Modern Container Coatings

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Modern Container Coatings

Robert C. Strand, EDITOR
American Can Company

A symposium sponsored by
the Division of Organic
Coatings and Plastics Chemistry
at the 174th Meeting of
the American Chemical Society,
Chicago, IL, August 29–
September 2, 1977.

ACS SYMPOSIUM SERIES **78**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1978

Library of Congress CIP Data

Modern container coatings.
(ACS symposium series; 78. ISSN 0097-6156)

Bibliography: p. 124 + ix.
Includes index.

1. Containers—Congresses. 2. Coatings—Congresses. I. Strand, Robert C., 1925- . II. American Chemical Society. Division of Organic Coatings and Plastics Chemistry. III. Series: American Chemical Society. ACS symposium series; 78.

TS198.3.C6M63 621.7'57 78-14801
ISBN 0-8412-0446-2 ACSMC8 78 1–124 1978

Copyright © 1978

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating new collective works, for resale, or for information storage and retrieval systems.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto.

PRINTED IN THE UNITED STATES OF AMERICA

American Chemical
Society Library
1155 16th St. N. W.
Washington, D. C. 20036

ACS Symposium Series

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Containers—metal, glass, and more recently plastic—are an essential part of our food and beverage distribution system. The technology of these containers, particularly metal cans, has developed steadily over the past 75 years. A key to the success of the metal container has been the development and availability of organic coatings which offer a wide range of performance properties.

Early coating materials such as C-enamel, which is used in corn cans, were relatively simple to manufacture and apply. They did not represent a high level of technical sophistication, but they did the job for a specific packaging need. Once a coating was developed, it tended to remain in use for many years because there generally was little reason to change it.

With the advent of newer can-making technology such as the drawing–redrawing and the drawing and ironing processes, newer and more sophisticated coating materials were needed. Environmental concerns and energy conservation pressures also have contributed to the demand for new and different coating materials. This trend is seen also in the glass container industry where safety coatings for beverage bottles are now in use. Much of the change in coating technology has taken place within the past four to five years and brings the latest, most modern coating technology to the container industry.

That segment of the coating industry which serves the packaging business is characterized by vigorous competition among suppliers and the use of extensive proprietary know-how. For these reasons it is difficult for coating chemists to discuss their company products or processes. For example, there are no papers in this symposium on the wash coating of two-piece beverage cans because the process involves proprietary technology on the part of several companies.

Despite these problems, this symposium succeeds in surveying the main areas of coating development and analysis currently used in the rigid packaging industry. I would like to thank the authors whose time and effort contributed to the success of this symposium.

ROBERT C. STRAND

American Can Company,
Barrington Technical Center,
Barrington, IL
May 31, 1978

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

1

Waterborne Spray Can Coatings

DAVID O. LAWSON

PPG Industries, Delaware, OH 43015

In preparing to cover this subject for this Symposium, it was difficult to determine how broadly to define water borne coatings and the reasons for their increased interest in the industrial coatings field. Other presentations here have and will mention some of the areas I wish to review. However, for understanding of water borne spray can coatings, we will explain the purpose of spraying the interior of metal cans, review why the various legislative actions of recent years have stimulated development of water borne sprays, give a general insight into coating formulations, and relate field experience with coating handling and equipment operation. From this, we will be able to have some feeling for the future of water borne spray can coatings.

The metal can industry supplies the major share of its production for the beer and soft drink markets. With calculations from various industry figures, this highly specialized business today is producing in the range of 45 to 50 billion cans annually. The three-piece can is produced from decorated flat stock, which has undergone a number of coatings operations. Handling of sheets through the coating stages and subsequent can forming operations can be expected to damage the interior basecoat through abrasion and scratching. Complete protection and coverage must be achieved with the steel substrates used for three-piece cans, because of the delicate flavor properties of beer and the corrosiveness, as well as taste considerations, of carbonated soft drink products. The interior spray, then is actually a repair coating and is the last operation in coating of the can body. Two-piece cans are taking over the major share of the beverage can market and are produced in the integral form of the drawn cup. Both aluminum and tinplated steel substrates are used today, and again protection of beverages from the metal and of metal from the product to be packaged requires the inside spray coating.

For some years, the interior sprays have been familiar organic coating types with organic solvents as the transport media. Reduction of organic solvent emissions from such coatings has

0-8412-0446-2/78/47-078-001$05.00/0

been a goal for some time and efforts increased with the advent of the famous Los Angeles Rule 66. Here it was proposed to allow solvent emissions if so-called Rule 66 exempt solvents were used. Five to six years later, other sections of the country had adopted Rule 66 and even added some more stringent requirements to attempt meeting governmental Air Quality Standards. Again, Los Angeles led the way with a modified Rule 66, but we in the coatings industry were given the opportunity to proceed with water borne coatings which, along with high solids coatings, were made exempt from any requirements of incineration of volatiles.

You should be aware that important progress was made in the development and commercialization of water reducible electrocoatings in the early 1960's. This commercialization and some better understanding of how to formulate water reducible polymers to meet the demands of industrial applications took place before the legislative pressures asking for reduced organic solvent emissions.

We were working closely with major can companies to see what place could be found for the efficient electrodeposition process. This led to spray applications of the water reducible polymer systems that were evolving for interior beer and soft drink contact. It was recognized that the spray application area in can plants is a source of high emissions, because of the spray operation and the use of low solids content coatings. The industry was moved toward changing to water borne interior sprays because solvent emissions could be reduced by as much as 70 to 80% over the low solids, organic solvent containing conventional systems. Remember, this coating operation takes place for every beer and soft drink can manufactured! As further incentive, the avenue of water borne spray offers continued use of existing equipment, which represents extremely high capital investment in the can industry.

The first challenge from these materials, then, is to spray apply on the various types of air and airless spray equipment in the many can producing plants. The coatings are also tailored to meet cure conditions dictated by the various substrates, side seam construction, and oven designs in use in the industry. Of major importance, of course, is meeting the higher temperature, shorter time cycle of the two-piece can cure. The final measure of acceptability for a can liner in contact with beer and soft drink products is to meet the performance and flavor characteristic requirements expected.

