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Water
Reducible
Polymers
in Food
Contact
Applications

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JOURNAL OF COATINGS TECHNOLOGY

Volume 53   Number 674

Features

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GOOD NEWS FOR PAINT MANUFACTURERS WHO HAVEN'T SWITCHED TO UCAR ACRYLICS.

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UNION CARBIDE

Coatings Materials

Comment

"Paint Is Paint"

The Vice-President of Research & Development of a large paint manufacturer spoke to one of our Societies recently and said that one of the problems plaguing the industry is the general impression that "Paint Is Paint."

To the consumer, the "bargain special" looks much the same as the can of higher-priced "name brand" paint. Why not save the $5 to $10 per gallon! Can there be that much difference between them?

Yes, indeed, there is a vast difference in quality, as we know. In the long run, the low-priced stuff will cost a great deal more in money and time than its more-expensive, and well-known competitor. What Mr. & Mrs. Consumer see, therefore, is not necessarily what they get.

The Southern Society is offering a good look at "Quality Paint" with the programming of its annual meeting this month.

Spotlighting the program is Chuck Finegan's Keynote Address, "We Need to Help Our Products Go First Class." There'll also be talks on paint quality from the point of view of: the paint manufacturer, the user, and the Consumers Union. We hope to publish some of the papers in the JCT.

Somehow, the industry must find a way to convince Mr. & Mrs. Consumer that "Paint Is Paint" is just so much "Humbug From Hillman."—FJB

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Cure in five minutes at 100°C. Promote outstanding adhesion. Allow non-critical mixing ratios.
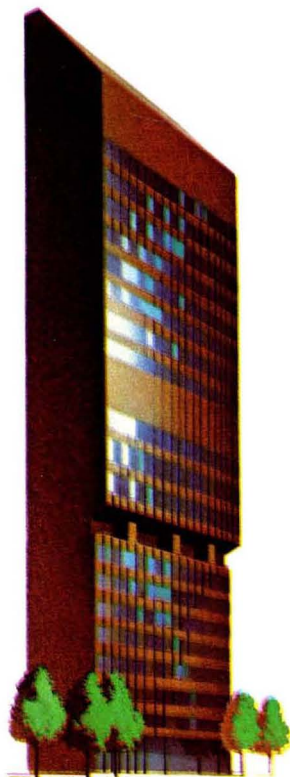
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Abstracts of Papers in This Issue

DESIGN OF WATER REDUCIBLE POLYMERS FOR USE IN FOOD CONTACT APPLICATIONS—P.V. Robinson

A number of methods of synthesizing hydrolysis resistant water-reducible polymers are described. In particular, polymer grafting techniques are explored and the application of some of these techniques to the synthesis of water-reducible polymers for use in contact with food is described. It is shown that in order to obtain the total balance of properties necessary for container coatings, significant levels of grafting to a main polymer backbone are necessary.

APPLICATION OF SIMPLEX LATTICE DESIGN EXPERIMENTATION TO COATINGS RESEARCH—K.K. Hesler and J.R. Lofstrom

A coating is a complex mixture of pigment, vehicle, solvent, and additives. Variations in the fractions of principal components comprising a coating produce significant changes in properties, performance, and cost. Applying methods for designed experiments with mixtures to coatings research has proven very useful in determining optimum principal component percentages for specific properties, maximum performance, and minimum cost. Simplex lattice design experiments are efficient; only a minimum of sample production is necessary, replication yields information about the experimental error of the test methods, and equation-fitting allows prediction over a broad composition region.

KINETICS OF SOLVENT DESORPTION FROM POLY (VINYL ALCOHOL) FILMS—M.G. Dodin

The mechanism of plastic film formation from solution and the possibility of creating a mathematical model for this process is considered. Molecular diffusion carries out the transportation of the solvent to the evaporation surface in the final stage of the process and its rate limits the overall process. Therefore, the application of the thermo-activation equation for solvent diffusion with a variable diffusion coefficient was examined for the case of solvent desorption from cast poly (vinyl alcohol) (PVA) films. The equation obtained is valid in a wide range of temperatures for binary and ternary PVA based systems. In this equation, the parameters of the casting process (time, temperature, and concentration of the residual solvent) were correlated with the physical constants of the polymer-solvent system. The equation can be used for guiding the production of films with specific physical and mechanical properties.

ANALYSIS OF PAINT—J. B. Lear

Various instrumental and chemical techniques are presented for the identification and determination of the binder, solvent, and pigment components of paint samples. Infrared spectroscopy, emission and X-ray spectroscopy, sodium fusion, and organic functional group analyses are discussed. A schematic procedure for analysis is included.

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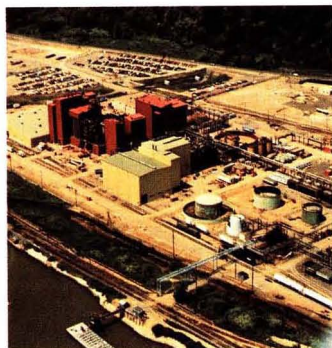
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The companies hold a leading
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- zinc oxide ● zinc dust ● zinc phosphate ● zinc chromate
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The history of the company began as far back as 1305 as the
forefathers of the present owners founded a glassworks in the
Thuringer forest. Porcelain was produced first in 1764, white
lead in 1847. The works in East Germany were lost in 1945.
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HEUCOTRON Yellow 5

■ **Less than 1 % Acid Soluble Lead**
■ **High SO$_2$-Resistance**

Reference sample

1 cycle Kesternich

5 cycles Kesternich

10 cycles Kesternich

Less than 1% Acid Soluble Lead

During recent years chrome yellow pigments have been partly substituted by organic yellow pigments as many authorities suspected the average content of 16 % acid soluble lead to be a potential hazard to human beings whereas there is no such danger with non-soluble lead and chrome combinations such as lead crystal or chrome steel.

HEUCOTRON-Yellow 5 is the first product of a newly developed generation of chromate pigments which contain hardly any acid soluble lead. According to the German DIN-Standard 55975 which simulates the solubility of lead in the human body, only 0.5% acid soluble lead (less than 1% is guaranteed) and no soluble chrome have been found in HEUCOTRON-Yellow 5. With this 32-times-reduction of the acid soluble lead content in HEUCOTRON-Yellow 5 the above mentioned supposition of a potential hazard to human beings has lost its basis. This Factor should eliminate the substitution of chrome yellows by organic pigments.

High SO$_2$-Resistance

The test panels were uniformly coated with an alkyd-melamine resin varnish containing 20% pigment and tested in accordance with DIN 50018 with 2 litres SO$_2$ in a Kesternich apparatus. HEUCOTRON-Yellow 5 was compared with two high performance pigments from the highly and medium stabilized series in the same shade range:

HEUCOTRON-Yellow 1064 - medium stabilized

HEUCOTRON-Yellow 123 - highly stabilized

HEUCOTRON-Yellow 5 - SO$_2$-stabilized

The Kesternich test has shown that HEUCOTRON-Yellow 5 possesses a significantly better resistance to SO$_2$ than the other two types. This characteristic predestinates HEUCOTRON-Yellow 5 for use in high quality paint systems such as those used for the final coat on cars and in other coating materials which are subjected to severe industrially induced atmospheric influences.

HEUCOTRON-Yellow	1064	123	5
SO$_2$ resistance	↓	↘	↑
Light fastness	↗	↑	↑
Weathering fastness	↗	↑	↑
Hue steps	↑	↗	↗

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Provides excellent overall balance of properties. Delivers exceptional cost/performance.

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Committee Activities

Progress Report on IUPAC's Supported Polymer Films Group

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

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

The following is a progress report of the Group by its Secretary, Dr. J. Sickfeld, of Germany. Included are the minutes of the Group's meeting in Copenhagen, held on October 9–10, 1980. It is felt that information on these activities will be of interest to all JCT readers.

MILTON A. GLASER,
Federation Liaison Committee

CHAIRMAN'S REPORT AND MEMBERSHIP

Incoming Chairman Dulog addressed the members and gave a report of the chairmen of working parties of IUPAC-Macromolecular Division (MMD) stressing two general points concerning the work of the MMD-working parties: All members should contribute to the work and the projects must be of a collaborative nature with the participation of at least two laboratories. Publication of the results are obligatory, preferably in *Journal of Pure and Applied Chemistry*, but upon written approval other journals may be chosen.

Chairman Dulog has accepted an invitation to report on the SPF Group's activities at the IUPAC-MMD symposium in Amherst, Mass. in 1982.

Mr. Zvonar, of Czechoslovakia, had asked to be dropped from the membership because, in his opinion, he would be unable to contribute to the work of the Group in the future. Because of his past merits he was asked to stay with the Group as an associate member. Two new members were welcomed to the Group: Mr. Gerster, of Switzerland, and Mr. Kollek, of Germany.

PROGRESS REPORTS

Analytical Group—A report on the "Analysis of Functional Groups in Amino Resins," was published by Christensen in *Progress in Organic Coatings*, Vol. 8, No. 3, pp 211–239 (1980) and included an appendix containing recommended methods for the "Analysis of Alkoxy Groups in Amino Resins by Zeisel/Merz Cleavage followed by Gas Chromatography"; "Proton-NMR-Spectroscopy"; and "Alkoxy Group Analysis by Transetherification plus GLC." The report by Kambanis on the determination of the nonvolatile content of amino resins was published in the JOURNAL OF COATINGS TECHNOLOGY, Vol. 52, No. 667, pp 61–64 (1980) under the title, "Nondestructive Drying of Amino Resin Solutions."

Literature Retrieval—This project will be finished shortly by Raaschou-Nielsen in cooperation with Fink-Jensen and will be published possibly in the JOURNAL OF COATINGS TECHNOLOGY before the next meeting of the SPF Group.

Adhesion Group—A brief report of past activities of the adhesion project was published in *Chemistry International*, No. 3, pp 39–40 (1980).

New results were presented by Zorll concerning the impact test for assessing adhesion. Characteristic of this method is that up to 80% of the energy exerted during the impact on the coated substrate is transferred to it, resulting in two different kinds of stresses—compressive stress and shear stress, the latter causing loss of adhesion. The size of the detachment area can be taken as a qualitative measure for adhesion and can also be used for calculating adhesion forces.

Kollek reported on the activities of the Fraunhofer Institut für Angewandte Materialforschung, in Bremen, in this field by application of new methods of surface characterization, remission photometry, and scanning microscope photometry. Some results have been published in *Farbe und Lack*, Vol. 86, pp 420–425 (1980) under the title, "Reaktivität und Morphologie von Metalloberflächen als Basis für ein Modell der Adhäsion." Using scanning microscope photometry on a metal surface after performing a peel test which resulted in adhesive failure, Kollek demonstrated that the whole surface was covered still by a layer of polymer material to an amount of $10-20 \ \mu g/cm^2$, and he failed completely in getting a real adhesive failure. After a lengthy discussion, it was decided that it is not sufficient to measure only adhesion forces in dealing with the protective properties of coatings. For the proper interpretation of adhesive phenomena it is equally important to describe the surface state before coating and after detachment of the film, and to study the effects occurring during detachment. As a practical consequence, one should be very careful in introducing absolute values of adhesion in specifications.

Solvent-Polymer Interaction—"Stability of Amino Resin-Containing Systems" was begun by Luthardt with the goal to distinguish between homocondensation reactions of the melamine resin and reaction with the respective binder (polyacrylate or polyester). A short-time storage of two binder compositions, each in two solvent mixtures, was carried out

at 50°C, which resulted in an increase in viscosity of the solutions. These changes in phenomenological properties could not be verified for the melamine-polyester blends by means of GPC and proton-NMR spectroscopy. Sickfeld could demonstrate small changes in peak height of the polyacrylate peak in GPC with the melamine-polyacrylate blends possibly indicating a reaction of the polyacrylate with melamine resin. Room temperature storage tests are being evaluated, and additional investigations will be carried out with different polyester model compounds in combination with a well defined commercially available methoxylated melamine resin also applying ^{13}C-NMR measurements.

New Analytical Projects—Because of financial difficulties, Hansen has assumed leadership of the project, "Analysis of Emulsion Paints." Participants (BAM, NIF, PPG, and Sandolin) will be sent samples of emulsion paints of known compositions. A draft for the project, "Properties of Supported Polymer Film and Related Bulk Polymers," was distributed and referral was made of the results during the GDCh meeting in Nurnberg published in *Farbe und Lack*, Vol. 86, pp 879–888 (1980). Oesterle was requested to more precisely define the objective of the project for the next meeting.

Miscellaneous Items—Other topics discussed were: investigation of the regulation of the water susceptibility of paints by the addition of additives (Oesterle); wood as a substrate for coatings and its interaction with water (Hansen); automatic continuous measurement of cadmium and other heavy metals (Dulog); determination of the solids content in pigmented and unpigmented solutions and dispersions of organic binders in volatile organic or aqueous liquids (Sickfeld); and problems connected with the classification of water-reducible paints with respect to their combustibility (Hansen).

The next meeting will take place in the Netherlands, October 1–2, 1981.

J. SICKFELD, *Secretary*

Design of Water Reducible Polymers For Use in Food Contact Applications

Peter V. Robinson

Glidden Coatings and Resins Division, SCM Corporation*

A number of methods of synthesizing hydrolysis resistant water-reducible polymers are described. In particular, polymer grafting techniques are explored and the application of some of these techniques to the synthesis of water-reducible polymers for use in contact with food is described. It is shown that in order to obtain the total balance of properties necessary for container coatings, significant levels of grafting to a main polymer backbone are necessary.

INTRODUCTION

Historically, polymers for use in coating the interior of metal food containers have been applied at relatively low concentrations in organic solvents. As pollution control legislation emerged during the last 15 years, it became necessary to develop coatings which could be applied to the interior of metal containers for food contact use which would comply with emerging pollution control standards. This paper describes some aspects of the background and history of a project which was established to develop nonpolluting can coatings for food contact use.

DISCUSSION

Many different polymers are used in the coatings industry. The list is extensive and generic species such as epoxies, polyesters, acrylics, vinyls, urethanes and the like have been available for many years for use by the industry. In order to make these polymers tractable for use in coatings, it was necessary to dilute the resins with

organic solvents for the purposes of application to the substrate, followed by evaporation of the solvent and cure by chemical or physical crosslinking.

With the advent of Rule 66 by Los Angeles County in the late 60's followed by EPA induced changes of similar nature, it became necessary to determine means by which polymers used by the paint industry could be used without the deleterious effects of high volatile organic solvent emissions. Clearly, it is possible to reduce the molecular weight of the polymer material such that it can be applied in the absence of solvent or with a significant reduction in the solvent content. This concept led to powder coatings, reactive diluent coatings, and high solids coatings. If the volatile organic solvent must be replaced by an environmentally acceptable diluent then, in the main, water is the diluent of choice. Water can be present as a solvent or as the continuous phase in an emulsion or suspension system. This paper concentrates on certain aspects of water solubility or dispersibility.

Because polymers such as epoxies, polyesters, acrylics, urethanes, and phenolics are required to be "soluble" in water for application and yet display marked insolubility in water as a protective coating, a careful formulation balance is necessary in their design. For example, a relatively easy method of providing water solubility to a hydroxyl group bearing polymer could be to react it with an appropriate amount of a cyclic anhydride such as phthalic, maleic, or succinic anhydride. This could then be followed by dissolution in water containing a volatile base. This chemistry is illustrated in *Figure* 1 using maleic anhydride as a typical reactant.

The technique does provide water solubility, but as is well-known, such polymers sometimes do not retain their water solubility for a commercially adequate length of time and package instability problems are the result. Turpin's[1] work was able to identify the causes of this instability and more importantly, indicated techniques for the synthesis of extremely hydrolysis resistant but intrinsically hydrolyzable polymer species.
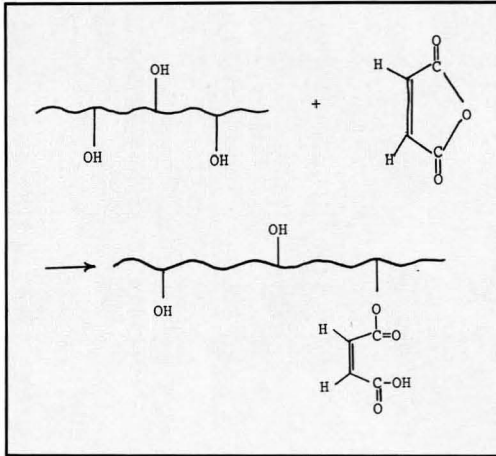
Figure 1—Water reducible polymer—anhydride half-ester

Figure 3—Epoxy polymer containing *pendant* carboxyl groups

As a result of these package stability considerations, a very important aspect of the author's work several years ago was to synthesize water soluble polymers which inherently were not sensitive to hydrolysis. At that time, the work was directed towards systems which would experience high operating dilution, relatively high operating temperature, and significant levels of agitation. If a polymer is hydrolyzable, such conditions are particularly severe in causing hydrolytic degradation of the polymer in industrial use. Accordingly, the project addressed means of providing water dispersibility to hydrophobic polymers without the critical placement of hydrolytically susceptible groups. If ester groups were to be used, then they would be hydrolysis resistant following Turpin's teaching as indicated earlier. Obviously, a hydroxyl bearing polymer made water soluble by reacting with a cyclic anhydride would be suspect for use in extreme conditions.

A very convenient technique for synthesizing such polymers is the copolymerization of ethylenically unsaturated carboxylic acids with other selected ethylenically unsaturated monomers via solution or emulsion polymerization techniques. This is shown schematically in *Figure* 2.

This methodology is highly utilized, but not without the sometimes difficult-to-tolerate property imbalance. Thus, the reality of coatings performance and economics requires the use of multiple comonomers in addition to the carboxylic monomer. The acid monomer is usually incorporated at a level such that approximately one carboxyl group is present for every 1000 parts of polymer (acid no. 50–60) as representing the best compromise between water dispersibility in the package and water insensitivity in the cured film. Production requirements and the well-known polymerization mechanism of acrylic or vinyl monomers are such that there is a wide distribution of polymeric types produced, some of which will contain large amounts of carboxyl groups and some of which will contain small amounts of carboxyl groups. For many coatings applications, this specie distribution represents a limiting restriction on the industrial use of such polymers. While these polymers do meet the criteria of providing carboxyl groups attached to a polymer backbone without the critical placement of hydrolytically sensitive linkages, the limitations mentioned caused other synthetic approaches to be studied and evaluated.

These approaches identified many potentially valuable

Figure 2—Carboxyl containing "acrylic" copolymer
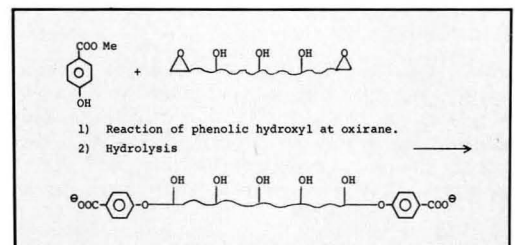
Figure 4—Epoxy polymer containing terminal carboxyl groups. Use of para-hydroxy benzoic acid
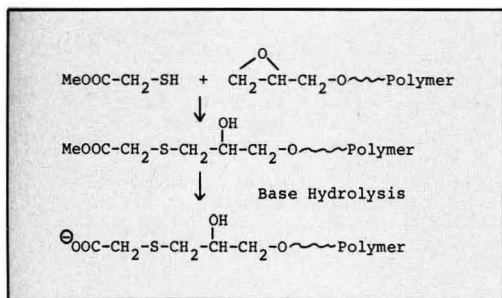
Figure 5—Epoxy polymer containing terminal carboxyl groups. Use of methyl thioglycolate

Figure 7—Urethane polymer containing *pendant* carboxyl groups

techniques for converting normally hydrophobic polymers into water dispersible forms when appropriately ionized. Thus, water soluble epoxy resins can be produced by replacing Bisphenol A by the methyl ester of diphenolic acid followed by hydrolysis of the methyl ester and neutralization.[2] *Figure* 3 illustrates this chemistry.

Such polymers are water dispersible and display excellent package and line stability. Similarly, epoxy resins can be made water soluble by reacting them with the methyl ester of para-hydroxybenzoic acid, again followed by hydrolysis and neutralization, as shown in *Figure* 4.[3]

A related chemistry is shown in *Figure* 5 where the methyl ester of thioglycolic acid is reacted with an oxirane containing polymer. The resultant adduct is hydrolyzed and neutralized for water dispersibility.[4]

Another technique for rendering epoxy resins water soluble is to react p-amino benzoic acid with an epoxy resin at the oxirane group. This forms a stable dispersion in suitable water/amine mixtures (*Figure* 6).[5]

A further example of the synthesis of water dispersible coatings polymers is one in which water dispersible urethanes are prepared by reacting dimethylol propionic acid with a diisocyanate (*Figure* 7).[6]

By utilizing these synthetic methods, either singly or in appropriate combination, placement of the acid functionality can be controlled with some precision.

Polymers produced by these synthetic methods for use in coatings are rarely water *soluble* in that the water diluted systems often have the appearance of emulsions.

It might be speculated that the carboxyl containing copolymers become distributed in such a way as to present as many ionized carboxyl groups as possible to the continuous, counterion containing water phase. A stabilized droplet would result in which the droplet interior would be anhydrous and comprised of hydrophobic polymer chains (*Figure* 8).

Many of these approaches were investigated simultaneously in several laboratories, including the author's, and this seems to indicate that when workers in the coatings industry are faced with a common problem they tend to respond with quite similar technology.

Further consideration of the need to attach a carboxyl group to a polymer backbone via nonhydrolyzable linkages led to the use of the well-known grafting reactions.[7] One technique by which this can be accomplished is to use one polymer as the "solvent" for the addition polymerization of a number of ethylenically unsaturated monomers. A particularly interesting graft polymer can be obtained when higher molecular weight Bisphenol A epoxy resin is used as the "solvent." Specifically, if about 80 parts of a medium to high molecular weight epoxy resin are used as solvent for the copolymerization of 20 parts of carboxyl containing ethylenically unsaturated monomers, water dispersible polymers of great utility are obtained.

These and many other similar concepts were studied and evaluated by another group which had been assigned the responsibility of designing a water reducible interior can coating. The can industry can be divided very roughly into two major sections for the purpose of this paper

Figure 6—Epoxy polymer containing terminal carboxyl groups. Use of para-aminobenzoic acid
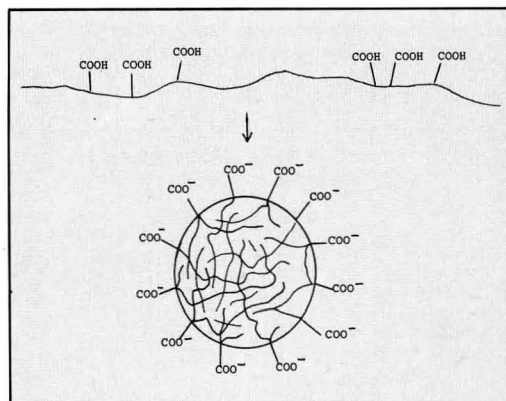
Figure 8—"Micelle" structure of typical water reducible polymers

Table 1—Market Use of Two- and Three-Piece Cans

	2 Piece	3 Piece
Beer and beverage	*	*
Other: 1) Sanitary		
2) Drums/large containers	—	*
3) Meat/fish/pet food		

Table 3—Typical Performance Requirements
For Water Reducible Can Coatings

1. Water reducible. VOC ≤ 520 grams/litre ($-$ Water).
2. Package stability. 6 months minimum.
3. Application via conventional equipment.
4. Cure latitude.
5. Neutral effect on flavor, odor, appearance.
6. Cured film complies with F&DA.

(*Table* 1). There are two and three-piece cans for the beer and beverage industry, and there are largely three-piece cans for all the remaining food and other container industries. In this paper, the beer and beverage segment will be addressed.

Traditionally, coatings for beer and beverage cans have been solvent-borne and limited to a very few chemical types (*Table* 2).

In three-piece cans, butadiene copolymers and epoxy resins crosslinked with phenolic resins have been used as basecoats. Topcoats for three-piece cans or single coats for two-piece cans have been formulated from epoxy resins crosslinked with aminoplasts, vinyl chloride/vinyl acetate copolymers, and various kinds of acrylic copolymers. Quite properly, the can industry is very conservative when coatings for use in contact with food are considered and, as a result, there is an understandable tendency to depend very strongly on those coatings which historically have been shown to work. Some requirements for a can interior coating are indicated in *Table* 3.

Given these criteria, it was decided to utilize the concepts described earlier for converting some of the chemical species described in *Table* 2 into water dispersible compositions. These compositions were chosen because they were already well-known and respected by the can industry and the compositions appeared in the Food and Drugs Section of the Code of Federal Regulations. It was felt that any attempt to design resins outside of these compositions would be fighting the double uphill task of meeting the requirements of the end-users *and* CFR in respect of their acceptability as food contact coatings.

The first approach involved the preparation of water dilutable versions of self-curing acrylics using the acrylamide crosslink. However, the problem of variable viscosity stability in the package was experienced, but much

more important, severe flavor problems for critical applications were very evident (*Figure* 9).[8]

The second approach was to prepare an epoxy resin of suitable molecular weight, cap it with a phenol or a carboxylic acid and then react the secondary hydroxyl groups spaced along the backbone with trimellitic anhydride in order to provide the appropriate level of ionizing capability (*Figure* 10).[9]

Ultimately, this approach had to be abandoned because of continuing stability problems related to hydrolysis in the package. Quite simply, the product continued to lose viscosity throughout its package life and accordingly, its application properties would change.

The third approach involved the use of a hydroxyl functional acrylic polymer made water dispersible by an appropriate level of carboxyl content and crosslinked by an aminoplast (*Figure* 11).

Unacceptable flavor properties were obtained, especially for critical applications, and the well-known formaldehyde induced beer haze problem was also experienced.

Concurrent with much of this activity, the use of vinyl chloride/vinyl acetate copolymer latexes and pre-emulsified high molecular weight solid epoxy resins were also being studied. These interesting approaches were abandoned because much more progress towards meeting the goals as set out in *Table* 3 was being made using the grafting technique.

Basically, this graft polymer is formed as follows. Epoxy resin is first synthesized, either with or without solvent and then a carboxyl containing monomer mixture is added to this preformed resin under conditions such that grafting via hydrogen abstraction along the epoxy backbone is high and grafting via carboxyl/epoxy esterification is low.

Table 2—Coatings Use by Type of
Two- and Three-Piece Cans

	Base Coat (3 Piece)	Top Coat (3 Piece)	Single Coat (2 Piece)
Epoxy/phenolic	*	—	—
Epoxy/aminoplast	—	*	*
Vinyl/copolymer	—	*	*
Butadiene	*	—	—
"Acrylics"[a]	—	*	*

(a) For non-critical applications.
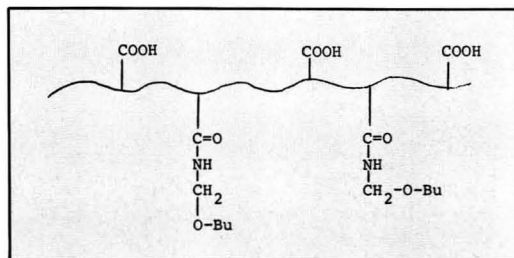
Figure 9—"Self-cure" water reducible "acrylic" copolymer utilizing the N-butoxymethylacrylamide crosslink
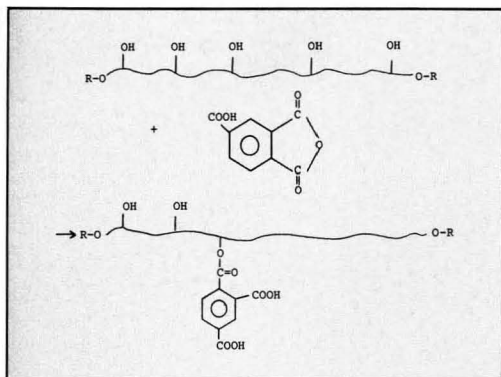
Figure 10—Epoxy polymer containing *pendant* carboxyl groups. Use of trimellitic anhydride

Figure 11—"Acrylic" copolymer containing both *pendant* carboxyl and hydroxyl groups for cure by reaction with melamine/formaldehyde resins

For can coating purposes, it is advantageous to use high epoxy levels and typical of this would be an epoxy resin content of 80% and an acrylic content of 20%. It was considered important to determine as nearly as possible the composition and structure of this graft copolymer and to that end, several techniques were used including gel permeation chromatography, ^{13}C nuclear magnetic resonance spectroscopy, multiple solvent fractionation analysis, and thermal analysis.

