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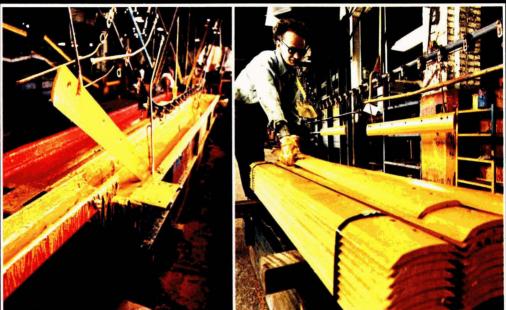
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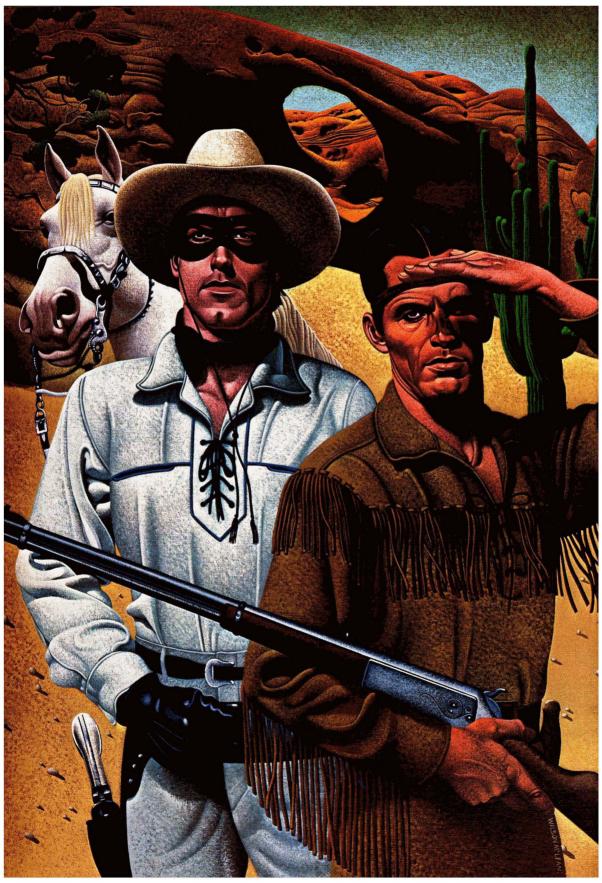
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Comment

The Left and Right Hands

The author of a "Letter to the Editor" in this issue feels that the coatings industry has all but thrown in the towel with regard to governmental regulations limiting the amount of volatile organic solvents in both trade sales and industrial coatings.

The result, he claims, will be "the further erosion of the paint industry as more and more surfaces are surrendered without a struggle."

Trouble is that either industry's voice has not been loud enough or government can't hear too well.

Anyway, now comes the hopeful word that the Department of Commerce has been made aware of these developments. The DOC Deputy Assistant Secretary for Environmental Affairs, after being briefed by NPCA, expressed concern about the fate of the small manufacturer if it turns out that only large companies will have the technical and manufacturing know-how to produce coatings that conform with strict governmental regulations.

And what will happen to the products themselves? DOC was advised that prices will certainly go up, but not necessarily performance characteristics.

Now that the right hand of government knows what the left hand is doing, perhaps there is a way to get them to shake on a deal the industry has been pushing for all along: quality coatings that do a job in protecting both the surfaces to which they are applied - and - the best interests of the consumer.—FJB

New A-C[®] 392

The key that opens giant new profit opportunities from the strippable coatings market.

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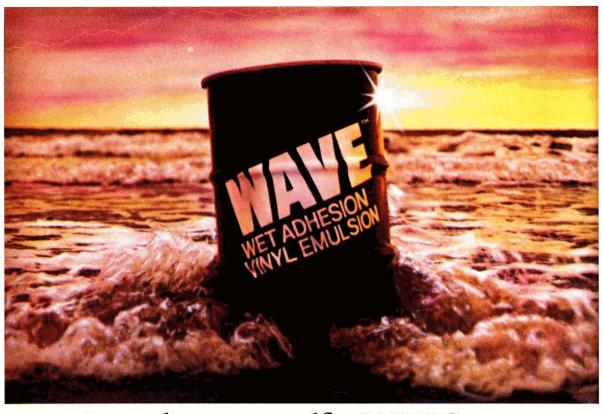
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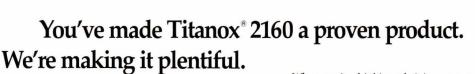
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EFFECT OF REACTION PATHWAY ON EMULSION POLYMER STRUCTURE—K.L. Hoy

Journal of Coatings Technology, 51, No. 651, 27 (Apr. 1979)

Most latexes offered commercially are produced by a semicontinuous batch process. In this process the particles are usually initiated from a batch charge of monomer, catalyst, surfactant, etc., and the remaining monomer is continuously added to the reaction vessel during the course of the polymerization. Other ingredients, such as additional catalyst, surfactant, stabilizer, buffer, etc., may also be added during the polymerization. The exact order of the additions are varied depending upon the effect desired by the latex chemist.

With such a wide latitude of operating procedures, it is not surprising that similar latex products produced by this general process exhibit strikingly different physical, formulation, and performance properties even though the actual compositions are nearly identical. The author attempts to delineate a "critical few" variables which are often employed by the latex chemist and to establish the effect that these variables have on the structure of the latex particle. Several novel methods of controlling the emulsion polymer structure to produce the desired performance properties are discussed. In addition, a method for the synthesis of gradient polymers and their respective properties as possible coatings polymers are reported.

COATING DURABILITY ON ORGANOLEAD-TREATED SOUTHERN PINE IN EXTERIOR EXPOSURE—H.M. Barnes

Journal of Coatings Technology, 51, No. 651, 43 (Apr. 1979)

Three coatings were applied to organolead-treated southern pine and exposed at 45° south. Significant improvement in the durability of a vinyl-acrylic latex and an alkyd paint on treated wood was demonstrated. No increase in the durability of a phenolic spar varnish was observed. Improved durability appeared to be independent of the type of organolead compound or the strength of treating solutions used.

STERIC STABILIZATION OF SURFACE-COATED TI-TANIUM DIOXIDE PIGMENTS BY ADSORBED METHYL METHACRYLATE COPOLYMERS—G.J. Howard and Choy Chow Ma

Journal of Coatings Technology, 51, No. 651, 47 (Apr. 1979)

The solution adsorption of some copolymers of methyl methacrylate onto a series of titanium dioxide pigments, which had been coated to impart various degrees of acidity to their surfaces, has been studied and, at the same time, the colloidal stability of the dispersions has been assessed. Homopolymers adsorb poorly from methyl ethyl ketone solutions and do not stabilize dispersions of the coated pigments; however, they are better adsorbed from their solutions in toluene and are then effective in dispersion.

Incorporation of a very small quantity of carboxylic acid groups into the macromolecular chain increases the adsorption and, provided the surface coverage is high, has a beneficial effect on dispersion stability. The extent of copolymer adsorption depends in considerable measure on the solubility parameter of the solvent. Copolymers with small amounts of nitrile, acrylamide, pyridyl, and hydroxyl groups also show enhanced adsorptions but do not, in general, improve dispersion stability except for some cationic copolymers on the more acid pigments. The relations between polymer adsorption and polymer structure, surface composition and solvent nature are discussed in terms of general acid-base interactions.

EFFECT OF TURNOVER RATE ON SOLID CONTENT IN DIP-COATING BATH—T. Sato

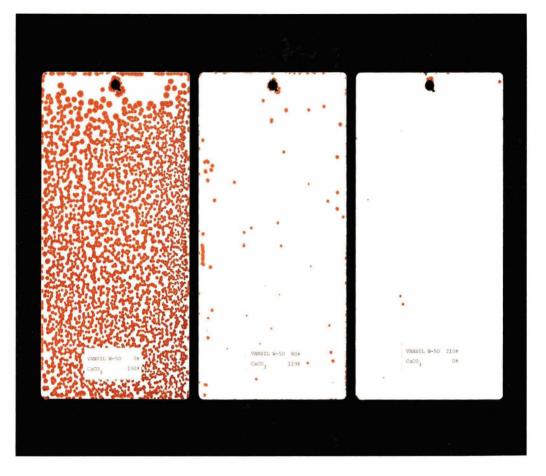
Journal of Coatings Technology. 51, No. 651, 61 (Apr. 1979)

The effect of turnover rate on the change in solid content of the dip-coating bath was theoretically calculated assuming that the evaporation rate of solvent is constant and the bath is replenished by the same paint as that in the original bath.

The results showed that the increase in the bath solid in m turnover, ΔC_m , is given by

(Continued)

Journal of Coatings Technology



Prevent early rusting from acrylic primers with VANSIL W.

The un-retouched lab photos above, dramatically demonstrate the rust-fighting property of VANSIL W (Wollastonite) compared with the popularly used extender, calcium carbonate. As the volume of VANSIL W was increased in these acrylic maintenance paint formulas, flash and early rusting diminished, then disappeared altogether.

The reason for VANSIL W's rust-inhibiting property is basic. VANSIL W acts as an effective buffer to maintain a desirable

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$$\Delta C_{m} = K_{t} \left\{ 1 - \left(1 - \frac{1}{t}\right)^{mt} \right\}$$
$$K = \frac{a C_{o}}{V}$$

where t is the number of days for one turnover, a is a volume of solvent evaporated, V is a volume of paint in the bath, and C_o is a solid content in the original bath. The solid content of replenish paint to maintain the bath solid constant, C_r , is given by

$$C_r = \frac{C_o^2}{C_o + K_t}$$

The validity of these equations was examined by a simulation experiment using sugar solution. The experimental results agreed well with the theoretical results.

INTERPLANT QUALITY CONTROL BY MEANS OF SIMPLE TRISTIMULUS COLORIMETERS—D.H. Cook

Journal of Coatings Technology, 51, No. 651, 64 (Apr. 1979)

The problem of color control of products made at different locations but marketed nationally with the same merchandizing aids has become increasingly acute, especially with frequent product changes to meet a competitive market.

The unreliability of wet standards has long been recog-

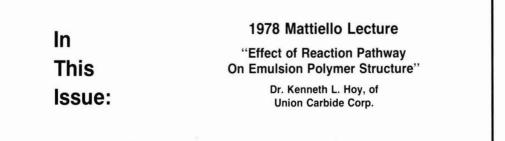
nized and the time needed to produce and maintain master standards makes them impractical for most latex or trade sales products. Establishment of working standards also becomes impractical when the manufacturing facilities are widely separated. Because of this it has become necessary to establish a way of communicating color, strength, and acceptable tolerances by means of finite instrumental figures to maintain not only batch-tobatch but plant-to-plant reproducibility of a product through the use of simple colorimeters.

A review of the methods used to establish and maintain a successful system is presented.

RE-SEARCH FOR OPPORTUNITY-C.M. Hansen

Journal of Coatings Technology, 51, No. 651, 66 (Apr. 1979)

A research institute with a permanent staff and modern equipment has the capacity to serve industry and government in a unique manner. Opportunities are presented in the form of authorized analyses and evaluations of coatings materials and performance, equipment evaluation prior to possible purchase by an industrial member, and a wide variety of projects (information-opportunity) ranging from waste disposal through fundamental concepts such as solubility, evaporation, permeation, colloid stability, rheology and the like. Problems and opportunities arising from environmental concern are increasing and research centers with combined industrial and governmental support are quite important in Scandinavia.



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HALOX Pigments offers formulating guidelines for paint producers

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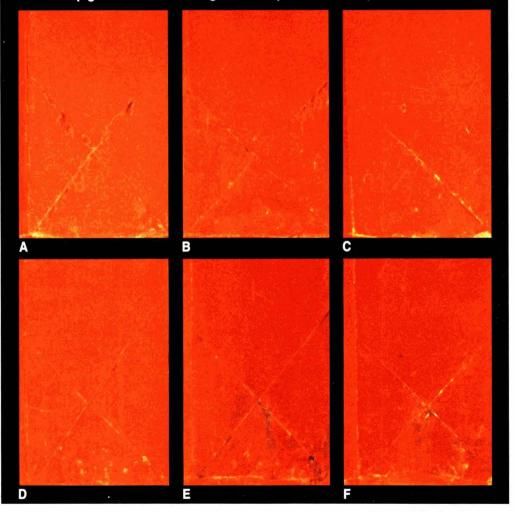
Extender Selection; Loading Levels and Inhibition; Oil Length Selection; Film Thickness; Halox Pigments in Alkyd, Chlorinated Rubber, Epoxies; Halox Pigments in Water-borne Vehicles; Halox Pigment Formulating Guide.

Technical Report TR8 "Halox Pigment & P.V.C.", is available now and we invite your inquiry for this information.



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CW221 at pigment volume loading from 47.3 percent to 18.7 percent.



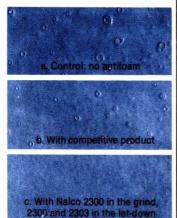
Journal of Coatings Technology

How to Select the Right Antifoam for Water-Based Paints

Results are What Count

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- 2. It should be persistent.
- It should not adversely affect color acceptance, gloss, water sensitivity, or intercoat adhesion.
- It should not cause surface defects such as crawling, pinholes, or fisheyes.

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A Systematic Approach

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

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

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

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



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

A Bank of Knowledge

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

A Broad Line of Products



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

How to Get Started

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

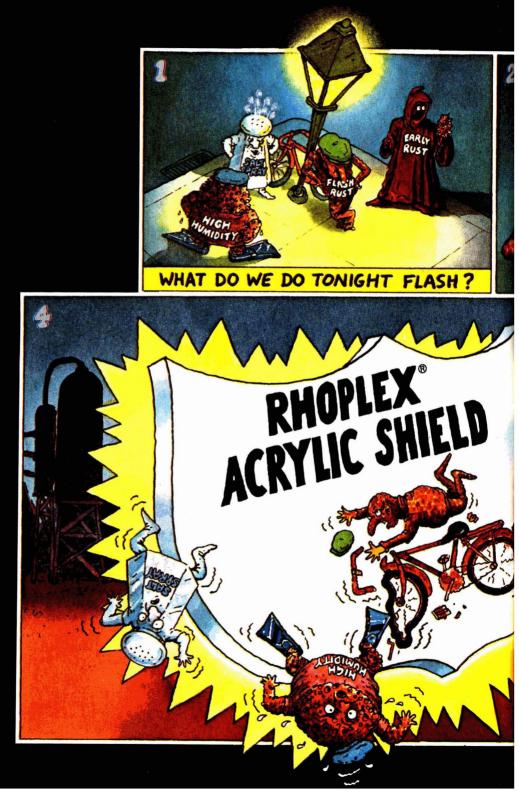
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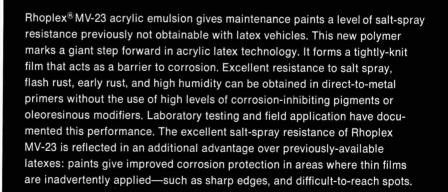
Vol. 51, No. 651, April 1979

RHOPLEX[®] MV-23 zaps salt spray, flash rust, early rust, high humidity, stains.





HIGH



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The barrier capability of Rhoplex MV-23 also has another valuable application ... in stain-resistant primers of many types. Exterior—over knots and staining woods such as cedar, redwood, and pine. Interior—for covering stained ceilings and walls. Write for a polymer sample and literature.



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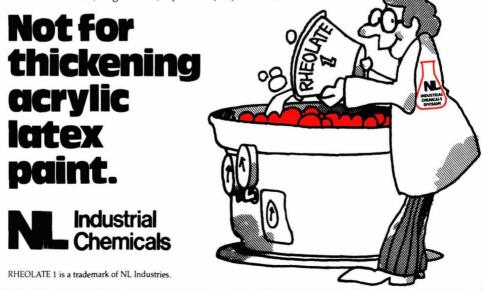
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Charles Kumins, of Tremco Inc., To Present 1979 Mattiello Lecture At Federation Annual Meeting in St. Louis

The Federation of Societies for Coatings Technology is pleased to announce that Charles Kumins, Director of Research and Development of Tremco Incorporated, Cleveland, Ohio, and Secretary and Trustee of the Paint Research Institute, will present the 1979 Joseph J. Mattiello Memorial Lecture at the 57th Annual Meeting of the Federation. to be held October 3-5 at the Convention Center, St. Louis, Mo.

Mr. Kumins will speak on "Physical Chemical Models for Organic Protective Coatings" at the morning session on October 5.

Early Career

A native of New York City, Mr. Kumins received the B.S. Degree in Chemistry from the College of the City of New York and the M.S. Degree in Physical Chemistry from the Polytechnic Institute of Brooklyn. He continued his graduate education in Physical Chemistry (while employed) at New York University.

He began his career at the Research Laboratory of the Titanium Div. of the former National Lead Co., Sayreville, N.J., where he worked on the chemistry of titanium oxides, particle size studies, and surface treatment of pigments to alter their performance properties. Later, in collaboration with A.E. Jacobsen, he took part in extensive studies on the photo-chemistry of titanium oxides and its relationship to chalking.

At a time when the exact role of light energy was being actively debated, it was shown by thermodynamic analysis, despite the very high free energy of formation of TiO₂ from its elements (about 50 K Cal/mol which made it one of the most stable oxides), that in organic media the combined action of absorbed light and water provided favorable energetics for the oxidation of the organic vehicle and the reduction of the TiO2 to Ti₂O₃. The variation in chalking of the same TiO2 in different vehicle systems could be accounted for by the difference in the value of the free energy change for the redoxreaction. It also offered an explanation for the observation that once chalking starts it continues at a rapidly escalating rate since the reduced product (Ti₂O₃) is easily reoxidized in the dark to TiO2. However, it is not of pigmentary grade, and on the next cycle of light exposure it easily participates in



the oxidation reduction process to destroy the binder with consequent chalking. Some of this work was part of Mr. Kumins' Master's Thesis.

As a result of these studies, a test for evaluation of the chalking properties of different TiO_2 pigments was devised which permitted obtaining results from as rapidly as five minutes to 24 hours. To obtain the same information, fence exposures from 8 weeks to 2 years (for the most resistant types) were usually required. The test, verified by years of cross-correlation with field exposure, has aided immensely in the research aimed at producing chalk-resistant pigments.

Work on Extender Pigments

Subsequently, Mr. Kumins became associated with the Michigan Alkali Co. (now Wyandotte Chemical Co.) where he was a group leader in the Extender Pigment Section. His efforts were directed toward the surface treatment of calcium carbonates, to make them compatible with aqueous and nonaqueous systems, particle-size control and measurement, and methods for preparation of the different crystal modifications of the calcium carbonate. Rheological studies on these modifications were made and published. They provided the first indications of the presence of long-range interactions between organic molecules. The work resulted in an extremely economical surface treatment which drastically improved the leveling properties of flat paints containing large amounts of the extender. Another achievement was the development of a method for the preparation of an exceptionally small particle size carbonate which imparted reinforcing properties to rubber formulations.

Paints for Production Of Zeolites

He next joined the Central Research Laboratories of the Interchemical Co. (now Inmont Corp.) as head of the Inorganic Laboratory. Research was devoted to high temperature solid state reactions, metallo organics, and fine particle pigments preparation.

During World War II, Mr. Kumins was concerned with projects under the auspices of the Office of Scientific Research and Development through the National Defense Research Committee. Returning to peacetime activities, his efforts resulted in several patented methods for the production of zeolites, customarily called "Molecular Sieves" in the industry. Based on crystallographic studies that the pigment ultramarine blue was a clathrate compound, whose polysulfide molecules were caged within the zeolites, new and rapid syntheses were developed to produce a colorant of exceptional strength. He also synthesized an iron organic oligomer from which transparent, extremely lightfast coatings could be prepared. He called it "Midas Gold". It has been marketed in several modifications, and is used extensively in metallic automotive finishes.

Later, he was appointed Assistant Director of the Central Research Laboratory and assigned the responsibilities for the Textile Printing Ink, the Industrial Finishes, Sealants and Adhesives, Dispersions, Electro static Copying and the Physical Chemistry Sections since the common denominator for all these sections included studies of the effects of surface chemistry and the interactions between multi-component liquid and solid phases. In these activities, he and his colleagues invented and patented foam-based printing systems, cationic (Continued)

1979 FSCT Annual Meeting Highlights St. Louis, Mo. October 3-5

Program

The 57th Annual Meeting program will open Wednesday, October 3, at the Convention Center in St. Louis.

Program Chairman Morris Coffino, of D.H. Litter Co., Inc., New York, has announced the following planned presentations:

- Keynote Address by Newscaster/TV Commentator Howard K. Smith (see March JCT).
- · Constituent Society Papers
- Roon Awards Papers
- Paint Research Institute Seminar

- Manufacturing and Education Seminars
- Overseas Papers

• Panel Discussions and Workshops Concurrent sessions will be held throughout the three-day meeting, but papers will be scheduled so as to avoid conflicting presentations.

Paint Industries' Show

To be held concurrently with the Annual Meeting in the Convention Center, the 1979 Paint Show will be the largest in history. To date, 130 supplier firms have

Kumins To Deliver 1979 Mattiello Lecture (Continued)

and anionic interaction printing systems for fast-set and durable textile inks, encapsulated reactive one part sealant formulation, poromerics and similar compositions.

At the urging and encouragement of Dr. Zeno Wicks, then Director of the Central Research Laboratories (now Professor and Head of Organic Coatings at North Dakota State University), he assembled a group of chemists to study. on a fundamental level, certain aspects of the physical chemistry of protective coatings. The results of the program were published in numerous papers in various scientific journals. These described changes in the glass transition temperature due to polymer sorption on surfaces, diffusion and solubility of gases and vapors in coatings, free volume effects, surface potential and polymer orientation on surfaces and their long range effect on polymer segment mobility.

Chemistry of Photoconduction

In 1967, Mr. Kumins accepted an offer to direct the Mt. Prospect, Ill. Research Laboratory of the Charles Bruning Co., then a subsidiary of Addressograph-Multigraph Co. There, in addition to administrative functions, he was concerned with the solid state physics and chemistry of photoconduction, electrostatic toners and papers for office copying machines, diazo compounds used in engineering drawing media, microfilm, electro-photography and lithography. During his four-year tenure, five patents were granted to his organization and 24 patent applications were filed.

In 1973, he was appointed Director of Research and Development for Tremco Incorporated, a manufacturer of roofing materials, high performance sealants for construction and insulating glass, glazing compounds, waterproofing materials, elastomeric tapes for the automotive and metal building industries. His present duties are in development of new sealant systems based on unique polymers synthesized by the Laboratory; penetrating compositions for roof treatment, and a continuing study of adhesion phenomena.

Author and Lecturer

Mr. Kumins has published 30 papers on polymer physical chemistry, analytical and surface chemistry, rheology, and transport processes through membranes. He has been granted over 100 U.S. and foreign patents on pigments, zeolites, adhesives, printing processes, poromerics, electrostatic toners, and roof sheeting. He has been an invited lecturer at numerous university seminars and conferences. He has presented papers at Gordon Research Conferences, and was elected Chairman for the 1969 Conference on the Science of Adhesion. Mr. Kumins assembled and chaired five American Chemical Society national symposia sponsored by the Divisions of Polymer Chemistry, Surface and Colloid Chemistry, and Organic Coatings and Plastic Chemistry.

He is the recipient of two Roon Awards for papers presented at Federation Annual Meetings.

Currently, he is Secretary and Trustee of the Federation's Paint Research Institute, Technical Coordinator for the Cleveland Society for Coatings Technology, member of the Editorial Board of *Progress in Organic Coatings*, and a member of the Executive Committee of the Adhesion Society. He was formerly on the Editorial Advisory Board of *Chemical and Engineering News and Product R & D*. reserved 318 exhibit spaces, some 15% more than the record number at last year's event.

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 3; 10:00 am to 5:30 pm on Thursday, October 4; 10:00 am to 4:00 pm on Friday, October 5.

Headquarters Hotel

The Sheraton St. Louis will be headquarters hotel, and Stouffer's Riverfront Towers will be co-headquarters. Other hotels with blocks of rooms set aside for the Annual Meeting are Bel Air Hilton, Breckenridge Pavilion, Holiday Inn Riverfront, Lennox, Mayfair, Rodeway Inn, and St. Louisian.

Free shuttle bus service will be provided between participating hotels and the Convention Center.

July 31 Deadline Announced For 1979 DCMA Award Entries

Authors wishing to compete for the 1979 DCMA Award, for the best paper prepared on any aspect of the science or usage of color, use of colorants or their behavior, which is presented to the Federation of Societies for Coatings Technology, are reminded that entries must be submitted by July 31, due to the advanced date of this year's Annual Meeting. The Award, offered annually by the Dry Color Manufacturers' Association, is presented at the FSCT Annual Meeting.

Papers are judged on the basis of originality and relevance to the coatings industry. Recipients are selected by the Inter-Society Color Council of the Federation, and only papers (manuscripts) submitted to the *Journal of Coatings Technology*, or those submitted for oral presentation at the FSCT Annual Meeting or at special regional meetings, will be considered.

Authors wishing to submit entries should contact either Robert Marcus. PPG Industries, Inc., 151 Colfax St., Springdale, Pa. 15144, (412) 274-4500 or Dennis Osmer, Pigments Dept., CIBA-GEIGY Corp., Ardsley, N.Y. 10502, (914) 478-3131.

Room Reservations

All requests for rooms and suites must be sent to the Federation Housing Bureau on the official form provided by the Federation. These have been mailed to all members, and additional copies are available from Federation headquarters.

Registration Fees

Regular "on-site" registration fees will be \$40 for Federation members and \$55 for non-members. Advance registration will be available for \$35 for members and \$50 for non-members.

There will again be a special \$15 advance registration fee for retired Federation members.

An advance registration form will be included in subsequent issues of JCT, and will also be mailed to Federation members in July.

Luncheon

The Federation Luncheon will be held Friday, October 5 at the Sheraton St. Louis.

Presentations will be made to recipients of the George Baugh Heckel 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 1979 Paint Industries' Show).

Program Committee

In addition to Mr. Coffino, the following members are serving on the FSCT Program Steering Committee:

Vice-Chairman — Hugh Lowrey, of Indurall Coatings, Inc., Birmingham, Ala.; Umberto Ancona, of McCloskey Varnish Co., Philadelphia, Pa.; Thomas Ginsberg, of Union Carbide Corp.,



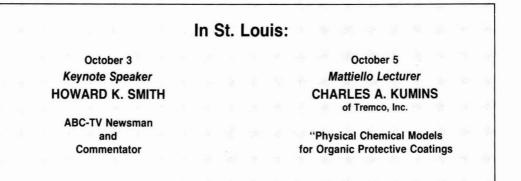
St. Louis will host the Federation's 57th Annual Meeting and 44th Paint Industries' Show on October 3, 4, and 5. Shown above is the St. Louis riverfront featuring the famed Gateway Arch. In background is Busch Stadium

Bound Brook, N.J.; William Mirick, of Battelle Memorial Institue, Columbus, Ohio; Colin D. Penny, of Hampton Paint Mfg. Co., Inc., Hampton, Va.; and Richard E. Wolf, of DeSoto, Inc., Des Plaines, III.

Meetings Committee

Members of the Kansas City and St. Louis Societies are serving on the Meetings Committee under General Chairman Howard Jerome, of Vane Calvert Paint Co. Chairing the various subcommittees are: Information Services — William Fitzpatrick, of Cook Paint & Varnish Co.; Operations — John Folkerts, of Plas-Chem Coatings; Luncheon — William Smith IV, of Conchemco, Inc.; Publicity — Herman J. Lanson, of Poly Chem Resins, Inc.; Busing — Floyd Thomas, Jr., of Thomas & English, Inc.

Mrs. Howard (Gene) Jerome is in charge of the Spouses' Program.



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Coating Materials

Effect of Reaction Pathway On Emulsion Polymer Structure

Kenneth L. Hoy Union Carbide Corporation*

Most latexes offered commercially are produced by a semicontinuous batch process. In this process the particles are usually initiated from a batch charge of monomer, catalyst, surfactant, etc., and the remaining monomer is continuously added to the reaction vessel during the course of the polymerization. Other ingredients, such as additional catalyst, surfactant, stabilizer, buffer, etc., may also be added during the polymerization. The exact order of the additions are varied depending upon the effect desired by the latex chemist.

With such a wide latitude of operating procedures, it is not surprising that similar latex products produced by this general process exhibit strikingly different physical, formulation, and performance properties even though the actual compositions are nearly identical. The author attempts to delineate a "critical few" variables which are often employed by the latex chemist and to establish the effect that these variables have on the structure of the latex particle. Several novel methods of controlling the emulsion polymer structure to produce the desired performance properties are discussed. In addition, a method for the synthesis of gradient polymers and their respective properties as possible coatings polymers are reported.

FORWARD

After I had recovered from the exhilaration of being named the Mattiello Lecturer for 1978, there was the awesome realization that I was expected to say something important. The thought came to mind that perhaps most Hollywood and TV celebrities repeat the usual trite cliches when honored by their respective societies because they have only played the parts and were not expected to write the script. However, the men of science who have preceded me in this honor always seem deserving as well as able to provide an insight into an interesting technical problem confronting the industry.

Some sought to give advice on what to say as well as how to say it. A few urged me to keep it entertaining; others to keep it technical (apparently these are mutu-

Presented at the 56th Annual Meeting of the Federation of Societies for Coatings Technology in Chicago, Ill., November 3, 1978.

*Chemicals and Plastics, R&D Dept., P.O. Box 8361, S. Charleston, W.Va. 25303.

ally exclusive). The Chairman of the Selection Committee, Mr. Dan Toombs, suggested that if possible I should make the lecture impinge on the changes taking place because of environmental concerns and the looming energy shortage.