Much of the successful application to date involves acrylic and epoxy chemistry, and we will direct our brief review for this presentation to those types of thermosetting materials. These coatings are processed via an additional polymerization of monomers initiated by thermal decomposition of a free radical initiator. Polymerization in a batch reactor uses a coupling solvent and chain transfer solvents to control molecular weight. Following proper polymerization, a portion of the organic acid groups along the polymer backbone are converted to amine salts, using an appropriate amine, to render the polymer reducible in water. As in many polymer systems, strict attention is given to raw materials, their proportions and addition rates, times, temperatures, and specific process check points. A multitude of processing factors affect successful manufacture of product, and each in turn would involve detailed study of engineering parameters. I will simply mention these for our purposes as: proper selection and preparation of equipment, careful control of polymerization conditions, and maintaining awareness of how such factors affect polymer molecular weight, particle size, etc. The performance of the water borne spray coating so produced is extremely dependent on processing procedures.

As we work with water borne spray coatings, our biggest challenge comes from the rheology and surface wetting characteristics that are so predominantly determined by the water present. Coated, as well as bare metal, substrates pose rather difficult problems. In the area of spray, of course, behavior of the coating material upon atomization through spray nozzles has a great bearing on the wetting and coverage also. Experience has been generally good in the handling of these coatings through conventional equipment. Some reeducation is required in the actual selection of spray nozzles because newer coatings cannot necessarily have the exact same solids, viscosity, and rheology properties of the conventional coatings they replace.

Overall, recognize the fact that line conditions vary widely in the industry. Such factors as temperature, type spray machine, can configuration, pressure available, can rotation speeds, and many more can and must be dealt with. To discuss these to any degree would consume a great deal of the time to which we are limited for one presentation. I believe other speakers will better describe some equipment details.

We are meeting these challenges and through experience the use of water borne spray coatings is becoming more familiar to the industry. With these low solvent coatings helping to meet Air Quality Standards, and the recognized safety aspects of storage and handling, we can certainly expect this technology to enjoy a great growth pattern and a long and useful life cycle.

RECEIVED MAY 22, 1978.

2

Fast-Cure Epoxy Powders as Beer and Beverage Can Interior Lacquers

PETER H. SCOTT, DONALD C. CLAGETT, and KENNETH V. FISCHER

Dewey and Almy Chemical Division, W. R. Grace & Co., 55 Hayden Avenue,
Lexington, MA 02173

The Clean Air Act of 1970 and related legislation has lead the coatings industry to consider alternatives to solvent based coatings (1, 2). These alternatives include waterborne coatings, powder coatings, non-aqueous dispersions, radiation cured total solids, and electrodeposition. Relative to coating the interior of beer/beverage cans with a solvent-free material, the Dewey and Almy Chemical Division of W. R. Grace & Co. has elected to pursue development of a powdered lacquer. Powdered coatings contain little or no volatile effluents and require low energy consumption for application and cure.

DISCUSSION

Any acceptable beer/beverage can coating must meet several general requirements. It must be formulated exclusively of materials approved for this use by the FDA (3). It must not affect the taste of the beverage packed in the can. It must be coated at low film weights (thin films) to minimize coating expense, and when used in a two-piece can it must cure within two minutes at a maximum temperature of 400°F to meet existing line specifications.

Other powder properties necessary to economically coat beer/beverage cans are:

1. Fine particle size powders on the order of 5-8 micron mean diameter.

2. Good bulk flow and fluidization such that the powder does not cake or cause blockage inside the application tubing. This is critical when dealing with very fine particle powders.

0-8412-0446-2/78/47-078-004$05.00/0

3. Minimal overspray and high transfer efficiencies.

4. The powdered material must be formulated such that it does not build up (impact fuse) on moving machinery parts inside the application device.

To meet the above requirements thermosetting epoxies and epoxy/phenolics were chosen for powder coating development at Grace. These resins have had a history of successful use as solvent base materials and thus the potential for obtaining a powder with the properties needed for an interior can coating was high. Typical epoxy powder formulations tested contained a bis-phenol A type epoxy resin, curing agent (acidic or basic), leveling agent, wetting agent and catalyst (4, 5).

Initial test results in our laboratory showed that coatings with acceptable physical properties could be produced but that cure times at 400°F were at least twice as long as required (Table 1). This was a key problem since an oven residence time of two minutes or less is a necessity on a commercial beer/beverage can line. Increasing oven temperatures above 400°F was one obvious option for reducing cure time, but that option was ruled out because of increased energy consumption and other commercial constraints. Therefore, we screened a variety of formulations to select curing systems with exotherms at or below 400°F as determined using differential scanning calorimetry (DSC).

Samples were prepared by micromilling raw material mixtures, and DSC scans were made using a duPont 990 instrument. The sample size was 17 ±1 mg., and the samples were heated in a nitrogen atmosphere at 0.3 mm positive pressure.

Our initial work showed that standard mixtures of epoxy and curing agent had exotherms at or above 400°F (Figures 1 and 2). Both acid and base catalyst, however, gave initial exotherms significantly lower than obtained with the uncatalyzed systems (Figure 3). Unfortunately, many of these formulations degraded other necessary properties, and some in fact resulted in unstable powder formulations. The survey revealed finally that trimellictic anhydride (TMA) cured epoxy powders could be catalyzed using either stannous octoate (Figure 4) or dicyandiamide (DICY) (Figure 5).

Based on this technology we have prepared epoxy powders with small particle size and narrow particle size distribution (Figure 6) which meet the requirements for an acceptable beer/beverage can coating. The properties of a typical epoxy powder cured with TMA and catalyzed with stannous octoate are given in Table II. It should be noted that both catalyst and curing agent are accepted by the FDA for use in can coatings as a result of successful petitions by W. R. Grace & Co. and Sherwin Williams Co.

