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Recent Developments

JCTAX 53 (678) 1-76 (1981)

JULY 1981

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Testing showed an increase in coating adhesion of 30 to 50% for solvent-based epoxy coatings modified with Hycar® RLP, over unmodified coatings. You can formulate two ways. Add an amineterminated polymer (ATBN) to the amine curing agent or add a carboxy-terminated polymer (CTBN) pre-react to the epoxy side.

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Volume 53

Number 678

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Comment

PRI—An Interim Report

One of the key reports at the Federation Spring Board meeting was submitted by the Ad Hoc Committee on the Paint Research Institute, whose members recently completed surveying all 26 Constituent Societies on the subject of PRI and its research efforts. The Committee's tentative conclusions are included in the Federation Newsletter in this issue (see page 17).

The complete Committee report, along with supplementary related comments on Paint Research Institute activities, will be published as part of the Report on the Spring Board Meeting in the August issue of JCT. For all members interested in the Federation and PRI, this should be "must" reading. However, it is well to keep in mind that the Committee's report "attempts to summarize faithfully the consensus of Society views of the Paint Research Institute, and is not to be interpreted as representing, at this time, the final conclusions and recommendations of the Ad Hoc Committee." More input is being sought from others in the industry to help identify ways to help improve the research effort, and the Committee will report again to the Board at its Fall meeting, October 27.

Research is as vital to the paint industry now as it was when PRI was founded almost a quarter century ago, and the efforts of the Ad Hoc Committee to determine how best to address them are of prime concern to the Federation. The Societies have had their say; now, additional input will be solicited to provide a broader perspective so as to develop a wider comprehensive data base upon which to draw for final conclusions and recommendations.—TAK

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Abstracts of Papers inThis Issue

MECHANISM OF CORROSION INHIBITION WITH SPE-CIAL ATTENTION TO INHIBITORS IN ORGANIC COAT-INGS—H. Leidheiser, Jr.

Journal of Coatings Technology, 53, No. 678, 29 (July 1981)

Proposed mechanisms by which inorganic and organic substances provide corrosion inhibition are reviewed. Special attention is paid to corrosion inhibition provided by lead compounds and chromates in organic coatings. Six requirements are described for an inhibitor to be used in organic coatings. Five programs of research are proposed that might assist in better understanding the mechanism of action of inhibitors in coatings.

INTERNAL STRESS IN PIGMENTED THERMOPLASTIC COATINGS—D.Y. Perera and D. Vanden Eynde

Journal of Coatings Technology, 53, No. 678, 40 (July 1981)

The effect of pigmentation on the development of internal stress in thermoplastic coatings is discussed. Three pigments (titanium dioxide, red and yellow iron oxides) and one filler (talc), a thermoplastic binder and a solvent were used to formulate a range of pigment volume concentration (PVC). A cantilever (beam) method was used to measure the internal stress (S).

It was found that, for PVC < CPVC (critical pigment volume concentration), S increases with increasing PVC, while for PVC > CPVC, S decreases with increasing PVC. This variation is mainly due to the dependence of the elastic modulus (one of the S-components) on the PVC. Such behavior indicates that internal stress measurements can also be used to determine the CPVC.

The low internal stress values obtained with the talc formulations were related to the lamellar shape of this extender.

RECENT DEVELOPMENTS IN MARINE ANTIFOULING COATINGS-M.H. Gitlitz

Journal of Coatings Technology, 53, No. 678, 46 (July 1981)

A brief overview of the state of the art in controlling or preventing undesirable marine growth on surfaces exposed to the marine environment using antifouling coatings is presented with emphasis on organotin toxicants. Recent developments in this area are described, especially in regard to organotin polymer technology where the toxicant and the binder are chemically linked in a film-forming polymer. These organotin polymer systems hold promise for truly providing the 30 month protection against fouling long sought by ship owners and operators.

CHARACTERIZATION OF ORGANIC COATINGS USING DIELECTRIC SPECTROSCOPY—J.V. Standish and H. Leidheiser, Jr.

Journal of Coatings Technology, 53, No. 678, 53 (July 1981)

A simple system is described for making dielectric measurements of coatings and films as a function of temperature. Illustrations are given of the applicability of the technique for studying (a) dielectric relaxations and determination of T_{0} , (b) water in coatings, (c) composition and structure of coatings, and (d) quality control of coating components. Examples are given for unpigmented poly (vinyl acetate) and epoxy-polyamide coatings.



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Pigment Level 53.4 lb./100 gal. Pigment Cost/Gallon\$1.80
Molyorange/Per Red Control
\$1.86

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Chrome Green Control

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\$1.30

nent Cost/Gallon

GREEN-SOLVENT & AQUEOUS SYSTEMS

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\$40.00

COBO HALL, DETROIT, MICHIGAN October 28–30, 1981

\$55.00

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- C
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- D
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- K 🗌 Government Agency
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for Retired Federation Members and their spouses \$20.00 each in advance only.

MAIL TO: Federation of Societies for Coatings Technology 1315 Walnut Street • Philadelphia, Pa. 19107

ANNUAL MEETING AND PAINT INDUSTRIES SHOW

	REGISTRATION FEES											
	Member	Non-Member	Spouses Activities									
ADVANCE	\$40.00	\$55.00	\$25.00									
ON SITE (FULL TIME)	\$45.00	\$60.00	\$30.00									
ON SITE (ONE-DAY)	\$25.00	\$35.00	-									

Spouses Activities

An interesting program has been planned for the spouses.

There will be a get-acquainted wine and cheese social in the Detroit Plaza Hotel on Wednesday, October 28. Continental breakfasts will be available on Thursday and Friday mornings in the Plaza and the Book Cadillac.

On Thursday, the spouses will be conducted on a sightseeing tour of Detroit and to the magnificent Meadow Brook Estate, home of the late Matilda Dodge Wilson. This estate, of over 100 rooms, exemplifies the elegance of 18th century England, and contains an abundance of antiques, wall hangings, and original Regency furniture. Luncheon will be served in the elegantly appointed dining room overlooking the green meadow.

The Annual Federation Luncheon will be held on Friday in Cobo Hall.

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MAIL TO: FSCT, 1315 WALNUT ST., PHILADELPHIA, PA 19107

HOTEL INFORMATION AND RATES

All room rates in Detroit are subject to an additional 4% charge-a Detroit tax. There is no hotel tax in Windsor.

Hotel	Singles	Doubles (D) Twins (T)	Parlor & 1 Bedroom	Parlor & 2 Bedrooms
	Hotels in Detroit			
BOOK CADILLAC*	\$50	\$58 (D) 70 (T) (DD)	\$175/250	\$225/300
DETROIT PLAZA	59/69/79	71/81/91	170/190/280	240/270/365
DOWNTOWN TRAVELODGE	38	40 (D) 42 (T)	-	-
HOWARD JOHNSON'S	40	52 (DD) 50 (T)	—	_
LELAND HOUSE*	30 to 45	35 to 55 (D) 40 to 55 (T)	45 to 65	65 to 85
PONTCHARTRAIN	64/69/74/79	79/84/89/94	140 to 225	200 to 285
SHORECREST	25 to 34	27 to 38 (D) 33 to 44 (T) 50 (DD)	65 to 90	_

	Hotels in W	indsor, Ontario, Canada	(All Rates in Canad	dian Dollars)
HOLIDAY INN	49	59 (D) 63.50 (T)	_	_
NATIONAL TRAVELLER	36	41 (D)	—	
RICHELIEU	46 to 52	52 to 60 (D)		
VISCOUNT*	40/42	42/44 (D) 46/48 (T) 50 to 62 (DD)	_	_

* These hotels require a one night's room deposit.



FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY 1981 ANNUAL MEETING AND PAINT INDUSTRIES' SHOW COBO HALL, DETROIT, MICHIGAN OCTOBER 28, 29, 30

(Wednesday, Thursday, Friday)

MAIL Coatings Federation Housing Bureau TO: 100 Renaissance Center, Suite 1950 Detroit, MI 48243

APPLICATION FOR ACCOMMODATIONS

Please indicate below the type of accommodations requested and your choice of hotels. Room reservations cannot be guaranteed unless this form is received by October 1. All reservation requests must be in writing and processed through the Housing Bureau. Phone requests will not be accepted.

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

CH	OICE OF HOTELS:
	(see below)
1st	
2nd	
3rd	
4th	

Hotel assignments will be made in the order received, and in accordance with availability. The Housing Bureau will send you an acknowledgment which will state the hotel to which you have been assigned. The confirmation of your reservation will come to you directly from the hotel, to whom you must direct all of your inquiries.

Note: Reservations for the Detroit Plaza will be accepted for arrival beginning Wednesday, October 28, only. Any requests for Plaza accommodations prior to Wednesday will be assigned to another hotel.

Please fill in the names and addresses of all occupants of the rooms you have reserved. (Bracket those rooming together.) Incomplete information will delay assignment of rooms. Type additional names on reverse side of this sheet. Please give accurate arrival and departure dates.

Type of			Dat	tes of
Room	Name	Address	Arrival	Departure

SEND CONFIRMATION	FOR ALL RESERVATIONS TO	1	Γ	IAL					
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CITY	STATE	ZIP	Convent	FOLLOW	sing Bure	tel/Motel	el/Motel	lest	sing Bure
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NUMBER 93J

JULY 1981

Societies for Coarries

ederation

REDERATION Newsletter

AD HOC COMMITTEE ON PAINT RESEARCH INSTITUTE ISSUES PRELIMINARY REPORT TO FSCT BOARD

In accordance with a directive from the Federation Board of Directors to undertake a comprehensive, in-depth study of the Paint Research Institute, members of the Ad Hoc Committee on PRI visited 23 Societies (3 surveyed by mail) for discussions on the research needs of the coatings industry generally, the perceived current role of the Paint Research Institute in addressing that need, and suggestions and recommendations for improving efforts in that regard.

Committee members are all Past-Presidents of the Federation. They are: James A. McCormick--Chairman (Baltimore); Newell P. Beckwith (Detroit); Neil S. Estrada (Golden Gate); Milton A. Glaser (Chicago); and John J. Oates (New York).

A standardized questionnaire was developed to uniformly survey areas of discussion with each Society. In addition, comments were solicited on any and all aspects of the PRI program.

The committee submitted a preliminary report to the Board meeting of May 15, in Denver, emphasizing that the <u>report attempts to summarize faithfully the consensus</u> of Society views on PRI, and is not to be interpreted as representing, at this time, final conclusions and recommendations of the Ad Hoc Committee.

Tentative Conclusions

The following are the tentative conclusions which represent the consensus response of those participating:

The overwhelming majority of the members of the Societies contacted:

- a. Know very little about PRI and how it operates;
- Are unhappy about PRI projects, the reporting of these projects to Federation members, and the practical applications of the research results to the needs of the medium-sized and smaller companies in our industry;
- c. Strongly criticized the poor management, poor communications and poor public relations emanating from both the Federation and PRI, on PRI programs, progress, etc.;
- d. Believe that future Federation research activities should emphasize participation of local Societies and members - from project selection, assignment at nearby universities, monitoring, and even financial support for research projects carried out in their area;

- e. Expressed unanimous willingness to support Federation research, even to significantly increased level of funding, provided membership was convinced of the practicality of the work, that projects were well managed, and reports were understandable;
- f. Expressed strong reluctance to solicit or accept government funding;
- g. Would like to hear about the progress of PRI projects on a regular basis, and in language that the average paint chemist can understand.

Majority of Society members were in favor of changing current PRI objectives from "basic" to "practical."

More input is being sought from others in the industry who can identify ways in which the research effort can be improved. This includes, among others, PRI Trustees (past and present), Technical Directors of various coatings firms, researchers who have worked on PRI grants, as well as a study of the programs of overseas coatings research groups and those serving other industries -- all designed to develop a data base resource to draw upon for further recommendations.

A subsequent report will be submitted to the Board for its meetings on October 27 in Detroit.

(More complete information on the findings of the Committee and related discussions will appear in the report on the Spring Meeting of the Board of Directors, to be published in the August issue of JCT.)

CLARKE BOYCE, OF TORONTO; TERRYL JOHNSON, OF KANSAS CITY, ARE NOMINATED TO FEDERATION OFFICER POSITIONS

A. Clarke Boyce, of Nacan Products Ltd., Toronto, Canada, has been nominated to be President-Elect of the Federation. Mr. Boyce, currently Treasurer, is a Past-President of the Toronto Society and has served as Society Representative to the Federation Board of Directors.

Terryl F. Johnson, of Cook Paint and Varnish Co., Kansas City, MO, has been nominated to the post of Treasurer. He is a Past-President of both the Kansas City Society and Kansas City PCA and has been KC Society Representative to the Federation Board for eight years.

The Nominating Committee also submitted the names of candidates for Board of Directors/Executive Committee positions:

Board of Directors as Members-at-Large--(two-year term for each): Stanley LeSota, of Rohm and Haas Co., Spring House, PA. He is the recipient of the 1979 George Baugh Heckel Award for his years of service to the Federation as Chairman of the Definitions Committee which culminated in the publication of the <u>Paint/Coatings</u> <u>Dictionary</u>. He is a Past-President of the Philadelphia Society.....and...... Helen Skowronska, Consultant, Cleveland, OH. She has been Chairman of the Federation's Technical Information Systems Committee for 10 years and is a member of the Editorial Review Board of the JCT. Ms. Skowronska is a Past-President of the Cleveland Society. Board of Directors as Past-President Member--(two-year term): Elder C. Larson, of Shell Development Co., Houston, TX. He served as President of the Federation in 1979-80. He is currently Chairman of the Federation Finance Committee.

<u>Society Representative to the Executive Committee--(three-year term)</u>: Horace S. Philipp, of Sherwin-Williams Co. of Canada Ltd., Montreal, Canada. A Past-Chairman of the Federation's Membership and American Paint Journal Awards Committees, Mr. Philipp is currently Chairman of the Program Awards Committee. He is a Past-President of the Montreal Society and has been its Society Representative since 1975.

Voting will take place on October 27 during the 1981 Federation Annual Meeting in Detroit.

DR. HERBERT L. FENBURR, OF CDIC SOCIETY, ELECTED HONORARY MEMBER OF FEDERATION

The Federation is pleased to announce that Dr. Herbert L. Fenburr, of Columbus, Ohio, was elected to Honorary Membership in the Federation during its Board of Directors meeting on May 15, 1981.

Dr. Fenburr, active in the Federation for more than 30 years, served as its President in 1967-68 and as a member of the Board of Directors from 1964-75. He also served as Chairman of the Finance, Investment, and Program Committees. He was President of the Paint Research Institute from 1970-73 and was a Trustee of PRI from 1969-76.

Dr. Fenburr received the Federation's George Baugh Heckel Award in 1976 for his many years of outstanding service to the Federation and the industry.

A Fast-President of the C-D-I-C Society, Dr. Fenburr retired in 1976 from Hanna Chemical Coatings Co., Columbus, Ohio, after more than 38 years of service with the firm.

He received the Ph.D. Degree in Chemical Engineering from Ohio State University from which he was awarded the Distinguished Alumni Award in 1967. He was also the recipient of the Man of the Year Award from Temple Israel in 1959.

Dr. Fenburr is a member of the American Chemical Society, the American Institute of Chemists, the New York Academy of Science, and the National Society for Professional Engineers. He is a Registered Professional Engineer in Ohio.

ACTION GIVEN PROPOSED AMENDMENTS TO STANDING RULES AND BY-LAWS BY FEDERATION BOARD AT MAY MEETING

The following are quick summaries (\underline{only}) of the actions of the Federation Board with regard to the Proposed Amendments to the By-Laws and Standing Rules presented at their meeting of May 15, 1981. Please consult the July and August JCTs for the full text of the proposed amendments.

<u>Adopted (Standing Rules)</u>--Changes in the boundaries of the Southern and Dallas Societies, transferring the State of Arkansas to Southern jurisdiction; and changes in the boundaries of the Baltimore and Piedmont Societies, transferring an additional portion of the State of Virginia to Baltimore jurisdiction.

First Reading (By-Laws)--A change to Article VI, which specifies that the Federation Board holds two meetings yearly.

Tabled (By-Laws)--Because of the continuing review of PRI activities/organization by the Ad Hoc Committee on PRI, this change (specifying that the Federation President annually nominates the Trustees of PRI) was tabled.

<u>Defeated (By-Laws)</u>--A proposal which would extend voting and office-holding privileges to all Federation members, regardless of class of membership.

WERNER BLANK, OF AMERICAN CYANAMID, WILL PRESENT MATTIELLO LECTURE AT ANNUAL MEETING IN DETROIT

Werner J. Blank, Manager of Resin Products at the Stamford, Conn. Research Center of American Cyanamid Co., will present the 1981 Joseph J. Mattiello Memorial Lecture at the Federation's Annual Meeting, October 28-30, at Cobo Hall in Detroit. Mr. Blank will speak on "Amino Resins in High Solids Coatings" at the morning session, October 30.

160 EXHIBITOR COMPANIES SIGN UP FOR 1981 PAINT INDUSTRIES' SHOW

One hundred and sixty exhibitor companies (highest ever) have contracted for exhibit space in the 1981 Paint Industries' Show at Cobo Hall in Detroit, October 28-30. Another record is the exhibit space they will occupy: nearly 38,000 net paid square feet.

COMING EVENTS

Sept. 23-24...Montreal and Toronto Societies Joint Symposium on "Coatings Directions for the 80's."
Oct. 28-30....Federation Annual Meeting and Paint Show. Cobo Hall, Detroit.
Mar. 10-12....Southern Society. Annual Meeting. Savannah, GA.
Mar. 23-24....Cleveland Society, Annual seminar on "Advances in Coatings Technology.". Baldwin-Wallace College, Berea, OH.
Apr. 3.....Baltimore Society. 50th anniversary celebration.
Apr. 22-24....Southwestern Paint Convention of the Dallas and Houston Societies. Shamrock Hilton Hotel, Houston.
Apr. 29-30....Federation Spring Meetings. Society Officers on 29th; Board of Directors on 30th. Boston.
May 6-8.....Pacific Northwest Society. Coatings & Ink Expo. Boxborough, MA.

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Annual Meeting Papers in Detroit Will Focus On Theme of "Challenge, Change, and Opportunity"

Three days of technical sessions keyed to the theme, "Challenge, Change, and Opportunity," will highlight the 1981 Federation Annual Meeting at Detroit's Cobo Hall, October 28-30. Program Committee Chairman Thomas J. Miranda, of Whirlpool Corp., has announced that papers are being developed on a wide variety of subjects of interest to coatings personnel.

General aspects of the theme topic will be addressed in extended sessions each day. On Wednesday, October 28, the program will feature "Innovation in Coatings," on Thursday, the focus will be on "Raw Materials to Finished Product," and on Friday, "Coatings Failure—\$70 Billion Challenge and Opportunity" will be highlighted. Presentations at these sessions will include discussion of such topics as renewable resources, high solids, analytical techniques, waste disposal, and causes of failure of trade sales and industrial coatings.

Other scheduled program features include:

- Keynote Address
- Mattiello Lecture, "Amino Resins in High Solids Coatings," by Werner J. Blank, of American Cyanamid Co., to be presented on Friday, October 30 [see May issue of JCT— Ed.]
- Paint Research Institute Seminar
- Manufacturing and Educational Committee Seminars
- Roon Awards Competition papers
- Constituent Society papers
- Papers presented on behalf of affiliated overseas coatings organizations

Concurrent sessions will be held throughout the meeting, but papers will be scheduled to avoid conflicting presentations.

Paint Show

To be held concurrently with the Annual Meeting, the 1981 Paint Show will be the largest in history. A total of 161 supplier companies have reserved booth space for displaying their products.

The Paint Show is the only national exhibit of raw materials and equipment

used in the manufacture of paints and related coatings, and participating firms will have their top technical personnel on hand to discuss the latest developments.

Show hours will be 12:00 to 5:30 pm on Wednesday, October 28; 9:30 am to 5:00 pm on Thursday, October 29; and 9:30 am to 4:00 pm of Friday, October 30.

Headquarters Hotel

The Detroit Plaza will be headquarters hotel, and the Detroit Cadillac will be coheadquarters. Blocks of rooms have also been reserved at other downtown hotels convenient to Cobo Hall.

Room Reservations

All requests for rooms and suites must be on the official housing form furnished by the Federation. Housing will be processed by the Detroit Convention & Visitors Bureau, who will accept only those reservations which are on the official form.

Housing forms have been mailed to all Federation members, and a form is included in this issue (see pages 14–15). Additional forms are available from the Federation headquarters office.

Registration Fees

Regular "on-site" registration fees will be \$45 for Federation members and \$60 for non-members. Advance registration will be available for \$40 for members and \$55 for non-members. Fee for spouses' activities will be \$30 on-site and \$25 in advance.

Once again there will be a special registration fee of \$20 each for retired members and their spouses.

Registration forms are included in this issue (see pages 12-13), and will also be mailed to all members of the Federation in August.

Luncheon

The Federation Luncheon will be held on Friday, October 30, at Cobo Hall.

Presentation will be made to the recipients of the George Baugh Heckel

Official Housing Form — pages 14-15 Advance Registration Form — page 12 Advance Spouses' Registration Form — page 13 Award (outstanding individual who has contributed to the advancement of the Federation) and the Flynn Awards (firms judged to have the best exhibit booths in the 1981 Paint Industries' Show).

A celebrity guest speaker will be featured.

Spouses' Program

A schedule of activities has been planned each day for spouses attending the Annual Meeting, and a Hospitality Room will be maintained at both the Detroit Plaza and Detroit Cadillac hotels.

Included in the spouses' registration fee will be a get-acquainted social on Wednesday afternoon, continental breakfasts on Thursday and Friday in the Hospitality Rooms, and a tour (including lunch) on Thursday.

NPCA Meets Same Week

The National Paint and Coatings Association will hold its Annual Meeting on October 26–28 at the Detroit Plaza Hotel.

The back-to-back scheduling of Association and Federation events provides coatings industry personnel with a full week of programming.

Program Committee

Assisting Chairman Miranda on the Program Steering Committee are: John C. Ballard (Vice-Chairman), of Kurfees Coatings, Inc., Louisville, Ky.; Darlene Brezinski, of DeSoto, Inc., Des Plaines, Ill.; Percy E. Pierce, of PPG Industries, Inc., Allison Park, Pa.; Peter Hiscocks, of Canadian Industries, Ltd., Toronto, Canada; Theodore Provder, of Glidden Coatings & Resins Div., SCM Corp., Strongsville, Ohio; and Walter Stuecken, of Group, Inc., Troy, Mich.

Meetings Committee

Members of the Detroit Society are serving on the Meetings Committee under General Chairman Jose G. Benavides, of Ford Motor Co. Chairing the various subcommittees are: Information Services—Bohdan (Dan) Melnyk, of Chrysler Corp.; Program Operations— Taki Anagnostou, of Wyandotte Paint Products, Inc.; Publicity—Jack Dentler, of Pfizer, Inc., MPM Div.; Luncheon— Fred F. Boehle, of Boehle Chemicals, Inc.; Society President—Walter Stuecken, of Grow Group, Inc.