Given that a typical experimental composition was 80 parts of epoxy resin and 20 parts of acrylic, it was a simple experiment to pre-form the two resins separately from each other and then blend them. If dissolution in a water/amine mixture led to an acceptable dispersion, then it could reasonably be concluded that grafting was not important in the composition. Such blending of separate components was totally unsuccessful and, accordingly, it was concluded that grafting had to take place in order to produce a satisfactory dispersion. It was also shown that while relatively low levels of polymerization initiator gave adequate conversion of monomer to polymer, it was only high levels of such initiator that gave satisfactory overall properties.

Table 4 shows the effect of increasing initiator level as the test dispersion series is traversed from 1 thru 6. Two critical parameters in the application of coatings to cans are coverage and blister resistance. Coverage refers to the property of obtaining a thin coating which is blemish and pin-hole-free. The minimum weight of dry polymer in the can that can be obtained while still maintaining blemish-free coatings is determined by an electrical test. Blister resistance, on the other hand, refers to the ability of the coating to produce a thick film without blistering during the bake process. *Table* 4 gives values of these parameters for several coatings. Clearly, a coating such as no. 1 or no. 2 would find limited utility on a commercial line because of critical application parameters. On the other hand, coatings represented by dispersions no. 5 and 6, represent systems of greater commercial utility in that coatings of different weights can be obtained from the same system for use in packaging different kinds of beverage. The coatings in the middle of the initiator sequence represent compositions which are on the borderline separating commercially viable coatings from those which are not viable.

In order to determine the composition of the graft,

Table 4—Effect of Increasing Initiator Level As Dispersion Series Move from 1–6

Test Dispersion No.[a]	Initiator Ladder		Coverage mg	Blister mg
	Dispersion NV[b]	AN[b]		
1	22.8	85.9	120	120
2	22.5	85.7	120	130
3	23.1	90.5	120	130
4	22.4	88.1	110	215
5	21.5	90.6	130	230
6	22.6	93.0	120	250

(a) Increasing initiator level.
(b) Abbreviations: NV—Non-volatiles
                                   AN—Acid Number (NV)

Note: All figures reported above are averaged from several observations.

Figure 12—Proposed mixture of components in epoxy/acrylic graft copolymer
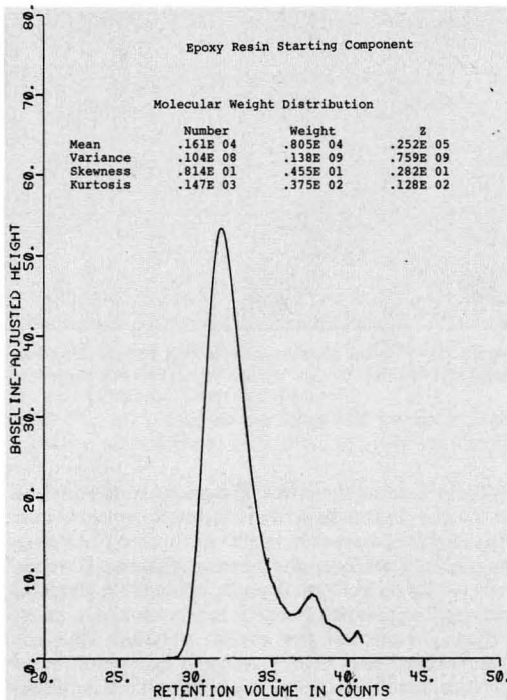
Figure 13—Gel permeation chromatography of epoxy resin
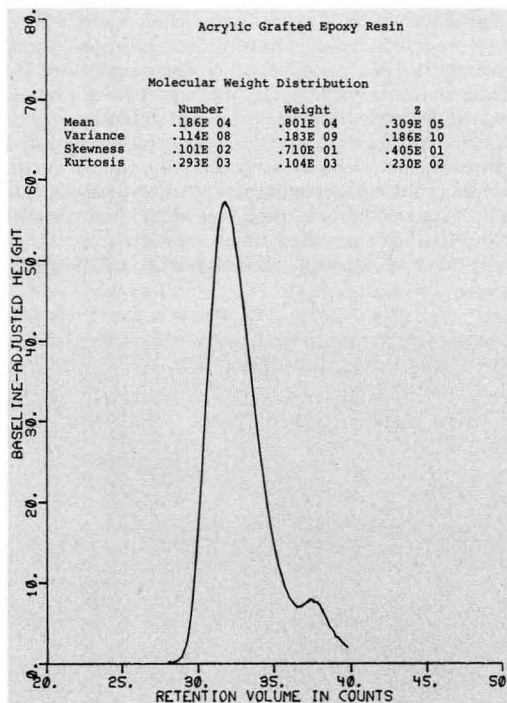
Figure 14—Gel permeation chromatography of epoxy/acrylic graft copolymer
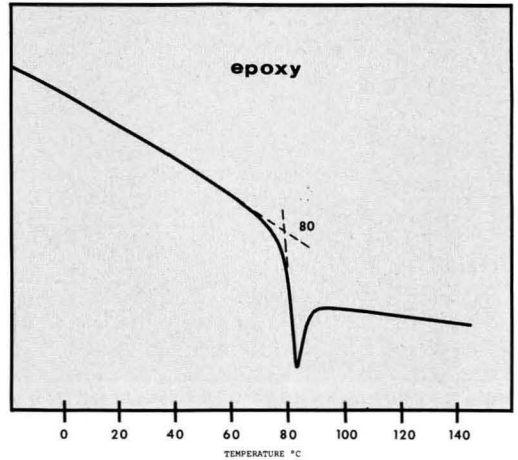
Figure 15—Differential scanning calorimetry (DSC) analysis of epoxy resin

graft copolymers were prepared in which the monomers used were essentially styrene and methacrylic acid and these made up 20% of the total composition; epoxy resin made up the remaining 80%. The styrene and methacrylic acid were added in their so-called azeotropic composition as determined from reactivity ratio data so that all acrylic polymer molecules and graft chains would have the same composition.

It was anticipated that the grafting efficiency was unlikely to be 100%, i.e., that the only specie present would be an acrylic chain grafted to an epoxy backbone.[10] Rather, it was assumed that the final composition would be comprised of a mixture of (1) acrylic grafted to epoxy backbone, (2) ungrafted acrylic, and (3) unmodified epoxy (*Figure 12*).

The problem was to determine the relative amounts of each. If the three components had different solubilities in different solvents, then even allowing for partitioning effects, some hint of the distribution of polymer species should be obtainable. Multicomponent solvent mixtures were identified which would extract the major components of the composition as described above. Obviously, epoxy resin which did not contain any graft should have zero detectable acidity while pure acrylic should have an acid number of 424. Anything that existed between zero and 424 would represent grafted epoxy and the acid number of this composition would give some indication of the degree of grafting. Analysis of the data indicated

Table 5—Components of Epoxy/Acrylic Copolymer As Found by Solvent Fractionation

Epoxy Resin—80 pbw
Acrylic   —20 pbw

(1) Epoxy/acrylic graft copolymer	60–45 pbw
(2) Acrylic copolymer	5–10 pbw
(3) Unmodified epoxy resin	35–45 pbw
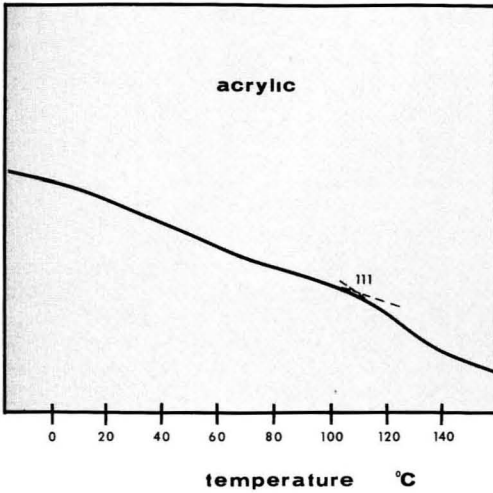
Figure 16—DSC analysis of acrylic copolymer
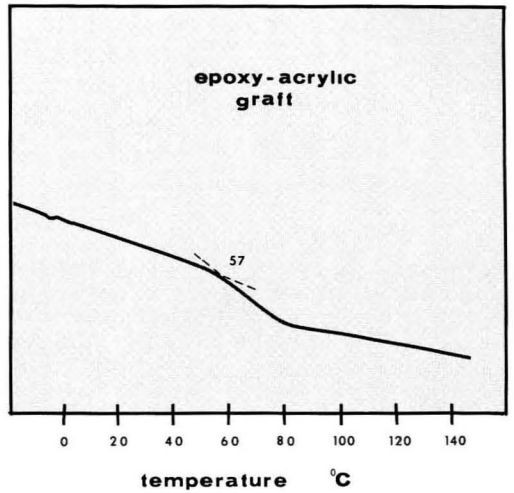
Figure 18—DSC analysis of epoxy/acrylic *graft* copolymer

that a large proportion of the original epoxy resin had been modified by acrylic polymer grafting. Correspondingly, unmodified epoxy resin and free acrylic copolymer were also found, confirming the composition speculations (*Table* 5).

Confirmation of these results via GPC was difficult in that there was little discernible difference in molecular size between the ungrafted epoxy resin starting component and the final product (*Figures* 13 and 14). This can be considered to be a consequence of the graft copolymer possessing a comb structure in which the branches are all short relative to the length of the main polymer backbone.

Further insights into the structure and composition of the graft blend were obtained from differential scanning calorimetry (DSC) studies. *Figure* 15 shows the curve obtained by DSC when the pure epoxy starting

Figure 17—DSC analysis of epoxy resin/acrylic copolymer *blend*

material was tested. There is a sharp transition at 80° C corresponding to the glass transition temperature of this particular grade of epoxy resin.

Figure 16 shows the results obtained when a model acrylic resin was used. The synthesis of this acrylic resin was carried out in reaction conditions which simulated the grafting copolymerization conditions, but in the absence of the epoxy backbone grafting site. There appears to be a transition at about 111° C. If this figure is real, it represents a temperature which is far too low as compared to what might be predicted from the Fox equation.[11] Probably, the explanation for this is that the molecular weight of the acrylic is so low that the true glass transition temperature for this composition cannot be obtained.[12]

Figure 17 shows the results obtained when the epoxy resin and acrylic resin are blended in a ratio of 80/20. This indicates a glass transition temperature of 78° C, which is almost the same as the results obtained for the pure epoxy.

The results obtained for the epoxy/acrylic graft are shown in *Figure* 18 where the transition occurs at 57° C. This result is probably a reflection of the short acrylic grafted chains internally plasticizing the main epoxy backbone and lending further support to the idea that the grafted copolymer has a comb-like structure. The DSC results are summarized in *Table* 6.

The available evidence indicated that the water dis-

Table 6—Glass Transition Temperature (Tg°)
Summary of DSC Analyses

Epoxy resin	Tg = 80° C
Acrylic resin	Tg = 111° C
Epoxy/acrylic *blend*	Tg = 78° C
Epoxy/acrylic *graft*	Tg = 57° C
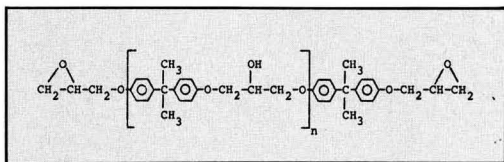
Figure 19—Idealized structure for epoxy resin

Figure 21—Most probable grafting locations on an epoxy resin in an epoxy/acrylic graft copolymer

persible composition was comprised of a mixture of epoxy resin, acrylic resin, and a true graft copolymer between epoxy polymer molecules and the acrylic components (*Table* 5). In order to determine the location of grafting along the epoxy backbone, carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) studies were carried out on both the actual composition and on model compounds designed to represent various segments of the polymer backbone. An idealized structure for a bisphenol A epoxy resin is shown in *Figure* 19.

In *Figure* 20 are shown two model compounds which represent portions of the polymer where it was thought grafting was likely to take place.

When these model compounds were used to replace epoxy resin in a typical graft polymerization experiment, ^{13}C NMR analysis determined that significant levels of grafting had taken place at the methylene groups alpha to the aryl ether groups. Surprisingly, high levels of grafting at methine carbon atoms could not be found. Analysis of an epoxy resin based composition confirmed these results but it was found that carbon-to-carbon grafting was also taking place at methine groups spaced along the epoxy polymer backbone (*Figure* 21).

^{13}C NMR peak assignment strategies are not discussed in this paper, but they will be the subject of additional papers in the future.

CONCLUSIONS

An attempt has been made to describe the strategy used in the development of a successful, commercial water soluble product. The goal was to establish water dispersibility without the introduction of hydrolytically susceptible groups.

A particularly viable synthetic route to meeting this goal was by grafting ionizible species to a hydrophobic polymer backbone. The resultant polymer was visualized
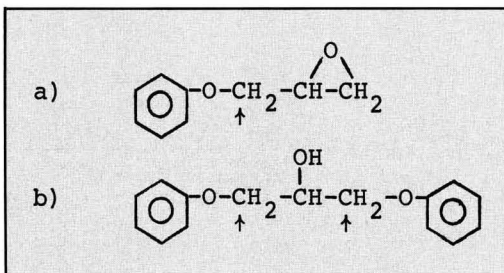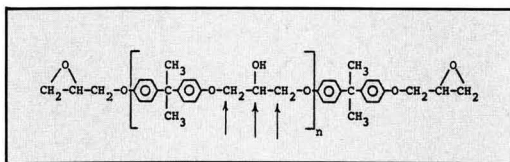
as having a comb-like structure with the grafted components being of short length compared to the length of the main backbone. As with most grafted copolymers, grafting efficiency was less than 100% and so the actual composition of the graft polymer was a mixture comprised of unmodified backbone polymer, polyacrylic components, and true grafted copolymer.

Additional requirements were that the product should be suitable for use in contact with food and beverage, and that the product be amenable to routine production at high volume in conventional production equipment. All of these goals were accomplished although how they were accomplished was not described in the present paper. As is usually the case, the conversion of a product concept or prototype into commercial reality consumed by far the largest proportion of the research and development resources used in the project.

ACKNOWLEDGMENTS

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Figure 20—Model compounds representing key structural locations in epoxy resins

Application of Simplex Lattice Design Experimentation to Coatings Research

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A coating is a complex mixture of pigment, vehicle, solvent, and additives. Variations in the fractions of principal components comprising a coating produce significant changes in properties, performance, and cost. Applying methods for designed experiments with mixtures to coatings research has proven very useful in determining optimum principal component percentages for specific properties, maximum performance, and minimum cost. Simplex lattice design experiments are efficient; only a minimum of sample production is necessary, replication yields information about the experimental error of the test methods, and equation-fitting allows prediction over a broad composition region.

INTRODUCTION

Coatings formulation research essentially involves finding the right combination of a number of ingredients to produce a system having a given set of properties, at a specific cost. The fact that there exist so many possible ingredients, and even more possibilities for combining them, makes modern, efficient coatings formulation a difficult task. The application of simplex lattice design experimentation to coatings research greatly reduces the difficulty of finding the appropriate materials, and the optimum proportions for the formulation of a specific coating. This paper will discuss one specific lattice design experiment with four components: prime pigment titanium dioxide, vehicle, and two extender pigments. The techniques presented are applicable to systems with fewer or more components, and references are provided for additional background and applications.

THEORY

Methods for designing experiments for the investigation of the intensive properties of multicomponent systems as a function of composition, have been published by Scheffé,[1] Gorman and Hinman,[2] and others[3,4] and are available in the form of professional seminars.[5] These methods recognize that for systems involving mixtures of materials, the sum of the proportions by weight, volume, etc., must be unity, and therefore, the experimental region can be represented by a regular simplex.

For three components, the experimental region would be a triangle, and four components, a tetrahedron. (See *Figure* 1). The experimental region is explored at points of composition corresponding to an ordered arrangement known as a lattice. The components may be pure compounds, or in the case of coatings, mixtures in themselves (pseudocomponents). The responses evaluated at the lattice point compositions are represented by simplified general polynomials. The coefficients in the polynomials are simple functions of the measured response. An estimation of the experimental error in the response measurements is obtained by replication. After the coefficients are calculated for a model (equation), an estimate of the model's (equation's) suitability is obtained by comparing observed vs predicted responses at checkpoint compositions in the lattice, and using statistical variance ratios.

EXPERIMENTAL

The experiment involved determining if a specific combination of prime pigment (titanium dioxide), vehicle (latex emulsion), and two extender pigments, could be developed to comprise a coating which would replace an existing formula (control), at a raw material cost savings, while maintaining equivalent performance parameters. The titanium dioxide and vehicle were common to the control formula, but the extender pigments
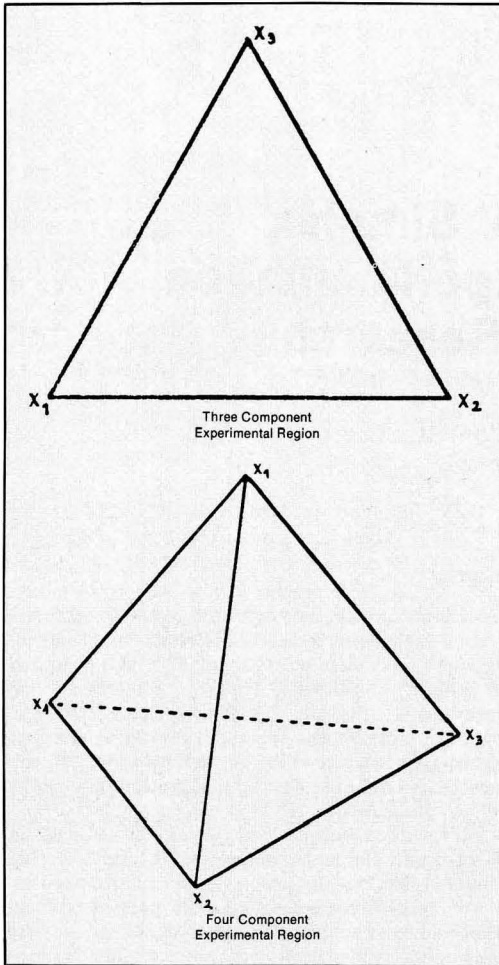
Figure 1—Three and four component simplex regions

Figure 2a—Lattice points of four component simplex design (pseudocomponent region)

Figure 2—Four component simplex (pure and pseudocomponent regions)
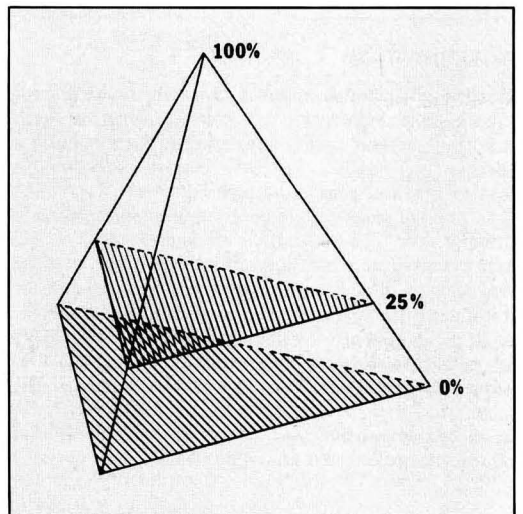
Figure 3—Selected response surface sections of the pseudocomponent region

Table 1—Four Component Simplex Design (Simplified)

Paint System	Level of Component				Type of Paint	Use in the Equation
	A	B	C	D		
1	1	0	0	0	Pure components	
2	0	1	0	0		
3	0	0	1	0		
4	0	0	0	1		Determining Points
5	1/2	1/2	0	0		
6	1/2	0	1/2	0		
7	1/2	0	0	1/2	Binary blends (blends of two paints)	
8	0	1/2	1/2	0		
9	0	1/2	0	1/2		
10	0	0	1/2	1/2		
11	1/3	1/3	1/3	0		
12	1/3	1/3	0	1/3	Ternary blends (blends of three paints)	
13	1/3	0	1/3	1/3		
14	0	1/3	1/3	1/3		
15	1/4	1/4	1/4	1/4	Centroid (middle of tetrahedron)	
16	5/8	1/8	1/8	1/8		
17	1/8	5/8	1/8	1/8	Smaller checkpoint tetrahedron (blends of four paints)	Checkpoints
18	1/8	1/8	5/8	1/8		
19	1/8	1/8	1/8	5/8		

were not. A four component simplex lattice mixture study was designed and implemented.

The four components were arranged as vertices of a tetrahedron, and a suitable formulation space within this tetrahedron was defined by: vertex 1 (a titanium dioxide-rich paint); vertex 2 (a vehicle-rich paint); vertex 3 (an extender A-rich paint); and vertex 4 (an extender B-rich paint) (See *Figure* 2). The term "rich", refers to the fact that systems 1–4 were not pure component systems, but rather mixtures in themselves, or pseudocomponents. The rich or vertex system in each case represented the high concentration of each specific component. Pseudocomponents were necessary because it was not possible to produce a practical coating containing pure components; e.g., only titanium dioxide, or only extender pigment, etc.

Based on simplex lattice design methodology, all of the component levels were varied by a constant percentage to maintain the equalsidedness, or simplex nature of the design. Nineteen lattice point compositions (four vertices, six binary blends, four ternary blends, and five ternary blend checkpoints) were prepared to determine the coefficients of the special cubic equation model. *Table* 1 enumerates the compositional design used for the four component lattice study shown in *Figure* 2A, and *Table* 2 enumerates the special cubic equation and its coefficients. *Table* 3 shows each lattice point more specifically in terms of pseudo and pure component levels. The "X", notation lattice code in *Table* 3 describes each paint in terms of its composition and general proportion of each vertex system.

The vertex systems were prepared and blended in the random order indicated in *Table* 3. Randomization of preparation and blending was used to control bias error. Only those coatings representing the lattice vertices (systems 1–4) were actually prepared. The remaining lattice point compositions (systems 5–19) were prepared by blending the four lattice vertex paints. The replications of the lattice vertex paints were coded 1A, 1B, 2A, 2B, 3A, 3B, 4A, and 4B. The remaining lattice point composition replicates were coded 5A, 5B, through 19A, 19B (See *Table* 3). Replication was necessary to establish experimental variation (random error). Blending calculations were based on the C.W.P.G. (centrifuged weight per gallon) of the lattice vertex paints, and the desired quantity of each test composition.

A 0.9 gal batch of each lattice vertex composition was produced, and blended to produce 1.0 pt of each remaining lattice point composition. The pure component levels in *Table* 3 represent the fractions of the variable N.V.M.

Table 2—Special Cubic Equation and Its Coefficients

$$y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4$$
$$+ b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4$$
$$+ b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4$$

$b_1 = \bar{y}_1$
$b_2 = \bar{y}_2$
$b_3 = \bar{y}_3$
$b_4 = \bar{y}_4$

$b_{12} = 4\bar{y}_{12} - 2(\bar{y}_1 + \bar{y}_2)$
$b_{13} = 4\bar{y}_{13} - 2(\bar{y}_1 + \bar{y}_3)$
$b_{14} = 4\bar{y}_{14} - 2(\bar{y}_1 + \bar{y}_4)$
$b_{23} = 4\bar{y}_{23} - 2(\bar{y}_2 + \bar{y}_3)$
$b_{24} = 4\bar{y}_{24} - 2(\bar{y}_2 + \bar{y}_4)$
$b_{34} = 4\bar{y}_{34} - 2(\bar{y}_3 + \bar{y}_4)$

$b_{123} = 27\bar{y}_{123} - 12(\bar{y}_{12} + \bar{y}_{13} + \bar{y}_{23}) + 3(\bar{y}_1 + \bar{y}_2 + \bar{y}_3)$
$b_{124} = 27\bar{y}_{124} - 12(\bar{y}_{12} + \bar{y}_{14} + \bar{y}_{24}) + 3(\bar{y}_1 + \bar{y}_2 + \bar{y}_4)$
$b_{134} = 27\bar{y}_{134} - 12(\bar{y}_{13} + \bar{y}_{14} + \bar{y}_{34}) + 3(\bar{y}_1 + \bar{y}_3 + \bar{y}_4)$
$b_{234} = 27\bar{y}_{234} - 12(\bar{y}_{23} + \bar{y}_{24} + \bar{y}_{34}) + 3(\bar{y}_2 + \bar{y}_3 + \bar{y}_4)$

Table 3—Four Component Simplex Design (Detailed)

System	Lattice Code	Randomized Test Order A	Randomized Test Order B	Pseudocomponent Level TiO₂	Pseudocomponent Level Vehicle	Pseudocomponent Level Extender A	Pseudocomponent Level Extender B	Pure Component Level[a] TiO₂	Pure Component Level[a] Vehicle	Pure Component Level[a] Extender A	Pure Component Level[a] Extender B
1	X_1	7	8	1	0	0	0	0.45	0.20	0.30	0.05
2	X_2	1	3	0	1	0	0	0.05	0.60	0.30	0.05
3	X_3	5	2	0	0	1	0	0.05	0.20	0.70	0.05
4	X_4	4	6	0	0	0	1	0.05	0.20	0.30	0.45
5	X_{12}	27	4	1/2	1/2	0	0	0.25	0.40	0.30	0.05
6	X_{13}	16	1	1/2	0	1/2	0	0.25	0.20	0.50	0.05
7	X_{14}	12	15	1/2	0	0	1/2	0.25	0.20	0.30	0.25
8	X_{23}	7	5	0	1/2	1/2	0	0.05	0.40	0.50	0.05
9	X_{24}	26	3	0	1/2	0	1/2	0.05	0.40	0.30	0.25
10	X_{34}	29	22	0	0	1/2	1/2	0.05	0.20	0.50	0.25
11	X_{123}	17	13	1/3	1/3	1/3	0	0.183	0.333	0.433	0.05
12	X_{124}	20	9	1/3	1/3	0	1/3	0.183	0.333	0.30	0.183
13	X_{134}	28	19	1/3	0	1/3	1/3	0.183	0.20	0.433	0.183
14	X_{234}	23	21	0	1/3	1/3	1/3	0.05	0.333	0.433	0.183
15	X_{1234}	30	25	1/4	1/4	1/4	1/4	0.15	0.30	0.40	0.15
16	X_{11234}	11	18	5/8	1/8	1/8	1/8	0.30	0.25	0.35	0.10
17	X_{12234}	24	14	1/8	5/8	1/8	1/8	0.10	0.45	0.35	0.10
18	X_{12334}	10	2	1/8	1/8	5/8	1/8	0.10	0.25	0.55	0.10
19	X_{12344}	8	6	1/8	1/8	1/8	5/8	0.10	0.25	0.35	0.30

(a) Percent of variable NVM volume.