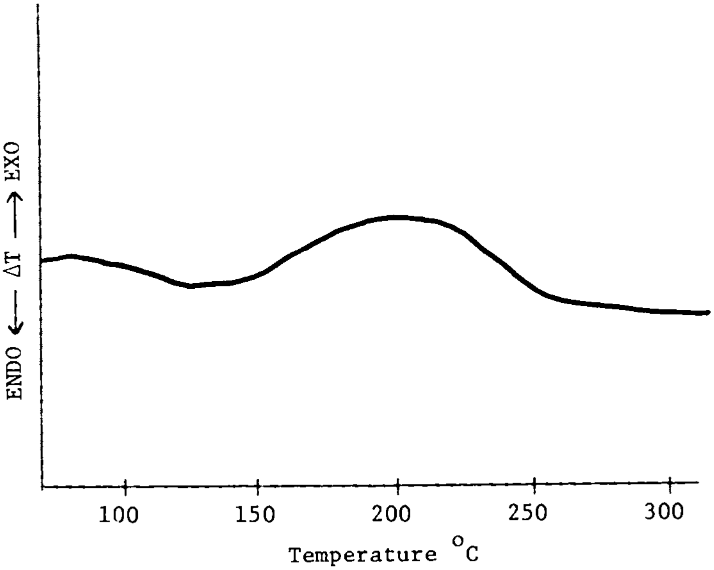


Figure 1. DSC scan of TMA/epoxy

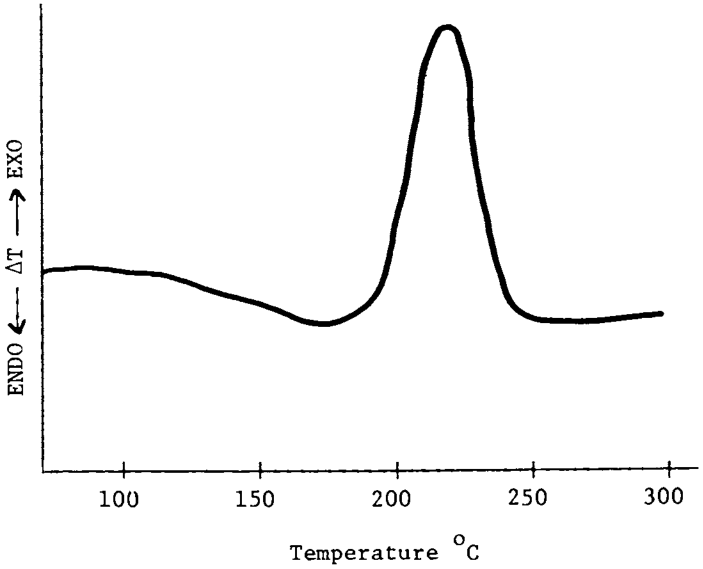


Figure 2. DSC scan of DICY/epoxy

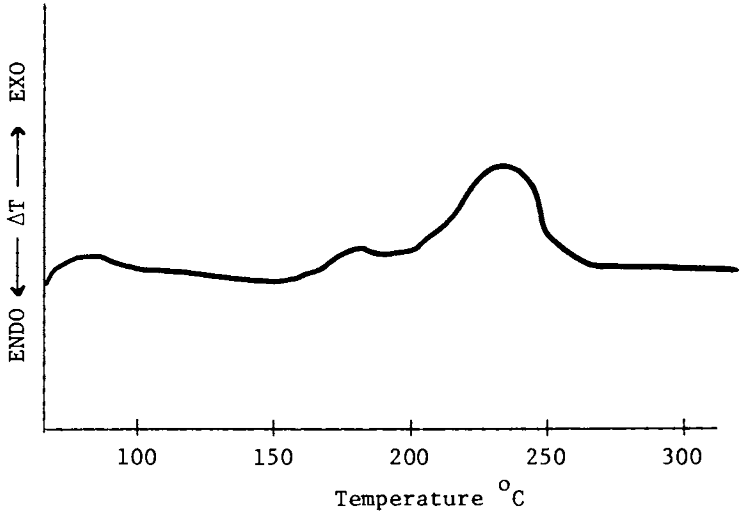


Figure 3. DSC scan of PAPA/epoxy with DICY catalyst

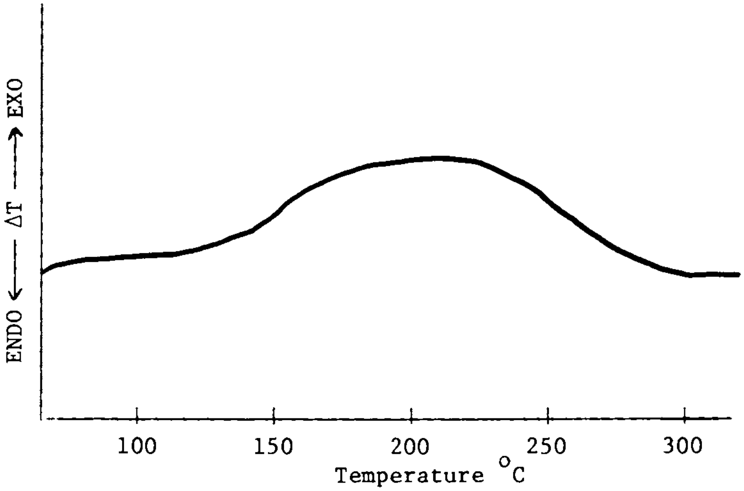


Figure 4. DSC scan of TMA/epoxy with stannous octoate catalyst

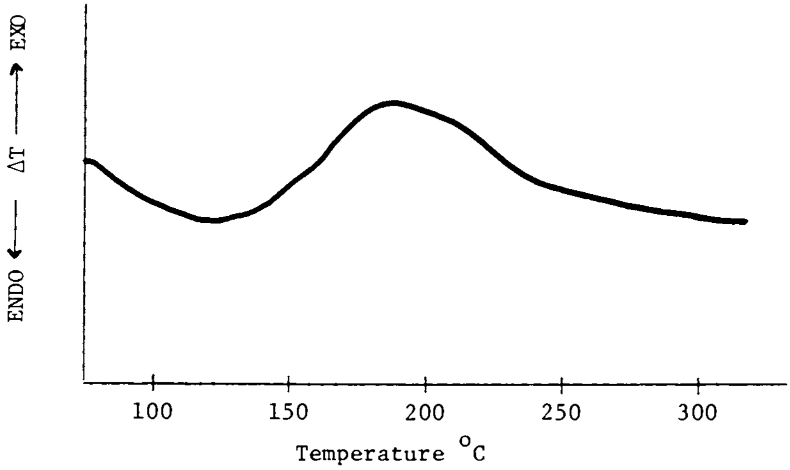


Figure 5. DSC scan of TMA/epoxy with DICY catalyst

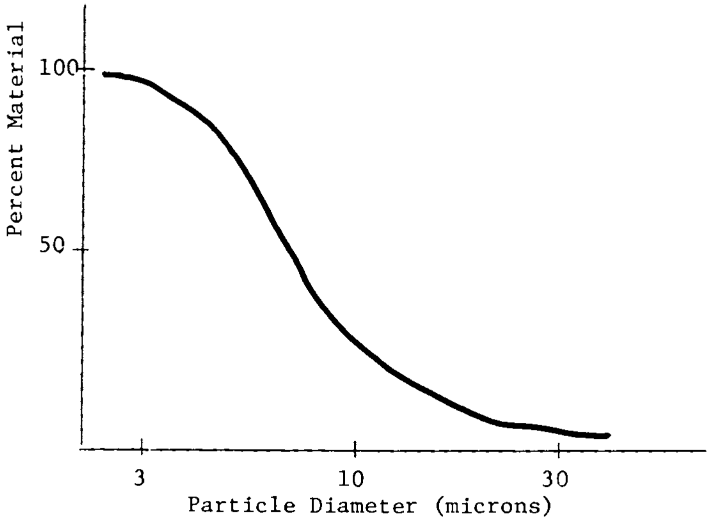


Figure 6. Particle size distribution for a typical W. R. Grace & Co. powdered-can lacquer

TABLE I

EFFECT OF CURING AGENT TYPE ON THE CURE: EPOXY/CURING AGENT RATIO = 1.5/1

AGENT	CURE TIME (minutes)
Trimellitic Anhydride	4
Polyazelaic Polyanhydride	5
Phthalic Anhydride	7
Dicyandiamide	8
XD 8038	15
Citric Acid	Variable
Phosphoric Acid	Variable

TABLE II

PROPERTIES OF DEWEY AND ALMY POWDERED CAN LACQUER FOR TWO-PIECE BEER/BEVERAGE CANS

PROPERTY	PERFORMANCE
Cross Hatch Adhesion in Boiling Water	pass
Reverse Impact on Parker Panels (160 in. lb.)	pass
Pasteurization Resistance (212°F/10 minutes)	pass
Flexibility (1/8 inch conical mandrel)	pass
Beverage Pack Resistance (beer and soft drink)	>1 month @ 100°F
Flavor Profile Testing	pass
Enamel Rater (WACO)	pass
Iron Pick-up	pass

As of now, equipment for applying Grace powders to two-piece can interiors is in commercial development at Coors in Golden, Colorado. We have succeeded in powder coating quality cans at commercial line speeds with no impact fusion and good transfer efficiencies.

SUMMARY

In conclusion, W. R. Grace & Co. has succeeded in developing air pollution-free powdered epoxy can lacquers whose reactivity allows curing at current commercial rates using existing can-maker ovens and settings. It is very likely that these powdered coatings will also allow reduction in energy input as compared to that required for solvent coatings.

Grace's developing powder technology represents an immediate solution to the can industry's needs for reducing plant emissions and conserving natural gas supplies.

REFERENCES CITED

1. Gardon, J. L. and Prane, J. W., Non-polluting Coatings and Coatings Processes, Plenum Press, New York, New York, 1973, pp 1-13.

2. Cole, Jr., G. E., Plastics Raw Materials to End Products and Coatings, American Chemical Society, Division of Chemical Marketing and Economics, 1974, pp 168-9.

3. Code of Federal Regulations, Title 21, paragraph 175.300.