With these thoughts in mind, I decided to introduce my subject "The Effect of Reaction Pathway on Emulsion Polymer Structure," by taking a lead from the man commemorated by this Lecture Series.

Basic principles must be stressed; they provide a groundwork for the serious student from which he may branch off on new developments of his own. Joseph J. Mattiello (1943)

Too often suppliers have failed to share the "basic principles" upon which they design their products, and coatings manufacturers conveniently disguise or omit certain "basic information or performance requirements." The net result of this "basic" misunderstanding is that the industry is not able to take advantage of all that can be done, and the products of our labor always seem to fall short of our expectations. A new polymeric binder is often evaluated in whatever is the most pressing problem or opportunity the coating formulator has at the moment, rather than in the system or environment for which it was intended. Thus, I have witnessed a new product, created from an elaborate synthetic program as a binder with improved barrier properties for a new maintenance coating, be misdirected for use in a temporary strip-coating application. I am sure that you can think of other examples in your own experience where a "coating of opportunity" failed ultimately by being over-designed or under-designed for the intended application. Indeed, many times, a "new-technology" tends to fail because we as coating chemists try to "force fit" our present products into the new need. In a sense, we often create what can be termed as a "Peter Principle Product". It is only fitting, then, that this lecture deal with some of the "basics" that we have learned about emulsion polymerization in the past few years in the hope that what is said can provide the groundwork for the design of coatings which can meet the changing needs of our society.



1978 MATTIELLO LECTURER KENNETH L. HOY

A native of Cheyenne, Wyoming, Dr. Hoy received the B.S. Degree in Pharmacy with honors from the University of Wyoming in 1950. He received the Ph.D. Degree in Medicinal Chemistry with a minor in Physical Chemistry and Pharmacology from the University of North Carolina in 1955. While at the University of North Carolina, he held the position of instructor of Pharmacy and actively taught Inorganic Preparation, Drug Analysis and Extraction Processes.

Dr. Hoy joined Union Carbide Corp. in 1955 at its Research Center in South Charleston, W. Va. His early work centered on the utilization of cycloaliphatic diepoxides in a variety of solvent-borne varnishes as well as in high solids coatings.

In response to the growing importance of water-borne systems to the Coatings Industry, Dr. Hoy was assigned in 1968 to establish a long-range, more fundamental investigation of latex technology. His new charter was to provide a firmer basis for the future of new water-borne systems.

On the polymeric synthesis side, he and his colleagues have been responsible for the introduction of poly(vinyl chlorideethylene) emulsions and vinyl acetatebutyl acrylate-vinyl chloride terpolymer emulsions; the latter forms the basis of his company's thrust into the exterior paint vehicle market.

Dr. Hoy has completed 24 years of service with Union Carbide Corp., where he currently holds the title of Corporate Research Fellow. He presently is a member of the Union Carbide Exploratory Basis Research Management Team, which is charged with the responsibility of defining future directions for the firm.

Dr. Hoy has many patents which are relevant to the coatings industry to his credit. They range from specular surface analysis to a process for controlling the molecular weight distribution of latex polymers. He is active in the field of organic polymer syntheses as well as the field of polymer physical chemistry.

He has published widely and has been a speaker at Gordon Research Conferences, Chemical Institute of Canada, ACS, Div. of Organic Coatings and Plastics Chemistry, University of Utah Polymer Conference, and various Constituent Societies of the Federation.

Dr. Hoy is a member of Gamma Sigma Epsilon (honorary chemistry), Rho Chi (honorary pharmacy), and Sigma Xi (honorary scientific).

INTRODUCTION

Most latexes offered commercially are produced by a semicontinuous batch process. In this process (Figure 1) the particles are usually initiated from a batch charge of monomer, catalyst, surfactant, etc., and the remaining monomer is continuously added to the reaction vessel during the course of the polymerization. Other ingredients, such as additional catalyst, surfactant, stabilizer, buffer, etc., may also be added during the polymerization. With such a wide latitude of operating procedures, it is not surprising that similar latex products produced by this general process exhibit strikingly different physical formulations and performance properties, even though the actual compositions are nearly identical. The exact order of the additions is varied depending upon the effect desired by the latex chemist. The effects of many of these process changes are well recognized, especially by those skilled in the art. As one might expect, they are recorded in the patent literature, but this is often confusing and at times even contradictory. The formulations chemist frequently is able to detect even minor changes not anticipated by the latex chemist by the reaction or interaction of an obscure ingredient or by tests not previously considered worth revealing to the latex chemist. Perhaps many of these results would be more understandable if we actually could measure the impacts that these process changes have on the structure of the individual latex particles.

PRESENT THEORY OF PARTICLE STABILIZATION

One of the accepted concepts of what the structure of a latex particle *might* be is owed to the development of Double Layer Theory.¹ In this model (Figure 2),² a polymeric spherical particle has adsorbed on its surface an anionic species (surfactant). Since this adsorbed layer is negatively charged, ion pairing creates a localized accumulation of positive cations in the immediate vicinity of the anionic layer. The layer of positive charges is called the Stern Layer. The Stern Layer is quite rigid and behaves as if it were physically a part of the particle, but it induces a much more diffuse concentration, although greater than in the bulk solution of anions surrounding the particle. When two particles approach each other these diffuse anionic layers create an electrostatic repulsive force which prevents flocculation and thus stabilizes the system.

Another model for stabilization^{3.4} of the latex particle involves the concept of a noinonic adsorbed hydrocolloid (*Figure* 3). In this theory, a slightly surface-active water-soluble polymeric material is adsorbed on the surface of the polymer particle. The hydrophobic segments of the hydrocolloid are at the polymer surface and the hydrocolloid are at the polymer surface in the aqueous phase immediately surrounding the particle. This mode of stabilization is often termed "entropic", since the stabilization system requires no localization of the ionic species to create a potential

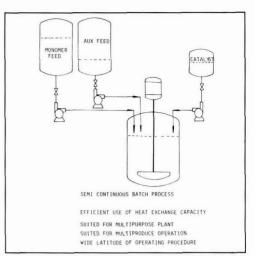


Figure 1—Simplified diagrams of a semicontinuous batch process

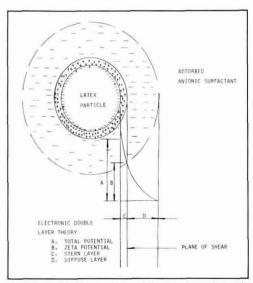


Figure 2—Model of latex particle stabilized via electronic double layer

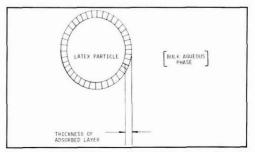


Figure 3—Model of latex particle stabilized via adsorbed hydrocolloid

energy barrier. Rather, the surface-free energy of the latex particles are dissipated by the adsorption and interaction of the hydrophobic segments of the hydrocolloid at the surface; the hydrophylic segments solvated by the aqueous phase form a steric barrier which prevents the particles from agglomerating.

PARTICLE STRUCTURE

Given those two models for stabilization, we decided to try to elucidate more of the fine structure details of the latex particles themselves. Ergo, a detailed study of latexes which incorporate certain functional groups seemed reasonable. In many modern latex polymers one or more monomers containing reactive functional groups are included in the polymerization recipe. In our study we elected to utilize carboxylic monomers because the acid function can be readily analyzed and many latexes of commercial interest contain acidic functions. Stability and rheology, for example, are the reasons often cited for the inclusion of carboxyl monomer; in the final film, carboxylic acid groups can provide reactive sites for crosslinking, adhesion, and other functions. The question then, is, if we are to understand the fundamental properties of these latexes, where are these functional (acid) moieties located in the latex? They could be present:

- (1) As polymeric acid in the aqueous phase.
- (2) At the interface between polymer and water.

(3) As randomly distributed between the surface and buried deep in the polymer particle.

It is well known that when certain acrylic acidcontaining latex polymers are neutralized to an alkaline

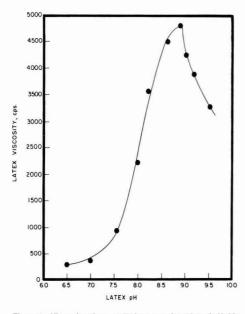


Figure 4—Viscosity of an acrylic latex as a function of pH, 60 rpm Brookfield, 46% total solids

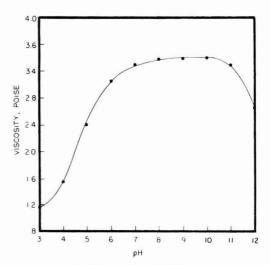


Figure 5—Viscosity of polyacrylic acid, 10% solution in water as a function of pH

pH, there is a marked increase in the viscosity of the system (Figure 4). Likewise, it is known that a solution of poly(acrylic acid) in water also increases in viscosity when the pH is increased (Figure 5). One could postulate from this limited information that the viscosity increase is caused by a soluble polyacid contained in the aqueous phase. However, when the latex polymer is separated from the water phase by centrifugation, very little, if any, soluble polymeric acid is found in the water phase; in contrast, only simple acidic residues (catalyst fragments, unpolymerized acids, etc.) are contained in the water. Following this lead, our laboratories developed a conductometric method of locating the residence of nearly all of the acid groups contained in the latex.5 Armed with this simple analytical tool, we can now ascertain the influence that compositional and process variables have on the location of the acid moieties of the latex polymer. In our studies we used a simple semicontinuous batch process in which we controlled the amount and type of acid, and where and when in the process it was introduced.

ACID LOCATION ANALYSIS

One set of experiments was directed at the effect of monomer structure. Since some monomeric acids, e.g., itaconic acid is not soluble in the bulk of the monomer mixture, they can be incorporated by using a separate aqueous feed or by dissolving them directly in the initial reactor charge. *Figure* 6 shows the results obtained using acrylic, methacrylic and itaconic acids when incorporated by the various methods cited. The single fact of note in these data is that the acid is readily accessible to the analysis and, therefore, is most probably at the interface.* Some is in the water phase but very little is buried or unaccounted for. In the case of

^{*}While accessibility to analysis is not in itself absolute proof of the surface location of the acid groups, other supporting data, some of which will be discussed later, lends credence to this assumption.

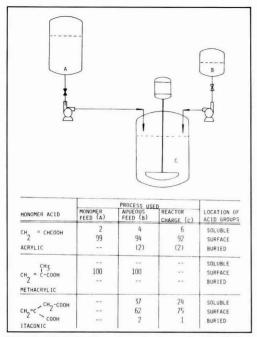


Figure 6—Effect of acid monomer structure and mode of incorporation on acid location

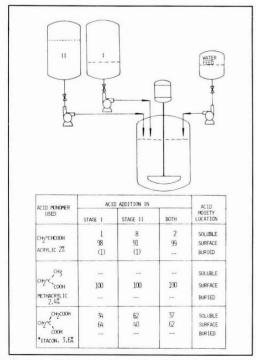


Figure 7—Effect of reaction stage on incorporation of acid monomer

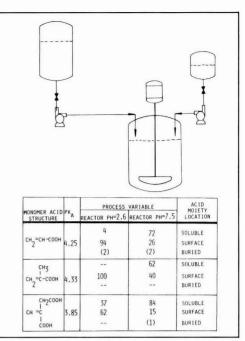


Figure 8—Effect of pH of reaction on incorporation efficiency and acid location

itaconic, the aqueous phase acid was identified as monomeric and not polymeric acid.

In the next set of experiments, the reaction scheme was modified to provide two separate monomer feed tanks. The monomer was divided in half and the acid monomer added either with the first half of the monomer, the second half of the monomer, or to both. From the data presented in Figure 7, it is obvious that if the acid is incorporated in the polymer it still tends to reside in the interface with little regard to the process pathway. A third set of experiments (Figure 8) demonstrates the effect of ionization on the acid incorporation and location. In the two experiments of this set, the polymerization was carried out at alkaline pH, and it is noted that, although the efficiency of incorporation was decreased markedly, the incorporated acid groups were still on the surface. In all cases the aqueous phase acid was either monomeric or very low molecular weight oligomers.

Thus, we can conclude from acid-location analysis that:

(1) Monomers containing carboxyl functions and perhaps other polar groups tend to be incorporated in such a manner that the carboxyl groups are at or very near the interface.

(2) The polymerizing carboxyl species which is incorporated in the latex particle is probably the unionized acid. (3) The process variables studied appear to have little effect on the location of the acid in the polymer particle.

After establishing these principles we were surprised that the viscosity-pH response of our latex products did not always follow the acid-location analysis. Some latexes with higher acid contents at the surface exhibited less viscosity response to pH change than did some with lower acid levels. It was soon concluded that there must be at least one other factor which controlled rheology. Just knowing acid concentration and location was not enough. Clearly, other process variables must influence how the acid monomers are incorporated rather than where.

MODEL FOR PARTICLE MORPHOLOGY

After much discussion, a working hypothesis was developed and a physical model of a latex particle proposed. The model (Figure 9) consists of a spherical particle (core), surrounded by an acid-bearing polymer layer which is caused to expand at alkaline pH by charge repulsion induced by neutralization and ionization of the carboxyl groups in the region of the interface. Continuous stabilization of the particle is accomplished by utilizing the double layer theory at acid pH and, at alkaline pH, a combination of ionic stabilization and an entropic layer generated by the expanding polymer segments. The degree of expansion of the acid polymer segments would, of course, depend not only upon the concentration of acid groups at the interface, but also on the frequency and length of the acid-rich polymer segments in the surface region. In this view, the process variables would influence the number and frequency of these segments. If this picture has any bearing on reality, then, clearly, measuring the degree of expansion and thickness of the postulated layer as the pH of the latex is changed from acidic to basic would have to be the next experimental thrust. Our approach to study the phenomena was twofold: (1) by Particle-Sedimentation in a Centrifugal Field, and (2) by Dilute Suspension Viscometry.

PARTIAL SEDIMENTATION

An analysis of the Stokes equation in terms of our model (*Figure* 9) allowed us to derive the equation for the relative rate of sedimentation:

$$\frac{S}{S_{o}} = \frac{R}{R+X} + \frac{\rho_{e} - \rho_{o}}{\rho_{e} - \rho_{o}} \left[-\frac{3R^{2}X + 3RX^{2} + X^{3}}{R^{2}(R+X)} \right]$$
(1)

Where

- S/S_0 = relative rate of sedimentation of particle
- R = radius of particle core
- X = thickness of expansion layer ρ_c = density of particle core
- $\rho_e = \text{density of particle core}$ $\rho_e = \text{density of expansion layer}$
- ρ_0 = density of medium

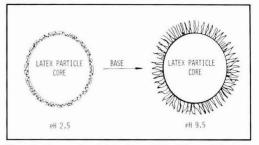


Figure 9—Proposed model of acid containing latex particle at pH 2.5 acid un-ionized and collapsed on surface; at pH 9.5 acid ionized and expanded (hydrated)

The key to the analysis of the equation resides in the densities of the three different zones considered. It may be assumed that the density of the expansion layer (ρ_e) must have as a limiting maximum the density of the core (ρ_e) and as a limiting minimum density that of the medium (ρ_o). In *Figure* 10 the predicted change in the sedimentation coefficient as a function of the ratio of the thickness of the layer to the radius of the particle (X/R) is shown; note that only in the case where ρ_e approximates ρ_o does the sedimentation coefficient decrease considerably with an increasing value of X/R. This is what actually happens in practice, and, therefore, we can make the assumption that $\rho_e = \rho_o$, and our equation simplifies and rearranges to

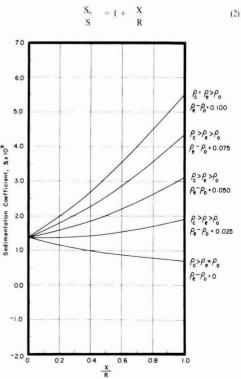


Figure 10—Variation of sedimentation coefficient with model layer thickness (X)

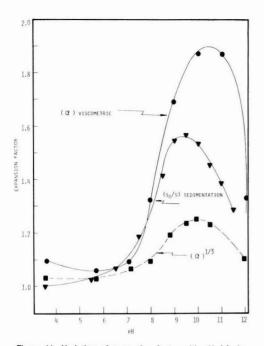


Figure 11—Variation of expansion factor with pH. [+] viscometric expansion factor (α); [=] viscometric expansion factor (S₀/S) for (S₀/S)

Therefore, S_0/S is directly proportional to the thickness of the layer, and a plot of S_0/S vs. pH would be very revealing. A plot typical of our results is given in *Figure* 11, which gives the results of not only the sedimentation experiment, but also the viscometric results which will be discussed in the following section. Of course, one could probably ask "What if you omitted all the acid?". This is illustrated in *Figure* 12. In this case one notes an apparent decrease in the layer thickness. Most assuredly this is caused by the collapse of the electronic double layer induced by the increased ionic strength resulting from the addition of base to neutralize the acid in the latex. This method, while experimentally very time consuming, proved to be the most revealing

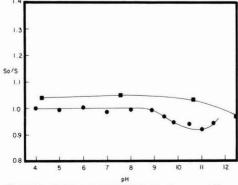


Figure 12—Variation of expansion factor of a non-acid bearing latex as a function of pH. [+] sedimentation; [=] viscometric

because of the uncomplicated low shear nature of the gravitational field. We will want to return to it later, but first I would like to verify our model via an independent measurement.

DILUTE SUSPENSION VISCOMETRY

Adaptation of the basic rheology expression of Einstein for dilute suspensions by Guth, Gold, and Simha provided us with the tool for a second evaluation of our theory. In this expression:

$$\eta = \eta_0 \left(1 + 2.5 \phi + 14.1 \phi^2 \right) \tag{3}$$

Replacement of the volume fraction, ϕ , with the "dry volume fraction", C, multiplied by an expansion factor (α) which would correct the volume fraction ϕ for the apparent increase in particle size caused by the expanded layer and substitution in the basic equation gives:

$$\eta = \eta_0 \left(1 + 2.5 \,\mathrm{C}\,\alpha + 14.1 \,\mathrm{C}^2\,\alpha^2 \right) \tag{4}$$

Solution of this equation for α gives:

$$\alpha = \frac{-2.5 + \sqrt{6.25 + 56.4 [\eta/\eta_0 - 1]}}{28.2 C}$$
(5)

Since η , η_0 can be measured in the experiment and C is known, then α can be readily calculated. A plot of α as a function of pH yields the data in *Figure* 11. Again the non-acid containing latex did not show a viscosity increase with pH (*Figure* 12). It should be noted that the values of α far exceed the values of S₀/S even for the same latex, but it should be remembered that:

$$\frac{S_{\alpha}}{S} = 1 + \frac{X}{R}$$
 while $\alpha = -\frac{(R+X)^3}{R^3}$

So that $\alpha^{1/3} \approx S_0/S$. When this correction is applied, then, the values of α are much too low. More recent studies in which the shear dependence was accounted for reconcile the two methods within the accuracy of the experiments. The extra correction for shear complicates the experiment, and so we decided to utilize sedimentation in the remainder of the study.

EFFECT OF REACTION PATHWAY ON PARTICLE MORPHOLOGY

The correlation of the two methods exceeded our hopes. Finally, we have had an analytical tool to study the effect of reaction pathway on the structure of the particle. The disadvantage of the method is that each latex characterized required at least 10 to 11 separate sedimentation experiments; nevertheless, we decided that the expenditure of time would be worthwhile. The effect that the reaction pathway had on particle expansion is shown in *Figure* 13 for acrylic acid (monomer fed); in *Figure* 14 the effect of the same reaction pathway but using an auxiliary aqueous feed for the acid is shown. *Table* 1 summarizes our results. From these data it is apparent that:

 Expansion is maximized when the acid monomer is added towards the final stage of the polymerization.

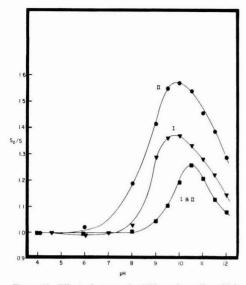


Figure 13—Effect of stage of addition of acrylic acid in polymerization on expansion factor (S_o/S vs pH); [•] Stage II; [♥] Stage I; [■] uniform feed

(2) Expansion is minimized when the acid monomer is fed throughout the process.

(3) The expansion trend is Stage II > Stage I >> Uniform.

(4) The use of water feed tends to equalize the formation of the expansion layer but lowers the incorporation efficiency.

(5) The trend for maximum effect in acid choice is Acrylic > Methacrylic >> Itaconic.

The effect of increasing the acid content is graphically presented in *Figure* 15, in which the amount of

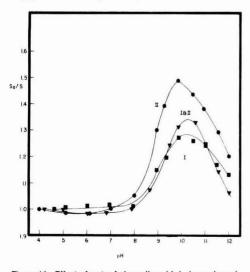


Figure 14—Effect of water-fed acrylic acid during polymerization on the expansion factor (S₀/S vs pH); [+] Stage II; [▼] uniform; [■] Stage I

Table 1—Summary of Process Variations on Location	
And Expansion Factors of Acid-Bearing Acrylic Latexe	s

	F				
Acid Monomer	Stage I	Stage II	Stage I and II	- Characterization	
Acrylic acid	2.0	2.0	2.0	% total acid	
in monomer	1.96	1.82	1.98	% in surface	
feed	744	1230	563	Å thick, layer	
	4000	4300	4400	Å particle size	
	4.0	4.0	2.0	% acid in feed	
Acrylic in	2.0	2.0	2.0	% total acid	
aux. H ₂ O				% in surface	
feed	800	1210	920	Å thick, layer	
	5600	5000	5400	A particle size	
	4	4	2.0	% acid in feed	
Methacrylic	2.4	2.4	2.4	% total acid	
in monomer	2.4	2.4	2.4	% in surface	
feed	484	725	422	Å thick, layer	
	4400	4600	4300	Å particle size	
	4.8	4.8	2.4	% acid in feed	

acid has been varied between 0.5% acrylic and 4.0%. In each case, the acid was fed at the Stage II point in the reaction. It is of interest to note that in each latex the maximum expansion takes place at a pH of 9.5-10; however, the onset of expansion does progressively decrease from pH 9 at 1% acid to pH \sim 5 at 4% acid. A latex containing only 0.5% acid does not even expand. *Figures*, 16, 17, and 18, depict several interesting effects that would be of interest to formulation specialists. The effect of simple bases (*Figure* 16) are all the same; polyvalent cations do, as expected, inhibit expansion and even cause collapse of the double layer. The effect of extraneous ionic species is illustrated in

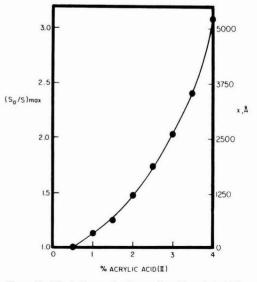


Figure 15—Effect of increasing the acrylic acid content of latex. Maximum layer thickness at pH 9.5

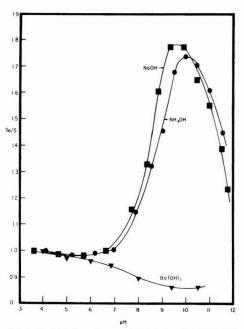


Figure 16—Variation of expansion factor—pH relationship with type of base used. [■] sodium hydroxide; [+] ammonium hydroxide; [▼] barium hydroxide

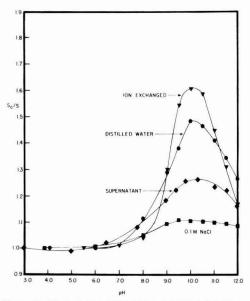


Figure 17—Effect of electrolyte on latex expansion. |♥] ion exchanged; |•] distilled water; [♦] supernatant; |■] 0.1 M sodium chloride

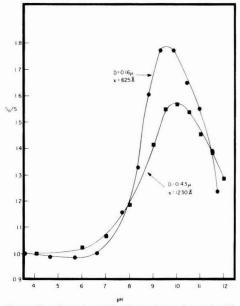


Figure 18—Effect of particle size on layer size at the 2% acrylic acid level. 0.16 μ , X = 625 Å, 0.43 μ , X = 1230 Å

Figure 17; dilution with 0.1 M salt solution suppresses expansion, while dilution of the latex with its own "natural" supernate indicates the degree of expansion in a whole neutralized latex. The expansion depicted with distilled water is typical of that observed in present experiments; however, the maximum expansion can be observed only when the catalyst fragments and added ionic species are removed by ion exchange or dialysis. The expansion is exaggerated if the layer size is maintained but particle size core is decreased (*Figure* 18).

EFFECT OF POLYMER STRUCTURE ON PARTICLE MORPHOLOGY

We finally believed that we had a method for measuring the effect that any change in the latex process would make on the product. We decided to change the model recipe and eliminate many of the copolymerization kinetic problems introduced by the choice of acrylate monomers. Our choice was to use essentially a styrene homopolymer to characterize the process variables.

You might imagine our surprise when it was found that styrene homopolymer behaved entirely differently from our model acrylic latex. What was determined is:

(1) Acid location analysis of styrene indicates much of the acid is buried (*Table 2*).

(2) Sedimentation study shows no expansion of the layer; in fact, a decrease similar to the core samples (*Figure* 19) is seen.

Soluble

Surface 58

Buried 39

Soluble 46

Surface 55

Buried 0

3

Late	exes Prepa	ared by Va	rious Proc	esses
	P	rocess Var	iable	
	Stage	Stage	Stage	
Acid Location	1	П	I and II	Acid Feed Stream

15

70

15

06

62

32

56

43

01

in monomer feed

as aux. H2O feed

Table 2—Distribution of 2% Acrylic Acid in Polystyren	e
Latexes Prepared by Various Processes	

Our firs	t reaction w	vas dis	belief bas	sed on	the prer	nise
	technician					
called-for						

periments gave the same results. After considerable discussion, one theory held that in this case the acid-rich polymer segments were constrained from expansion by the rigidity (high Tg $\sim 100^{\circ}$) of the styrene acid copolymer, and that the reason the acid seemed to be buried was that the stiffness of the polymer chain prevented the carboxyl groups from diffusing to the interface.

To test this postulate, a methyl methacrylate homopolymer latex (also Tg of $\sim 100^\circ$) was made and its response to pH measured. Indeed, it behaved just as the polystyrene latex (Figure 19). Again, a check of the "core" polymer produced the expected result. A further check of this hypothesis was carried out by preparing a series of copolymers in which the monomer ratios were adjusted to control the glass transitions of the base polymers. The results (Figure 20) indicate that the stiffness of the polymer segments is indeed an important factor in controlling the expansion of an allacrylic latex and hence its rheology.

Now we felt confident that we understood the problem with the styrene homopolymer latex and, therefore, we prepared two latexes, one a 50/50 copolymer of styrene/ethyl acrylate and another a 50/50 copolymer of methyl methacrylate/ethyl acrylate.

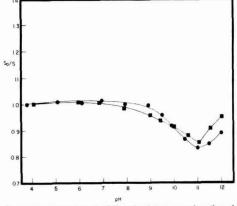


Figure 19-Expansion of acid bearing latexes as a function of pH. [+] polystyrene; [*] methyl methacrylate

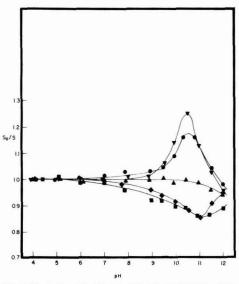
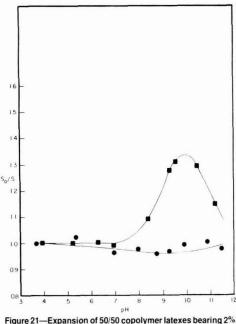


Figure 20-Expansion of butyl acrylate/methyl methacrylate copolymer acid bearing 2% latexes. [♥] 50/50, Tg 15°C; [·] 37.5/62.5 Tg 33°C; [▲] 31/69 Tg 44°C; [■] 25/75, Tg 54°C; [◆] 0/100 Tg 105°C

These two polymers had very nearly the same Tg. However, again we found the acrylate expanded while the styrene copolymer behaved differently (Figure 21).

We were now confronted with the inescapable conclusion that somehow styrene latexes were different. Finally, it was theorized that the polarity of the polymer was the remaining factor. In this modification of our



acrylic acid. [=] MMA/EA Tg 29°C; [·] Sty/EA Tg 27°C

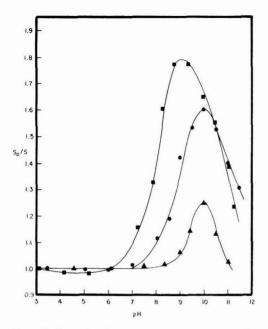


Figure 22—Expansion of acrylic copolymer latexes bearing 2% acid, II. [■] MMA/EA/BA 40/52/6 Tg 15°C; [+] MMA/EA/BA 40/58/0 Tg 18°C; [▲] MMA/EA/BA 49/0/49 Tg 15°C

theory, the polar character of the polymer segments led them to interact with the extremely polar aqueous phase which plasticized the polymer, thus permitting the alkaline expansion to take place. If this was true, then, a series of latexes having about the same Tg $\sim 15^{\circ}$ C but in which the non-polar/polar character of the monomers was varied would show a predictable response (*Figure 22*). Such is the case. Further, one might be able to affect the expansion by increasing the polarity, causing latexes with higher Tg to expand. Again, the evidence confirms this thought (*Figure 23*). *Figure* 24 illustrates the interaction of these two factors, stiffness and polarity of the polymer segments at the 2% acid level.