Table 4—Raw Hiding Power and Scrub Data

System	Hiding Power (SX)	Scrub Loss (mg/100 cycles)	System	Hiding Power (SX)	Scrub Loss (mg/100 cycles)
1A	35.9297	874 / 1011	10B	8.3325	317 / 281
1B	29.7952	703 / 670	11A	14.1177	74 / 72
2A	3.6462	41 / 33	11B	14.8811	83 / 73
2B	3.7958	41 / 43	12A	12.1778	112 / 165
3A	9.1919	305 / 202	12B	12.5247	140 / 127
3B	9.3583	186 / 120	13A	16.1728	418 / 399
4A	7.8443	1155 / 569	13B	18.3400	331 / 397
4B	7.9464	440 / 592	14A	5.8653	60 / 81
5A	15.2316	72 / 63	14B	5.9111	82 / 81
5B	17.2584	93 / 111	15A	11.5817	99 / 128
6A	23.5910	424 / 317	15B	11.9729	115 / 114
6B	21.6864	353 / 349	16A	22.7653	334 / 409
7A	19.7911	471 / 502	16B	21.4274	360 / 333
7B	20.4723	578 / 670	17A	6.2245	53 / 52
8A	5.4543	39 / 46	17B	6.3531	34 / 24
8B	5.4747	57 / 50	18A	10.4461	62 / 151
9A	4.5314	44 / 41	18B	10.8127	120 / 139
9B	4.8960	56 / 66	19A	9.9654	415 / 395
10A	8.4333	458 / 315	19B	11.1309	252 / 241

Table 5—Statistical Analysis of Hiding Power Data

Sample	Avg. Value	Std. Dev.	Variance
1	32.8625	4.33773	18.8159
2	3.721	0.105785	0.0111904
3	9.2751	0.117642	0.0138397
4	7.89535	0.0721335	5.20325E-03
5	16.245	1.43316	2.05396
6	22.6387	1.34674	1.81372
7	20.1317	0.481595	0.231934
8	5.4645	0.0144848	2.09808E-04
9	4.7137	0.257813	0.0664673
10	8.3829	0.0712824	5.08118E-03
11	14.4994	0.539798	0.291382
12	12.3513	0.245255	0.0601501
13	17.2564	1.53241	2.34827
14	5.8882	0.03233	1.04523E-03
15	11.7773	0.2766	0.0765076
16	22.0964	0.946022	0.894959
17	6.2888	0.090941	8.27026E-03
18	10.6294	0.259229	0.0671997
19	10.5482	0.824117	0.679169

Pooled variance = 1.44445
Pooled std. dev. = 1.20185
Degrees of freedom = 19
Your 95% Confidence Limits are +/− 1.77871 SX units.

Table 6—Statistical Analysis of Scrubbability Data

Sample	Avg. Value	Std. Dev.	Variance
1	749.	109.503	11991.
2	39.5	4.43471	19.6667
3	203.25	76.5566	5860.92
4	533.667	81.9289	6712.34
5	84.75	21.5465	464.25
6	360.75	45.1396	2037.58
7	555.25	88.7295	7872.92
8	48.	7.52773	56.6667
9	51.75	11.5	132.25
10	342.75	78.5891	6176.25
11	75.5	5.06623	25.6667
12	136.	22.4648	504.667
13	386.25	38.0296	1446.25
14	76.	10.6771	114.
15	114.	11.8603	140.667
16	359.	35.5996	1267.33
17	40.75	14.1745	200.917
18	136.667	15.6312	244.334
19	325.75	91.9832	8460.92

Pooled variance = 2634.04
Pooled std. dev. = 51.3229
Degrees of freedom = 54
Your 95% Confidence Limits are +/− 52.592 mg/100 cycle units.

volume of the formula. Additive levels were held constant in each vertex formula, and only a specific portion (93%) of the total formula N.V.M. was varied among the four major components.

Duplicate hiding power (SX) and abrasive scrubbability determinations were made on each lattice point composition and replicate, based on ASTM methods D2805-70, and D2486-74 A (proposed revision). *Table 4* enumerates raw hiding power and scrubbability data.

RESULTS AND DISCUSSION

The raw hiding power and scrubbability data were analyzed statistically. Means $\bar{y}$, variances σ^2, and standard deviations σ were determined. Variances and standard deviations were pooled, and 95% Confidence Limits were calculated (See *Tables 5* and *6*).

Using the mean $\bar{y}$ responses from the four lattice vertex compositions, the six binary lattice compositions, and the four ternary lattice compositions (systems 1-14,

respectively), the coefficients for the special cubic equation were calculated (see *Table 7*, and review *Table 2*). These equations for hiding power and abrasive scrub resistance were solved at the five lattice quaternary blend checkpoint compositions (systems 15-19). These hiding power and scrub resistance values were "predicted" values, and were compared with "observed values" in *Table 8*. The "lack of fit variance", σ^2L.F., was calculated from the differences between predicted and observed values, and then the "error variance", σ^2 error, was calculated from pooled variances. The variances were arranged as a fraction whose value is greater than unity, and this variance ratio was compared to the value

Table 7—SX and Scrub Loss Equations

Y (SX Value) = $32.86x_1 + 3.72x_2 + 9.28x_3 + 7.90x_4$
$- 8.19x_1x_2 + 6.28x_1x_3 - 0.99x_1x_4$
$- 4.13x_2x_3 - 4.38x_2x_4 - 0.81x_3x_4$
$- 3.12x_1x_2x_3 - 26.16x_1x_2x_4$
$+ 2.18x_1x_3x_4 - 1.08x_2x_3x_4$

Y (mg. paint lost) = $749x_1 + 39.5x_2 + 203.25x_3 + 533.67x_4$
(100 scrub cycles)
$- 1238x_1x_2 - 461.5x_1x_3 - 344.34x_1x_4$
$- 293.5x_2x_3 - 939.34x_2x_4 - 102.84x_3x_4$
$- 908.25x_1x_2x_3 - 662.49x_1x_2x_4$
$- 218.49x_1x_3x_4 - 928.74x_2x_3x_4$
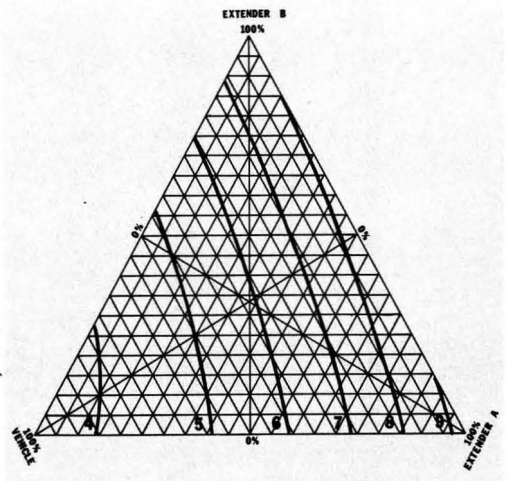
Figure 4—SX values at 0% TiO₂ pseudocomponent
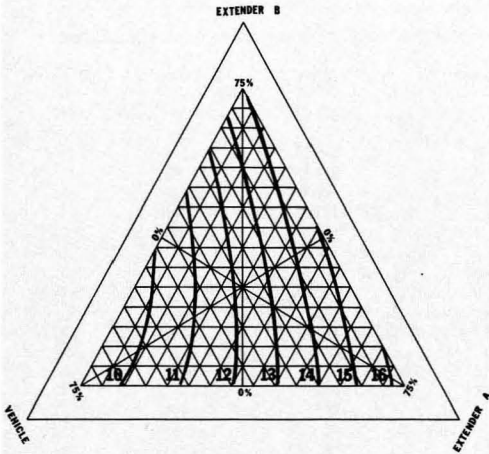
Figure 5—SX values at 25% TiO$_2$ pseudocomponent
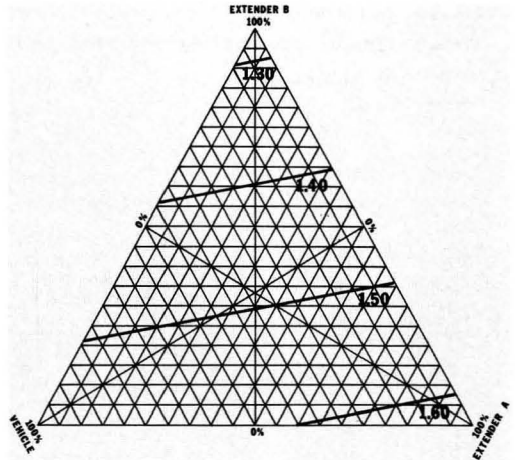
Figure 8—RMC/gal at 0% TiO$_2$ pseudocomponent
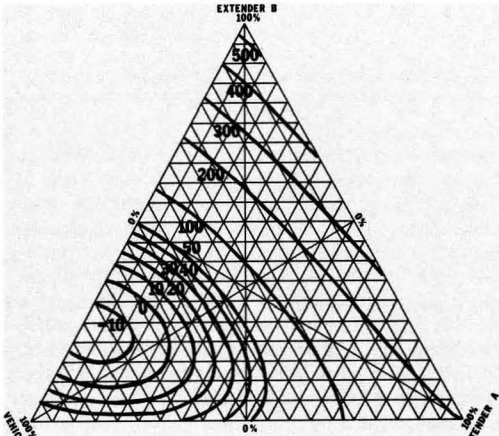
Figure 6—Scrub loss (mg/100 cycles) at 0% TiO$_2$ pseudocomponent
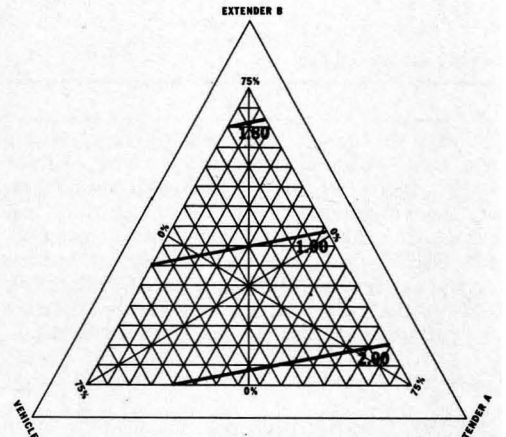
Figure 9—RMC/gal at 25% TiO$_2$ pseudocomponent
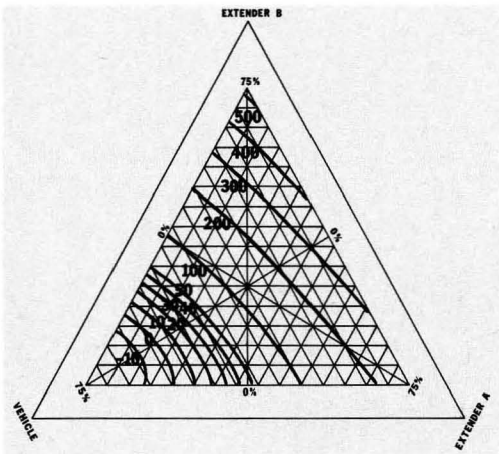
Figure 7—Scrub loss (mg/100 cycles) at 25% TiO$_2$ pseudocomponent
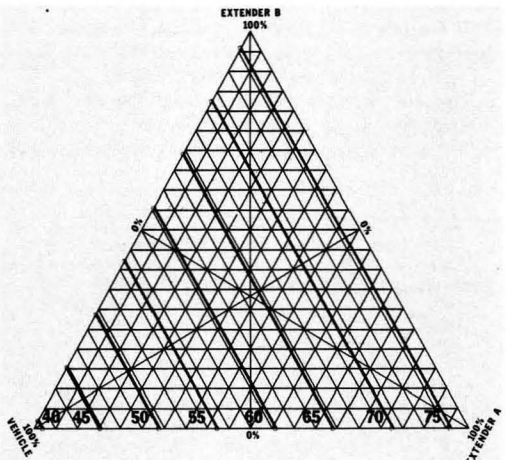
Figure 10—PVC at 0% TiO$_2$ pseudocomponent
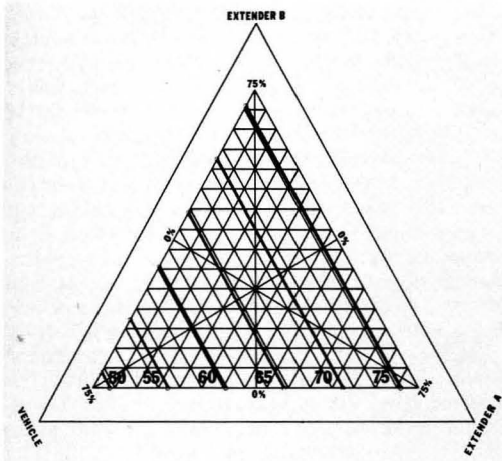
Figure 11—PVC at 25% TiO₂ pseudocomponent
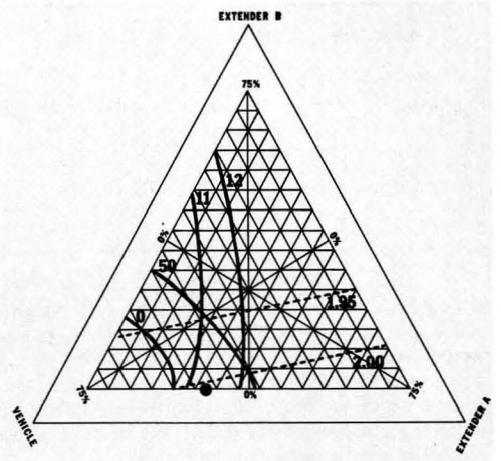
Figure 12—Composite of response contours at 25% TiO₂ pseudocomponent

Table 8—Lack of Fit Tests

Test Point	Predicted SX	Observed SX	Difference	Predicted Scrub[a]	Observed Scrub[a]	Difference[a]
15	12.23	11.78	0.45	127.67	114.00	13.67
16	22.51	22.10	0.41	365.35	359.00	6.35
17	7.05	6.29	0.76	−21.64	40.75	−62.39
18	11.18	10.63	0.55	164.52	136.67	27.85
19	9.84	10.55	−0.71	298.60	325.75	−27.15

$^{b}\sigma^2$ L.F. = 0.354
$^{c}\sigma^2$ error = 0.7223
F-Ratio = σ^2 error/σ^2L.F. = 2.040
Tabular F-Ratio F_5^{19} (.05) = 4.56

$^{b}\sigma^2$ L.F. = 1126.49
$^{c}\sigma^2$ error = 658.51
F-Ratio = σ^2L.F./σ^2error = 1.711
Tabular F-Ratio F_{60}^{5} (.05) = 2.37

(a) mg. lost/100 cycles

(b) σ^2L.F. (Lack of Fit Variance) = $\frac{1}{r}$ (sum: i = 1,r)$[\bar{Y}oi-Ypi]^2$

  where $\bar{Y}oi$ = observed average response at the ith checkpoint
  Ypi = predicted response at the ith checkpoint based on model, derived without using checkpoint data.
  r = number of checkpoints.
(c) σ^2error (Replication Error Variance) = σ^2pooled/n
  where: n = number of observations at each checkpoint.

Table 9—Pseudocomponent to Pure Component Transformation Equations

		Minimum Level of Pure Component		Experimental Variation of Simplex		Level of Pseudocomponent		Level of Pure Component
TiO₂ level	=	0.05	+	[(0.40)	×	(0.25)]	=	0.15
Vehicle level	=	0.20	+	[(0.40)	×	(0.475)]	=	0.39
Extender A level	=	0.30	+	[(0.40)	×	(0.275)]	=	0.41
Extender B level	=	0.05	+	[(0.40)	×	(0)]	=	0.05

Table 10—Comparison of System Properties

Property	Control	Experimental	
		Predicted	Observed
SX	9.93	11.35	10.15
Scrub loss			
(mg/100 cycles)	108	16	52
RMC	$2.06	$2.01	$2.01
PVC	43.8	58.9	58.9

in an F table, established using the appropriate degrees of freedom. Since the calculated F-Ratios were less than the tabulated F-Ratios, it was concluded that the observed vs predicted differences were not real, but due to random variations. The model, therefore, is a good predictor of the particular response for this mixture system, within the experimental error of the data.

The response equations for R.M.C. and P.V.C. are obtained using the same coefficients (*Table 2*) as used for hiding power and scrubbability, except that only the R.M.C.'s and P.V.C.'s of the lattice vertices are used, since there are no blending interactions (all binary and ternary coefficients are equal to zero). R.M.C. and P.V.C. equations are as follows:

$$RMC \ (\$/gal) = 3.2651x_1 + 1.5604x_2 + 1.6269x_3 + 1.2741x_4$$
$$PVC = 76.53x_1 + 39.31x_2 + 76.53x_3 + 76.53x_4$$

Inspection of the coefficients in the equations for hiding power and scrubbability will reveal interaction, or nonlinear blending effects. Positive blending effects are called "synergisms", and negative blending effects are called "antagonisms." The interactions between the components are better observed, however, with response-surface contour plots.

Response-surface plots of the four component mixture study are shown graphically as three component sections or slices out of the tetrahedron (*Figure 3*). These three-component slices are obtained by holding one component level constant, and varying the other three. *Figures* 4–11 show surface response contour plots, at constant titanium dioxide pseudocomponent levels of 0% and 25%. The response-surface contour plots for hiding power and scrubbability show synergism, or positive nonlinear blending, in their curvilinearity, while the R.M.C. and P.V.C. slices or sections show only linear responses. The significance of nonlinear blending effects (synergism or antagonism) is that a blend of components produces a greater or lesser response than predicted from the individual components themselves.

Inspections of the response-surface plots were made to determine if a composition could be found yielding equal or better hiding and abrasive scrubbability than the control paint system, at lower R.M.C. Overlaying of the contour plots revealed a composition corresponding to: 25% pseudocomponent 1 (15% titanium dioxide), 47.5% pseudocomponent 2 (39% vehicle), 27.5% pseudocomponent 3 (41% extender A), and 0% pseudocomponent 4 (5% extender B) (See *Figure* 12). Equations used for these transformations are shown in *Table 9*. *Table* 10 enumerates the control system in terms of hiding power, abrasive scrubbability, R.M.C., and P.V.C., and the suggested experimental composition in terms of predicted and observed values of these properties.

The data indicate that an acceptable experimental system composition was obtained from the study. The observed values were in good agreement (within the 95% Confidence Limits of variation) with the predicted values.

SUMMARY

The application of simplex lattice design experimentation methodology resulted in obtaining a successful coating formula. A particular combination of four principal components was developed yielding a coating with specific performance parameters. A minimum of paint sample production (in this case, four original systems) yielded performance parameter information over a broad composition region. Replication and statistical analysis of the data yielded estimates of the reproducibility of the test methods and performance parameters.

ACKNOWLEDGMENT

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Kinetics of Solvent Desorption
From Poly(vinyl alcohol) Films

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The mechanism of plastic film formation from solution and the possibility of creating a mathematical model for this process is considered. Molecular diffusion carries out the transportation of the solvent to the evaporation surface in the final stage of the process and its rate limits the overall process. Therefore, the application of the thermoactivation equation for solvent diffusion with a variable diffusion coefficient was examined for the case of solvent desorption from cast poly(vinyl alcohol) (PVA) films. The equation obtained is valid in a wide range of temperatures for binary and ternary PVA based systems. In this equation, the parameters of the casting process (time, temperature, and concentration of the residual solvent) were correlated with the physical constants of the polymer-solvent system. The equation can be used for guiding the production of films with specific physical and mechanical properties.

INTRODUCTION

PVA films can be used for different industrial purposes and specifically as a separator material in alkaline batteries. The particular nature of the PVA polymer is the coincidence of decomposition temperature with the melting point.[1] Therefore, casting from aqueous solution is the simplest method of producing PVA films. Certain quantities of residual solvent (water) are usually present in the film after completion of the formation process. Physical properties of the PVA cast films are dependent on the amount of solvent in the film. Consequently, it is desirable to propose a relationship which correlates

preparation parameters with the quantity of residual solvent in the film in order to better control the production process.

The mechanism of solvent cast film formation is basically known[2] and can be illustrated in the example of the desorption curve (*Figure* 1). There are two main stages in the process of film formation. The first stage is evaporation from a free liquid surface. During this stage, the principal movement of solvent to the evaporation surface is carried out by convection. Since evaporation is slower than the convective mass transfer, the rate of evaporation is approximately constant and limits the rate of the overall process in this stage. The temperature of the film on the evaporation surface is constant and equal to the temperature of the wet thermometer during this stage.

The second and last stage is evaporation from the surface of the solid polymer film. The movement of the solvent to the evaporation surface is performed by diffusion. Diffusion is slower than evaporation and, therefore, the rate of diffusion limits the formation process during the last stage. The temperature of the film is equal to the temperature in the drying chamber.

There is a period between these two stages when convective mass transfer develops into diffusion and both kinds of transport occur simultaneously. The temperature of the evaporation surface increases from the temperature of the wet thermometer to the temperature in the drying chamber during this period.

The mathematical description was restricted to the last stage where the rate of the overall process is limited by the rate of diffusion. Analytical solutions of the diffusion equation under known conditions can sometimes be used for calculating the rate of diffusion. Since solvent diffusion through a polymer involves a change of the diffusion coefficient with the quantity of the residual solvent in the film, the diffusion equation does not have a

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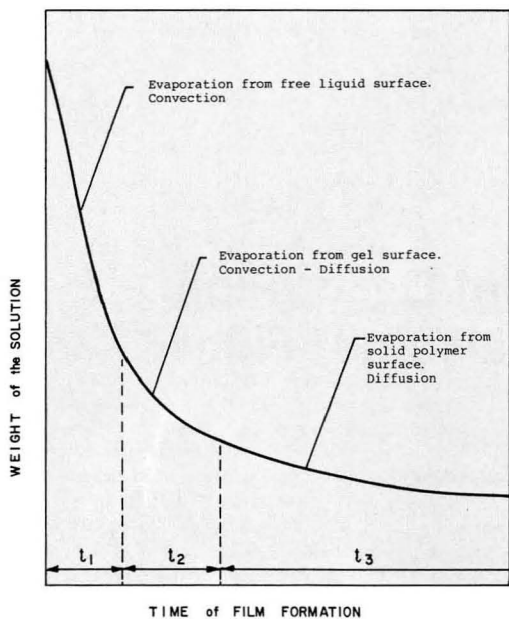
Figure 1—Desorption curve. t_1—is time of the first stage of film formation; t_2—is time of period of changing the mechanism of solvent transport; t_3—is time of the last stage of film formation. Inscriptions near the curve are processes which occur during each stage
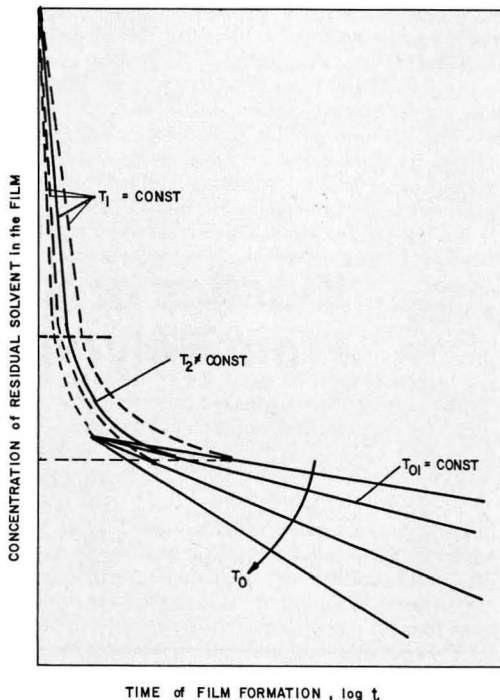
Figure 2—Desorption curves for different temperatures of film formation. T_{01}—is temperature in the drying chamber; T_1—is temperature on the surface of the film during the first stage; T_2—is temperature of the film during the period of changing the mechanism of solvent transport

reasonable analytical solution. Thus, generally, it is non-Fickian or anomalous diffusion. Several approximate models have been obtained.[3-6] The models were based on the assumptions that: (1) diffusion coefficients are constant during relatively short periods of time and change from one period to another,[3-5] (2) the dependence of the coefficient on concentration is given,[5] and (3) the rate of diffusion does not depend on the concentration of the residual solvent at all.[6] The assumptions generate various models which describe the desorption process only qualitatively.

An attempt was made to find an equation based on experimental data which could describe solvent diffusion with a variable diffusion coefficient.[7-9] Thermoactivation theory of diffusion in polymers was used as a basis. According to this theory, the following correlation was applied for guiding the experimental procedure.

$$t \sim 1/D \sim e^{Q/RT} \qquad (1)$$

Where:

t = time to obtain a definite quantity of residual solvent

Q = effective activation energy of diffusion which depends on the quantity of residual solvent (C)

T = formation temperature, ^{K}

D = diffusion coefficient

According to the mechanism of film formation discussed and the correlation proposed, the desorption curves for different constant temperatures at constant

initial film thickness should have the form of convergent straight lines at the last stage of film formation (see Figure 2). This idea was based on the fact that the temperature in the drying chamber essentially influences the rate of the formation process only during the last stage. The form of the desorption curves at the diffusion limited last stage is determined by the dependence of effective activation energy of diffusion (Q) on the concentration of the residual solvent in the film (C). The first assumption was that such dependence would be linear. Therefore, desorption curves on Figure 2 are presented in coordinates C vs log T. The above suppositions permitted the start of experimental study of the solvent diffusion process with a variable diffusion coefficient.

The concentration of the residual solvent in films was determined to find the equation which correlates production parameters of solvent cast films with quantity of residual solvent in the film. Eleven binary and ternary polycarbonate and polysulfone based systems were tested over a wide range of temperatures which spans the normal solvent boiling point. The following equation for the description of solvent diffusion with a variable diffusion coefficient was obtained for the polymer-solvent systems tested.

$$t = \beta \exp \left[\frac{Q_0 - \alpha C}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right] \qquad (2)$$

Where:

β = constant

Q_0 = activation energy of diffusion when the amount of solvent in polymer is equal to zero

T_p = temperature at which straight lines intersect in log t vs $1/T$

C = concentration of the solvent in film, %

The form of equation (2) and the value of its constants suggest that the equation has clear physical meaning. Besides, the semiempirical way of obtaining the equation allows calculation of any technological component of the production process of polymer films from solution, i.e., (t, T, C).

The present study was undertaken to determine whether the previous equation is effective for PVA based systems and if so, to study their features. PVA is a partly crystalline polymer which contains crystalline and amorphous zones in the structure. The process of crystallization, which occurs during formation of films from solution, results in squeezing out the solvent from the crystalline regions to amorphous zones. Consequently, the local concentrations of solvent in the amorphous zones are much higher than the average concentration in the film. Movement of the solvent takes place through amorphous zones and effective activation energy of diffusion is a function of the local concentration of residual solvent. However, the concentration of solvent which can be measured is the average concentration in the film. Therefore, effective activation energy of solvent diffusion in *crystalline* polymers should always be lower than effective activation energy of solvent diffusion in *amorphous* polymers for the same average concentration of residual solvent in the film (see *Figure* 3). Based on this theory, there is no principal difference between polymer-solvent interaction in amorphous and crystalline polymers. Consequently, equation (2) should be valid for PVA based systems although a difference in dependence of effective activation energy on concentration of residual solvent in film may be expected.

Strong hydrogen bonds between PVA and water should result in a very high value of activation energy of diffusion (Q_0). PVA polymer is produced with different degrees of hydrolysis. Fully hydrolyzed PVA does not contain acetate groups. Partly hydrolyzed PVA has a certain quantity of residual acetate groups which weakens hydrogen bonding between the intra- and intermolecular hydroxyl groups. Activation energy of diffusion of the solvent bonded to the polymer should depend on the strength of the polymer-solvent bonds. Therefore, the constant Q_0 should be different for PVA polymers with various degrees of hydrolysis and should be higher for fully hydrolyzed PVA than for partly hydrolyzed polymer.

