has been appointed District Sales Manager for the Des Moines and western Iowa territory; **Alford Markham** has been named Production Manager, as assistant to **Russell Luecke**, Vice-President of Manufacturing; and **Bill Johnson** has been promoted to Head Tinter.

Robert Chellew has been named a Sales Representative for the Chemical Coatings Div., Pratt & Lambert, Inc. His territory will include parts of Pennsylvania, New Jersey, New York, Connecticut, Massachusetts, and Rhode Island.

Helge Meyer has joined the staff of NIFAB, Scandinavian Paint Consultants Ltd., of Stockholm/Copenhagen, a firm which is working with the Scandinavian Paint and Printing Ink Research Institute. Mr. Meyer, who has many years of experience in Sweden's coatings industry, has been President of SLF (the Federation of Scandinavian Paint and Varnish Technologists), and a Vice-President of the Oil and Colour Chemists' Association. He is currently Chairman of the Danish Paint and Varnish Chemists' Association, a corresponding member of GDCH, and the Editor of "Farg och Lack."

Merck & Co., Inc. has announced the formation of three separate divisions from the distinct business operations that formerly had been combined in the Merck Chemical Div. (MCD). The new divisions are: Merck Chemical Manufacturing Div., Merck Animal Health Div., and Merck Chemical Div. **Thomas B. Davis** has been elected Vice-President and General Manager of the division that retains the Merck Chemical Division designation — formerly the industrial and fine chemicals area of MCD. In this position, Mr. Davis reports to **Howard F. Powers**, who has been elected to the newly created position of Group Vice-President in charge of the firm's industrial and environmental health businesses. Mr. Powers had been Executive Vice-President of MCD before the reorganization. **Dr. Hilmer L. Jones** has been elected Vice-President and General Manager of the Animal Health Div., formerly the animal health and feed products area of MCD. **Spencer A. Stouffer** has been elected Vice-President and General Manager of the Chemical Manufacturing Div., formerly the operations area of MCD.

Richard C. Drexler has been appointed Product Manager, Surfactants and Specialties for the Distribution Division of Chemtech Industries. He joined the firm in 1973, and most recently served as a Technical Sales Representative.

Ralph A. Wobser has been appointed a Sales Representative for the Industrial Chemical Division of PPG Industries, Inc. He will work out of the firm's regional sales office in Houston.

The Chemical Products Division of Cargill, Inc. has announced a series of personnel changes. **Mark B. Spitz,** Assistant Vice-President, has been named General Manager of four subsidiary companies — Tennant Strapping Systems, Griplock of Canada, Elastomers, and Agricultural Chemicals; and **James F. Lawrence** has been named General Manager of resin production and sales. In addition to his new duties, Mr. Spitz will continue to supervise the firm's resin business from corporate headquar-

ters in Minneapolis. Mr. Lawrence, formerly Resin Account Manager of Cargill's central region offices in Carpentersville, Ill., will move to Minneapolis to assume his new post. **Thomas M. Tolle** succeeds Mr. Lawrence as Account Manager at Carpentersville, while **David E. Tweet,** currently head of resin research, succeeds Mr. Tolle as Assistant Account Manager. In the company's eastern resin production and sales area, **Thoms C. Donnelly** will leave his position as Account Manager to head a special division project. Assistant Account Manager **Robert P. Hislop** has been named Account Manager in the region's Philadelphia office. **G. Wallace Meyer,** National Accounts Manager for coatings resins, has been given responsibility for polyester industries, and will supervise the division's market development programs.

Obituary

Vincent G. Florentine, Manager of Quality Assurance for Benjamin Moore & Co., died January 8. A member of the New York Society for Coatings Technology, he served as its President in 1973-74, and was the 1961 recipient of the Roy H. Kienle Award in recognition of his technical achievements and outstanding service to the Society's Technical Committee and its Subcommittees.

M. R. Matteson, 79, founder of Matteson Ridolfi, Inc., manufacturers representatives, died December 23. He had spent over 50 years in the coatings industry.