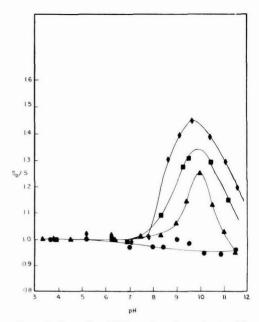


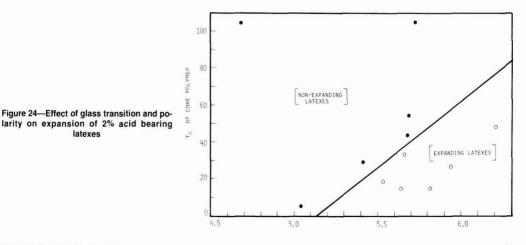
Figure 23—Expansion of 50/50 copolymer latexes bearing 2% acrylic acid. [♦] MMA/MA Tg 49°C; [■] MMA/EA Tg 29°C; [▲] MMA/BA Tg 15°C; [•] MMA/2EHA Tg 5°C

In this figure Tg was used as an indication of the temperature at which the stiffness (modulus) of all the polymers studied was approximately the same, and as a measure of total polarity, the "polar solubility parameter" was used:

polarity =
$$\sqrt{\delta_{\rm H}^2 + \delta_{\rm p}^2}$$

Thus far, we have identified the major factors which influence the alkaline response of the particles; summarized, they are:

- (1) Carboxyl groups at the surface.
- (2) Process variables (how and when acid fed).
- (3) Glass transition of surface polymer segments.



(4) Polar/non-polar character of the surface segments.

It is my belief that the coating formulator, utilizing the "basic" concept of the latex particle presented here and fully aware of the effects that can be created, can more understandably formulate and attain the desired properties of latex coatings. It is my hope that he can use this information as a groundwork "from which he may branch off on new developments of his own."

EFFECT OF PROCESS ON REACTION PATHWAY

Thus far, I have given you the thrust of perhaps several years of work, and we have still not exhausted all the possible process variations which we could study using this methodology. But now I should like to return to Mattiello's quote and place it back in the context of his original thought.

"Basic principles must be stressed. They provide a groundwork for the serious student from which he may branch off on new developments of his own. The suddenness of conception is only apparent. It is safe to say that few great discoveries are the result of chance or sheer inspiration. More often they are the result of chance plus a long course of study, training, and work. Each new discovery builds on the past, and new basic principles are developed from the old ones, produced by the same labor which produced the old ones. The mainstream of discovery has a perceptible continuity."

During the course of our work, several basic questions kept recurring which did not seem to fit the generally accepted theories; the most serious one was: "How does the particle grow during polymerization and why does the acid accumulate on the surface?" Conceptually, the accepted theory supposes the existence of polymer particles swollen with monomer. These swollen particles are in equilibrium with the much larger monomer drops which serve as a reservoir of monomer. The mass transport of monomer through the liquid monomer-water interface and subsequently through the water-polymer interface is not considered to be a limiting factor, since the surface areas involved are extremely large. The swollen polymer particles eventually encounter a radical species, are "stung" and rapidly polymerize. At any one time about half of the particles are actively polymerizing (live), and the other half are inactive (dead) towards polymerization but are swollen with monomer. A particle which is in the active polymerization phase becomes inactive when a second radical enters the particle and combines with the growing polymer chain, or when the growing polymer chain transfers with a species which is able to escape the polymer particle. At any rate, the accepted theories demand a kinetic control of the polymerization and not a diffusion or mass transfer control. The data presented

here do not easily conform to the accepted model. Indeed, some serious discrepancies must be accounted for, such as:

(1) Why does the acid tend to accumulate on the surface at all?

(2) Why is the particle expansion different when the reaction path of acid is changed from Stage I to Stage II?

(3) Why do the styrene and methyl methacrylate tend to bury the acid monomer? In a particle swollen with monomer, mobility of polymer segment should not be a factor and yet we know it is.

A strict interpretation of the expansion data would tend to indicate that the polymerization was occurring very near if not on the surface. The polymer particle is almost in an unswollen state. That is, the reaction is more diffusion-dependent than kinetic. There is a caveat that we must invoke. The literature mechanism is describing a simple batch polymerization, while the latexes described in this work have been made by a semicontinuous batch process.

Before we confront these two different ideas, let me describe another set of experiments we performed. Using our two-stage reaction system we made two latexes of the same overall final composition but with varying compositions for the two stages. The first was made with a uniform 50/50 BA/MMA in both stages and with 2% acrylic acid only in the second stage. For the second latex the first stage (core) was 75/25 BA/MMA (Tg - 15°) and the second stage (shell) was a 25/75 BA/MMA (Tg + 54°C) with 2% acrylic acid. If surface growth took place then one would expect the first latex to exhibit a typical expansion while the second would not. *Figure 25* shows the results of our experiment and this is exactly what happens.

A second experiment, Figure 26, is similar to the first except that the uniform polymer was a 25/75 BA/MMA. Tg 54°C, and the staged polymer had a 100% methyl methacrylate core, Tg 105°C, and a 50/50 BA/MMA (Tg 15°C) shell. In this case the latter latex exhibited expansion characteristics as predicted while the uniform copolymer did not. Clearly, from these data, the polymerization appears to take place in a zone near the surface of the particle and not in a uniformly swollen particle. Yet the postulate can be made that since these two polymer compositions are not compatible, in the particle they would tend to separate into two distinct polymer phases, perhaps a core-shell morphology. Dynamic mechanical measurements of polymer films of the latexes in question do verify that the polymer exists in two distinct polymer phases. It is difficult to understand why the proponents of this line of reasoning would expect core and shell morphology rather than a random microphase separation of the two polymers. The work of Sperling⁶, et al, on Emulsion Polymerized IPN, might at first glance support the random microphase morphology; however, on closer examination, it is to be noted that this group also utilized a semicontinuous batch process,* and, therefore, provides no basis for choice between these two concepts. Perhaps, then,

^{*}A few staged batch polymerizations were also carried out, but the results were nearly identical.

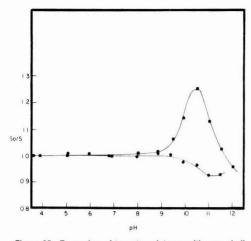


Figure 25—Expansion of two-stage latexes with core-shell morphology. $[\bullet]$ uniform copolymer 50/50 BA/MMA (Tg + 15°C) with 2% acrylic acid in second stage; $[\cdot]$ soft core 75/25 BA/MMA (Tg - 15°C) and hard shell 25/75 BA/MMA (Tg + 54°C) with 2% acid in second stage

there is something unique about the semicontinuous batch process used commercially, and we should examine some of the characteristics of the commercial reaction system:

(1) The reaction is carried out as warm (hot) as possible because the better utilization of cooling capacity minimizes investment.

(2) The monomer is fed to maintain temperature of reaction, thus utilizing the ΔH of polymerization to heat the reactor. Therefore, monomer is added at or near the rate of polymerization which just maintains the temperature of the reaction.

(3) Under the reaction conditions, a large monomer pool does not exist. Indeed, we refer to it as "starved

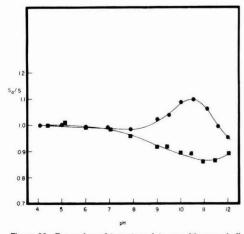


Figure 26—Expansion of two-stage latexes with core-shell morphology. [■] uniform copolymer 25/75 BA/MMA (Tg + 54°C; I·] hard core 100 MMA (Tg 100°C) and soft shell 50/50 BA/MMA (Tg + 15°C) with 2% acrylic acid in the second stage

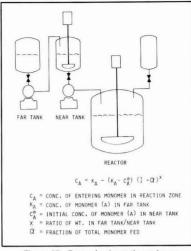


Figure 27—Power feed reaction scheme

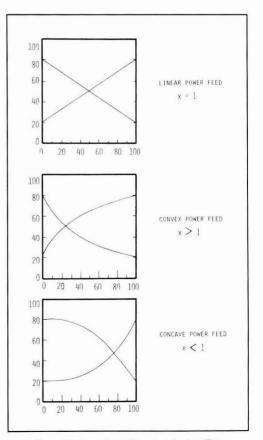


Figure 28-Several possible power feed profiles

feed", and we intuitively feel that the solubility of the monomer in water is seldom exceeded.

Under the operating constraints cited it may be that the implied monomer \neq water \neq polymer equilibrium doesn't apply. An argument can be made that chemical reaction kinetics are not a factor in the limiting reaction rate, but rather heat transfer is the rate controlling factor. Heat transfer is, of course, seldom a factor in a laboratory reactor because of the better agitation, smaller volume to surface ratios, and nonscalable character of the reactor itself as a heat sink. At any rate, the more important observation is that this reaction configuration is able to provide apparent diffusion control which ultimately leads to core and shell morphology.

POWER FEED A NEW REACTION PATHWAY

Following this lead we began to discuss potential utility of such a morphology, and it was proposed that any number of shells could be constructed provided we wished to keep changing the composition of the monomer mix. Early latexes in which this was accomplished did not form very attractive films. Most were weak, opaque, sticky, and uninteresting from a coatings point of view. Finally, it was realized that this gross incompatible character might be eliminated if we could devise a method of gradually changing the composition of the entering monomer during the course of the polymerization. Such a reaction scheme is shown in Figure 27. In this reaction scheme two monomer feed tanks are arranged in series. The monomer (W1) of composition K_A, contained in the far tank is transferred at rate (R_1) to the agitated near tank in which the monomer (W_2) has an initial composition of C_A^0 . Monomer is transferred from the near tank to the reactor at such a rate (R_{a}) that both the near and far tanks empty at the same instant in time. The analysis of the mass transfer gives the equation:

$$C_A^{t} = K_A - (K_A - C_A^{o}) (1 - \alpha)^{X}$$

Where

 C_A^i is the concentration entering monomer A at any time K_A is the concentration of monomer A in the far tank C_A^i is the initial concentration of monomer in A in the near tank α is the fraction of the monomer fed at time t or $[R_2l/(W_1+W_2)]$ X is the weight ratio of far/near tanks W_1/W_2

It is to be noted that this general equation is a power function of X, the ratio of the weights contained in the feed tanks. For this reason, in our laboratories, this technique has been given the name "Power Feed." The Power Feed equation provides a graphic means of representing the feed profile of the various monomers in the reaction; in *Figure* 28, several types of feed profiles are illustrated. The first illustration is a case where the concentration of monomer is varied in a linear fashion with time. The power of the feed is one; hence, the term a linear power feed. Polymers made by this feed profile are often termed gradient polymers. The next two examples illustrate situations where the exponent is greater than one and less than one. It is apparent that the total amount of the monomer feed is equal to the

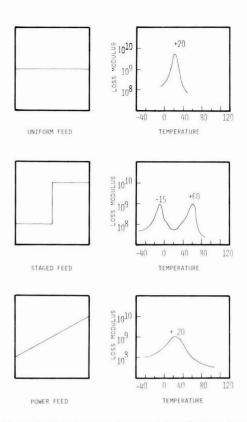


Figure 29—Dynamic mechanical properties of uniform feed latex; stage fed latex, and power feed latex

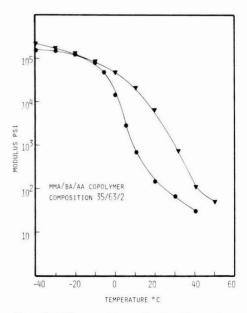


Figure 30—Stiffness modulus as a function of temperature for [·] uniform feed latex, [▼] power feed latex

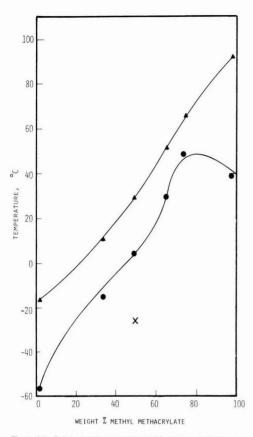


Figure 31—Brittle ductile transition of [•] uniform-fed latexes; [X] power fed latex; [▲] Tg of uniform-fed latex

area under the curve. More complex feed profiles can be constructed by the use of three feed tanks in a series, e.g., parabolic, sigmoidal, etc. However, a complete discussion of these mathematical forms is beyond the scope of the present discussion. I would like, therefore, to limit our discussion to the linear Power Feed profile and how the gradient polymers prepared by this reaction pathway differ from those made by conventional uniform or staged reaction pathways. Figure 29 illustrates the dynamic mechanical properties of three latexes made by uniform feed, a staged feed and a linear power feed. It will be noted that the uniformly fed material has a rather narrow peak at $\sim 20^{\circ}$ C, the staged feed latex has two peaks at -10 and 60°C, and the power feed material has a single broad peak covering a range of -10 to 40°C. Further, only the uniform polymer and the Power Feed polymer (gradient polymer) formed films of any consequence. The major difference is the flexible, non-tacky character of the gradient polymer when compared to the soft, rather sticky feel of the uniform polymer. This is perhaps best illustrated by the relationship of modulus of the polymers as a function of temperature, Figure 30, which demonstrates the advantage of the power fed gradient polymer over the random copolymer. It will be noted that the use temperature of the gradient polymer is fully 20-25°C higher than that of the random copolymer.

In another instance, it was found that the toughness (ductility) of a polymer could be increased by providing a unique feed profile. Using a linear power feed system the brittle point (as measured by its brittle-ductile transition, T_{BD})⁷ of a 50/50 methyl methacrylate/ethyl acrylate copolymer was decreased from 0° for the random copolymer to -24° for the gradient copolymer without affecting the apparent hardness of the coating (*Figure* 31).

Since these initial experiments were performed several years ago, we have found that this type of experimental approach has had a profound effect upon our experimental methodology of product development. We have stopped thinking of a latex as an aqueous dispersion of a random copolymer, rather we are convinced that the particle infrastructure as created by the reaction pathway plays an extremely important role in the overall performance of a water-borne latex coating. It is only through a mutual understanding by both polymer chemists and formulators of this "particle infrastructure" that the ultimate performance can be attained. We are committed to the idea that the polymer chemists working in conjunction with the coating formulator will be able to markedly improve the performance of latex coatings, not only in the familiar Trade Finish Area but also in the emerging Industrial Finish Applications, and, perhaps, meet the challenge of economics, energy and ecology.

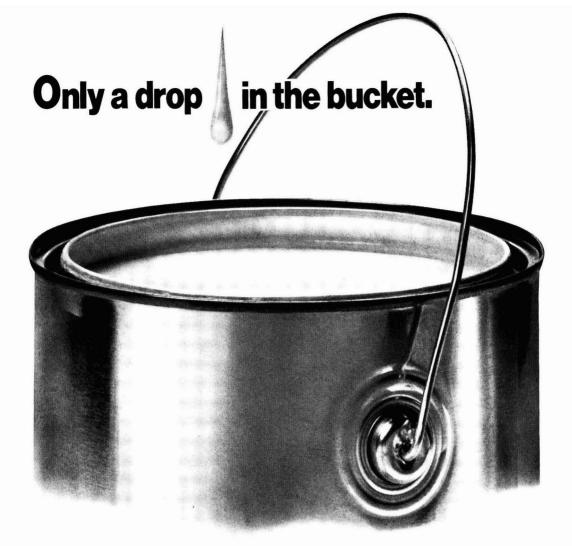
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Without the efforts of these persons, this lecture would not be possible.

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Coating Durability On Organolead-Treated Southern Pine In Exterior Exposure

H.M. Barnes Mississippi State University*

Three coatings were applied to organolead-treated southern pine and exposed at 45° south. Significant improvement in the durability of a vinyl-acrylic latex and an alkyd paint on treated wood was demonstrated. No increase in the durability of a phenolic spar varnish was observed. Improved durability appeared to be independent of the type of organolead compound or the strength of treating solutions used.

INTRODUCTION

In a recent report¹ the durability of coatings applied to southern pine substrates treated with organolead compounds and artificially weathered was discussed. No discernible differences between treated and untreated samples in any coating group were indicated. Durability appeared to be independent of treatment level. It should be noted that treatment level represented the strength of the treating solutions and not the amount of preservative in the wood structure. It was suggested that exterior durability of coatings on treated material might be better than the durability on untreated controls.

In this paper the results from the exterior weathering of similarly treated and coated samples are presented after 36 months of exterior exposure.

MATERIALS AND PROCEDURES

Selected southern pine boards with a nominal measurement of $1 \times 6 \times 18$ in. [45.7 cm (long) $\times 13.9$ cm (wide) $\times 1.9$ cm (thick)] were conditioned at 22°C and 50% relative humidity prior to treatment. All lumber was flat-sawn, clear stock averaging six to nine rings per inch and containing no heartwood. Randomly assigned samples were pressure treated with a treatment regimen of 30 min of vacuum [25 in. Hg (63.5 cm Hg) or better] and 2 hr of pressure at 160 psi (11.25 kg/cm²) with

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0.1, 0.5, or 1.0% (weight basis) solutions of trimethyllead acetate (TMLA)/water, triethyllead acetate (TELA)/ethanol, tributyllead acetate (TBLA)/toluene, or dibutyllead diacetate (DBLD)/water. The threshold retention value for these compounds of 0.15 lb/ft³ is within the range of threshold values for the principal wood preservatives (chromated copper arsenate, pentachlorophenol). Following treatment, the samples

Table 1—Composition of Topcoats Tested						
Raw Material	% By Weight					
LATEX						
Pigment						
Rutile TiO ₂						
CaCO ₃	17.6					
ZnO						
Vehicle						
Vinyl acetate/acrylic resin						
Water						
Linseed-castor phthalic-erythritol						
alkyd resin	11.86					
Water, aromatic hydrocarbon						
Water, aromatic nyurocaroon						
ALKYD						
Pigment	44.8%					
TiO ₂						
ZnO						
CaCO ₃						
Silicates						
Vehicle						
Linseed-castor modified alkyd resin .						
Mineral spirits						
Drier						
Mineral spirits						
CLEAR						
Tung oil, linseed oil, dehydrated						
Castor oil, phenolic resin, drier	53.7					
Mineral spirits, dipentene						
UV absorber (benzophenones)						
· · · · · · · · · · · · · · · · · · ·						

Treatment	Vin	yl-Acr	ylic	Modi	Modified-Alkyd			
		Years			Years	5		
	1	2	3	1	2	3		
Control	8	3	0	7	1	0		
Trimethyllead Acetate	8	6	2	9	5	2		
Triethyllead Acetate	7	5	2	8	2	1		
Tributyllead Acetate	8	5	3	8	5	2		
Dibutyllead Diacetate	7	5	2	8	2	1		

Table 2—Overall Exterior Performance of Two Coating Systems On Organolead-Treated Southern Pine At Three Exposure Times.³

(a) A rating of 10 indicates no defect.

were reconditioned at 22°C and 50% relative humidity and edge-sealed with a phenol-resorcinol adhesive.

Treated samples were coated by brush with either one coat of a white alkyd-modified, vinyl-acrylic latex paint, one coat of a linseed-castor-modified alkyd paint, or three coats of a clear phenolic spar varnish containing an ultraviolet absorber. Samples coated with the pigmented systems were first primed with one coat of a white linseed-soya, alkyd-base primer. Touch sanding was done between coats of the clear system. All coatings were locally purchased proprietary finishes. Their compositions are given in *Table 1*. For the treated samples, four replications for each coating × chemical × concentration were used. In addition, 12 untreated control samples were coated with each finish, yielding a total of 180 coated samples.

Coated samples were attached to a 45° south, exterior-exposure fence. The samples were inspected periodically and were evaluated using exposure standards.²

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RESULTS AND DISCUSSION

No consistent differences in the performance of the vinyl acrylic with respect to treatment or treating solution strength were noted. Therefore, exposure ratings for all solution strengths were combined. These are shown in *Table 2* along with values for the untreated coated control.

Failure of this coating on the untreated sample accelerated after one year's exposure. Coating failure was primarily by checking and cracking arising from the advent of mildew and decay organisms. The wood under the coating was spongy due to deterioration by decay organisms. *Fusarium sp.*, *Botrydiplodia sp.*, and *Schizophyllum commune* were isolated from the control panels. The treated panels exhibited mildewing, but after three years' exposure, no invasion of the substrate by decay organisms was noted. Typical treated and untreated panels after three years' exposure are shown in *Figure* 1.

Results from the exposure of the modified alkyd are also shown in *Table 2*. The control samples failed completely prior to three years' exposure. Treated panels

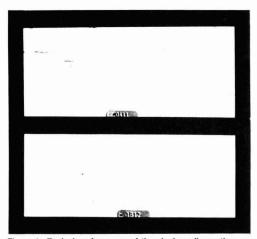


Figure 1—Typical performance of the vinyl-acrylic coating on untreated (top) and treated (bottom) samples after three years of exterior exposure at 45° south.

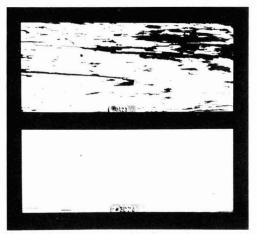


Figure 2—Typical performance of the alkyd coating on untreated (top) and treated (bottom) samples after three years of exterior exposure at 45° south.

performed much better and were rated below those coated with the vinyl-acrylic system. Samples treated with TMLA and TBLA performed slightly better after two years of exposure. At the end of three years, however, there were no differences among the treatment compounds. A set of typical panels is shown in *Figure 2*.

All untreated samples coated with the spar varnish completely failed after 14 months of exposure. The treated samples performed only slightly better, with complete failure occuring after 18 months. Unfortunately, the treatments examined in this study did little to aid the durability of a clear exterior finish over woody substrates.

These results also serve again to demonstrate the differences between Weather-Ometer³⁶ exposure results and those found in actual exposure, a fact recently demonstrated by Feist and his coworkers.³

SUMMARY

This study indicates that organolead wood preservatives are compatible with typical coating systems in use

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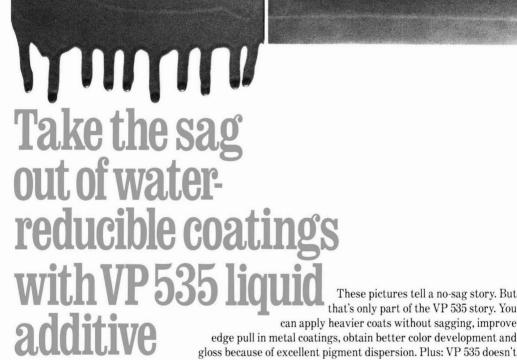
today. By reducing the attack by microorganisms, they increase the durability of pigmented coating systems. They offer little protection for wood coated with clear systems, since these coatings fail by ultraviolet degradation prior to being seriously affected by decay and mildew organisms.

ACKNOWLEDGMENT

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Steric Stabilization Of Surface-Coated Titanium Dioxide Pigments By Adsorbed Methyl Methacrylate Copolymers

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The solution adsorption of some copolymers of methyl methacrylate onto a series of titanium dioxide pigments, which had been coated to impart various degrees of acidity to their surfaces, has been studied and, at the same time, the colloidal stability of the dispersions has been assessed. Homopolymers adsorb poorly from methyl ethyl ketone solutions and do not stabilize dispersions of the coated pigments; however, they are better adsorbed from their solutions in toluene and are then effective in dispersion stabilization.

Incorporation of a very small quantity of carboxylic acid groups into the macromolecular chain increases the adsorption and, provided the surface coverage is high, has a beneficial effect on dispersion stability. The extent of copolymer adsorption depends in considerable measure on the solubility parameter of the solvent. Copolymers with small amounts of nitrile, acrylamide, pyridyl, and hydroxyl groups also show enhanced adsorptions but do not, in general, improve dispersion stability except for some cationic copolymers on the more acid pigments. The relations between polymer adsorption and polymer structure, surface composition and solvent nature are discussed in terms of general acid-base interactions.

INTRODUCTION

Dispersions of particulate matter in nonaqueous media may be stabilized against coagulation by macromolecular species present at the phase interface; very efficient stabilization may be obtained when the chains are permanently bound to the surface.¹ To obtain a good degree of colloid stability from physicially adsorbed polymers, however, it is necessary that the chains are well anchored. Modern theories of steric stabilization predict that stability is improved by thicker interfacial layers, higher segment densities and, most importantly, good solvency conditions for those chain segments extending into the dispersion medium.² Relatively small alterations in polymer structure have been found^{3,4} to have significant effect on dispersion stabilization as a consequence of either the strength of anchoring or the conformation of the adsorbed chains.

The adsorption of a polymer at a solid surface is strongly influenced by the chemical structures of the polymer, the surface, and the solvent from which adsorption is made. In the present report we show how methyl methacrylate copolymers are adsorbed by a series of titanium dioxide pigments which have been coated so as to possess a gradation in surface character. We show also how the colloidal stability of pigment dispersions is affected by alteration of polymer composition, pigment surface chemistry, and solvent nature.

MATERIALS AND METHODS

Materials

Five surface-treated rutile pigments are supplied by Tioxide International Ltd. The surface coating of the titanium dioxide pigment was obtained by treating the base pigment with solutions of sodium silicate, followed by aluminum sulphate (or aluminum nitrate in the case of V). Surface basicity was controlled mainly by adjusting the pH during this process and the values are included in Table 1. All pigments contained approximately the same amount (10%) of coating. High resolution transmission electron micrographs supplied by the manufacturer show a continuous coating to the titanium dioxide particles which is approximately 5-7 nm thick. The crystal size (specifically for pigment III) is approximately 220 nm and the surface areas quoted in Table 1 were determined by nitrogen adsorption at 77°K (BET analysis taking area of nitrogen molecule to be 0.162 nm²). The compositions of the surface coatings are taken from x-ray fluorescence measurements made by the manufacturer.

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			Surface C	omposition		Surface Area	pH of
Pigment	Preparation pH	% Al ₂ 0 ₃	% SiO ₂	% SO42	ppm NO ₃	m ² g ⁻¹	Aqueous Slurry
I	5.0	4.28	2.30	1.05		9.2	4.25
11	7.0	4.45	2.20	0.53		9.9	5.00
III	8.5	4.38	2.84	0.09		13.6	5.78
IV	10.5	4.35	2.40	0.07	—	19.8	6.80
	then to 8.0						
V	8.5	4.43	2.43		5.25	21.6	6.45

Table 1—Characteristics of Rutile Pigments

A simple method to characterize the various pigment coatings is via the pH of the aqueous slurry obtained by shaking 2g of pigment with 50 cm³ water for 15 min and centrifuging off the larger particles. The main difference between pigments I, II, and III arise from their different pH's at preparation. Sulphate ions are retained in the coatings at lower pH's and inhibit the formation of crystalline alumina which is responsible for surface basicity; nitrate ions do not exhibit this effect. Pigment III is a commercial product and had received a more intensive milling than the other, laboratory-made, pigments. Pigment II was prepared later during these studies and was little investigated. All pigments were vacuum dried at 110°C and kept *in vacuo* until required.

Methyl methacrylate homopolymers were prepared as follows. The monomer (BDH Ltd) was the middle cut from a reduced pressure distillation and was polymerized as a 25% solution in toluene at 60°C under nitrogen using recrystallized azoisobutyronitrile (0.4% on monomer) as initiator. After some 20% conversion, the polymer was precipitated by pouring the reaction mixture into petroleum ether. After thorough washing with further petroleum ether, the powdery product was filtered off and dried *in vacuo*.

Three commercial polymethylmethacrylates (Acryloid[®], Rohm and Haas Ltd.) were used extensively. These were supplied in solution and solid polymer was isolated by thinning with 2.5 parts acetone and precipitation with petroleum ether. After washing well with further nonsolvent, the dried polymer was redissolved in pure acetone and again precipitated, washed and dried *in vacuo*. During the course of our studies, it became evident that these commercial polymers had a slightly acidic functionality which was not removed by repeated dissolution and reprecipitation. Acid contents were found by titration against 0.1M sodium hydroxide

		Table 2—Ch	aracterizatior	of Polymers		
Polymer Code	% Comonomer in Feed	% Copolymerized Units in Polymer	$[\eta]^a$	Μ _v ^b	$\overline{\boldsymbol{M}}_{\boldsymbol{w}}/\overline{\boldsymbol{M}}_{\boldsymbol{n}}^{\mathrm{c}}$	Remarks
			Homopolymers	3		
PMM-1	zero		0.157	37000		
PMM-2	zero	-	0.310	96000		
PMM-3	zero	-	0.477	175000		
PMM-4	zero	—	0.571	223000		
PMM-A10-Meth	—	-	-	49000 ^d	-	methylated PMM-A10
		A	cidic Copolym	ers		
PMM-MA	2.0	3.2	0.156	37000"		
PMM-A10		0.7	0.188	49000"	1.9	Commercial
PMM-A21LV	—	0.7	0.232	68000°	1.7	'homopolymers'
PMM-A21		0.7	0.264	78000	2.0	(see text)
PMM-A10-Hydrol.1	_	2.7		49000 ^d		
PMM-A10-Hydrol.2		3.2		49000 ^d		hydrolyzed PMM-A10
		C	ther Copolyme	rs		
PMM-AM-1	0.5	0.6	0.493	183000°		
PMM-AM-2	1.0	0.7	0.515	194000°		
PMM-4VP-1	0.5	1.2	0.488	181000°		4-vinyl pyridine
PMM-4VP-2	1.0	2.0	0.520	197000°		comonomer
PMM-2HEM	1.0	1.7	0.491	182000°		2-hydroxyethyl
						methacrylate comonome
PMM-AN	1.0	0.8	0.561	218000°		acrylonitrile comonomer

(a) dl.g⁻¹, in toluene at 25°C.

(b) From equation of Chinai, et al⁷ $[\eta] = 7.1 \times 10^{5} (M_{\chi})^{0.23}$.

(c) From gel permeation chromatography in tetrahydrofuran.(d) Assuming no chain seission during methylation.