EXPERIMENTAL

Poly(vinyl alcohol) polymers with 88 to 89% and 99 to 100% hydrolysis were used in powder form and dissolved in water or in a mixture of water and methanol (75:25 v.p.). Boric acid was added to PVA as a crosslinking agent in a quantity of 15% by weight of PVA. Initial concentration of the polymer in solution was 10 to 15%
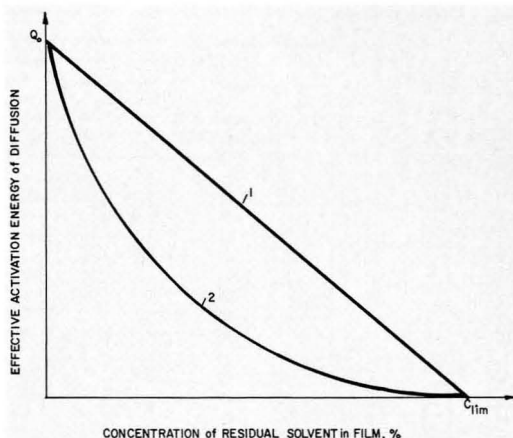
Figure 3—Dependence of effective activation energy on concentration of residual solvent in film. (1) Amorphous polymers; (2) Crystalline polymers

by weight. The reagents were pure and not subjected to additional cleaning. Systems tested included:

(a) 88 to 89% hydrolyzed PVA + water
(b) 88 to 89% hydrolyzed PVA + water + methanol (75:25)
(c) 99 to 100% hydrolyzed PVA + water
(d) 99 to 100% hydrolyzed PVA + water + boric acid (15%)
(e) 99 to 100% hydrolyzed PVA + water + methanol (75:25)

Films with 1.5 ± 0.1 mil to 2.5 ± 0.1 mil thickness were formed by a doctor blade on a metal sheet in a drying oven. The time of formation varied over a wide range for each constant temperature. Concentration of the residual solvent was calculated by the equation:

$$C = \frac{P_w - P_d}{P_w} \cdot 100\% \qquad (3)$$

Where:

C = concentration of residual solvent in film
P_w = wet weight of the film
P_d = dry weight of the film after drying to constant weight

The specimens were weighed on an analytical balance. Experimental data were introduced into the computer and constants of the equation obtained were calculated. Correlation coefficients between experimental data and data calculated by the equation were determined.

RESULTS AND DISCUSSION

The concentration of the residual solvent in films, formed under different conditions, was determined in order to control the preciseness of Correlation 1 for PVA based systems. The results obtained are shown in *Tables* 1–5. Examination of the applicability of equation (2) consists of plotting the data on the graphs with coordinates C vs log t for various constant temperatures of film

Table 1—Quantity of Residual Solvent in PVA Films Formed at Various Conditions for 88–89% Hydrolyzed PVA + Water System
(thickness of the film, δ = 2.5 mil)

No.	Temperature of Formation, °C	Time of Formation min	Quantity of Residual Solvent, %	log t Experiment	log t Calculation
1	21	910	9.2	2.9590	2.7363
2	21	1450	7.5	3.1614	3.0613
3	21	1760	7.3	3.2455	3.1043
4	21	2900	6.6	3.4624	3.2646
5	30	360	9.4	2.5563	2.4984
6	30	950	6.7	2.9777	2.9599
7	30	1100	6.4	3.0414	3.0224
8	30	2900	4.4	3.4624	3.5331
9	40	290	8.0	2.4624	2.4673
10	40	400	6.3	2.6021	2.7362
11	40	960	4.7	2.9823	3.0659
12	40	1080	4.4	3.0334	3.1401
13	55	150	7.3	2.1761	2.1925
14	55	180	6.0	2.2553	2.3487
15	55	210	5.6	2.3222	2.4036
16	55	285	6.7	2.4548	2.2608
17	55	1250	2.6	3.0969	3.0145
18	55	1300	2.2	3.1139	3.1475
19	70	60	8.9	1.7782	1.7495
20	70	80	6.7	1.9031	1.8903
21	70	90	4.7	1.9542	2.0661
22	70	110	4.1	2.0414	2.1338
23	70	145	3.1	2.1614	2.2724
24	70	180	2.7	2.2553	2.3409
25	70	240	2.0	2.3802	2.4897

Table 2—Quantity of Residual Solvent in PVA Films Formed at Various Conditions for 88–89% Hydrolyzed PVA + Water + Methanol System (T ≤ 65°C)
(thickness of the film, δ = 2.5 mil)

No.	Temperature of Formation, °C	Time of Formation min	Quantity of Residual Solvent, %	log t Experiment	log t Calculation
1	19	282	10.6	2.4502	2.4117
2	19	316	12.0	2.4997	2.2465
3	19	355	10.2	2.5502	2.4629
4	19	376	9.35	2.5752	2.5788
5	19	408	8.8	2.6107	2.6595
6	19	5145	4.27	3.7114	3.6224
7	19	7225	3.98	3.8606	3.7160
8	19	8135	3.17	3.9104	4.0190
9	19	14145	3.55	4.1506	3.8682
10	19	29000	2.7	4.3802	4.2327
11	40	120	8.4	2.0792	2.2144
12	40	166	6.03	2.2201	2.4889
13	40	200	7.6	2.3010	2.2972
14	40	250	7.25	2.3979	2.3363
15	40	332	4.9	2.5211	2.6607
16	40	872	3.5	2.9405	2.9394
17	40	980	3.15	2.9912	3.0266
18	40	1000	3.14	3.0000	3.0279
19	50	60	12.9	1.7782	1.7338
20	50	100	7.25	2.0000	2.0861
21	50	126	5.0	2.1004	2.3133
22	50	174	4.15	2.2405	2.4272
23	65	40	11.2	1.6021	1.6036
24	65	50	7.25	1.6990	1.7386
25	65	112	2.46	2.0492	2.0741

Table 3—Quantity of Residual Solvent in PVA Films Formed at Various Conditions for
99–100% Hydrolyzed PVA + Water + Methanol System (T ≤65°C)
(thickness of the film, δ = 2.5 mil)

No.	Temperature of Formation, °C	Time of Formation min	Quantity of Residual Solvent, %	log t Experiment	log t Calculation
1	23	300	11.9	2.4771	2.3677
2	23	405	10.5	2.6075	2.5455
3	23	450	9.7	2.6532	2.6581
4	23	460	10.1	2.6628	2.6007
5	23	940	8.1	2.9731	2.9142
6	23	1450	6.3	3.1614	3.2713
7	23	1500	7.0	3.1761	3.1216
8	23	2200	5.6	3.3424	3.4387
9	40	210	10.0	2.3222	2.2281
10	40	990	4.8	2.9956	2.9302
11	40	1100	4.6	3.0414	2.9709
12	40	1150	5.0	3.0607	2.8911
13	40	1200	4.5	3.0792	2.9919
14	50	80	11.1	1.9031	1.9459
15	50	120	9.0	2.0792	2.0940
16	50	150	6.8	2.1761	2.2920
17	50	180	6.2	2.2553	2.3572
18	50	240	5.4	2.3802	2.4548
19	50	360	4.0	2.5563	2.6667
20	55	140	6.1	2.1461	2.2102
21	55	250	3.8	2.3979	2.4879
22	60	100	6.3	2.0000	2.0412
23	60	120	5.0	2.0792	2.1501
24	65	45	14.5	1.6532	1.5968
25	65	50	9.2	1.699	1.7599
26	65	62	8.0	1.7924	1.8100
27	65	80	6.6	1.9031	1.8790
28	65	118	4.2	2.0719	2.0410
29	65	145	2.9	2.1614	2.1738

formation. Straight lines in these coordinates indicate that equation (2) is probably valid for a description of the results. However, the data in *Tables 1–5* do not fall on straight lines in coordinates C vs log t. Thus, in *Figure 4*, log C is plotted against log t; the points fall on convergent straight lines. The next step consists of replotting the data on the coordinates log t vs $10^3/T$ (*Figure 5*). Since the points fall on convergent straight lines with these coordinates too, it was possible to calculate values for Q(C) from the slope of the curves log t vs $10^3/T$ according to the formula:

$$Q(C) = 2.3R \frac{\Delta \log t}{\Delta (10^3/T)} \qquad (4)$$

The linear dependence of Q on log C (*Figure 6*) insures the validity of the following equation to the PVA based systems and the determination of its constants.

$$t = \beta \exp\left[\frac{Q_o - \alpha \log C}{R} \left(\frac{1}{T} - \frac{1}{T_p}\right)\right] \qquad (5)$$

The straight lines in coordinates log t vs $10^3/T$ have a break at the temperature equal to the boiling point of methanol (~ 65°C) for the PVA + water + methanol systems and, therefore, form two temperature ranges

(*Figure 5*). Every temperature range has different values of the constants for equation (5). Only one temperature range below the boiling point of water is found for PVA + water and PVA + boric acid + water systems. The dependence of Q on log C is linear for each system over any temperature range tested, which indicates a difference between equations (2) and (5). According to the data obtained, effective activation energy of solvent diffusion in PVA is lower than the effective activation energy of solvent diffusion in amorphous polymers for the same average concentration of residual solvent, if constants in equations (2) and (5) are the same. The validity of equations (5) for polyamides which are also high crystalline polymers was shown recently.[9] Consequently, equations (2) and (5) represent the same mechanism of diffusion. The form of these equations suggests that diffusion of the solvent through the polymer is realized by thermal fluctuations which create the conditions for molecules to overcome a potential barrier Q. The specific nature of crystalline polymers is manifested in another dependence of Q(C) comparable to polycarbonate and polysulfone based systems. However, the physical meaning of the equation remains unchanged.

It was expected that the equilibrium quantity of the residual solvent in the film would be in conformity with

**Table 4—Quantity of Residual Solvent in PVA Films Formed at Various Conditions for
99–100% Hydrolyzed PVA + Water + Methanol System (65 ≤ T < 100°C)**
(thickness of the film, δ = 1.5 mil)

No.	Temperature of Formation, °C	Time of Formation min	Quantity of Residual Solvent, %	log t Experiment	log t Calculation
1	65	45	14.5	1.6532	1.5912
2	65	50	9.2	1.6990	1.7488
3	65	62	8.0	1.7924	1.7972
4	65	80	6.6	1.9031	1.8639
5	65	118	4.2	2.0719	2.0205
6	65	145	2.9	2.1614	2.1488
7	70	40	11.7	1.6021	1.6292
8	70	50	6.6	1.6990	1.7967
9	70	60	5.2	1.7782	1.8665
10	70	70	5.9	1.8451	1.8295
11	70	90	3.5	1.9542	1.9823
12	70	120	2.5	2.0792	2.0808
13	85	30	13.1	1.4771	1.5103
14	85	36	4.7	1.5563	1.6540
15	85	40	4.3	1.6021	1.6664
16	85	45	2.5	1.6532	1.7425
17	85	55	1.3	1.7404	1.8341
18	85	60	2.2	1.7782	1.7604
19	85	69	1.1	1.8388	1.8576
20	85	76	1.5	1.8808	1.8141
21	85	80	1.25	1.9031	1.8396

earlier data.[2] No equilibrium amount of residual solvent in the PVA films was obtained after drying the film for about 400 hr at room temperature.

Equation (5) was valid for all PVA based systems tested. The values of the constants in equation (5) for the systems evaluated are presented in *Table 6*.*

The constants Q_o obtained at low temperature ranges (below the boiling point of the solvents) had very high values, greater than the Q_o for any systems studied before.[7–9] Such high values of Q_o can be attributed to very strong hydrogen bonds between PVA and water. The presence of residual acetate groups in partially hydrolyzed PVA results in decreasing the value of Q_o. These data indicate that Q_o is a function of chemical structure of the polymer and solvent and depends on the strength of the physical bonds between polymer and solvent. It is found that the addition of a crosslinking agent and methanol does not influence the value of Q_o at low temperatures. But Q_o changes when the temperature of film formation exceeds the normal boiling point of methanol (~65° C) for the PVA + water + methanol system. The value of the jump in energy is a characteristic of a solvent whose boiling point borders between two temperature ranges and does not depend on the correlation of components in the polymer-solvent system.[8] Therefore, the difference in value of Q_o for high and low temperature ranges is almost the same as for fully hydrolyzed and partly hydrolyzed PVA (see *Table 6*).

Both α and Q_o are defined by the polymer-solvent system and their values change similarly by the variation of components in the system. Such a relationship results from the stability of concentration of the residual solvent at the intersection point in *Figure 4* ($C_{lim} \approx 23\%$) for all tested PVA based compositions (*Table 6*). Constants Q_o and α are correlated by the formula which follows from equation (5) and at the intersection point, can be rearranged to the following form:

$$Q = Q_o - \alpha \log C_{lim} = 0 \qquad (6)$$

Constancy of C_{lim} leads to a direct proportion of changing the values of Q_o and α.

Thus, the concentration of solvent in a polymer at the point of intersection (C_{lim}) marks a limit for the use of equation (5); $C_{lim} \approx 20\%$ for polycarbonate, polysulfone, and PVA based systems.[8] Existence of a similar concentration limit in the applicability of equations (2) and (5) probably relates to a change of the diffusion mechanism at about 20% of a solvent in a polymer. It is possible to assume that equations (2) and (5) are valid at the last stage of film formation when the solvent bonded with the polymer takes part in the diffusion process. Approximately 20% of the solvent is necessary in order to localize intermolecular interaction in a polymer.[10] If the solvent concentration in the polymer is higher than 20%, transference of the solvent to the evaporation surface is carried out by self-diffusion of the solvent. The process of self-diffusion proceeds with an activation energy, which is essentially lower than the value of Q_o in equations (2) and (5) and does not depend on the solvent concentration in the polymer.[11] Of course, the change of diffusion mechanism takes place not at the point of C_{lim} but at the

---

*Correlation coefficient between experimental data and data calculated by equation (6) has values from 0.952 to 0.993 for different systems. Moreover, values of constants which were found from graphs are close to the value of constants determined by the computer. These facts show that equation (6) describes experimental data with a high degree of precision and that the conclusions made about physical meanings of constants are reliable.

Table 5—Quantity of Residual Solvent in PVA Films Formed at Various Conditions for 99–100% Hydrolyzed PVA + Water + Boric Acid System
(thickness of the film, δ = 1.5 mil)

No.	Temperature of Formation, °C	Time of Formation min	Quantity of Residual Solvent, %	log t Experiment	log t Calculation
1	21	270	14.5	2.4314	2.3564
2	21	380	12.9	2.5798	2.5688
3	21	950	10.6	2.9777	2.9254
4	21	1000	11.0	3.0000	2.8582
5	21	1100	10.5	3.0414	2.9427
6	21	1150	10.55	3.0607	2.9340
7	21	2400	8.9	3.3802	3.2429
8	21	5400	6.9	3.7324	3.7052
9	40	125	22.0	2.0969	1.5755
10	40	256	11.5	2.4082	2.4073
11	40	325	10.2	2.5119	2.5611
12	40	400	9.1	2.6021	2.7075
13	40	1020	6.6	3.0086	3.1193
14	40	1120	6.7	3.0492	3.1001
15	40	1200	6.9	3.0792	3.0623
16	40	1250	6.75	3.0969	3.0905
17	63	90	13.0	1.9542	1.9274
18	63	105	12.0	2.0212	1.9848
19	63	155	8.3	2.0212	1.9848
20	63	180	8.7	2.1903	2.2490
21	63	800	3.8	2.9031	2.8089
22	63	1120	2.8	3.0492	3.0278
23	77	50	13.5	1.6990	1.7363
24	77	60	9.5	1.7782	1.8800
25	77	80	7.2	1.9031	1.9933
26	77	90	7.1	1.9542	1.9991
27	77	120	4.7	2.0792	2.1677
28	85	42	11.0	1.6232	1.6983
29	85	48	9.5	1.6812	1.7340
30	85	53	9.7	1.7243	1.7289
31	85	63	5.2	1.7993	1.8809
32	85	80	3.9	1.9031	1.9510
33	85	85	3.6	1.9294	1.9705

region of concentrations near this point, and the real limit of applicability of equation (5) is lower than that of C_{lim}.

T_p does not depend on the conditions of film production nor on the composition of the solvents in the polymer-solvent system. The value of T_p remains constant for the PVA + water and PVA + boric acid + water in the low temperature range and for PVA + water + methanol in the middle temperature range: $\approx 100°$ C. These ranges were found to be the highest temperature ranges for PVA based systems and $100°$ C is the upper temperature extreme of equation (5). Therefore, it is important to determine the physical meaning of this temperature for PVA. According to the earlier data, the value of T_p in the high temperature range is close to the melting point of the polymer. If the polymer and solvent form stable complexes, the T_p in the high temperature range is displaced to temperatures closer to the decomposition temperature of the polymer, e.g., polycarbonate + methylene chloride + toluene.[8] However, the temperature of $100°$ C is not equivalent to the melting point or the temperature of decomposition of PVA since both are between 220 and $230°$ C.[1] A simple experiment was performed to determine the temperature of thermo-oxidation of the PVA used in our investigation. The PVA film was put in an oven at a temperature of $100°$ C for four to five days; during this time the film became brown. The same result was obtained when the film was formed from the solution at a temperature of $120°$ C for one to two hours.

The exposure of PVA film in an oven at $90°$ C showed that the film did not turn brown or change weight. The experiments indicate that the process of thermo-oxidation starts in dissolved PVA at a temperature range close to $100°$ C. Results obtained can explain the absence of high temperature ranges (above the boiling point of water) in PVA based systems and confirms the presence of physical meaning for the constant T_p.

T_p at a low temperature range, below the boiling point of methanol for PVA + water + methanol systems, is equal to $82°$ C. This value of T_p is related to properties of the solvent whose boiling point is at the upper end of the temperature range[7-8] and does not depend on the composition of the solution or the nature of the polymer employed in the system.

Constant β depends on certain factors such as the nature and initial concentration of the polymer in solution, the thickness of the films, the nature of the solvent,
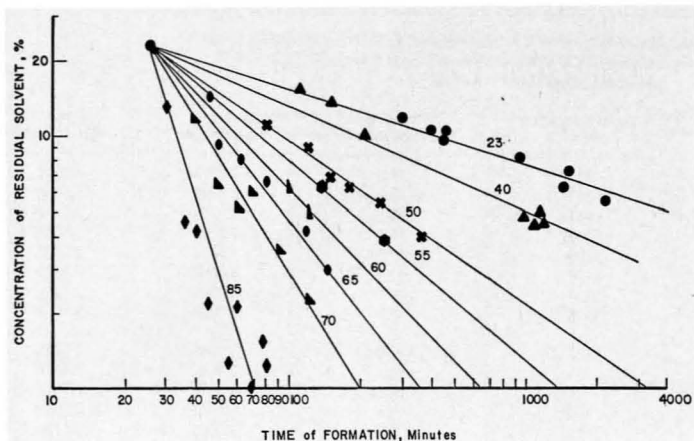
Figure 4—Residual solvent concentration as a function of the time of film formation for 99–100% hydrolyzed PVA + Water + Methanol system. Numerals near straight lines are temperatures of formation in °C

and the design of the casting machine. However, β is one constant which does not vary during transition between the high and middle temperature ranges for ternary systems and between high and low temperature ranges for binary systems.[8] Equation (5) cannot be applied for the time of film formation less than the time at the intersection point in *Figure* 4, that is β. However if equation (5), can be employed, the time calculated is the whole time of film formation. All time prior to the diffusion period of film formation is counted in the value of β.

Very often, the process of the production of PVA cast

films from solution is divided into several stages: (1) formation with drying by casting machine, (2) additional drying in other zones of the machine to a definite humidity, and (3) additional drying out of the machine. The formula from equation (5) can be applied for the process of additional drying (stages 2 and 3), for surface controlled evaporation:

$$t_{a.d.} = \beta \exp \left[\frac{\alpha (\log C_\beta - \log C)}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right] \qquad (7)$$

Where:

$t_{a.d.}$ = time of additional drying
C_β = concentration of the residual solvent, when additional drying was begun
β = 1

Any component of casting technology (t, C, T) can be calculated by applying equation (5) or the following equations:
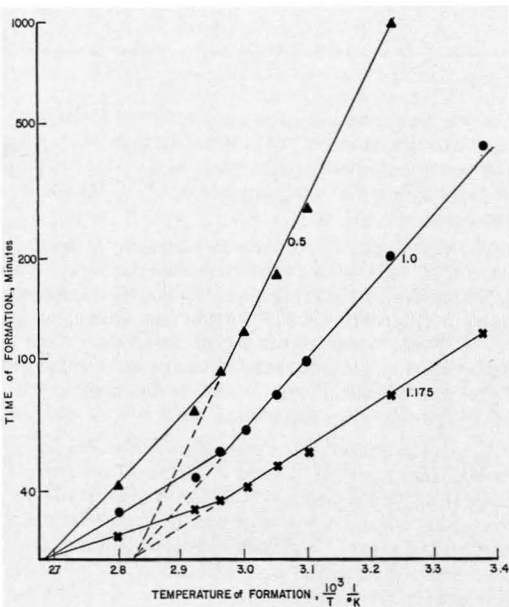
Figure 5—Formation time as a function of the temperature for 99–100% hydrolyzed PVA + Water + Methanol system. Numerals near straight lines are concentration of residual solvent in %
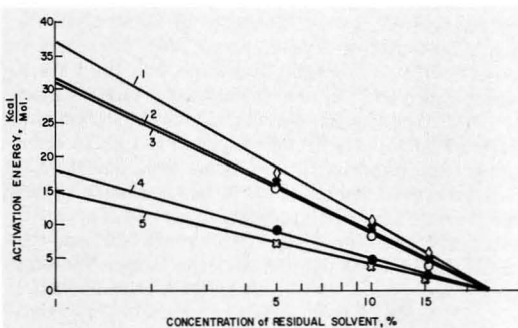
Figure 6—Activation energy for diffusion of solvent as a function of residual solvent concentration. (1) 99–100% hydrolyzed PVA + Water + Methanol; (2) 88–89% hydrolyzed PVA + Water; (3) 88–89% hydrolyzed PVA + Water + Methanol (T < 65°C); (4) 99–100% hydrolyzed PVA + Water + Methanol (T < 65°C); (5) 88–89% hydrolyzed PVA + Water + Methanol (100 < T < 65°C)

Table 6—Constants of Equation (6) for PVA Based Systems

System	$Q_o, \dfrac{Kcal}{mol}$		$\alpha, \dfrac{Kcal}{mol}$		$T_p, °C$	β, min		C_{lim}, %	Correlation Coefficient
	by graphs	by computer	by graphs	by computer		by graphs	by computer		
PVA (88–89% hydrolyzed) + Water	32.0	30.91	23.45	22.71	100	17.2	18.96	23	0.978799
PVA (88–89% hydrolyzed) + Water	32.5	33.98	23.87	24.95	98	19.0	16.39	23	0.978072
PVA (88–89% hydrolyzed) + Water + Methanol (75:25) (T < 65°C)	31.6	33.54	23.21	24.64	82	24	19.68	23	0.986978
PVA (88–89% hydrolyzed) + Water + Methanol (75:25) (65°C < T < 100°C)	14.9	14.14	10.94	10.38	100	24	25.36	23	0.987168
PVA (99–100% hydrolyzed) + Water	37	38.91	27.21	28.57	100	15.9	13.54	23	0.993685
PVA (99–100% hydrolyzed) + Water + Boric Acid (10%)	37.3	37.85	27.39	27.80	98	33	33.63	23	0.981097
PVA (99–100% hydrolyzed) + Water + Methanol (75:25) (T < 65°C)	36.5	37.16	26.8	27.28	82	27	25.72	23	0.987345
PVA (99–100% hydrolyzed) + Water + Methanol (75:25) 65°C < T < 100°C	18.0	19.51	13.22	14.38	100	27	24.1	23	0.952007

$$\log C = \frac{Q_o}{\alpha} - \frac{2.3R}{\alpha\left(\frac{1}{T} - \frac{1}{T_p}\right)} \cdot \log \frac{t}{\beta} \qquad (8)$$

$$T = \left(\frac{1}{T_p} + \frac{2.3R}{Q_o - \alpha \log C} \cdot \log \frac{t}{\beta}\right)^{-1} \qquad (9)$$

Formulas (8) and (9) give expressions for quantity of residual solvent in film and temperature of film formation correspondingly for a given time of film formation, t. It is possible to calculate the concentration of the residual solvent in the film which was subjected to step drying. The essential parameters of the casting machine can be found by employing equations (5) and (7) if properties of the polymer-solvent system and constants of the equations are known.

CONCLUSIONS

- The applicability of the kinetic equation for solvent diffusion with variable diffusion coefficient is shown for the formation process of PVA films from solution.
- The equation obtained is valid for binary and ternary PVA based systems and allows calculation of any component of casting technology (t,T,C).
- The constants of the equation have been determined and their physical meaning have been examined for PVA based systems.
- Dependence of the effective activation energy of diffusion on quantity of residual solvent in the PVA film is different from analogous dependence, typical of polycarbonate and polysulfone based systems.

Such distinction is related to the partly crystalline structure of the PVA polymer.
- Strong hydrogen bonds between PVA and water result in very high activation energy of diffusion in PVA + water systems.
- The modification of the kinetic equation was obtained in order to calculate the parameters of additional solvent removal in the casting machine or in an oven.

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Analysis of Paint

James B. Lear
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Various instrumental and chemical techniques are presented for the identification and determination of the binder, solvent, and pigment components of paint samples. Infrared spectroscopy, emission and X-ray spectroscopy, sodium fusion, and organic functional group analyses are discussed. A schematic procedure for analysis is included.

Introduction

The purpose of this paper is to describe the analysis of paint. The discussion is meant to describe consumer and industrial paints, and is not intended to cover such specialty areas as marine paints, inorganic paints, or similar specialty products. The discussion will apply to liquid paint samples, since the analysis of paint films is another subject. Also, this discussion will not include any analysis of paint additives, which is also a subject that must be dealt with separately.

Like Gaul, paint is essentially divided into three parts, namely, binder, pigment, and solvent. This generally applies whether the paint is solvent-based or water-based, the latter being of continually greater importance for environmental reasons. Of course, it should be noted that while all coatings do contain binder and solvent, there are many clear coatings, aside from those containing a transparent mineral flatting agent, that contain no pigment, which simply eliminates some of the separation steps. The separation and identification

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of the components of a paint is the subject of this paper.

The first thing that must be determined is whether the paint is solvent-based or water-based. Because of the difference in solubility, these two types of paint must be handled differently.

A small amount of the paint may be reduced with water and with an organic solvent such as methyl ethyl ketone (MEK) or tetrahydrofuran (THF), and mixed. Water-based paints will not generally disperse in organic solvents and vice versa.

An exception to the above is the case of paints in which the binder is a polymer which contains carboxylic acid groups that have been neutralized with amine. Paints containing such a binder can be reduced with either THF or MEK and will disperse. Likewise, they will disperse with the addition of water. The ability of a paint to be dispersed in both organic solvent and water indicates the presence of such a binder.

Separation of Binder

The binder is really the backbone of any paint and, as such, its identity is probably the most critical information that can be obtained from the analysis. Therefore, the isolation of the vehicle is the first step.

In the case of solvent-based paint, the removal of the pigment is generally accomplished by dilution of the paint with solvent, and centrifuging. One part of paint can be reduced with one part of a solvent, usually MEK, mixed well and centrifuged until a clear supernatant layer is obtained. Using a relatively high speed centrifuge (ca. 15,000 rpm), this

can generally be accomplished in 20–30 min. If a low speed centrifuge is used (ca. 3000 rpm) this can take from 1–4 hr.

After centrifugation is finished, the clear supernatant layer is transferred to a suitable container (a glass vial with a plastic stopper serves well) and the centrifuge tube containing the pigment is also stoppered and retained.

As stated above, paints containing an amine-solubilized binder can be similarly reduced with either water or MEK and centrifuged to remove the pigment. THF may also be used as a reducing solvent and is often the solvent of choice as this makes handling the supernatant layer easier.

With the majority of water-based paints, which are only water-reducible, one cannot use centrifugation to isolate the binder from the pigment. The reason for this is that latex or emulsion binders will be separated from the vehicle if centrifuged and will appear mixed with the pigment rather than in the supernatant layer. As a result, such paints must be handled differently to isolate the binder.