4. Talen, H. and Teringa, P. M., Powder Coating, Elsevier Sequoia Patent Report No. 4, Elsevier Sequoia, S. A., Lausanne, Switzerland, 1974, pp 3-13.

5. Miller, E. P. and Taft, D. D., Fundamentals of Powder Coating, Society of Manufacturing Engineers, Dearborn, MI, 1974, pp 16 and 162, 211-220.

6. Zorll, Ü., Progress in Organic Coatings, 4, pp 124-125, (1976).

RECEIVED MAY 22, 1978.

Waterborne Two-Piece Body Spray

L. A. WATSON

Technical Coatings Co., North & 25th Avenues, Melrose Park, IL 60160

The epoxy resins have served the container coatings industry well for many years. Solvent based epoxy systems have been designed for utilization in almost every segment of can-closure manufacture. If not as the basic backbone (component) of the coating system, the epoxy resin found merit as a modifier for other resinious materials.

With the increased emphasis for ecologically acceptable coating, epoxy chemistry has been directed toward meaningful water borne systems. New water borne epoxy ester coatings have been developed in recent years which are fairly equivalent, in performance, to their solvent counterpart. Film integrity, such as fabrication, steam processing and moderate corrosion resistance can be maintained. Applied cost of the water borne system VS its solvent counterpart is lower mainly because of the restricted use of expensive solvents.

Recent developments have produced interior can coatings which meet the FDA requirements as per Regulation 121.2514, now 175.300. Formulating latitude with the water borne epoxy systems have allowed the chemist to circumvent the problems of taste, odor and turbidity when exposed to beer packaging. Application of spray linings can be tailored to provide adequate coverage over both steel and aluminum D&I containers.

Commercial acceptance of epoxy water borne spray lining for the beer and beverage container is on the rise. This article will relate to the interior spray application.

0-8412-0446-2/78/47-078-011$05.00/0

DISCUSSION:

Water borne epoxy interior coatings can be classified into three different groups:

a) Water Dispersible Epoxy Coatings
b) Water Epoxy Emulsion Coatings
c) Water Borne Epoxy Coatings-Solution Type

From the above classifications the chemist must survey the known data for the necessary physical parameter conducive toward the proposed end use (interior spray lining in this case). Negative aspects sometimes play the more aggressive role in the choice of vehicle development.