Co-chairing the Spouses' Activities Committee are Mrs. Fred (Rosemary) Boehle, Mrs. Walter (Lorraine) Stuecken, and Mrs. Jose (Lorraine) Benavides. At a time when wax looks like it's waning, we're expanding our tank car fleet over 30% – to get you all the hard, high-melting-point BARECO* Microcrystalline Wax you need. We're committed to wax and polymer manufacturing. We're here to stay, and spending millions to grow. Millions for more tank cars, new plant construction, increased production capability, expanded research and development facilities, and expanded technical services. And, because we can rely on our long-established rawmaterials sources, you can rely on us for unmatched delivery. Order Bareco. We're with you for the long haul.



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Action Given to Proposed Amendments to Federation By-Laws And Standing Rules By Board of Directors on May 15, 1981

This report summarizes the actions of the Federation Board of Directors with regard to the Proposed Amendments to the By-Laws and Standing Rules presented at their meeting of May 15, 1981.

ADOPTED

The following amendments to the Standing Rules (Article SR I-Constituent Societies) were adopted.

Article SR I—Constituent Societies

WHEREAS the Southern Society has requested that the State of Arkansas be included within its boundaries and WHEREAS the Dallas Society has agreed to transfer the State of Arkansas from within its boundaries to the boundaries of the Southern Society, be it

RESOLVED that Standing Rules Article SR I, Section B, be revised as follows:

"Dallas Society—That part of the States of Texas and Louisiana lying north of the 31st parallel, plus the entire State of Oklahoma."

"Southern Society—All of the following States: Arkansas, South Carolina, Georgia, Florida, Tennessee, Alabama, Mississippi, and all of Louisiana east of the Mississippi River and south of the 31st parallel."

WHEREAS the Baltimore Society has requested that additional territory in the State of Virginia be included in its boundaries and

WHEREAS the Piedmont Society has agreed to transfer this territory from within its boundaries to the boundaries of the Baltimore Society, be it

RESOLVED that Standing Rules Article SR I, Section B, be revised as follows:

"Baltimore Society—The State of Maryland, District of Columbia, and that portion of the state of Virginia east of a north-south line through Roanoke and north of a line from the northeast corner of Roanoke to a point defined by the junction of the Virginia & North Carolina borders at the Atlantic Ocean."

"Piedmont Society—All of the State of North Carolina, plus that part of the State of Virginia west of a north-south line through Roanoke and south of a line from the northwest corner of Roanoke to a point defined by the junction of the Virginia & North Carolina borders at the Atlantic Ocean."

* * * * * *

GIVEN FIRST READING

The following amendment to the By-Laws (Article VI— Annual Meeting) was given first reading. It will be presented for adoption at the Board of Directors meeting of October 27, 1981.

Article VI—Annual Meeting

WHEREAS By-Laws Article III, Section B, Sub Paragraph (1) k specifies that at least two Board meetings be held each year and

WHEREAS By-Laws Article VI deals with only the Annual Meeting, be it

RESOLVED that By-Laws Article VI be amended as follows:

"ARTICLE VI-MEETINGS"

"A. Time, Place, and Program

(1) The Spring Meeting of the Federation Board of Directors shall be held in the second quarter of the year, the exact time and place to be determined by the Board of Directors. This meeting shall include the presentation of reports by Officers and Committees, and a business session.

(2) The Annual Meeting of the Federation shall be held in the last quarter of the year, the exact time and place to be determined by the Board of Directors. The Annual Meeting shall include: the presentation of technical papers and seminars; the Paint Industries' Show; the Fall Board of Directors meeting, at which shall be presented reports by Officers and Committees; the presentation of annual awards; the induction of new officers; and a business session."

"B. Resolution From the Floor

Any Active Member may propose a resolution addressed to the Federation Board of Directors from the floor during the business sessions of the Federation Board."

TABLED

Because of the continuing review of PRI activities/ organization by the Federation Ad Hoc Committee on PRI, the following amendment to the By-Laws (Article III— Organization) was tabled. (It had received first reading at the October 28, 1980 meeting).

Article III—Organization

WHEREAS an important annual duty of the President is to nominate the Trustees of the Paint Research Institute for election by its Members, who are the Federation Board of Directors, and

WHEREAS this duty is not currently included in the Federation By-Laws, be it

RESOLVED that By-Laws Article III, Section C, Paragraph (1) be amended by adding new sub-section e., as follows:

"e. Nominate annually the Trustees of the Paint Research Institute for election by its Members (Federation Board of Directors."

.

DEFEATED

The following amendment to the By-Laws and Standing Rules (re equal voting and office-holding privileges for all members) was presented for first reading and was defeated. The vote was 17 against, 15 for. (24 is required for approval).

Amendment to By-Laws and Standing Rules Re Equal Voting and Office-Holding Privileges

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

RESOLVED that the Federation By-Laws and Standing Rules be amended wherever applicable in order to extend voting and office-holding privileges to all members, regardless of class of membership.

Clarke Boyce, of Toronto; Terryl Johnson, of Kansas City, Are Nominated to Federation Officer Positions

A. Clarke Boyce, of Nacan Products Ltd., Toronto, Canada, has been nominated to be President-Elect of the Federation of Societies for Coatings Technology. Mr. Boyce, currently Treasurer, is a Past-President of the Toronto Society and has served as Society Representative to the Federation Board of Directors.

Terryl F. Johnson, of Cook Paint and Varnish Co., Kansas City, MO, has been nominated to the post of Treasurer. He is a Past-President of both the Kansas City Society and Kansas City PCA and served as Society Representative to the Federation Board of Directors. He is a past member of the Federation Executive Committee and current chairman of the MMA Awards Committee. Mr. Johnson has been with Cook since 1947.

The Nominating Committee also submitted the names of candidates for Board of Directors/Executive Committee positions:

Board of Directors as Members-at-



elected):

Society.



T.F. Johnson

Large-(two-year term; two to be

Stanley LeSota, of Rohm and Haas

Co., Spring House, PA. He is the

recipient of the 1979 George Baugh

Heckel Award for his years of service to

the Federation as Chairman of the

Definitions Committee which culmi-

nated in the publication of the

Paint/Coatings Dictionary. He is a

Past-President of the Philadelphia





S. LeSota

H. Skowronska

Helen Skowronska, Consultant, Cleveland, OH. She has been Chairman of the Federation's Technical Information Systems Committee for 10 years and is a member of the Editorial Review Board of the Journal of Coatings Technology. Ms. Skowronska is a Past-President of the Cleveland Society.

Board of Directors as Past-President Member-(two-year term; one to be elected):

Elder C. Larson, of Shell Development Co., Houston, TX. He served as President of the Federation in 1979-80. He is currently Chairman of the Federation Finance Committee.



E.C. Larson

Society Representative to the Executive Committee-(three-year term; one to be elected):



Horace S. Philipp, of Sherwin-Williams Co. of Canada Ltd., Montreal, Quebec. A Past-Chairman of the Federation's Membership and American Paint Journal Awards Committees, Mr. Philipp is currently Chairman of the Program

Awards Committee for the 1981 Annual Meeting. He is a Past-President of the Montreal Society and has been its Society Representative since 1975.

Voting will take place on October 27 during the 1981 Federation Annual Meeting in Detroit, MI.

TECHNICAL COMPUTER APPLICATIONS IN THE COATINGS INDUSTRY A Bibliography

JOURNAL OF COATINGS TECHNOLOGY Reprint

This 11-page bibliography consists of references grouped into the following sections:

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PROCEEDINGS/NUMBER 145

Mechanism of Corrosion Inhibition With Special Attention To Inhibitors in Organic Coatings

Henry Leidheiser, Jr. Lehigh University*

Proposed mechanisms by which inorganic and organic substances provide corrosion inhibition are reviewed. Special attention is paid to corrosion inhibition provided by lead compounds and chromates in organic coatings. Six requirements are described for an inhibitor to be used in organic coatings. Five programs of research are proposed that might assist in better understanding the mechanism of action of inhibitors in coatings.

INTRODUCTION

Many of the important metals of commerce, such as iron (steel), aluminum, and zinc (as galvanized steel), owe their importance to the fact that their tendency to corrode can be controlled by organic coatings. The satisfactory performance of the organic coating, in turn, depends on the fact that corrosion inhibitors in the coating, or at the interface between the coating and the metal substrate, permit the metal to resist the attacks by water, oxygen, and ions that penetrate through the coating to the metal.

It is the purpose of this article to accomplish the following:

(1) To define inhibitors;

(2) To discuss proposed mechanisms by which inhibitors operate;

(3) To outline the requirements for an ideal inhibitor for use in organic coatings; and

(4) To suggest specific research programs that might be carried out to improve the understanding of the mechanism of corrosion inhibitors in coatings.

Corrosion inhibitor research falls broadly into two categories, those studies concerned with corrosion in very acidic solutions and those concerned with corrosion in slightly acid, neutral, and slightly alkaline media. Strong acidic environments are used in the pickling of steel and corrosion inhibition is important to permit removal of the scale without severe attack of the steel. Some petroleum wells also operate under conditions where metallic structures are exposed to acidic environments. Painted

^{*}Center for Surface and Coatings Research, Bethlehem, PA 18015.

PRI Director's Preface

Dr. Leidheiser wrote a down-to-earth article on corrosion inhibitors, and our impression is that it is both practical and understandable. However, we have heard enough background noise concerning papers in JCT that are primarily theoretical that a few words of explanation are in order.

The PRI Trustees commissioned this work and assigned the rather restricted title so that the scope would hit a target familiar to any coatings manufacturer faced with the ultimate loss of chromate inhibitors. Look upon this survey as our opening shot in a revitalization of a research program in corrosion control.

For further background, see JOURNAL OF COAT-INGS TECHNOLOGY, 45, No. 584, 61-64 (1973) which recognizes four general areas of research as conceived by a panel of experts inside the industry after confronting a group of outside experts in related academic fields. It amused Dr. Leidheiser that explicit mention of the mechanism of inhibition was not made at that time. The closest we can come is to include this report in the category "Interference With the Chloride-Induced Corrosion Mechanism."

Other categories of research which PRI wishes to support are:

- (1) Barrier Properties of Coatings on Metals.
- (2) Bonding of Freshly-Exposed Iron to Various Species.
- (3) Localization of Anodic Areas.

Whether or not these categories explicitly encompass corrosion inhibitors, the name of the game practiced by coatings companies is to find inhibitors. Basic research should be guided by concepts as handled in the latter part of Dr. Leidheiser's survey, and to this end we invite research proposals from interested parties. Federation members who read this account can do one of two things: (1) send us practical ideas to be converted into action plans by us, or (2) contact a potential bidder of your acquaintance and ask for a preproposal to be submitted to us.

> RAYMOND R. MYERS Kent State University Kent, Ohio 44242

metals are not generally exposed to highly acid conditions and, thus, the research of pertinence to coatings involves inhibitors that function in the mildly acidic to mildly alkaline region, i.e., pH 4 to 10. Corrosion reactions under a coating often lead to pH's outside this range, but the extreme pH values only occur after considerable corrosion has taken place.

BASIC CORROSION THEORY AS APPLIED TO ORGANIC COATINGS

Corrosion reactions will only occur beneath an organic coating when the following conditions are met: (1) an aqueous phase exists, (2) ions are present, and (3) a conductive pathway exists between the anodic and cathodic areas. Under many service conditions, the cathodic reaction is $H_2O + 1/2O_2 + 2e^- = 2OH^-$ and, thus, oxygen is also necessary. However, cathodic reactions not requiring oxygen can serve as the electronconsuming reaction in some circumstances. If the above conditions are met, corrosion does not necessarily occur because the metal surface may be protected against either or both the anodic and cathodic reactions by the formation of an unreactive interface between the substrate and the coating. It is the task of the coatings scientist to understand those conditions where corrosion does not occur even though corrosion might be expected.

The anodic reaction of importance to organic coatings is the ionization of the metal, $Me - ne^- = Me^{+n}$. The kinetics of this reaction are generally studied by determining the rate of the reaction as a function of the applied potential. Active metals dissolve according to the relationship $E = \beta \log i + \text{constant}$, where E is the electrode potential and i is the current. Many of the important metals of commerce, and iron in particular, exhibit a steady-state relationship between electrode potential and current in some environments such as that shown in *Figure* 1. In the potential region between B and C, the very low and the metal is said to be passive. Additives to the solution that result in a corrosion potential between B and C inactivate the metal for dissolution.

The mechanism of the cathodic reaction can be studied in the same way as the anodic reaction by applying a potential and noting the current that flows as a function of potential. In the case of the important cathodic reaction, $H_2O + 1/2O_2 + 2e^- = 2OH^-$, the rate is controlled, when oxygen is present in excess, by the catalytic activity of the metal, or oxided metal, for the reaction. Under quiescent conditions, the rate of the reaction may be controlled by the rate at which oxygen reaches the metal surface.

In the absence of an applied potential, as for a normal coating in service, the rate of the overall corrosion reaction at the metal/coating interface may be controlled by (a) the anodic reaction, (b) the cathodic reaction, or (c) the resistance of the conductive path between the anodic and cathodic regions.

Some electrochemical techniques for studying the kinetics of corrosion beneath organic coatings and through defects in the coating have been described previously.¹⁻⁶ These techniques provide useful informa-



Figure 1—Classic anodic polarization curve shown by a metal exhibiting passivity. This shape of curve is obtained under potentiostatic conditions when sufficient time is allowed for steady-state current conditions to be obtained. The section to point B is known as the active region; the section from B to C is known as the passive region; and the section beyond point C is known as the transpassive region

tion in understanding the rate of water uptake by a coating, the development of conductive paths in a coating, changes in the anodic/cathodic area ratio as corrosion proceeds, and the identification of the site of coating defects. However, the major shortcoming in the application of these techniques is the absence of data which relate the electrical measurements to the performance of coatings in service. Research in this area is needed.

Limited types of corrosion control may be obtained through the use of coatings that contain high pigment or filler concentrations that reduce the rate of transport of water, oxygen, or ions through the coating. Corrosion control is also possible through the selection of polymers that have good adherence to the substrate and restricted segmental motion at and near the coating/substrate interface as pointed out by Kumins.⁷

DEFINITION OF CORROSION INHIBITORS

Inhibitors are specific chemical agents naturally present in the environment, or purposely added to the environment, that significantly reduce the corrosion rate that is observed in the absence of the inhibitor. For the purposes of this article, a substance that significantly reduces the corrosion rate is defined as one that reduces the corrosion rate by at least 50%.

The term "inhibitor" describes those chemical agents that reduce the corrosion rate by virtue of interacting with the metal surface and, thereby, reducing its corrosion tendency. This reduction is accomplished by chemical products on the metal surface which are effective at thicknesses of less than 10 nm. The inhibitor may, or may not, be an integral part of the chemical product on the metal surface. The term "passivator" is limited to those inhibitors that perform this function by promoting the



Figure 2—Anodic polarization curve obtained with iron in 0.01N dichromate solution at pH 3.9. Surface area of anode is 0.32 cm². Curve obtained under potentiodynamic condition, i.e., steadystate conditions not achieved as in *Figure* 1. See Reference 12

development of a protective film on the metal surface which includes the substrate metal as a component. The most common film is an oxide. Passivators are, thus, a class of inhibitors which perform their function in a very specific way. To make a distinction between inhibitors and passivators requires some knowledge of the mechanism by which corrosion reduction is achieved. We prefer to use the more general term "inhibitor" and avoid the use of the term "passivator". Corrosion inhibitors include many organic compounds, inorganic substances, and metallic cations. Inhibitors which function by oxide film formation include such materials as nitrates, nitrites, chromates, molybdates and other oxidizing agents. Examples of the activity of these substances in reducing corrosion rates will be given in this report.

The restrictive definition outlined previously eliminates corrosion protective materials that function by removal of a specific aggressive environmental constituent. For example, a substance such as hydrazine which functions by removing oxygen from a closed system will not be considered an inhibitor. A phosphate used in a phosphating pretreatment that develops a phosphate coating thicker than 10 nm on the metal surface will not be considered an inhibitor. This cut-off point is purely arbitrary. It is an effort to separate inhibition from the simple barrier-type protection obtained with a coating.

MECHANISM OF OPERATION OF INHIBITORS

Four major classes of inhibitors will be discussed: oxidizing inhibitors with chromate as the example; organic compounds; metallic cations; and nonoxidizing inorganic and organic salts.



Figure 3—Thickness of oxide film formed on iron as a function of time of exposure to 0.01N dichromate solution at pH 3.9. Note: Actual film thickness is a function of the optical parameters selected for determining film thickness, so there is a measure of uncertainty in absolute values of film thickness. Data obtained from Reference 12

Mechanism of Corrosion Inhibition By Oxidizing Inhibitors

Oxidizing inhibitors include such materials as chromates, nitrates, nitrites, hydrogen peroxide, and, in limited cases, even oxygen. These materials all function by the formation of a thin oxide coating on the surface, a major cation of which is the substrate metal. Thin and protective oxide films can also be formed by anodic polarization of metals in environments containing anions such as sulfate, borate, oxalate, tartrate, etc.⁸ Anodicallyformed oxides will not be considered in this paper.

The most widely used oxidizing inhibitor is chromate. Commercial metals are often exposed to chromate solutions before shipment in order to avoid corrosion during transit or during storage. Phosphate pretreatments for corrosion protection are often followed by a chromate treatment. Metals are often chromated before the application of an organic coating and chromates are used in coatings to provide long-term corrosion protection. This wide use of chromate, and the need to design inhibitors to substitute for chromate because of environmental restraints, led to a decision to concentrate the discussion on a single oxidizing inhibitor, namely, chromate.

There is a consensus that chromate is an effective corrosion inhibitor for iron, zinc, aluminum, and many other metals as well. In general, chromates are effective in aerated and deaerated solutions and in acid, neutral, and alkaline environments. They are one of the most versatile inhibitors. However, there is a decided lack of consensus with respect to views on the mechanism by which chromate provides the inhibition.

Iron, when anodically polarized in deaerated chromate solutions, exhibits a potentiodynamic polarization curve such as that shown in *Figure* 2. The shape of the curve is consistent with the presence of a film on the iron surface. The current in the plateau region is of the order of $1 \text{ amp/m}^2 (10^{-4} \text{ amp/cm}^2)$ with no dependence on pH in the range from 3.9 to 12. Under steady-state

Table 1—⁵¹Cr Remaining on Surface of Iron after Immersion In Chromate Solutions for One to Several Hours

pН	Chromium Remaining on Surface	Reference
1.9	3×10^{16} atoms/cm ²	10
4	1.2×10^{16}	9
Not Given	5.5×10^{15}	11
7.5	5.2×10^{15}	9
9	4×10^{15}	9
11	Not measurable	9

conditions (potential constant rather than changing at a fixed rate), the current may be as low as 10^{-4} amp/m² $(10^{-8} \text{ amp/cm}^2)$. Measurements, using ellipsometry, indicate that there exists a film on the surface of the iron during exposure to the chromate solution, and the film thickness is a function of the time of exposure and the potential to which the iron is polarized. Data are given in Figure 3 which show that the film thickness for an unpolarized specimen is of the order of 4 nm after one hour exposure and the thickness increases with time of exposure. The ellipsometric studies support measurements using radioactive ⁵¹Cr in which iron specimens were dipped in chromate solutions at different pH's and the chromium remaining on the surface was determined after washing the residual fluid from the surface. Data from several authors are summarized in Table 1. Powers and Hackerman⁹ showed that the chromium uptake as a function of pH followed the HCrO4 ion concentration in the equilibria involving HCrO₄, H⁺, CrO₄, and $Cr_2 O_7^{=}$.

The detailed composition of the film on the surface of iron exposed to chromate solutions is uncertain. The radioactivity measurements indicate that chromium is a component of the film and Szklarska-Smialowska and Staehle¹² have concluded, on the basis of a study of the optical parameters of the film, that it is a mixture of iron and chromium hydroxides in the absence of polarization, and that the composition is a function of experimental conditions. When the iron is polarized into the plateau region of *Figure* 2, the surface film appears to be largely Fe₃O₄ with an outer skin of γ -Fe₂O₃.

The many suggestions made as to how chromate functions as an inhibitor for the passivation of iron have been condensed into four. These may be summarized as follows.

Uhlig¹³ believes that passivation of iron is the result of adsorption of oxygen on the surface, with consequent lower reactivity. This mechanism may apply under certain laboratory conditions; but, it certainly does not apply under practical conditions since there is no doubt that a film exists on the surface after chromate treatment, and that it does contain chromium. It is also possible, in some circumstances, that the oxide surface has adsorbed oxygen on it. The suggestion of Uhlig will not be discussed further because it is considered not to have pertinence to painted metals.

A second hypothesis states that during exposure to the chromate solution, the iron reacts to form soluble ferrous ions. These ions react with the chromate in solution to form a film on the surface consisting of a mixture of hydrated ferric and chromic oxides.¹⁴ This proposal was amplified later by stating that the protective value of the oxide is related to the reduced ability of iron ions to diffuse through the film.¹²⁻¹⁵

A modification of the hypothesis outlined above has been proposed by Robertson¹⁶ and further elaborated by Powers and Hackerman.⁹ These workers believe that chromate is adsorbed on the surface and, by direct reaction with iron, forms unhydrated γ -Fe₂O₃ which serves as a better barrier to diffusion than a film of hydrated oxides.

The explanation which is favored by the author is based on the relative solubilities of chromium oxide and the metal oxides of the metals which can be passivated by chromate. *Table* 2 lists nine metals which may be made more resistant to corrosion in mild media by prior exposure to the chromate ion. The second column lists the pH at which the metal ion at 10^{-4} M is in equilibrium with the oxide or the hydrated oxide of the metal. In order to make a proper comparison, the values, with the exception of the more noble metal copper, are those at a similar value of the potential of -0.2 v vs the NHE. This value is not far from the corrosion potential of the metals in a 0.5M NaCl solution.

What this table shows is that the resistance to attack (dissolution) of hydrated chromium oxide at a low pH is much greater than that of the oxides or hydrated oxides of cadmium, iron, lead, cobalt, nickel, zinc, copper, and aluminum. The oxide of chromium has a pH-dependent solubility approximately the same as that for tin oxide. The data shown in *Table* 2 suggest that chromium oxide should be resistant to acids down to a pH of the order of 2. In confirmation of this conclusion, Brasher et al.¹⁷ have noted that pure iron passivated in chromate solution to a pH of this order. At pH 1.6, ion dissolution in chromate solution occurs at a very low but measurable rate.

It is likely that chromate is such an effective inhibitor because it is incorporated in the natural oxide on the surface of the inhibited metal as $Cr(OH)_3$, or Cr_2O_3 , which then protects the underlying metal by a very low solubility. The high solubility of alkali chromate (thus mobility in the aqueous phase) and the reducibility of Cr(VI) to Cr(III) in the presence of a metal immersed in the solution, assure that the $Cr(OH)_3$ phase will be present over the entire surface of the oxide film on the metal.