The technique used is to spread a thin film of the paint on a glass plate (6″ × 6″ plate is convenient). The film is allowed to air dry and then is removed by scraping with a razor blade. The film is placed in a plastic stoppered vial along with MEK and the vial shaken for several hours on a wrist-type shaker. After shaking is completed, the vial is allowed to sit to permit insoluble material to separate, or the mixture can be centrifuged. In either case, the clear supernatant layer is removed and retained.

Thus, the binder of solvent-based and amine-solubilized water-soluble paints is removed from the pigment by centrifugation, while the binder is removed from

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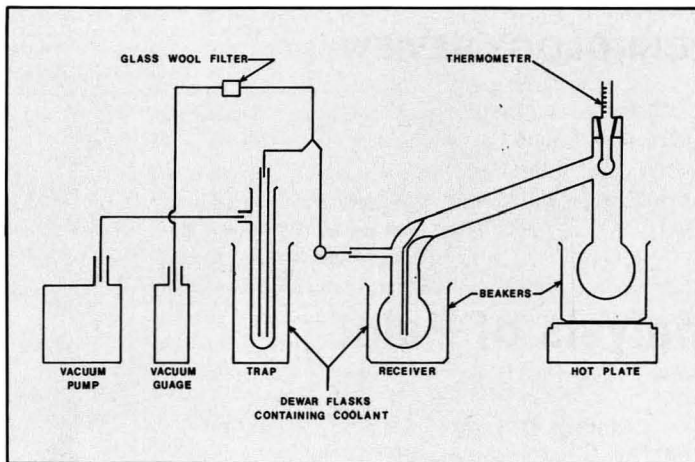
HOT PLATE

DEWAR FLASKS CONTAINING COOLANT

Figure 1—Vacuum distillation apparatus

water-based paints by solvent extraction of an air dried film. The identification and analysis of the isolated binder will be discussed later.

Separation of Pigment

As outlined above, the pigment in solvent-based and amine-solubilized water-soluble paints can be isolated by centrifugation. A quantitative determination of the amount of pigment in the paint can be obtained along with the separation of the binder. The centrifuge tube is weighed empty, paint is added, and the tube weighed again. The reducing solvent is added, the paint and solvent are mixed, and then centrifuged. After the separation and removal of the clear supernatant layer to be used in the binder analysis, more solvent is added to the centrifuge tube. The pigment is mixed with the solvent and then recentrifuged. This step is repeated twice to wash all the binder from the pigment. After the final washing and centrifuging, the solvent is decanted and the tube is dried in an oven at 105° C for two hours. After removal from the oven and cooling, the tube is reweighed. From the initial weight of paint and the weight of pigment isolated, the pigment content of the paint can be calculated. The dried pigment is removed from the centrifuge tube and retained for analysis.

Because of the inability to remove pigment from vehicle in water-based (latex) paints by centrifuging, another technique must be used. By ashing the sample after drying, to remove water, one

can obtain the inorganic pigment, free of binder.

The total paint or portion of the dried film used to isolate the binder from water-based paints may be used. If the total paint is used, the sample is weighed into a preweighed porcelain crucible and dried in a 105° C oven until all water has been removed. After drying, the crucible is heated with a Bunsen burner to carbonize the sample and then placed in a 600° C muffle furnace until all traces of carbon are gone. After cooling, the crucible is weighed and the percent ash is calculated. The technique using the dried film is the same, but the drying step in the oven is deleted.

The potential problem in the ashing technique is the possible volatilization of some pigments. In general, most of the common inorganic pigments in paint are not volatile under the conditions of ashing, but there is a problem with carbonates and in some cases with chromates. The loss of CO_2 with prolonged heating of carbonates is well known. However, experience has found that if one avoids prolonged heating at the carbonizing step and also if the time in the muffle furnace is kept to a minimum, there is very little loss of CO_2 from paints containing carbonates. The lack of a better way to isolate pigments from water-based paint forces one to use ashing in pigment isolation, the problems notwithstanding.

Solvent Separation

As in previous separations, the method of isolation of the solvent from paint is

again different depending on whether it is solvent-based or water-based.

In the case of solvent-based paint, our preferred method is to isolate the solvent by vacuum distillation. Alternately, the paint can be diluted with a suitable low boiling solvent and directly injected into a gas chromatograph. Although this method avoids the stripping step, it does introduce a reducing solvent that may interfere with one or more of the components in the solvent when it is chromatographed. There is no way of knowing beforehand if this will be the case. This is one objection to direct injection. A second is that only retention time can be used for the identification of a particular peak, and this can lead to difficulty if components of the same or very similar retention times are present in the same solvent. The technique of chromatographing the paint on two columns of different polarity is often suggested as a remedy, but this has been known to fail on occasion. Another disadvantage of this technique is the eventual fouling of the chromatographic column with the nonvolatiles of the paint which are injected on the column with each injection of paint.

As a result, isolation of the solvent by vacuum stripping is seen to have two overwhelming advantages. First, the solvent is isolated as is, and contains no added reducing solvent, and second, a portion of the stripped solvent can be examined by IR spectroscopy, giving invaluable information as to the types of solvent present, and some idea as to their amounts. With this information, the use of retention times on the chromatographic trace becomes considerably more meaningful.

The apparatus (*Figure* 1) for use in the distillation is a simple apparatus consisting of a sample flask, an adapter containing a thermometer port and a side arm leading to a water-cooled condenser, another adapter with a side arm leading to vacuum and a connection to a receiving flask. All joints are ground glass. The source of heat on the sample flask is a boiling water bath, and the receiver is immersed in a dry ice acetone bath. The vacuum used is about 1–2 mm Hg.

About 15–20 mL of paint is placed in a 250 mL round bottom one-necked flask. The flask is connected to the adapter containing a thermometer to measure head space temperature, to a vacuum pump by means of vacuum tubing, and also to the receiving flask (50 mL, round bottom, one-neck).

The receiving flask is immersed in a dry ice acetone bath in a Dewar flask. A vacuum is pulled for about 4–5 min with
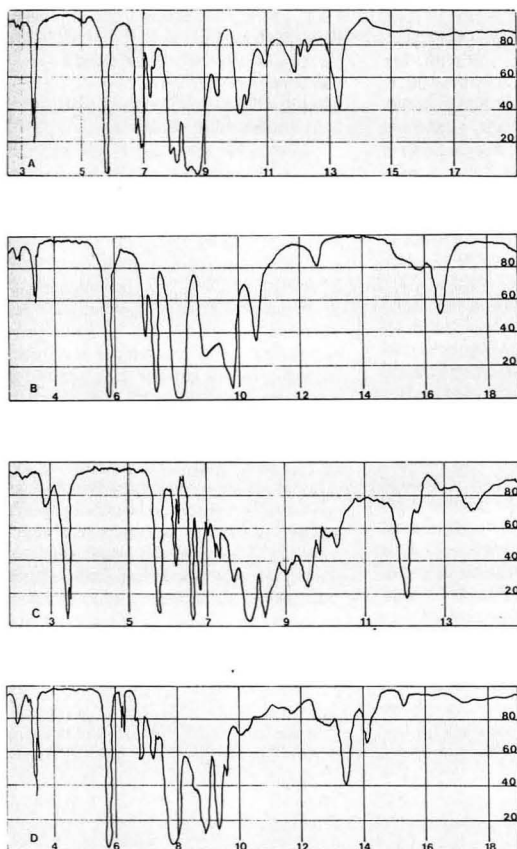
Figure 2—IR spectra of ester-containing polymers. (A) poly-
methyl methacrylate (B) polyvinyl acetate (C) epon ester
(D) phthalic alkyd
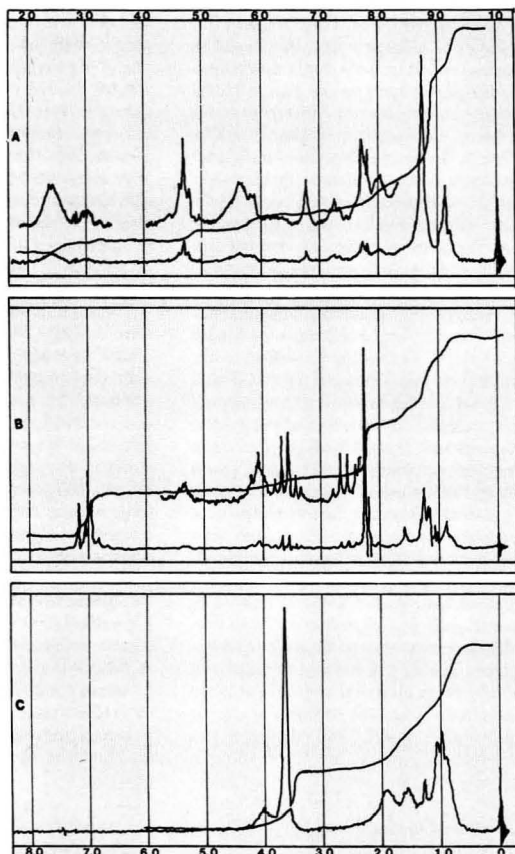
Figure 3—NMR spectra of (A) phthalic alkyd (B) epoxy ester
(C) methyl/butyl methacrylate

no heat on the sample flask. After that
time, the sample flask is immersed in a
boiling water bath and the stripping
continued for another 15 min under
vacuum. Then the heating bath is re-
moved and the vacuum released slowly.
After vacuum is fully released, the
receiver is removed from the cooling bath
and disconnected from the distillation
apparatus. The isolated solvent is trans-
ferred to a plastic stoppered vial and
retained for analysis.

The use of vacuum stripping of the
solvent is not satisfactory in the case
of water-based paints because of the
difficulty of vacuum stripping samples
that contain large amounts of water
leading to the incomplete isolation of
water and whatever water-miscible sol-
vents that may be present.

As a result, the most satisfactory tech-
nique is the dilution of the water-based
paint with THF, thorough mixing, either
allowing the mixture to settle or centri-

fuging to remove the pigment, and then
direct injection of the supernatant into a
suitable chromatographic column. The
same objections to this technique as
stated above apply in this case, but in the
case of water-based paints it is the lesser
of evils. A saving factor is that there are
really a limited number of water-miscible
solvents that are commonly used in such
paints, and as a result, the possibility of
overlap in the use of retention times as a
method of identification is significantly
decreased.

Analysis of Binder

INSTRUMENTAL METHODS: The first
step in the identification of the binder is
generally an examination of the IR curve
of the binder to determine generic type.

In both cases of binder separation,
the solvent and reducing solvent-based
paint, and the extracting solvent in the

case of water-based paint, must be re-
moved to examine the vehicle. This is
done by placing a drop of the solution
on a salt plate and spreading the drop
over the central area of the plate. The
plate is then placed under a heat lamp for
5 min, and heated to about 150°C.

After the salt plate is cooled, it is
placed in an appropriate cell and the IR
spectrum of the binder is obtained. Since
the composition of the binder is of great
importance to end use and performance
of the paint, the information obtained
from the IR spectrum is of prime interest.
The interpretation of the spectrum is in
the final analysis essentially a matter of
experience, but there are several collec-
tions of IR spectra that aid greatly in the
identification of polymer spectra.[1-4]

An examination of the spectrum will
indicate the type of organic functional
groups and resin types (e.g., ester, ether,
hydrocarbon, aromatic, vinyl, nitrile,
urethane, amine resin, nitrocellulose,

etc.). Following a tentative decision on the type of binder present, the use of the various collections of spectra makes confirmation relatively simple. *Figure* 2 illustrates the considerable differences in a series of ester-containing polymers. Obviously, the more complicated the binder system, the more difficult the interpretation. At this point, experience is a definite factor, since knowledge of possible combinations of polymers, as related to end use of the paint, can be used to eliminate many polymer types.

Pyrolysis is another technique that has been shown to be effective in binder analysis.[5-8] The technique involves the controlled rapid heating of the binder to produce degradation of the polymer and permits identification of the pyrolysis products. It is particularly effective in the analysis of acrylic and vinyl polymers by identification of their monomers.

One of the most effective methods of pyrolysis is to deposit a film of the polymer on a wire (Curie Point method) or to place some of the dried polymer on a narrow flat piece of metal. The wire or metal strip is placed in a pyrolysis chamber attached to a gas chromatograph. The wire or metal strip is actually a part of an electrical circuit, and when the circuit is closed, the wire or strip is electrically heated and the pyrolysis products are swept into the chromatographic column, where they are separated. The use of polymers of known compositions establishes retention times of various monomers and allows for quantitation of the technique.

Many polymers do not pyrolyze as cleanly and neatly as acrylics or vinyls, but do, in most cases, give pyrolysis products that are constant in composition under the same conditions. The technique can be extended to such polymers if one has known polymers to use in calibration. The key to pyrolysis is the maintenance of specific conditions. If conditions can be repeated time after time, the technique yields valuable information.

Other instrumental techniques of significant use are two types of nuclear magnetic resonance (NMR): ^{1}H (proton NMR), and ^{13}C NMR. The techniques give information as to the structural configuration of organic compound present, which can be used to determine what and how much of a particular species is present.

^{1}H (proton NMR) gives information about the types of protons present and their environment ($-CH_3, -CH_2,$

$$-\overset{O}{\underset{\|}{C}}-H,$$ phenyl, etc.), and ^{13}C NMR gives similar information but in respect to the carbon atom and its environment. One of the difficulties with ^{1}H NMR is

that due to the relatively high molecular weight of polymers and, thus, their relatively high viscosity in solution, the spectra produced are not of the quality generally available for ^{1}H NMR of low molecular weight, essentially pure compounds. As a result, the interpretation of polymer spectra is impeded due to peak overlap and poor resolution. For this reason, the use of ^{13}C NMR is beginning to come to the fore in the NMR analysis of polymers, since these difficulties are largely overcome.

There are many articles in the literature on the NMR analysis of polymers,[9-13] particularly as applied to acrylic and vinyl polymers, polyesters, alkyds, and polyurethanes. These studies often contain NMR spectra that can be used as references. It would appear that ^{1}H NMR is useful in polymer analysis in the case of relatively simple polymer systems (copolymers, etc.) (*Figure* 3), but more complex polymers and mixtures of polymers yield spectra too complex to interpret satisfactorily. The hope is that ^{13}C NMR will alleviate this problem to a greater extent and allow useful information to be extracted from ^{13}C NMR spectra.

Again, the collection and compilation of NMR spectra of a wide variety of polymers and their mixtures will greatly facilitate the use of NMR in polymer analysis.

CHEMICAL METHODS: One of the chemical techniques that is quite useful is sodium fusion.[14] This technique will show whether the binder contains the elements N, S, halogen, and P. The technique is very old, and the advent of analytical instrumentation has somewhat overshadowed its use. However, the information it yields is very important and relatively easy to obtain.

The presence of Cl, for instance, can confirm the presence of vinyl chloride in a polymer or the use of a chlorinated plasticizer. The presence of F could indicate vinyl fluoride or vinylidene fluoride resin. The presence of nitrogen could indicate an amine resin (urea-formaldehyde and/or melamine-formaldehyde resins), a urethane resin, an amide resin (nylon), a nitrile resin, etc. The presence of S could indicate the presence of polysulfide resin, toluene sulfonamide resin, etc. The presence of P could indicate the presence of phosphate plasticizer, a resin containing a phosphorous-containing polyol, etc.

The strength of a sodium fusion test is that it establishes what elements other than C, H, and O are present, and as a result will verify or eliminate the presence of certain resin systems and greatly aid in identification of the binder.

Of course, the amount of any of the elements found in the sodium fusion test can be quantitatively determined by various methods, and in the case of a small sample, only a few milligrams will suffice for elemental microanalysis.

Another chemical technique, particularly useful in the case of alkyd resins, is saponification. The well known Kappelmeier technique has been well documented,[15] and by using this method one can obtain quantitative values for dibasic acid, fatty acid, and polyol components of an alkyd. General saponification methods reported in the literature[16,17] involve the saponification of the sample and direct injection into a gas chromatograph for complete separation and quantification of the components. Unfortunately, acrylic esters and cellulosic esters do not respond to this technique, but vegetable oils do. The use of acid hydrolysis can also be used, and is reported to be effective in the analysis of both polyurethanes and polyamides.[18] There exists a whole series of chemical tests that may be used to obtain information about the binder. In addition to the use of elemental analysis discussed above to determine the percentages of N, Cl, S, and P, the use of wet chemical analysis can yield information as to the functionality of the binder and its amount.

If the IR curve of the binder indicates a carboxylic acid, an acid number determination can be used to determine the amount. The same is true of hydroxyl functionality using a hydroxyl number determination. The use of an epoxy equivalent determination to determine the equivalent weight of any epoxy resin present in the binder, and an isocyanate equivalent determination to find the isocyanate equivalent weight of a binder containing unreacted isocyanate groups, are just two more among the examples of the use of wet chemical analysis in binder analysis. Amine equivalents and unsaturation equivalents are more examples. Almost any wet chemical method suitable for determination of functionality or equivalence can be used in binder analysis. Some modification may be necessary if evidence from the IR spectra or an elemental analysis indicate that such functionality exists in the binder.[19]

Extraction techniques are very useful, particularly in binders that contain plasticizer. Many vinyl, acrylic, and cellulosic binder systems require the use of plasticizer to give reasonably flexible films. Many of the plasticizers used are esters (phthalates, adipates, benzoates, vegetable oils, epoxidized oils, etc.), but many also include such materials as hydrocarbon oils, chlorinated paraffins, chlorinated polyphenyls, and phosphate esters. In most cases these materials are soluble in such solvents as ethyl ether

and/or hexane, while most polymers are reasonably insoluble in these solvents. It is a simple matter to extract the isolated binder with such a solvent and determine if any plasticizer is present. Obviously, the original examination of the IR curve of the binder will generally give an indication of the presence of a plasticizer, so extraction need not be done unless necessary. The extraction can be done quantitatively, and an IR spectrum is very helpful in its identification. Again, there exist several collections of the IR spectra of common plasticizers which aid in identification.[20-22]

Pigment Analysis

The pigment can be isolated by centrifugation or ashing, depending on the type of paint being analyzed. Once the pigment is separated, several instrumental or chemical methods of analysis may be used, although the chemical methods are rarely used because of time and tediousness of such techniques.

INFRARED:[3,23] As in the case of binder analysis, a fairly rapid, relatively easy method of finding out what pigments are present in the isolated pigment is desired. IR spectra again offer some success, but the fact that most oxides, with the exception of SiO_2, are transparent in the normal IR region($2-15\mu$), present a problem since some of the most commonly used paint pigments (TiO_2, ZnO, iron oxides, etc.) are oxides. But conversely, pigments such as silicates, sulfates, carbonates, chromates, hydrated yellow iron oxide, etc., do have IR spectra that can be used in identification. In addition, the IR spectra of pigments in the far IR($15-40\mu$) do include identifiable spectra for most of the oxide pigments. If such instrumentation is available, reasonable pigment identification can be done by IR.[4] It should be noted that the identification is generally indicative of the anion present and is relatively nonspecific as to the cation present, particularly in the case of carbonates, sulfates, and chromates. Considering the overall advantages and disadvantages of the use of IR spectra, the technique does provide considerable information as to type and amount of pigment present. The use of nujol mull or KBr pellet techniques can be used to obtain pigment spectra.

EMISSION SPECTROSCOPY:[13,24] Because of the general inability of IR spectra to yield information concerning the cations present in the pigment, other techniques are required to obtain this information. One of the older techniques is the use of emission spectroscopy. The technique involves placing the pigment in a high temperature arc or spark, thereby raising the cations to a high energy state and recording the line spectra as the various cations return to the ground state. Numerous characteristic lines are produced for each element, and the spectra are scanned for various elemental lines. As a result, the spectra show what elements are present, and semiquantitatively, the amount of each, with the exception of the elements H, O, C, S, the halogens, and to an extent, P.

Thus, for a pigment mix containing TiO_2, $CaCO_3$, and china clay, the spectra would indicate Ti, Ca, Al, and Si. These data, coupled with IR spectra, which would show silicate, carbonate, and the so called "halo effect" from TiO_2, would fairly well characterize the pigment.

Because of the matrix effect always present in emission spectra (the effect resulting from the influence of other pigments present on the intensity of the particular element spectrum), the method can be used only semiquantitatively without standards. By using standards that closely approximate the pigment to be analyzed, one can obtain quantitative data. The preparation of good standards is somewhat time consuming and tedious and must be performed for each pigment mixture.

X-RAY:[13,24-26] Another technique available to obtain information on the nature of the cations present in the pigment is x-ray fluorescence. Either wavelength or energy dispersive instruments can be used. The technique involves the bombardment of the sample with x-rays and the collection of the characteristic x-rays of the elements present in the sample, which are scattered due to the original bombardment. As a result, the data from the x-ray analysis gives information as to which elements are present. In this technique, both S,P, and the halogens give characteristic emissions, and as a result, the presence of sulfate, phosphate, and halogen-containing pigments can be confirmed. The intensity of the characteristic x-rays emitted gives an indication of the amount of each element present, but as in the case of emission spectroscopy, the matrix effect is again present and standards of composition similar to that of the pigment being analyzed must be used to obtain quantitative data. The matrix effect is limiting in both types of x-ray fluorescence.

Probably the best quantitative technique for pigment analysis is the use of x-ray diffraction spectroscopy. In this technique, because of the crystal structure of each solid compound, a distinctive scattering pattern is obtained for each compound. Large collections of almost every crystalline compound have been compiled and are available for searching in order to identify crystalline solids. The problem present in pigment analysis is that in a multicomponent mixture, such as a pigment mixture, there is the possibility of some overlap in the scattering pattern, making the interpretation somewhat difficult.

One can determine, by the use of one or more of the techniques mentioned above, essentially the individual pigments that are present in the pigment mixture. With this information at hand, an x-ray diffraction pattern of the mixture becomes relatively simple to interpret and can yield a very definitive analysis of the pigment.

CHEMICAL METHODS: The use of chemical analysis of inorganic mixtures can, of course, be used as a basis for pigment analysis. Various schemes are available in the literature[15] for such analyses, generally based on the solubility of various pigments in different acids and acid mixtures. These methods are generally multioperation procedures and are usually fairly tedious and complicated. With the advent of instrumental methods, they have generally fallen into disuse unless the necessary instrumentation is not available.

Solvent Analysis

As stated previously, the solvent of a paint may be isolated from the binder and the pigment by a vacuum distillation, and examined by IR to determine the types of solvents present. The ability to obtain such information is a big advantage as far as subsequent gas chromatographic analysis is concerned, since one does not have to rely simply on retention times from the chromatograph for identification.

GAS CHROMATOGRAPHY:[27-29] After it has been ascertained which solvents are most likely to be present, the solvent is injected into a gas chromatograph containing a column deemed suitable for making the desirable separation of the solvent mixture, and a chromatogram is obtained (*Figure* 4). If it is suspected that the original column choice may possibly result in some incomplete separation or overlap of peaks, the sample can be injected on a different column with different separation characteristics to achieve the desired separation. The area under the various peaks of the chromatogram, along with data obtained on the particular column with regard to the response factors of the various solvents, can be used to give quantitative data on the solvent mixture. The retention times of the pure solvents must be determined on the particular column used in the separation, so that identification of the various peaks can be accomplished.

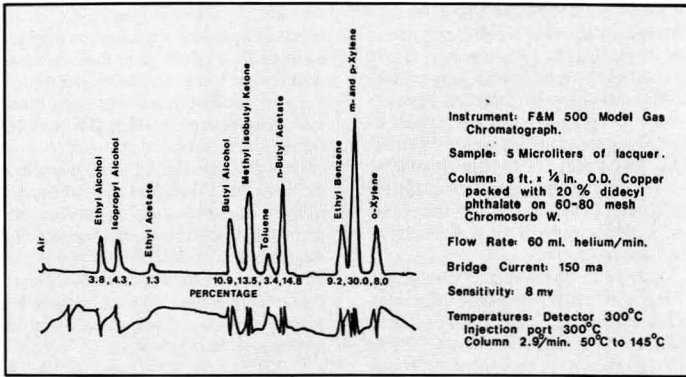Separations are not always clear-cut.

Figure 4—Quantitative determination of solvents in a nitrocellulose automotive lacquer

Often the difficulty is the results of the presence of naphtha solvents. Naphtha solvents are multi-component mixtures of normal hydrocarbons, cyclic aliphatic hydrocarbons, and in some cases aromatic hydrocarbon. Such solvents are widely used in the paint industry and are frequently encountered in solvent mixtures. An examination of a chromatogram of a typical naphtha run on a packed column will contain upwards of 20 peaks, and considerably more on a capillary column. The presence of such a mixture, along with the other components of a solvent mixture, may make quantification of the chromatogram difficult.

SEPARATION: A solution to this difficulty is to separate the hydrocarbon portion of the solvent mixture. This is accomplished by shaking a known volume of the solvent mixture with 80% sulfuric acid. The hydrocarbon portion is insoluble in the sulfuric acid, while any oxygenated solvent will dissolve in the acid. If the shaking of the solvent mixture with the acid is done in a graduated cylinder, the hydrocarbon portion will float to the top. This allows the measurement of the volume of hydrocarbon solvent in the total mixture, and the percent of hydrocarbon solvent present can be determined if the total volume of the solvent mixture used in the separation is known.

In addition, the hydrocarbon portion is easily removed and can be examined by IR to determine if it is an aliphatic or an aromatic naphtha. Also, the hydrocarbon is then reinjected into the chromatograph and its chromatogram obtained. The chromatogram of the hydrocarbon portion can then be compared to the original chromatogram of the total solvent; the peaks related to the hydrocarbon as well as the peaks of the oxygenated solvents present can all be identified. Any skew in the total analysis due to overlap can then be adjusted using the

data from the two chromatograms. Note that this revision is possible only because the total solvent has been isolated from the paint. It is not possible if the direct injection of the total paint is used as a basis for solvent analysis.

Isolating the oxygenated solvents from the sulfuric acid is not possible because the strong acid has a very deleterious effect on these solvents. A technique has been used at PPG that at least partially removes some of the oxygenated solvents from a mixture containing both oxygenated solvent and naphtha. It is not quantitative and works best for such oxygenated solvents that have at least some water solubility (alcohols, alcohol ethers, certain esters, and most of the common ketones).

A portion of the isolated solvent is put in a vial and an equal volume of distilled water is added. The vial is stoppered and shaken on a wrist type shaker for about 15 min. The mixture is transferred to a separatory funnel and the mixture allowed to separate. The top layer will contain any naphtha plus a portion of a oxygenated solvent that remains in the hydrocarbon phase. The lower layer contains H_2O and any H_2O-soluble oxygenated solvents.

After the mixture has separated, the lower layer is withdrawn from the separatory funnel into a long, narrow vial. Potassium carbonate is added to saturate the water, the vial is stoppered and shaken vigorously. The oxygenated solvents will separate from the water and form a top layer, which can be removed with a micropipet. IR spectra and a chromatographic separation can be used to yield further information on the oxygenated solvents present.