GROUP A - WATER DISPERSIBLE EPOXY COATINGS

In water dispersible epoxy coatings, the epoxy resin is dispersed with the aid of a suitable dispersing agent. These systems are heterogeneous in nature and have several distinct disadvantages:

1. The dispersant must be held to an absolute minimum because of possible flavor contamination in packaged beer or beverage.

2. Solvent tolerance of the resultant dispersion is rather limited and extremely critical. Because of this factor separation is generally noted.

3. Extended storage generally produces settling within the finished goods (product).

4. Spray application of the epoxy dispersion systems is extremely difficult. (Poor substrate wetting).

GROUP B - WATER EMULSIFIABLE EPOXY SYSTEMS

1. Similar to the epoxy dispersion family, but much more complex.

2. Need for an emulsifying agent and other surface active agents to protect the encapsulated particle.

The necessity for such additional additives, to maintain the emulsion system, increases the possibility of flavor off - notes of the packed media.

3. Possibility of water sensitivity generally caused by the presence of the various surface active agents.
4. Lowest gloss factor of the three variables under consideration.
5. Spray application much better than the epoxy dispersion system.

GROUP C - WATER BORNE EPOXY SOLUTION SYSTEMS

The solution type water borne epoxy coatings are generally epoxy resins esterified with different acids. These esters are subsequently neutralized with amines. Water and a suitable cosolvent are then added to reduce the polymer to the desired non-volatile content. Curing agents of various types (such as Melamines, Urea-Formaldehyde or Phenolics) may then be added to optimize the system. The resultant epoxy system exhibits excellent gloss, flow and film formation. This type of coating system is very comparable to solvent based epoxy coatings even in product resistance.

Having resigned ourselves to concentrate on the development of the solution type water borne epoxy, several major parameters must be satisfied. These are:

1. Taste and Odor Profile - (The coating material should neither impart or distract any flavor connotations from the packaged media).
2. Turbidity Resistance - (Maintain the desired clarity of the packaged goods).
3. Application - (Sprayability).
4. Shelf Stability - (Hydrolitic stability).

EXPERIMENTAL DETAILS

All coating systems were evaluated over the 12 oz. (211 x 413) two piece aluminum container (D&I). The treatment on these containers were both Alodine 401-45 and 404. The steel D&I can was also included in our investigation. Dry film deposition for the aluminum container was 120-140 mgs./can and the stoving cycle 2 minutes @ 400°F. For the steel container the film weights were increased to 180-200 mgs./can and cured 2 minutes @ 400°F.

The coated containers were evaluated for beer and water pasteurization at 160°F. for 30 minutes. Taste and odor profiles were generated as well as beer turbidity definition.

The attached data indicates the results of the different water borne coatings evaluated in our laboratory.

TABLE I

Having established a vailid coatings candidate (solution water borne epoxy) our next step was to define reproducibility and stoving latitude.

TABLE II

Indicates our findings with System A - Laboratory Batch: B - 1st Pilot Batch.

TABLE III

Represents our taste and odor characterizations. Having successfully demonstrated the validity of our approach utilizing the solution type epoxy, one major hurdle remained: That being application. Because of various profiles of the D&I container being used in the industry, sprayability (uniform coverage) can be very evasive. Assistance from the spray equipment people was enlisted to maximize our efforts.

Collectively, we were able to achieve good film distribution of side wall coverage from 3.0 to 3.5 mgs./4 in.^{2} and yield enamel rater readings of an average of 5 ma. Total film weight in the container was roughly 120 mgs. Temperature, pressure and solvent balance seemed to have more influence on our material than did initial viscosity. Better atomization at the lower fluid volume output seems to be the key.

TABLE I. WATER BORNE COATINGS

System	Type	Water Past. 160°F. 30 Min.	Beer Past. 160°F. 30 Min.	MEK Rubs	Adhesion	Turbidity Resistance After 3 Mos. @ 105°F.	Taste	Flavor	Application Characteristic	Stability 6 Months @ 77°F.
Coating A	Vinyl	Sl.Blush	Sl.Blush	10-15	ok	Satisfactory	ok	ok	Not Satisfactory	Satisfactory
Coating B	Epoxy/ Acrylic Emulsion	ok	ok	>50	ok	Excellent	ok	Not Satisfactory	ok	ok
Coating C	Epoxy Dispersion	ok	ok	>100	ok	ok	ok	ok	ok	ok
Coating D	Epoxy Solution Type	ok	ok	>100	ok	ok	ok	ok	ok	ok

*Coating A & B gave inferior results on steel cans compared to aluminum. However, coating C and Coating D has equivalent performance on both aluminum and steel cans.

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

TABLE II

			H_2O Past. 30' @ 160°F. X Scotch Tape	Beer Past. 30' @ 160°F. X Scotch Tape
404 Alumn.	2' @ 360°F.	A	0-0	0-0
401 Alumn.	2' @ 360°F.	A	10-10	8-2
Steel	2' @ 360°F.	A	10-10	0-0
404 Alumn.	2' @ 360°F.	B	10-8	9-8
401 Alumn.	2' @ 360°F.	B	0-10	0-7
Steel	2' @ 360°F.	B	10-10	0-0
404 Alumn.	2' @ 385°F.	A	10-10	10-9
401 Alumn.	2' @ 385°F.	A	10-10	10-8
Steel	2' @ 400°F.	A	10-10	10-10
404 Alumn.	2' @ 385°F.	B	10-10	10-10
401 Alumn.	2' @ 385°F.	B	10-10	10-10
Steel	2' @ 400°F.	B	10-10	10-10

Lab Batch Orig. A
1st Pilot Batch - B

Legend: 0 - Complete Failure
10 - Perfect

TABLE III

All samples and the control were prepared using unpasteurized beer. The samples were then pasteurized and held for approximately 30 days before the flavor evaluation was conducted. The taste panel consisted of 8 panelists.

CODE SHEET

Lab Number	Collective Panel Rating	Distribution*
Control (Blank)	+1.3	7/0/1
Sample A	+1.4	8/0/0
Sample B	+1.3	8/0/0
Sample C (Solvent base epoxy control)	+1.0	7/0/1

*In the rating distribution, the first figure indicates how many panel members gave a plus (+) opinion; the second figure indicates how many gave a zero (0); the third figure signifies how many gave a minus (-) rating.