F. E. Wellersdieck, retired executive of Benjamin Moore & Co., died December 26. He was 83. He began his career with the company in 1910, and at the time of his retirement in 1957 was serving as Corporation Director of Purchases.

Earl D. Flood, founder and Chairman of the Board of the Flood Co., died December 14. He was a member of the National Paint and Coatings Association's 50-year club, and was a Past-President of the Master Painters Association, predecessor of the Painting and Decorating Contractors of America.

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Meetings

Three Courses on Color Technology Being Offered in June at Rensselaer Poly

For the 12th consecutive year, The Rensselaer Color Measurement Laboratory at Rensselaer Polytechnic Institute is offering a program of three intensive continuing-education courses in color technology.

The following courses will be offered: "Principles of Color Technology" (June 7-11); "Color Technology for Management" (June 15-16); "Advances in Color Technology" (June 21-25).

The courses are under the direction of Dr. Fred W. Billmeyer, Jr., Professor of Analytical Chemistry at Rensselaer. Assisting him will be Max Saltzman, recently retired as Manager of Color Technology, Allied Chemical Corp., and Adjunct Professor of Chemistry at Rensselaer.

"Principles of Color Technology" is intended to provide both theory and practice in the description, specification, and measurement of color, and will be of particular interest to industrial personnel responsible for color matching and color control. Both theoretical concepts and practical applications of the science of color will be emphasized. Laboratory sessions will be held daily for instrumental measurements, computations, and problem solving. Those without advanced degrees and whose practical experience in the field is a substitute for a college degree should find the course of particular value.

"Color Technology for Management" is a two-day course designed to aid executives responsible for research, production, or marketing of colored products in reaching correct management decisions based on the principles of color technology particularly where instrumental or computational techniques are involved. The course will describe what can and what cannot be expected from programs of instrumental color measurement and control, and from computer color matching, and those attending will learn how to recognize realistic programs in these areas and how to avoid highly inflated proposals not based on reality.

"Advances in Color Technology" is limited to applicants having two or more years of experience in instrumental color measurement, or a shorter period of experience plus completion of "Principles of Color Technology" or an equivalent course. Topics covered are instrumentation for color measurement, data reduction and colorimetric calculations, color perception, color difference calculations and color spaces, turbid-medium theory and color matching, and geometric aspects of color and appearance. Included are selected advanced laboratory workshops on such topics as the photometric and wavelength calibration of color-measurement spectrophotometers, the separation of fluorescence and true reflectance, the variables of perceived color, and geometric aspects of color measurement.

Complete information on the courses is available from the Office of Continuing Studies, Color Technology Program, Rensselaer Polytechnic Institute, Troy, N. Y. 12181.

Baltimore Society Seminar Focuses on Technology Update

"An Update on Emerging Technologies" is the title of a seminar being sponsored by the Baltimore Society for Coatings Technology at Martins-West, Baltimore, on February 25, from 3:00 pm to 9:00 pm.

The following papers will be presented:

"Recent Developments in the Field of Powder Coating Technology" — John Miller, of Farboil Corp.

"Radiation Cured Coating Technology: Development and Application of UV and EB Cured Coatings" — Dr. R. A. Hickner, of Dow Chemical Co.

"Development Application and Handling of Pigment Slurry" — M. C. McGuire, of J. M. Huber Corp.

"Formulation, Development and Application of Electrocoat Systems" — Dr. George Brewer, Consultant.

The after-dinner speaker will be Dr. Harrison, of University of Maryland, who will speak on "Ecological Failures and Their Consequences."

Hunterlab Inaugurates Series Of Mini Shows/Seminars

Hunter Associates Laboratory, Inc. recently inaugurated a series of exhibits to be held in conjunction with its traditional area seminars at selected locations in the field.

The combined events provide a no-cost opportunity for interested individuals to discuss color problems and possible instrumental solutions.

Day-long informal exhibits are followed the next day by a seminar at which Hunterlab staff personnel present background on colorimetry and the theory of color science, as well as effective methods for the measurement of appearance attributes.

The Mini Show/Seminar Spring schedule is:

Chicago—Mar. 8-9.

Indianapolis—Mar. 11-12.