Obviously, the original IR spectrum of the isolated solvent can be used to detect
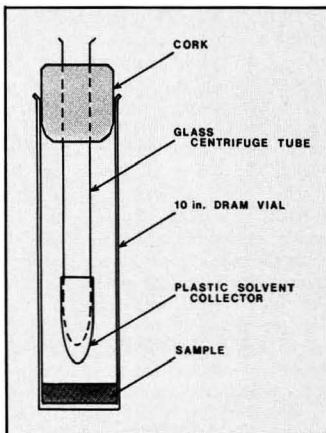

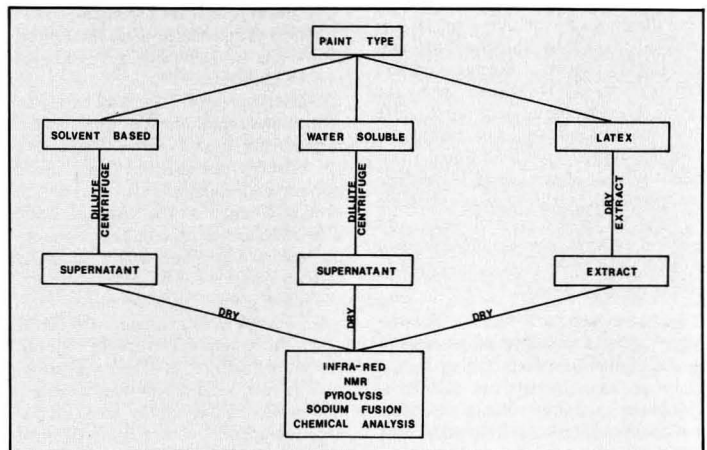Figure 5—Simplified solvent distillation apparatus

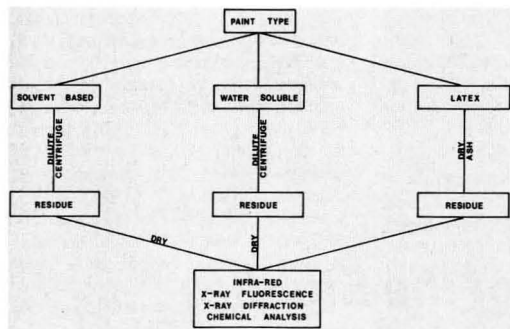

Figure 6—Scheme for binder analysis
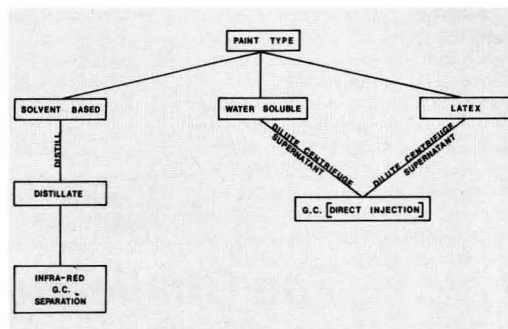
Figure 7—Scheme for pigment analysis

Figure 8—Scheme for solvent analysis

the presence of naphtha in the total solvent, and if not present, the preceding is not necessary.

SIMPLIFIED SOLVENT SEPARATION: The isolation of the solvent from the total paint by vacuum distillation is of great help in the solvent analysis, but is time consuming and somewhat meticulous, and the clean-up of the sample flask is laborious. Therefore a simpler method of solvent separation was sought.

An apparatus (*Figure 5*) was devised that required a heating block, 10-dram disposable vials, a small glass centrifuge tube which serves as a cold finger, and a plastic centrifuge tube which fits over the cold finger to collect the solvent.

The heating block, which can be heated to 150° C, is drilled to contain a hole into which the 10-dram vial can be placed. About one inch of the vial is surrounded by the heating block. The glass centrifuge tube is fitted into a one-hole cork so that it can be suspended into a 10-dram vial about ½ in. above the bottom of the vial. The plastic centrifuge tube is cut and slotted so that it fits over the end of the glass centrifuge tube to catch the solvent when it is volatilized.

About 2 mL of the paint sample is placed in the vial, and the glass centrifuge tube containing the plastic collector is suspended in the vial by means of the cork stopper. The centrifuge tube is filled with crushed ice and the vial is inserted into the preheated block. The solvent volatilizes, and some of it condenses on the cold finger and drips into the plastic collector.

After 15 min, the vial is removed from the heated block. The apparatus is disassembled and the solvent is recovered from the collector with a micropipet. About two drops of the collected solvent is placed on salt plates and the IR spectrum is obtained. The remaining solvent is transferred to a small septum vial and used to obtain a gas chromatograph of the solvent.

In all, about 0.25 mL of solvent is collected, although somewhat more could be collected by using a larger collector. This is certainly sufficient for IR and gas chromatographic analysis. At present, work is underway to establish if the technique provides a quantitative solvent separation. This is done by subjecting the paint in question to solvent separation by both vacuum distillation and the above technique. Preliminary work indicates reasonable success in most cases, but paints containing very high boiling solvents may present a problem.

Conclusion

The analysis of a paint sample is predicated on the separation of the primary parts, the identification of the components of each part and the quantification of the components within each part (*Figures 6-8*). Methods (primarily instrumental) are suggested for the separation processes and techniques, and are described for identification and quantification. As in most endeavors, experience comes with time and practice, and the seemingly complicated becomes relatively simple.

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The Challenges of the Eighties
In Coatings and Graphic Arts

Harvey F. George
Gravure Research Institute*

This is a meeting of coating experts. My personal background is in the graphic arts or printing. We will focus here on the major challenges that will face the printing industry and to large extent your industry, in the next decade or next two decades. Printing and coating both deal with the controlled application of substances to surfaces. Thus, some of the developments that will be discussed are applicable to printing as well as coating. Common challenges are related to environmental concerns and the energy and oil situation. Challenges that are specific to printing are the result of the revolutionary advances in electronic image manipulation and transmission technology which now affect the preparatory end of the printing industry. Even here there is a crossover of new technology such as in computerized color matching.

Environmental concerns have taken solid roots within the American electorate as a whole. Every time there is trouble with a dump site or atomic installation, those concerns are reinforced across the board. As job holders, consumers and taxpayers, the same voters are by and large conscious of their stake in industrial productivity, employment and the need to control costs and inflation. These concerns are not lost on elected officials or those who hope to be elected, and are reflected in existing legislation governing the drafting of environmental rules and guidelines as well as in the current campaign rhetoric. As an

example, the Federal Clean Air Act, including the Amendments of 1977, is a 181-page document that charges the EPA to prepare detailed documentation regarding the impact of any guidelines or regulations on cost, energy consumption and employment.

Federal, state and local regulatory agencies cannot have the detailed technical expertise to draft realistic rules or guidelines without industry input for every industry that may be regulated. This expertise exists in the industry. Thus, the Clean Air Act spells out the requirement for hearings and time periods for comment by environmental groups, industry or employees whose jobs are adversely affected. It is essential that members of the technical staff of plants which may be affected, are aware of the rules and guidelines which are in the drafting stage and that they attend the hearings. The industry positions that are presented to the agencies, preferably through recognized industry associations like your own, should be well organized and documented on technical grounds. This is a time-consuming and costly task but lacking this effort the final regulations may well reflect the overly optimistic opinion of some manufacturers of emissions or effluent control equipment or the record-breaking performance of a plant not typical of the industry as a whole.

There are similarities between coating materials and printing inks as far as materials and their method of manufacture are concerned. By comparison with coating, the printing processes themselves impose certain restraints which have to be reflected in emission control legislation. Webster's dictionary defines

"coating" as "to cover with a finishing, protecting or enclosing layer." Judging by your own trade press, the range of materials used for coatings and the methods of application is very wide indeed. The same dictionary gives some examples of the usage of the word "print", usually having to do with pressure. Printing is simply defined as "the act, art or practice of a printer." This act, art or practice of a printer implies the transfer of ink from a form to paper or some other substrate, to form type or images of high resolution and controlled optical density and color tone values. In process color, the individual color values are synthesized by the controlled overprinting of dots of the subtractive primary colors. The printing copy is usually changed every few hours or days. All these requirements place severe restraints on the chemical composition and rheological state of the inks at the time of printing. Control of emissions from coating operations is based on such documents as the Federal EPA OAQPS Guidelines "Control of Volatile Organic Emissions from Stationary Sources— Volume II, Surface Coating of Cans, Coils, Paper, Fabrics, Automobiles and Light Duty Trucks" of May 1977.[1] These guidelines, with their heavy emphasis on water borne and high solids coating are just not applicable across the board to the printing industry.

The major printing processes are letterpress, offset lithography, gravure and flexography. Other less used printing processes include screen printing or serigraphy, electrostatic printing and ink jet printing.

The printing industry is characterized by the large number of firms, close to

50,000, who manufacture printed products. This makes printing the largest of all manufacturing industries, in terms of the total number of establishments. However, most of these are small companies. Only 18% employ 20 or more employees and the larger firms, with 100 or more employees, number approximately 2,000 or 4% of the industry total. Most of what we discuss here will relate to these larger firms who produce the bulk of the printed products as well as contribute most of the controllable emissions and effluents to the environment.

The EPA initially tended to lump gravure printing and flexography with coating. Vigorous objections that could be substantiated on technical grounds were raised by individual printers, ink makers and the printer's technical associations, such as the Flexible Packaging Association, the Flexographic Technical Association and the Gravure Industry Emission Control Committee. This Committee, of which I am Chairman, is jointly sponsored by the Gravure Technical Association and the Gravure Research Institute. As the arguments were in the technical area and GRI has an experienced scientific and engineering staff familiar with gravure printing, GRI had to do the largest share of the work in coordinating this effort and had to provide technical support. The OAQPS Guidelines "Control of Volatile Organic Emissions From Existing Stationary Sources—Volume VIII: Graphic Arts, Rotogravure and Flexography"[2] were issued in December, 1978 and followed by a section in an EPA document "Guidance to States and Local Agencies in Preparing Regulations to Control Volatile Organic Compounds From Ten Stationary Source Categories"[3] of September 1979. This latter document also contains compliance schedules. These compliance dates can be postponed by the states if a printer can show that he needs more time to develop new control technology.

The EPA guidelines to the states specify the following emission reductions:

(A) Publication gravure using solvent blend inks:

    75% overall emission reduction
    90% efficiency of the solvent recovery or equivalent control system
    75%–85% capture efficiency

(B) Packaging gravure using solvent based inks:

    65% overall emission reduction
    90% efficiency of the solvent recovery or equivalent control system
    75%–85% capture efficiency

(C) Flexography using solvent based inks:

    60% overall emission reduction
    90% efficiency of the solvent recovery or equivalent control system
    65%–75% capture efficiency

Alternate methods of compliance with RACT guideline can be achieved by either of the following methods: (1) Using water borne inks where the volatile portion contains 75% or more water and 25% or less organic solvent; and (2) Using high solid inks with a 60% or greater nonvolatile content by volume. This percent is calculated after the water is removed. It is also specified that "all units of a machine which has both coating and printing units will be considered to perform a printing operation. A typical operation is as follows: The first unit applies a uniform background color; subsequent units print additional colors; the final unit applies a varnish overcoat."

The LAER (Lowest Achievable Emission Rate) guidelines for new sources in non-compliance areas specify figures generally 5% more stringent than those cited above.

Specialty printers are those that do not fall into the publication or packaging categories. This includes the printing of wallpaper, woodgrains, high pressure laminates, floor coverings, shower curtains, decorative wrapping paper, paper cups and plates, paper napkins and even part of the postage stamp production by the U.S. Department of the Treasury, Bureau of Engraving and Printing in Washington, D.C. These are not mentioned in the above guideline documents—we assume due to an initial oversight—but now the EPA wants to apply coating guidelines. Freedom from objectionable odors and non-toxicity are as important for paper plates and postage stamps as they are for many packaging products. Besides the difficulty of drying water base inks on non-absorbent substrates, the high surface tension, even of water containing liberal amounts of additives, prohibits the printout of a smooth ink layer on most films. Further, the coating guidelines specify emission control in terms of coating formulation parameters, i.e., volatiles in pounds per gallon of coating which is completely unsuited to gravure printing operations with their high dilution ratios and minimum film thickness. As matters now stand, the EPA position regarding specialty printing creates a great deal of uncertainty. However, our committee has persisted in its efforts to get EPA to change its unreasonable position and we expect shortly that an EPA memorandum will be sent by the Control Pro-

grams Development Division to the EPA Regional Directors and through them to the various states, reversing their present position and indicating that specialty gravure is to be treated under the RACT guidelines for graphic arts.

"New Source Performance Standards For Publication Rotogravure" are scheduled to be published in the Federal Register this week. After publication the industry has 60 days for comment. The standards, which apply to new press installations and additions of press units to existing presses, are to reflect the capabilities of the state of the art vapor collection and control technology. For publication gravure, usually operating with solvent blends consisting of toluene and aliphatic hydrocarbons, this means activated carbon solvent recovery and steam regeneration of the solvent beds. The solvents are not water miscable and can be separated for reuse from the steam condensate by decanting. The EPA surveyed data from most existing plants and questioned manufacturers of emission control equipment. This may have resulted in excessively high expectations regarding efficiency and cost effectiveness. The EPA and their contractor then ran weeklong tests at two plants. GRI engineers were running parallel tests. As a result of data from one plant, the EPA was inclined to require that 90% of the solvent going into the fountains as part of the ink used for ink dilution and evaporation makeup as well as solvent used for press cleanup, be recovered. As a result of the parallel tests we found some oversights in the EPA data, such as lack of temperature correction on a meter and infiltration of vapors from the other pressroom. The EPA retested the pressroom in question and collected more plant data and we expect a combined collection and recovery requirement of 84%.

Future advances in plant engineering will be fundamental. Compliance with environmental regulations on hazardous waste, waste water treatment and above all, air emission control, will require highly competent professional staff. For efficient solvent recovery or incineration, vapor concentrations in dryers or ducts should be in the 1,500 to 3,000 ppm range. Even with widely varying ink coverage on the substrate from job to job, peak concentrations must stay below limits set by safety considerations and the underwriters. Concentration monitoring equipment requires periodic maintenance and recalibration by competent personnel. Recovered publication solvents can usually be reused after decanting with minor adjustments. Most packaging solvents are more corrosive to

the solvent recovery and have to be redistilled to separate solvent from the desorption steam condensate. With the rise in solvent cost, recovery where applicable, is probably the most effective way of controlling emissions. Solvent recovery is however, a heavy user of steam and reductions in steam consumption depend on the way the plant is operated as well as on design. Efforts to recover low temperature heat from the solvent recovery or regenerative incineration for use in press dryers, general purpose or boiler feed hot water and space heating have been successful. A boiler system is under construction that burns low grade bindery waste with a high ash content to supply the base heat load for a large printing plant. Most large printers have energy supply programs with alternative fuel supplies and conservation measures.

As for ink developments in the 80's, the type of inks that will probably emerge in the paste ink category for compliance with emission regulations include high solids heat set inks, ultra-violet curing inks, electron-beam curing inks, infrared setting inks and chemically reactive inks.[4,5] In the liquid ink category water base inks have been on the market for many years but were usually limited in application to less demanding segments of the market such as household paper products, corrugated board and paper bags. The pressures of environmental regulations and the energy and oil situation are now motivating the development of water base inks for the more sophisticated market segments. Rotogravure newspaper supplements are now being printed with water base inks on an increasingly frequent basis. More sophisticated packaging and specialty gravure products are also being produced with aqueous inks. The outlook for increased use of water base inks in gravure and flexography is very good. The prospects for high solids inks or low solvent technology for gravure and flexography are not nearly as optimistic. This is recognized by EPA which in its approval of delayed compliance plans is allowing up to five years additional time for the development of the new ink technologies. Among the candidates are catalytic inks or two part systems and radiation curable inks sensitive to the same radiation sources mentioned above for paste inks, except with liquid inks the low initial viscosity requirements, particularly in gravure, make the curing problem all the more difficult at high speeds. The use of heated fountains can provide some assistance but considerable research by ink and coating suppliers will be required before viable systems are on the market. In my own opinion, as more and more printers install add-on devices such as incineration and solvent recovery to meet compliance deadlines, and as water base inks become more prevalent, there will be less incentive for these sophisticated high solids systems to be developed. I do expect, for gravure at least, that they will not capture a significant market share except perhaps for top coatings and other special applications.

The challenges of rapidly evolving new technology, particularly in electronics and data communications, as well as the constraints of environmental regulations and energy and materials availability, will require that printers and suppliers of printing and coating materials keep well informed of these developments, plan, and respond as required. I am confident that this will be the case and that the future of the coatings and graphic arts industries will be both exciting and bright.

References

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(2) "Control of Volatile Organic Emissions From Existing Stationary Sources—Vol. VIII: Graphic Arts—Rotogravure and Flexography" EPA-450/2-78-033, OAQPS No. 1.2-109, December 1978, Research Triangle Park.

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(4) Bassemir, R. W., "Ink Technology For Coated Paper—Developments For The 1980's," *TAPPI*, (Jan. 1980).

(5) Funk, E. T., "Radiation—Curable Inks—The Concept of High Solids Content and Impact on EPA Regulations," *ibid.*, (Sept. 1980).

United Kingdom Orders of FSCT Educational Literature

In the United Kingdom, Federation publications and other industry aids are available from the Birmingham Paint, Varnish and Lacquer Club. Please contact: Mr. Ray Tennant, Carrs Paints Limited, Westminster Works, Alvechurch Rd., Birmingham B31 3PG, England.

Society Meetings

Baltimore Society—
Virginia Section   December 10

Rich Johnson, of Cargill, Inc., spoke on "WATER-REDUCIBLE AND HIGH SOLIDS COATINGS."

CARL MINCHEW, *Secretary*

Birmingham   Dec. 4

Mr. P. Green, of Binks Bullows Ltd., presented a talk on "High Speed Electrostatic Discs and Bells."

High speed electrostatic equipment, when used on automotive production lines, has been shown to give better standards of finish and greater economies than other electrostatic application methods. Mr. Green pointed out that many of the limitations normally associated with electrostatic paint spraying are reduced, allowing a wider range of materials to be used.

Mr. Green described the various methods used. Originally, electrostatic charge was applied by directing a conventional spray gun towards the grounded workpiece via a charged grid. Later, he said, the Ransburg No. 2 gun was employed using centrifugal force to throw the paint off the rotating head, while high electrostatic forces caused atomization of the paint particles. Such methods, now known as Low Speed Electrostatic applications, had certain limitations such as resistivity, viscosity,

and surface tension. Because of these, some paints (e.g., water-based) are not suitable for Low Speed Equipment.

According to Mr. Green, many equipment manufacturers have therefore worked to develop High Speed Equipment. He said that when rotational speeds exceeded 15,000 rpm centrifugal forces contributed directly to the degree of atomization.

Using slides, Mr. Green described the equipment and discussed its advantages and limitations. A series of graphs depicted the effects of various parameters on the size of atomized particles. Increasing the rotational speeds gave smaller particles while lower speeds increase particle size. Also, the resistivity and viscosity of materials was found to be less critical with high rotational speeds. Therefore, component paints, acrylics, and water-borne paints could all be applied by this method, he said.

Mr. Green concluded the presentation with a film showing the British Leyland "Mini Metro" line which demonstrated the versatility of the equipment. In the future, Mr. Green said, robotics will play an important part in the efficient application of paints.

Q. Since electrostatic forces represent only 1% to 2% of atomization, why is a charge necessary?

A. To improve transfer of particles to the object. Shroud air is only to limit

sideways spread. British Leyland achieves 85% utilization with High Speed guns.

Q. Can the same paint mixture be hand sprayed or will the high boiling solvents necessary for H.S.E. be a problem?

A. Paint from the same pots can be used for hand touch-in operations. Alkyds applied on the 'Bounty' line are used like this.

Q. Does low resistivity give problems?

A. Some metallics work well, although loss of voltage caused by tracking to earth can be a problem. Insulation of the pressure pot could overcome this.

Q. What is the function of the serrations on the disc?

A. An aid to atomization. Paint comes off the head in a sheet and is broken up by statics. Serration breaks the sheet into strings which are then split into discrete particles.

Q. Since higher speed of rotation leads to drier films, can H.S.E. be used for spraying polychromatics or hammers which really need a wet surface to achieve full effect?

This has never been tried. The slower bells are still available for such work.

Q. Can powders be applied by this method?

A. No. Better means are available.

Q. What type of programming method was used for the robotics on the 'Metro' line?

A. V.D.U. and keyboard. The articulator copying method was not used.

Q. Could the differences in particle orientation caused by electrostatics give rise to problems in the Quality Control of polychromatics applied by H.S.E.?

A. Non-metallic polychromatic finishes might be an answer. The application of a final coat by non-electrostatic means might be another. The effect is not unknown in straight colors and variations are accepted.

M. GRIFFITHS, *Publicity Officer*

Mexico Society Officers for 1980–81. Seated (left to right): Secretary—Teresa Suarez; President—Rogelio Cuellar; and Vice-President—David Juarez. Standing (left to right): Past-President—Roberto Garcia; Member-at-Large—Alejandro Garnica; Member-at-Large—Antonio Diaz; Treasurer—Pedro Romero; and Member-at-Large—Salvador Gallardo

Chicago   Jan. 5

Dr. Andrew Mercurio, of the Rohm & Haas Co., presented "AQUEOUS GLOSS ENAMELS." A presentation entitled, "ENZEMATIC RESISTANT HYDROXY ETHYL CELLULOSE," was given by Dr. Edward Glass, of North Dakota State University.

L. F. KINNEY, *Secretary*

Cleveland   Jan. 22

Dr. S.T. Krotine, of The Sherwin-Williams Co., discussed his role as Vice-President of research and development and commented on "THE PRESENT CLIMATE OF THE INDUSTRY AND ITS FUTURE."

Mr. Krotine, in regard to the industry's innovation, said that innovative research is really the creation of new knowledge; where the basic research is taken through development, pilot plant, market development, and on to the market place. Innovation is effected by both productivity and capital formation. Research and development should help to increase productivity.

Mr. Krotine also discussed the nation's energy and petroleum dependence. He said that the coatings industry uses only .025% of the total of the oil and gas. If one removes the water from coatings, an average of 40% of the material remaining depends directly or indirectly on petroleum. According to Krotine, there are two issues in energy: one is cost and the other is availability.

With regard to industry regulation, Mr. Krotine felt that the 1970's was a period of legislation and interpretation; the 1980's will be a time of enforcement. The coatings industry will remain the target industry; however, this does provide an opportunity for change in product application. In the 80's, he said, the changes will be in the industrial plants regarding wastes.

CARL J. KNAUSS, *Secretary*

Dallas   Jan. 15

Mike Markowitz, of Rollins Environmental Services (Texas), spoke on the subject of "WASTE DISPOSAL."

According to Mr. Markowitz, recovery for reuse of waste streams is the first priority, but if wastes are produced which cannot be recycled after concentrating, then it is necessary to comply with the RCRA Act regulations and agencies. In Texas, the agencies include the EPA, DOT, and the Texas Department of Water Resources. A slide presentation depicted the illegal disposal at the Love Canal, abandoned liquid mixtures, and abandoned drum sites.

WILLIAM A. WENTWORTH, *Secretary*

Kansas City   Jan. 8

Russell Koch, of Universal Color Dispersions, gave a talk and slide presentation on "THE WONDERFUL WORLD OF COLOR."

Mr. Koch said that it is not unusual for a coating manufacturer to use 24 differ-

Louisville Society Officers for 1980–81. Left to right: Treasurer—Fred E. Newhouse; President-Elect—Philip W. Harbaugh; Society Representative—Joseph A. Bauer; President—John K. Menefee; Secretary—John A. Lanning; Past-President—Gary W. Gardner

ent prime pigments in order to produce a wide range of colors. If a company produces 11 different generic-type coatings, this would result in (11 generics $\times$ 24 pigments) 264 colorants that would have to be produced and stored.

It is becoming more and more economical for a coatings manufacturer to explore the possibility of replacing many of their various generic-type colorants with universal dispersion, Mr. Koch explained. There are color dispersions available today that are compatible with different generic-type coatings. It, therefore, may be possible to replace as many as 264 colorants with only 24 universal color dispersions, according to Mr. Koch. He pointed out that manufacturers must check color dispersion compatibility with their own generic formulations before a decision is made.

MIKE BAUER, *Secretary*

Los Angeles   Jan. 14

A presentation entitled, "EXTENDERS, THE INORGANIC BACKBONE OF FLATS AND PRIMERS," was given by Tom Brown, of Engelhard Minerals and Metals Corp.

Mr. Brown stated that there are three names describing the materials found within the title extenders: extenders, fillers, and inerts. He then discussed the characteristics of extender pigments. They included: inorganics, natural, crystal structure, particle size distribution, shape, surface chemistry, surface area, and porosity. Mr. Brown then compared the criteria for formulations of flats, semi-gloss, and gloss paints with respect to inerts.

According to Mr. Brown, the paint industry is the second largest user of extenders. The greatest sales volume is

Officers of the C-D-I-C Society for 1980–81. Left to right: Past-President—Robert Broerman; President—W.J. Frost; and Past-President—Lloyd Reindl. Standing: Vice-President—Robert D. Thomas; Council Representative—William Mirick; Treasurer—Robert A. Burtzlaff; and Secretary—Nelson W. Barnhill

found with clay; calcium carbonate is second. He predicted that extender usage will increase in the 80's.

A discussion of various extenders followed which included kaolin, carbonates, talcs, natural silicas, and synthetic silicas.

Mr. Brown concluded with a discussion of the difficulty of making mathematical considerations for multi-pigment, multi-extender latex systems. He offered a practical, simple guide for the formulator. He suggested using the seven-step approach for the selection of extenders and determining the amounts. These steps are: (1) shape, (2) size, (3) volume, (4) rhelogical effect, (5) special requirements, (6) dispersion, and (7) CVPC calculations.

Q. What method do you use to determine particle size distribution? Does the pigment or extender industry work on a standardized method?

A. Sedimentation method. There is no standard method.

L. LLOYD HAANSTRA, *Secretary*

Louisville   **Jan. 29**

A presentation entitled, "NEW APPROACHES TO WATER BORNE EPOXY PERFORMANCE," was given by Clifford Dukes, of Celanese Resins Division.

Mr. Dukes described three water borne epoxy systems compared to a standard organic solvent based polyamide cured epoxy for performance. All three of these systems meet C.A.R.B. numbers for VOC less than 250 grams per liter. Two of the systems utilize an epoxy/amine curing mechanism while the third uses an epoxy/carboxy acrylic cure mechanism. He concluded the presentation by showing data concerning weatherability, pigmentation, compatibility with hydrophobic extender, and economics, indicating that overall performance of water-borne epoxies is comparable to existing solvent based systems.

JOHN LANNING, *Secretary*

New York   **Jan. 13**

Gabriel Malkin, Consulting Engineer, presented "VENTILATION IN A PAINT PLANT."

He began by describing the problems found by OSHA and EPA. The various aspects of ventilating in a paint plant were presented. Mr. Malkin concluded his talk by discussing the many faults in intake and outlet ventilating systems and described ways to correct them.

TED YOUNG, *Secretary*

Piedmont   **Jan. 21**

Elio Cohen, of Daniel Products Co., discussed "FACTORS GOVERNING TINTER PERFORMANCE."

A brief history of tinting colors was discussed. Mr. Cohen then presented five factors governing tinter performance. These included: (1) the dispersing medium, (2) pigments, (3) solvents, (4) dispersing equipment, and (5) tinter interactions.

SARA ROBINSON, *Secretary*

Rocky Mountain   **Jan. 12**

Tom Brown, of Engelhard Minerals and Metal Corp., spoke on "EXTENDERS, THE INORGANIC BACKBONE OF FLATS AND PRIMERS."

The presentation was divided into three subjects: first, existing products in the extender area which are appropriate for paints; second, a brief synopsis of the technical concepts that apply to extenders; and third, a series of seven suggestions for formulators in terms of the application of extenders in paint products.

DONALD R. BAGGE, *Secretary*

Future Society Meetings

Baltimore

(Apr. 16)—Education Committee program.

(May 21)—Technical Steering Committee program on PAINT APPLICATION METHODS.

Birmingham

(Apr. 2)—"SOME ASPECTS OF AMINO RESINS"—J.E. Sreeves, B.I.P. Ltd, Chemical Div.

(May 7)—"COATING WINDOW FRAMES"—G.W. Rothwell, Building Research Establishment.

Chicago

(Apr. 6)—FSCT SLIDE SHOW—Federation Officers; "MULTI-FUNCTIONAL EPOXIDES"—M. Gaschke, CIBA-Geigy Corp.