(e) Assuming $[\eta] / M$, relation as for homopolymer.

of a known mass of polymer (ca 1g) dissolved in acetone and are expressed in Table 2 as the equivalent weight % of methacrylic acid. Careful infrared spectroscopy demonstrated that a laboratory-made copolymer containing 0.5% methacrylic acid units shows a broad absorption between 2400 and 2700 cm⁻¹ which is absent in a laboratory-made homopolymer of methyl methacrylate. The commercial polymer (Acryloid A-21) exhibits a weak absorption in this region of the infrared spectrum which may represent carboxylic acid, but the absorption is not as strong as the measured acidity would require. Inspection of the other spectral regions characteristic of COOH groups does not enable a clear differentiation between these three polymers to be made and we cannot definitely specify the nature of the acidic comonomer in the commercial materials. However, one of them (Acryloid A-10) was successfully methylated in toluene solution by addition of ethereal diazomethane. After precipitation and a further solution-precipitation cycle, the polymer was dried in vacuo. This sample was found to have zero acidity on titration.

The same commercial polymer (PMM-A10) was partially hydrolyzed in a heterogeneous system following the technique of Glavis.5 About 10g of polymer were added to a mixture of sodium hydroxide (20g), water (18 cm³), and isopropanol (150 cm³) and then heated at $82 \pm$ 2°C with constant stirring for 60 min in one case and 90 min in the other.

After filtration, the polymer was washed with dilute hydrochloric acid and dissolved in acetone. Following further treatment with dilute hydrochloric acid, the polymer was precipitated by petroleum ether, dried, redissolved in acetone, reprecipitated, and, finally, dried in vacuo. The acid content was found as before.

Copolymers containing low amounts of methacrylic acid, acrylamide, 4-vinyl pyridine, acrylonitrile, and 2-hydroxyl-ethylmethacrylate were prepared to low conversion by radical polymerization using the same technique as for the laboratory-made homopolymer samples. Acrylamide was used as received, 4-vinyl pyridine was fractionally distilled under reduced pressure and the inhibitor removed from the other monomers by adsorption on a silica gel column. Characterization data are listed in Table 2. For the polymers made with acrylonitrile, acrylamide, and vinyl pyridine comonomers, the compositions are from nitrogen contents found on elemental analysis (Microanalytical Services, Chemistry Department, U.M.I.S.T). The hydroxyl content of P-2HEM was measured by acetylation.⁶ The M_w/M_n ratios from gel permeation chromatography data are based on a calibration with polystyrene and can be taken only as a guide to the width of the molecular weight distribution. The viscosity-average molecular weights are from the calibration published by Chinai, et al⁷ which was based on light-scattering studies of polymethylmethacrylate fractions covering the molecular weight range of our samples; it is unlikely that the small comonomer contents will lead to significant error in the estimation of the molecular weights from intrinsic viscosity data.

Methyl ethyl ketone and acetone were fractionally distilled at atmospheric pressure and dried over molecular sieve; other solvents were of analytical reagent grade and were used without further purification. Water contents were measured by the Karl Fischer titration method.

Methods

Solution adsorptions were measured by shaking a known quantity of pigment (ca 500mg) with 25 cm³ of polymer solution of known concentration contained in a carefully stoppered conical flask. The agitation was made in a horizontal plane (amplitude 25mm, 90 cycles/min) in a thermostat at 25.0±0.1°C for 40 hr. Supernatants were centrifuged in closed tubes and equilibrium solution concentrations found gravimetrically. Measurements were made in duplicate, suitable blank determinations being made with each set. The solution concentrations of methyl isobutyrate (model compound) were determined by gas chromatography and by refractometry.

Dispersion stability was assessed by two methods. When a moderately concentrated dispersion of titanium dioxide particles is allowed to stand at constant temperature and without agitation, some coarse particles, or larger flocs, settle rapidly to form a thin layer of sediment. Above this is a layer which settles slowly, having a definite boundary with the hazy supernatant. The settling process is characterized by mutual interference between particles and the rate of settling is not given by Stokes' Law.

About 500mg pigment was weighed accurately into a 50 cm³ conical flask to which was added 25 cm³ polymer solution of known concentration; this is the same adsorbent/solution ratio as used in adsorption measurements. Twenty glass beads, approx. 3 mm diameter, were added to each flask which was then subjected to 1 min ultrasonic agitation before shaking vigorously on a mechanical wrist-action shaker for 150 min. Immediately after shaking, 5 cm³ of dispersion were transferred to a tube ($75 \times 11 \text{ mm i.d.}$) and allowed to stand at room temperature $(23\pm2^{\circ}C)$. Three such tubes were prepared for each test. The height of the subsiding boundary was measured at various times by use of a cathetometer: the data are plotted as the relative sedimentation height, h_t/h_o , where h_t is the height of boundary at time t and h_o the initial height, against the time of sedimentation. The initial slope of the nearly linear plot is presented as a relative measure of dispersion stability and is reproducible to better than $\pm 5\%$.

After standing for five days, 0.2 cm³ of the hazy supernatant was removed by a pipette at a fixed depth (25 mm) from the bottom of the tube: this sample was diluted with 5 cm³ of the original polymer solution, subjected to ultrasonic irradiation for 5 min, and immediately transferred to a 10 mm optical cell for measurement of its optical density at 530 nm, using polymer solution as reference. By careful standardization of the procedure, a reproducibility of about ± 5% was obtained. The relative rating of dispersion stabilities from optical densities concurred well with that given by set-

Table 3—Adsorption of Polymethylmethacrylates

	Plateau Adsorption (mg g ⁻ⁱ) From Methyl Ethyl Ketone From Toluene									
Sample Code Pigment	1	111	IV	v	1	ш	IV	v		
PMM-1	-4.0	-3.0	0.7	2.0	_	_	_	_		
PMM-A10										
Meth.	1.0	1.0	1.0	2.0	12.9	18.9	20.5	20.8		
PMM-2	-2.2	-1.0	1.5	1.7	20.9	25.1	30.7	26.6		
PMM-3	3.4	2.5	8.8	9.9		_	-			
PMM-4		-		_	30.4	36.4	51.1	45.2		

Table 4—Pigment Stability in Pure Liquids

Solvent	Pigment I	Ш	ш	IV	۷
Toluene	0"	0	0	0	0
Methyl ethyl ketone	0	0	2	4	0
Methylene chloride	0	0	0	0	0
Acetone	0	0	1	3	0
Water	$\infty^{\mathbf{b}}$	5	$0^{\rm c}$	0	0

(a) 0 = clear, 1-5 increasing turbidity.

(b) Fully stable dispersion.

(c) Much slower to clear than other unstable systems.

Table 5—Dispersion Stability in Toluene Solutions Of Homopolymers

	Relative Settling Rate ($h^{-1} \times 10^3$)						
Sample Code	Pigment I	ш	IV	v			
PMM-A10 Meth.	31.5	32.6	∞^{ii}	x			
PMM-2	28.8	29.6	x	x			
PMM-4	25.8	23.7	28.0	30.8			

(a) Settles out in a few minutes.

tling rates and greater prominence to the latter technique was given.

RESULTS

First, adsorption and dispersion stabilization behavior exhibited by methyl methacrylate homopolymers were considered. Two tests were made of the time necessary to ensure adsorption equilibrium. Polymer PMM-A10 reached a constant level of adsorption on pigment V from toluene in 2 hr but required about 8 hr with pigment IV from methyl ethyl ketone. On the basis of these results, it is considered that the standard procedure which has a contact period of 40 hr is adequate for all systems investigated. Polymer PMM-A10 was adsorbed from a constant volume of methyl ethyl ketone at a constant concentration onto pigment IV in a range of masses (200 mg to 2000 mg); no change in the adsorption, which would correspond to the plateau region of the isotherm, was found. Thus, independence of the pigment/polymer ratio was confirmed.

Adsorption isotherms of methyl methacrylate homopolymers were found on four pigments and the data are summarized in *Table* 3 in terms of the plateau adsorption. Adsorptions are normally very small from a polar solvent, methyl ethyl ketone, negative results being found in some cases. Only the higher molecular weight homopolymer (PMM-3) shows any significant extent of interaction with titanium dioxide pigments and then only with those having the more basic surface coatings. Negative adsorptions imply a preferential adsorption of solvent; appropriate "blank" determinations with pigment in solvent eliminate the possibility that these results are a consequence of material being leached from the solids.

On the other hand, finite adsorption is found from toluene, and to an extent that is clearly molecular

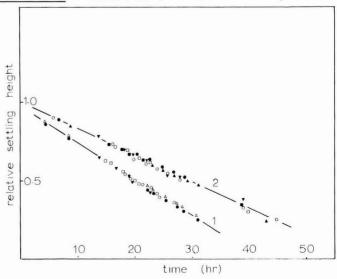


Figure 1—Relative settling height against time: Curve 1, pigment IV, PMM-A10 methyl ethyl ketone; Curve 2, pigment III, PMM-A10, toluene. Agitation time 2hr ⋅ 4hr ₀, 7hr ■, 9hr □, 14hr ▲, 15hr △, 23hr ▼

Sample code		Plateau Adsorption (mg.g ⁻¹) From Methyl Ethyl Ketone From Toluer							ne
	% methacrylic acid	Pigment I	ш	IV	۷	I	ш	IV	۷
PMM-A10 Meth.	Zero	1.0	1.0	1.0	2.0	12.9	18.9	20.5	20.8
PMM-A10	0.7	5.3	24.0	28.8	24.8	19.9	30.0	35.3	39.3
PMM-A10 Hydrol-1	2.6	20.8	31.4	37.6	37.6	_			_
PMM-A10 Hydrol-2	3.2	23.5	28.1	39.2	37.0	38.0	46.5	54.2	43.8
PMM-MA	3.2	11.5	15.2	17.4	16.5	28.9	39.1	44.8	40.1

Table 6—Adsorption of COOH-Containing Polymethylmethacrylates

weight dependent. The exponent of the empirical equation⁸

$$A = KM^{\alpha}$$
(1)

was found by plotting the data of *Tables* 2 and 3 and lies in the range 0.44 to 0.60 for the various pigments. Although these values are approximate, being based on three samples only, they are clearly higher than those reported in several other polymer/solvent/adsorbent systems.^{8,9}

Before studying the effect of adsorbed polymethylmethacrylate on dispersion stability, and in view of the different adsorption rates observed in different solvents, a preliminary experiment was made to find the effect of various times of agitation on the consequent settling rate. Dispersions of pigment IV in methyl ethyl ketone and pigment III in toluene solutions of PMM-A10 were prepared with times of shaking varying between 2 and 23 hr. The results are given in *Figure* 1 and show that the sedimenting boundary falls linearly with time and that the rate is independent of the period of agitation.

The stability of the pigments in pure liquids was assessed by visual observation of the supernatant after standing for three days (*Table* 4). No pigment is stable in the nonpolar liquids, all the particles separating out in a few minutes. Pigments III and IV in polar liquids have a degree of stability and fines are still present in the supernatant after several weeks. The more acidic pigments I and II are relatively stable in water, particularly the former which is more stable in pure water than in most of the polymer solutions. This is an example of charge stabilization since, on addition of sodium chloride, a gradual coagulation is observed.

The effect of methylmethacrylate homopolymers on the dispersion stability of the pigments is summarized in

Table 5. In this and subsequent tables, the initial polymer concentration is approximately 1% (w/v) and the measurements referred to previously confirm that this concentration is high enough to correspond to the plateau of the adsorption isotherm. None of the homopolymers would stabilize any pigment in methyl ethyl ketone; this is true even for the higher molecular weight samples which were adsorbed to a small but finite, extent. In toluene, the more basic pigments are stabilized only by high molecular weight homopolymer, even though the adsorption is quite high. Table 5 also shows that higher molecular weight polymers are better stabilizers. It is not possible to compare settling rates directly between the different pigments as these will have different particle sizes, and pigment III, which had been more extensively milled, will be inherently more stable. Unfortunately, it is not possible to express the results in terms of stability ratios since the dispersion in the pure solvents are too unstable to provide an accurate settling rate.

The effect of small amounts of copolymerized acid groups on polymer adsorption is shown in *Table* 6.

The adsorption of homopolymers from methyl ethyl ketone solution is greatly enhanced by the presence of a very few acid groups, especially on the pigments of high basicity, and the same pattern is evident from toluene solutions. From both solvents, polymer PMM-A10 on the most acidic pigment (I) exhibits the smallest improvement. The laboratory-made copolymer (PMM-MA) is not as well adsorbed as the hydrolyzed commercial polymer (PMM-A10 Hydrol-2); there are several possible reasons for this. It is of lower molecular weight and may have a different molecular weight distribution; the exact composition of the parent compositional homogeneity of the hydrolyzed sample.

Table 7—Relative Settling R	lates of Pigments with	COOH-Containing Polymers
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				S	ettling Rate	(h ^{.1} × 10 ³)			
	%	From Methyl Ethyl Ketone				From Toluene			
Sample Code	Acid	Pigment I	III	IV	v	1		IV	v
PMM-A10 Meth	zero	20	x	x	œ	31.5	32.6	x	œ
PMM-A10	0.7	x	28.6	24.1	33.8	23.0	18.0	21.1	21.7
PMM-A10 Hydrol-1	2.6	23.3	_	24.9	25.5		-	—	-
PMM-A10 Hydrol-2	3.2	21.1	29.4	25.0	24.7	67.6	78.7	166.2	105.4
PMM-MA	3.2	œ	84.8	28.3	47.9	—	—		-

			Ρ	olymer	PMM-A10				Polyme	r PMM-	A21	
	Solubility			Plateau	Adsorptio	n (mg/g)			Plateau Adsorp		rption	tion (mg/g)
Solvent	Parameter ^a	$[\eta]^{b}$	Pigment I	Ш	Ш	IV	v	$[\eta]^{b}$	1	Ш	IV	v
Carbon tetrachloride	8.6	-	(26.6) ^e	-	(32.9) ^c 36.0 ^d	(39.5) ^c	(35.4) ^c	—	-	-	—	_
Xylene	8.8	-	_	_	36.0 ^d	—	_	—	-	-	—	-
Toluene	8.9	0.188	19.9	18.3	30.0	35.3	39.3	0.264	25.9	35.0	41.4	41.0
Methyl ethyl ketone	9.3	0.195	5.3	18.8	24.0	28.8	24.8	0.310	22.5	27.6	38.2	37.2
Methylene chloride	9.7	0.311	12.1		17.3	24.0	26.2	0.485	16.7	24.1	33.7	34.8
Acetone ^e		0.165	1.0	_	5.9	9.1	6.7	0.270	16.8	25.8	30.6	30.2
Acetone ^f	9.9		4.5	-	12.8	21.4	16.9	_		_		

Table 8—Adsorption of COOH-Containing (0.7%) Polymethylmethacrylates from Several Solvents

(e) normal grade.

(f) special acid-free.

The changes in adsorption due to incorporation of acid functionality into the macromolecular chains affect the stability of the pigment dispersions and the results are summarized in *Table 7*.

The lack of stability of pigment I in methyl ethyl ketone solutions of PMM-A10 and PMM-MA compared to the slightly higher molecular weight sample PMM-A10 Hydrol-2 also follows the pattern of the adsorption

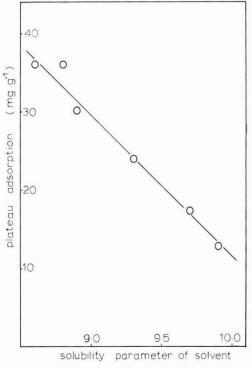


Figure 2—Adsorption of PMM-A10 onto pigment III from several solvents. (Solubility parameter in cal^{1/2} cm^{-3/2})

data. However, the relatively poor performance of PMM-A10 Hydrol-2 in toluene solution does not correlate at all with adsorption.

The solvent dependence of adsorption was examined further with the acidic (commercial) copolymers. The data of Table 8 show how the pattern of adsorption varies with the solvent nature. Solvent dependence is in the same order with both polymers. Acetone, of whatever quality, seems out of order in terms of a coil size dependence, i.e., adsorption is inversely related to intrinsic viscosity. A satisfactory relation to the solvent solubility parameter is found for the most extensive set of data (Figure 2), and similar behavior has been reported with some other systems.^{10,11} Thus, with any given pigment coating, the level of adsorption is strongly determined by the polymer-solvent interaction. Normally, redistilled acetone gives a lowered adsorption because its slight acidic impurity (equivalent to 0.7% acetic acid) competes for surface sites. The data of Table 8 also show a fairly strong molecular weight dependence of adsorption, particularly in the ketonic solvent.

Measurement of adsorption from a mixed solvent system may help to describe the relative affinities of the various components for the surface. Solutions of PMM-A10 in toluene were made and quantities of methyl ethyl ketone added in the range 1 to 20% (v/v). Adsorptions were then studied on pigments I and IV. these representing the extremes of surface acidity. As may be seen from Figure 3, the plateau adsorption decreases as the content of methyl ethyl ketone is increased, the effect being most marked at small additions, and tends to reach the level found from pure methyl ethyl ketone. This result could be interpreted as showing that solvent-surface interactions play a part in fixing the amount of polymer adsorption. Methyl ethyl ketone is a basic solvent and might be expected to adsorb preferentially on the surface acidic sites; hence, the greater effect on the more acidic pigment I. As the intrinsic viscosity of the polymer is much the same in

⁽a) $cal^{1/2} cm^{-3/2}$. (b) $dl.g^{-1}$.

⁽c) at concentration $\sim 2 \text{ g } l^{-1}$ (d) extrapolated.

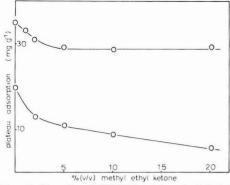


Figure 3—Adsorption of PMM-A10 from toluene/methyl ethyl ketone mixtures: Curve 1, pigment I; Curve 2, pigment IV

both solvents (0.188 and 0.195 dl g⁻¹ in toluene and methyl ethyl ketone respectively), it might be thought that small additions of the polar solvent would have little effect on adsorption by virtue of improving the polymer solubility. However, this argument may not be correct: although a very wide spread of values for the solubility parameter of polymethyl methacrylate is reported¹² it may well be that PMM-A10 has a solubility parameter between that of the two solvents, and small additions of one liquid to the other might markedly improve the net polymer-solvent interaction.

The amount of polymer (PMM-A10 and PMM-A21) adsorbed generally increases with the surface basicity, as judged by the pH of an aqueous dispersion, but this trend is not always shown, for example, as with adsorption of PMM-A10 from toluene (*Table* 8). Since the more basic pigments tend to be of higher surface areas (*Table* 1), it may also seem that polymer adsorption is determined by the superficial area of the pigment: indeed, in methylene chloride, the relation is linear but it is less so with the other solvents, where pigment IV.

The low adsorption of PMM-A10 from methyl ethyl ketone onto pigment I is associated with a curiously-shaped isotherm (*Figure* 4): normal isotherms are found with the other pigments and with PMM-A21 on I. Furthermore, isotherms are normal from toluene (*Figure* 5). Although the experimental results at lower surface coverages are limited, the data have been tested against

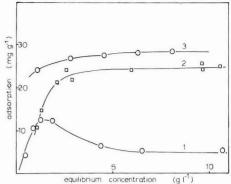


Figure 4—Adsorption from methyl ethyl ketone: Curve, PMM-A10 on pigment I; Curve 2, PMM-A21 on pigment I; Curve 3, PMM-A10 on pigment IV

the Langmuir¹³ isotherm and against the limiting form of the Simha, Frisch, and Eirich equation.¹⁴ The latter does not provide a satisfactory representation of the experimental adsorptions, but, rather surprisingly, the Langmuir equation, originally derived for an entirely different adsorption situation, is satisfactory.

The colloidal stability in various solvents was also measured with polymers carrying a few carboxylic acid groups (Table 9). Several points should be noted. Although efficient adsorption is found from a poor solvent, carbon tetrachloride, none of the pigments are stable in this medium. However, the poor polymer solubility in this solvent restricts measurements to concentrations below 2 g/l and the plateau of the adsorption isotherm would not be attained. The other two examples of complete absence of any stabilization correspond to systems where the level of polymer adsorption is low. Direct comparison between the different solvents is difficult since they are of differing viscosities; the pigments tend to be less well stabilized the higher the solubility parameter, the polar methyl ethyl ketone appears to give even poorer dispersions than might be expected on solubility grounds alone.

The concentration dependence of dispersion stability may be seen from *Figures* 6-9. Both settling rates and supernatant turbidities show that the stabilization effect is manifest only at solution concentrations corresponding to the isotherm plateau, and the two methods

Table 9—Settling Rates (h⁻¹ × 10³) of Pigments in Solutions Of COOH-Containing (0.7%) Polymethylmethacrylates

		Polymer PMM-A10				Polymer PMM-A21						
Solvent	Solubility ^a Parameter	[η] ^b	Pigment I	II	ш	IV	v	[η] ^b	i	ш	IV	v
Carbon tetrachloride	8.6		x	_	x	x	x	_	_	_	_	_
Toluene	8.9	0.188	23.0	_	18.0	21.1	21.7	0.265	20.5	17.9	20.7	19.1
Methyl ethyl ketone	9.3	0.195	x	∞	28.6	24.1	33.8	0.310	28.9	27.5	27.2	28.8
Methylene chloride	9.7	0.311	33.0	-	19.2	27.5	30.0	0.485	-	_		
Acetone	9.9	0.165	x	_	39.7	32.5	37.6	0.270	_	-	_	_

(a) cal^{1/2} cm^{-3/2} (b) dl g⁻¹.

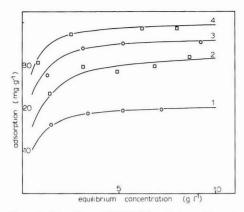


Figure 5—Adsorption of PMM-A10 from toluene: Curve 1, pigment I; Curve 2, pigment III; Curve 3, pigment IV; Curve 4, pigment V. Solid lines, Langmuir equation

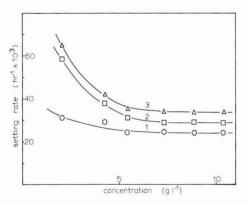


Figure 6—Settling rate against concentration of PMM-A10 in methyl ethyl ketone; Curve 1, pigment IV; Curve 2, pigment III; Curve 3, pigment V. (Pigments I and II unstable)

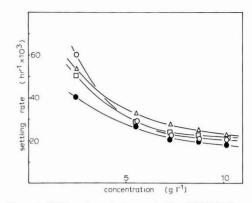


Figure 8—Settling rate against concentration of PMM-A10 in toluene; Δ , pigment I, •, pigment III; \circ , pigment IV; \Box , pigment V

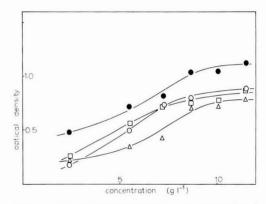


Figure 9—Supernatant optical density against concentration of PMM-A10 in toluene; symbols as in Figure 8

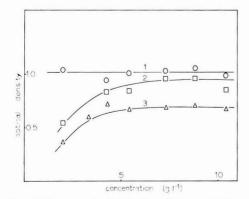


Figure 7—Supernatant optical density against concentration of PMM-A10 in methyl ethyl ketone; Curve 1, pigment IV; Curve 2, pigment III; Curve 3, pigment V

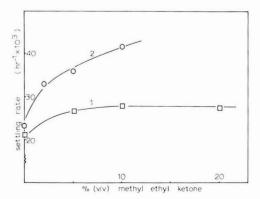


Figure 10—Settling rate against %(v/v) methyl ethyl ketone in toluene; Curve 1, PMM-A10, pigment IV; Curve 2, PMM-A10, pigment I

				P	lateau Adsorp	tion (mg g ')	
Sample Code	Comonomeric Group	Content of Comonomer (%)	$[\eta]^{a}$	Pigment I	Ш	IV	v
PMM-3	None	Zero	0.477	3.4	2.5	8.8	9.9
PMM-A21	-COOH ?	0.7	0.264	22.5	27.6	38.2	37.2
PMM-AM-1	-CONH.	0.6	0.493	14.5	17.5	21.7	23.5
PMM-AM-2	-CONH ₂	0.7	0.515	21.0	22.5	27.2	32.4
PMM-4VP-1	-C ₅ H ₄ N	1.2	0.488	19.0	22.7	19.2	16.3
PMM-4VP-2	-C-H ₄ N	2.0	0.520	30.3	33.1	30.8	25.8
PMM-2HEM	-COO CH ₂ CH ₂ OH	1.7	0.491	14.5	23.9	30.3	31.3
PMM-AN	-CN	0.8	0.561	15.9	6.0	6.9	11.3

Table 10—Adsorption of Methacrylate Copolymers from Methyl Ethyl Ketone

give concordant assessments. As the surface coverage is reduced, the dispersions become less stable. Although not shown, precisely the same result is found from solutions of PMM-A10 in acetone and in methylene chloride.

Addition of methyl ethyl ketone to toluene solutions of PMM-A 10 markedly reduces adsorption (*Figure* 3); a parallel worsening in dispersion stability is also exhibited (*Figure* 10). With pigment IV, 5% addition of the polar cosolvent brings the stability to a new level which is about the same as that in pure methyl ethyl ketone. Pigment I is unstable in pure methyl ethyl ketone and an addition of 20% methyl ethyl ketone to toluene is sufficient to produce the same result in that the pigment settles immediately after cessation of agitation.

The effect of comonomer units other than carboxylic acid was briefly investigated in terms of polymer adsorption from solutions in methyl ethyl ketone and the summarized data are given as *Table* 10.

The amounts of comonomer were deliberately kept low since it was clear that the effect of carboxylic acid groups is manifest at small contents; furthermore, it was hoped that the low level of comonomeric units would cause little alteration in polymer solubility. With the exception of the commercial polymer PMM-A21, included in *Table* 10 for comparison purposes, the copolymers are quite similar in molecular size, to judge from their intrinsic viscosities. All modifications improve the adsorption over that of the homopolymer.

With acrylamide comonomeric units, the adsorption increases with surface basicity of the titania pigment and the improvement is most noticeable with pigments I and 11 where the adsorption approaches that of the commercial polymer. Hydroxyl groups are also favorable for adsorption although not quite as good as carboxylic acid. Again, although the adsorption increases with surface basicity, the relative improvement is best with the more acidic surfaces. Although nitrile groups increase adsorption on to pigment I, their effect with the other pigments is small. The best overall performance is with 2% 4-vinyl pyridine units. This most cationic modification is particularly well adsorbed on the less basic pigment surfaces and gives high adsorptions on all four pigments examined.

The dispersion stabilization data provide an interesting commentary on the adsorption results of *Table* 10. The settling rates for dispersions of the pigments in methyl ethyl ketone solutions of the same set of copolymers were measured and the results given in *Table* 11. Although all the copolymers adsorb on all the pigments and, in most cases, to a quite high level, nonetheless, stability is, with a few exceptions, very poor and the most basic pigments IV and V are hardly stabilized at all. The best results are with the more cationic copolymers of 4-vinyl pyridine.

The effect of a small amount of water, such as might be experienced in practice, was examined from both a nonpolar (toluene) and a polar (methyl ethyl ketone) liquid. Toluene was saturated with water before making up solutions of the commercial polymer samples and the amount before and after contact with the pigments determined by the Karl Fischer method. The adsorption data are tabulated in *Table* 12.

Table 11—Settling Rates ($h^{-1} \times 10^3$) of Pigments In Methyl Ethyl Ketone Solutions of Methacrylate Copolymers

				Settling Ra	te	
Sample Code	Comonomer Group	Content of Comonomer (%)	Pigment I	W	IV	۷
PMM-3	None	zero	x	x	x	x
PMM-A21	-COOH ?	0.7	28.9	27.5	27.2	28.8
PMM-AM-1	-CONH ₂	0.6	53.8	200.0	x	∞
PMM-AM-2	-CONH.	0.7	33.6	133.3	x	∞
PMM-4VP-1	$-C_3H_4N$	1.2	29.6	20.8	∞	x
PMM-4VP-2	$-C_3H_4N$	2.0	98.1	36.6	130.9	x
PMM-2HEM	-COOCH ₂ CH ₂ OH	1.7	333.3	œ	œ	00
PMM-AN	-CN	0.8	206.2	x	×	x

	PMM	-A10	PMM	I-A21	PMM-A10
Pigment	% Water at Equilibrium	Adsorption (mg/g)	% Water at Equilibrium	Adsorption (mg/g)	Adsorption (mg/g)
I	0.040	18.1 (19.9) ^c	0.034	25.3 (25.9)	7.0 (5.3)
III	0.040	27.9 (30.0)	0.033	34.7 (35.0)	24.1 (24.0)
IV	0.040	33.4 (35.3)	0.034	40.0 (41.4)	29.1 (28.8)
v	0.038	28.9 (39.3)	0.036	41.2 (41.0)	25.8 (24.8)

Table 12—Adsorption of COOH-Containing Polymethylmethacrylates from Wet Solvents

(c) Values in parentheses: adsorption from dry solvent

With PMM-A10, complete adsorption of water from toluene solution has only a slight effect on the adsorption except for the more marked fall with pigment V: the adsorption of the higher molecular weight sample is hardly affected. In methyl ethyl ketone, the slight enhancement of adsorption is barely outside experimental error; difficulties with the Karl Fischer technique in this solvent prevented an estimate of the final water content so it is not known if water competes with solvent molecules for surface sites in this case. Corresponding measurements of settling rates were also made in the presence of traces of water (Table 13).

The higher molecular weight polymer, which is slightly the superior in toluene solution, is made slightly worse by being saturated with water: its adsorption too. is slightly reduced (Table 12). However, sample PMM-A10, which also has its adsorption level cut a little by water, is now noticeably better in stabilizing the pigment dispersions. More dramatic results are found in methyl ethyl ketone from the pigments at the ends of the range. Pigment I, which is not stabilized in dry solutions of PMM-A10, is markedly improved whereas pigment V, which has some nitrate surface groups, is made unstable by addition of a small quantity of water.