Low solubility of the chromium oxide, however, cannot be expected to provide permanent protection in the absence of a reservoir of chromate ions. The corrosionresistant lifetime of a chromated metal is limited, and exposure to an aqueous phase over extended periods results in loss of the chromium and the regaining of the normal corrosion rate of the metal in that environment. It is known, however, that chromated metals do have a finite lifetime and that the chromium oxide will provide protection for a longer period than expected on the basis of simple barrier protection. Thus, the coating must have some self-repair properties. The ability to provide additional $Cr(OH)_3$ (or Cr_2O_3) at points of breakdown is a

pH at which Me ⁺ⁿ Ion (10 ⁻⁴ M) Exists in Equilibrium with Oxide or Hydrated Oxide at a Potential of −0.2 v vs. NHE ¹⁸
7.9
7.2
7.2
7.0
6.4
5.7 (at +0.4 v)
2.5
2.1 (for Cr (OH) ₃)
3.7 (for 10^{-6} M)
3.7 (for 10 ⁻⁶ M)

Table 2—Metals Made More Resistant to Corrosion In Mild Media by Prior Exposure to the Chromate Ion

consequence of the presence in the coating of a sufficient amount of the chromate ion such that the anodic part of the corrosion process (in the case of iron), $Fe - 2e^- =$ Fe^{++} , occurs simultaneously with the cathodic reaction $Cr^{+6} + 3e^- = Cr^{+3}$. The trivalent chromium remains in the film as protective oxide.

The inhibiting effect of chromate on the pitting of aluminum has been attributed by Pryor^{19,20} to the preferential adsorption of chromate ions and exclusion of the chloride ion. Recent work by Koudelkova, Augustynski, and Berthou,²¹ using X-ray photoelectron spectroscopy, has shown that chloride ions are incorporated into the surface film on aluminum exposed to mixed chromatechloride solutions, or exposed to chloride solutions after exposure to the chromate solution. These workers found, additionally, that the oxide film on aluminum contained Al(III) oxide, Cr(III) oxide, and Cr(VI) species. These species were present on the aluminum surface independent of whether the aluminum was exposed without an applied potential or if the aluminum was polarized anodically.

It is not generally recognized that oxidizing and nonoxidizing inhibitors in some cases show exceedingly good inhibition of the cathodic reaction: the greatest attention has been paid to effects on the anodic reaction. Szklarska-Smialowska and Mankowski²² have pointed out the cathodic inhibition in the case of solutions of HPO₄⁻, WO_4^{\pm} , As O_4^{\pm} , and Si O_3^{\pm} containing calcium ions. In this case, the inhibition is due to the formation of a thin layer of sparingly soluble calcium salts on the surface of the iron. The layer is claimed to be effective by limiting access of dissolved oxygen to the metal surface. Cathodic reduction of oxygen on platinum electrodes was also observed to be inhibited in similar solutions. Szklarska-Smialowska may have interpreted her work correctly, but our own laboratory investigations indicate that chromated iron shows a reduced catalytic activity in some environments for the reduction of oxygen as compared to an unchromated surface, and the inhibition increases with increase in time of exposure to the chromate solution.²³ Data illustrating this effect are shown in Figure 4.




Additional confirmation of the hypothesis that the oxide formed on iron in chromate solution is a poor catalyst for the oxygen reduction reaction is found in the work of Cartledge,²⁴ who observed the following:

(1) Cathodic polarization of freshly passivated iron at a current density above $10^{-2} \text{ amp/m}^2 (10^{-6} \text{ amp/cm}^2)$ in 0.01M chromate solution at pH 5.4 led to a reduced cathodic current; and

(2) The exchange current density for oxygen reduction on iron is "somewhat higher than 10^{-13} amp/m² (10^{-17} amp/cm²)" in chromate solution. This value is very low compared to typical exchange current densities for hydrogen evolution in HCl or H₂SO₄ solutions.

The above studies suggest that chromate is an effective inhibitor because it has four important characteristics: (1) the chromium oxide formed by the process $Cr^{+6} + 3e^- = Cr^{+3}$ has a low solubility; (2) chromate ions are incorporated in the oxide film on the surface of the inhibited metal and serve as a reservoir to repair defects in the oxide; (3) the oxide formed in the presence of the inhibitor reduces the rate of the anodic reaction; and (4) the oxide formed in the presence of the inhibitor is a poor catalyst for the cathodic reaction, $H_2O +$ $1/2O_2 + 2e^- = 2OH^-$. Ideas on research to confirm or refute these suggestions are summarized in a later section.

Mechanism of Corrosion Inhibition By Organic Compounds

The number of publications dealing with corrosion inhibition by organic compounds is legion. Corrosion inhibition is a regular topic at the international conferences on corrosion and every five years a symposium on corrosion inhibitors is held at the University of Ferrara in Italy. The most recent meeting was held in September 1980: 75 papers appeared in the published proceedings, the great majority of which dealt with organic corrosion inhibitors. The book, "Corrosion Inhibitors", published by NACE,²⁵ contains 25 separate articles, many of which deal with organic inhibitors. Three recent reviews of corrosion inhibition treat organic corrosion inhibitors.²⁶⁻²⁸ Many publications that deal with organic corrosion inhibitors are concerned with effects in acid solutions since an important use of organic inhibitors is as additives to pickling baths, in storage vessels holding acids, and in petroleum recovery from wells where the pH is low. Thus, organic corrosion inhibitors are often utilized where the predominant cathodic reaction is $2H^+ + 2e^- = H_2$, i.e., when the pH is below four.

The mechanism of acidic corrosion inhibition by organic compounds is considered to be primarily by adsorption of the organic compound and insulation of the metal from the environment. Evidence for the presence of the organic compound at the metal surface during corrosion comes from ellipsometry, electrochemical measurements, solution depletion, radiotracer measurements, spectroscopic measurements, and studies of the double layer. Circumstantial evidence comes from corrosion inhibition data which are interpretable in terms of adsorption isotherms.

Riggs²⁹ gives the structure of 207 organic compounds that are used as corrosion inhibitors. These compounds all have the common feature that they are polar in nature and contain an active group capable of strong bonding to a metal surface. Typical groups include acetylenic bond; primary, secondary, and tertiary amines; ether; thioether; aldehyde; carboxyl; nitrogen in a ring; sulfur in a ring; hydroxy; thiol; sulfoxide; and phosphonium; as well as compounds containing arsenic or selenium. Much research has been done on homologous series of compounds or compounds containing a single active group incorporated into molecules in a different way. Generalizations are drawn on the basis of polarity, molecular size, geometry of the molecule, multiple adsorption sites in the molecule, geometrical configuration on the metal surface, effects on the double layer, etc. These generalizations are often interesting from a scientific point of view, but less interesting from a practical point of view since the ability to use a specific inhibitor under service conditions is generally limited by cost, solubility, resistance to deterioration, properties such as odor and toxicity, and possible deleterious effect on the process in which the liquid is being utilized.

MECHANISM OF CORROSION INHIBITION



Figure 5—The rate of cathodic delamination of 10µm thick polybutadiene coatings on galvanized steel as a function of prior exposure to 0.1M CoCl₂ solution. Note that preexposure to the CoCl₂ solution reduces the rate of cathodic delamination. Codes by each curve represent particular manufactured lots of galvanized steel

Corrosion potential and corrosion rate measurements in the presence and absence of the inhibitor are the criteria used to determine whether the inhibitor affects primarily the anodic or cathodic half reactions or affects both to approximately an equal extent. It is generally true that organic inhibitors affect both half reactions, but not necessarily to the same extent. These electrochemical measurements are supportive of the concept that organic compounds function primarily by adsorption with consequent lowering of the metal area available to the aqueous solution.

Mechanism of Corrosion Inhibition By Metallic Cations

A recent review of metallic cations as corrosion reduction agents³⁰ outlines 11 means by which the action occurs. These include: (a) participation in the cathodic reaction. (b) substitution of another reaction for the anodic corrosion reaction, (c) reduction of a corrosionpromoting species, (d) control of the pH of the medium, (e) catalysis of polymer formation, and six mechanisms which involve inclusion of the cation, or the reduced metal atom, in a coating on the surface of the corroding metal, (f) effect on the cathodic reaction, (g) change in morphology of corrosion product or corroding metal, (h) change in protective nature of oxide on the surface, (i) formation of an insoluble barrier layer at the metal surface, (j) formation of intermetallic compounds, and (k) adsorption of cations or metal atoms. Only the latter six mechanisms fit the restrictive definition of an inhibitor used herein. Reference 30 should be consulted for a more complete survey of corrosion inhibition by metallic cations. Remarks that follow are limited to corrosion inhibition by three cations that have importance in coatings science and technology, namely, cobalt, nickel and lead.

The predominant cathodic reaction in aerated, neutral aqueous solutions is $H_2O + 1/2O_2 + 2e^- = 2OH^-$. Since the solution is aerated, the metal is generally covered with a thin oxide or hydrated oxide film. In the case of zinc under laboratory conditions, this film is 10 nm in thick-

ness.³¹ The cathodic reaction, thus, must take place on the oxided metal, and the catalytic properties of this oxide control the rate of the cathodic reaction under certain circumstances. For example, the rate of the cathodic reaction on aluminum in aerated 0.5M NaCl solution is approximately 1/50 the rate of zinc.³² An outstanding example of the inhibition of the cathodic reaction in aerated NaCl solution is the effect of cobalt and nickel on the cathodic behavior of zinc.33 Small amounts of these metals decrease the cathodic current at potentials slightly negative of the corrosion potential and decrease the corrosion rate significantly. It has been proposed^{34,35} that the inhibition is a consequence of incorporation of small amounts of cobalt or nickel in the oxide on zinc which, in turn, changes the catalytic activity of the surface for the reaction, $H_2O + 1/2O_2 + 2e^- = 2OH^-$.

Additional evidence for the "poisoning" of the catalytic reaction by cobalt is found in cathodic delamination studies. The delamination of an organic coating from a metal surface upon cathodic treatment of a scratched coating is attributed to the occurrence of the cathodic reaction underneath the coating at the periphery of the delaminating area. The lower rate of delamination of a polybutadiene coating from a zinc surface after pretreatment in a cobalt-bearing solution,³⁵ as shown in *Figure* 5, provides confirmation that the cobalt reduces the rate of the cathodic reaction on zinc.

Lead compounds are widely used as corrosioninhibitive pigments in coatings. Early studies of the mechanism of the inhibition are those of Ragg,³⁶ Lewis and Evans,³⁷ and Burns and Haring.³⁸ Mayne³⁹ showed that the protective action of lead pigments was due to a soluble species leached from the pigments by distilled water. Additional extensive studies confirming this fact were reported by Pryor.⁴⁰ Extracts of the pigments provided excellent protection to steel exposed to the aerated aqueous solution for up to 100 days. In deaerated solutions the inhibiting effect was lost and the potential of the steel remained in the active range. In aerated solutions the potential of the steel in the extracts was approximately + 0.25 v vs NHE, a value characteristic of passivated steel. Pryor determined that the steel was covered

Table 3—Approximate Concentration Above Which
Inhibitor Becomes Effective Against Corrosion of Mild Steel
In Aerated Salt Solutions at pH 5.5 to 7 046

Salt Solution	Concentration	
Nitrite	0.0001M (oxidizing anion for comparison)	
Phosphate	0.001	
Carbonate	0.01	
Bicarbonate	0.1	
Fluoride	1.0	

with a thin film of γ -Fe₂O₃ and that the lead content of the film was less than 10⁻⁵ mg/cm². Unfortunately, sensitive surface analysis tools were not available at the time Pryor did his research. His experiments bear repeating using techniques such as Auger spectroscopy, X-ray photoelectron spectroscopy, or secondary ion mass spectrometry to determine the extent of incorporation of lead in the iron oxide film.

The active component of the extract from litharge (PbO) was interpreted by Pryor to be a mixture of Pb(OH)₂ and PbOH⁺. These species, with appreciable buffering capacity, were assumed to be available to react with H⁺ ions formed at anodic areas by hydrolysis reactions involving Fe(II) or Fe(III). This local buffering action is presumed to promote film repair either by inclusion of lead in the film or by promoting the incorporation of additional Fe(III) in the film. In the words of Pryor: "Inhibition is considered to be primarily due to oxygen dissolved in solution which adsorbs on the surface of iron and takes part in a heterogeneous reaction with surface iron atoms to form a thin film of γ -Fe₂O₃, probably in a manner similar to that by which oxide films are formed in air." A modified hypothesis will be presented later in the report.

Mayne³⁹ has addressed the mechanism of inhibition when the lead pigment is included in a paint as follows: "So long as a lead pigment is sufficiently basic to form soaps when incorporated in a drying oil, it will yield a paint film which can render water noncorrosive, even in the presence of small quantities of electrolytes and atmospheric CO_2 . When water diffuses through a paint film which contains lead soaps, it breaks the soap down slowly to water-soluble products and corrosion inhibition is provided by the soluble lead component." Mayne believed that the inhibition is a consequence of adsorption of an unknown lead species on the surface of the metal substrate.

Mechanism of Corrosion Inhibition By Nonoxidizing Inorganic and Organic Salts

An excellent review on this subject has recently been presented by Thomas.⁴¹ Compounds representative of this class are sodium phosphate, sodium hydroxide, sodium carbonate, sodium borate, sodium acetate, and sodium benzoate. These compounds provide corrosion inhibition in aerated solutions but they are ineffective in deaerated solutions.⁴² They have in common the fact that the corrosion potential becomes more active in deaerated 0.01N solutions and becomes more noble in aerated solutions.^{42,43} The noble potential achieves a value characteristic of passivated steel. The surface film formed on the steel is largely γ -Fe₂O₃ with inclusion of phosphate or FeOOH, depending upon the inhibitor.^{44,45}

Corrosion inhibition by nonoxidizing anions takes place only if the anion concentration exceeds a certain value. Some representative values are given in *Table* 3.⁴⁶ Also, there exists a critical pH for inhibition by anions⁴⁷⁻⁴⁹ as shown by the data given in *Table* 4. Increasing the oxidizing nature of the environment, by increased oxygen pressure or addition of hydrogen peroxide, decreases the concentration of inhibitor required for corrosion protection.⁵⁰⁻⁵²

The mechanism of corrosion inhibition, as advanced by Pryor and Cohen,⁴² is very similar to that proposed by Pryor for corrosion inhibition by lead pigments. The inhibition is proposed to be due to a protective film of γ -Fe₂O₃ maintained in constant repair by dissolved oxygen. The film is proposed to be formed by adsorption of oxygen, followed by heterogeneous reaction and thickening until it reaches an equilibrium thickness of approximately 20 nm, at which thickness the outward diffusion of iron ions is prevented. The nonoxidizing inhibitor ions are not assumed to participate directly in the formation of the oxide film; their function is confined to the discontinuities in the oxide film. The rate of corrosion must be sufficiently slow to prevent undermining of the film and the inhibitor may play an additional role in controlling the pH of the solution in the vicinity of the metal surface.

Pore plugging of defective areas in the ferric oxide is provided by precipitation of the anion. Another role of dissolved oxygen is the rapid conversion of dissolved ferrous ions to the ferric state. Ferric salts are generally less soluble than ferrous salts and precipitation is, thus, favored at the site where the ferrous ion is formed, i.e., at defects in the film. Evidence for such precipitation comes from studies using radioactive anions.⁵³⁻⁵⁵ Autoradiography has indicated that the uptake of the anion is localized, in agreement with a pore plugging concept. Evidence for the precipitation at the metal surface of a species containing the anion in commercial paints has been cited by Harrison.⁵⁶ He noted that phosphate is observed at the metal surface after several years in the case of a coating that was pigmented with Zn₃(PO₄)₂.

The number of defect areas is apparently a function of the surface condition of the metal. Brasher and Mercer⁵⁷ have shown, for example, that corrosion inhibition of a grit-blasted iron surface required a benzoate concentration 100 times greater than that required for an abraded surface.

REQUIREMENTS FOR AN IDEAL INHIBITOR FOR USE IN ORGANIC COATINGS

All exterior coating systems designed for corrosion protection require one or more inhibitors as a constituent. In some cases the inhibitor is present only in the primer coat, whereas in other cases inhibitors are present in the top coats as well. In the comments that follow it will be assumed that the pigments being discussed have no deleterious physical properties that make them unsuitable for use in a coating. The discussion will be concerned only with those properties that relate directly to corrosion inhibition.

All organic coatings are permeable to water, oxygen, and ions; they differ only in degree of permeability when the coating is first applied and when it is aged under service conditions. Thus, the constituents necessary for a corrosive environment can reach the metal surface through the organic coating even in the absence of a gross defect in the coating. The function of an inhibitor is to reduce to a negligible rate the corrosion reaction that does occur when the constituents are present at the coating/substrate interface.

Following are requirements for an ideal inhibitor for use in organic coatings. These requirements are based on the assumption that water as an aqueous phase, i.e., aggregates of more than 25 water molecules, may form at the coating/substrate interface when the system is exposed to high relative humidity or to an aqueous solution. The formation of this aqueous phase at the interface is reversible. Once the system is exposed to dry conditions, water exits from the coating and the polymer/metal bonds are re-established. The evidence for this assumption is qualitative and is based on the observation that in many systems the coating/metal adherence falls to a very low value when the system is exposed to hot water. The coating/metal adherence regains its pre-water-exposure value if the coating is allowed to dry before the adherence property is determined. This assumption provides that inhibitors perform their function at those portions of the interface where an aqueous phase exists.

THE INHIBITOR MUST BE EFFECTIVE AT PH'S IN THE RANGE OF 4 TO 10 AND IDEALLY IN THE RANGE OF 2 TO 12: Local conditions at the coating/substrate interface may yield very high or very low pH since the aqueous liquid volume may be very small. Superficial corrosion or leaching of a constituent, or impurity, from the coating into a liquid volume that may be as small as 25 molecules may be the precursor to a corrosion site. It is highly desirable that the inhibitor prevent the initial corrosion reaction so that the water nucleus may dissipate before a high molarity solution forms with an osmotic force to increase the liquid volume.

THE INHIBITOR SHOULD REACT WITH THE METAL SUR-FACE SUCH THAT A PRODUCT IS FORMED WITH A MUCH LOWER SOLUBILITY THAN THE UNREACTED INHIBITOR: A unifying and simplifying theme which runs through the mechanisms by which a wide variety of inhibitors function is that the product which forms at the metal surface has a much lower solubility in the environment than that of the unreacted inhibitor. The very low solubility of chromium oxide at low pH, relative to the solubility of other metal oxides, as shown in *Table* 2, explains the generality of γ -Fe₂O₃, as shown by its presence on the surface of iron upon anodic polarization in many media, explains the corrosion inhibition of iron in the

Table 4—Values of the pH Above Which Corrosion
Of Mild Steel Occurs at a Very Low Rate in the Presence
Of Corrosion Inhibitors 48

Inhibitor	Critical p Concentration Value		
Phthalate	0.01M	6.2	
	0.025	6.55	
	0.05	6.8	
	0.10	7.1	
Benzoate	0.01	5.2	
	0.025	5.6	
	0.05	5.9	
	0.10	6.2	
Salicylate	0.01	4.2	
	0.025	4.6	
	0.05	4.9	
	0.10	5.2	
m-Aminobenzoate	0.01	5.7	
	0.025	6.1	
	0.05	6.4	
	0.10	6.6	

presence of inhibitors such as borate, carbonate, and benzoate. The low solubility of ferric phosphate helps to explain the inhibition of iron by phosphate in aerated solutions. Organic inhibitors by virtue of their adsorption at the metal surface confirm the fact that the metal/inhibitor or metal oxide/inhibitor complex has a lower solubility than the inhibitor alone.

The ideal inhibitor is one which yields a product on reaction with the metal which has a negligible solubility in environments over a wide range of pH and ionic constituents. Coatings used under atmospheric conditions require an inhibitor reaction product which has a low solubility over a narrow temperature range, but coatings exposed to aggressive environments at high temperature require inhibitor reaction products with a low solubility at operating temperatures.

THE CORROSION INHIBITOR SHOULD HAVE A LOW BUT SUFFICIENT SOLUBILITY: Corrosion inhibitors in general are effective only when there is a reservoir of the inhibitor in the environment sufficient to repair defects in the film or to interact with bare metal should the coating be damaged in service. A sufficient solubility is required to maintain this reservoir in the coating, but the solubility must be small enough that the inhibitor is not leached from the coating by rain or other aqueous environments to which the coating is exposed.

THE CORROSION INHIBITOR SHOULD FORM A FILM AT THE COATING/SUBSTRATE INTERFACE THAT DOES NOT RE-DUCE THE ADHESION: This requirement, stated in a negative manner, should perhaps be stated in a positive way, i.e., the inhibitor should enhance the adhesion between the coating and the substrate. Inhibitors that yield surface films that change in composition or structure with time and become hygroscopic in nature are an obvious class with undesirable characteristics. THE CORROSION INHIBITOR MUST BE EFFECTIVE BOTH AS AN ANODIC AND A CATHODIC INHIBITOR: Corrosion beneath an organic coating is electrochemical in nature, with the anodic area generally at that region where bulk water has collected and the cathodic area being either peripheral to the anodic area or at a more remote location under the coating. When the anodic area is at a break in the coating, the cathodic area is under the coating.⁵⁸ Both anodic and cathodic areas are injurious to the coating—rust occurs at the anodic area and delamination, with subsequent rusting, occurs at the cathodic area.⁵⁹

THE CORROSION INHIBITOR SHOULD INHIBIT THE TWO IMPORTANT CATHODIC REACTIONS, $H_2O + 1/2O_2 + 2e^-=$ $2OH^-$ AND $2H^+ + 2e^+ = H_2$: The predominant reaction that occurs on the substrate surface when oxygen is present is that which involves water and oxygen. Generally, sufficient oxygen is available to support this reaction. However, there may be conditions where oxygen is scavenged from the environment by biodegradable matter, or the oxygen concentration at the coating/ aqueous phase interface may be low for another reason. Under these conditions the hydrogen evolution reaction dominates. An effective inhibitor must have the capability of reducing the rate of both these reactions.

SUGGESTED PROGRAMS OF RESEARCH DEALING WITH INHIBITORS IN COATINGS

Cathodic Polarization Behavior Of Metals Exposed to Inhibitors

It has been assumed herein, on the basis of very limited experimental data, that good inorganic and oxidizing corrosion inhibitors yield a film on a metal surface that is a poor substrate for both the anodic and cathodic corrosion half reaction. Much information is available in the literature on the anodic polarization behavior of metals in solutions containing inhibitors, but very little information is available on the cathodic polarization behavior of these types of inhibitors. Cathodic polarization data are available for many organic inhibitors. The limited evidence on the cathodic behavior has come from the work cited in References 22 and 24, from much suggestive work in our laboratory, and from polarization studies of painted metals in which the paints contained chromate pigments.⁶⁰

It is thus proposed that cathodic polarization data be accumulated for metals previously exposed to solutions containing inhibitors such as chromate, tungstate, molybdate, phosphate, benzoate, and others. Many metals should be used and the environments in which the polarization curves are determined should be both aerated and deaerated. The important variables in the medium in which the polarization curves are determined include pH, stirring and ionic species. Polarization curve data should be supplemented with actual corrosion measurements in the same media.