COMMENTS

CONTROL SAMPLE

Dull aroma. Reasonably fresh. Rather full in body and flavor. A trace of harshness. The hop bitter and aftertaste are of average intensity. The flavor is moderately aromatic and malty, rather dry and estery, slightly astringent with a grainy note. Good drinking quality.

SAMPLE A

Slightly fresher tasting and smoother palate than the Control Sample. Very good drinkability.

SAMPLE B

Smoother palate and diminished dry overtones. Good panel acceptance.

SAMPLE C (Solvent Base Epoxy Control)

A trifle fresher tasting with smoother palate and lessened dry notes. Reasonably good drinking quality.

SUMMARY

While other approaches directed toward the interior spray application of the D&I container have merit, we feel that the water borne solution epoxy offers the best latitude. Coating systems based on this technology require very little deviation from the norm with respect to resin manufacture and subsequent letdown. This is a very prominent factor to consider because most of the previous knowledge of solvent type epoxy systems can be readily applied. Indications are that some energy conservation and improved economics can also be achieved.

ACKNOWLEDGMENT

Many thanks to D. Merchant for his exhausting resin development input and Herb Goldt for his meticulous laboratory investigation. Thanks also to the Nordson people for their valuable contribution.

RECEIVED JUNE 12, 1978.

4

Container Coatings Based on Dispersions of Epoxy Resins in Water

FRANK N. JONES, THOMAS H. GLADNEY, WILLIAM T. SOLOMON,
JOHN R. GREENWALD, JOHN E. MASTERS, and DAVID A. SHIMP

Celanese Polymer Specialties Co., Technical Center, 9800E Bluegrass Parkway,
Louisville, KY 40299

Coatings based on epoxy resins have been used to line food and beverage containers for over twenty-five years. These coatings are based on blends of resin (idealized structure in Fig.1) with a small proportion of crosslinker, usually an aminoplast which reacts predominately with the secondary hydroxyl groups along the backbone of the resin. Baking produces a film which has much of the toughness and chemical resistance of a thermoset coating yet retains considerable elasticity and is capable of excellent adhesion. These characteristics give epoxy coatings an outstanding combination of properties for container interiors - chemical inertness, physical damage resistance, little or no effect on flavor and the ability to protect metal from contents and vice versa.

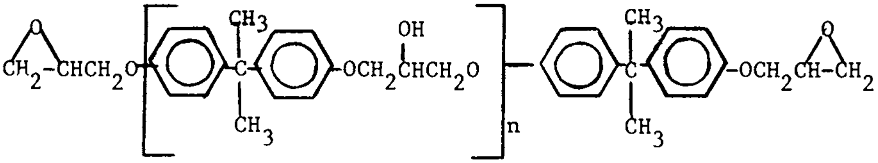


Figure 1.

Soon after the development of the two-piece drawn and ironed beverage can, epoxies were recognized as a preferred coating. In addition to adhesion and toughness, epoxy coatings are able to overcome a number of irregularities that occasionally arise during two-piece can production. They cover surface scratches well, they protect container contents from substances such as drawing lubricants which are occasionally left on the metal surface, and they are somewhat tolerant of variations in metal pretreatment, application and bake conditions.

Most epoxy resins used in container linings are especially tailored for the purpose. Molecular weights are relatively high, ranging from 2500 to 8000 (n = 8 to 27 in Figure 1).

0-8412-0446-2/78/47-078-019$05.00/0

Lower molecular weights are usable, but molecular weights above 2500 impart superior elasticity to the film and are believed to reduce the potential for food or beverage contamination from traces of uncrosslinked substances in the cured film.

Epoxy coating technology has not been static. In recent years "low-bake" formulations based on specific resins, crosslinkers and solvent blends have been developed. Low-bake coatings can be cured at oven temperatures 20°C. to 40°C. lower than first generation epoxy coatings and they have broader bake latitude. Oven temperatures can vary over a 30°C. range without serious adverse effects.

Historically the reliability of epoxy container coatings has been superb. Over 10^{11} cans have been coated, and the frequency of major coating-related problems has been very low. Epoxy coatings have established an excellent reputation among brewers for their ability to protect beer from flavor variations and among food canners for their ability to protect metal from aggressive contents.

Container coatings are usually applied by rollcoating flat stock or by high-speed automatic spray into formed cans. Both methods require the resins to be used as dilute solutions in organic solvents to achieve low viscosity, substrate wetting and film-thickness control. Current formulations usually are sprayed at 20% to 23% solids by weight and are rollcoated at 28% to 42% solids. Application in this form causes air pollution and it wastes solvents and energy. Therefore, new physical forms for epoxy coatings are needed.

The industry is seriously examining coatings based on four technologies:

(1) Water-dilutable epoxy resins
(2) Emulsions of liquid epoxy resins in water
(3) Dispersions of solid epoxy resins in water
(4) Epoxy powders

Each of these technologies has some attractive features, but each involves major technical problems. Our group has been exploring all of them for more than a decade. In recent years we have been working intensively with the third, epoxy dispersions. This paper is a generalized report on how this technology is progressing.

CURRENT DISPERSION COATING FORMULATIONS.

An epoxy dispersion container coating is based on a small particle size dispersion in water of solid resins and crosslinkers very similar to those used in solvent-borne coatings. Small amounts of dispersants are required to stabilize the dispersion, and other substances are usually added to adjust rheology for application. The total weight of non-volatile additives may be 2% to 8% of the weight of the film. Particle diameter is predominately 0.5 μm to 3 μm, although this may not be the optimum range. Spray formulations contain 25% to 30%

solids by weight; relatively high solids are possible because the dispersed resin adds little to the viscosity of the medium. The formulation complies with all applicable requirements of Section 175.300 of Title 21 of Code of Federal Regulations for food contact coatings (1). Such coatings have been manufactured in production equipment.

Originally it was hoped that such dispersions could be applied on present-day spray equipment with almost total pollution abatement. However, most current formulations incorporate 18% to 20% by volume of organic solvent to improve sprayability and to promote formation of uniform films.