Charlotte, N.C.—Mar. 31, Apr. 1.

Metropolitan New York—Apr. 14-15.

Minneapolis—May 12-13.

Syracuse, N.Y.—May 26-27.

Meanwhile, Hunterlab's 1976 Workshop will be held at company headquarters in Fairfax, Va., Nov. 10-12. This event is designed to provide a more thorough understanding of appearance properties and their measurement.

For detailed information, or to register, write Hunter Associates Laboratory, Inc., 9529 Lee Highway, Fairfax, Va. 22030.

Conference on "Colorants" To Be Held May 12-14 in Ottawa

The Fourth Annual Conference of the Canadian Society for Color in Art, Industry and Science will be held at the University of Ottawa on May 12-14.

The Conference theme will be "Colorants," and the program will include presentations on various aspects of pigments and dyes. Papers will explain the relation between the physical properties of colorants and the perceived color; characteristics of colorants that are important to technologists, designers and artists; calculation of colorant mixtures to produce a particular color; and the control of color in industrial processes.

An "Open House" in the Optics Section of the National Research Council is also planned.

Program Chairman is Dr. A. R. Robertson, of the Division of Physics, National Research Council, Ottawa, Ontario, Canada.

SYMCO '76 Set for March 9 and 10

The Sixth Annual Chicago Coatings Symposium, SYMCO '76, will be held March 9 and 10 at the Sheraton Oak Brook, Oak Brook, Ill.

Sponsored jointly by the Chicago Society for Coatings Technology and the Chicago Paint and Coatings Association, the symposium will focus on coatings developments over the years, with the theme, "Coatings Past, Present and Future — 1776-2176."

The following presentations will be featured:

"Past Preludes to Future Coatings" — Dr. J. C. Weaver, Consultant and former Director of Research at Sherwin-Williams Co.

"Photoinitiators in UV Curing" — Dr. Peter Pappas, of North Dakota State University.

"Corrosion Resistant Coatings" — T. M. Muzyczko, of Richardson Co.

"A New Look at Agriculture for Coatings Raw Materials" — L. H. Princen, of Northern Regional Research Center, U. S. Department of Agriculture.

"A Direct Method for Measuring the Chalky Surface Adhesion of Latex House Paints" — O. E. Brown, of Union Carbide Corp.

"The Future of the Coatings Industry Over the Next Two Hundred Years" — Dr. Howard L. Gerhart, of Carnegie-Mellon University and formerly Vice-President of Research and Development with PPG Industries, Inc.

"Current Research on the Fire Hazards of Materials" — Dr. G. E. Hartzell, of Dow Chemical Co.

"Pigment and Surfactant Selection in Trade Sales Paints" — Ralph Edelman, of E. I. du Pont de Nemours & Co., Inc.

"The Cracking and Splitting of Latex Films" — Dr. J. W. Vanderhoff, of Lehigh University.

"Performance of Construction Coatings" — Joseph Stein, of Tishman Realty & Construction Co.

Registration fees are $25 for one day and $40 for both days if paid in advance. On-site registration is $27 for one day, $45 for two days. The fees include lunch and coffee. Checks should be made payable to Education Fund, Chicago Paint and Coatings Association. To register, write Ms. Dolores Thomas, Chicago Paint and Coatings Association, Suite 1710, 33 N. Dearborn St., Chicago, Ill. 60602.

Colorant Formulation Course Slated for Lehigh, May 3-7

An intensive five-day course and symposium on "Colorant Formulation; Theory and Practice" is being offered by the Consortium for Color Technology on May 3-7 at the Jennie H. Sinclair Conference Center at Lehigh University. The May 7 symposium may be attended independently by those who do not register for the entire course.

Colorant formulation techniques will be covered in detail, starting with the basics and proceeding to the latest advances. Instruction and practice are provided in the use of the computer for colorant formulation by Kubelka-Munk single and two-constant theories, and the application of Mie and radiative transfer theory. No previous knowledge of color theory is required, but some familiarity with elementary calculus is desirable. All other mathematical tools, including matrix operations, are presented in the course. Afternoons will be devoted to computer exercises.