Accelerated Corrosion Tests For Inhibitors in Formulated Coatings

Many different screening tests are used to determine the efficacy of an inhibitor, but no satisfactory accelerated test has been developed for formulated coatings. Service experience and salt spray tests have been the tests on which coatings scientists have had to rely. It is suggested that the efficiency of a coated metal to serve as a cathode as determined by electrical measurements and the anodic and cathodic polarization curves obtained on a damaged coating may provide the basis for a good accelerated test. Electrical measurements have the advantage over salt spray tests in that information may be generated that provides clues as to the mechanism by which the inhibitor functions.

Cyclic Dissolution and Precipitation Of Inhibitive Pigments in Coatings

As discussed herein, a requirement of an inhibitor in an organic coating is that it have a low but sufficient solubility. When the coating is wetted by water (rain), water absorption by the coating is rapid and some of the inhibitor enters into solution and migrates to the metal interface by a diffusion process. It is thus available at the metal/coating interface whenever the coating is wet. As the coating dries, the inhibitor probably reprecipitates. It is important to obtain a better picture of the behavior of the inhibitor on repeated solution and precipitation as the coating cyclically takes up water and dries during its lifetime.

A nondestructive technique for studying this phenomenon is based on Mössbauer spectroscopy. Ferromagnetic and antiferromagnetic materials yield a Mössbauer spectrum, the character of which is dependent upon particle size. Within a size range, which depends upon the temperature, the spectrum is a composite of the ferromagnetic behavior and the paramagnetic behavior. If the pigments used at the start of the experiment yield a spectrum which contains the paramagnetic component, the method would be ideally suited to determining the changes in particle size upon repeated wetting and drying.

The following suggestion has been proposed in print previously:⁶¹ "It is proposed that an organic coating be formulated with a ferromagnetic or antiferromagnetic material that will serve as a model for a corrosion inhibitor. A cobalt additive should be doped with 57 Co and the emission spectrum should be determined immediately after the coating is formulated and then after the coating has been alternately wetted and dried over many cycles. The emission spectrum should be taken as a function of temperature and changes in particle size or particle size distribution should be sought by means of Mössbauer measurements as a function of temperature. Candidate materials that might serve as a model for a corrosion inhibitor include Co₂VO₄, MnCo₂O₄, LiCoPO₄, CaCoSiO₄, and Fe₃(PO₄)₂ \cdot 4H₂O doped with ⁵⁷Co. The criteria in the choice of the model for the corrosion inhibitor are its solubility and the rate of solution.

The solubility behavior of the known corrosion inhibitor, $SrCrO_4$, should be approximated by the model inhibitor.

Nature of Inhibitor Components Included in Film on Metal Surface

The inclusion of components of the inhibitor in the corrosion resistant film on the metal surface is well accepted. The radioactivity measurements on chromium summarized in *Table* 1 are one example and many more could be cited. The exact chemical nature of the included component is unknown, however. It is suggested that surface analytical tools such as Auger spectroscopy, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry be utilized to determine the chemical nature of corrosion inhibitors such as benzoate, borate, silicate, chromate, and the extract from litharge after becoming incorporated in the surface film. Such measurements should, of course, be combined with electrochemical measurements and corrosion studies.

Character of Interfacial Oxide At Metal/Organic Coating Interface as a Function Of Time of Exposure to an Inhibitor

The objective of these studies is to determine how this interfacial oxide changes with time of exposure to an aggressive environment when the coating contains an inhibitive pigment. Techniques which are candidates for such study include ellipsometry, emission Mössbauer spectroscopy, and Raman microprobe analysis. Each technique has a severe limitation. Ellipsometry is limited by the transparency of the coating and the ability to interpret the results in terms of the optical constants. Mössbauer spectroscopy is limited by the need to utilize ⁵⁷Co at the interface and the ability to interpret the results unambiguously. Interest in cobalt as a substrate material is minimal, but it may be acceptable as a model system. Raman microprobe studies are limited by the lack of sensitivity when the film is thin. Raman microprobe studies are in their infancy and perhaps techniques will develop that design around thickness limitations.

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Internal Stress In Pigmented Thermoplastic Coatings

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The effect of pigmentation on the development of internal stress in thermoplastic coatings is discussed. Three pigments (titanium dioxide, red and yellow iron oxides) and one filler (talc), a thermoplastic binder and a solvent were used to formulate a range of pigment volume concentration (PVC). A cantilever (beam) method was used to measure the internal stress (S).

It was found that, for PVC < CPVC (critical pigment volume concentration), S increases with increasing PVC, while for PVC>CPVC, S decreases with increasing PVC. This variation is mainly due to the dependence of the elastic modulus (one of the S-components) on the PVC. Such behavior indicates that internal stress measurements can also be used to determine the CPVC.

The low internal stress values obtained with the talc formulations were related to the lamellar shape of this extender.

INTRODUCTION

The development of internal stress in organic coatings is recognized¹⁻⁹ as one of the major causes of damage in a coating system and must be accorded high priority when formulating coatings. The presence of a high internal stress can induce loss of adhesion and/ or cracking of the coating. During film formation, the coating tends to shrink. As long as this can occur freely (i.e., the paint can flow) internal stress does not develop, but when shrinkage is restrained (e.g., by film adhesion to a substrate and/or hindrance of the mobility of macromolecular segments) internal stress develops.

It follows that all the factors affecting skrinkage, chief among them the coating composition, will affect the formation of the internal stress.

Pigments/ fillers are one of the principal components of coatings, and might be expected to play an important role in the development of internal stress.

As far as we know, relatively few studies, $^{2,4,9-12}$ most of them of a qualitative character, have been carried out in this field. The methods used to measure the internal stress and the equations used to calculate it are, in some cases, of debatable validity. The data given by these papers indicate that, as a function of the pigment content, the internal stress can increase, decrease or be unaffected. In one case² (aluminum powder-filled polystyrene) it was found that the internal stress decreases with increasing pigment content. In our opinion this may be the case during the first period of drying, but we question whether this is so when the coating is dry. It is worth mentioning the paper of Croll, ¹³ although the study concerns only the effect of one pigment (titanium dioxide) on internal strain.

In the present paper, three pigments and one filler in a thermoplastic binder were investigated. The aim of the study was to analyze as quantitatively as possible the effect of pigmentation on the development of internal stress.

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Table 1—Characteristics of th	e Pigments/Filler Used
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	TIO ₂ ^b	Iron oxide		
		Red ^c	Yellow ^d	Talc ^e
Density (g.cm ⁻³)	4.1	5	4.1	2.75
Oil absorption (g. linseed oil/100 g)	~ 20	~ 25	~ 65	~ 30
Specific surface area $(m^2 \cdot g^{-1})$	10	_	-	12.2
Shape	Sª	Sª	A*	Lª

(a) S = spherical; A = acicular; L = lamellar.
(b) TiO₂ = rutile titanium dioxide (*Kronos*® RNCX).

(c) Red iron oxide = 130 B (Bayer). (d) Yellow iron oxide = 930 (Bayer).

(e) Talc = Mistron® 755 (Cyprus Industrial Minerals Corp.).

EXPERIMENTAL

Materials

The following materials were used:

(a) A thermoplastic binder: Polyisobutyl methacrylate, Röhm Plexigum P-675; density = 1.05; Tg (glass transition temperature $\simeq 53^{\circ}$ C (determined by Differential Scanning Calorimeter).

(b) Solvent: toluene (analytical grade)

(c) Three pigments and one filler. Their characteristics are given in Table 1.

Paint Preparation

The different pigment volume concentrations (PVC) were obtained by dilution of concentrated pastes with binder. The concentrated pastes were prepared in white (porcelain) ball mills. The PVC were verified by ashing known weights of dry free films.

The paints were applied on different substrates (steel, tinplate) with a doctor blade or the filmograph I.V.P.

Methods of Measurements

The following types of measurement were carried out: internal stress, mechanical properties, evaporation kinetics and gloss. All the measurements were carried out at $T(^{\circ}C) = 21 \pm 0.8$ and $RH(\%) = 52 \pm 1$.

INTERNAL STRESS: The internal stress (S) values were measured with a cantilever (beam) method.¹⁴ Briefly, this method consists of registering the deflection of a cantilever substrate, coated on one side and vertically clamped at one end to a support. One of the advantages of this method is that the deflection can be measured at different lengths from the clamping point. This enables one to select the cantilever substrate correctly and to eliminate errors due to clamping.

The S-values were calculated by applying Corcoran's equations.3,14

MECHANICAL PROPERTIES: The mechanical properties of free films were determined by stress-strain measurements with an Instron apparatus. The dimensions of the specimens were 15 mm wide and 50 mm distance between the jaws.

EVAPORATION KINETICS: The evaporation kinetics measurements were made gravimetrically by recording the decrease in weight of a coated plate as a function of time, until a constant weight was obtained.

The retained solvent in the "dry" coating was determined by first dissolving the film in analytical grade n-amyl acetate, and the solution obtained analyzed in a gas chromatograph (Perkin Elmer, Sigma 3) equipped with a Head Space (HS6).

GLOSS: The gloss measurements were made with the Gardner Glossmeter (60°).

RESULTS

The results (mean values of five measurements, experimental error = 5 to 7%) obtained are given in Figures 1-5. Figures 1-4 show the development of internal stress as a function of time for the formulations investigated (different PVC). Figure 5 shows the dependence of the maximum internal stress (Sm) on PVC and on the reduced pigment volume concentration (A). A is defined¹⁵ as the ratio between the PVC and the critical pigment volume concentration (CPVC).

The following conclusions could be drawn:

(a) As a function of time, S increases to a maximum value (Sm) and then decreases until an apparent stationary state is reached.

(b) In all cases, excepting the talc formulations, the time necessary to reach Sm decreases with increasing PVC.

(c) Sm increases with increasing PVC up to a particular PVC. Above this PVC, Sm decreases. As will be shown later, this PVC corresponds to the CPVC $(\Lambda = 1)$. This indicates that internal stress measurements can also be used to determine the CPVC.

(d) The talc formulations (for the same PVC) develop the smallest internal stress values and require a longer time to reach the Sm (this is discussed later).

CONCLUSIONS AND DISCUSSION

The results obtained can be explained if the factors affecting S are taken into consideration.

Assuming that the coatings investigated behave like Hookean materials (an assumption which is sufficient for the purpose of the present discussion) for a biaxial stress situation, one can write:7,8

$$Sm = \frac{M_c \cdot \epsilon_c}{1 - \nu_c}$$
(1)

where M_c , ϵ_c and ν_c are, respectively, the elastic modulus, the internal strain, and the Poisson's ratio of the coating.

Mathematical relationships for ϵ_c have been proposed in the literature.^{7,8} By assuming that ϵ_c is related to the



Figure 1—Titanium dioxide. Development of Internal stress, S(MPa), as a function of time [hour(h) and day(d)]. The numbers in the figure indicate the different pigment volume concentrations (%) investigated



Figure 2-Red iron oxide. idem Figure 1

Figure 3—Yellow iron oxide. Idem Figure 1





Figure 4—Talc. idem Figure 1



Figure 5—Maximum internal stress, $S_m(MPa)$, vs PVC(%) and λ ; x (Titanium dioxide); \bullet (Red iron oxide); Δ (Yellow iron oxide); \bigcirc (talc)

volume of solvent evaporated after the coating solidification (ΔVs), Croll⁷ suggests that:

$$\epsilon_{\rm c} = \frac{1}{3} \cdot \frac{\Delta V_{\rm s}}{V_{\rm T}} = \frac{\phi_{\rm s} - \phi_{\rm r}}{3(1 - \phi_{\rm r})}$$

(2)

where

 V_T = volume of coating at solidification

 ϕ_s = solvent volume fraction at coating solidification

 ϕ_r = solvent volume fraction retained in "dry film"

The determination of the solidification point and consequently of ϕ_s is a point of discussion. Croll identifies ϕ_s as the solvent concentration at which the glass transition temperature (Tg) of the coating coincides with the experimental temperature. This implies the determination of Tg as a function of solvent concentration with all the experimental and theoretical difficulties involved.^{7,13,16,17}

We suggest determining ϕ_s in a simpler way, namely by combining the measurements of internal stress with those of solvent evaporation kinetics (see *Figure* 6). In this case ϕ_s is given by

$$\phi_{\rm s} = 1 - \phi_{\rm FS} \tag{3}$$

where ϕ_{FS} is the solid volume fraction when the internal stress starts to develop (i.e., at time T_s).

The values of ϕ_i (mean value of five measurements, experimental error $\approx 8\%$) obtained by this procedure are given in *Table* 2. The error introduced by using this procedure is mainly due to the difficulty in determining T_s accurately. In general, the solvent evaporation is more important at the edges of a cantilever (beam) substrate. As a result, for coatings developing rapid and large S, the possibility exists that a deflection might be noticed before the bulk of the coating reaches the ϕ_s . In such cases the values of ϵ_c will be overvalued.



Figure 6—Schematic description of the dependence of $\phi_{\rm F}$ (solid volume fraction) and S (internal stress) on time

A comment on the validity of equation (2) is necessary. This equation can correctly evaluate ϵ_c only if a number of conditions are met (e.g., ϵ_c is linear and isotropic). In addition, if the relaxation process and the decrease of the coating thickness are marked after the coating solidification, the value of ϵ_c will be overvalued. This point will be discussed in a further paper.

As mentioned previously, Sm increases with increasing PVC up to a particular PVC. Above this PVC, Sm decreases markedly (see *Figure 5*). Measurements of gloss, density, and mechanical properties (see *Table 3* and

Table 2—Internal Strain (ϵ_c) and Solvent Volume Fraction	ns
At (1) Coating Solidification (ϕ_s) and (2) Retained in th	e
Dry Film (ϕ_r)	

	PVC %	ф ×10²	ф, ×10²	€c %
TiO ₂	5	12	0.55	3.8
	15	11.2	0.55	3.6
	25	11	0.61	3.5
	35	10.7	0.61	3.4
Talc	5	13	0.50	4.2
	15	13	0.40	4.2
	25	12	0.40	3.9
	35	11.8	0.40	3.8
red	5	12.7	0.3	4.1
iron	15	12.5	0.25	4.1
• oxide	25	12.2	0.4	4
	35	11.2	0.5	3.5
vellow	5	12	0.35	3.9
iron	15	12.2	0.35	3.9
oxide	25	11	0.52	3.5
	35	-	-	-



Figure 7—Density, d (g/cm³), vs PVC (%) for the coatings investigated

Figure 7) show that this PVC represents the critical pigment volume concentration (CPVC).

Equation (1) indicates that the dependence of Sm on PVC (or Λ) will be a resultant of the dependence of the Sm components (M_c, ϵ_c , and ν_c) on PVC.

In general, for coatings filled with inorganic pigment [Modulus (pigment) > Modulus (binder)],¹⁸ when PVC < CPVC, M_c increases and ν_c decreases with increasing PVC. Since for most coatings M_c is dependent on the strain rate and the temperature, it is difficult to evaluate accurately. In our opinion, M_c can be approximated if the formation rate of S is taken into account and the master curve¹⁹ of the coating can be determined. The latter is, however, a laborious procedure.

In Figure 8 Young's elastic moduli (Ec) determined at room temperature and one strain rate are given. For two cases Ec could be determined for PVC > CPVC. For the other two cases the films obtained were too brittle to be handled.

Table 3—CPVC (%) Values Obtained by Measuring Internal Stress (S), Gloss (G), Density (d), and Mechanical Properties (ultimate stress, σ_u)

	s	G	d	σ_{u}
TiO ₂	51 ± 1	50 ± 2	51 ± 1	-
Red iron oxide	41 ± 1	43 ± 2	41 ± 1	-
Yellow iron oxide	27 ± 1	26 ± 2	28 ± 1	27 ± 2
Talc	48 ± 1	46 ± 3	49 ± 1	48 ± 2



Ec

Figure 8—Young's elastic modulus, E_c (GPa) of the coating investigated, 3 months old, determined at T (°C) = 21 \pm 0.8, RH(%) = 52 \pm 1 and strain rate 1.66 \times 10⁻⁴(s⁻¹). x (Titanium dioxide); \oplus (Red iron oxide); \triangle (Yellow iron oxide); \bigcirc (Ialc)

In spite of the fact that the M_c values are certainly different from those of Ec, probably much smaller, the values given in Figure 8 indicate that below the CPVC the elastic modulus increases with increasing PVC. Since ϵ_c appears to be practically independent of PVC (see *Table 2*), it follows that the increase of Sm with PVC (see Figure 5) is mainly due to the effect of PVC on the elastic modulus.

As already mentioned, above the CPVC Sm decreases with increasing PVC. This is due to the decrease of the elastic modulus as a result of the increasing film discontinuity.^{15,20} The decreasing rate of the internal stress after reaching Sm increases with PVC (see *Figures* 1—4). Since no detachment or fissures were observed visually during experiments, this finding is probably due to the fact that the internal stress developed is sufficient to promote a break of pigment/binder bonds and/or to form microfissures, all factors relieving the stress.

The difficulties in accurately determining the internal stress components (i.e., M_c , ϵ_c , and ν_c) prevent us from

Table 4—Time (days) to Reach the Maximum Internal Stress For the Titanium Dioxide and Talc Formulations						
PVC (%)	5	15	25	35	45	
TiO ₂	36	33	30	28	25	
Talc	46	49	54	60	115	

Film thickness = 70 microns

explaining quantitatively the way in which each pigment affects the development of internal stress. Despite this drawback, it is interesting to discuss the case of talc because it develops (at the same PVC or Λ) the lowest Sm values. Similar results were noted with some pigments (e.g. aluminum powder^{2,9}). The cause of this behavior seems to be the lamellar shape of the pigment/filler particles. In the literature⁹ it is stated that the talc particles are parallel to the coating surface. This arrangement reduces resistance to shrinkage and so favors a reduced development of the internal stress.

On the basis of the present study we suggest that another mechanism may be involved. Lamellar particles, due to the high tortuosity factor²¹⁻²³ (ratio between the actual distance a solvent molecule has to travel across a layer and the layer thickness), retard the solvent evaporation more than other morphologies (e.g., spherical, cubical, etc.). This situation will also affect the development of the internal stress, since the time necessary to reach Sm is much longer for talc formulations than for other pigments (see Figures 1–4 and Table 4). The longer the solvent remains in the film (solvent acts as a plasticizer) the longer the period during which the internal stress can relax, thus producing smaller Sm values.

SUMMARY

The present study shows that below the CPVC, S increases with increasing PVC, while above the CPVC, S decreases with increasing PVC. This behavior is mainly due to the dependence of the elastic modulus on the PVC. This investigation indicates that internal stress measurements can also be used to determine the CPVC. The low internal stress values obtained with talc formulations were related to the lamellar shape of the talc particles.

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Recent Developments In Marine Antifouling Coatings

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A brief overview of the state of the art in controlling or preventing undesirable marine growth on surfaces exposed to the marine environment using antifouling coatings is presented with emphasis on organotin toxicants. Recent developments in this area are described, especially in regard to organotin polymer technology where the toxicant and the binder are chemically linked in a film-forming polymer. These organotin polymer systems hold promise for truly providing the 30 month protection against fouling long sought by ship owners and operators.

BACKGROUND AND HISTORY

The objective of antifouling coatings is to control or prevent the growth of marine organisms on surfaces exposed to the marine environment. In these days of high fuel costs, the economic cost of fouling is exceedingly important and can no longer be ignored by even the smallest ship owner or operator.

The economic cost of fouling can be demonstrated using the example of a VLCC (very large cargo carrier) operating at 15 knots. A ship of that size consumes fuel at a rate of 170 tons per day. For a 300 day operational year, the fuel cost (at \$80/ton) amounts to over \$4 million. Moderate fouling can easily increase the fuel required to maintain speed by 30%, or over \$1 million!

The contribution of fouling to structural failure can be significant, and is best illustrated by some recent data showing that accumulation of 10 lb of fouling per square foot of surface area exposed to the marine environment in six months is not unusual. Under these circumstances corrosion is inevitable through accelerated coating failure.

Marine fouling as an aesthetic issue is probably underrated, but important. Except to a marine biologist, fouling is not pretty, especially to the owner of a new \$75,000 yacht.

For these reasons, man has waged a battle against fouling for over four thousand years. Originally, marine resistant woods, tar and pitch coatings^{*}, and copper or lead sheathing were used to control fouling and were successful for a period of time. With the advent of metal hulls this latter method had to be abandoned because of the rapid galvanic corrosion. In the middle 1800's, the emergence of "patent paints" based on mercury and/or arsenic oxide in an oleoresinous vehicle was probably the first attempt to use a paint consisting of a toxicant dispersed in a polymeric vehicle. Subsequently, rapid developments based on this concept resulted in the copper oxidebased paints, many of which are still in use today.

Many other unusual and innovative ways to prevent fouling have been proposed. Some of the more interesting ones are:

- (1) Low energy surfaces (e.g. Teflon)
- (2) Barnacle cement enzyme
- (3) Electrochemical generation of chlorine
- (4) Copper-nickel cladding
- (5) Radioactive technetium-99 coatings

When Teflon[®] became commercially available in the late 1940s, its antistick and low friction surface led many

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For a fascinating account of how changes in the supply pattern of these bitumenous antifoulants influenced the emergence of chemistry in Western Europe, the interested reader is referred to James Burke's recent best-selling book "Connections," Chapter 7, Little, Brown & Co., Boston (1978).

Teflon is a registered trademark of E.I. duPont de Nemours & Co.

Table 1—Conventional Methods of Fouling Control

	Historical Perspective			
Ancient	Resistant woods			
	Copper sheathing			
	Bituminous coatin	gs		
Late/Middle	Mercury/arsenic o	xides		
19th Century	9th Century Copper powder			
	"Patent paints"			
Recent Past	All copper oxide			
	Various binders, including vinyl			
	Mostly copper oxi	de (80%)		
	Insoluble matrix	Soluble matrix		
	Vinyl resin,	Vinyl/Rosin		
	Chlorinated rubber			
	Contact, High loading			
Present	Some organotin/copper of	oxide combinations.		
	TBTO, TBTF alor TBTF/TPTF com	ne binations		
	Organotin/polymers			
Future	?			

to believe that the perfect antifouling coating had been found. Unfortunately, fouling organisms find it easy to bond to Teflon. Moreover, its insolubility and relatively high softening point make it difficult to apply conveniently. Recently, there has been renewed interest in coatings where Teflon is dispersed in fluorinated polyurethanes, as done by Griffith and coworkers at the Naval Research Laboratory.¹ These coatings did not prevent fouling, but enabled the growth to be readily removed. The cost of such coatings is not expected to be competitive with the newer antifoulings in most commercial applications, however, and scrubbable systems based on copper oxide are already in existence.

There has been a continuing interest in the proteinaceous cement excreted by barnacles, with which they attach themselves to a substrate.² Although some of this work is targeted towards improved dental cements, considerable research has been done on the chemistry of the cement in an attempt to find an enzyme which will interfere with its production by the barnacle or its curing on the substrate. While interesting from a biochemical standpoint, the stability of such an enzyme for the period of time necessary for coating manufacture, storage, application, and fouling prevention is of doubtful attain ability, and this approach has been largely abandoned as impractical. Moreover, many fouling problems are algae-related.