The effect of a model plasticizer, dioctylphthalate, added at 30 parts per 100 parts PMM-A10, was found by measuring adsorption on pigment V from toluene solutions. The results are shown in Figure 11, which also gives the isotherm for dioctylphthalate solutions. The gravimetric method was used, and trial experiments

Table 13—Settling Rates (h⁻¹ × 10³) Of COOH-Containing Polymethyl Methacrylates **From Wet Solvents**

	Settling Rate in Toluene ^a			
Pigment	PMM-A10	PMM-A21	PMM-A10	
I	18.3 (23.0)°	21.6 (20.5)	51.0 (∞)	
III	14.4 (18.0)	18.2 (17.9)	30.0 (28.6)	
IV	15.1 (21.1)	21.5 (20.7)	27.8 (24.1)	
v	15.9 (21.7)	21.9 (19.1)	∞ (33.8)	

(a) Initial water content 0.060%, PMM-A10, 0.056%, PMM-A21 (b) Initial water content 0.40%

(c) Values in parenthesis; rates in dry solvent.

showed that none of the plasticizer was lost on solvent evaporation. After obtaining the total mass of polymer plus dioctylphthalate, the latter was extracted completely by three portions of diethyl ether and the weight of polymer found. Single point experiments with two other pigments (Table 14) confirm that the polymer adsorption is reduced although the adsorption of plasticizer is small. Settling rates were measured in the presence of dioctylphthalate in systems corresponding to the experiments of Figure 11 and Table 14. In no case does the plasticizer affect dispersion stability.

All the previous adsorption and dispersion stabilization results have been taken from experiments in dilute solutions where the isotherm levels off to an apparent plateau at equilibrium solution concentrations around 4 to 6 g/l and stays at this value up to at least 10 to 12 g/l. We also report some very limited observations on adsorption from much more concentrated solutions, up to 100 g/l: the experimental problems of high viscosity and small concentration changes on adsorption lead to a reduced accuracy. Figure 12 shows the behavior from a polar and nonpolar solvent. In both cases, after the dilute solution plateau of the isotherm, now at the extreme left of the curve, a further increment of adsorption occurs. In the case of toluene a second near-plateau is followed by yet further adsorption, whereas from

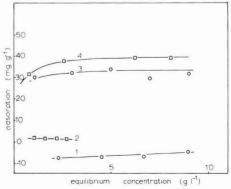


Figure 11-Adsorption of PMM-A10 and dioctylphthalate: Curve 1, dioctyphthalate in absence of polymer; Curve 2, dioctyphthalate in presence of polymer; Curve 3, PMM-A10 in presence of dioctylphthalate; Curve 4, PMM-A10 in absence of dioctyphthalate

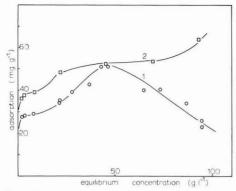


Figure 12—Adsorption from concentrated solution; Curve 1, PMM-A21 on pigment III from methyl ethyl ketone; Curve 2, PMM-A21LV on pigment IV from toluene

methyl ethyl ketone a maximum in the adsorption occurs. The difference in adsorption levels exhibited by the different pigments seems to be maintained in these concentrated solutions (*Table* 15).

Stabilities are much higher from concentrated polymer solutions (*Table* 16), particularly for the more severely milled pigment III. The higher stabilities may be a direct consequence of the improved adsorption from concentrated polymer solutions or may be merely the effect of the greater solution viscosities. Pigment II, which is not stabilized by PMM-A10 in methyl ethyl ketone in dilute solution, remains unstable when the polymer concentration is raised to 50 g/l. The particles settle less rapidly than in dilute solution but are still too fast to measure.

DISCUSSION

Methyl methacrylate homopolymer is adsorbed much more strongly from toluene than from methyl ethyl ketone; in both solvents the amount adsorbed increases with basicity of the pigment coating. The difference in performance from the two solvents may be a consequence of better solvency in the ketone but it should be noticed that the exponent of the Mark-Houwink equation, which is sensitive to the strength of polymer-solvent interactions, is reported¹² to be about the same in both liquids. Thus, a stronger competition for surface sites by the basic methyl ethyl ketone may

Table 14—Combined Adsorption of PMM-A10	
And Dioctylphthalate from Toluene	

	Dioctylph	thalate	PMM-A10			
Pigment	Equilibrium Concentration (g/l)	Adsorption (mg/g)	Equilibrium Concentration (g/l)	Adsorption (mg/g)		
III	2.78	0.8	9.27	26.9 (30.0) ^a		
IV	2.49	0.5	9.15	32.9 (35.3)*		

(a) adsorption (mg/g) in absence of plasticizer.

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be largely responsible for the low adsorptions from this solvent. Certainly, the molecular weight dependence of adsorption from toluene is unusually high which might be indicative of a diffuse, looped, surface conformation. Methyl isobutyrate, which is the analogous model compound for the polymer repeat unit, is not adsorbed from solutions in toluene and it must be presumed that the intrinsic strength of attachment of ester units to the coated pigments is relatively weak, whatever the solvent.

The observations on the stabilizing effect of adsorbed copolymers that are summarized in *Figures* 6-9 point clearly to the necessity of a high degree of surface coverage. The effects of polymer structure, solvent and pigment coating on dispersion stability are, therefore, discussed in terms of systems corresponding to plateau levels of polymer adsorption.

Methyl methacrylate homopolymer dissolved in the polar liquid methyl ethyl ketone is unable to stabilize any of the pigments because its adsorption is very low. However, even in toluene, from which it is quite well adsorbed, only the more acidic pigments are stabilized. This sensitivity to the nature of the pigment coating could arise from various causes; firmness of bonding to the surface, extension of the polymer layer, or the magnitude of the particle-particle attraction.

When a few polar groups are introduced into the polymer chain structure the adsorption is greatly increased. Carboxylic acid groups are particularly beneficial in this respect and a very small incorporation is adequate. The source and nature of the acidic groups on the commercial polymethylmethacrylates are not known although the content seems a little too high to be attributed to initiator fragments at chain ends. By having these anchor points on the molecule, the consequent higher adsorptions makes possible a fuller test of the effect of solvent structure. Generally speaking, the level of polymer adsorption correlates well with the solubility parameter of the solvent although the influence of solvent-surface interactions cannot be eliminated. Inspection of Table 8 shows that adsorption from methyl ethyl ketone is low in several cases. There is, for instance, the curiously-shaped isotherm observed with PMM-A10 when in contact with pigment I in methyl ethyl ketone, while on the other pigments. and on all pigments from the other solvents, normal isotherms are found. Whatever the explanation of the maximum in the isotherm, it is noteworthy that the anomalous behavior arises on the most acid surface

Table 15—Adsorption of PMM-A21 from Concentrated Solutions In Methyl Ethyl Ketone

Pigment	Equilibrium Concentration (g/l)	Adsorption (mg/g)
I	50.1	41.4
III	49.9	49.2
IV	49.5	67.8
V	49.8	51.8

Pigment	Equilibrium Concentration (g/l)	Settling Rate
I	50.1	13.7 (28.9) ^a
111	49.9	11.6 (27.5)
IV	49.5	15.6 (27.2)
v	49.8	15.2 (28.8)

Table 16—Settling Rates (h⁻¹ × 10³) from Concentrated Solutions Of PMM-A21 in Methyl Ethyl Ketone

with a basic solvent, i.e., where the selectivity for polymer adsorption is critically balanced. Crowl and Malati¹⁵ have reported adsorption maxima at low equilibrium solution concentrations of polyadipates with several adsorbents. Interestingly, the effect is more evident with the hydroxyl-ended polyesters and, although present with a surface-treated rutile pigment, is not shown with pure rutile. Other than the exceptional case of PMM-A10 on pigment I from methyl ethyl ketone, the isotherms are of the usual shape with a quite well-defined plateau at low concentrations; the data fit the form of the Langmuir equation, but we hesitate to attribute any special significance to this observation.

When the methacrylate chain is modified to include a few carboxylic acid groups, the pigments are, in general, stabilized in methyl ethyl ketone (*Table 7*). However, polymer PMM-A10 does not stabilize pigment I at any concentration in methyl ethyl ketone, even that corresponding to the maximum of the adsorption isotherm. In toluene it seems clear that a very low level of acidic comonomer is superior; perhaps PMM-A10 Hydrol-2, although better adsorbed, presents exposed acid groups in the adsorbed loops which, thereby, weaken the steric repulsion on approach of a second covered particle either by direct interactions or by being too close to Θ -conditions.

Although there is a general trend between adsorption and dispersion stability (*Tables* 8 and 9), high adsorption *per se* does not necessarily ensure stabilization, as the behavior of solutions in carbon tetrachloride shows. Polymethyl methacrylate in carbon tetrachloride is close to Θ conditions at *ca* 23°C; thus, it is very well adsorbed but the unfavorable polymer-solvent interactions prevent the generation of a steric repulsion.

When mixtures of methyl ethyl ketone and toluene are used, the level of polymer adsorption drops to the level found from the polar solvent alone (*Figure* 3). Correspondingly, the dispersion stability worsens (*Figure* 10). If the former effect was due to the mixed liquid acting as a better solvent than either one, separately, modern treatments of steric stabilization¹⁶ would predict an improvement in colloid stability. Since the opposite is observed, it seems more likely that the action of methyl ethyl ketone is to block surface sites.

Improvement in the adsorption of polymethylmethacrylate is also obtained by the incorporation of comonomeric groups other than carboxylic acid. Thus, the cationic acrylamide and pyridyl groups are particularly good at raising the adsorption onto the more acidic pigment coatings, while hydrogen bonding from primary hydroxyl groups improves adsorption more generally across the spectrum of surface treatments. Nitrile groups are the least efficient of those tried and it should be noted that all the laboratory synthesized polymers will have at least one nitrile group per chain derived from the radical initiator. However, the incorporation of these various groups, although generally improving the level of polymer adsorption, does not noticeably improve the dispersion stabilization. The only significant effects being shown are by low vinyl pyridine copolymers on acidic pigments to which, it may be presumed, they are relatively firmly anchored.

The surface characteristics of the adsorbents used have a substantial control over the level of polymer adsorption and subtle changes in the pattern arise on altering polymer structure or solvent character. In the surface treatment of titanium dioxide pigments, the modifying species such as silica are coated via a solution precipitation process and these materials will be in high concentration at the surface. Some measurements were made for comparison purposes of the adsorption of PMM-A10 from toluene and from methyl ethyl ketone onto uncoated, high surface area, samples of silica, alumina, and titania (Table 17). The adsorption onto aluminum oxide from both solvents is much higher than on the other pigments. This may be in part a consequence of its higher surface area, but it is doubtful if all the surface accessible to nitrogen molecules (used for surface area determination) would be available to polymeric adsorbates. The negative adsorption onto silica from methyl ethyl ketone must result from the enhanced solvent competition for this acidic surface; in contrast, adsorption on alumina is enhanced.

Returning to the coated pigments, it seems that the basic alumina groups are the important surface sites for the adsorption of our polymers, especially in polar media; silicas are weakly acidic and any titania groups will be amphoteric. Mixed silica/alumina catalysts are known¹⁷ to contain both Brönsted and Lewis sites; pure alumina has Lewis sites only.¹⁸ and the surface activity of pure silica is likely to reside only in hydrogen bonding sites.¹⁸ Sherwood, *et al*¹⁹ studied the solution adsorption of stearic acid onto titanium dioxide pigments

Table 17—Adsorption of PMM-A10 on Oxide Surfaces

	Surface	Point of Zero	Plateau Ads	sorption (mg/g)
Adsorbant	Area (m²/g)	Charge (pH scale)	From Toluene	From Methyl Ethyl Ketone
Silica ^a	50	_	70	-17
Titania ^b	50	6.6	145	104
Alumina	100	9.0	316	342

(a) aerosil 0X50 > 98% SiO₂

(b) > 97% TiO₂

(c) $\geq 97\%$ Al₂O₃

coated with graded proportions of silica and alumina; the amount of acid adsorbed increased directly to the alumina content. Pure rutile has two types of isolated hydroxyl groups together with hydrogen bonded pairs; Lewis, but not Brönsted, sites are also reported.²⁰ Thus, it seems likely that the five pigments studied can be discussed in terms of three types of adsorption site: basic sites from alumina, plus a few from titania groupings; acid sites from silica/alumina (and some titania sites); and more acidic sites from sulphate and nitrate groups. Although the relative quantities of these sites are not known, the acidity of aqueous slurries and the coating formulations give the series of decreasing acidity as I>II>II=V>IV.

Comparison of adsorption on the various pigments is complicated by their differing surface areas since the more basic pigments tend to have the greater surface areas. However, these differences may be more apparent than real in that the pigment coatings are known to be porous and some of the area detected by nitrogen will be excluded to polymeric adsorbates. The geometrical surface area, as estimated from the crystal size of the pigments, is of the order of 6 m²g⁻¹. Of course, if the true area available for polymer adsorption where known, it would be possible to make comparisons in terms of polymer adsorption per unit of surface area. The problem is highlighted by the adsorption of unmodified homopolymer from toluene (Table 3) where the adsorption variation from pigment to pigment may be partially determined by the areas available for adsorption on the various solids.

Polymethylmethacrylate is known to bind to silica hydroxyl groups through hydrogen bonding with the ester carbonyl.²¹⁻²³ Ester groups will also interact with surface acidic sites so, at first sight, higher adsorptions might be expected with less basic pigments, but this is not observed (*Table* 3). When a few acid groups are present, additional polymer-surface binding will result from ionized interaction at basic alumina sites. This has been shown for the case of stearic acid on aluminacoated titanium dioxide by Sherwood and Rybicka.²⁴

From a solvent such as methyl ethyl ketone, it may be presumed that the acidic sulphate and silica/alumina sites are occupied by solvent molecules and they are unlikely to be displaced by ester groups. Incorporation of carboxylic acid residues then gives a much enhanced adsorption through their interaction with basic alumina sites, unaffected by solvent competition. Increase of the polymer carboxylic acid content beyond a certain level does not much alter the adsorption and this observation is in line with the behavior reported of some other copolymer series.^{23,25} The specific effect of acid groups in the adsorbate molecule has also been shown by Ottewill and Tiffany²⁶ for fatty acids on rutile, and by Hamann²⁷ for polyesters on anatase.

When the copolymer has some cationic groups such as pyridyl units, some of the methyl ethyl ketone must be displaced by the polymer and the more acidic pigments now give higher adsorptions (*Table* 10). On the more basic pigments the vinyl pyridine copolymers are less well adsorbed than copolymers with either acrylamide or methacrylic acid units.

Water is barely soluble in toluene and would be expected to accumulate at almost any solid interface presented to "wet" toluene. That this has so little influence on the level of adsorption (Table 12) on any of the pigments suggests that it is either adsorbed on lower energy sites not normally available to polymer segments or that polymer segments are bound to wateroccupied sites. The location of water molecules from solutions in methyl ethyl ketone is not known, but polymer adsorption is practically unchanged. However, traces of water produce complex effects on dispersion stability (Table 13). In toluene, water has little effect in the presence of the higher molecular weight, carboxyl-containing polymer, but improves the performance of the other polymer sample (PMM-A10) on all pigments. With methyl ethyl ketone as dispersion medium, small water contents make pigment I relatively stable but destabilize pigment V.

Most studies of polymer adsorption are limited to quite dilute solution concentrations, even though many pigment dispersions of practical importance may have quite high polymer contents. One literature report²⁸ suggests that the behavior in concentrated solutions cannot necessarily be inferred from adsorption isotherms restricted to low concentrations. In a recent study of the adsorption of several polymers onto glass powder, from moderately concentrated solutions, Lipatov²⁹ found continuously increasing adsorptions, the isotherm data fitting the Freundlich equation. This author explained the behavior as due to the adsorption, not of single polymer molecules, but of molecular aggregates formed in the solution phase at higher concentrations; similar views have been expressed elsewhere.30

Stability against coagulation is improved when the polymer concentration is increased to around 50g/l. It is not clear to what extent this is due to the higher medium viscosity although the observation with pigment II shows that this factor alone, in the absence of significant adsorption, cannot impart colloidal stability.

SUMMARY

In summary, the general feature which determines the adsorption of our polymers is that of acid-base interaction. It is pertinent to note that this same view is taken by Fowkes and his co-workers³¹ in a discussion of adhesion phenomena. Not only is there the complex balance between the polymer-surface, solvent-surface, and polymer-solvent interactions, but it must also be appreciated that the pigment surfaces are not energetically homogeneous. Instead, they carry several sorts of surface groups of a range of acidities, which are difficult to fully characterize. Furthermore, adsorbed polymers do not necessarily impart colloidal stability to a pigment dispersion. They may be insufficiently anchored to resist the approach of a second particle or, if too close to Θ conditions, the loops may be incapable of generating sufficient repulsive free energy.

The influence of the coating composition on the titanium dioxide pigments' stability when dispersed is not readily separated from the present results. In polar

media the pigments show some differences in their inherent stability. When the polymer carries no additional anchoring groups, stability in toluene is better with the more acidic pigments. In methyl ethyl ketone, where such anchoring groups are necessary, carboxyl acid groups give a complex pattern (*Table 7*) but cationic comonomers act best on acidic pigments (*Table 11*).

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Effect of Turnover Rate On Solid Content in Dip-Coating Bath

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The effect of turnover rate on the change in solid content of the dip-coating bath was theoretically calculated assuming that the evaporation rate of solvent is constant and the bath is replenished by the same paint as that in the original bath.

The results showed that the increase in the bath solid in m turnover, ΔC_m , is given by

$$\begin{split} \Delta C_m &= K_t \left\{ \begin{array}{cc} 1 - (1 - & \frac{1}{t})^{mt} \\ K &= & \frac{a \, C_o}{V} \end{array} \right. \end{split}$$

where t is the number of days for one turnover, a is a volume of solvent evaporated, V is a volume of paint in the bath, and C_0 is a solid content in the original bath. The solid content of replenish paint to maintain the bath solid constant, C_r , is given by

$$C_r = \frac{C_o^2}{C_o + K}$$

The validity of these equations was examined by a simulation experiment using sugar solution. The experimental results agreed well with the theoretical results.

INTRODUCTION

The solid content of dip-coating bath tends to increase during coating process due to the evaporation of solvent if the composition of replenishment paint is the same as that of the original bath. This is particularly evident when the turnover rate is slow. It is important to understand the material balance of the bath during the continuous coating process for the quality control, since the change in the solid content affects the viscosity of the bath and, thereby, the coating weight. No systematical work, however, has been found on the solid change of dip-coating bath.

In the present work, the theoretical equation for the solid content of the bath was calculated based on some assumptions and the applicability of the equation was examined on a simulation experiment.

COMPUTATION

Assuming that the bath is replenished once a day and one turnover is accomplished in t days, a volume of paint removed, by coating, from the bath per day is V/t, where V is a volume of paint in the bath. Assuming that the volume of solvent evaporated per day is a, the total volume of paint removed from the bath (by coating and evaporation) per day, v, is

$$v = a + V/t \tag{1}$$

Since the same volume of paint should be added to the bath to keep the volume of paint constant, the volume of solid added to the bath per day, s, is

$$s = v \cdot \frac{S_o}{V} = (\frac{V}{t} + a) \frac{S_o}{V}$$
 (2)

where S_0 is a volume of solid in the original bath. The volume of solid removed from the bath per day is

Therefore, the volume of solid in the bath at the end of the first day of coating, S_1 , is

$$S_1 = S_0 + s - S_0/t = S_0 p + s$$
 (4)

where
$$p = 1 - \frac{1}{t}$$
.

The volume of solid in the bath at the end of the second day, S_2 , is

$$S_2 = S_1 + s - S_1/t = S_1 p + s$$

In the same manner, the volume of solid in the bath at the end of the nth day, S_n , is

$$S_n = S_{n-1} + s - S_{n-1}/t = S_{n-1} p + s_{n-1}$$

Therefore,

$$S_{n} = S_{o}p^{n} + s (p^{o} + p^{1} + p^{2} + ... + p^{n-1})$$

$$S_{n} = S_{o}p^{n} + s \cdot \frac{1 \cdot p^{n}}{1 \cdot p}$$
(5)

Substituting equations (2) and (4) for s and p

$$S_n = S_o + \frac{atS_o}{V} \left\{ 1 - (1 - \frac{1}{t})^n \right\}$$
(6)

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Solid concentration in the bath after n days, C_n , is $C_n = S_n/V$, and the change in the solid content in n days, ΔC_n , is

$$\begin{split} \Delta C_n &= C_n - C_o = S_n / V - S_o / V \\ &= \frac{at S_o}{V^2} \left\{ 1 - (1 - \frac{1}{t})^n \right\} \end{split} \tag{7}$$

or

$$\Delta C_n = \frac{atC_o}{V} \left\{ 1 - \left(1 - \frac{1}{t}\right)^n \right\}$$
(8)

The change in solid content in m turnovers, ΔC_m , is

$$\Delta C_{\rm m} = \frac{{\rm at} S_{\rm o}}{V^2} \left\{ 1 - \left(1 - \frac{1}{t}\right)^{\rm mt} \right\}$$
(9)

If t is very large

$$\lim_{t \to \infty} (1 - \frac{1}{t})^{mt} = e^{m} (e = 2.72)$$

Therefore,

$$\operatorname{mt} \to \infty \Delta C_{\mathrm{m}} = \frac{\operatorname{atS}_{\mathrm{n}}}{\mathrm{V}^2} \quad (1 - \mathrm{e}^{\mathrm{-m}})$$
⁽¹⁰⁾

if m is large

$$\Delta C_{\rm m} = \frac{{\rm at} S_{\rm o}}{V^2} \tag{11}$$

RESULTS

The changes in solid content in the bath with the number of days and the number of turnover are given by equations (8) and (9). Assuming a, S_0 , and V are constants, C_n is a function of t and n.

$$\Delta C_n = K \cdot F(t, n)$$
$$\Delta C_m = K \cdot F(t, m)$$

 $F(t, n) = t \left\{ 1 - \frac{1}{2} \right\}^{n}$

Where $K = \frac{aC_e}{c}$

and

F (t, m) = t
$$\left\{ 1 - (1 - \frac{1}{t})^{mt} \right\}$$
 (13)

The change in F (t, n) with n and the change in F (t, m) with m are given in *Figure* 1 and *Figure* 2, respectively. The figures show that when the turnover rate is faster (t is smaller), the solid content reaches plateau in shorter

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(12)

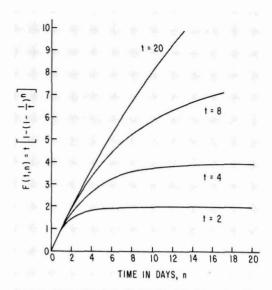


Figure 1-Change in F (t,n) with time for various turnover ratio

time and the final solid content is smaller. The increment of solid content at equilibrium is inversely proportional to the turnover rate (1/t) as shown in *Figure* 2.

The number of turnovers at which the solid content of the bath approaches equilibrium is calculated. The numbers of turnovers to reach 90% [m (0.90)] and 99% [m (0.99)] of equilibrium state are calculated by the following equations:

$$m(0.90) = -\frac{1}{t \log(1 - \frac{1}{t})}$$
(14)

$$m(0.99) = -\frac{2}{t \log(1 - \frac{1}{t})}$$
(15)

In any case, the solid content nearly reaches equilibrium in two turnovers. After two turnovers, there is no significant change in the solid content with turnover.

In order to maintain the bath solid constant, the solid concentration of replenish paint should be lower than that of the bath paint. The volume of solid to be added per day to maintain the bath solid constant is S_o/t and the solid concentration of replenish paint, C_r , is

$$C_r = \frac{S_o/t}{V} = \frac{C_o^2}{C_o + K_t}$$
(16)

EXPERIMENTAL

The change in solid content of the bath with turnover was measured by a simulation experiment using a sugar solution. The solution used for turnover equipment consisted of 600g of food-grade sugar dissolved in 2000ml of water (0.231 g/ml). Six 100ml glass beakers were filled with 100 ml of the sugar solution and allowed to evaporate at 60°C. When approximately 10ml of water had evaporated, various amounts of the solution were removed from the baths by pipets. The greater the

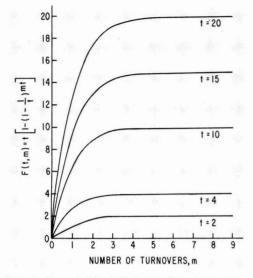


Figure 2—Change in F (t,m) with turnover for various turnover rates

amount of removal of the solutions, the faster the turnover rate. The baths were then replenished by solution so that the volumes were kept constant. The two solid concentrations of the replenish solutions used in this work are (a) the same as that of the bath and (b) calculated from equation (16).

The baths were again stored at 60°C for evaporation and amounts of the solution were removed from the baths followed by replenishment, in the same manner as the first cycle.

This procedure was repeated ten times. Therefore, the total volume of water evaporated was 100ml. The solid content in the solution was determined by measuring the weight of the nonvolatile material by drying approximately 2g of the solution for 5 hr at 120°C.

The experimental results are shown in *Figure* 3. Open circles and solid circles show the experimental results with the replenish solution containing the same solid concentration as the bath and those with the replenish solutions containing the solid concentration calculated from equation (16), respectively.

In the case of this experiment

$$C_0 = 0.231 \text{ g/ml}$$

a = 10 ml
V = 100 ml

$$n = 10$$

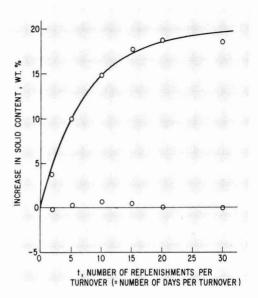


Figure 3—Change in the solid content by ten times replenishment vs. number of replenishments per turnover. Legend: open circles—experimental results; solid line—theoretical curve

Therefore, the change in the solid content in weight is

$$\Delta C_{n} = 0.0231 t \left\{ 1 - (1 - \frac{1}{t})^{n} \right\}$$
(17)

The solid content of replenish paint to maintain the bath solid constant is

$$C_{\rm r} = \frac{C_{\rm o}^2}{C_{\rm o} + K_{\rm t}} = \frac{2.31}{10 + {\rm t}}$$
(18)

The theoretical solid content change calculated by equation (17) is shown by the solid line in the graph. The figure shows that the theoretical results on the solid content change in the bath with continuous coating process agree well with the experimental results.

APPENDIX

SYMBOLS

a	=	amount of evaporation of solvent per day
Cn	=	solid content in bath after n days
C_{m}	=	solid content in bath after m turnovers
Cr	=	solid content in replenish paint to maintain the bath solid constant
S	=	volume of solid added to bath per day
Sn	=	volume of solid in bath at the end of the nth day
t	=	number of days for one turnover
V	=	volume of paint removed from bath per day
V	=	volume of paint in bath

Interplant Quality Control By Means of Simple Tristimulus Colorimeters

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The problem of color control of products made at different locations but marketed nationally with the same merchandizing aids has become increasingly acute, especially with frequent product changes to meet a competitive market.

The unreliability of wet standards has long been recognized and the time needed to produce and maintain master standards makes them impractical for most latex or trade sales products. Establishment of working standards also becomes impractical when the manufacturing facilities are widely separated. Because of this it has become necessary to establish a way of communicating color, strength, and acceptable tolerances by means of finite instrumental figures to maintain not only batch-to-batch but plant-to-plant reproducibility of a product through the use of simple colorimeters.

A review of the methods used to establish and maintain a successful system is presented.

Introduction

For many years individual batches of paint were produced at regional locations by Standard T Chemical Company and marketed within that region by its parent company, Montgomery Ward. These batches were controlled for color against either spectrophotometric curves or acrylic lacquer "Bowles" chips. Each location used an abridged spectrophotometer which, when properly maintained, was reproducible, but did not necessarily correspond to those at other locations.

As marketing and production demands changed, it became obvious that quality control methods must also change. As a major marketing device, most types of consumer or trade sales finishes are now offered in a wide choice of colors. The range of colors offered is so large that the use of pretinted or ready mix paints is precluded from an inventory or supply position. These colors, selected by the customer, are tinted at the store level using colorants dispensed into short filled color bases. These color bases must be controlled so that the resulting paint matches the color chip from which the customer made his selection.

The manufacture of these items at widely separated locations is determined by the demand for the product, the type of product, package size, delivery time, and many other variables. The end result is that items made at more than one location would be furnished to the same marketing outlet and sold together as a package. This, of course, also demands that these items made at any location match those made at any other location.

Concurrent with the marketing change were changes in the supply, cost, and form of raw materials. Slurries of pigments became more prevalent and economical. Thus, it became necessary to make frequent changes in formulations, as well as having alternate formulations for the same end product. While the physical characteristics of the product, i.e., viscosity, weight per gallon, pH, and gloss, could be communicated by figures, strength or shade could not.

In the past, samples of the finished product were furnished each plant,

along with drawdowns of tinted paint and readings taken at the Central Laboratory. The use of wet samples of paint was considered, but delays in shipping, loss of samples, and inability to ship latex products during winter months all contributed to what we considered an unacceptable condition. Dried paint films drawn down and read at one location did not correspond to readings at a different location, due to the change in the film itself and instrument variations. To facilitate quick approval of production batches, measurements were needed which could be duplicated at any location. It was then decided to establish means for rapid and accurate communication of strength and color of tinted whites and color bases.