The one-day symposium will be general in nature and will be of interest to anyone concerned with color. Speakers will include Fred W. Billmeyer, Jr., David L. MacAdam, Roland Derby, Sol Panush, and Eugene Allen.

Fee for the course and symposium is $350, which includes notebooks, lunches, and a banquet; one representative from each Consortium member company may attend free of charge. Fee for attendance at the symposium only is $70; all representatives of Consortium member companies may attend the symposium free.

The course and symposium are under the direction of Eugene Allen, Professor of Chemistry at Lehigh. For complete program information or to register, write Mr. Allen, c/o Color Science Laboratory, Lehigh University, Bethlehem, Pa. 18015.

Toronto Hosting Mar. 29-31 Powder Coating Conference

The Fourth North American Conference on Powder Coating, to be held March 29-31 at the Inn-on-the-Park, Toronto, will provide an in-depth look at advances in equipment and materials and the future of powder coating around the world.

The first two days of the event will feature presentations.

The Powder Coating Show will be open March 30-31 with exhibits of the latest equipment, materials and methods, with live demonstrations of powder applications.

Complete information and a registration form may be obtained from the sponsor, *Canadian Paint and Finishing*, 481 University Ave., Toronto, Canada, M5W 1A7.

FATIPEC Conference to be Held May 2-7 on French Riviera

The 1976 International Conference of FATIPEC (Continental European Federation of Associations of Paint, Varnish, Enamel and Printing Technicians) will be held May 2-7 in the Convention Centre of Antibes — Juan-les-Pins, on the French Riviera.

Some 1500 to 2000 participants are expected to attend.

The program will feature 150 papers, with 10 general sessions and five symposium discussions.

The symposium discussions, in which both producers and consumers will be represented, will cover building paints, industrial paints, protection of civil engineering structures, packaging, and printing inks.

The Fifth Specialized Exhibition will bring together approximately 100 European firms.

Complete information and registration forms are available from Mr. G. Eyraud, Secretary, FATIPEC, 5, Rue de la Poudriere, 69001, Lyon, France.

New Course on Current Topics To Begin March 3 in New York

An update on a variety of subjects of current interest is available to qualified chemists and coatings technicians through a new semester of the seminar-style course in "Current Topics in Coatings Technology," to be offered at the New York Community College, beginning March 3. Sponsored by the Joint Education Committee of the New York Society for Coatings Technology and the New York Coatings Association, the course consists of 13 evening sessions, and features a different guest lecturer each week.

The series follows an earlier one which ended on January 28.

Lectures will focus on Adhesions; Measurement of Film Integrity; Color Measurement and Matching; Effect of Environmental and Safety Regulations on the Formulator; Solvent Recovery Systems; New Industrial Coatings Equipment; Plastisols and Organosols; Trends in Lacquer Formulation; and many more.

The courses are coordinated and directed by Don Brody, of M&T Chemicals Inc., Rahway, N. J., who is also Chairman of the Joint Education Committee.

Registration fee is $100. To be eligible, applicants must have completed a course in the fundamentals of coatings technology or have at least two years' industry experience.

Applications should be directed to Mr. Saul Spindel, David Litter Laboratories, 116 E. 16th St., New York, N. Y. 10003.

Literature

Coatings Brochures

A 24-page reference guide is now available which describes briefly a list of technical brochures on paint, coating and caulk applications for chemical intermediates, polymers, and solvents. Organized by application area, the guide particularly emphasizes low pollution coatings incorporating intermediates such as trimellitic anhydride and isophthalic acid. Write Amoco Chemicals Corp., MC 4102, Dept. ADV-JPAT, P. O. Box 8640A, Chicago, Ill. 60680.

Computer Color Matching

Addition of a color matching computer aids in the preparation of the prescribed standards set forth by customers, and is said to eliminate costly color matching mistakes. A sample submitted by a customer is measured for tristimulus values and chromaticity coordinates. The computer then predicts the best possible formulation with available colorants or gives a choice of formulations, indicates the degree of metamerism to be expected, and plots a predicted spectral curve against that of the standard. For complete information, contact Munsell Color Products, Macbeth Div., Drawer 950, Little Britain Rd., Newburgh, N. Y. 12550.