FILM PROPERTIES OF DISPERSION COATINGS

The resins used in dispersion coatings are Bisphenol-A/epichlorohydrin types crosslinked with amino resins, similar to those used in solvent-borne epoxy can coatings. There is no need to reduce the molecular weight of the epoxy resin or to chemically bond solubilizing groups to make it water-dilutable. Molecular weight is within the 2500 to 8000 range preferred for film physical properties and flavor. This advantage is being realized in practice. Industry requirements for properties such as solvent resistance, adhesion, pasteurization resistance and absence of volatiles in the cured film have been met or exceeded. For example, dispersion coatings resist the necking and flanging of two-piece cans better than current coatings based on water-soluble resins. Dozens of beer flavor tests of various formulations have given consistently good results, usually equalling controls and sometimes surpassing them. Of course, substantial effort was required to find dispersants and modifiers which do not adversely affect coating properties. Crosslinkable modifiers which meet this requirement have been identified.

METAL PRETREATMENT

Dispersion coatings have excellent adhesion to detergent-washed aluminum, to aluminum treated with the standard pretreatments and to most of the surfaces encountered in steel cans. However, it is recommended that in converting to water-borne coatings of any type the industry should take extra care with washing and pretreatment procedures until the boundaries of acceptable practice can be defined. Such care might prevent coating failure caused by adhesion loss or poor wetting.

Formulators of any water-borne container coating face an inherent problem: the surfaces to be coated are designed to be easily wetted by solvent-borne coatings whose surface tensions usually range from 26 to 28 dynes/cm. Water has a very high surface tension, 72 dynes/cm. at 25°C., and it will not wet low energy surfaces. Additives are available which are capable of reducing surface tension to about 32 dynes/cm. and which are acceptable for use in food contact coatings, but the ideal 26 dynes/cm. level is difficult to achieve. Even if low surface tension is achieved, it is doubtful that water-borne coatings can be as effective as solvent-borne ones in "biting" into oil-contaminated surfaces.

APPLICATION

The most troublesome obstacles to developing water dispersion coatings lie in the application area. The formulator is faced with the formidable task of applying a dispersion on equipment designed to suit the rheological characteristics of a solution. The rheology of the dispersion is grossly different. Further, the dispersion offers relatively little latitude for adjusting solvent evaporation rates.

In the early stages of development application difficulties characterized by poor substrate wetting, blistering, poor atomization during spray, spray nozzle plugging, instability at elevated temperatures and poor flow during rollcoating were encountered. These problems have been overcome in the spray area as evidenced by a series of successful runs in two-piece can plants under representative production conditions. They were solved mainly by formulation refinements combined with minor equipment changes.

Dispersion coatings having excellent application characteristics have recently been formulated. Only minor set-up adjustments are needed to convert a two-piece can line from solvent-borne to aqueous dispersion spray coatings. Beer film weights (90-120 mg./can) can be achieved, and the relatively high solids of dispersion coatings are advantageous for soft-drink film weights (160-220 mg./can). Special spray nozzles now being designed especially for water-borne coatings may offer advantages.

To prevent spray nozzle plugging all solid particles large enough to plug a 70 µm orifice have been scrupulously eliminated. Particle diameter is under good control in the 0.5 µm to 3 µm range, and few if any particles as large as 10 µm are present in current formulations. No instance of nozzle plugging has occurred in more than two years of laboratory and production trials.

Dispersion coatings have several advantageous application characteristics:

(1) Spray line start up is easy; the opacity of the wet coating allows the operator to visually check uniformity of coverage.
(2) Clean up is easier than with any other coating type.
(3) Less filter blockage occurs than with other types of water-borne coatings.

Also, dispersion coatings offer potential energy savings. Baking temperatures are similar to those of "low-bake" epoxy coatings, and the cure rate is such that the first oven zone can be operated at reduced temperature. Further, the low proportion of solvent could reduce the amount of heated air which must be exhausted to stay safely below the lower explosive limit.

TABLE I.

AIR POLLUTION ABATEMENT POTENTIAL OF SPRAY-TYPE EPOXY INTERIOR CAN COATINGS.

Coating Type	% Solids By Weight	Ratio of Water to Organic Solvent By Volume	Ratio of Water to Organic Solvent By Weight	Weight Ratio Organic Volatiles to Solids	Organic Solvent Reduction
Solvent borne, standard solids	20.6	-	-	3.85:1	Standard
Solvent borne, maximum solids	23.0	-	-	3.35:1	13%
Water borne, dilutable resin	20.0	70:30	74:26	1.04:1	73%
Water borne, dilutable resin	20.0	80:20	83:17	0.68:1	82%
Water borne, dispersed resin	27.5	80:20	83:17	0.45:1	88%
Water-borne, dispersed resin	38.0	95:5	96:4	0.066:1	98%
Powder Resin	99	-	-	-	99%

Formulations for three-piece cans, end stock and side-seam stripe are not yet as well refined as those for two-piece cans, but we believe that dispersion technology will soon find uses in these areas.

AIR POLLUTION ABATEMENT

Current dispersion coatings are formulated to meet all present and proposed U.S. environmental regulations. The volatile portion contains at most 20% of organic solvent measured by volume.

Current coatings based on water-dilutable epoxy resins are frequently formulated at a 70:30 water:organic solvent volume ratio to meet interim regulations. The proportion of solvent can be reduced, but technical problems multiply as coupling solvent is subtracted. An 80:20 ratio appears feasible, but it may be near the limit of what can be accomplished without substantial trade off.

In contrast, coatings based on water dispersions have the potential to far exceed current EPA regulations and to meet the very stringent regulations being proposed abroad. Coatings which are virtually solvent free are possible, and a formulation having a 95:5 water:organic solvent ratio shows considerable promise. However, such formulations cannot be properly applied to two-piece cans using presently available equipment. The application problems could probably be overcome with concentrated engineering effort.