Partly because we were familiar with colorimeters and color differences in our industrial and colorant manufacture, we concentrated on these instruments, even while recognizing their limitations. Unfortunately, none of the commercial instruments then on the market met our demands. Over a year was spent working with the manufacturer establishing the specifications and tolerances considered essential. The resulting colorimeters for all locations were purchased at one time through the Central Research Laboratory. Prior to their installation, all instruments were correlated against each other, tested by both the supplier and ourselves. Through their correlation and the control of the variables, it has become possible to deal in finite figures.

Discussion

It has long been established that colorimeters, by the nature of their design, cannot be reliably considered for measuring absolute standards. They are, however, excellent for making fast, ac-

^{*10}th and Washington Sts., Chicago Heights, Ill. 60411, Presented at the Symposium on Color and Appearance Instrumentation of March 14, 1978, Cleveland, Ohio,

curate, and reproducible measurements between two nearly identical colors. Changes in the pigmentation, gloss, surface characteristics, or film thickness affect the accuracy of the readings. Control of these variations as follows has allowed us to establish "go-no-go" release tolerances.

Formulations are developed in a central laboratory and furnished to each manufacturing location. Each specific formulation has listed the tests and tolerances established for that product, including the tristimulus readings. Raw materials used, listed by code, are specific and no variation can be made without laboratory approval.

Each formulation also specifies the order of addition, type of equipment to be used, and manufacturing procedures in detail. This information is developed by the Corporate Processing Laboratory based on laboratory work and test batches. All must be approved by the Corporate Process Engineer. We have, thus, eliminated differences in pigmentation, surface characteristics, and gloss by raw material selection and order of addition. From these laboratory batches and/or test batches, the physical measurements of the product are established.

The tinting or white strength is established by adding a volumetric measure of colorant to a weighed quantity of the base, shaking the tinted paint, and drawing down with a Bird Applicator. The dried films are read on a Gardner colorimeter against a white standard and the tristimulus values and accepted tolerance are entered on the formula. These figures can now be used by the control laboratories as release or approval standards.

Because a wide variation of products are manufactured, test methods have been written for testing each type of paint - the quantity of paint, the volume of tint or colorant to be added, the film thickness, drving time, etc., are specified. This eliminates the variation in panel preparations. Each laboratory is supplied with dispensing canisters and the same lots of tint or colorant, which eliminates the possibility of metamerism. A sample of each production batch is tinted following the prescribed test method and is approved if the resulting readings meet the tolerances for that product.

Raw Materials

We have worked on the theory that the same controlled raw materials, added in the same order under controlled procedures, will produce the same end product. Each raw material has its specification agreed on between Standard T and the supplier. A copy of that specification, signed by the supplier, is furnished to each plant laboratory. Each shipment of each raw material is tested prior to its use at any location. Shipments meeting all specifications are approved by the testing technician. Shipments which vary from specification are accepted or rejected by the Plant Laboratory Manager.

All variations are reported to the suppliers, Corporate Purchasing, and Corporate Quality Assurance in writing.

Production and Quality Control

Each laboratory completes a batch history report for each product made on a form supplied by the Corporate Quality Assurance (QA) office. These forms are sent to the QA office daily, listing all additions made, the results of the physical tests, etc. Any deviation from standard is circled for emphasis.

After review by the Corporate QA office, the completed forms are sent to the formulator of the products involved. Constant additions or variation from standard leads to a review and, if necessary, modification of that particular formulation. At specific time intervals, retains from each batch are retested to insure the stability of the product which, in turn, insures uniform color when the product is tinted at the store level. Any change is reported to the Corporate QA office for review.

Instrument Control and Maintenance

To insure the continued accuracy and correlation of the colorimeters, periodic readings are made at each location of the same set of ceramic tiles. Products made at each producing location are also sent to the Central Research Laboratory for comparison to each other and to the previously determined standard.

A preventive maintenance program is currently in progress at Standard T in which the unit from one location is returned to the supplier for inspection and, if necessary, replacement of parts. A previously tested unit is supplied the individual plant during the time its unit is under test. Upon receipt of their own unit, the "loaner" is forwarded to the next plant so that their unit can be sent back to the supplier.

The same procedure is followed with other laboratory equipment, i.e., selection and testing is done by the Central Research Laboratory. A Corporate Purchase Order is placed and all units are replaced at one time.

Ours is a system of checks and balances. Parts of the system seem tedious but it can and does work.



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Red Cross. The Good Neighbor.

Re-Search for Opportunity

Charles M. Hansen

Scandinavian Paint and Printing Ink Research Institute*

A research institute with a permanent staff and modern equipment has the capacity to serve industry and government in a unique manner. Opportunities are presented in the form of authorized analyses and evaluations of coatings materials and performance, equipment evaluation prior to possible purchase by an industrial member, and a wide variety of projects (information-opportunity) ranging from waste disposal through fundamental concepts such as solubility, evaporation, permeation, colloid stability, rheology and the like. Problems and opportunities arising from environmental concern are increasing and research centers with combined industrial and governmental support are quite important in Scandinavia.

Introduction

Recent discussions within the United States have indicated that there are opportunities for expanded coatings research.1.2 This is also true overseas and one of several coatings research institutes in Europe where such work takes place is located in Scandinavia. Whatever course of action is ultimately decided upon in the United States, it must be the result of numerous compromises, available funding and personnel, and the need to serve the parties which have taken upon themselves the task of starting such a cooperative research effort. Such an institute as described here may not be the answer for every concern, however.

The Scandinavian Paint and Printing Ink Research Institute, with its permanent staff and modern equipment, has the capacity to serve Scandinavian industry, government, and universities in a unique manner. It also frequently cooperates with sister Scandinavian institutes having other areas of specialization.

Figure I shows that the Institute is not identified absolutely with any one segment. Cooperating to achieve the goals and objectives of each allows the maximum utilization of resources. Creativity, scientific understanding, and good common sense are all necessary ingredients to success. One measure of success is growth. The Institute's financial growth has primarily resulted from the increasing number of vital person to person contacts with representatives of local (Scandinavian) industries and governments. The contacts with universities and other institutes have led to another kind of growth — expanded interests in coatings. This interest fosters activities which otherwise would never have been conceived. The recent workshop at Kent State University (see September 1978, JCT, p. 135) has also demonstrated this type of synergism.

The Institute's present income is now over a million dollars per year, which is well over four times as large as that reported for 1971 by the previous (and first) director, Mr. H.K. Raaschou Nielsen, in his Mattiello lecture "Cooperation - National and International. Do We Realize Its Potentialites."3 This same visionary report ranks high on potential impact for our industry - if only we could or would cooperate more -how much further might we now be as an industry, both nationally and internationally. In 1977 the Finnish coatings industry and the Swedish printing industry joined into the cooperative effort represented by this Institute. Others are welcome

Still further examples of cooperation can be cited showing that the Institute's purpose is to serve creatively, using resources wherever they may be, to further its constituents needs. The Institute has, for example, obtained government funding not only for its "own" projects, but also to support work at universities (or elsewhere), obtained academic funding to give an insight of our industry to advanced engineering students (about 130 have had contact with coatings in this way, including myself as a graduate student from 1962-1967), and obtained industrial funding for both specified and unspecified projects.

Increased funding is not necessary to increase effectiveness when cooperative efforts function as they should. The Institute has divided and expanded efforts for the "Environmental Literature Review" between the Netherlands, and IARIGAI institutes in England, Finland, Italy, East Germany, and Norway.

Every attempt has been made to avoid activity in projects which can be handled by the Danish Technological Institute, for example, which has specialists in the "applied" coatings industry. Their efforts are primarily directed toward professional painters. builders, and architects, rather than coating manufacturers. Examples of other forms of cooperation such as ASTM, ISO, and IUPAC are well presented,3 as are the more organizational and historical aspects of the Institute. In addition, the Institute is affiliated with the Danish Academy of Technical Sciences (ATV).

Challenges of an Institute

The challenge of an institute is to satisfy its constituents so that they in turn can provide the necessary financing, either directly or in the form of recommendations for grants from government. In other words, no recommendation — no grant. This requires agreement among the member companies on what the institute 'should be doing. There is surprising agreement on the general areas of activity which are desired. Agreement among member com-

^{*14} Odensegade, Copenhagen, Denmark,

Presented by Mr. Hansen at the 56th Annual Meeting of the Federation of Societies for Coatings Technology in Chicago, Ill., November 3, 1978.

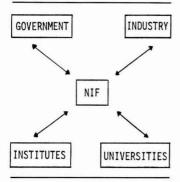


Figure 1 — The Scandinavian Paint and Printing Ink Research Institute (NIF) and its interactions on behalf of the coatings industry

panies on what should *not* occur is also necessary. Competition among the member companies is felt to be influenced by certain activities, particularly those which might be called formulation. As in every cooperative adventure, one must give something to get something and compromises are required. These discussions and years of experience have led to the following areas of desired activity.

ENVIRONMENTAL ACTIVITIES: Here, each company need not do the same kind of work, and results obtained by an institute are regarded by all parties as being of an objective character. Solvent evaporation, waste disposal, monomer retention, analytical methods for toxic substance, labelling, and behavior of amines are all useful activities in this area. Further needs will arise and be met with fundamental knowledge.

FUNDAMENTAL ACTIVITIES: While everyone is in agreement that fundamental knowledge is a good thing, some smaller companies have felt they had less immediate need for this than for other activities of a more practical nature. Thus, in addition to continuing such projects related to principles of formulation such as: solvent properties; diffusion and permeation of water and solvents; rheology after application and evaporation from water borne coatings: pigment dispersion stability; surface tension effects; internal stress; improved adhesion based on receding contact angle plots; and the like, a series of applied research projects relating to the consumer products area was started. Here the emphasis is on substrates, such as concrete, wood, and plastic, and their problems related to coatings, for instance, how coatings should behave to perform properly on substrates in practice.

ANALYTICAL ACTIVITIES: Its analytical capacity, combined with a knowledge of coatings, places the Institute in a particularly valuable position for serving the coatings industry in all its various aspects. For example, these analyses can be quite important in determining proper labelling; or providing documentation for an expert witness situation or other forensic effort: or in controlling the contents of sample A for ingredient X, which may have caused a special problem or produced a special effect. The Institute has the standard instrumentation of a well-equipped analytical laboratory, including infrared, UV-visible, gel permeation chromatography, gas chromatography, atomic absorption, thin layer chromatography, and scanning electron microscopy with x-ray analysis. Wet analyses are also performed according to standardized procedures. Should the Institute lack equipment for more advanced analytical techniques, this can generally be used on a per problem basis at a cooperating institute. The Institute has been particularly active in helping to develop standard analytical procedures by cooperating with ISO, ASTM, and IUPAC groups.

GENERAL TESTING: The Institute is equipped to perform almost all standardized test methods for coatings and printing inks, whether Scandinavian, ASTM, DIN, or ISO. Here again, experience in the coatings industry is an advantage and all the pitfalls and advantages of accelerated testing methods such as salt-spray. Weather-Ometer^{\$\$}, blister box, and dirt retention must be recognized at all times.

In addition, such specialized testing as internal stress, tensile strength, rheological profiles, surface characterization by contact angles, and solubility parameters are carried out as required. These are examples of specialized capabilities which are centralized at one place and carried out by trained personnel who can recognize problems and special situations which unexperienced personnel may not.

OTHER SERVICES: The Institute maintains other services which are particularly well suited for a cooperative venture. A specialized coatings library is one. Coatings literature is reviewed and cards are sent out which can be used for current awareness or filed for future searches. An environmental service of this type is also functioning on a cooperative basis as mentioned above. The Institute's staff provides a large number of less visible services, such as providing lectures: functioning in various coatings related work groups, societies, or guiding groups for other institutes: and answering a large number of inquiries by phone or letter. These all, directly or indirectly, increase the effectiveness of the industry as a whole.

It has long been one of the goals of the Institute to employ and train younger engineers for a few years and then, by mutual agreement, attempt to find them a position in the coatings industry. While this program has not always functioned as one might hope, a renewed effort is being made, based on recent growth. to establish a turnover among the younger engineers.

As previously mentioned, the Institute also provides the opportunity for Master's level students to do research within the industry. Some of the best exploratory research done recently at the institute is a result of just such projects.

Scandinavian Paint Consultants

An independent organization, Scandinavian Paint Consultants, whose purpose is to market the Institute's capabilities has also been growing. In addition to this function, courses are arranged, audio visual programs dealing with coatings have been developed, and contacts with a large segment of Scandinavian industry are maintained. Ove Säberg is director of this activity. This organization also markets the Säberg adhesion tester which has been standardized in Sweden and West Germany. This is a portable instrument for measuring vertical, pull-off adhesion of coatings (and concrete cohesion). A recent development is a device to determine film thickness in the field. A 45° angle, small hole, is drilled through the coating into the substrate. Microscopic examination then allows film thickness measurement. There is no visible scratch or scar as a result of this measurement.

Publications

The usual reporting procedure is to send members, and selected other institute's and people, copies of Institute reports wherever a project has progressed to a given point or perhaps been completed. Frequently, requests are received to publish these in the literature for all to benefit from the results. This may be in the American. English, or German coatings literature or in conjunction with a conference or congress, but most often they are published in the Scandinavian journal, *Färg och Lack*.

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C.M. HANSEN

This excellent publication usually prints its articles in a Scandinavian language. It is the official journal of the SLF (Federation of Scandinavian Paint and Varnish Technologists). Unfortunately, because of the language problem, numerous excellent articles may not reach a larger audience. Partly because of this, the title page of *Färg och Lack* and other European journals have been sent to the JOURNAL OF COATINGS TECHNOLOGY for early publication in the English language. A few articles published in *Färg och Lack* by personnel from the Institute are listed in the Appendix.

Conclusion

What the coatings industry in the United States ultimately decides to do with broader research activities is a matter which only they can decide. The rest of the industry can only hope that coatings research activities increase, and that the results are published, primarily for the benefit of the local industry, but also for the benefit of all. *Re-search means opportunity*.

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- (2) Gardon, J.L., JOURNAL OF COATINGS TECHNOLOGY, 50, No. 644, 135 (1978).
- (3) Nielsen, H.K.R.N., JOURNAL OF PAINT TECHNOLOGY, 45, No. 576, 37 (1973).

APPENDIX

Articles in Färg och Lack Authored by Employees Of the Scandinavian Paint and Printing Ink Research Institute

- In Press: E. Nilsson: Coatings on Wood and Moisture C. Hansen, K. Skaarup: Surface Resistance in Diffusion and Permeation
 - K. Nielsen: Behavior of Amines in Water-Borne Coatings. Free Amine and Evaporation.
- 1978 A. Saarnak: Choice of Solvents for Cleaning Production Equipment - A Solubility Parameter Consideration
 - W. Hansen: Standardization Concerning Printing Inks
 — Use and Misuse
 - W. Hansen: Treatment of Waste in the Coatings and Print. Ink Ind.
- 1977 C. Hansen, K. Skaarup: Diffusion with Resistance at the Surface
 - A. Saarnak: Interaction between Pigment/ Binder/Solvent and Dispersion Stability
 - B. Lindberg: Painting Plastics II
 - E. Nilsson: Internal Stresses in Coatings — Temperature and Moisture
 - C. Hansen: Vinyl Chloride Monomer Retention in

Films Formed from Solution

1976

- C. Hansen: Receding Contact Angles and Coatings Performance — The Cos θ Plot
 - B. Lindberg: Painting Plastics I. Adhesion Studies
 - H. Meyer: People and Coatings — Interview with H.K. Raaschou Nielsen
 - B. Rogers, W. Hansen: Printability of Films
 - K. Eng: On Nomenclature

1975

- E. Nilsson: Internal Stresses in Coatings
 H.K. Raaschou Nielsen: International
- Standardization and Test Methods (ISO) K. Eng: Analysis of Heavy
- Metals in Coatings by Atomic Absorption Spectroscopy

1974

- Ove Säberg: Dirt Retention, Particle Adhesion to Coated Surfaces
 - A. Saarnak: Study of Methods to Evaluate the Resistance of Coatings to Biological Attack

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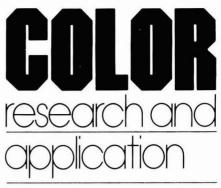
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Society Meetings

Baltimore

Feb. 1

Ron Campbell, of Union Carbide Corp., presented a movie titled "MAY 19TH, 1981." Following the movie, he spoke on "PLACARDING AND TRANS-PORTATION OF HAZARDOUS MATERI-ALS."

GORDON ALLISON, Secretary

Birmingham

Feb. 1

Graham Robinson, of Synthetic Resins Ltd., spoke on "WATER-BORNE FINISHES."

Conventional solvent-based coatings have been under scrutiny for the last ten years, and of the many developments, the field of water-based coatings is only one, said Mr. Robinson. Water-borne coatings are unique in that the environment contains a large amount of the solvent used, i.e., water. Initially, solvent-based resin solutions in a water dilutable form were used for industrial coatings, but water soluble alkyds are now available as a possible resin solution, he continued.

On stoving, the paint film gives off solvents, amines, aldehydes, ketones, and acids. Mr. Robinson presented figures showing the solvent and gaseous product evolved for solvent-based, water-based, and powder coatings. As the water-based coating contains 3-4% of amines on final stoving, it is a case of less air pollution rather than no pollution. Mr. Robinson mentioned that there is a need for better analytical methods to measure the pollution products.

He concluded by naming some interesting applications including an automotive metallic topcoat, gravure and flexographic printing inks, anti-graffiti paints, and all weather sports surfaces.

Q. Isn't the emission from aqueous stoving paints, such as aliphatic amines, injurious to health?

A. Yes, hence the need for a reliable method of analysis.

BRIAN F. GILLIAM, Publicity Officer

Chicago

Honored guests in attendance included James McCormick, Federation President and Frank Borrelle, Federation Executive Vice-President. Mr. McCormick thanked the Society for its help, cooperation, and support for the Federation's recent Chicago convention.

Mr. Borrelle made a brief slide presentation concerning the Federation's recent reorganization and the Federation in general.

Bruce R. Harris, of Stepan Chemical Co., spoke on "SURFACTANTS AS RE-LATED TO THE PAINT INDUSTRY."

RICHARD M. HILLE, Secretary

Cleveland

This was a joint meeting with the Cleveland Paint and Coatings Association.

Mike Malaga acted as moderator for the panel discussion, "LIVING WITH GOVERNMENT REGULATIONS." The panel included Robert L. Knarr, of OSHA; Harold Harkins, of DOT; and Roger Grimes, of EPA.

JACK S. MALAGA, Secretary

Dallas

Jan. 11

Jan. 23

H.S. Ritter, of PPG Industries, Inc., spoke on "COLLOID PROPERTIES OF LATEX PAINTS,"

Dr. Ritter discussed the fact that various colloids are needed to formulate latex paints and that colloid properties must balance to achieve desired results.

RICHARD WILLIAMSON, Secretary

Golden Gate

Feb. 12

Feb. 21

Tom Dowd, of the E.T. Horn Co., was presented with a special award for his contributions to the education committees from both the Golden Gate Society for Coatings Technology and the Golden Gate Paint and Coatings Association.

Judy Thompson, an interior decorator with Lifestyle West, spoke on "A New HOUSE AT THE SAME ADDRESS."

SHARON VADNAIS, Secretary

Louisville

Feb. 5

William Hare, of Morehouse Industries, Inc., spoke on "DISPERSION TECHNIQUES PERTAINING TO HIGH SPEED DISPERSERS."

J. KIRK MENEFEE, Secretary

Montreal

Mr. Robert Rauch, of Tioxide of Canada, Inc., and Mr. Karmazyn, of Rohm and Haas Co., spoke on "FLOW IMPROVEMENT IN LATEX GLOSS AND SEMI-GLOSS PAINTS."

Mr. Rauch showed how the enamel grade type of titanium dioxide can influence flow and levelling. He also described a test method using the Rotovisco which measures the degree of flow and levelling of glossy emulsion paints.

Mr. Karmazyn discussed the use of alkali soluble resins to modify improvement in flow and (usually) gloss, and final paint film appearance. He also discussed the emulsion particle size and emulsion stabilization and its relation to the flow of glossy emulsion paint.

CUTHBERT A. MCWADE, Secretary

New York

Feb. 5

Feb. 7

This was a joint meeting of the New York Society and the New York Paint and Coatings Association.

A "LEGISLATIVE UPDATE" was held, chaired by Milton Goll, of Cosan Chemical Corp. It consisted of a panel of industry representatives. The following topics were discussed.

CONSUMER PRODUCT SAFETY — Wes Pollitt, of Sapolin Paints, Inc.

The Consumer Product Safety Commission can assess civil and criminal penalties and can require the recall of products, said Mr. Pollitt. In a ranking of 260 general products as hazardous, paints were ranked as the 23rd most hazardous type. The lead standard, continued Mr. Pollitt, is a maximum of 0.6% by weight of nonvolatile of paints. This applies to consumer paints and paints for toys and furniture. Coatings for metal furniture are exempted. HUD regulations for lead are still unresolved, while OSHA allows a maximum of 50 micrograms of lead or chromium per cubic meter of air in the workplace. In discussing labeling, Mr. Pollitt said that combustible paint products must be labeled as hazardous. This applies to products with a flash point range of 80 to 150°F, Tag Open Cup. He said that the new labeling guide supplement is ready.

Q. Are there any label requirements for flammable paint strippers other than

Society Meetings (Continued)

those of the Consumer Products Safety Commission?

A. Yes, the labels of the outer packaging in which shipments are made are subject to DOT regulations.

DEPARTMENT OF TRANSPORTATION — Rocco Parrella, of International Paint Co.

Mr. Parrella mentioned that a hazardous materials newsletter is being published monthly. He also discussed new. regulations on tank cars and trucks resulting from explosions such as the one at Waverly, Tenn. Modifications are expected to cost \$10,000 per tank car. The trend is to build tank cars smaller than before, to limit damage from accidents. An amendment has been proposed, he concluded, to ban direct unloading from tanks into drums.

SOLID WASTES — Al Eilender.

The Resources Conservation and Recovery Law passed recently by Congress will gradually become very important to paint manufacturers and will involve considerable expense, said Mr. Eilender. Subtitle C involves identification, treatment, storage, and inspections of hazardous waste. Hazardous wastes listed include water-based paint and latex sludge. A key provision involves the means of determining whether waste is hazardous, he continued. A list of hazardous wastes has been published. Wastes can be exempted if they pass certain specific tests, but these tests are costly to run.

AIRBORNE PARTICLES — John Woodruff, of Whittaker, Clark & Daniels.

There have been no changes in regulations since last year. Mr. Woodruff advised manufacturers to continue to request Material Safety Data Sheets from their suppliers and to follow good housekeeping procedures.

HEAVY METALS — Bill Stewart, of Tenneco Chemicals.

The Consumer Product Safety Commission has not specified a test for lead in paint, but GSA is using Atomic Absorption as a test. This will probably set a precedent, said Mr. Stewart. He also mentioned that there has been some concern as to the use of polychlorinated biphenyls in phthalocyanine pigments, but suppliers assure that the vel is less

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than 100 parts per billion, which is no problem.

AIR AND WATER POLLUTION — Gabe Malkin, Consultant.

The California Air Resources Board restrictions on solvent emissions from paints are now being studied by several other states. The previous limit on ozone levels in the atmosphere of .08 ppm is being raised to .12 ppm, and the American Petroleum Industry is trying to get the limit raised further, to .25 ppm. Water quality guidelines were presented some time ago, said Mr. Malkin. Solvent effluent was set at zero, and water effluent guidelines have not yet been firmed up. Promising work is being done on paint plant sludge recovery, he concluded.

OSHA UPDATE - Leo Chaison.

In regard to lead, Mr. Chaison said that a maximum airborne level of 50 micrograms per cubic meter of air is permitted, including lead driers and inorganic pigments. Companies have one year to comply. The lead level must actually be measured, and if above 30 micrograms there are many requirements, including periodic medical checks. The regulation is being challenged in court, he said. With regard to benzene, Mr. Chaison mentioned that the new ruling limited emissions to one ppm, but this was struck down by a Federal Court. The Federal government is petitioning the Supreme Court for a review of the ruling. The third item mentioned, acrylonitrile, is limited to 2 ppm over an eight hour period. Acrylonitrile may be present in some latexes used in paints. Paint manufacturers are exempted if they obtain a letter from their supplier stating that the latex resin will not generate vapors of 2 ppm.

TOXIC SUBSTANCES ACT — Leo Chaison.

A distinction is made between manufacturers of basic raw materials and processors who produce mixtures of these raw materials. Paint manufacturers produce mixtures and are exempted from TOSCA regulations, provided that their raw material suppliers have registered their products, said Mr. Chaison. Manufacturers of chemicals, including resins, must file such information as physical data, flash point, and toxicity data, as well as an indication of their customers' intended use of the product. The cost of testing new products can vary from \$50,000 to a maximum of about \$1 million, he continued. An initial inventory of toxic substances will be published this Spring. Paint manufacturers should check to be sure that all of their raw materials are on this list. If not, either they or their raw material suppliers must file information on the unlisted raw materials within 210 days, concluded Mr. Chaison.

A "ROUND-TABLE DISCUSSION," also chaired by Milton Goll, followed.

PASSAIC VALLEY SEWER COMMISSION — Frank D'Assencio.

Mr. D'Assencio said that when the system is completed it will be able to treat 300 million gallons of waste water per day. Five types of waste are prohibited. They are fire hazards (solvents), corrosive substances (of pH less than 5 or more than 9), solid or viscous wastes (sand, gravel), wastes interfering with plant operations (latex sludge, greaseballs), and heat which would upset the biology of the plant (above 40°C in stream). As to toxic substances, he said, guidelines have not yet been published, but plants must show effective removal.

Q. How are discharges in the Passaic Valley system traced to a specific plant?

A. There are 160 sub-areas, each with a key manhole. All areas are sampled and the results are fed into a computer.

PRACTICAL METHODS OF WASTE DIS-POSAL — Dr. Samuel Lee, of SCA Chemical Waste Disposal Co.

Dr. Lee said that the U.S. lags behind other countries in waste disposal because large areas of open land were available. New laws such as TOSCA and the Resources Conservation and Recovery Act are forcing development of new methods. The SCA Co. was formed to provide solid and chemical waste disposal. The philosophy of operations include extraction of valuable materials where possible, process control through analysis, and flexibility of operation. He described a scientific landfill site in North Carolina which has the following features: 1) geologically sound site on clay soil, 2) cavity construction is both above and below ground, with impermeable liner, 3) internal sumps to collect liquids, and 4) back-up waste treatment system. Specific treatment of paint industry waste includes solvent recovery, coagulation of water and latex waste, etc.

Q. How practical is the landfill system?

A. The people running the sites are forever responsible for the waste and this is bound to be costly. Recycling will be a better answer when the technology is developed.

ANTICIPATION OF LEGISLATION IN 1979 — Larry Thomas, of the National Paint and Coatings Association.

Mr. Thomas felt that what is really needed is a respite from new regulations and re-interpretation of present laws. The top priority of Congress now is inflation and the "tax revolt." Therefore, the budgets of regulatory agencies may be tightened. Bills have been introduced based on the idea that excessive regulation is inflationary and stifles innovation, he said. Mr. Thomas then talked about the following proposed legislation: Congressional oversight of agencies, forcing cost analysis; relaxation of regulations for small business; postponement of Clean Air Act compliance for one year; amendments to OSHA favoring small business; extension of Resources Conservation and Recovery Act, and giving the agency involved more powers; TOSCA legislation involving Federal government testing for carcinogens; and suspension of the duty on imported nitrocellulose until 1980.

Q. How does the government define

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Constituent Society Meetings and Secretaries

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

BIRMINGHAM (First Thursday—Calthorpe Suite, Edgbaston). BRIAN J. ADDENBROOKE, Croda Paints Ltd., Brodesley Green Rd., Birmingham B94TE, England.

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

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

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

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

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

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

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

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

LOS ANGELES (Second Wednesday—Steven's Steak House). JAN P. VAN ZELM. 5412 Calle de Arboles, Torrance, Calif. 90505.

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

MEXICO (Fourth Thursday—meeting sites vary). MAURICIO ESQUIVEL, Pinturas Azteca.

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

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

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

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

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

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

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

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

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

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

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

TORONTO (Second Monday—Town and Country Restaurant). A.G. MORRIS, L.V. Lomas Chemical Co., 6365 Northwest Dr., Mississauga, Ont., Canada.

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

small business?

A. This is not definite, and varies with each bill introduced.

U.S. Senator Harrison Williams, of New Jersey, spoke on "OSHA."

Senator Williams, one of the original sponsors of the legislation, reviewed its origins. He indicated that the administration of the Act has not always promoted the basic aims of the original legislation. However, he continued, this is gradually being corrected. Rules and procedures are being simplified and OSHA is now concentrating on standards for high hazard industries.

Q. Is the Senate considering the sale of Alaskan oil to Japan, in view of the difficulties of transporting the oil to the U.S.?

A. Yes, it is being considered. MARVIN J. SCHNALL, Secretary

Piedmont

Jan. 17

Don Kession, of Spencer Kellogg Div., Textron, Inc., spoke on "CORRO-SION RESISTANCE IN WATER-RE-DUCIBLE COATINGS."

Mr. Kession explained the classification of WD resins — emulsions, dispersions, and solutions (colloids). Aided by a slide presentation, he discussed such topics as emulsion constituents, emulsion film formation, emulsifiers, emulsion paint film properties, and types of water-soluble resins.

Mr. Kession concluded by saying that water-soluble paint dispersion's film properties have the advantages of higher gloss, better flow and rheology, and use of thinner films. Disadvantages include slower drying, less stability, and the need for crosslinking or oxidation.

Q. Are there any rust inhibitors in the white test formulas?

A. No.

W.J. CUNANE, Secretary

Toronto

Jan. 8

Ada Nielsen, of Nalco Chemical Co., spoke on "SCREENING PROCEDURES OF ANTI-FOAMS — DILEMMA OF PREDICT-ING SUCCESS IN USE."