Chlorine gas has been used in several shipboard systems to control marine growth in sea water intake chests. While such a system has the advantage of convenient on/off operation via gas valves, it is impractical for fitting to a whole ship and would be expected to accelerate the corrosion of steel or aluminum hulls.

Alloys of copper and nickel are resistant to fouling, and their use either as the solid alloy or as a cladding on

Table 2—Soluble Matrix Copper Oxide Antifouling Paint

U.S. Navy 121/63 Formula	1	
Ingredient	Pounds	Gallons
Cuprous oxide	1440	50.0
Rosin	215	24.1
Vinyl resin (VYHH) ^a	55	4.7
Tricresyl phosphate	50	11.7
Xylene	115	16.1
MIBK	165	24.7
Antisettling agent	7	1.0
	2047	132.3

1:4 Resin: Rosin Ratio

(a) Union Carbide

steel has been proposed for materials of construction for oil rigs and container ships.³ Trials have been carried out on small boats over the past few years and the results are encouraging.⁴ However, the high cost of these alloys, compared to the normal materials of construction, and the special fabrication requirements make the method practical only for special applications where cost is not a major consideration.

One of the more imaginative approaches to control of marine fouling is the use of coatings of radioactive technetium-95.⁵ Unsuitable for hull coatings, the radioactivity of this system and the difficulty of application make it of questionable practicality except possibly for the most specific uses such as instrumentation.

There has been continuing interest in the use of organic biocides as marine antifoulants but none has attained commercial importance. A review of the work in this area is beyond the scope of this article.

The evolution of so-called "conventional" methods of fouling control, on which this review focuses, is summarized in Table 1. Copper oxide-based systems have been refined over the years and basically fall into two categories. One is the "insoluble matrix" type, usually based on copper oxide in a vinyl resin binder which may or may not contain cobinders like chlorinated rubber, and the other is the "soluble matrix" type based on vinyl resin and rosin as the water-sensitive component of the binder. Most of the copper oxide-based systems in use today are based on the soluble matrix concept. An example of such a system is the U.S. Navy 121/63 formula, the composition of which is shown in Table 2. This type of formula, characterized by its high loading of copper oxide and high rosin content, is believed to function via a microchanneling mechanism. The action of sea water on the copper oxide and rosin, both of which have a low but finite sea water solubility, promote channeling into the film which serves as a pathway for release of the toxicant. Unfortunately, these "microchannels" are easily clogged by organic debris and copper sulfide, formed by the action of hydrogen sulfide present in polluted waters, on the various chlorocuprates which are the actual leaching species in sea water. Such coatings display an exponential decay of toxicant leaching, characteristic of diffusion-controlled release coatings.

Table 3-Vinyl Rosin Marine Antifouling Paint

	Parts/Wt.
Red iron oxide	. 15.12
Talc	. 11.22
Zinc oxide	. 7.08
VAGH ^a	. 11.16
Rosin	. 3.73
Methyl isobutyl ketone	. 20.31
Xylene	. 18.84
Bentone 27	. 0.51
Methanol 95% J prewet	. 0.17
bioMeT TBTF Marine Antifoulant ^b	. 11.86

(a) Union Carbide.

(b) bioMeT is a registered trademark of M&T Chemicals, Inc

Wt./Gal	10.82	lbs.
% Solids (wt.)	60.68	
% Solids (vol.)	38.74	
Vinyl/Rosin	3/1	

Typical systems' lifetimes are 14–18 months. Because of the logarithmic relationship, to double the lifetime would require four times the initial toxicant loading. This is not practical because of the film thickness required to carry this much copper oxide.

Various approaches to overcome the decay or deactivation of cuprous oxide paints have been proposed. Among these, the so-called scrubbable coatings are perhaps the most widely publicized. Theoretically, the scrubbing procedure should reactivate a copper oxide paint which contains enough toxicant to permit the reestablishment of the necessary concentration gradient for a proper leaching rate. However, the practical problems attendant in controlled mechanical scrubbing under water, in a low visibility marine environment, without damaging the remaining antifouling coating or the anticorrosive primer are not to be underestimated.

In addition, there is concern that the scrubbing procedure, while temporarily improving the situation, actually encourages rapid regrowth of fouling organisms. Even with scrubbable coatings, one cannot defeat the exponential law of diffusion which requires a fourfold increase in the toxicant concentration to double the fouling-free lifetime.

ORGANOTINS AS ANTIFOULANTS

In the mid 1950's, Van der Kerk and coworkers, in their systematic exploration of the biological activity of organotin compounds, discovered that tributyltin compounds had broad spectrum biocidal properties.⁶ By the early 60's, the excellent antifouling properties of the tributyltins were discovered and commercialized. Various data have been reported in the literature comparing organotins to copper in antifouling activity. In the laboratory, the tributyltins show control of barnacle larvae and seaweed spores at one-one hundredth the level required for copper oxide.⁷ Under more practical conditions, however, such as those reported by Chromy et. al.⁸ one-tenth to one-twentieth the amount of organo-

Table 4-Chlorinated Rubber Marine Antifouling Paint

	Parts/Wt.
Red iron oxide	20.0
Talc	8.5
Zinc oxide	9.4
Bentone 27	0.7
Methanol 95% } prewet	0.2
bioMeT TBTF Marine Antifoulant	15.7
Parlon ^a S-20 (50% in xylene)	13.8
WW Gum rosin (60% in xylene)	23.0
Xylene	8.7
	100.0

(a) Hercules Incorporated.

100.00

Wt./Gal	12.42
% Solids (wt.)	80.91
% Solids (vol.)	57.25
Resin/Rosin	1/2

tin as compared to copper is required for full algae and barnacle control. These figures refer to "available" organotin. In poorly designed formulations, organotins do not perform better than copper oxide.

Organotins, used initially as cotoxicants in high performance copper paints, gradually came to be used in all-organotin systems. They offered a wide scope of formulating approaches with respect to pigments and binders, and they did not contribute to corrosion on steel or aluminum, which can be a problem with copper oxide paints.

The preferred tributyltin derivatives are the bis-oxide, TBTO®, and the fluoride, TBTF. In theory, any tributyltin derivative will function as well as any other tributyltin compound since the biological activity of these compounds resides in the organotin cationic portion of the molecule and is independent of the nature of the anion, providing of course that the anion is biologically inert.⁶ The physical properties, however, are a function of the anion.

The bis-oxide offers the paint formulator an easily handled, solvent-miscible liquid toxicant. Its liquid form and relatively high (for a tributyltin compound) sea water solubility (25 ppm) enable it to be used when a relatively fast leaching antifouling paint, with good control of hard shelled and vegetative fouling organisms, is required. Its plasticizing action on the paint film limits the level that can be added to a typical vinyl system to about 13% by weight or 20% by volume (dry film). Although TBTO can be used as the sole toxicant in an antifoulant paint at levels of about 0.6 lb/gal, today its commercial usage is largely as a cotoxicant in cuprous oxide-based paints at levels of 2 to 5 weight % (dry film).

Probably the most popular tributyltin compound in use today as an antifoulant toxicant is tributyltin fluoride. The pure chemical is a white, high melting powder which is insoluble in the common paint solvents. Its pigment-like properties allow it to be used at levels of

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Figure 1-Toxicant release vs. time

30% of the total paint volume solids. It is somewhat less soluble in sea water than TBTO (< 10 ppm) and functions well as the sole toxicant in vinyl/rosin and chlorinated rubber/rosin based antifoulant paints. Typical formulations are shown in Table 3 and Table 4. TBTF has also been used as a cotoxicant in commercial cuprous oxide formulations. Water-sensitive pigments such as zinc oxide, shown in these formulations, and rosin are necessary ingredients to permit greater water diffusion into the film, assisting diffusion of the toxicant to the surface. Recent studies' have shown that when tributyltin fluoride is exposed to sea water, hydrolysis occurs at a slow rate, forming compounds such as tributyltin chloride and TBTO which can diffuse through the paint film. The leaching rate of coatings based on TBTF is determined by loading, film permeability, and thickness. Tributyltin fluoride is now also available in premilled paste form for more convenient handling and easy incorporation by high speed mixing.

One of the newer antifoulants available to the U.S. market is triphenyltin fluoride. This material has been in use as an antifoulant in Europe for almost 10 years. Triphenyltin compounds have had an excellent record of human and environmental safety as agricultural fungicides in the U.S., Europe, and Asia for over 10 years. Their ready degradation in the environment to lower phenyltin compounds and inorganic tin has been documented in the literature.¹⁰ Triphenyltin fluoride, as well as the hydroxide and chloride, are excellent long-term antifoulants providing protection for over two years when compounded in the proper formulations.

Triphenyltin fluoride in pure form is a white solid, infusible and insoluble in the common paint solvents. It has the lowest sea water solubility of the organotin antifoulants, less than 1 ppm, and undergoes hydrolysis at a much slower rate than tributyltin fluoride. Furthermore, the hydrolysis products, triphenyltin chloride and triphenyltin hydroxide, while having somewhat greater solubility in water than the parent compound, are solids and will not readily diffuse through the paint film. Thus, the triphenyltins are most effective when used in eroding or dissolving type coatings. Our work has shown¹¹ that the use of tributyltins, especially TBTF, in conjunction with triphenyltin fluoride can improve the antifouling performance, especially against early algae challenge, and also the paint film properties. Typical formulations recommended for triphenyltin fluoride systems use chlorinated rubber as binder and relatively high levels of water-sensitive zinc oxide and rosin to promote controlled erosion. A formulation of this kind has demonstrated, over a 24 month period, performance against the severe fouling challenge in Biscayne Bay, Florida. It is also being patch-tested on some large tankers where it has presently resisted fouling for 18 months.

While triphenyltin fluoride is registered as an antifoulant with the U.S. Environmental Protection Agency, no paint based on triphenyltin fluoride is yet registered in the U.S., although many are commercially available in Europe and Japan.

More detailed information on the toxicology and environmental chemistry of organotin antifoulants can be found in Reference 21.

ORGANOTIN POLYMERS

Probably the most exciting development in marine antifoulants in recent years has been the emergence of organotin polymer-based antifoulant coatings. Much of this enthusiasm is due to the realization by ship owners and marine paint companies that these systems can truly provide the long term fouling control long sought by the marine industry.

Polymers of trialkyltin acrylate esters were first described by Montermoso et. al. in 1958¹² in a search for thermally stable polymers. The use of organotin polymers to protect surfaces against the attack of marine organisms was described by Leebrick.¹³ Interest in polymeric organotin antifoulants was kindled in the late 1960's and early 1970's with research and development proceeding in the U.S., Europe, Australia, and Japan. In the U.S., the potential of organotin polymers was recognized by researchers at the David W. Taylor Laboratory of the U.S. Naval Ship Research and Development Center in Annapolis.¹⁴ By the mid 1970's, paints based on organotin polymers were available in Europe and Japan. In the U.S., such paints first received EPA approval in 1978.

As discussed earlier, conventional antifoulant systems based on copper or tributyltin toxicants rely on a leaching mechanism to transfer the toxicant to the surface of the paint film. Since the mechanism is diffusioncontrolled, availability of toxicant decreases logarithmically with time as shown in *Figure* 1.

An important consequence is that, in such conventional leaching-type paints, toxicant remains in the paint film although its leaching rate is insufficient to control fouling. To compensate for such effects and to achieve a reasonable service life, more toxicant must be incorporated in the paint film than is really necessary were it delivered at a constant rate. The efficiency of such a system when 2-3 year fouling control is required is less than ideal, and residual toxicant remains in the depleted



Figure 2—Mechanism of antifoulant release

film even though it is no longer effective. The necessity of removing the spent antifoulant prior to recoating is a nuisance and adds to maintenance expenses.

These limitations do not apply to properly formulated paints based on organotin polymers. In these polymer paints, the organotin is chemically bound to the binder backbone, usually an acrylate polymer. Attack by sea water on the film surface causes hydrolysis of the organotin-ester linkage. The organotin moiety is released into the surroundings where it can prevent fouling. The depleted outer layer of the paint film, now containing hydrophilic free carboxylate groups, has little integral strength and is easily eroded by moving sea water, exposing a fresh surface layer of organotin acrylate polymer. This hydrolysis and erosion mechanism is continually repeated until no paint is left on the substrate. The process is illustrated in *Figure 2*.

Thus, while conventional antifouling paints with copper or tributyltin additives function by a leaching mechanism, antifoulant paints based on organotin acrylate polymers rely on a controlled hydrolysis and erosion of the paint film to deliver the toxicant. The hydrolysis and erosion mechanism of toxicant release from a properlydesigned, polymer-based system can result in a constant rate of toxicant release with time as shown in *Figure* 3.

Thus, in polymer-based systems, the service life of the antifouling coating is a direct linear function of film thickness, providing the hydrolysis/erosion rate is above a minimum value necessary for fouling control. This is the major difference between these systems and conventional systems where the service life is more dependent on factors which affect the diffusion of toxicant out of the paint film, such as initial toxicant loading and film permeability. Conventional antifoulings have service lifetimes proportional to the logarithm of their film thickness, as previously described, and erosion in such systems is not as significant a contributor to toxicant release as in polymer systems. Because of these intrinsic character-



Figure 3—Toxicant release vs. time

istics, organotin polymers offer great versatility to the coatings chemist.

The advantages claimed for organotin polymer-based antifouling paints include:

- (1) Constant toxicant delivery vs. time
- (2) Erosion rate/toxicant delivery controllable
- (3) No depleted paint residue to remove and dispose
- (4) 100% Utilization of toxicant
- (5) Polishing at high erosion rates
- (6) Self-cleaning
- (7) Continuously reactivated

With these advantages, it is not surprising that most manufacturers of antifouling paints are either already marketing an organotin polymer system or have such a system under development.

FORMULATING ORGANOTIN POLYMER PAINTS

In order to derive all these benefits from polymerbased antifoulant paints, they must be formulated knowledgeably. The principles governing their performance are different from conventional additive antifoulants.

Since, in polymer-based paints, the coating itself is consumed in releasing toxicant, the erosion rate of the paint and the film thickness essentially dictate the service life. The service life is then an inverse function of the erosion rate and a direct function of the total film thickness:

$$t_e = \frac{x}{E}$$

where $t_e = service$ life

- E = erosion rate
- $\mathbf{x} = \text{film thickness}$

The erosion rate of antifoulant paints based on tributyltin methacrylate copolymers is strongly influenced by a number of formulation variables. Dominant variables are:

- (1) Composition and structure of the copolymer
- (2) Levels of water-sensitive pigments in the formulation

- (3) Levels of inert pigments
- (4) Level and nature of auxiliary toxicant
- (5) Level and nature of other paint additives (when present)
- (6) Pigment volume concentration

In addition, the erosion of the polymer film, being governed by a chemical hydrolysis reaction, is a function of temperature and ship's speed.

Control over the first variable is exercised by the polymer raw material supplier, and different polymers are available to give erosion rates suitable for different service conditions and formulation needs. Atherton, et al.¹⁵ described the effect of polymer composition on hydrolysis and erosion rate. Some companies have taken a different course. International Paint Company, for example, has claimed in their patents¹⁶ that the erosion rate of polymer paints can be controlled by the incorporation of hydrophobic additives of low sea water solubility and vapor pressure in the formulation. Examples of such retarders include chlorinated waxes and silicones. Recent patent applications¹⁷ by Hempel's Marine Paints claim the use of chlorinated rubber and polyacrylate esters as erosion retarders.

The sensitivity of the erosion rate to the above formulation variables should not be underestimated. A minor formulation change, if the effect of the change is not understood, can turn a fine paint into one destined for early failure either because it erodes too fast or does not erode at all. The performance of some eroding paints can also be affected by the nature of the anticorrosive substrate, but this effect is now understood and can be compensated for.

Although organotin polymers which contain a sufficiently high organotin concentration can provide excellent antifouling performance by themselves, this is frequently achievable only at the expense of a high erosion rate and/or poor film qualities. In a formulation balanced for good paint film properties, most paint suppliers have found it beneficial to incorporate a cotoxicant in the formulation. Suitable cotoxicants for use in polymer systems include TBTF and copper oxide, although the formulations will be somewhat different to compensate for their differing effect on the erosion rate. An alternate approach is to chemically bond an organic cotoxicant to the organotin polymer backbone¹⁸ although the cost/effectiveness of this approach is not proven.

In formulating organotin polymer paints, two main approaches are being followed. The first, pioneered by International Paint (UK), focuses on relatively rapid eroding systems which show a definite decrease in surface roughness with time. This polishing effect is claimed to contribute to increased ship fuel efficiency over and above the economic advantage obtained from keeping the hull free from fouling. Polishing antifoulings are somewhat more expensive to the ship owner since as many as four, $100 \,\mu$ m (16 mil total) coats (dry film) must be applied in order to achieve a 2–3 year service life. Erosion rates of such systems are of the order $10-12 \,\mu$ m per month. Christie¹⁹ has reviewed this approach in some detail. The other approach, first developed in Japan, concentrates less on the smoothing characteristics of the coating but fully utilizes the potential of organotin polymers to provide long-term antifouling performances. Such coatings also erode in service but more slowly than the polishing type. Typical erosion rates for such systems are 3–6 μ m per month so that two, 100 μ m coats can provide the required protection. An example of such a system is Takata LLL developed by Nippon Oils and Fats Ltd.²⁰

Since the erosion rate of coatings based on organotin polymers can be controlled, systems with erosion rates inside these limits can also be achieved.

SUMMARY

There is no doubt that the organotin polymer systems are the most exciting new development in marine antifoulants. Their benefits have been demonstrated in service in Europe and the Far East, and there is proof that they can truly provide long-term protection against fouling when properly formulated and properly applied. One note of caution, however, even with our ever improving "bag of tricks" we cannot perform miracles on poorly maintained, rough, and pitted hulls. Most companies supplying fast-eroding polymer paints do not recommend the application of such systems when hull roughness is of the order of $> 200 \ \mu m$, since that is the operating film thickness for many of these smoothing systems.

The problem of maintaining underwater surfaces free of marine fouling for extended periods of time has been one of the most difficult problems coatings science and technology have ever addressed. Soaring fuel prices have provided greater incentive than ever before to solve the problem. There is convincing evidence that better tools than ever before are available to accomplish this, if they are formulated and applied intelligently.

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United Kingdom Orders of FSCT Educational Literature

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Characterization of Organic Coatings Using Dielectric Spectroscopy

John V. Standish and Henry Leidheiser, Jr. Lehigh University

A simple system is described for making dielectric measurements of coatings and films as a function of temperature. Illustrations are given of the applicability of the technique for studying (a) dielectric relaxations and determination of T_a , (b) water in coatings, (c) composition and structure of coatings, and (d) quality control of coating components. Examples are given for unpigmented poly(vinyl acetate) and epoxy-polyamide coatings.

INTRODUCTION

If a polymer film is placed between two metal electrodes, a parallel plate capacitor is created where the polymer film is the dielectric of the capacitor. An experimental procedure, referred to as dielectric spectroscopy, involves measuring the change in electrical properties of the polymeric dielectric as a function of temperature. Dielectric spectroscopy has long been used to characterize polymers, but it is an experimental procedure which is not widely used in the coatings industry. This paper presents an experimental method for conducting dielectric spectroscopy which is more attractive than the bridge balancing methods which have traditionally been used for making dielectric measurements. Further, experimental results (using unpigmented films prepared from poly (vinyl acetate) or from epoxy resins cured with polyamide resins) are presented to demonstrate that dielectric spectroscopy is a very useful means for characterizing organic coatings.

BACKGROUND

Dielectric measurements are used by materials engineers for evaluating the properties of polymer insulators and dielectrics. There is already much literature which describes the theory of dielectric measurements. This literature also indicates ways in which dielectric spectroscopy can be used to study polymers, as well as polymer composites such as organic coatings. Some examples are given below.

Two texts, one by Hedvig¹ and the other by McCrum et al.² discuss cases where dielectric spectroscopy has been used, for example, to investigate the effectiveness of various plasticizers in poly (methyl acrylate), the effect of curing temperature on curing rate of polyester resins, and the degradation of polymers by heat and radiation. An annual review of the dielectric literature³ is also available.

Devay et al.⁴ used dielectric spectroscopy to investigate the aging of urethane coatings during atmospheric exposure. The type of pigment used (rutile or anatase TiO₂) influenced the aging process of the coatings.

Bair, Johnson et al.⁵⁻⁷ have used dielectric spectroscopy to identify the presence of water condensed as a second phase within polymers such as polycarbonate and polyethylene. The water was contained in the polymers in concentrations as low as 0.37 weight percent. Experiments have been conducted which show that dielectric spectroscopy is capable of identifying the presence of water layers as thin as $0.5 \,\mu$ m at the interface of an epoxy-polyamide film and a metal electrode.^{8,9}

Dielectric measurements have traditionally been conducted by placing the polymer sample in one arm of a capacitance bridge as shown schematically in Figure 1. When an alternating excitation voltage is applied across the arms of the bridge, the values of the equivalent parallel capacitance, CP, and the equivalent parallel

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Figure 1—Schematic diagram of a capacitance bridge



Figure 2—Vector diagram showing relationship of I_T , I_L , I_C , and θ

resistance, R_P , are determined for the polymer sample by adjusting the variable capacitor and resistor, wired in parallel, until zero current flows through the detector. Several references discuss bridge balancing techniques in detail.¹⁰⁻¹⁴ The bridge balancing procedure must be repeated for each temperature change during dielectric spectroscopy. Bridge balancing is time consuming and tedious when many values have to be determined and is, therefore, an unattractive experimental procedure. An alternate, more simple and less time-consuming procedure for conducting dielectric spectroscopy is described below.

EXPERIMENTAL PROCEDURE

Dielectric Measurements

The alternate approach involves applying an alternating excitation voltage to a dielectric sample and analyzing the current which develops in the electric circuit. Referring to Figure 2, I_T is the total current in the circuit which leads the excitation voltage by a phase angle θ . I_T is considered a vector quantity and so can be resolved into its components. One component called the loss current, I_L , is inversely proportional to R_P and is in-phase with the excitation voltage. The second component is called the charging current, I_C , and is 90 degrees out-of-phase with the excitation voltage.

Equations (1) and (2) show the relationship between I_L and R_P , and I_C and C_P , respectively.

$$I_{L} = \frac{V}{R_{P}}$$
 (1)

$$I_{\rm C} = \omega C_{\rm P} V \tag{2}$$

In the equations above, ω is the angular frequency of the excitation voltage ($\omega = 2\pi f$), and V is the RMS value of the excitation voltage.

Dielectrics are often characterized by quantities known as the dielectric constant, ϵ' , and the dielectric loss, ϵ'' (ϵ' and ϵ'' are, however, more specifically referred to as the real and imaginary components of the complex dielectric constant). Values of ϵ' and ϵ'' can be calculated using the following relationships:

$$C_o = \epsilon_o A/d \tag{3}$$

$$\epsilon' = I_{\rm C}/V C_{\rm o} \tag{4}$$

$$\epsilon'' = I_{\rm L}/V C_{\rm o} \tag{5}$$

In equation (3), c_0 is the vacuum capacitance of the sample holder, ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85 \times 10^{-14}$ Farads/cm), A is the area of the electrodes, and d is the spacing between the electrodes.