Polyurethane Coating Systems

A new 32-page technical manual on polyurethane coatings, adhesives and latices provides a comprehensive technical treatment of the subject and should be a valuable source of basic performance information. Included are basic descriptions of the transfer and direct coatings techniques, together with complete technical information and "Instron" tensile curves on more than 30 topcoats, skincoats, direct coating, adhesive and latex polymers. Write for a copy of "The Polyurethane Coatings Book" to Millmaster Onyx Corp., Polyurethane Specialties Div., 624 Schuyler Ave., Lyndhurst, N. J. 07071.

Pigment Dispersions Catalog

Now available is a new technical catalog for the coatings, ink, and allied industries which compiles all pertinent information on a wide variety of colored pigment dispersions for solvent-thinned and water-thinned coatings. Also included is detailed information on slip agents, flatting bases, dispersing agents, and foam suppressors. Write Daniel Products Co., 400 Claremont Ave., Jersey City, N. J. 07304.

Coming Events

FEDERATION MEETINGS

(May 14)—Spring Council Meeting. Sheraton Four Season Hotel, Toronto, Canada.

(Oct. 27-29)—54th Annual Meeting and 41st Paint Industries' Show. Sheraton Park Hotel, Washington, D. C. (FSCT, Suite 830, 1315 Walnut St., Philadelphia, Pa. 19107).

SPECIAL SOCIETY MEETINGS

(Mar. 9-10)—Chicago Society. SYMCO '76. Sheraton Oakbrook Hotel, Oakbrook, Ill. "Coatings — Past, Present, and Future — 1776-2176." (Miss Delores Thomas, Chicago Paint and Coatings Association, 33 N. Dearborn St., Chicago, Ill. 60602).

(Mar. 17-19)—Southern Society Annual Meeting. Fairmont Hotel, Atlanta, Ga. (Bobby D. Moore, Interstate Paint Corp., P. O. Box 1038, Brunswick, Ga. 31520).

(Apr. 8-10)—Dallas and Houston Societies. Southwestern Paint Convention, Dallas, Texas. (Donald D. Wilson, Dal-Worth Paint Mfg. Co., P. O. Box 173, Mesquite, Texas 75149).

(Apr. 26)—Philadelphia Society Seminar on "Thermoplastic and Thermosetting Anti-Corrosive Water-Reducible Coatings." Cities Service Research Center, Cranbury, N. J. (Donald Romanofsky, Harad Paint Co., 5525 Grays Ave., Philadelphia, Pa. 19143).

(May 6-8)—Pacific Northwest Society. Spring Symposium. Bayshore Inn, Vancouver, B. C., Canada. (B. D. Lamb, Harrisons & Crossfield (Canada) Ltd., 3070 Kingsway, Vancouver, B. C., Canada V5R 5J7).

OTHER ORGANIZATIONS

(Mar. 1-5)—World Conference on Oilseed and Vegetable Oil Processing Technology. RAI Centre, Amsterdam, Netherlands. (American Oil Chemists' Society, 508 S. Sixth St., Champaign, Ill. 61820).

(Mar. 2-4)—Plastics Institute of America course on "Polymers for Decorative and Durale Coatings." University of Louisville, Louisville, Ky. (PIA, Castle Point Station, Hoboken, N. J. 07030).

(Mar. 8-9)—Regional Technical Conference on "Plastics Coatings for Electrical Applications." Hotel Toronto, Toronto, Canada. Cosponsored by Ontario Section and Electrical and Electronics Div. of Society of Plastics Engineers. (Walter Ambriki, Honeywell Ltd., 740 Ellesmere Rd., Toronto, Ontario MIP 2V9, Canada).

(Mar. 10-12)—Annual Marine Coatings Conference. Sea Pines Plantation, Hilton Head Island, S. C. (John Montgomery, National Paint and Coatings Association, 1500 Rhode Island Ave. N. W., Washington, D. C. 20005).