(May 9)—AWARDS NIGHT. Installation of 1981–82 Officers.

C-D-I-C

(Apr. 13)—PLANT TOUR of Battelle Memorial Institute.

(May 11)—"PIGMENT DISPERSION AND MILLING IN THE PAINT AND RELATED INDUSTRIES"—Edward Carter, Morehouse Industries, Inc.

Houston

(Apr. 8)—"CHLORITE: A NEW FAMILY OF PAINT EXTENDERS"—William Meadows, Cyprus Industrial Minerals.

Los Angeles

(Apr. 8)—"POLYMERIC ORGANIC DISPERSANTS FOR PIGMENTS: PRINCIPLES AND PRACTICES"—Robert D. Athey, Jr., Swedlow, Inc.

(May 12)—"PLANT DESIGN: BUILD NEW—REDESIGN OLD"—Jim White, Hockmeyer Equipment Corp.

Montreal

(May 7)—PAST-PRESIDENTS' NIGHT
(May 9)—50TH ANNIVERSARY BALL. Ritz Carlton Hotel

New York

(Apr. 14)—"DISPERSION EQUIPMENT" —Panel Discussion.
(May 12)—PAVAC AWARD NIGHT.

Philadelphia

Technical Committee Meetings

(Apr. 2)—"NEW GENERATION COATINGS—APPLICATION WORKSHOP: PART II—TWO COMPONENT AND POWDER"— speakers from Mobay Chemical, Polymer Corp., and Nordson Corp.
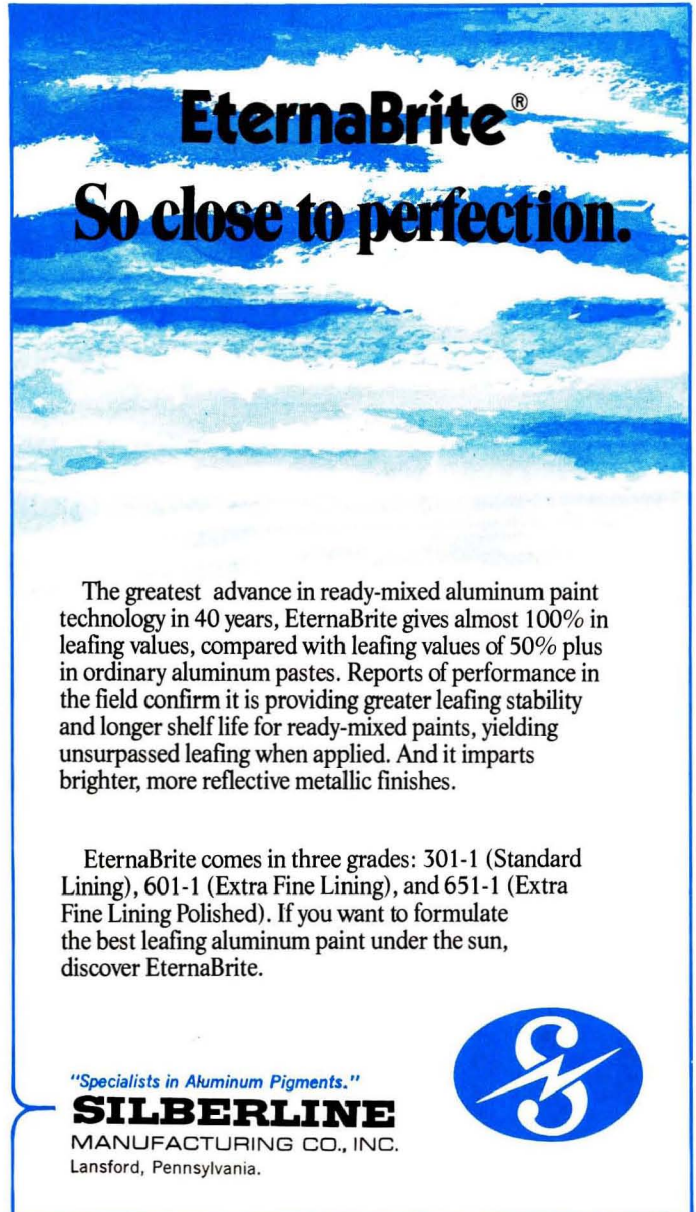
(May)—Society Technical Committee Seminar on "INTERFACES REVISITED."

Pittsburgh

(Apr. 6)—"KNOW YOUR ENEMY— THE WEATHER"—George W. Grossman, The Q-Panel Co.

(June 1)—"ART AND ALCHEMY"— John C. Pavlik, Fisher Scientific Co.

Elections

BIRMINGHAM

Active

PLANTE, ANDREW C.—Carrs Paints Ltd., Westheath, Birmingham, England

TYE, TERENCE T.—Carrs Paints Ltd., Westheath.

YATE, M.J.—Inmont Ltd., Wednesfield, Staffordshire, England

LOS ANGELES

Active

AGIN, ROBERT W.—Tnemec Co. of Cal., Inc., Compton, CA

ALY, M. MOSELHY—Edoco Technical Prod., Long Beach, CA

ARAKAWA, BARON M.—Custom Bldg. Products, Bell, CA

BLACKBURN, ROY E., JR.—Western Spec. Coating, Los Angeles, CA

BRAITBERG, HYMAN D.—Deft, Inc., Irvine, CA

BRUNSMA, STEVE—Ameritone Paint Corp., Long Beach.

CHENG, CHI HUA—Essex Chemicals, La Mirada, CA

CHERN, TSUEY F.—Cargill, Inc., Lynwood, CA

CLARK, DENNIS S.—Harshaw Chem. Co., Sylmar, CA

CURADO, A.L.—Old Quaker Paint Co., Carson, CA

CUSICK, GARY—Silco Coatings Co., Ontario, CA

DESILVA, DODWELL P.—McCloskey Varnish Co., Los Angeles.

FLORIANI, ROBERT J.—Deft, Inc., Irvine.

FRASCA, LEONARD V.—Harshaw Chemical Co., Sylmar.

FUENTES, GILBERTO—Universal Paint Corp., Industry, CA

GEORGE, DONALD J.—Edoco Technical, Long Beach.

GILLETTE, ANDREW H.—Major Paint & Varnish, Torrance, CA

GRAY, DAN—Ameritone P.T. Corp., Long Beach.

GUERRA, JOHN—Major Paint, Torrance.

HOLMES, FRANK D., SR.—Whittaker Coatings, Colton, CA

IMADA, RANDOLPH H.—Evr-Gard Coatings Co., Paramount, CA

JENKINS, V.C.—Consultant, Irvine.

KAPADIA, SAILAN, J.—Zolatone Process, Inc., Los Angeles.

KAY, CARL J.—Products Research, Glendale, CA

KING, FRED B.—McCloskey Varnish Co., Los Angeles.

KIRAKOZ, YOUSIF D.—Deft, Inc., Irvine.

KUNDALKAR, BHAGYASHREE R.—Sinclair Paint, Los Angeles.

LANDER, ARTHUR G.—Custom Building Prdts., Bell.

LI, TEH C.—Aerospace Corp., Los Angeles.

MAY, ROBERT D.—Mero Corp., Baldwin Park, CA

MINAMYER, MARK A.—Ameritone Paint, Long Beach.

MORALES, EZEQUIEL—Pinturas Calette S.A., San Ysidro, CA

NANO, VICTOR N.—Koppers, Inc., Los Angeles.

ORTEGA, FRED—C.H. Tripp Finishing Co., San Diego, CA

PALACIOS, EDUARDO R.—Harshaw Chem. Co., Sylmar.

PHONG, DAVID—Leeder Chemicals, Inc., La Mirada.

RICARDO, TEANO—National Paints, Inc., Los Angeles.

ROACH, RALPH M.—Tnemec Co. of Cal., Inc., Compton.

ROSENFELD, NORMAN—Chemical Technology Labs., Lynwood.

SALTZMAN, MAX—Consultant, Color Tech., Los Angeles.

SANDOKE, ALPHEWS—Modern Coatings, Inc., Cerritos, CA

SCHNEIDER, CHARLES W.—Chemical Technology Labs, Lynwood.

SCHNEIDER, RAYMOND S.—Reichhold Chemicals, Azusa, CA

SHAW, TIMOTHY J.—Hill Brothers Chemical, City of Industry, CA

SOKOLIN, STUART—Ameritone Paint Corp., Long Beach.

STARK, RON—Intl. Animated Film Soc., Agoura, CA

TERAN, IVAN—PPG Industries, Torrance.

TORRES, CHARLIE—Textured Coatings, Los Angeles.

VAN ZELM, JAN P.—Byk Mallinckrodt, Redondo Beach, CA

VATZ, JAMES—Bostik West, Marina Del Rey, CA

Associate

ALLEX, STEVE—E.T. Horn Co., La Mirada, CA

BERG, JERRY—Badische Corp., Diamond Bar, CA

BOLLENBACH, DENNIS—Celanese Plastics, Los Angeles, CA

BREDE, WALLACE—Spencer Kellogg, Long Beach, CA

CARTER, EDWARD—Morehouse Industries, Fullerton, CA

COURTAIN, ROCKY A.—Morehouse Industries, Fullerton.

DICKINSON, RANDY J.—E.T. Horn, La Mirada.

DICKMAN, ROBERT F.—Spencer Kellogg, Long Beach.

GOODWIN, DENISE R.—Union Carbide Corp., Long Beach.

JACKSON, WHARTON—Wharton Jackson & Sons, Laguna Beach, CA

KIM, KEITH—Int'l Minerals & Chem. Corp., Los Angeles.

LEON, PETE—Union Camp Corp., Orange, CA

MITTELMAN, ELKIN S.—Western Paint & Decorating, North Hollywood, CA

O'FARRELL, ROLAND—Cargill, Inc., Lynwood, CA

OLQUIN, LITA M.—John K. Bice Co., Inc., Los Angeles.

SMITH, JEFFREY B.—Van Waters & Rogers, Los Angeles.

TARANTINO, JACQUELINE—Allo Chemical Co., Ontario, CA

TAYLOR, CARL E.—Charles E. Thomas Co., Gardena, CA

TAYLOR, CHRISTOPHER L.—Buckman Laboratories, Santa Ana, CA

TRUDEAU, ROBERT G.—Double R. Company, W. Covina, CA

WENDT, BILL—NL Industries, Inc., Tustin, CA

WRIGHT, DAVE—Agechem, Inc., Long Beach.

ZYWOCIENSKI, JOHN M.—Stay & Day Materials, Los Angeles.

Educator and Student

MISLANG, HERMENEGILDO—Dunn-Edwards Corp., Downey, CA

ONG, ROMEO—Student, Los Angeles, CA

NEW YORK

Active

CERQUEIRA, JOE E., JR.—Proctor Paint & Varnish, Yonkers, NY.

CRISTINO, ANTHONY—Engelhard Industries, East Newark, NJ.

JAFARY, ISHRAT H.—Peerless Paints, Brooklyn, NY.

MEHTA, ASHOK K.—Tenneco Chemicals, Piscataway, NJ.

POLESTAK, W.J.—George Kaolin Research, Springfield, NJ.

VALLE, RAFAEL—Reichhold Chemicals, Tuxedo, NY.

NORTHWESTERN

Active

FLIGGE, GERALD C.—Stewart Paint Mfg. Co., Minneapolis, MN.

HAMRE, JOAN—Cargill, Inc., Wayzata, MN.

Associate

CLARK, JENNIFER L.—Union Chemical Co., Minneapolis, MN.

KILIAN, MICHAEL R.—Union Chemical Co., Minneapolis.

POST, RUSSELL—Cyprus Industrial Minerals, Clayton, MO.

Educator and Student

GLASS, J. EDWARD—North Dakota State University, Fargo, ND.

JACOBS, GREGORY F.—North Dakota State University, Fargo.

NILL, KIMBALL R.—North Dakota State University, Fargo.

Meetings/Education

Gordon Research Conferences Scheduled for June and July

A Gordon Research Conference on "Physics and Chemistry of Coatings and Films," will be held June 15–19 at Plymouth State College, Plymouth, NH.

The following presentations are scheduled:

(June 15) "New Methods to Assess Pigment Dispersion and Flocculation"— J. Lichtenbelt; "Light Scattering by Titanium Dioxide Pigment in Coatings"—W.D. Ross; "Barrier Mechanism of Corrosion Protective Coatings"—W. Funke.

(June 16) "The Exploitation of Sorption and Transport Measurements for the Characterization of Aging in Glassy Polymers"—H.P. Hopfenberg and A.R. Berens; "Encapsulation and Separations by Liquid Surfactant Films"—N.N. Li; "Solvent, Polymer and Pigment Interactions in Urethane-Melamine Coatings"—W.T. Short; "Molecular Orientation in Solvent Cast Films and Polymer-Polymer Blends"—W.M. Prest, Jr.

(June 17) "Surface Tension Forces and Coatings Defects"—P.E. Pierce; "Mechanics of Electrostatic Atomization, Transport and Deposition of Coatings"—G.C. Bell, Jr. and J. Hochberg; "Adhesion of Coatings in a Liquid Environment"—J. Schultz.

(June 18) "Study of the Curing of Solid Phenolic Resins by High Resolution ^{13}C NMR"—A. Rudin; "Amino Resins for High Solids Coatings"—W.J. Blank; "Interplay of Macromolecular Conformation, Extensional Viscosity and Roll Application Speeds in Ribbing Phenomena"—J.E. Glass; "Ultrafiltration and Electrophoresis for the Recovery of Electrocoating Paints"—J.M. Radovich.

(June 19) "Effect of Liquid Particle Size on Liquid and Solid-State Properties of Latex Paints"—F.L. Floyd; "Mechanistic Studies on Sterically Hindered Amines as Protective Agents in the Photochemically Induced Oxidation of Hydrocarbons"—B. Felder.

Another conference entitled "Microbiological Degradation" will be held July 27–31 at Brewster Academy, Wolfeboro, NH.

Presentations are as follows:

(July 27) "Aspects of Plasmid Behavior"—G.A. Jacoby; "Role of Plasmids in Biodegradation"—P.A. Williams; "Chemical Feedstocks from Biomass"— S. Shoemaker.

(July 28) "Microbial Interactions and the Selection of Microorganisms in the Natural Environment"—J.H. Slater; "Biochemical Bases for Symbiosis Between Termites and Their Intestinal Microbiota"—J.A. Breznak; "Physiology of Thermophilic and Extreme Thermophilic Microorganisms that Degrade Starch and Cellulose"—L.G. Ljungdahl.

(July 29) "Measurement of Microbial Hydrocarbon Degradation in Environmental Samples"—R.M. Atlas; "Sensitive Analytical Methods for the Biomass, Metabolic Activity, and Community Structure of Marine Detrital and Benthic Microbiota"—D.C. White; "Assessment of Biodegradation Potential of Chemicals—An Industrial Point of View"— W.E. Gledhill.

(July 30) "Natural History of a Degradative Metabolic Pathway"—L.N. Ornston; "Experimental Evolution of New Metabolic Functions"—B.G. Hall; "Chemosynthesis at Deep Sea Hydrothermal Vents"—H.W. Jannasch.

(July 31) A summary of the conference and final discussion will be chaired by Douglas E. Eveleigh.

For additional information, contact Dr. Alexander M. Cruickshank, Director, Gordon Research Conference, Pastore Chemical Laboratory, University of Rhode Island, Kingston, RI 02881.

NPCA to Sponsor 21st Annual Marine Coatings Conference

The National Paint and Coatings Association (NPCA) will present the 21st Annual Marine and Offshore Coatings Conference, April 1–3 at the Del Monte Hyatt Hotel, Monterey, CA.

The conference will provide a forum to discuss new developments in marine coatings and new application techniques.

On April 1 and 2, sessions will undertake an extensive review of current and prospective bottoms systems.

The final session, on April 3, will feature "New Coatings Technology." A presentation by John Toomey, Farboil Corp., and David Bloodgood, Consultant, on the use of powder coatings in new construction, will be featured. John Peart, of Avondale Shipyard, will follow with a paper entitled, "Citric Acid Cleaning of Steel." J.A. Gise II, of Complete Abrasive Blasting Systems, Inc., will then speak on "Utilization of Steel Grit in Conjunction with Dehumidification."

Selected speakers will conclude the session with an update on regulatory issues affecting the marine industry.

For further information, contact John Montgomery or Mark Padow, NPCA, 1500 Rhode Island Ave., N.W., Washington, D.C. 20005.

Golden Gate Conference to Focus on Regulations

The Manufacturing Committee of the Golden Gate Society for Coatings Technology will host an all-day conference, "Safety and Government Regulations," on June 15 at A. Sabella's, San Francisco, CA.

The conference, designed to help manufacturers cope with the myriad of laws, regulations, and agencies which govern their operations, will cover the areas of the workplace, shipment of material, and disposal of hazardous waste.

Presentations for the conference are scheduled as follows:

"Necessity for Reasonable Regulation"—M.J. Patterson, San Francisco Fire Dept.

"State Regulation and Waste Management"—Dr. Storm, Dept. of Health Services of the State of California.

"Federal Regulation and Waste Management"—Presented by the Environmental Protection Agency.

"Storage and Disposal of Hazardous Waste"—H.M. Schneider, Romic Corp.

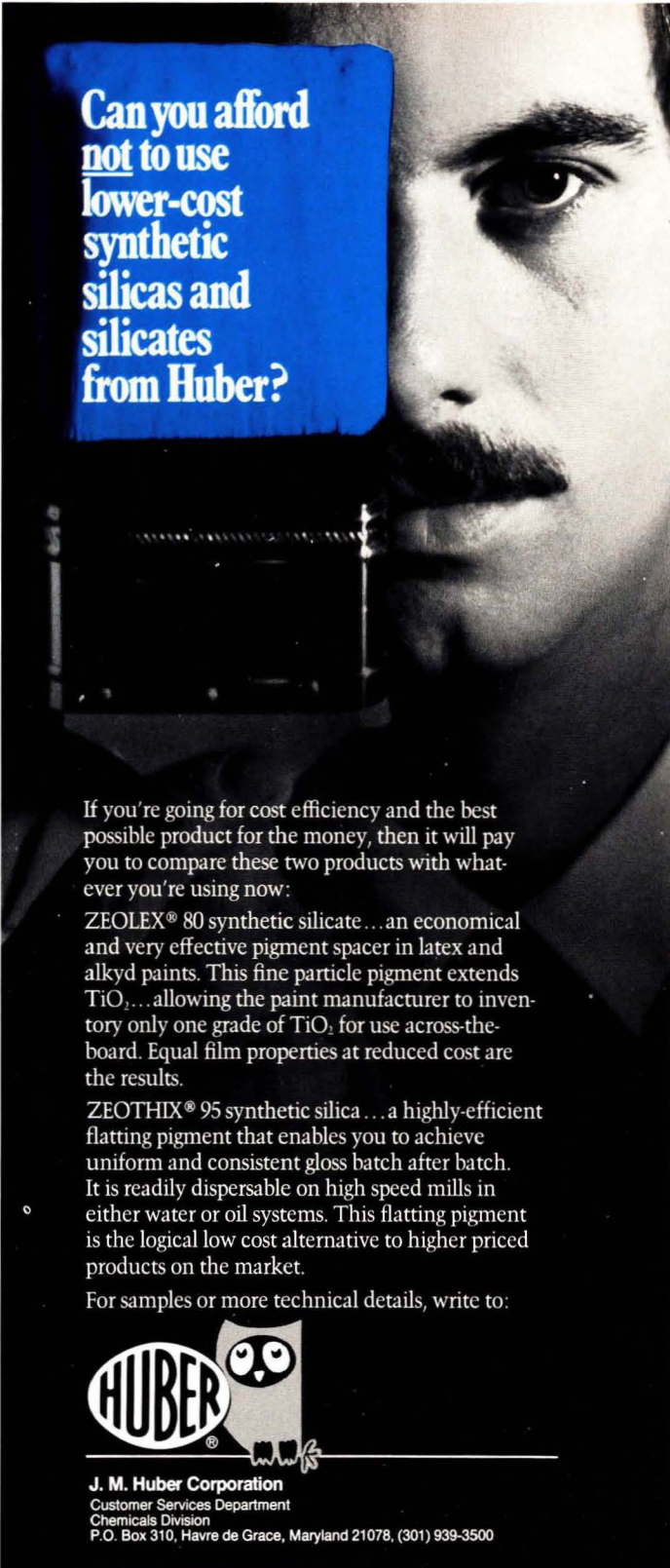"By-Product Reutilization"—Dr. Palmer, Zero Waste Systems.

"Motor Carrier Safety"—J.W. Spivey, Dept. of Transportation.

"The Insurance Role in Assisting Industries in Compliance with Government Regulation—or—Is OSHA for Real?" —J. Aparton, Clifton and Co.

"An Industry Point of View"—N. Estrada, Reichhold Chemicals, Inc.

"Results of OSHA Paint Industry Survey"—C. Erickson, State of California OSHA Consultants.

Registration fee for the conference is $40, which includes lunch and dinner. For additional information, contact Louie Sanguinetti, Manufacturing Committee Chairman, Jasco Chemical Corp., P.O. Drawer J, Mountain View, CA 94042.

Deadlines Announced For Society Papers

Societies planning to submit papers in competition for the A.F. Voss/*American Paint and Coatings Journal* Awards in 1981 should advise the AFV/APCJ Awards Committee of their intentions to participate by May 1, 1981. The announcement was made by Committee Chairman Albert Seneker.

Papers must be received at the Federation headquarters office no later than July 30 to be eligible for the 1981 competition.

Notification of intent to compete should be sent to Albert Seneker, c/o Ameron Corporate Research, 4813 Firestone Blvd., South Gate, CA 90280.

Coatings Lab Course Offered By Minneapolis Area Firm

Hennepin Technical Centers, Plymouth, MN, has announced a new 24-month course to train persons as coating materials lab technicians. The course will be offered beginning in June.

The course was developed with the assistance of an advisory board whose members are in the coatings industry in the Minneapolis/St. Paul area. Instruction at the centers is competency-based. Students attend classes six and one-half hours per day, five days per week, year round.

The first year of the program is basic laboratory technician training, including three weeks of on-job training in industry. Training subjects will include: mathematics, physics, safety, communications, testing specs and standards, lab techniques and procedures, heating, sublimation, evaporation, and centrifuging, interjoint glassware, determination of physical properties, weighing, basic chemistry, volumetric analysis, organic chemistry, polymer chemistry, testing, occupational relations, and basic laboratory practice.

Upon completion of the training program, certificates will be awarded. These certificates include specific listing of the job skills in which the student is competent. A job placement service is offered.

Fee for the course is $128 per quarter for Minnesota residents and $320 per quarter for nonresidents.

Further information may be obtained by writing, Hennepin Technical Centers, District Office, 1820 N. Xenium Ln., Plymouth, MN 55441.

Stability/Stabilization of Coatings Systems is Subject of PRI Symposium at Battelle

The Paint Research Institute will hold a symposium devoted to the topic, "Stability and Stabilization of Coatings Systems," on May 4 and 5 at the Battelle Memorial Laboratories, Columbus, Ohio.

The two-day meeting will be divided into four sessions directed mainly toward the coatings formulator; however, anyone engaged in finishing manufactured articles using organic coatings is urged to register.

The opening day of the symposium will feature the following sessions:

Controllable Factors in Making Stable Coatings Systems

"Colloid Principles"—Richard J. Ruch, Kent State University

"Pigment Dispersion"—Seymore Hochberg, E. I. duPont de Nemours & Co., Inc.

Session Chairman—William Mirick, Battelle Memorial Laboratories

Specific Chemistry of Stabilization

"Factors Influencing Package Stability and Pot Life of Isocyanate Systems"—Zeno W. Wicks, North Dakota State University

"Factors Influencing the Stability of Fully-Alkylated Melamine Resins"—Werner J. Blank, American Cyanamid Co.

"Characterization of the Charge on Model Latices"—Kirk J. Abbey, Glidden Coatings & Resins Div. of SCM Corp.

Session Chairman—Otto C. C. Lin, E.I. duPont de Nemours & Co., Inc.

The banquet speaker, Thursday evening, will be Irving N. Einhorn, of Springborn Laboratories, who will discuss, "Stable Coatings for Solar Applications."

The second day sessions will feature the following:

On-Line Stabilization Problems

"Surface Flaws and the Stabilization of Coatings Properties"—Gordon Bierwagen, Sherwin-Williams Co.

"Key Factors in Stabilization of Pigment Dispersions"—Geoffrey D. Parfitt, Carnegie-Mellon University

"Stabilization of Industrial Coatings with Regard to Application Problems"—Robert S. Bailey, Lilly Industrial Coatings

"Factors Influencing Stability of Trade Sales Water-Based Paints"—Girish C. Dubey, Cambridge Coatings, Inc.

"On-Line Powder Painting"—Peter R. Gribble, Glidden Coatings & Resins Div. of SCM Corp.

Session Chairman—Charles A. Kumins, Sherwin-Williams Co.

Research Ideas for Stabilization

Session chairman and speakers will take part in a mini-encounter between scientists who will emphasize the aspect of solutions looking for problems and industrial personnel well-versed in problems seeking solutions.

The registration fee of $150 covers attendance, lunches, and banquet. Housing is available on request.

To register, or to obtain additional information, please contact William Mirick, Battelle, Columbus Laboratories, 505 King Ave., Columbus, OH 43201; or phone (614) 424-5543.

Glidden Pigments Group of SCM Corp., Baltimore, has appointed **J. Corson Smith,** Vice-President of Marketing.

Gary G. Maxwell has been appointed Assistant Plant Manager for Witco Chemical Corporation's Isocyanate Products Division, New Castle, DE.

American Hoechst Corp. has promoted **Eckhard E. Mulhauser** to the position of Director of the Chemicals Department, Industrial Chemicals Div. Somerville, NJ. The company has also named **Dr. Luis M. Herz** Vice-President of Manufacturing for the division.

Body Bros., Inc., Bedford, OH, has announced the election of **Jack D. Harris** as President, Chief Operating Officer and Treasurer. **Robert W. Body** will remain active as Chairman and Chief Executive Officer.

J.C. Smith	G.G. Maxwell	J.T. Gormley	H. Gosch

Rust-Oleum Corp. has named **Gary R. Guth** to the position of Manufacturing Manager at the company's Evanston, IL coatings production facility. He will assume responsibility for the manufacturing and warehousing operations as well as coordinating the extensive renovation and modernization efforts for the facility.

Sun Chemical Corp., in a series of appointments, has announced the following. **John T. Gormley** was named Business Manager-Dry Color Products. He assumes responsibility for marketing the firm's dry colors and presscakes. Appointed to the position of Business Manager-Flush Color Products was **Heinz Gosch.** He will assume responsibility for marketing the company's flush colors. **Maurice Carruthers** was appointed Technical Service Manager, responsible for all customer service activities. **Thomas Herbe** has been named Flush Development Supervisor.

It was announced that ALCHEMY-South, Ltd., Doraville (Atlanta), GA, a manufacturers' agent for resins and pigments, has been formed by **William G. Welch** and **Paul H. Eliot** , both of the Southern Society. Mr. Welch, formerly of Chemcentral-Atlanta, and Mr. Eliot, previously associated with Ciba-Geigy Corp., will concentrate marketing efforts in Georgia, Alabama, Tennessee, and South Carolina.

The Organic Chemicals Div. of W.R. Grace & Co. has named **Peter Kosberg,** Senior Chemical Salesman, at the firm's Los Angeles division. Also, **Janet Webb** has joined the company as Sales Representative in Philadelphia.

Douglas E. Steadman has been named District Sales Manager for the Pigment & Chemicals Co., Ltd., Milton, Ontario.

NL Industries, Inc. has appointed **Walter F. Schultz** to the new position of Vice-President Operations Services. He will be responsible for manufacturing and operating services, materials management, engineering services, management services and facilities management.