Values proportional to I_c and I_L can be determined continuously and automatically by using a phase sensitive detector known as a lock-in amplifier (LIA). The circuit diagram which was used is shown schematically in *Figure 3*. A one volt RMS excitation voltage was applied to the polymer sample. The resulting current in the circuit was amplified and converted to a voltage proportional in value to the current by a current sensi-

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tive amplifier (Princeton Applied Research Model 181). The voltage output of the amplifier was input to the LIA (Princeton Applied Research Model 5204). The LIA yields DC voltages proportional to Ic and It which were recorded on the y axis of x-y recorders. A thermocouple placed near the sample was used to drive the x-axes of the recorders. Samples were cooled in liquid N2 and values proportional to I_c and I_L were recorded continuously as the samples were warmed at a rate of a few degrees per minute. Since the thermocouple was placed immediately adjacent to the sample (see Figure 4), it is assumed that there was little temperature difference between the sample and the value that was recorded by the thermocouple. Measurements can be made conveniently with the LIA at constant frequency, over the frequency range of 10 to 50.000 Hz.

Commercial dielectric sample cells are available, but sample holders can also be easily constructed in the laboratory. One such holder is shown in *Figure* 4. This holder employed circular electrodes of tin plate. The area of the smaller electrode was 9.62 cm^2 . The sample (either as a free film or on a tin plate substrate) was placed between the electrodes and the holder, and was clamped under moderate pressure with "C" clamps. It is recognized that small air gaps may exist between the coating and an electrode, but these gaps will not introduce a significant error in most cases. Hedvig^{1,15} has also used an LIA for conducting dielec-

Hedvig^{1,15} has also used an LIA for conducting dielectric measurements. Additional details concerning the procedure and equipment can be found in References 8 and 9. It is interesting to note that LIA's are also useful for other types of investigations concerned with organic coatings, corrosion, and electrode processes.^{8,9,16-18}

Preparation of Coatings

Samples were prepared by mixing stoichiometric amounts of epoxy and polyamide resins using toluene, n-propanol, and methyl isobutyl ketone as solvent. The epoxy resins used were Epon[®] 1002 and 825. The polyamide resins used were Versamid[®] 100 and 125 and Emerez[®] 1511.

Coatings were prepared by spraying the coating solution onto a substrate, or by pipetting the solution onto the substrate. Coated substrates were generally baked in a forced-air oven at 100° C for 20 min, after which the temperature was raised to 150° C over a time period of about 5 min. The coated substrate was removed from the oven and stored in a desiccator. Some samples were allowed to cure at room temperature in the laboratory atmosphere. The purpose of the baking step was to minimize the effects of aging such as additional curing or solvent release from the coating over time. The coating over time. The coating sprepared were in the range of 125 to $150 \,\mu$ m in dry film thickness as measured by a micrometer.

It is recognized that the solvents used, time between mixing and application, method of application, curing



Figure 3—Schematic diagram of experimental equipment

conditions, and other factors may affect the properties of epoxy coatings. No strict efforts were made to control or study these variables.

Dielectric measurements were also made with a film of poly(vinyl acetate) (PVAc) which is a wellcharacterized polymer.

RESULTS AND DISCUSSION

Dielectric Relaxations and Determination of Tg

Generally, as a polymer is heated from low temperatures, values of I_L and I_C increase as a result of both increased thermal vibrations of the polymer molecule and increased mobility of low molecular weight or ionic



Figure 4—Schematic diagram of holder used to make dielectric measurements. (A) electrode leads; (B) insulated metal plates; (C) rubber; (D) electrode, 9.62 cm²; (E) grounded guard ring; (F) thermocouple; (G) sample

Epon 1002 and 825 are registered trademarks of Shell Chemical Co. Versamid 100 and 125 are registered trademarks of Henkel Corp. Emerez 1511 is a registered trademark of Emery Industries.



Figure 5—Dielectric results obtained for a film of poly (vinyl acetate) (1000 Hz)

species in the sample. In addition, over narrow temperature ranges the sample develops sufficient free volume to allow molecular groups (dipoles) along the polymer chain, and eventually the polymer chain itself, to rotate freely in the alternating electric field. The rotation of molecular groups also gives rise to increases in I_L and I_C known as dielectric relaxations. As an illustration of these phenomena, *Figure 5* shows results obtained for a 120 μ m thick film of PVAc at 1000 Hz.

In Figure 5 the general increase in both I_L and I_C is observed with increasing temperature as are dielectric relaxations at -76° and 61° C. The relaxation at -76° C is a result of the rotation of the acetate groups located along the polymer chain. The relaxation at 61° C represents the glass transition temperature, T_g , of the polymer.



Figure 6—Dielectric results obtained for a film of Epon 1002/Versamid 100 at (A) 1000 Hz, and (B) 10 Hz



Figure 7—Dielectric results obtained at 10 Hz for a film of Epon 1002/Versamid 100 after exposure to various relative humidities. (A) 0% RH, 0 wt % H₂O; (B) 20% RH, 0.47 wt % H₂O; (C) 43% RH, 0.95 wt % H₂O; (D) 65% RH, 1.54 wt % H₂O; (E) 83% RH, 2.02 wt % H₂O; (F) water immersion, 2.18 wt % H₂O. Plots were successively offset one division on the y axis for clarity

Figure 5 also shows that the increase in I_L and I_C accompanying T_g is often so large that a scale change is necessary to show both low and high temperature data. Hedvig¹ reports that dielectric relaxations for PVAc occur at about -65° to -75°C and at about 55° to 65°C. Hedvig also reports that the increase in ϵ' ($\Delta\epsilon'$) which results in passing from temperature below to above T_g is 5. Finally the room temperature values of ϵ' reported for PVAc is 3.2.¹⁹ These literature values agree favorably with the data shown in Figure 5.

Those familiar with dynamic mechanical spectroscopy (where a sinusoidal strain is applied to a sample, and the resulting stress is measured as a function of temperature) will recognize that the information obtained dielectrically is often similar to that obtained mechanically.^{1,2} It should be pointed out that dynamic mechanical tests are often run at frequencies on the order of one Hz and that results obtained by either dielectric or mechanical means are frequency dependent. The frequency dependence of dielectric results is discussed below.

Dynamic mechanical experiments generally require that a polymer sample be about 1 mm in thickness or be supported on a glass braid. An obvious advantage of dielectric measurements is the fact that experiments can be run with free films, or with coatings supported on or separated from metal substrates. References 20 and 21 discuss the use of dynamic mechanical methods for characterizing coatings.

Figure 6A shows results obtained at 1000 Hz for a film of Epon 1002/Versamid 100 after storage at 20% relative humidity. The relaxation at 75° C is associated with the glass transition temperature of the sample. An additional maximum in I_L is seen at about -20° C and a shoulder is seen at about -80° C. The increase in I_C which is expected to be associated with the maxima at -20° C is too small to be seen and is perhaps overshadowed by the increase in I_C from thermal effects. The molecular origin of the lower temperature relaxations apparent in Figure 6 are discussed elsewhere.⁸

It is interesting to compare the results in Figure 6A at 1000 Hz to those in Figure 6B at 10 Hz. Reducing the



Figure 8—Dielectric results obtained at 1000 Hz for a coating of Epon 1002/Versamid 100 after (A) storage in a desiccator, (B) after one day at 65% relative humidity, and (C) after one day immersion in water. The I_L data for C are very similar to those of B and are not shown

measurement frequency reduces the conductivity resulting from the rotation of molecular groups along the polymer chain, and therefore, the ionic component of the conductivity becomes greater relative to the dipole component. The result of reducing the measurement frequency is that the relaxation at T_g is not as clearly resolved at 10 Hz as it is at 1000 Hz. In fact, at 10 Hz the ionic conductivity masks any maximum in I_L at T_g although the corresponding increase in I_C can be seen. The temperature of each transition decreases as the measurement frequency decreases. Finally, the lower temperature transitions are slightly more resolved at 10 Hz than at 1000 Hz.

Water in Coatings

It is often necessary to specify the relative humidity to which a sample has been exposed.¹¹ Figure 7 shows that even small changes in relative humidity can cause changes in the dielectric spectrum of epoxy/polyamide coatings. The weight of water contained in the sample as determined with a microbalance is also given in Figure 7. Note that the relaxation at about -60° C becomes more intense as water content increases and that the maxima shift slightly to lower temperatures. Also notice that the I_c curve shows a more pronounced change corresponding to the relaxation as the water content increases.

The value of T_g can also be influenced by the water content of a polymer sample as shown in *Figure* 8. Exposure to 65% RH reduces T_g by about 12° C while immer-



Figure 9— $\Delta \epsilon'$ at T₉ measured at 1000 Hz for films of (A) Epon 1002/Versamid 100; (B) Epon 1002/Emerez 1511; (C) Epon 1002/Versamid 125; (D) Epon 825/HMDA; (E) Epon 1002/HMDA

sion in deionized water for one day reduces T_g about 23° C. In Figure 8, the value chosen for T_g was taken as the inflection point of the I_C plot. The increased water content at 65% RH increased the ionic conductivity in the sample such that no maximum in I_L was observed. Finally, it is interesting to note that while water content influenced T_g to a large extent, it had only little affect on the temperature of the secondary transitions below T_g (see Figure 7).

Reduction in T_g for epoxy samples exposed to water has been reported by others.^{22,23} Plasticization of coat-



Figure 10— $\Delta\epsilon'$ at Tg at 1000 Hz for films of Epon 1002/Versamid 100 (A) cured at 100°C and (B) cured in laboratory atmosphere



Figure 11-Dielectric results obtained at 10 Hz for Epon 825 after exposure to laboratory atmosphere

ings by water may be an especially significant phenomenon in the case of corrosion resistant coatings since the permeability of water, oxygen, and ionic species is generally expected to increase as Tg decreases. Coating properties such as hardness and impact or abrasion resistance may easily be influenced by water content of the film. Also, the energy required for crack propagation is often reduced in polymers containing water.24

Effects of Coating Composition and Structure

Figures 9 and 10 show ϵ' vs temperature for various epoxy films. Values have been normalized in terms of ϵ' to account for variations in film thickness from sample to sample. T_g values for these samples range from about 65° to 85°C. The magnitude of change in ϵ' in passing through T_g is dependent upon the composition and conditions of curing of the films. An air-dried Epon 1002/Versamid 100 film has a $\Delta \epsilon'$ of about 7 while the same film baked in an oven has a $\Delta \epsilon'$ of about 4.3. This difference most likely reflects the lower degree of crosslinking in the air-cured film. The $\Delta \epsilon'$ values for films of Epon 1002 cured with Versamid 125 and Emerez 1511 are 2.5 and 2.8, respectively. The equivalent weight of these polyamides is Versamid 100 > Emerez 1511 > Versamid 125. The value of $\Delta \epsilon'$ appears to be influenced by the amount of polyamide resin in the film and/or by the fact that the lower the equivalent weight of the polyamide the smaller the distance between crosslinks. If the value of $\Delta \epsilon'$ is influenced by crosslink density, it is likely that $\Delta \epsilon'$ could be related to diffusion rates through a coating.

Quality Control of Coating Components

Samples which are liquids can also be evaluated by dielectric spectroscopy. Figure 11 shows results obtained for Epon 825 (with no curing agent) which is a liquid at room temperature. The relaxations at -145° and -80° C result from rotation of the diphenylpropane and glyceral groups of the epoxy molecule, respectively.8 The relaxation at -10° C is T_g for Epon 825. Since the magnitude and temperature of a given relaxation can be influenced by the molecular weight, chemical composition, and

purity of a sample, dielectric measurements may be useful in some cases for quality control of resins used in coatings.

CONCLUSIONS

An experimental procedure for conducting dielectric spectroscopy was described which is more automated and less time consuming than the traditionally used bridge balancing techniques. Results reported above, and in the literature, demonstrate that dielectric spectroscopy is a very useful method for obtaining information concerning the physical and chemical properties of organic coatings. The experimental procedure described above makes dielectric spectroscopy a method for characterizing coatings which should be considered by many laboratories.

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Baltimore— Virginia Section Apr. 22

Ken Hagenson, of Buckman Laboratories, presented a talk and slide show featuring, "CURRENT ALTERNATIVES TO LEAD AND CHROMATE RUST INHIBITIVE PIGMENTS."

CARL B. MINCHEW, Secretary

Birmingham

Mar. 5

J. Sreeves, of B.I.P. Ltd., presented "SOME ASPECTS ON AMINO RESINS."

The class of materials which Mr. Sreeves discussed were defined as the condensation products of low molecular weight amino compounds with aldehydes, optionally etherified with alcohols. He explained that although the amino resins used in surface coatings were almost exclusively etherified, the bulk of their production was of the nonetherified type, for use in adhesives, moulding compound and paper.

According to Mr. Sreeves, the main purpose of etherification was to impart solubility, compatibility and stability to the base resin. It also gave the required viscosity and reactivity.

Three amino compounds in general use are urea, melamine, and benzoguanamine. Normally, formaldehyde was the other reactant. Mr. Sreeves explained that these intermediates have relatively low dependence on petroleum feedstocks and, therefore, any oil shortages should affect costs to a lesser degree. The manufacture of alcohols from coal is relatively easy, also.

A series of graphs showed that prices of raw materials such as methanol and formaldehyde were lower than in the early 1970's.

From the environmental aspect, methylated aminos were very interesting, allowing the development of high solid and waterborne formulations. However, according to Mr. Sreeves, their present use has been delayed due to the high cost of solvent per unit solid and the need for more specialized manufacturing plants. Mr. Sreeves felt that these materials were ahead of their time and would increase in use when volume solids became a more important factor to paint manufacturers and users.

Paint manufacturers generally consider amino resins as brittle and hard, for use as a minor component of the resin mixture. This is no longer the case, according to Mr. Sreeves. An example showed a paper-laminate impregnated with a medium containing 80% urea. It was suggested that the industry look to higher levels of amino, using other resins to modify performance.

In the future, compounds such as caprolactone might be used as reactive diluents to give high solids content at working viscosities. Newly developed raw materials such as triazone, urone and the ethylene urea derivatives might also provide interesting resins. It is important though, explained Mr. Sreeves, that the level of free formaldehyde in the resins be kept at an acceptable level.

Mr. Sreeves concluded that aminos would become relatively cheap and readily available, providing high solids, low bake and cold curing systems.

BRIAN ADDENBROOKE, Secretary

Mar. 19

Cleveland

The first speakers were Clarke Boyce, Treasurer of the Federation, followed by Frank Borrelle, Executive Vice-President of the Federation.

Mr. Boyce pointed out the accomplishments of the Cleveland Society and its membership which include five pastpresidents, four committee chairmen, twelve Federation committee members and a PRI Director.

Mr. Borrelle presented a slide show featuring the Federation and its people. He explained the Federation's budget, publications, and activities such as the Annual Meeting and Paint Show.

The technical speaker was Dr. Louis Freimiller, of Rohm and Haas Co. He discussed "THE ROLE OF RHEOLOGY MODIFIERS IN LATEX PAINTS."

Dr. Freimiller explained that latex flat paints make up a large percentage of the exterior (79%) and interior (94%) flat market, but latex paints account for a lower portion of the gloss and semi-gloss market (60% interior and 33% exterior). The superior rheology of the alkyd based paints is the major reason that they are high in the gloss markets.

Dr. Freimiller showed that an alkali soluble resin acts to depress the leveling viscosity but does not add to the viscosity itself and must be used with conventional thickeners. The alkali soluble emulsion acts as a true thickener and has more desirable viscosity profile than celluloses, has a higher high shear viscosity and has a lower leveling viscosity.

The main advantage of the alkali soluble emulsion, according to Dr. Freimiller, is its structure that makes it function as it does. Photomicrographs showed that the modifiers can link latex particles together showing a critical association concentration of 1.75% in water. Another modifier showed an association concentration of 1.5% in water. A critical association concentration for the latter was 0.65% in latex. This modifier provides results that are hard to distinguish from unthickened latex, according to Dr. Freimiller. Similar results were presented with TiO₂ and this thickener gave a greater gloss and low splatter.

By replacing up to 7.5% of the binder with the alkali soluble rheology modifier, flow and gloss can be upgraded without reducing alkali resistance, concluded Dr. Freimiller. But, it must be remembered that the pH must not drop below neutral or excessive viscosity develops. A pH range of 8.0-8.5 is best.

CARL KNAUSS, Secretary

Dallas

Apr. 9

Honored guests at the meeting included Howard Jerome, Federation President-Elect and Frank Borrelle, Executive Vice-President of the Federation.

William D. Meadows, Technical Service Manager, Talc Division, of Cyprus Industrial Minerals Co., spoke on "CHLORITE—A NEW EXTENDER PIG-MENT FOR THE COATINGS INDUSTRY."

Mr. Meadows explained that chlorite, found in Montana, is magnesium aluminum silicate with a small percentage of iron content. It is produced in three grinds; 200 mesh, 360 mesh, and superfine.

Chlorite, Mr. Meadows said, is almost a drop-in substitute for delaminated clay. Slides displayed comparisons of the chemical properties of talc, chlorite, and clay; the price per pound; and viscosities in a pigmented 70% alkyd.

Comparisons of gloss, according to Mr. Meadows, show that chlorite flats less, so that a higher solids paint with higher gloss is possible.

Q. Have you completed any exposure studies?

A. Yes. Fade and chalk resistance will be better than talc and better than calcined clay.

A twelve minute slide/tape presentation prepared by the Montreal Society was shown, entitled "An Introduction to Resin Manufacture."

WILLIAM A. WENTWORTH, Secretary

Kansas City

Apr. 9

Apr. 8

Federation President William H. Ellis and Field Services Director Thomas Kocis gave a talk and slide presentation on the Federation's aspects and activities. MIKE BAUER, Secretary

Los Angeles

Dr. Robert Athey, of Swedlow Corp., presented "POLYMERIC ORGANIC DIS-PERSANTS FOR PIGMENTS."

Dr. Athey's discussion featured five parts: (1) a review of colloid science,

(2) evaluation methods of dispersants,
(3) potential pitfalls in evaluations,
(4) organic structures, and (5) evaluation of commercial systems.

According to Dr. Athey, Stokes Law is the basis for settling. No dispersion is infinitely stable. The particles are large and dense, causing them to settle. Therefore, you need to protect the dispersion from settling. Higher viscosity will cause particles to fall down slower. Also, particle size breakdown will help. And, finally there are additives, protective colloids and ionic systems.



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Dr. Athey, then presented pigment dispersant evaluation methods. "Viscositydosage plot" and the "Daniels flow point method" can be used.

The pitfalls in evaluations were discussed such as determining pH, salinity, water, temperature, etc.

A slide presentation featuring organic dispersants was shown. According to Dr. Athey, organic dispersants are generally good for viscosity stability on aging, good rewetting or scrubability, accepted by EPA, and pigment-surfactant interaction. Dispersants shown included cellulosics, casein, and many non-ionic and cationic dispersants. Using examples with these various surfactants, Dr. Athey illustrated the pH effect, the dosageviscosity curves, and the effect of molecular weight, and the effect of salt.

Dr. Athey concluded by discussing the value of the organic dispersants. Although costly, sensitive to pH, and often interfered by cations, the organic dispersants aid in aging stability and modify rheology.

Q. What correlation is there between heat aging and room temperature aging?

A. Only about half of the time you can find a direct correlationship. Sometimes, under heat you cause a reaction to happen that does not happen at room temperature.

Q. Do you state that to obtain the optimum usage of the dispersant used, the pH should be raised regardless of the Zeta potential of the pigment?

A. No, the pH is going to be affected by what ionization you are going to get by the pigment itself.

Q. How "universal" can we expect any dispersant ever to be? Discuss criteria.

A. No, there never will be a truly universal dispersant. I have shown you some dispersants that will work well with titanium dioxide but are terrible with clay.

Q. Can you comment on HLB relationships?

A. For hydrophobic systems, like talcs, you need good wetting. For easily wetted systems, like TiO_2 , you can get away with less wetting. Dispersants are low molecular and they are not surfactants, they don't change the surface tension. Therefore, you may want to add a small amount of surfactant when you have a hydrophobic system.

Q. How do you select a dispersant of a pigment mixture, especially mixtures that incorporate moderately soluble pigments?

A. It is a fallacy that you can do this by running a "dosage-viscosity" test of the dry blend, especially when there are moderately soluble pigments present. For insoluble pigments, it may work. You have to test first the most water soluble pigment and find the best dispersant and after that the rest of the pigments.

L. LLOYD HAANSTRA, Secretary

Piedmont

Apr. 15

Apr. 6

Jim Albright, of the Lilly Co., presented a program entitled "How TO PLAN AND PLANT A FLOWER GARDEN." Using slides and a taped program, the various effects of careful planning and the use of flower varieties were shown. Mr. Albright explained how this could enhance a yard or home, and offered suggestions on planting and raising flowers successfully.

SARA ROBINSON, Secretary

Pittsburgh

George Grossman, of the Q-Panel Co., presented "KNOW YOUR ENEMY—THE WEATHER."

Mr. Grossman discussed an instrument which duplicates the weather for testing purposes. The instrument, Mr. Grossman explained, is set up to a timer with sunlight (ultra violet), wetness, and temperature.

The sunlight spectrum and how it affected materials exposed to ultra violet light was discussed. The instrument is capable of duplicating sunlight at certain wave lengths which reproduces UV effects of sunlight in accelerated testing.

In conclusion, Mr. Grossman described the instrument as a "duplication of Mother Nature in weathering."

Q. Are the instrument's effects on pigments the same as the polymer? A. There are strong differences, depending on the pigment colors.

BILL CIBULA, Secretary

Rocky Mountain Apr. 6

Dr. Robert Athey, of Swedlow, Inc., gave a talk entitled "POLYMERIC OR-GANIC DISPERSANTS FOR PIGMENTS— PRINCIPLES AND PRACTICES."

DONALD R. BAGGE, Secretary

Southern

Mar. 10

Rich Johnson, of Cargill, Inc., gave a presentation entitled "COM-PARING HIGH-SOLIDS AND WATER-BORNE COATINGS TO CONVENTIONAL ENAMELS." He outlined some of the problems encountered in the use of each. B.L. BUDZIEN, Secretary

Toronto

Apr. 13

A talk entitled "WATER SOLUBLE ACRYLIC RESINS" was given by David Hickson.

R. KUHNEN, Secretary



Southern Society Officers for 1981–82. Left to right: President—Franklin D. Rector; President-Elect—Dan M. Dixon; Vice-President—William G. Early; and Secretary-Treasurer—James E. Geiger.



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Elections

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- ADESKO, PAUL L.—E.I. du Pont de Nemours & Co., Inc., Troy, MI.
- BALATAN, SERGIO E.-Inmont Corp., Detroit, MI.
- BROWN, WILLIAM B.—GM Research Laboratories, Birmingham, MI.

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ENDO, MACKENZIE K.—Argo Paint & Chemical Co., Westland, MI.