(Mar. 16-17)—Association for Finishing Processes of SME Seminar on "Modern Finishing Processes for Flat Line Board Products." Thunderbird Jantzen Beach Motor Inn, Portland, Ore. (Flat Line Seminar, AFP/SME, 20501 Ford Road, P. O. Box 930, Dearborn, Mich. 48128).

(Mar. 22-24)—Fifth Annual Gas Chromatography Short Course. Occidental College, Los Angeles, Calif. (Dr. R. L. Amey, Department of Chemistry, Occidental College, Los Angeles, Calif. 90041).

(Mar. 22-26)—National Association of Corrosion Engineers. Materials Performance and Corrosion Show. Hyatt-Regency Hotel, Houston. (NACE, P. O. Box 1499, Houston, Tex. 77001).

(Mar. 23-26)—OCCA — XXVIII. Oil and Colour Chemists' Association Annual Technical Exhibition. Alexandra Palace, London, England. (Director and Secretary, OCCA, Priory House, 967 Harrow Road, Wembley, Middlesex HAO 2SF, England).

(Mar. 29-31)—Fourth North American Conference on Powder Coating. Inn-on-the-Park, Toronto, Canada. (M. J. Palmer, **Canadian Paint and Finishing**, 481 University Ave., Toronto, Ontario, Canada M5W 1A7).
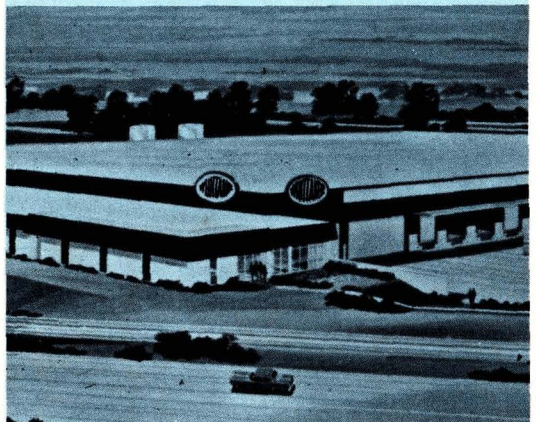
Coming Events (Continued)

(Apr. 4-9)—100th Anniversary Meeting of American Chemical Society. New York, N. Y. (ACS, 1155 16th St. N. W., Washington, D. C. 20036).

(Apr. 5-9)—Scanning Electron Microscopy Symposium and Workshops. Four Seasons Sheraton Hotel, Toronto, Canada. (Dr. Om Johari, IIT Research Institute, 10 West 35th St., Chicago, Ill. 60616).

(Apr. 7-8)—Air Pollution Control Association's 4th Annual Government Affairs Seminar. International Inn, Washington, D. C. (APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213).

(Apr. 12-13)—Washington Paint Technical Group's 16th Annual Symposium. Marriott Twin Bridges Hotel. (Mildred A. Post, c/o U. S. Dept. of Commerce, National Bureau of Standards, Washington, D. C., 20234).

(Apr. 21-23)— Chemical Coatings Conference. Cincinnati Convention Center, Cincinnati, Ohio. (Jerry L. Colness, National Paint and Coatings Association, 1500 Rhode Island Ave., N. W., Washington, D. C. 20005).

(Apr. 26-29)—Society of Plastics Engineers 34th Annual Technical Conference. Chalfonte-Haddon Hall, Atlantic City, N. J. (Eugene E. Wilson, Society of Plastics Engineers, 656 W. Putnam Ave., Greenwich, Conn. 06830).

(May 2-5)—Color Marketing Group. Copley Plaza, Boston, Mass. (Color Marketing Group, 1000 Vermont Ave., N.W., Washington, D.C. 20005).

(May 2-7)—XIIIth FATIPEC Congress. Convention Centre of Antibes — Juan-les-Pins, France. (G. Eyraud, Secretary, FATIPEC, 5, Rue de la Poudriere, 69001, Lyon, France).