Literature

High Shear Mill

A bulletin describing a high shear mill designed for laboratory evaluations and very small batches of paint, ink, chemical and other formulas, is available. The machine serves as a dissolver, ball mill, sandmill, attritor, and mixer. Aqueous or solvent formulas can be tested. For bulletin LM-980, write, Epworth Manufacturing Co., Inc., 1400 Kalamazoo St., South Haven, MI 49090.

Storage Containers

Literature describing a new series of portable bulk handling and storage containers has been recently published. These drums and bins, ranging in capacity from 250-575 gal, can be fabricated from mild steel to stainless steel to meet user requirements. For further information, contact, Mr. Dean Olinger, Product Manager, Clawson Tank Co., P.O. Box 350, Clarkston, MI 48016.

Phosphate Catalyst

Literature is now available describing a new phosphate catalyst for accelerating the cure of polymeric methylated and butylated amino crosslinking agents. Contact, King Industries, Inc., P.O. Box 588, Norwalk, CT 06852.

Surfactants

A guide to surfactants suggested for evaluation as dispersing aids in oleophilic or hydrophilic liquid media is now available. This bulletin describes 12 surfactant products used in the dispersion of pigments, fillers, and other particulate materials in inks, dyes, protective coatings, and other applications. Copies of Bulletin No. 210 may be obtained by writing Witco Chemical Corp., Organics Div., 3230 Brookfield St., Houston, TX 77045.

Products Guide

A 16-page, full-color bulletin which describes a company's lines of hydrocarbon resins, plasticizers, nonstaining antioxidants and chlorinated paraffins has been prepared. A brief description of ten product categories, the chemical and physical properties of each product grade, and tabular outlines of general compatibility and solubility characteristics are featured. For further information, contact Mark H. Buchta, Neville Chemical Co., Neville Island, Pittsburgh, PA 15225.

Can Lining

A recently published four-color bulletin describes water-borne spray coatings for the interior of beer and soft drink cans. These modified epoxy coatings have lower solvent levels. For information, contact John M. Hafeli, Market Manager, Metal Decorating and Containers, Glidden Chemical Coatings, 900 Union Commerce Bldg., Cleveland, OH 44115.

Transducer

A compact, non-contact transducer for measuring and monitoring the linear density of film, paper, wire insulation, coatings, and adhesives is featured in a new technical bulletin. For complete details, contact John S. Piso, Micro Sensors, Inc., New Englander Industrial Park, Holliston, MA 01746.
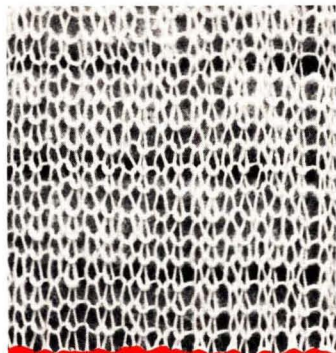
Fungicide/Microbiocide

Production of a new, finer-particle size grade of nonmetallic organic fungicide and microbiocide with a wide range of applications is described in recently released literature. The low toxicity compound is for use in both nonaqueous coatings and caulks and in vinyl formulations. For additional information, contact Interstab Chemicals Inc., Coatings Technical Service Dept., 500 Jersey Ave., P.O. Box 638, New Brunswick, NJ 08903.

Surface Modifier

The high-performance anti-wetting and anti-sticking properties of a surface modifier are detailed in a new four-page brochure. Included are a discussion of typical properties and methods of removal, as well as instructions for storage and handling. For a copy, contact 3M Company, Dept. CH80-20, P.O. Box 33600, St. Paul, MN 55133.

Pinhole Detectors

Literature is available describing a new line of pinhole detectors designed to detect pinholes and holidays in nonconductive protective coatings applied to metal, concrete, or asbestos cement. Contact KTA-Tator Associates, Inc., 2020 Montour St., Coraopolis, PA 15108.

Liquid Chromatography

Five new technical bulletins dealing with various analysis techniques and new liquid chromatography data processing developments in liquid chromatography are now available. Titles include "Instrumental Sources of Error in High Precision Quantitative LC Analysis" (TN-75); "LC Systems Control by a Basic Program" (TN-76); "LC Data Processing in Basic Language" (TN-77); "Spectroscopic Solutions to LC Separation Problems" (TN-78); and "A Discussion of Gradient Systems Pre-Pump vs. Dual Pump" (TN-79). For a free copy of these documents, request the appropriate order number from the Perkin-Elmer Corp., Main Ave., Mail Station 12, Norwalk, CT 06856.

Color Correction

A new line of batch color correction computer systems for pigment application has been introduced. The systems are designed to accept tristimulus measurement data from a wide range of colorimeters and spectrophotometers. For additional information, contact Applied Color Systems, Inc., P.O. Box 5800, U.S. Highway One, Princeton, NJ 08540.

Process Monitoring

New literature on oxygen analyzers used for flue gas, food, safety, heat-treating, and general process monitoring is now available. Copies of the eight-page Bulletin 4206 may be obtained by contacting Beckman Instruments Inc., Process Instruments Div., Technical Information Section, 2500 Harbor Blvd., Fullerton, CA 92634.

Infrared Spectrophotometers

A product line of microprocessor-controlled infrared spectrophotometers has been introduced in literature. The new line is designed for industrial quality control, routine analytical applications, and for a variety of teaching environments. For further information, write the Perkin-Elmer Corp., Maine Ave., Mail Station 12, Norwalk, CT 06856.

Porosimeter

A compact, bench-top, mercury intrusion porosimeter is described in newly published literature. The instrument is designed to measure pore diameters from 500 to 0.006 micrometer. For additional information, write Micromeritics Instruments Corp., 5680 Goshen Springs Rd., Norcross, GA 30093.

Pumps

Literature concerning a new series of double pumps, suited to many applications in the industrial and mobile markets, such as mixing, metering, etc., is presented in bulletin SP-1470. Also available, is literature featuring high speed pumps, which are ideal for handling thin liquids at full motor speeds of 1200–1800 rpm. Contact, Viking Pump Division, Houdaille Industries, Inc., Cedar Falls, IA 50613.

Pigment Grinding Aid

A new grinding aid for organic pigments is described in a recent brochure, which highlights its technical properties, features charts, graphs, and photographs, and describes its characteristics and capabilities in pigment grinding. For a copy of the brochure, contact Air Products and Chemicals, Inc., P.O. Box 538, Allentown, PA 18105.

Corrosion-Inhibiting Pigment

A bulletin describing an improved, molybdate-based corrosion-inhibiting paint pigment is available. The pigment is designed for solvent-based paint vehicles, including oils, alkyds, modified alkyds, epoxies, epoxy esters, polysters, and similar types. To obtain Technical Bulletin 361, write: Sherwin-Williams Chemicals, Publications Dept., 10909 S. Cottage Grove Ave., Chicago, IL 60628.
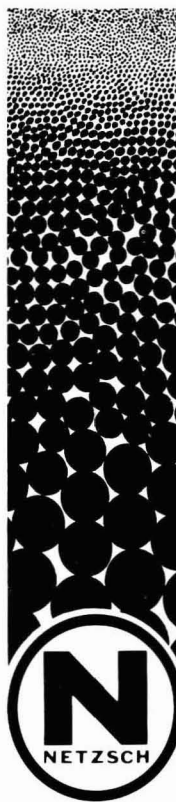
Polymeric Dispersant

Technical literature has been recently published concerning a polymeric dispersant with exceptional surface activity. The bulletin details typical properties, coating applications, and higher solids pigment dispersion data. For a copy of the technical bulletin, #2300–011, write: GAF Corp., Commercial Development, 140 West 51st St., New York, NY 10020.

On-Line Recording Gloss System

A new on-line recording glossmeter that provides continuous numerical gloss indication of material flowing on a continuous web is the subject of recent literature. For more information, contact Gardner Laboratory Div., Pacific Scientific Co., P.O. Box 5728, 5521 Landy Lane, Bethesda, MD 20014.

IR Spectrophotometer

Information is available concerning a new IR spectrophotometer which can be used in a wide variety of color applications in numerous industries. Write, Hunter Associates Laboratory, Inc., 11495 Sunset Hills Rd., Reston, VA 22090.

World Surface Coatings Abstracts

World Surface Coatings Abstracts, a source of information for the paint industry since 1928, is a monthly journal covering articles, patents and books on paints, varnishes, lacquers and their components, application and uses, printing inks, recording materials, and adhesives.

Produced manually until the mid-70's, the January 1976 issue saw a new departure—computerization. A logical enhancement of the service follows from this. Magnetic tapes of WSCA abstracts from January 1976 onward are now being supplied to Lockheed Missiles and Space Co., Inc., in California, for incorporation into their Lockheed Dialog on-line service. This enables owners of teletype-compatible terminals to connect, via the telephone network, with the Lockheed computers and retrieve abstracts on chosen topics, either directly or subsequently through the mail. The cost of this service to users is $65.00 per hour at the terminal and $.15 per print through the mail (telecommunications charges must be added to these figures). The WSCA database is called Surface Coatings Abstracts to distinguish it from the printed version. For more information, contact Dr. N.R. Morgan, Paint Research Institute, Waldegrave Rd., Teddington, Middlesex TW11 8LD, England or Lockheed Dialog Information Retrieval Service, 3460 Hillview Ave., Palo Alto, CA 94304.

Solvent Recovery

An automatic, compact system for solvent recovery is the subject of recently issued technical literature. Intended for paint, varnish, adhesive, or rubber solvent manufacturers, this packaged system is factory-assembled, pre-piped, and pre-wired, with a capacity of up to 400 gallons an hour. For details, write Chemetron Process Equipment, Inc., P.O. Box 35600, Louisville, KY 40232.

Antifoulants

An eight-page booklet focusing on organotin antifoulants for ship bottom paints has been prepared. The four-color brochure describes the products and how they protect ship bottoms against barnacles, algae, and other marine organisms for up to 36 months. For a copy of booklet AF-10, write M&T Chemicals Inc., Rahway, NJ 07065.

Glossmeter

A glossmeter system which consists of a signal processor and a choice of six optical sensors with different geometries is the subject of a recently issued product bulletin. Details can be obtained from Hunterlab, 11495 Sunset Hills Rd., Reston, VA 22090.

Elcometer

Literature is now available describing a battery-operated digital-readout ultrasonic wall thickness gauge. Designed for convenient hand-held use, it is pre-calibrated for the direct measurement of wall thickness in steel ranging from 1.5 to 99.9 mm. To obtain a free two-page catalog sheet, write Elcometer, Inc., P.O. Box 1203, Birmingham, MI 48012.

Urethane Elastomer

A lower cost resin to compliment standard water reducible urethane resins is described in recently issued literature. For further details, contact, Spencer Kellogg, H.A. Kasprzak, Product Manager, Box 807, Buffalo, NY 14240.

Psuedo-water Soluble Pigments

A new line of psuedo-water soluble pigments is the topic of recent literature. These pigments are used in aqueous paints and printing inks, and are readily dispersed and exhibit high color value. For more information, contact, Sandoz Colors and Chemicals, East Hanover, NJ 07936.

New Silicate Binder

Literature is available concerning a new inorganic binder, developed primarily for single package zinc-rich coatings. The new alkyl silicate binder reportedly represents a major advance in the technology of inorganic composites. Further information can be obtained from Union Carbide Corp., Coatings Materials Division, Dept. JLS, Danbury, CT 06817.

Microprocessors

Members of the Paint Research Association recently completed a study reviewing microprocessor control of paint manufacture. Their report can be obtained by writing, Mrs. Caroline Veitch, Publications Co-ordinator, Information Dept., Paint Research Association, Waldegrave Road, Teddington, Middlesex TW11 8LD, England

Notes to Industry

Available from the Paint Research Association are recent copies of "Notes to Industry." They include: "Analysis of Air Pollution in the Production and Use of Paint and in Welding"; "Odour Problems from the Stoving of Industrial Paint" and "Equipment for the Application of Powder Coatings." Please contact, Mrs. Caroline Veitch, Information Dept., Paint Research Association, Waldegrave Road, Teddington, Middlesex, TW11 8LD, England.

Book Review

INDUSTRIAL ORGANIC CHEMICALS IN PERSPECTIVE
Part I: Raw Materials and Manufacture

Authors
Harold A. Wittcoff
and
Bryan G. Reuben

Published by
John Wiley and Sons
New York, NY
1980 (298 pages) $29.50

Reviewed by
Dr. Thomas J. Miranda
Whirlpool Corp.
Benton Harbor, MI

Part one consists of six chapters on the raw materials and manufacture of industrial organic chemicals. In the initial chapter, the authors describe the structure of the book and its forthcoming part II. A useful source of journals, books, patents and bibliography of industrial chemicals is presented.

The reader is then treated to an overview of the chemical industry, its enormous size and its relationship to the national economy; the anatomy of the chemical industry, its growth, research and development, competition, capital intensity and economies of scale are then presented. The chapter closes with a list of the top chemical companies and the top chemicals. The remaining chapters discuss chemicals from natural gas and petroleum. The synthesis and reactions of chemicals is well presented in tables and flow sheets, and by equations. In addition, much detail is presented in the text such as reaction conditions, time, temperature, pressures and yields. Process advantages are compared such as co-products processes and preferred processes. Chemicals derived from ethylene, propylene, c_4 stream, benzene, toluene and xylene are presented, comparing processes on the way. This is followed by a chapter on chemicals derived from other sources including coal, Fischer-Tropsch reaction, natural fats and oils, carbohydrates and fermentation.

Chapter four describes how polymers are made. Topics covered include functionality, polymerization processes, block, graft and living polymers. Also included are brief treatments of thermosets and polymer properties.

Chapter five is devoted to industrial catalysts and includes definition, historical development, acid, base, metal, coordination and enzyme catalysts.

The book concludes with a discussion of the future of the chemical industry and the effects of social and political pressures on the industry. Of interest are some specific examples of major problems brought on the industry by overzealous enforcement of regulations such as the acrylonitrile copolymer bottle.

This text covers the worldwide petrochemical system which is viewed as another asset in its favor by this reviewer. The authors also include, on the inside covers, conversion units and special units used in the chemical industry, i.e., 1 bbl = 42 U.S. gallons.

This volume is required reading for chemists. It goes a long way to provide a concise and very readable picture of an industry which has had an enormous impact on the history and progress of man. For those in the coatings industry it is a valuable tool to provide background to new entrants in the industry and to those practicing in the field. As a text for a course in industrial chemistry it should be welcomed on the college campus.

FOURTH INTERNATIONAL CONFERENCE IN ORGANIC COATINGS SCIENCE AND TECHNOLOGY

Edited by
G.D. Parfitt
A.V. Patsis
Technomic Publishing Co., Inc.
Westport, CT 06880
1980   (294 pages) $55.00

Reviewed by
Thomas J. Miranda
Whirlpool Corp.
Benton Harbor, MI 49022

This book is the bound proceedings of the titled conference held in Athens, Greece in 1978. There are twenty-one papers covering the following areas: Formation of Polymer Dispersions; Theory and Practice, Characterization of Latices; Coatings for Automotive Applications, i.e., Resins, Non-Aqueous Dispersions; Color Formulations and Control; Electrocoating by Autophoresis; Electroplating; Corrosion; Ink Printing and Textiles; High Solids Coatings; Crosslinking Mechanisms; Marine Coatings; Container Coatings and Powder Coatings.

For those in the coatings industry, this volume provides a variety of topics representing an overview of current research and practice, as well as some specific subject areas, such as water-soluble polymer behavior in water-borne coatings. A number of the articles are well referenced, providing the reader with a useful guide to additional reading; others, unfortunately were prepared without a bibliography.

The high cost of this volume will probably limit its circulation to key industrial and technical information centers.

Coming Events

FEDERATION MEETINGS

(May 14–15)—Spring Meetings. Society Officers on 14th; Board of Directors on 15th. Hilton Hotel, Denver, CO. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

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

1982

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

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

PAINT RESEARCH INSTITUTE MEETING

(May 4–5)—Paint Research Institute Symposium on "Stability and Stabilization of Coatings Systems," Battelle Memorial Institute, Columbus, Ohio. (Dr. Raymond R. Myers, Chemistry Dept., Kent State University, Kent, Ohio 44242).

SPECIAL SOCIETY MEETINGS

(Apr. 21–22)—Chicago Society. SYMCO '81. "Impact of Environment, Cost, and Technology in 1981." Fountain Blue Restaurant, Des Plaines, IL. (Dolores Thomas, Chicago PCA, Suite 1936, 35 E. Wacker Dr., Chicago, IL 60601).

(May 1–2)—Pacific Northwest Society. Annual Symposium. Washington Plaza Hotel, Seattle, WA.

(May 5)—Detroit Society FOCUS Conference, "Color and Appearance in Changing Times." Management Education Center, Troy, MI. (Bohdan Melnyk, Detroit Society for Coatings Technology, 765 Dellwood Dr., Ann Arbor, MI 48103).

(May 9)—Montreal Society. Fiftieth Anniversary dinner-dance, Montreal, Que.

(June 15)—Golden Gate Society Seminar, "Safety and Government Regulations." (Louie Sanguinetti, Jasco Chemical Corp., P.O. Drawer J, Mountain View, CA 94042).

1982

(Mar. 10–12)—Southern Society Annual Meeting. Savannah, Ga.

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

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

1983

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

OTHER ORGANIZATIONS

(Apr. 1–3)—National Paint and Coatings Association 21st Annual Marine and Offshore Coatings Conference. Del Monte Hyatt Hotel, Monterey, CA. (John Montgomery, NCPA, 1500 Rhode Island Ave. N.W., Washington, D.C. 20005).

(Apr. 6–10)—"Introduction to Paint Formulation" Short Course. University of Missouri–Rolla, Rolla, MO. (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri–Rolla, Rolla, MO 65401).

(Apr. 6–10)—National Association of Corrosion Engineers "Corrosion/81." Sheraton-Centre and Hotel Toronto, Toronto, Ontario, Canada. (Conference Coordinator, NACE, P.O. Box 218340, Houston, TX 77218).

(Apr. 7–8)—NACE T6 Symposium on Underfilm Corrosion. Sheraton Centre Hotel, Toronto, Canada. (National Association of Corrosion Engineers, 1440 South Creek, Houston, TX 77084.)
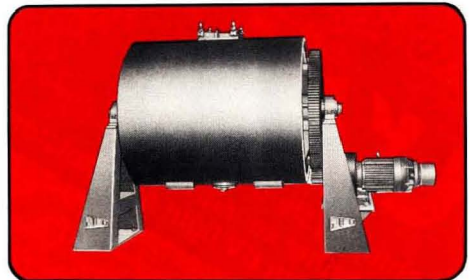
(Apr. 13-14)—Washington Paint Technical Group Annual Symposium. "New Decade, New Ideas." Marriott Twin Bridges Motel, Washington, D.C. (WPTG, P.O. Box 12025, Washington, D.C. 20005).

(Apr. 13–17)—"Advanced Paint Formulation" Short Course. University of Missouri–Rolla, Rolla, MO (Norma Fleming, Co-ordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(Apr. 15–17)—Hunterlab Workshop, "Appearance Properties of Materials." Reston, VA. (Hunterlab Associates Laboratory, Inc., 11495 Sunset Hills Road, Reston, VA 22090).

(Apr. 26–28)—Inter-Society Color Council Annual Meeting. Roosevelt Hotel, NY. (Dr. Fred W. Billmeyer, Secretary, ISCC, Rensselaer Polytechnic Institute, Troy, NY 12181.)

(Apr. 28–30)—OCCA-32. Oil and Colour Chemists' Association 32nd Annual Technical Exhibition. Cunard International Hotel, London, England. (The Director and Secretary, OCCA, Priory House, 967 Harrow Rd., Wembley, Middlesex HAO 2SF, England.)

(May 4–7)—Society of Plastics Engineers. 39th Annual Technical Conference. Sheraton-Boston Hotel, Boston, MA. (Nancy Rein, SPE Conference Dept., 14 Fairfield Dr., Brookfield Center, CT 06805.

(May 10–12)—"Refresher for Contractors, Maintenance Engineers and Inspectors" Short Course. Sheraton-Valley Forge Hotel, Philadelphia, PA (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(May 17–21)—American Oil Chemists' Society 72nd Annual Meeting. Fairmont Hotel, New Orleans, LA. (American Oil Chemists' Society, 508 S. Sixth St., Champaign, IL 61820).

(May 18–22)—"Dispersion of Pigments and Resins in Fluid Media" Short Course. Kent State University, Kent, OH. (Carl J. Knauss, Chemistry Dept., Kent State University, Kent, OH 44242).

(May 19–20)—"Practical Waste Management for the Coatings Industry" Short Course. Granada Royale, Kansas City, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

(May 31–June 5)—"Polymer Blends and IPN's" Short Course. Lehigh University, Bethlehem, PA (Jone Svirzofsky, Lehigh University, Bethlehem, PA 18015).

(June 8–12)—"Adhesion Principles and Practice for Coatings and Polymer Scientist" Short Course. Kent State University, Kent, OH. (Carl J. Knauss, Chemistry Dept., Kent State University, Kent, OH 44242).

(June 8–12)—"Advances in Emulsion Polymerization and Latex Technology" Short Course. Lehigh University, Bethlehem, PA. (Dr. Mohamed S. El-Aasser, Dept. of Chemical Engineering, Whitaker Lab. #5, Lehigh University, Bethlehem, PA 18015).

(June 14–17)—Dry Color Manufacturers' Association Annual Meeting. The Greenbriar, White Sulphur Springs, WV. (P.L. Lehr, DCMA, Suite 100, 1117 North 19th St., Arlington, (Rosslyn) VA 22209.)

(June 15–19)—"Applied Rheology for Industrial Chemists" Short Course. Kent State University, Kent, OH. (Carl J. Knauss, Chemistry Dept., Kent State University, Kent, OH 44242).

(June 17–20)—Oil and Colour Chemists' Association Conference, "Alternative Technologies in Coatings." Beaufort Hotel, Bath, England. (The Director and Secretary, OCCA, Priory House, 967 Harrow Rd., Wembley, Middlesex HA0 2SF, England.)

(June 21–26)—Air Polution Control Association 74th Annual Meeting & Exhibition. Philadelphia Civic Center, Philadelphia, PA (Public Relations Dept., Air Pollution Control Association, P.O. Box 2861, Pittsburgh, PA 15230).

(June 21–24)—American Society for Testing and Materials Committee D-1 on Paint and Related Coatings and Materials Meeting. Biltmore Plaza, Providence, RI. (Jane R. Turner, ASTM, 1916 Race St., Phila., PA 19103).

(June 29–July 3)—SURTEC (International Congress and Exhibition on Surface Technology). International Congress Center, Berlin, West Germany. (Dieter von Schramm, AMK Berlin, 1735 Eye St. N.W., Washington, D.C. 20006).

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

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

(Sept. 7–11)—"Advanced Paint Formulation" Short Course. University of Missouri-Rolla, Rolla, MO (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, MO 55401.

(Sept. 13–16)—Canadian Paint Manufacturers Association. Four Seasons Hotel, Vancouver, B.C: (Lydia Palazzi, Canadian Paint Manufacturers Assn., 2050 Mansfield, Montreal, Que., Canada H3A 1Y9.)

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

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

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

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

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

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

(Oct. 25–27)—"Women in Coatings—Meeting the Challenges" Short Course. Detroit, MI (Norma Fleming, Coordinator, Arts & Sciences Continuing Education, University of Missouri-Rolla, Rolla, MO 65401).

Advertisers Index

'Humbug' from Hillman

Out of desk drawers, company archives, dusty shelves and pleasant memories have come contributions from the pages of old issues of "RBH Dispersions," that wonderful, little magazine of quotes, jokes and philosophical quips. Its editor, I recall, was Stewart Hoagland, a man of great wit and perception, it seemed to me. I trust that the RBH folks will consider the contributions below a belated tribute to them and to Stewart Hoagland.

—*Herb Hillman*

From our old friend, Harold Werner, we have the following stolen from RBH issues of the past—

If you have failed to get the thought across, your efforts are in vain. The following excerpt will give you an indication of what can happen when you misuse grammar.

EXAMPLES OF UNCLEAR WRITING—Sentences taken from actual letters received by the Welfare Department in applications for financial support:

"I am forwarding my marriage certificate and six children. I have seven, but one died, which was baptized on a half sheet of paper."

"Mrs. Jones has not had any clothes for a year, and has been visited regularly by the preacher."

"I cannot get sick pay. I have six children. Can you tell me why?"

"I am glad to report that my husband who is missing is dead."

"This is my eighth child. What are you going to do about it?"

"Please find out for certain if my husband is dead. The man I am living with can't eat or do anything until he knows."

"I am very annoyed to find you have branded my son illiterate. This is a dirty lie as I was married a week before he was born."

"I am forwarding my marriage certificate and three children, one of which is a mistake as you can see."

"My husband got his project cut off two weeks ago, and I haven't had any relief since."

"Unless I get my husbands money pretty soon, I will be forced to lead an immortal life."

"I want money as quickly as I can get it. I have been in bed with the same doctor for two weeks, and doesn't do me any good. If things don't improve I will have to send for another doctor to help him."

From the "Pipet" he sends

TO THOSE WHO USE LAB STOOLS FOR OTHER PURPOSES

I hope that that stuff was water,
    that wet stuff on the stool.
For I sat down inadvertently
    And one part of me is cool.
That wetness isn't there now,
    The stool is almost dry.
But the rear of my anatomy
    Tells me the reason why.
I pray that that was water
    Instead of HCl,
'Cause hydrolysis of protein
    Progresses pretty well.
I want that to be water
    And not con. alkali.
The cloth is thin where it went in,
    And I'm extremely shy.
My pants are made of woolens
    And I'm a protein too.
So I'm really up against it
    When the solution soaks on thru.
I fain that that was water,
    Just good old H_2O.
But I'll apply some litmus'
    For now's the time to know.
Oh happy day — — oh lucky me!
    'Tis water — — so no worry,
But I'll be darned if I sit down
    Again in the laboratory.

Al Seneker sent the following attempts to improve on our "Structural Damage." Al disclaims any parentage of the formulae—only a good memory.
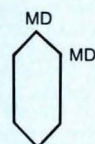
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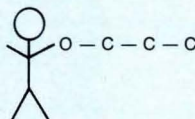
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That shouldn't be surprising.

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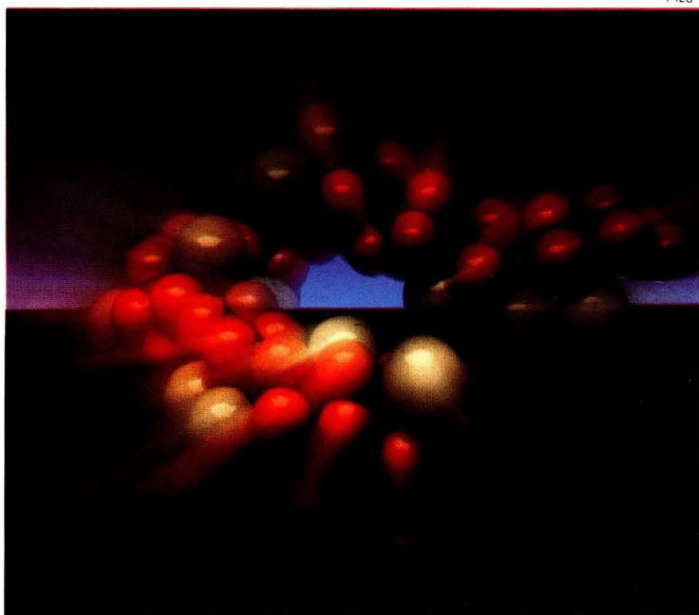
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Organics Division.

For more information, write to Witco Chemical Corporation, Organics Division, Dept. CC5, 3230 Brookfield Street, Houston, TX 77045. Or call (713) 433-7281.

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