- HEMENWAY, KEVIN-Kush Industries, Roseville, MI.
- HENDRICK, PATRICIA A.—Wyandotte Paint Products, Inc., Troy.
- LELE, SUBHASH S.— BASF Wyandotte Corp., Holland, MI.
- SAGE, MARVIN-Grow Group, Inc., Troy.
- SAPPOK, REINHARD J.—BASF Wyandotte Corp., Holland.
- SCHELL, CHARLES E.—Precision Coatings, Walled Lake, MI.
- STEVENSON, WARREN-Inmont Corp., Detroit.

WROBBEL, MARK T.-Grow Group Inc., Troy.

Associate

CHERASARO, NICHOLAS J.—Tenneco Chemicals, Inc., Troy, MI.

MULLINS, ALLAN BOYD-Seibert Oxidermo, Inc., Detroit, MI.

KANSAS CITY

Active

MCFADDEN, RICHARD I.—Cook Paint & Varnish Co., North Kansas City, MO. REED, MICHAEL—The Valspar Corp., Kansas

City, MO.

LOUISVILLE

Active

- BUENTE, ROGER W.-Red Spot Paint & Varnish Co., Evansville, IN.
- LUTTERBACH, MARK A.—Red Spot Paint & Varnish Co., Evansville.
- WILLENBRINK, J.L. III—Willenbrink Enterprises, Louisville, KY.

Associate

GRISWOLD, JAMES H.—Diamond Shamrock, Louisville, KY.

SALTSMAN, JANICE A.—United Catalysts, Inc. Louisville.

NEW ENGLAND

Active

- ENSCOE, JOHN R.—Technical Coating Laboratories, Avon, CT.
- KARP, HERBERT E.—Technical Coating Laboratories, Avon.
- LONGHI, GERALD A.—Technical Coating Laboratories, Avon.
- PARKS, EDWARD W.—Parks Corp., Middleboro, MA.
- POLLANO, GAIL—Polyvinyl Chemical Industries, Wilmington, MA.
- ROBERTS, JAMES F.—Samuel Cabot, Inc., Chelsea.
- WARREN, ROBERT V.—Waterlac Industries, Inc., Danvers, MA.
- WILSON, WYMAN D.—Technical Coating Laboratories, Avon.

Associate

ARMSTRONG, RICHARD—Ropak Central, Inc. Wellesley, MA.

FLEMING, JAMES S.—American Can Co., Chestnut Hill, MA.

PENNINGTON, SAM-Tri State Corp., East Hartford, CT.

- VAN BEUSICHEM, WILLIAM-NL Chemicals/ NL Industries, Inc., Londonderry, NH.
- WOLKENBREIT, STEVEN—Uniroyal Chemical Co., Naugatuck, CT.

NEW YORK

Active

- ARGIRIADI, ANDREW—Camrex Reliance Paint Co., Brooklyn, NY.
- BECK, R. NORMAN-NL Chemicals/NL Industries, Inc., Hightstown, NJ.
- ERENRICH, ERIC H.-Allied Chemical Co., Morristown, NJ.
- FINK, KENNETH D.-Passonno Corp., Watervliet, NY.
- FLAUMENHAFT, FRANK-Lacquer & Chemical Corp., Brooklyn, NY.
- GREENE, MURRAY-Eastern Paint Co., Hawthorne, NJ.
- GREGG, DAVID E.-Engelhard M&C Corp., Edison, NJ.
- KICKI, EDWARD M.—Aurachem Corp., Harrison, NJ.
- MASCIALE, MICHAEL J.-Mobil Chemical Co., Edison, NJ.
- NANGRANI, KHEMCHAND—Dart Industries, Paramus, NJ.
- ROQUE, SALVADOR LUZ-United States Testing Co., Jersey City, NJ.

Associate

- BRAND, RICHARD J.—Tenneco Chemicals, Inc., Fords, NJ.
- BURRY, DONALD L.-Rohm and Haas Co., Elmwood Park, NJ.
- CARDIN, E. ROBERT-Rohm and Haas Co., Colts Neck, NJ.
- ERRICO, WALTER G.-O.A. Both Corp., Stockton, NJ.
- SHIBATA, KOICHI-Takeda Chemical Industries Ltd., New York, NY.

NORTHWESTERN

Active

- DANICK, CHUCK—Cargill, Inc., Minneapolis, MN.
- EDWARDS, JAMES N.-Valspar Corp., Minneapolis.

PACIFIC NORTHWEST

Active

DIBRINO, ANDREW W.-Drew Paints, Inc., Portland, OR.

Associate

- AMBROSE, C.M., JR.-C.M. Ambrose Co., Redmond, WA.
- CLELAND, EDWARD, D.—Chemcentral, Portland, OR.
- HOLTON, JAMES-Cyprus Industrial Minerals, Beaverton, OR.

Retired

LAUGHNAN, DON F.—Laughnan Consulting, Inc., Bellevue, WA.

SOUTHERN

Active

- BALKUS, ROBERT A.—AZS Chemical Co., Atlanta, GA.
- GAVLAK, WILLIAM M.-PPG Industries, Inc., East Point, GA.
- ROOT, RICHARD ALLEN-NER Data Products Co., Blytheville, AR.
- RUTHERFORD, HENRY S.-PPG Industries, Inc., East Point.
- SICKELS, EARLE F.—Delta Laboratories, Ocala, FL.
- WELLS, KYLE-Buckman Laboratories, Memphis, TN.

Associate

- BRUMBACK, CARL F.-Monsanto Co., Atlanta, GA.
- FOSTER, KEVIN D.-Alcoa Co., Atlanta.
- KENLINE, MARK A.—Spencer Kellogg Div., Atlanta.
- LIZZIO, WILLIAM T.—Union Chemicals Div., Memphis, TN.
- PENNARTZ, PHILLIP L.-E.I. duPont de Nemours & Co., Inc., Charlotte, NC.
- URANN, DAVID W.—Union Chemicals Div., Tampa, FL.
- WILLIAMS, FLOYD J.-Mobay Chemical Corp., Hendersonville, TN.

WESTERN NEW YORK

Associate

O'SHAUGHNESSY, JIM-Steep Rock Calcite Div., Gouverneur, NY.

FUTURE SOCIETY MEETINGS

Note to all Society Program Chairmen:

All Program Chairmen are urged to forward their Society's meeting agenda for the 1981–82 meeting season to Federation headquarters as soon as possible.—Ed.

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PNW Hosts Over 250 at Annual Symposium

A total of 262 members, guests, and spouses attended the 34th Annual Spring Symposium of the Pacific Northwest Society, held April 30, May 1 and 2 at Seattle's Washington Plaza Hotel.

President Curt Bailey, of Jarvie Paint Mfg. Co., presided at the event.

The Symposium Committee was headed by Bob Hogg, of Preservative Paint Co. Assisting him were: Curt Bailey, Dennis Hatfield, Joe McCambly, Bill Clary, Brad Wear, Bill Helzer, Lou Waldron, Bill Shackelford, Walt Sadowski, Ron Wade, Lynne Bailey, Diane Wear, Bob Osterlund, and Jim Roberts.

Technical program presentations featured the following:

"Flammability Potential of Coatings"—Elder Larson, of Shell Development Co. "Identifying and Correcting Film Surprises/Irregularities in Water-Borne and High Solids Industrial Coatings"— Cyriac P. Alexander, of Cargill, Inc.

"Reclaiming Waste Solvents Through In-Plant Distillation"—C. Kenneth Claunch, of Finish Engineering Co. (Presented by Sharon Vadnais, of E. T. Horn Co.).

"Water-Borne Maintenance Coatings"—David B. Norby, of Spencer-Kellogg Div. of Textron, Inc.

"High PVC Exterior Latex Paints"— G. W. Buttrich, of Union Carbide Corp.

"Dispersion of Carbon Black in Coatings Systems"—James W. Joudrey, of Columbian Chemical Co.

"Recycling Latex Wash Water—A Review of the Use of Paint Additives in Modern Coatings"—John J. Oates, of Troy Chemical Corp. "Safety Program for Mixers and High Speed Dispersers Used in the Coatings Industry"—Gloria Myers, of Myers Engineering Co.

Officers for the coming year will be: President—Dick Stewart, of Westcan Industrial Coatings Ltd.; President-Elect—Steve Norton, of Tenneco Chemicals; and Secretary—Bob Hogg, of Preservative Paint Co. The Treasurer's position has not yet been filled, and will be announced later. Deryk Pawsey, of Rohm and Haas of Canada Ltd., continues as Society Representative.

A Special Service Award was presented to former Society Representative John J. Filchak, of General Services Administration, for his outstanding contributions to the Pacific Northwest Society.

The 1982 Symposium will be held at the Bayshore Inn, Vancouver, on May 6-8.





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The conference will provide a forum for the discussion of new and improved processes, governmental environment, the present and future requirements of the industry, and results of new research.

The Association for Finishing Processes of the Society of Manufacturing Engineers, now invites the submission of abstracts of proposed papers on the various aspects of radiation curing.

All inquiries should be made to Susan Buhr, Technical Administrator, Association for Finishing Processes of the Society of Manufacturing Engineers, One SME Dr., P.O. Box 930, Dearborn, MI 48128.

Subcommittee Focuses on Zinc Rich Standards

With the purpose of developing standards, guides, and test methods for zinc rich and other galvanic protective coatings, members of Subcommittee D01.48 on Zinc Rich, an ad hoc group of Committee D-1 on Paint and Related Coatings and Materials of the American Society for Testing and Materials (ASTM), met in Orlando, FL, January 19.

The group, formerly Task Group D01.46.09 on Zinc Rich, was elevated to its new status by the Executive Committee with D-1. It is comprised of four groups, focusing on the determination of cure, laboratory evaluation, film integrity and solids by volume, and top coatings.

Elected Chairman of the group is Michael D. Tellor, of the Carboline Co., St. Louis, MO. Seymore Mark, of G & W Natural Resources Corp., Bethlehem, PA, was elected Vice-Chairman and serving as Secretary will be Ernest W. Horvick, of the Zinc Institute, New York, NY.

For further information on Subcommittee D01.48 meetings, contact Jane Turner, ASTM Standards Development Div., 1916 Race St., Philadelphia, PA 19103.

Powder Coating Institute Formed

Principal manufacturers serving the powder coating industry established The Powder Coating Institute on May 1, 1981. This nonprofit organization was formed for the purpose of advancing the utilization of powder coating as an economical, nonpolluting high quality finish for industrial products. For more information, contact Gordon E. Cole, Jr., PCI, 44 Husted Lane, Greenwich, CT 06830.

SUNY to Sponsor Adhesion Course

The State University of New York, Institute In Science and Technology, New Paltz, NY will sponsor a course entitled, "Fundamentals of Adhesion: Theory, Practice and Applications," October 7-9.

Designed for chemists, physicists, material scientists, and engineers, the course will feature the fundamentals of adhesion and a comprehensive review of the latest developments in the field of adhesion. Through lectures, theory, practical problems and the solutions which have been devised to "cure" adhesion-related problems will be discussed. In addition to lectures, technique demonstrations and hands-on experience will be presented.

For further information, contact Dr. Angelos V. Patsis, Director, Institute In Science and Technology, State University of New York, CSB 209, New Paltz, NY 12561.







Celanese Plastics & Specialties Co. has appointed Carolyn J. Hanson Senior Sales Representative for Specialty Resins. Headquartered in Charlotte, NC, Ms. Hanson will be responsible for the sale of the firm's epoxy resins, curing agents and acrylic resins which are used in industrial coatings, adhesives, and other uses in the Southeast. Ms. Hanson is a member of the Piedmont Society.

Also announced by the firm was the appointment of Linwood L. Creekmur, Jr. as Senior Sales Representative for Specialty Resins in Chicago, IL.

David A. "Skip" McDonnell was appointed Account Executive for Specialty Resins. Mr. McDonnell is a member of the Louisville Society. Dennis K. Bollenbach has been named regional Sales Manager, West, for Specialty Resins, Los Angeles, CA. Mr. Bollenbach is a Los Angeles Society member.

Don L. Mazzone has been promoted to General Manager of Operations for the Southwestern Region of The O'Brien Corp. He will be responsible for operations in the Southwestern Region, which is based in Houston, TX. Mr. Mazzone is a Golden Gate Society member.

George H. Wihelm has been appointed Director of Marketing for Spencer Kellogg Division of Textron, Inc. Also, Henry A. Kasprzak has been named Market Manager. Mr. Kasprzak is a member of the Western New York Society. Transferred to the Los Angeles Sales Office for the firm, was Perry A. Ciambella, Sales Representative. Mr. Ciambella is a C-D-I-C Society member.

Thomas H. Haag has been promoted by Rohm and Haas Co. to Market Area Manager, Trade Sales Coatings, in the Polymers, Resins & Monomers North America Business Team. He has been with the company since 1953.

Edward E. Raswyck, formerly Sales Manager, has been appointed Vice-President, Chemical Coatings, Reichhold Chemicals, Inc. Mr. Raswyck assumes the position formerly occupied by L.J. "Rocky" Rochenbach, who has retired after 40 years with the firm.









C.J. Hanson

D.L. Mazzone

Charles A. Kumins has formed his own Consulting Service at Epping Rd., Gates Mills, OH 44040. Mr. Kumins has 35 years of R&D experience in the coatings industry, 25 of which were as R&D director and Vice-President of three major firms. He holds more than 100 U.S. and foreign patents and has published extensively in scientific journals. He is Secretary of the Paint Research Institute and he presented the Mattiello Lecture at the Federation's 1979 Annual Meeting. Mr. Kumins was Chairman of the Gordon Research Conference on the Science of Adhesion in 1969.

NL Chemicals/NL Industries, Inc. has announced the appointment of George B. Wright as Lake Central Region Sales Manager. Mr. Wright is a member of the Cleveland Society.

Reliance Universal Inc. has appointed Walter M. McMahon, Director of Copon Technical Services. Also, Michael G. Falcone has been named Technical Director of the Houston operation. Mr. McMahon and Mr. Falcone are Houston Society members.

The Eastern Region Chemical Coatings staff of Glidden Coatings & Resins has announced the appointments of **Richard A. Wamsher**, as Field Sales Manager, Chemical Coatings and John M. Shaw, as Technical Service Manager. Both will be headquartered in Reading, PA.

Also announced by the firm, was the appointment of **Alan F. Lang**, as Product Manager, Coil Coatings for Glidden Chemical Coatings.

C. Joe Spangler has been named Regional Technical Manager for the southwest region of SCM Glidden Coatings & Resins, Dallas, TX. Mr. Spangler is a Southern Society member. C.A. Kumins

J.B. Converse

The appointment of Jeffrey B. Converse as National Sales Manager—Paint Additive Division has been announced by the office of the U.S. Marketing Division of Byk-Mallinckrodt Chemische Produkte GmbH Ltd.

Chemical Manufacturers Association has announced the appointment of **Dr. Carlos D. Stern** as Director of Environmental Programs.

Midland Division, The Dexter Corp. has made the following appointments. **Paul C. Waidzunas** has been promoted to the position of Senior Project Chemist of the Beer and Soft Drink Interior Spray Group of the Packaging Laboratory. **Robert M. Baker** has been named Senior Project Chemist, coordinator of the End Enamel Group in the Packaging Laboratory. Mr. Baker is a Chicago Society member.

NL Industries, Inc. has appointed William E. Parker, Corporate Vice-President. Mr. Parker also continues as President of NL Baroid, headquartered in Houston, TX.

Sun Chemical Corp. has announced several new Vice-Presidential appointments. Donald S. Bunin was named Vice-President and Group Director of Engineering and Manufacturing Services; Peter Ludwig, Vice-President and General Manager of the Pigments Division; William E. Morris, Vice-President and General Manager of the Chemicals Division, and Michael Pisetzner, Vice-President and Assistant General Manager of the Chemicals Group.

The appointment of **Richard W. Davis** as Sales Representative in New England for the Pigment and Additive Group was announced by Sandoz Colors and Chemicals. DeSoto, Inc., Des Plaines, IL, presented three of their scientists with the 1980 "Researcher of the Year" Award. **Robert Ansel and Fred Hawker**, Senior Research Chemists, and Victor Pietryga, Research Chemist, were honored for their accomplishments and developments for the firm. They are members of the Chicago Society.

Interstab Chemicals, Inc. has appointed **Robert William Diederich** as Southwest Regional Sales Manager for the Thermoset Process Chemical Division. He is a member of the Louisville Society.

Hercules Incorporated has named William E. Hosker Western Region Director. He will be headquartered in San Francisco, CA.

Tenneco Chemicals, Coatings and Colorants Department, has announced the following promotions within the Marketing Department. Samuel J. Bellettiere was appointed Product Manager, Coatings Additives. He is a member of the Philadelphia Society. James A. Dye was named Regional Manager, West Coast. Mr. Dye is a Los Angeles Society member. Wayne C. Cochran was promoted to Regional Manager. Chicago region, and Anthony L. DeGisi was named Louisville Regional Manager. Mr. DeGisi is a C-D-I-C Society member. Appointed Regional Manager of the Cleveland area was John T. McGroarty. He is a member of the Chicago Society.

Donald P. Miller has been named Manager of Marketing, Colorants, for the Organics Division of Tenneco Chemicals, Inc.

John A. Wright, Executive Vice-President, St. Joe Minerals Corp., President of St. Joe Lead Co., and St. Joe Resources Co., has been re-elected Chairman of the Board of Directors of Lead Industries Association, Inc.

Elected First Vice-Chairman was Allan K. Booth, President, Amax Lead & Zinc, Inc. and Keith C. Hendrick, President, Noranda Sales Corp., Ltd. was named Second Vice-Chairman. Others elected were Harold A. Krueger, General Manager, Ozark Lead Co.—Secretary; Wilbur R. Wenzel, Vice-President, Amax Lead & Zinc, Inc.—Treasurer; and L.A. Weible, Vice-President, Finance, St. Joe Lead Co.—Assistant Treasurer.

Officers elected included Werner T. Meyer, President; Jerome F. Smith, Vice-President; Helen L. Wilbur, Assistant Secretary; and D.L. Moore, Assistant Treasurer.



Fred Hawker, Senior Research Chemist; Victor Pietryga, Research Chemist; and Robert Ansel, Senior Research Chemist were presented with DeSoto, Inc.'s "Researcher of the Year" Award for 1980

Edward Erickson, Vice President of Stewart Paint Manufacturing Co., has retired after more than 43 years of service to the industry. Mr. Erickson was President of the Northwestern Paint and Varnish Production Club (now the Northwestern Society for Coatings Technology) in 1953, serving previously as Treasurer, Secretary, and Vice-President. Mr. Erickson was recently elected to honorary membership in the Northwestern Society.

D.H. Litter Co., Inc. has appointed **David Penichter** Technical Sales Representative, responsible for the New York and New Jersey areas.

Marilyn Unruh has been promoted to Technical Sales Representative at Thompson-Hayward Chemical Co., for the Industrial Chemical Division.

The Valspar Corp. has promoted **Robert Edenborg** to Senior Chemist of long-range development for the Chemical Coatings Division.

Illinois Minerals Co., Cairo, IL, has announced the recent appointment of George Wrape as National Sales Representative.

Frank Frey has joined the Textile Chemical Division of Dexter Chemical Corp. as a Technical Representative for the New York, New Jersey, and Pennsylvania areas. Harold L. Synder has been named Sales Manager for Chemcentral/Atlanta. Mr. Synder is a Southern Society member.

The Jones-Blair Co. has promoted William Yeargan to Corporate Purchasing Manager in Dallas, TX.

Robert E. Burks, Jr., has been named Acting Chairman of the Department of Polymer Science at the University of Southern Mississippi. Mr. Burks is a member of the Southern Society.

Robert D. Mangan has been named Sales Manager of 3M's Chemical Resources Division.

Buckman Laboratories, Inc. has announced the recent election of **Dr. Fred W. Raths** to Vice-President-Operations.

Drew Chemical Corp., Boonton, NJ has announced the following appointments. Robert G. O'Brien has been named Vice-President and General Counsel. Appointed Marketing Manager for the International Industrial Chemicals Division was Ronald J. Delavan. Bjorn Mattsson was named Market Manager for Food Processing Chemicals. David C. Longmore was appointed Product Manager, Specialty Chemicals, Europe, for the International Industrial Chemicals Division. Named as Supervisor, Environmental/Safety Assurance was Valerie L. Frankoski. James Donnelly has joined Deeks & Co., Inc., as a Sales Representative. Mr. Donnelly is a member of the Southern Society.

Dr. Peter Kamarchik has been named to the position of Research Associate for PPG Industries, Coatings & Resins Div., Research and Development Department. Dr. Kamarchik is a Pittsburgh Society member. Mark W. Kelly has joined TCR Industries, Carson, CA, as Northern California Sales Manager. Mr. Kelly has been associated with the industry for more than 30 years. He is a member of the St. Louis Society.

Jack D. Linn has been appointed Manager of Coil, Container and Appliance Products for PPG Industries' Coatings and Resins Division.



The Detroit Society for Coatings Technology has voted **Dr. Newell P. Beckwith**, Honorary Member.

A native of Omaha, NE, Dr. Beckwith is a graduate of North Dakota State University. He recently retired from Inmont Corp. after serving as Vice-President Managerial Operations Inmont U.S. and Vice-President of



Inmont U.S. and N.P. Beckwith Vice-President of International Marketing.

Dr. Beckwith is a Past-President of the Federation (1955) and has been a member of the Detroit Society for over 40 years. He has been active in the Paint Research Institute, serving as Secretary and Trustee. During 1980-81, Dr. Beckwith was an Ad Hoc Committee member for PRI.

Obituary

John Lawson, 96, died on February 13, 1981. He was former President of Enterprise Paint Manufacturing Co. In 1921, Mr. Lawson founded the Federal Varnish Co., which merged with Enterprise in 1926. He served on the National Paint and Coatings Association's Flax Development Committee, was NPCA Regional Vice-President, and was active in the Association's Scientific Section.

John W. "Jack" Callaghan, 65, a Sales Representative for the Minerals, Pigments, and Metals Division of Pfizer Inc., died on April 9. He was a member of the New York Society.

Arthur E. Stauderman, 82, died on April 24. A native of Brooklyn, NY he received a Chemical Engineering Degree from Pratt University. Mr. Stauderman was President of the Louisville Society in 1928 and was Federation President in 1938-39. He began his career in the paint industry in 1922 with Colonial Paint Co. in New York. From 1924 to 1942. Mr. Stauderman was associated with Peaslee-Gaulbert Co., Jones-Dabney Co. (part of Devoe & Raynolds), in Louisville. He then joined Schaefer Varnish Co., Louisville, until 1968, when he retired. He was a member of ASTM and ACS and was an Honorary Member of the Federation and the Louisville Society. He also taught several coating technology subjects at the University of Louisville and at Schaefer Varnish.

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SCAQMD Extends Amendments to Rule 1113

The Southern California Air Quality Management District (SCAQMD) Board of Directors has delayed ruling on amendments to the district's Rule 1113, which governs allowable levels of volatile organic emissions from architectural surface coatings.