Ms. Nielsen described defoamers as destroyers of foam, whereas anti-foams not only prevent foams from forming, but also act as defoamers. A good description was given of the differences between pin-holing, fish eyes, and cratering.

If problems with color development are encountered, she said, it is necessary to ensure that enough surfactant present: Some anti-foams may have less effect on color development than others. Evaluating anti-foams is not a simple matter. A good knowledge of the resin system, pigments, surfactants and other additives is necessary, as well as any previous work done on like systems, she added

ALUN G. MORRIS, Secretary

Western N.Y.

Jan. 9

Paul R. Guevin, of Hughson Chemicals, discussed "The MEASUREMENT OF SLIP RESISTANCE."

Mr. Guevin described the instruments now being used and the work of the ASTM committees on correlation and standardization of methods.

GEORGE C. REID, Secretary

Western New York Feb. 13

James W. Joudry, of NL Industries, Inc., spoke on "RHEOLOGY AND THE PROPER USE OF RHEOLOGICAL AD-DITIVES."

Mr. Joudry pointed out that most of the equipment used for measuring viscosity gave the values at low shear, but applications are usually at high shear. He suggested the use of a plate-andcone viscometer in order to obtain a viscosity profile. He discussed clay and organic additives for increasing viscosity.

GEORGE C. REID, Secretary

Future Society Meetings

Birmingham

(May 3) — "CATHODIC ELEC-TRODEPOSITION—CURRENT STATUS" — E. Millington, of International Paints.

C-D-I-C

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

Cleveland

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

Golden Gate

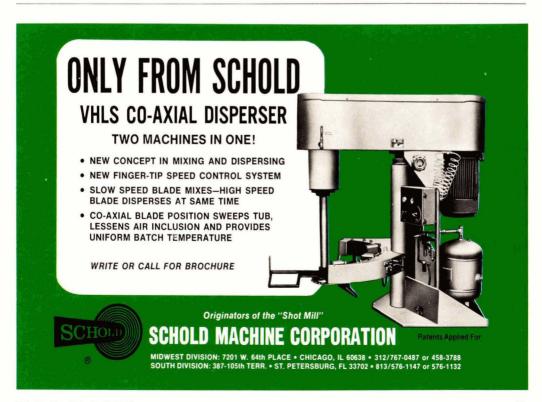
(May 14) — "USE OF ORGANO TITA-NATES IN COATINGS" — Salvatore J. Monte, of Kenrich Petrochemicals, Inc.

(June 18) — Manufacturing Seminar, "Mixing Time '79."

Los Angeles

(May 9) — "USE OF ORGANO TITA-NATES IN COATINGS" — Salvatore J. Monte, of Kenrich Petrochemicals, Inc. Also, Manufacturing Seminar, "Computers for the Paint Industry."

NOTE TO ALL CONSTITUENT SOCIETY SECRETARIES: Future Society Meeting notices for the 1978-1979 meeting season conclude with this issue. All Secretaries are urged to forward their Society's meeting agenda for the 1979-1980 meeting season to Federation headquarters as soon as possible. — Ed.



Vol. 51, No. 651, April 1979

Elections

BIRMINGHAM

Active

HODGSON, PHILIP JOHN — Sandoz Products Ltd., Horsforth Leeds, Yorkshire, England.

CHICAGO

Active

- ABACAN, CRISPIN D. Standard T Chemical Co., Chicago Heights, Ill.
- BISHOP, MIRIAM A. Cargill, Inc., Carpentersville, III.
- BROWN, ORVILLE E. Rust-Oleum Corp., Evanston, III.
- BRUNSON, JOHN E. Graham Paint & Varnish, Chicago, Ill.
- COATES, H. RANDOLPH Midland Div., Dexter Corp., Waukegan, Ill.
- COLLINS, ROBERT L. Sherwin-Williams Co., Chicago.
- DAVIES, DONN T. Davies Imperial Coatings, Inc., Hammond, Ind.
- DAVIS, LIONEL Valspar Corp., Chicago.
- DORFMAN. ROBERT Inchemco Ltd., Skokie, III.
- DUHANEY, DONALD C. Rust-Oleum Corp., Evanston.
- EMSHOFF. WILLIAM G. The Enterprise Companies, Chicago.
- FISHER. PETER K. Rust-Oleum Corp., Evanston.
- Fox, EDWARD L. United Coatings Inc., Chicago.
- FREEMAN, RICHARD A. Jordan Paint Mfg. Co., Forest Park, Ill.
- GRAHAM. JOHN C. DeSoto, Inc., Des Plaines, Ill.
- GRUBESIC, JOHN O'Brien Corp., South Bend, Ind.
- GYSSLER, WAYNE E. DeSoto, Inc., Des Plaines.
- HUNT, JAMES G. Jordan Paint Mfg. Co., Forest Park.
- JAKUBOWSKI, GERALD C. Dupli Color, Elk Grove, Ill.
- JANISZEWSKI, GEORGE A. Whittaker Coatings, Rockdale, III.
- JONES. OSBURN B. Elliott Paint & Varnish Co., Chicago.
- JORDAN, FRANCIS H. Mobil Chemical Co., Kankakee, III.
- JURSS, LARRY J. Thiem Corp., West Allis, Wis.
- KAMRADT. MIKE Martin Varnish Co., Chicago.
- KINNEY, LAYTON F. Standard T Chemical Co., Chicago Heights.
- KIRKEGAARD. PHILLIP V. Midland Div., Dexter Corp., Waukegan.
- LAWSON, DAVID Inchemo Ltd., Skokie.
- LEAHY, JOHN T. Moline Paint Mfg. Co., Moline, III.
- LEEP. GUS W. Seymour of Sycamore Inc., Sycamore, III.
- MAJKRZAK, EDWARD P. DeSoto, Inc., Des Plaines.

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- MOONEY, RAYMOND M. Valspar Corp., Chicago.
- MUZYCZKO, T. Bingham, Franklin Park, III.
- NEAR, WILLIAM R. Rust-Oleum Corp., Vernon Hills, III.
- NOWICKI. GERARD Cellofilm Corp., Chicago.
- OLHOFT, GARY V. Union Carbide Corp., Alsip, III.
- PLOOY, RONALD J. Northwest Chemical, Waukesha, Wis.
- SATZGER. DAVID DeSoto, Inc., Des Plaines.
- SCHIFFMAN, ELLWOOD Jordan Paint Mfg. Co., Chicago.
- SHEPPARD, THOMAS F. United States Gypsum Co., Des Plaines.
- SOLLE, HENRY A. Union Carbide Corp., Alsip.
- STECH, CLIFFORD E. Rockford Chemical Coatings, Rockford, Ill.
- SULLIVAN, JERRY Midland Div., Dexter Corp., Waukegan.
- SUPERCZYNSKI, WAYNE O'Brien Corporation, South Bend.
- TODD. BRUCE H. Chemetron Corp., Holland, Mich.
- ULMER. ROBERT W. Masonite Corp., St. Charles, III.
- VARGO, SUSAN T. Cargill, Inc., Carpentersville.
- VRANDACK, MARIANNE E. John L. Armitage & Co., Elk Grove.
- WALDON, ROBERT J. Midland Div., Dexter Corp., Waukegan.
- WEST. ALVIN C. Mobil Chemical Co., Kankakee.
- WHITE, ROGER G. The Enterprise Companies, Chicago.

Associate

- BLACKER, ROGER P. Whittaker, Clark & Daniels, Inc., Willowbrook, Ill.
- CAPREL. WILLIAM T. Kraft Chemical, Chicago, Ill.
- CARPENTER, OWEN G. Cyprus Ind. Minerals, Glen Ellyn, Ill.
- GRIMM. WILLIAM A. Pluess-Staufer Ind., Inc., Des Plaines, III.
- HOLLY, BRUCE E. Tenneco Chemicals, Inc., Chicago.
- KALLAL, JR., WILLIAM L. Tenneco Chemicals, Inc., Chicago.
- LOBERMANN, JAMES Whittaker, Clark &
- Daniels, Inc., Willowbrook. MCGROARTY, JOHN T. — NL Industries,
- I.C.D., Bensenville, III. MILLS. DAVID R. — Nalco Chemical Co., Hillside III
- MURDOCK. ROBERT N. Murdock Co., Inc., Arlington Heights, Ill.
- PAYNE, GARY L. Hilton-Davis, Cincinnati, Ohio.
- STAPLES III, PAUL C. Air Products & Chemicals, Inc., Hillside.

CLEVELAND

Active

- GHELANI, SHIRISH V. Limbacher Paint & Color Works, Inc., Lakewood, Ohio.
- HOWARD, DENNIS D. Hughson Chemicals Co., Erie, Pa.
- MCKINSTRY, JAMES E. Mobil Chemical Co., Cleveland, Ohio.
- ORCH. WILLIAM M. Glidden-Durkee Div., SCM Corp., Strongsville, Ohio.
- SHAW. JULIE Ceilcote Co., Berea, Ohio.
- TUCKERMAN, THOMAS D. Body Brothers, Inc., Bedford, Ohio.
- WICHACHEEWA. PETER Glidden-Durkee Div., SCM Corp., Strongsville.
- WILLIAMS, CONSTANCE F. Glidden-Durkee Div., SCM Corp., Cleveland.

Associate

CAMPAGNA. JOSEPH — Davies Can Co., Solon, Ohio.

HOUSTON

Active

- ALLEY, MILTON Alco Paint Mfg. Co., Inc., Stafford, Tex.
- BLEUEL, PAUL T. Mobil Chemical Coatings, Beaumont, Tex.
- BURST. JOHN F. Dresser Minerals Div., Houston, Tex.
- COOK, HERBERT L. Oil Center Research, Houston.
- HERRANZ, ANGEL Cook Paint & Varnish Co., Houston.
- LEZNICKI, CHRISTOPHER Z. Russco Paint Mfg. Co., Beaumont.
- REYES, FELIMON S. PPG Industries, Inc., Houston.
- TRZOS. THEODORE S. Dresser Minerals Div., Houston.
- TUNGLAND, BARRY J. Matcote Company, Inc., Houston.
- VARDY, JOEL M. PPG Industries, Inc., Houston.
- WEISMANTEL, GUY E. Consultant, Houston.

Associate

- JACKSON, THOMAS A. Sun Chemical, Pigments Div., Plano, Tex.
- SCHMIDT, LEO A. Johns Manville, Houston, Tex
- SPARKS. STEVEN W. Delta Solvents -Chemical Co., Houston.

LOUISVILLE

Active DAGHIR, DAVID M. — M & T Chemicals, Inc.,

DUNHAM, JOHN D. - Celanese Coatings Co.,

Journal of Coatings Technology

Carrollton, Ky.

Jefferstown, Ky.

HOWARD, JR., ROBERT D. — M & T Chemicals Inc., Carrollton.

POWELL, RICHARD L. — Reichhold Chemicals, Inc., Louisville, Ky.

WOLFE, GORDON S. — Porter Paint Co., Louisville.

NEW ENGLAND

Active

- BRILLINGER. JAMES H. W R Grace & Co., Lexington, Mass.
- BUNDOCK, JR., HOWARD G. California Prod. Corp., Cambridge, Mass.
- MULVEY, GEORGE M & M Paint Mfg. Co., Pawtucket, R.1.
- PARKS, JOHN W. Parks Corp., Somerset, Mass.

Associate

FRIEDMAN, STEVEN R. — Abcor, Wilmington, Mass.

NEW YORK

Active

- ABRASH. MURIEL Engelhard Industries, Inc., East Newark, N.J.
- AHDIEH, HARRY B. Cellofilm Corp., Woodridge, N.J.
- IYER. MOHAN R. CIBA-GEIGY Corp., Ardsley, N.Y.
- KAYE, JEFFREY C. Maas & Waldstein Co., Newark, N.J.
- LEVINE, CHARLES Consultant, Brooklyn, N.Y.
- MOHAMMAD. IQBAI. Hoboken Paints, Inc., Lodí, N.J.
- SCHMIDT, GEORGE A. Engelhard Minerals & Chemicals Corp., Edison, N.J.
- SKLAK, BRUCE Z. Hartin Paints & Filler Corp., Kearny, N.J.
- SLIVA, THOMAS J. D/L Laboratories, New York, N.Y.

Associate

WESER. JACK — Columbia Can Co., Inc., Linden, N.J.

PACIFIC NORTHWEST

Active

- AYERS. TIM C. Laurence-David, Inc., Eugene, Ore.
- CHENG. CAMILLO C. Drew Chemical Corp., Seattle, Wash.
- Соок. DICK Technical Research Co., Seattle.
- DAVIS. DONALD D. American Tar Co., Seattle.
- FRYE, WILLIAM Forrest Paint Co., Eugene.
- PHANEUF, RAYMOND F. Jarvie Paint Mfg. Co., Seattle.
- STEVENS, RICHARD G. Forrest Paint Co., Eugene.

Associate

BROWN, L. SCOTT — Nalco Chemical Co., Littleton, Colo.

- HELZER. WILLIAM C. Helzer Chemical Co., Seattle, Wash.
- KLATT, JR., ROBERT W. Pacific Coast Chemical, Portland, Ore.

Ромрео. В. Р. — American Cyanimid Co., Los Angeles, Calif.

PHILADELPHIA

Active

- DAVIDSON, HUGH R. Davidson Colleagues, Tatamy, Pa.
- HEGEDUS, CHARLES R. Naval Air Development Center, Warminster, Pa.
- MILLER. WALTER G. Delkote, Inc., Pennsgrove, N.J.

REYNOLDS, THOMAS W. — C.J. Osborn Chemicals Co., Merchantville, N.J. ROESCH, THELMA — Davidson Colleagues, Tatamy.

WESTERN NEW YORK

Active

- CHADWICK, GEORGE F. Mesch and Associates, Lockport, N.Y.
- INTORP, NORBERT B. Hooker Chemicals, Niagara Falls, N.Y.
- ROBEY, JAY Spencer Kellogg Div., Buffalo, N.Y.



Southern Society Holds 43rd Annual Meeting

An attendance of about 300 was recorded at the 43rd Annual Meeting of the Southern Society for Coatings Technology in Buena Vista, Florida, March 14-16. The President, A. Roy Neal, of Rico Chemicals, Inc., was the Presiding Chairman. Alfred L. Hendry of A.L. Hendry & Company, served as Program Chairman.

Technical Session

The meeting opened with a keynote address, "Energy Dilemma — Possible Solution" by John W. Fetzer, of Marathon Oil Co.

Other presentations at the meeting were:

"Florida School Property Management Association Paint Specifications" by Billie Williams, of Devoe & Raynolds Co.

"Practical Rheology for the Coatings Chemists" by James W. Jourdrey, of N L Industries, Inc.

"Water Reducible Resins for Coatings" by Robert Mate, of Goodyear Chemicals Co.

"Data and Telecommunications" by Alex Serraes and Sheila Tyle, of Southern Bell Telephone Co.

"Weatherable Epoxy Resins" by Jack W. Klarquist, of Shell Chemical Co.

"Economics and Use of Iron Oxide

Pigments" by David S. Young, of Pfizer, Inc.

"The Orlando Plant of DeSoto, Inc." by Kenneth W. Erdman, of DeSoto, Inc.

Two students from the Polymer Coatings Course at the University of Southern Mississippi also presented brief papers covering their work.

The Federation was represented by James A. McCormick, President, and Frank J. Borrelle, Executive Vice-President.

Business Session

During the business session, the Society presented a \$500 contribution to the Paint Research Institute and another of \$5,000 to the Polymer Science Department of the University of Southern Mississippi for scholarships.

New Officers

Officers elected for 1979-30 were: President — Alfred L. Hendry, of A.L. Hendry & Co.,; President-Elect — Thad T. Broome, of Precision Paint Co., Vice-President — Franklin D. Rector, of Indurall Coatings Inc.,; and Secretary-Treasurer — Dan M. Dixon, of Freeport Kaolin Co.

The 1979 Annual Meeting will be held at the Terrace Garden Inn, Atlanta, March 19-21.

Conference on Mixing Equipment to be Hosted By Golden Gate Society on June 14

The Manufacturing Committee of the Golden Gate Society will sponsor an all day conference on the use of equipment for mixing and blending of paints, inks, and varnishes on June 18, at A. Sabellas' Fisherman's Wharf, San Francisco. This program will emphasize the economics as well as the latest techniques for mixing and blending of surface coatings. Registration fee of \$35 includes lunch and dinner.

Scheduled for presentation are the following:

"Practical Guide to Rheological Studies of Inks and Paints" — Norman Nigard, of California Ink Co.

"Additives for Dispersing and Mixing Pigments" — W.J. Stewart, of Tenneco Chemicals, Inc.

"Mixing Equipment for Dispersing Inks and Pastes" — Hugh Purcell, of Morehouse Cowles. "Factors Governing Tinter Performance" — Fred Daniel, Elio Cohen, and Ray Pinario, of Daniel Products Co.

"Theory and Use of Attritor Mills for Dispersing" — Roy Nelson, of Epworth Mfg.

"Concept of Horizontal Milling" – Myron Segal, of Premier Mill Corp.

"Small Media Mills and Media" — Speaker to be announced from Chicago Boiler Co.

"Designs of Hi Speed Dispersers" — Jim Wight, of Big H Equipment Corp.

"Dispersing with Ball Mills" — Speaker to be announced from Paul O. Abbe, Inc.

"Use of Different Type Media for Closed Mills" — Geoff Daly, of Jaygo, Inc.

For further information, contact E. Harmon, Borden Chemical Co., 41100 Boyce Rd., Fremont, Calif. 94538.

CIBA-GEIGY to Again Hold Colorimetry Seminar, May 22-24

A repeat of last year's successful two-and-one-half-day seminar on "Colorimetry and Optics of Pigmented Systems," will be offered by CIBA-GEIGY Corp.'s Colorimetry Laboratory in Ardsley, N.Y., May 22 to 24.

The seminar will provide practical information on the optical behavior of pigments in various materials. The course will acquaint participants with the application of the science of colorimetry, color measurement, and the theories of colorant formulation and pigment dispersion to the solutions of typical problems found in industry.

The seminar will be useful for color technicians, chemists, and others involved in colorant formulation and control. Cost is \$185.

Instructors for the seminar are Ruth Johnston-Feller, Color Consultant to CIBA-GEIGY, and Dennis Osmer, Manager of the Colorimetry Laboratory.

For additional information, or to register, contact Dennis Osmer, Colorimetry Laboratory, Pigments Dept. CIBA-GEIGY Corp., Ardsley, N.Y. 10502.

Two-Phased Polymer Systems Topic of Lehigh Short Course

An introductory short course on "Polymer Blends, Grafts, and Blocks (Two-Phased Polyer Systems)," will be held at Lehigh University, Bethlehem, Pa., June 10-15.

Organized as part of Lehigh's polymer science program, the course will stress the interrelationships among synthetic detail, morphology, mechanical behavior, and processing. Examples will be given of industrially important materials such as impact-resistant plastics, thermoplastic elastomers, polymer impregnated wood and concrete, multilayer films, polymeric surfactants, low creep fibers, and insulating materials.

The course is based on the book "Polymer Blends and Composites," by Drs. Leslie H. Sperling and John A. Manson, of Lehigh, who will conduct the course.

Registration fee of \$500 includes a copy of the book.

For additional information contact Materials Research Center, Lehigh University, Bethlehem, Pa. 18015.

Dispersion Short Course Scheduled at Kent State, May 21-25

A short course on "Dispersion of Pigments and Resins in Fluid Media" will be held at Kent State University, Kent, Ohio, from May 21 to 25. Lectures will be conducted in the areas of surface chemistry fundamentals, pigment-vehicle treatments, water and classic systems, and the mechanics of dispersion.

Presentation will be followed by practical experiences with commercial systems and discussions on dispersion equipment and plant practices.

Program Chairman Carl J. Knauss, of the Chemistry Dept. of Kent State, announced the following presentations:

MAY 21

"Fundamentals of Dispersion Preparation" — Dr. Richard J. Ruch, of Kent State University.

"Surfactants and HLB" — William C. Griffin, of ICI America, Inc.

"Polymeric Organic Chemicals as Dispersants for Pigments" — Dr. Robert D. Athey, Jr., of Carnegie-Mellon Institute of Research.

"Surface Chemistry of Pigment-

Vehicle Systems" — Charles A. Kumins, of Tremco Corp.

MAY 22

"Methods of Dispersion Modification" — Dr. Ruch.

"Dispersion of Classic Solvent Systems" — George R. Pilcher, of Sherwin-Willams Co.

"Pigment Dispersion Technology in Water-Base Systems" — Dr. Robert F. Conley, of Mineral and Resource Technology.

"Particle Size Distribution Analysis of Pigments, Latexes, and Coatings" — Dr. Theodore Provder, of Glidden Coatings & Resins Div., SCM Corp.

MAY 23

"Mechanisms of Dispersion Stabilization" — Dr. Ruch.

"Dispersion of TiO₂ as a Determinant of Hiding Power" — Fred B. Stieg, of PigmenTech Consulting.

"Dispersion of Carbon Black and Other Pigments in Fluid Vehicle for Printing Inks" — Dr. John W. Vanderhoff, of Lehigh University.

"Factors Governing Tinter Perform-

ance" - Elio Cohen, of Daniel Products Co.

MAY 24

"Flow and Processing Mechanics of Liquid-Solids Systems" — David G. Bosse, of Maginet-Projects.

"Practical Aspects of Compounding of Powder Coatings Formulations" — Stan Jakopin, of Werner Pfleiderer Corp.

"Theory and Application of Mixers in Blending and Dispersion" — Dr. James Y. Oldshue, of Mixing Technology of Mixing Equipment Co.

"Principles of Ball and Pebble Milling" — John M. Rahter, of Paul O. Abbé, Inc.

MAY 25

"High Shear Dispersion and Sandmilling" — William Hair, of Morehouse Industries, Inc.

"Elastomer-Black Interaction During Mixing" — Merton Studebaker, Consultant.

Additional information may be obtained from Carl Knauss, Chemistry Dept., Kent State University, Kent, Ohio 44242.

Quality Assurance is Topic of New York/Phila. Joint Technical Seminar

A two-day joint coatings symposium on "Maintaining Quality Under Pressure," will be hosted by the New York and Philadelphia Societies for Coatings Technology at the National Conference Center, Exit 8, New Jersey Turnpike, May 30 and 31.

Scheduled for presentation are the following:

MAY 30

"What's Happening to Paint Quality?" — Joseph Csernica, of Consumers Union.

"Laboratory Evaluation, Friend or Foe?" — Martin B. Freedman, of Rohm and Haas Co.

"Do You Know How Good Your Exterior Paint Is?" — Dr. Louis R. Freimiller, of Rohm and Haas Co.

"Improving Quality of Paints with Additives" — Marvin J. Schnall, of Troy Chemical Corp.

"Color Communication" — Dale N. Mosler, of Macbeth Div.

MAY 31

"People Make or Break an Instrumental Color Control System" — Dr. Robert Marcus, of PPG Industries, Inc.

"Factors Governing Tinter Performance" — Ramon E. Pineiro, of Daniel Products Co. "Volumetric Computer Color Matching" — Bruce H. Todd, of Chemetron Corp.

"The Dynometer — A Sedimentation Analysis Instrument" — Frank Zurlo, of Byk-Mallinckrodt.

"Measurements of Optical Properties of Paints" — S. Upton Jenkins, of Hunter Associates Laboratory.

In addition, following the first day's presentations, there will be a "handson" display of testing and color measurement instruments. Exhibiting companies are: Byk-Mallinckrodt, Gardner Laboratory, Hunter Associates Laboratory, and Macbeth Div.

Registration fees are \$40 for one day and \$70 for both days. On-site accommodations are available.

For further information, or to register, contact either of the Symposium Co-Chairmen, Elio Cohen, Daniel Products Co., 400 Claremont Ave., Jersey City, N.J. 07304 (201-432-0800), or Stanley LeSota, Rohm and Haas Co., Springhouse, Pa. 19477 (215-643-0200).

Macbeth Shortens Color Seminar to Regional Meetings

Macbeth, a division of Kollmorgen Corporation, has shortened its normal five day color course to a two day regional seminar.

The color seminar is designed to give a good understanding of the problems and solutions associated with color and its quality and production control. Appropriate use of visual standards, proper lighting and instrumentation will be discussed and demonstrated.

The first day is devoted to lectures and practical demonstrations. The fee for the first day is \$95 and includes reference material and lunch. The second day is an informal session of hands-on use of lighting control and instrumentation. Technical experts will be on hand to discuss any color problems that attendees bring with them. There is no charge for the second day.

The dates are: Boston, Mass., April 26 and 27; Chicago, Ill., April 30-May 1; Atlanta, Ga., May 17 and 18; Cleveland, Ohio, June 7 and 8; and Charlotte, N.C., June 14 and 15.

Additional information and application forms can be obtained from Lorraine Richard, Macbeth, Little Britain Rd., P.O. Box 950, Newburgh, N.Y. 12550.

FATIPEC Invites Papers for 1980 Congress

The XVth Congress of FATIPEC (Federation of the Associations of Technicians in the Paint, Varnish, Lacquer and Printing Ink Industries of Continental Europe) will be held from June 8-13, 1980, at the Rai Congress Centre in Amsterdam, Netherlands.

In order to attain an accurate and well integrated program, the Congress hopes to present information from varied and internationally oriented sectors of the coatings industry. Therefore, authors are invited to submit discussion papers focusing on the theme. "Activities of the Coatings Industry in the Framework of Ecology. Energy and Economy Problems." Acceptance of submitted papers will be determined by the Technical-Scientific Committee, part of the Dutch organizing structure, on the basis of its effectiveness in dealing with the Congress theme.

Registration of papers from speakers from FATIPEC member countries should be made to the respective national FATIPEC association. Speakers from other countries are requested to register their papers directly to the Congress Secretariat: C. Korf, Oostenrijklaan 43, Haarlem, Netherlands.

Authors must send their names and titles of papers to Mr. Korf by June 1; the abstract by September 1; and the full text by January 1, 1980. Both plenary lectures and discussion papers will be presented in one of the three official FATIPEC languages: English, French or German.

Congress Circular #1, with a preliminary registration form is now available from either FATIPEC or the Federation office at 1315 Walnut St., Phila., Pa. 19107. Circular #2 will be distributed later this year to those who have returned the registration form.

During the XIVth Congress held in May 1978, the Annual General Meeting of the FATIPEC elected Dr. Milt F.



eration. Dr. Kooistra received a degree in Chemical Engineering in 1950 from Delft Technical University. In the same year, he joined Sikkens Paint Co. in Sassenheim,

Kooistra Presi-

dent of the Fed-

M.F. Kooistra in Sassenheim. Holland and began his research in coat-

ings technology. After developing and promoting innovative research in various positions with the company, he was promoted to Research Manager.

When Sikkens became incorporated into Akzo Coatings, a division of Akzo, Dr. Kooistra began to serve in his present position of Research Coordinator within the Akzo Coporate Research Laboratories at Arnhem, Holland.

Dr. Kooistra is President of the Dutch N.V.V.T., the Association of Dutch Paint Technicians, which will be the host group for the FATIPEC Congress. Internationally, he is known as the current President of ISO-TC35, the worldwide organization on standardization in the field of coatings.

Innovations/Challenges, Topics Of NCCA Annual Meeting

The annual meeting of the National Coil Coaters Association will be held at the Marco Beach Hotel and Villas, Marco Island, Fla., on April 30-May 2.

Focusing on the theme, "Innovations and Future Challenges," the Opening General Session on Monday, April 30, will highlight such topics as "The Future of the Steel Market" — Peter F. Connor, Inland Steel Co. and "The Future of the Aluminum Market" speaker to be named. Also scheduled for this session is the presentation of the winners in the 11th Annual NCCA Design Competition.

The afternoon session will feature open Technical Committee meetings and will include workshops on processing techniques, aluminum-based coil stock, and color. The business session on Tuesday morning is scheduled to include the NCCA Membership Meetings and the election of NCCA Board of Directors.

Featured among the morning presentations on May 2 are: "Future Material Requirements for the Automotive Industry" — T.C. Lasko, of Fisher Body Div. of General Motors Corp. and an examination of the culvert stock market by A.P. Warr, of B & K Machinery International Ltd.

Concluding the meeting on Wednesday will be an address by Dr. Michael H. Mescon, of Georgia State University, who will speak on "A Conscious Approach to Excellence."

Additional information may be obtained from Don White, NCCA, 1900 Arch St., Philadelphia, Pa. 19103.

Energy Efficiency to be Topic of SPE ANTEC, May 7-10

The 37th Annual Technical Conference (ANTEC) of the Society of Plastic Engineers (SPE) will be held at the Hyatt Regency Hotel. in New Orleans. La., on May 7-10. The theme of ANTEC '79, "Plastics—Efficient Use of Resources," will be the subject of four plenary session speakers, 30 different educational seminars, 100 exhibits, and several special events, including a luncheon address by Governor Edwin Edwards of Louisiana.

Some 205 technical papers will cover the areas of fabrication, materials, and end uses. Special sessions will feature 56 papers on resource efficiency with plastics, plastics in the public interest, plastic analysis, and plastics in education, the latter of which will include five award-winning student papers. Some of the key papers of general and technical interest that will be presented by industry representatives at the conference are:

"World Petroleum Availability" — U.S. Geological Survey.

"The National Energy Outlook, 1980-1990" — Shell Oil Co.

"The Role of Plastics in Energy Conservation" — Ethyl Corp.

"Consumer Safety and Plastic Products" — Consumer Product Safety Commission.