(May 6-7)—International Symposium on Flammability and Fire Retardants. Four Seasons Sheraton Hotel, Toronto, Canada. (V. M. Bhatnagar, 209 Dover Rd., Cornwall, Ontario, Canada K6J 1T7).

(May 9-12)—National Coil Coaters Association Annual Meeting. Marco Island Hotel, Marco Island, Fla. (NCCA, 1900 Arch St., Philadelphia, Pa. 19103).

(May 10-13)—International Meeting on Radiation Processing. Cerromar Beach Hotel, Dorado Beach, Puerto Rico.

(June 2-4)—Symposium on "Energy Savings through Reactive Coatings." North Dakota State University, Fargo, N. D. (Dr. Zeno W. Wicks, Jr., Polymers and Coatings Dept., North Dakota State University, Fargo, N. D. 58102).

(June 6-10)—The Chemical Institute of Canada's 59th Canadian Chemical Conference. London, Ontario, Canada. (Don Emmerson, CIC, Suite 906, 151 Slater St., Ottawa, Ont. K1P 5H3, Canada).

(June 7-11)—Principles of Color Technology. Rensselaer Polytechnic Institute, Troy, N.Y. (Office of Continuing Studies, Color Technology Program, Rensselaer Polytechnic Institute, Troy, N. Y. 12181).

(June 8-11)—International "Conference on Colour Studies," sponsored by Hungarian Naitonal Color Committee. Budapest, Hungary. (Dr. Fred W. Billmeyer, Jr., Dept. of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. 12181).

(June 15-16)—Color Technology for Management. Rensselaer Polytechnic Institute, Troy, N. Y. (Office of Continuing Studies, Color Technology Program, Rensselaer Polytechnic Institute, Troy, N. Y. 12181).

(June 21-25)—Advances in Color Technology. Rensselaer Polytechnic Institute, Troy, N. Y. (Office of Continuing Studies, Color Technology Program, Rensselaer Polytechnic Institute, Troy, N. Y. 12181).

(June 27-30)—American Society for Testing and Materials Annual Meeting. Chicago, Ill. (ASTM, 1916 Race St., Philadelphia, Pa. 19103).

(June 27-July 1)—Air Pollution Control Association's 69th Annual Conference & Exhibition. Memorial Coliseum, Portland, Ore. (APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213).

(July 18-24)—Intersociety Conference and Exposition on Transportation. Los Angeles Hilton Hotel, Los Angeles, Calif. (Thomas P. Woll, U. S. Dept. of Transportation, Federal Railroad Administration, 2100 2nd St. S.W., Room 4108, Washington, D. C. 20590).

(Sept. 14-16)—"Powder Coating 4." Cincinnati, Ohio. (Society of Manufacturing Engineers, 20501 Ford Rd., Dearborn, Mich. 48128).

(Sept. 29-Oct. 1)—Convention of Scandinavian Federation of Paint Technologists. Congress Hotel Kalastajatorppa, Helsinki, Finland. (Federation of Paint and Varnish Technologists, Boks 828—2100, Copenhagen, Denmark).

(Sept. 30-Oct. 1)—National Coil Coaters Association Fall Technical Meeting. Hyatt Regency O'Hare, Chicago, Ill. (NCCA, 1900 Arch St., Philadelphia, Pa. 19103).

(Oct. 7-9)—South African Section of OCCA and Council for Scientific and Industrial Research Symposium on "Nonconventional Coatings." Port Elizabeth, South Africa. (Council for Scientific and Industrial Research, Symposium Secretariat — S.125, P. O. Box 395, Pretoria 0001, South Africa).
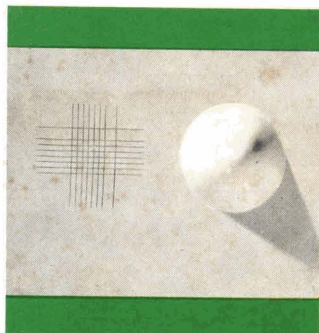
(Oct. 25-27)—National Paint and Coatings Association Annual Meeting. Washington Hilton Hotel. (Alan N. Darrow, NPCA, 1500 Rhode Island Ave., N.W., Washington, D. C. 20005).

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