At the April 3rd meeting in El Monte, CA, the board extended current emission limits (350 grams per liter of interior coatings and 250 grams per liter of exterior coatings) until September 4. During this period, the board will attempt to determine if proposed reductions in allowable amounts of volatile organic compounds (VOCs) will diminish the quality of affected coatings, make necessary more frequent painting, and thus increase rather than decrease the total amounts of emissions in the air.

Larry L. Thomas, Executive Director of the National Paint and Coatings Association, told the board that VOC limits of 400 grams per liter of nonflat coatings and 250 grams for flat coatings would allow the industry to maintain high product quality and make a positive contribution to clean air in California. (NPCA is also advocating use of "flat" and "nonflat" designations for coatings in the rule rather than the currently-used terms of "interior" and "exterior").

Thomas also stated the NPCA's opposition to the proposed May 1, 1983 deadline for further VOC reductions, and asked that certain product exemptions under Subsection (d) of Rule 1113 be made permanent rather than be allowed to expire within the now-prescribed 18 months. He stressed that it is not technically possible for the industry to meet the lower VOC levels suggested for 1983, but pointed out that if and when new technologies become available, deadlines and exemptions can be changed to reflect that availability.

Decisions on the 1983 deadline, on the "flat" and "nonflat" designations and on the permanency of the section (d) exemptions were also postponed by the board.

The April 3rd hearing was the most recent in a series of steps taken by California's South Coast Air Quality Management District in regard to Rule 1113 requested by the California Air Resources Board (CARB). CARB has requested SCAQMD to examine possible modifications and regulatory alternatives to the rule.

Battelle to Study PCB Destruction Technology

Researchers at Battelle's Columbus Laboratories have proposed a study to develop information concerning the current state-of-the-art of polychlorinated biphenyl (PCB) destruction technology.

The project, sponsored on a multiclient basis by several companies, is designed to meet the decision-making needs of firms that must safely dispose of PCB wastes, manufacturers of disposal equipment, and independent disposal contractors.

A number of conventional and alternative disposal techniques presently exist, according to William H. Mink, director of the program. However, the technical and economic feasibilities of degrading specific types of PCB wastes, while meeting pollution control guidelines, have not been comparatively analyzed. This information is essential to provide companies with a more rational basis for choosing the most promising destruction methods to solve their particular PCB disposal problems.

To obtain this information, the Battelle program will identify PCB waste disposal methods that appear promising for use with a number of common PCBcontaminated wastes.

The results of the program will benefit any firm facing a PCB-waste disposal problem. For the processors of small volumes of waste, the study will provide the necessary information to determine whether disposal options offered by different waste disposal firms are technically sound for their individual wastes. For processors of large waste streams, it will identify the economics for various disposal processes, confirming laboratory data on the processes, the process steps necessary to implement a disposal system, and the technical drawbacks for other than conventional incineration disposal processes. Equipment manufacturers and waste disposers will similarly benefit.

Participation in the 18-month study is open to companies at an investment of \$25,000 per company. Additional information can be obtained from William H. Mink, Battelle's Columbus Laboratories, 505 King Ave., Columbus, OH 43201.

Battelle Proposes Research On Wear-Resistant Coatings

Battelle's Columbus Laboratories have proposed a program to study the development of low-cost, wear-resistant protective materials. Researchers will center their study on Battelle's newly developed cubic boron nitride coatings.

During the program, which is sponsored by several companies, researchers will adapt the methodology used in producing these coatings to production line use. Potential coating applications include complex parts such as drill bits, mining tools, and dyes, as well as valve components, pump impellers, and engine parts. Additionally, the method could be used to apply cubic boron nitride to long service-life products and to coat large surfaces in one continuous process.

According to Battelle's Dr. Harry A. Beale, Director of the proposed research team, cubic boron nitride is an attractive coating because of its hard, wearresistant characteristics. Presently, it can only be produced by costly high-pressure technology.

The Battelle method, explained Dr. Beale, shows promise of economically applying the coating onto various base materials. With the method, boron and selected cubic phase stabilizers are evaporated in the presence of ammonia gas to deposit a cubic boron nitride coating.

As part of the study, Battelle initially will prepare boron alloy stock, study melting and evaporation of the stock, and characterize the coatings and optimize their wear-resistant properties. Experiments will accumulate engineering data for use in applying cubic boron nitride coatings. Samples will be prepared and distributed to member companies for their testing.

Experts in both materials and tribiology will conduct the project. Material specialists will concentrate on the improvement of materials and production and the identification of future applications. Tribiology experts will provide insight on wear mechanisms and processes and on the physical properties required for satisfactory performance.

Companies may join the two-year study for an investment of \$15,000 per year. Sponsors will receive licenses to Battelle patents in this field, whether these result from the group study or from applicable research previously conducted.

Additional information may be obtained from Dr. Harry Beale, Battelle's Columbus Laboratories, 505 King Ave., Columbus, OH 43201.

Methods for Unloading Acetic Acid

Two audiovisual presentations describing safe handling and proper methods for unloading acetic acid from tank cars and tank trucks are now available. One program details the various properties of acetic acid that should be considered when handling. The other offers step-by-step procedures for unloading acetic acid to help assure customer and shipper safety. For more information about the free programs, contact Air Products and Chemicals, Inc., Industrial Chemicals Div., P.O. Box 538, Allentown, PA 18105.

Production Control Programs

A newly issued four-page brochure describing computer programs designed for formula design and production control in paint and coatings operations is available. With the program package, users of manufacturer's color control systems can quickly and accurately design new coatings formulas, generate production batch tickets, store and retrieve formulas and maintain complete control over production and inventory. A flow chart illustrating operation of the system is contained in the brochure. For more information, contact Applied Color Systems, P.O. Box 5800, Princeton, NJ 08540.

Ultrasonic Filling System

A six-page brochure featuring a new ultrasonic filling system for paint and stain is now available. For a free brochure, contact Beltron Corp., P.O. Box 1000, Megill Rd., Farmingdale, NJ 07727.

Polyethylene Gels

A technical report describing the properties and preparation of polyethylene gels for paints and finishes is now available. The six-page report describes how low molecular weight polyethylene gels in various solvents are useful as a means of distributing polyethylene in a very finely divided state into products such as cosmetics, polishes, inks, paints, and lacquers. Various figures and tables illustrate explanations in the report. For a copy of "The Properties and the Preparation of A-C Polyethylene Gels," contact Allied Chemical Corp., Fibers and Plastics Co., A-C Polyethylene Dept., P.O. Box 2332R, Morris Township, NJ 07960

Air Quality Document

The Air Quality Committee of the Canadian Paint and Coatings Association has developed a concise document explaining air quality to the coatings industry's customers. Entitled "Coatings Industry Introduction to Air Quality," it is available in a three-ring, looseleaf format. Topics covered include a general background concerning air quality, how the coatings industry fits into the overall air quality picture, and the various options available for emission abatement. Also featured in the manual is a workbook section that enables an industrial applicator to determine the magnitude of any air quality problem. Priced at \$15, including two annual updates, the document is available to CPCA paint and coatings manufacturing members for distribution to their industrial coatings applicator customers. Write CPCA, 2050 Mansfield, Suite 800, Montreal, Quebec, Canada H3A 1Y9.

NETZSCH

Acrylic Emulsion

A comprehensive technical bulletin describing an acrylic emulsion, designed for use in the formulation of industrial maintenance topcoats and metal finishes has been published. For a copy of the free brochure, write Marketing Service, Rohm and Haas Co., Independence Mall West, Philadelphia, PA 19105.

Pigments

Corrosion-resistant and tannin-stainblocking pigments which contain no lead or toxic, heavy metal compounds are described in a four-page "Pigment Product Guide." The brochure summarizes features, specifications and suggested applications for corrosion-resistant boroand phospho-silicate based products and pigments. For a copy, write Halox Pigments, 425 Manor Oak One, 1910 Cochran Rd., Pittsburgh, PA 15220.

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Platy Talcs

A new technical bulletin featuring platy talcs is now available. These platy talcs are refined from naturally occurring hydrous magnesium silicates, a unique class of nonmetallic minerals exhibiting low abrasion, heat resistance and easy dispersion in a variety of systems. The bulletin can be obtained from Minerals & Chemicals Div., Engelhard Minerals & Chemicals Corp., Menlo Park, Edison, NJ 08837.

On-Line Color Measurement

A new scanning color eye on-line color measurement system is the subject of recently published literature. The system has the capability of scanning the entire width of a web and measures color at many variable points rather than at one fixed point, allowing the user to compare the color across the entire web. For more information, contact Color Communications, Macbeth, P.O. Box 950, Newburgh, NY 12550.

Pigment Particle

A brochure featuring the technical advantages of flushed color over traditional dispersions has been published. A copy is available from the Hilton-Davis Chemical Div., Color Dept., 2235 Langdon Farm Rd., Cincinnati, OH 45237.

Vinyl Resins

Vinyl resins for coatings are described in a 38-page technical booklet and a 6-page fold-out selection guide which have been recently published. This literature discusses ten vinyl resins, produced by a proprietary solution polymerization process, which provides advantages in vinyl coatings. An applications table indicates the suitability of each resin in packaging, product finishes, building products, marine and maintenance, magnetic tapes, inks and adhesives. Copies of the technical booklet, "UCAR Solution Vinyl Resins for Coatings," (F-48210) and the "Selection Guide," (F-48258), are available from Union Carbide Corp., Coatings Materials Div., Dept. K3442, Danbury, CT 06817.

Pumps

An entire line of progressive cavity pumps is discussed and illustrated in a new, four-page brochure. Applications, general specifications, and available options are featured for each pump. For a free copy of the brochure, write Netzsch, Inc., Nemo Pump Div., Pickering Creek Industrial Park, Lionville, PA 19353.

Thermoplastic Polyimide

New technical data on the processing, application, and properties of a thermoplastic polyimide soluble in common solvents is featured in recent literature. To receive this information, write Resins Dept., CIBA-Geigy Corp., Saw Mill River Rd., Ardsley, NY 10502.

Epoxy Coating, Water-Borne Primer

A new silicone epoxy coating for metal surfaces and a new turbine-grade waterborne alkyd primer to protect exterior metal surfaces are featured in two recently published brochures. The applications, advantages, and features are described for both. For more information, write General Electric Co., Insulating Material Product Section, Dept. 812, One Campbell Rd., Schenectady, NY 12345.

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Information Services

The National Technical Information Service (NTIS) of the U.S. Department of Commerce is a central source for the public sale of Government-sponsored research, development, and engineering reports and other analyses. Most reports are available in paper copy or microfiche. Some reports are available in other forms, such as magnetic tape, punched cards, or 16mm microfilm (reel or cartridge). A recent issue of one of their annually indexed abstract newsletters. Materials Science, contained such topics of interest as "Scale-up of a Titanium Carbonitride Coating System for Titanium Alloys," "Method of Coating Silicon Nitride Bodies," and "Ultra-Black Coating Due to Surface Morphology." The NTIS Information Center can be contacted by calling 703-487-4600. The abstract newsletter, Materials Sciences, can be ordered, at an annual subscription cost of \$70, by writing NTIS, 5285 Port Royal Rd., Springfield, VA 22161, or by calling 703-487-4630.

Leveling Agent

A water reducible, anti-cratering leveling agent, designed for water soluble and emulsion based coatings to improve appearance and application, is the subject of new literature. For more information, write Paint Chemicals, Inc., 8012 S. Chicago Ave., Chicago, IL 60617.

Chromatography Products

Literature describing a new line of unique chromatography products, designed to improve speed, reproducibility and efficiency in areas which have relied on more classical, time-consuming and manual operations, is available. For further information, write Contact Product Manager, Separation Sciences, J.T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ 08865.

Adjustable Stator for Pumps

Literature featuring an adjustable stator option for cavity pumps, designed to compensate for changes in the size and shape of the internal pump cavity due to wear or thermal variations, has recently been published. For more information, write Netzsch Inc., Pickering Creek Industrial Park, Lionville, PA 19353.

Pin Hole Detectors

A new series of pin hole detectors for detecting coating flaws in paint, plastics, varnish, and epoxy, when applied to any conductive substrate, is the subject of new literature. For information, write Mr. Frank Rueter, Vice-President Marketing, Zorelco Ltd., P.O. Box 25468, Dept. B 18, Cleveland, OH 44125.

Atomic Spectroscopy Data System

New literature is available featuring a new atomic spectroscopy data system for graphite furnace work. It describes the system which includes a terminal with graphics board, interface, connectable cable, and graphics software. For more information, write the Perkin-Elmer Corp., Main Ave., Mail Station 12, Norwalk, CT 06856.

Colorimeter System

A colorimeter quality control instrument which has the ability to measure extremely large and bulky objects that cannot be readily presented to a conventional colorimeter is the subject of new literature. For more information, write Reva Goldman, Advertising and Sales Promotion, Pacific Scientific, Gardner Laboratory Div., P.O. Box 5728, 5521 Landy Lane, Bethesda, MD 20014.

Chlorinated Rubber

A six-page color brochure is available describing the advantages of chlorinated rubber as an important raw material in paint formulations to offset the effects of acids, alkalies, salts, fungi, fresh and saltwater. For a copy of "Corrosion Protection," write Hercules Incorporated, Product Inquiry, 910 Market St., Wilmington, DE 19899.

Flame Retardant Latexes

Halogenated based latexes, which combine inherent flame retardancy and low smoke generation with the safety and easy handling of standard latexes, are the subject of recent literature. For more information, write Arapahoe Chemicals, Inc., Applied Products Dept., 2075 North 55th St., Boulder, CO 80301.

Acrylic Emulsions

Two complete and up-to-date technical bulletins featuring acrylic emulsions have been published. The first features a hydroxyl functional acrylic emulsion polymer, designed for use in formulation coil coatings for aluminum and galvanized steel. The other bulletin discusses a water-borne thermosetting acrylic polymer designed for use in formulating coil coating primers. Physical and rheological properties, starting point formulations, formulation techniques, cure profiles, and safe handling information are featured. For more information on Rhoplex AC-1533 and Rhoplex AC-1561, contact Marketing Services, Rohm and Haas Co., Independence Mall West, Philadelphia, PA 19105.

Thickness Gauge

Literature featuring a new portable coating thickness gauge is available. Write Zorelco Ltd., P.O. Box 25468, Cleveland, OH 44125.



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Corrosion Coatings. (WC) (To 40)
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Marine Coatings. (SO) (To 37)
Analytical Chemist, Midwest (34+)
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Self-starter with strong interpersonal skills and demonstrated record of accomplishment. Send resume and cover letter to Marianne Levine, James River Graphics, Inc., 28 Gaylord Street, South Hadley, MA 01075.

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Coming Events

FEDERATION MEETINGS

(Oct. 28-30)—59th Annual Meeting and 46th Paint Industries' Show. Cobo Hall, Detroit, MI. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

1982

(Apr. 29-30)—Spring Meetings. Society Officers on 29th; Board of Directors on 30th. Boston, MA. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

(Nov. 3-5)—60th Annual Meeting and 47th Paint Industries' Show. Sheraton Washington Hotel, Washington, D.C. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

SPECIAL SOCIETY MEETINGS

(Sept. 23-24)—Montreal and Toronto Societies Joint Symposium on "Coatings Directions for the 80's."

1982

(Mar. 10-12)—Southern Society Annual Meeting. Hyatt Regency, Savannah, Ga. (Dan Dixon, Freeport Kaolin Co., P.O. Box 337, Gordon, GA 31031). (Mar. 23-24)—25th Annual Technical Conference of the Cleveland Society for Coatings Technology. Baldwin-Wallace College, Berea, OH.

(Apr. 22-24)—Southwestern Paint Convention. Shamrock Hilton Hotel, Houston, TX.

(May 6–8)—Pacific Northwest Society. Annual Symposium. Vancouver, B.C.

1983

(Feb. 23-25)—16th Biennial Western Coatings Societies' Symposium and Show. Hyatt Regency, San Francisco, CA.

OTHER ORGANIZATIONS

(Aug. 10-14) —"Introductory Short Course on Composition of Coatings." University of Missouri-Rolla, Rolla, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(Aug. 31-Sept. 4) —"Introduction to Paint Formulation" Short Course. University of Missouri-Rolla, Rolla, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).



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Please make checks payable in U.S. funds. Pennsylvania residents, please add 6% sales tax. (Sept. 7–11) — "Advanced Paint Formulation" Short Course. University of Missouri-Rolla, Rolla, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, MO 55401.

(Sept. 13–16)—Canadian Paint Manufacturers Association Annual Meeting. Four Seasons Hotel, Vancouver, B.C. (Lydia Palazzi, Canadian Paint Manufacturers Assn., 515 St. Catherine St. W., Montreal, Que., Canada H3B 1B4.

(Sept. 14–16)—Second International Conference on "The Durability of Building Materials and Components." Gaithersburg, MD. (Dr. Geoffrey Frohnsdorff, B348, Bldg. 226, Center for Building Technology, National Bureau of Standards, Washington, D.C. 20234).

(Sept. 20-25)—4th Congress of the Association Internationale de la Couleur, "COLOR 81." International Congress Centre (ICC), Berlin (West), Germany. (Prof. Dr. Heinz Terstiege, (AIC COLOR 81), Bundesanstalt fur Materialprufung (BAM), Unter den Eichen 87, D-1000 Berlin 45, Federal Republic of Germany).

(Sept. 21–22) — "Techniques and Mechanics of Marketing Specialty Chemicals" Short Course. Hilton Plaza Inn, Kansas City, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri–Rolla, Rolla, MO 65401).

(Sept. 23-24)—"Managing for Innovation in Coatings" Short Course. Hilton Plaza Inn, Kansas City, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(Sept. 28–29) —Golden Jubilee of Colour in the CIE. The Colour Group (Great Britain). Imperial College, London, England. (Ms. M.B. Halstead, Thorn Lighting Ltd., Great Cambridge Rd., Enfield, Middlesex EN1 1UL, England).

(Oct. 7–9)—"Fundamentals of Adhesion: Theory, Practice and Applications" Course. State University of New York, Institute In Science and Technology, New Paltz, NY. (Dr. Angelos V. Patsis, Director, Institute In Science and Technology, State University of New York, CSB 209, New Paltz, NY 12561).

(Oct. 13–15)—Association for Finishing Processes of the Society of Manufacturing Engineers. "Finishing '81" Conference and Exposition, "Economics, Compliance, and Energy." Cobo Hall, Detroit, MI. (William J. Yeates, Executive Director AFP/SME, One SME Dr., P.O. Box 930, Dearborn, MI 48128).

(Oct. 13-16) — "Formula 81". RAI Exhibition Centre, Amsterdam, Holland.

(Oct. 25–27)—"Women in Coatings—Meeting the Challenges" Short Course. Detroit, MI (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401). (Nov. 2-4)—American Society for Testing and Materials Committee D-33 on Protective Coating and Lining Work for Power Generation Facilities Meeting. Monteleone Hotel, New Orleans, LA. (ASTM, 1916 Race St., Phila., PA 19103).

(Nov. 3–4) — Decorating Plastic RETEC, 5th Annual Regional Technical Conference, Society of Plastic Engineers, Decorating Division. Louisville, KY. (Edward S. Stumpek, General Electric, One Plastics Ave., Pittsfield, MA 01201).

(Nov. 4–6)—American Society for Testing and Materials Committee, Utilities Nuclear Coating Work Committee Meeting. Monteleone Hotel, New Orleans, LA. (ASTM, 1916 Race St., Phila., PA 19103).

(Nov. 10–12) — "Refresher for Painting Contractors, Maintenance Engineers and Inspectors" Short Course. Hilton Plaza Inn, Kansas City, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(Nov. 17-19) — "Job Estimating Workshop for Painting Contractors." Granada Royale, Kansas City, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(Dec. 9)—American Society for Testing and Materials Symposium on Selection and Use of Wear Tests for Coatings. Phoenix, AZ. (ASTM, 1916 Race St., Philadelphia, PA 19103.)

1982

(Feb. 7-10)—Inter-Society Color Council. Williamsburg Conference, Williamsburg, VA.

(May 9-14)-XVIth Congress of FATIPEC, Brussels, Belgium.

(Oct. 11–13)—10th Congress of the Federation of Scandinavian Paint and Varnish Technologists. Copenhagen, Denmark. (G. Christensen, Sadolin & Holmblad Ltd., Holmbladsgade 70, DK-2300, Copenhagen S, Denmark).

1983

(July)—25th Annual Pacific Coatings Convention. Melbourne, Australia. (O.C.C.A.A., 1983 Pacific Coatings Convention, C/- Tioxide Australis Pty. Ltd., Private Bag 13, Ascot Vale, Victoria, 3032, Australia).

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Vol. 53, No. 678, July 1981

Humbug' from Hillman

Lewis Hosfeld has sent along a few profound definitions.

Serendipity—Looking for a needle in a haystack and finding the farmer's daughter.

Standing Ovation-Laying an egg without sitting.

A Finagle Law—Once a job is fouled up, anything you do makes it worse.

And from Milt Glaser, your friendly Past President, we have-

Law of Thermodynamics-

- 1. You cannot win.
- 2. You cannot break even.
- 3. You cannot get out of the game.

"Humbug from Hillman" has been dedicated to a policy of offering educational services. Therefore, in keeping with the modern educational trend of spending more time in filching exam questions than in studying, we publish below an examination sent to us in error by an anonymous filcher. All you have to do is to find the appropriate course.—Herb Hillman

FINAL EXAM

Instructions: Read each question carefully. Answer each question. Time limit— 4 hours. Begin immediately.

MUSIC:

Write a piano concerto. Orchestrate and perform it with flute and drum. You will find a piano under your seat.

BIOLOGY:

Create life. Estimate the difference in subsequent human culture if this form of life had developed 500 million years earlier, with special attention to its probable effect on the English parliamentary system. Prove your thesis.

HEALTH

You have been provided with a razor blade, a piece of gauze, and a bottle of Scotch. Remove your appendix. Do not suture until your work has been inspected. You have fifteen minutes.

LANGUAGES:

2,500 riot-crazed aborigines are storming the classroom. Calm them. You may use any ancient language except Latin or Greek.

PSYCHOLOGY:

Based on your knowledge of their works, evaluate the emotional stability, degree of adjustment, and repressed frustrations of each of the following: Alexander of Apfrodasias, Ramses II, Gregory of Micea, and Hammurabi. Support your evaluation with quotations from each man's work, making appropriate references. It is not necessary to translate.

SOCIOLOGY:

Estimate the sociological problems which might accompany the end of the world. Construct an experiment to test your theory.

MANAGEMENT SCIENCE:

Define Management. Define Science. How do they relate? Why? Create a generalized algorithm to optimize all managerial decisions. Assuming an 1130 CPU supporting 50 terminals each terminal to activate your algorithm; design the communications interface and all necessary control programs.

ENGINEERING:

The disassembled parts of a high-powered rifle have been placed in a box on your desk. You will also find an instruction manual, printed in Swahili. In ten minutes a hungry Bengal tiger will be admitted to the room. Take whatever action you feel appropriate. Be prepared to justify your decision.

POLITICAL SCIENCE:

There is a red telephone on the desk beside you. Start WW III. Report at length on its socio-political effects, if any.

EPISTEMOLOGY:

Take a position for or against truth. Prove the validity of your position.

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