"Polyacrylate — A Tough, New Engineering Polymer" — Union Carbide Corp.

"Low Density Film Resins of the Future" — Dow Chemical Co.

"Applications and Design of a Novel

Polymer Processing Machine" — Farrell Machinery Group.

Additionally, approximately 25 technical and general interest industry films on plastics will be shown each day, concurrently with the technical paper sessions. The movies will cover such topics as vinyl plastics, reinforced plastics, PVC, moldmaking, polyolefins, polypropylene, polymers and fire, and safety with extrusion and injection molding, as well as other subjects.

Advance registration fees are \$60 for SPE members and \$85 for non-members for the entire conference.

For additional information, or to register, contact Eugene W. Wilson, Society of Plastics Engineers, 656 W. Putnam Ave., Greenwich, Conn. 06830.

Colloidal and Surface Phenomena is Subject of Fundamentals Course at Carnegie-Mellon

Carnegie Institute of Technology will present a series of five-day courses on "Fundamentals for Dealing with Colloidal and Surface Phenomena" at Carnegie-Mellon University, Pittsburgh, Pa. Course dates are May 21-25 and September 24-28, 1979.

Presentations will benefit those persons who encounter in their work the unique effects which surface conditions and degree of dispersion exert upon the properties of materials and their performance in industrial processes. Participants will develop an understanding of the basic theoretical concepts in the field.

Areas to be covered include: Types of Colloids, Preparation and Purification of Colloids; Surface Energy and Surface Tension; Examples of Completely Polarizable and Non-Polarizable Colloids; Physical Chemistry of Surfactant Solutions; Electrokinetic Phenomena (Electro-osmosis, Streaming Potential, Electrophoresis); Contact Angle, Wetting and Adhesion, Friction and Lubrication; Critical Coagulation Concentration; Adsorption on Solid Surfaces from the Vapor Phase and from Solution; Solid Surface Characterization through Adsorption Measurements; Methods of Determining Physical Properties of Colloids; and Comparison of Different Techniques for Studying Surfaces.

The course format includes lectures, problem-solving sessions, and laboratory demonstrations, all designed to provide a foundation in the fundamentals and to introduce specific research techniques.

The registration fee, which includes text, course notes, and laboratory fee, is \$675. Lodging is available at a special rate to registrants.

To obtain more information, or to register, contact Margaret Morrison, Post College Professional Education, Carnegie Institute of Technology, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pa. 15213.

Color Technology Program to be Held at Rensselaer in June

The principles, management, and development of color technology will be examined during the three intensive continuing-studies courses offered by Rensselaer Polytechnic Institute, Troy, N.Y., June 4-29.

"Principles of Color Technology," (June 4-8 and 11-15) will study the areas of color description, measurement principles, and color-difference calculations, as well as the use of computers in color matching and colorant properties. Hands-on experience will be provided in laboratory exercises. The course will be of particular interest to industry personnel responsible for color matching and color control.

"Color Technology for Management," (June 18-19) is designed to aid executives responsible for research, production, or sales of colored products in reaching correct management decisions based on the principles of color technology.

"Advances in Color Technology," (June 25-29) will utilize both lectures and laboratory workshops in providing the latest information on the developments and techniques of color science and technology. Attendance is limited to those applicants having advanced knowledge and experience in color, or those who have completed the course, "Principles in Color Technology." Tuition is \$425 for both the "Principles" and "Advanced" course, and \$250 for the "Management" course.

For additional information, or to register, please contact Richard J. Teich, Office of Continuing Studies, Rensselaer Polytechnic Institute, Troy, N.Y. 12181.

Leadership and Evaluation Are Topics of Chicago's Management Seminar

The Joint Education Committee of the Chicago Society and the Chicago Paint and Coatings Association will hold its ninth annual Management Development Seminar on April 26 at the Fountain Blue Restaurant, Des Plaines, III.

Dr. Albert H. Hastorf, of Stanford University's Graduate School of Business, will conduct both the morning and afternoon sessions. The initial session, "Leadership Style and the Situation," will review some of today's popular management styles, contrasting the task-oriented, centralized style with a more participative style. Also examined is the proposition that the effective style depends on the particular situation.

The afternoon session, "Evaluating People in Organizations," will use filmed case studies in examining the evaluations of people and communication with them.

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People

Wyandotte Paint Products Co. has acquired the business of Dumar Paints and Chemicals, Ltd., Rexdale, Ontario, effective February 1, 1979. William Dunn, one of the former owners of Dumar Paints, will continue to manage that facility for Wyandotte Paint. Mr. Dunn is a Past-President of the Federation of Societies for Coatings Technology.

Meanwhile, **Taki J. Anagnostou** has been named Vice-President, Research and Development for Wyandotte. Mr. Anagnostou is a member of the Detroit Society for Coatings Technology.

William F. Abercrombie has been promoted to the position of Manager, Research Laboratory, of the J.M. Huber Corp., Clay Div. In his new capacity, he will be responsible for the administrative activities of the laboratory and the coordination of quality control for the division.

Southern Protective Products Company of Atlanta, Ga., has appointed **Patrick G. DeCelles** Manager of its new manufacturing plant in Houston, Tex. His responsibilities will include supervising the production of caulking, sealants, adhesives, and spackling and glazing compounds manufactured for customers in the Southwestern United States.

Shu-Jen Wu Huang has been promoted to the position of Group Leader for the Organic Chemicals Div. of The Richardson Co.

Meanwhile, **Wayne Stancel** has been named Group Leader—Product/Process Development of the division. Ms. Huang and Mr. Stancel are both members of the American Oil Chemists Society.

In a reorganization of the management of its Organic Chemicals Div., the SCM Corp. has made the following appointments: John A. Faber-Vice-President, Administration and Planning, and Assistant to the President: William B. Stoufer-Vice-President, Technology, and Assistant to the President; George A. Frank-Director of Employee and Community Relations; John M. Heijmans-Division Controller; Ralph E. Close-Group Vice-President and General Manager of the Terpene Products Group; Charles W. Morris-Group Vice-President and General Manager of Sylvachem; and W. Arnold Dinkins-Group Vice-President of PCR, the company's new acquisition.









A. S. Adkins

G. W. Bovenizer

Albert E. Cash has been appointed a Vice-President of the O'Brien Corp. Promoted last March to the office of Sales Manager for the Western states region, Mr. Cash will continue to carry out his responsibilities in this position at the company's headquarters in South San Francisco, Calif.

Meanwhile, Adrian S. Adkins has been named Corporate Technical Director of the firm. Mr. Adkins is a member of the Golden Gate Society for Coatings Technology.

Richard L. White, previously Director of the Technical Marketing Dept., Mobay Chemical Corp., has been appointed Director of Corporate Planning. Mr. White is a member of the Pittsburgh Society for Coatings Technology. Dr. Arthur L. Baron, Director of the Plastics and Coatings Div., has assumed the additional duties of Director of Technical Marketing, and Dr. Gerard E. Reinert, has been named Manager of Research for the division.

The ACNA Div., Montedison, Inc., has appointed Eric H. Hill National Sales Manager for organic pigments. He will be aided by George Morehouse, mid-western regional Sales Manager.

Reliance Universal, Inc. has named Charles J. Fisher President and Chief Operating Officer. James Z. Hoffman, has succeeded Mr. Fisher as Vice-President and General Manager of the Specialty Chemicals Div. William J. Rutledge has assumed Mr. Hoffman's duties as Vice-President, Corporate Operational Services, and Herbert A. Champlin has been named Vice-President, Marketing and Commercial Development.

EZ Paintr Corp. has announced that **David Bruce LaBott** has been appointed to the position of Vice-President/Controller for the company.

In a series of promotions, NL Titanium Pigments has named James W. Hartsgrove to the position of Western Regional Sales Manager, George W. Bovenizer to Chicago District Sales Manager, and Robert W. Blackford to New York District Sales Manager, Mr. Hartsgrove is a member of the Chicago Society for Coatings Technology and Mr. Bovenizer belongs to the Northwestern Society, In addition, William R. VanBeusichem, Charles D. Maisch and William Powell have been appointed Sales Representatives in the Eastern, Lake Central, and Central Regions respectively.

Absolute Coatings, Inc. has engaged **Dr. Berthold Winston** as Technical Consultant. Dr. Winston, associated with the coatings industry for the past 30 years, has been a member of the New York Society for Coatings Technology, the American Chemical Society, and the Association of Corrosion Engineers.

Hillar M. Rootare has joined the Research and Development Laboratory of Micromeritics Instruments Corp. as a Research Scientist. In this position, he will be responsible for mercury porosimetry development and consultation on electrophoresis applications.

Peter B. Statham has been appointed Marketing Manager for The Flood Co., Hudson, Ohio. He will be responsible for the development and implementation of all sales and marketing programs in connection with Flood's entire line of specialized coatings and paint additives.

Interstab Chemicals, Inc., of New Brunswick, N.J., has appointed John B. Watson Manager of its newly established regional sales office in Dallas, Tex. Under his supervision, the sales office will serve the plastics and paint industries in the southwestern United States. Dr. A.C. Zettlemoyer, Provost and Vice-President of Lehigh University, Bethlehem, Pa., has been appointed an "Honorary (Foreign) Member" of the Chemical Society of Japan, Division of Colloid and Surface Chemistry. This is the first such honorary membership conferred by the society.

Dr. Zettlemoyer, following 38 years of service including more than 10 years in his present position, will retire, effective June 30, 1980. He will continue in research as University Distinguished Professor, effective July 1, 1980, and will continue to report to the President of Lehigh.

A native of nearby Allentown, Pa., he earned his B.S. and M.S. Degrees at Lehigh and his Ph.D. Degree at M.I.T. He joined the Lehigh faculty in 1941 and has been Provost and Vice-President since 1969. In addition, he was one of the founders of the National Printing Ink Research Institute and the Center for Surface and Coatings Research, both at Lehigh.

Among the numerous honors Dr. Zettlemover has received are the Mattiello Award from the Federation of Societies for Coatings Technology, Kendall Award from the American Chemical Society, Honor Scroll from the American Institute of Chemists, Voight Award from the Graphic Arts Industry, Hillman Award from Lehigh, Ault Award from the Printing Ink Industry, Bond Medal from the American Oil Chemists' Society, Honorary Doctor of Science from Clarkson College of Technology, and Honorary Doctor of Letters from the China Academy.

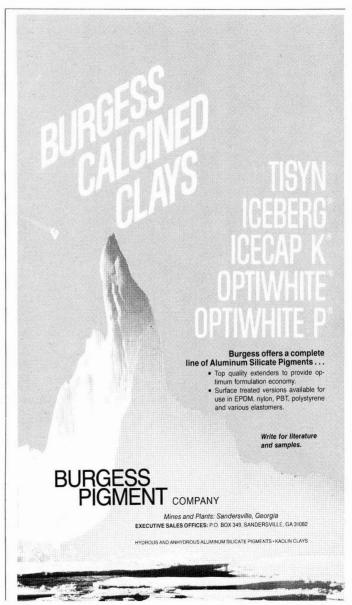
He has been a consultant to several governments and has lectured widely in the U.S., U.S.S.R., China, Japan, and Europe. His research in colloid and surface chemistry is of international recognition and importance. He has been elected to Tau Beta Pi and Sigma Xi.

In a series of managerial appointments, Filterite has named Royal R. Swanson-Manager of Field Service Operations; William M. Sporer-Product Manager for Industrial Filter Products; Eugene R. Reahl-Regional Sales Manager for the West Coast; Robert D. Evans-Zone Manager for the Filter Group in Houston, Texas; Paul S. Masaschi-Sales Manager for Industrial Filter Products; D. Randy Culley-Regional Sales Manager for the Chicago area; John R. Scheidel-Regional Manager for the Northeastern area; and Vincent B. Fadoul-General Sales Manager and William McCaffery-Operations Manager for Filterite and Fluid Dynamics Products.

Lonza Inc., Fair Lawn, N.J., has named **Gerald R. Schiller** Senior Vice-President. Formerly the Vice-President of Manufacturing and Engineering, Mr. Schiller will share with **Bernard D. Allen**, President, some of the responsibility for company operations.

Hunter Associates Laboratory, Inc., Fairfax, Va., has appointed **Robert C. Rumsey** to its Marketing Department as Area Manager of the Middle Atlantic States. He will be headquartered in Runnemede, N.J. John M. Pachuta has been promoted to Marketing Manager for the Thiokol Corp. Chemical Division's line of acrylated monomers and urethane oligomers. Mr. Pachuta is a member of the Chemical Marketing Research Association.

Whittaker Corp. has named **David P.A. Fabrizio** President of its newest subsidiary, ToxiGenics, Inc. Mr. Fabrizio is a recognized authority in the determination of mutagenicity, carcinogenicity, and toxicity.



Mixer/Blender

A newly published data sheet describes a new vibratory system for mixing and blending various powders to give intermixing of particles irrespective of varying specific gravities. The data sheet includes applications and technical specifications. For more information, write The Boulton Corp., 801 S. Great Southwest Parkway, Grand Prairie, Texas 75051.

Pigment Blacks

The surface chemistry of pigment blacks is discussed in a new technical bulletin. Noting that "several hundred different blacks were still on the market in 1973." the booklet details how manufacturing processes determine the differences between blacks, as well as their value in various applications. To receive a copy of this bulletin, write Pigments Div., Degussa Corp., Route 46 at Hollister Rd., Teterboro, N.J. 07608.

Deuterium Gas

The specifications and principle uses of deuterium gas (D2) are defined in a recently issued data sheet. Deuterium gas is a nonradioactive isotope of natural hydrogen identical in chemical properties, but different in atomic weight. To obtain a copy of data sheet 6647, write Adv. Dept., Liquid Carbonic Corp., 135 S. LaSalle St., Chicago, Ill. 60603.

Dimethylformamide

The properties of DMF (dimethylformamide) are discussed in a brochure now available. The versatility of DMF in neutrality, miscibility, chemical and thermal stability, and other characteristics make it suitable for a wide variety of commercial applications. For additional information, write Air Products & Chemicals, Inc., Industrial Chemicals Dept., P.O. Box 538, Allentown, Pa. 18105.

Polymer Emulsions

Comprehensive data on physical and chemical properties of two polymer emulsions are available in a completely revised and updated brochure. The bulletins discuss total solids, viscosity, and average particle size. Applications include interior and exterior flat and semi-gloss paints, industrial finishes. caulks, and textile treatments. For more information, write Organic Chemicals Div., W.R. Grace & Co., 55 Hayden Ave., Lexington, Mass. 02173.

Electric Airless Sprayers

Four new airless sprayer features are described in literature recently completed. The new features are a selfcleaning tip, three foot whiphose, larger tires, and a hose rack. For additional information, write Michael Kline, Adv. Dept., Grace, Inc., P.O. Box 1441, Minneapolis, Minn., 55440.



Dust Control

Two basic methods of dust control, unit collectors and central systems, are described and compared in new literature. Both systems are described and their respective advantages and disadvantages in areas such as energy use, flexibility, engineering, reliability, maintenance, and dust disposal are outlined. To obtain a reprint, write DCE Vokes, Inc., Suite 900, Plainview Plaza, 10101 Linn Station Rd., Jeffersontown, Ky, 40223.

Antifungal Agent

A new mildewcide, which is now registered as an antifungal agent for use in adhesives and sealants, is described in literature recently completed. Physical properties, suggested use level recommendations for various applications, safety, handling, and toxicity information are included in bulletin 77A-29. For further information, write Abbott Laboratories, Chemical and Agricultural Products Div., D-902, North Chicago, Ill. 60064.

Detectors

A six-page applications bulletin which describes the use of two UV detectors has been prepared. The first detector is shown to be useful in recording only selected components of a complex mixture based upon a particular functional group. The second detector is said to be valuable for identifying aromatic compounds in complex matrices. For a copy of bulletin GCD-45, write Perkin-Elmer Corp., Instrument Div., Main Ave., Mail Station 12, Norwalk, Conn. 06856.

Rotary Table

A rotary table with dual alignment fixtures is the subject of literature now available. The table allows exposure of one mask while the operator unloads and loads the previously exposed substrate. For further information, contact Charles Yost, Sales Engineer, Oriel Corp., 15 Market St., Stamford, Conn. 06902.

Equipment Catalog

A completely revised laboratory and pilot plant equipment catalog containing descriptive information and engineering information has been issued recently. The 80-page catalog includes information on testing equipment for batch and continuous operations such as crushing, grinding, classification, and concentration. To obtain a copy of catalog 0179, write SEPOR Laboratory Supply, P.O. Box 1252, Wilmington, Calif. 90748.

Fineness of Grind Gage

An eight-page brochure has been released which describes fineness of grind gages that are used for checking particle size in paste form of products such as resins, plastisols, chemicals, and paint and varnish. The pamphlet includes method of use, scales available, list of industries that use such gages, complete specifications, and current price list. To obtain a copy, write to Paul N. Gardner Co., P.O. Box 6633, Station 9, Fort Lauderdale, Fla. 33316.

Methods Development

An 18-page, step-by-step manual details the methods development process involved in attacking a liquid chromatography separation problem. Included are column and detector selection, sample pretreatment, and chromatographic optimization. Attached are useful solvent property charts, and detailed descriptions of the solvent and sample filtration kits. For a copy of TN-69, write Perkin-Elmer Corp., Instrument Div., Main Ave., Mail Station 12, Norwalk, Conn. 06856.



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Reader Asks: Will Structures Survive CARB?

TO THE EDITOR:

I have just attended the 1979 Western Coatings Symposium in San Francisco. Aside from one plaintive plea. I watched an industry calmly accept CARB without a murmur of protest.

The audience and panel on that Friday afternoon session, "Dealing with Government Agencies and Regulations", were encouraging the further decay of the Paint Industry.

As I drove about the next day I wondered how many wooden homes and steel structures would exist in America today if they had first been painted with CARB-complying primers. Because government bureaucrats say we must change, the paint industry is accepting a ruling that says future wooden homes and steel structures will be painted with paints using vehicles with little or no moisture-vapor resistance. These latex primers still allow moisture to flow through the film to the substrate.

How can one predict from accelerated tests how a piece of painted wood or steel will survive after 50, 75 or even 200 years? Salt spray tests have little correlation with actual exposure; there is no accelerated test to duplicate dry rot and decay. Decay allows the repairman to push a nail into the wood with the pressure of his finger.

Until the industry can develop latices with moisture resistance (this will become increasingly difficult under another proposed regulation concerning premanufacture notification of new chemical substances) steel and wood surfaces can be painted only with a definite risk of premature failure. To the truthful manufacturer who is well aware of product liability, these surfaces may be lost as far as painting is concerned. Thus we have the further erosion of the paint industry as more and more surfaces for painting are surrendered without a struggle.

Why can't the paint industry raise it's voice and be heard? Is it necessary to accept government regulations that are not in the best interest of society and the industry?

R.G. GOHMAN Technical Director & Vice President Jones-Blair Co. Dallas, Tex.

Book Review

PIGMENT + FÜLLSTOFF TABELLEN 1 Auflage

PIGMENT + EXTENDER TABLES First Edition

Olaf Lückert Kiebitzweg 4 D-3014 Laatzen 1 West Germany

Reviewed by Percy E. Pierce PPG Industries, Inc. Pittsburgh, Pa.

Pigment + Füllstoff Tabellen (Pigment and Extender Tables) is a guide to the commercially available pigments and extenders in West Germany which are used in the coatings, printing ink, and related industries. The tables are written in German, but Olaf Lückert has made available an English guide for using the tables which will assist the English speaking reader. The book is logically organized so that the reader will have little difficulty using the tables even if he has a minimum facility with the German language. A section on the addresses of pigment manufacturers as well as their agents is included.

The main index is organized so that color pigments, including white, are grouped together followed by functional pigments, metal pigments, special effect pigments, extenders, and special effect extenders. Each of the above broad classes are further subdivided. For example, under color pigments are listed white pigments, yellow pigments, orange pigments, etc. Each of these subheadings are further broken down into more specific categories. A page reference is given for each entry in the index so that the user can go directly to the page corresponding to the particular type of pigment.

A key word index based on pigment name, chemical name, and trade name is also provided at the end of the volume for those who desire to look up a specific pigment, pigment type, or product trade name.

A useful feature of the tables is the brief general discussion of the pigments which proceeds each table section, giving the reader a general overview of the types of pigments, advantages, technically important considerations for applications, and specific applications of the pigments covered in that section.

I heartily recommend the Pigment Tables especially to company libraries. It is a most useful reference. It is also a useful overview of the commercial pigments area. The reader cannot help but come away from examining Lückert's Pigment + Füllstoff Tabellen better informed and with a clearer conception of the commercial pigment choices available. It is regrettable that a similar table is not available covering domestic U.S. pigments.

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Coming Events

FEDERATION MEETINGS

(May 17-19)—Federation Spring Meetings. Third-ranking Society Officers—17th; Board of Directors—18th; Executive Committee—19th. Hilton Hotel, New Orleans, La. (FSCT, Suite 832, 1315 Walnut St., Philadelphia, PA 19107).

(Oct. 3-5)—57th Annual Meeting and 44th Paint Industries' Show. St. Louis Convention Center, St. Louis, Mo. (FSCT, Suite 830, 1315 Walnut St., Philadelphia, Pa. 19107).

PAINT RESEARCH INSTITUTE MEETING

(May 1-2)—Paint Research Institute Symposium on Analytical Methods Used to Monitor Product Compliance With Regulations. Battelle Institute, Columbus, Ohio, (Dr. Raymond R. Myers, Chemistry Dept., Kent State University, Kent, Ohio 44242).

SPECIAL SOCIETY MEETINGS

(May 3)—Detroit Society FOCUS Seminar, "Recent Advances in Automotive Coatings." Michigan Inn, Detroit, Mich.

(May 3-5)—Pacific Northwest Society. Thirty Second Annual Spring Symposium. Bayshore Inn, Vancouver, B.C., Canada. (B.D. Lamb, Harrisons & Crosfield (Canada) Ltd., 810 Derwent Way, Annacis Industrial Estate, New Westminster, B.C., V3M5R1, Canada).

(May 9)—Los Angeles Society Manufacturing Seminar, "Computers for the Paint Industry."

(May 22)—Pittsburgh Society Spring Symposium, "Controlling Corrosion with Organic Coatings." Duquesne University, Pittsburgh, Pa. (Jim Jones, PPG Industries, Inc., 151 Colfax St., Springdale, Pa. 15144).

(May 30-31)—New York and Philadelphia Societies Joint Symposium, "Maintaining Quality of Coatings Under Pressure," National Conference Center, Hightstown, N.J.

(June 18)-Golden Gate Society Manufacturing Seminar, "Mixing Time '79."

1980

(Mar. 19-21)—Southern Society Annual Meeting. Terrace Garden Inn, Atlanta, Ga. (Thad Broome, Precision Paint Co., 5275 Peachtree Industrial Blvd., Atlanta, Ga. 30341).

OTHER ORGANIZATIONS

(May 7-10)—Society of Plastics Engineers, 37th Annual Technical Conference, "Plastics—Efficient Use of Resources." Hyatt Regency Hotel, New Orleans, La. (SPE, Eugene E. Wilson, 656 W. Putnam Ave., Greenwich, Conn. 06830).

(May 10-11)—"Control of Volatile Organic Compound Emissions," sponsored by the U.S. Environmental Protection Agency, National Paint and Coatings Association, Association of Finishing Processors of the Society of Manufacturing Engineers, and Air Pollution Control Association. New Otani Hotel, Los Angeles, Calif. (Mr. Michael R. Taylor, JACA Corp., 550 Pinetown Rd., Fort Washington, Pa. 19034).

(May 11-12)—National Paint and Coatings Association. Production Planning and Inventory Management Seminar, Part II—Advanced. Stouffer's Inn On The Square, Cleveland, Ohio. (Everett Call, NPCA, Rhode Island Ave., N.W., Washington, D.C. 20005).

(May 14-18)—Institute of Applied Technology, Training Course, "Nuclear Quality-Assured Coating Work." Jackson, Mich. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(May 21-25)—"Colloids and Surfaces." Carnegie-Mellon University. (Mrs. Gerry Cohen, Course Coordinator, Post College Professional Education, Carnegie Institute of Technology, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pa. 15213).



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(May 21-25)—Short Course on "Dispersion of Pigments and Resins in Fluid Media." Kent State University, Kent, Ohio. (Carl J. Knauss, Chemistry Dept., Kent State University, Kent, Ohio 44242).

(May 22-23)—Institute of Applied Technology, Mini Course, "Coating Inspection: Instruments and Practices." Washington, D.C. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(June 4-8)—Tenth Annual Short Course, "Advances in Emulsion Polymerization and Latex Technology." Lehigh University, Bethlehem, Pa. (Dr. Mohamed S. El-Aasser, Dept. of Chemical Engineering, Whitaker Lab. #5, Lehigh University, Bethlehem, Pa. 18015).

(June 4-8 and 11-15)—"Principles of Color Technology." Rensselaer Polytechnic Institute, Troy, N.Y. (R.J. Teich, Office of Continuing Studies, Rensselaer Polytechnic Institute, Troy, N.Y. 12181).

(June 8-13, 1980)—XVth Congress of FATIPEC. RAI Congress Centre, Amsterdam, Netherlands. "Activities of the Coatings Industry in the Framework of Ecology, Energy, and Economy Problems." (Congress Secretary is C. Kork, Oostenrijklaan 43, Haarlem, Netherlands).

(June 10-13)—ASTM Committee D-1 on Paints and Related Coatings and Materials, Shoreham Hotel, Washington, D.C. (J.H. Bystrom, ASTM, 1916 Race St., Philadelphia, Pa. 19103.)

(June 11-15)—Institute of Applied Technology, Training Course, "Painting and Coating for Industry." Houston, Tex. (Institute for Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(June 14-15)—Society of Plastics Engineers, European Sections RETEC, "Latest Improvements in the Development and Processing of Polyolefins." Ghent, Belgium, (Jacques de Craene, RIGI p.v.b.a. Noorderlaan 98/36 2030-Antwerpen-Belgium).

(June 17-20)—Dry Colors Manufacturers Association, Annual Meeting. The Greenbrier, White Sulpher Springs, W. Va. (J.L. Robinson, DCMA, Suite 100, 1117 N. 19th St., Arlington, Va. 22209).

(June 18-19)—"Color Technology for Management." Rensselaer Polytechnic Institute, Troy, N.Y. (R.J. Teich, Office of Continuing Studies, Rensselaer Polytechnic Institute, Troy, N.Y. 12181). (June 20-23)—Oil and Colour Chemists' Association Conference, "The Challenge to Coatings in a Changing World." Stratford Hilton Hotel, Stratford-on-Avon, England. (The Director and Secretary, OCCA, Priory House, 967 Harrow Rd., Wembley, Middlesex HAO 2SF, England).

(June 24-29)—Air Pollution Control Association 72nd Annual Meeting and Exhibition, Cincinnati Convention-Exposition Center, Cincinnati, Ohio. (Public Relations Dept., Air Pollution Control Association. P.O. Box 2861, Pittsburgh, Pa. 15230).

(June 25-29)—"Advances in Color Technology." Rensselaer Polytechnic Institute, Troy, N.Y. (R.J. Teich, Office of Continuing Studies, Rensselaer Polytechnic Institute, Troy, N.Y. 12181).

(Aug. 11-15)—"Corrosion Control by Organic Coatings," sponsored by National Association of Corrosion Engineers. Lehigh University, Bethlehem, Pa. (Prof. Henry Leidheiser, Jr., Sinclair Lab. #7, Lehigh University, Bethlehem, Pa. 18015).

(Aug. 26-31)—Short Course on "Advances in Emulsion Polymerization and Latex Technology." Davos, Switzerland. (Dr. Gary W. Poehlein, Director, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Ga. 30332).

(Sept. 11-12)—Institute of Applied Technology, Mini Course, "Coating Inspection: Instruments and Practices." St. Louis, Mo. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

(Sept. 23-26)—67th Canadian Paint Manufacturers Association Convention, sponsored by the Ontario Paint Association. Harbour Castle, Toronto, Ont. Canada. (R.E. Green, 1666 Aimco Blvd., Mississauga, Ont. L4W 1V4 Canada).

(Sept. 24-28)—Institute of Applied Technology, Training Course, "Painting and Coating for Industry." Honolulu, Hawaii. (Institute of Applied Technology, Suite 600, 1776 K St., N.W., Washington, D.C. 20006).

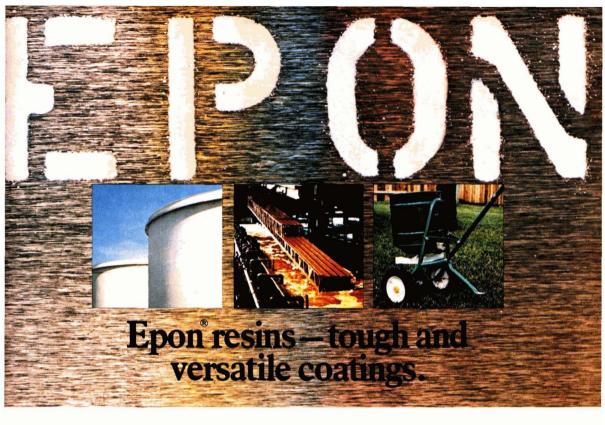
(Sept. 24-28)—"Colloids and Surfaces." Carnegie-Mellon University. (Mrs. Gerry Cohen, Course Coordinator, Post College Professional Education, Carnegie Institute of Technology, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pa. 15213).

(Sept. 30-Oct. 2)—National Coil Coaters Association Fall Technical Meeting. Hyatt Regency O'Hare Hotel, Chicago, III. (Don White, National Coil Coaters Association, 1900 Arch St., Philadelphia, Pa. 19103).

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