Even when formulated at an 80:20 water:solvent ratio, dispersion coatings are ecologically attractive because they can be applied in more concentrated form than water-dilutable types. The situation is summarized in Table I, from which it can be seen that to apply a given weight of solids from a water-dilutable coating containing 20% solids by weight requires about 50% more solvent than to apply it from a dispersion coating containing 27.5% solids. This factor is expected to increase in importance in future years. The trend in U.S. regulatory philosophy is toward controlling total organic effluent and away from the less fundamental approach of controlling water:solvent ratio.

SUMMARY

The feasibility of using epoxy dispersion coatings formulated at an 80:20 water:organic solvent volume ratio for two-piece cans has been firmly established. The technology is expected to be broadly applicable to other container interior uses. It offers a number of advantages including the potential for almost total pollution abatement. In the future, as environmental regulations tighten, the advantages of dispersion technology may become compelling.

LITERATURE CITED

(1) Title 21 was recently reorganized; the former section 121.2514 is now section 175.300. Federal Register 42, No.50, page 14545 (1977).

RECEIVED MAY 23, 1978.

Coatings for Drawn Tinplate and Chrome-Coated Steel Food Containers

G. W. GERHARDT, K. G. DAVIS, and J. R. HALL

Mobil Chemical Co., Packaging Coatings Dept., 2000 Westhall St.,
Pittsburgh, PA 15233

Drawn containers made from tinplate and chrome-coated steel are beginning to make a significant penetration into the food container market. Utilization of these substrates for the production of a single draw or draw-redraw container has been prompted primarily by three factors:

1. The success of the drawn aluminum container in this market.
2. The increasing concern with the possibility of introducing trace quantities of lead into the packed product when lead-containing solders are used in making three-piece soldered side seam containers.
3. The continuing desire by industry to investigate whether better or lower cost containers than those already on the market can be made commercially.

The manufacturer of a single or multiple draw container requires coatings which have much better fabrication properties than those commonly used on tinplate and chrome-coated steel three-piece containers where the coating must withstand only a simple forming, or is applied after fabrication of the container. The drawn container is fabricated from precoated metal to yield a container with a wall thickness essentially equal to the thickness of the bottom of the container and, in turn, equal to the thickness of the original flat metal stock. There is very little thinning or thickening of the metal, but the metal is drastically reformed, particularly on the sidewall near the top of the can. From a practical standpoint, the industry would like to form the container to the maximum capability of the metal being used. Thus, it is necessary that the coatings industry develop coatings which will perform under severe drawing conditions. Also, to

0-8412-0446-2/78/47-078-025$05.00/0

provide extra strength in the wall of the container, many cans have circumferential beads in the body. The beading operation is done after drawing of the can and thus adds further deformation.

Coatings for food containers, by necessity, must have the ultimate in physical properties. In addition to the requirement that the coating not change the food in any way, the coating must possess a multitude of other requirements. Sterile food packs are produced by processing the container after packing of the food or by aseptically packing a sterile product in a sterilized container. The elevated temperatures to which the container is exposed during these processes require that the coatings perform under elevated temperatures as well as at normal storage temperatures. The particular properties which the coatings must possess are that they not change in any way during the processing cycle, and the coating on the exterior of the container must have exceptional scuff resistance at elevated temperature since that coating is in direct contact with the sterilizing equipment.

After the container is filled and processed, then the organic coating must protect the food product during storage periods as high as 100°F. for periods as long as two or three years.

Experimental

The primary problems in the evaluation of coatings for drawn containers is to obtain meaningful test results in a short period of time so that significant progress can be achieved rapidly.

Early in our work we found that we could not duplicate the drawing of a container by any simple fabrication test. We therefore procured equipment for drawing a 202X200 can utilizing a 44% reduction in the first draw and 22% in the second draw. After we did considerable work with this straight-walled container, we found that it was not quite as severe in fabrication as commercial containers, so we procured a set of tools which beads the can. A deep bead near the flange area gives us as extreme fabrication as we have seen on most commercial cans.

After fabrication of the container, the cans are packed, seamed with an end which has a product resistant coating on it and processed. We prefer using a 90 minute at 250°F. process, even though some products do not require such stringent sterilizing conditions. After cooling of the containers, the exterior and interior are examined for coating performance and, presuming the coatings pass this initial screening, duplicate containers are placed on storage at room temperature and at 120°F. We recognize that no food products are stored at 120°F., but we use this temperature to accelerate breakdown of the coated can.

The best way of developing a coated can for a particular product is to pack that product under commercial conditions. Since we are not always certain as to what products will be packed, we must simulate pack conditions. Quick tests for coating integrity are generally run with a solution consisting of 10 parts hydrochloric acid/20 parts $CuSO_4 \cdot 5H_2O$/70 parts water. Exposure times to this test solution may vary from several minutes to several hours. This test is simply a screening test to determine whether the coating has fabricated properly and whether that system should be put on long term packs. Products which we test pack representing various types of foods are shown in Table 1. We do not pack foods the way they would be packed commercially; that is, from the basic food ingredients. Our packs are all actually repacks. We feel, however, that by repacking a standard commercial product, we can insure ourselves good control of the characteristics of that product without requiring extended food preparation time.

Results

Early in the test work we determined that the coatings which performed the best were those which showed the best initial fabrication. Typical fabrication and process properties of coatings are presented in Table 2. Of those which showed good fabrication, a few were quickly eliminated because they did not have the required hydrolytic stability or the resistance to softening by fats and oils that are required of many foods. The primary development work then centered around the formulation of polyvinyl dispersion type coatings and epoxy formulations.

Since the data in Table 2 shows that the PVC dispersion vinyls as a rule have better fabrication than the epoxies, we tried to use the PVC dispersions on both the interior and the exterior of the can. However, in studying exterior coatings, we discovered that the PVC dispersions are not really thermosetting; and, consequently, they will resoften slightly during processing of the filled container. Also, any movement in the sterilizer will abrade the PVC dispersion off of the metal. Epoxy coatings which thermoset during the bake are not subject to this type of adhesion

TABLE 1.

TEST MEDIA

Type of Food		Product Packed
High acid	or	5% acetic acid/3% salt in water Lemon pudding
Fatty		Vienna sausage
High sulfur	or	Pea and ham soup Tuna in brine
Highly aromatic		Barbecue sauce

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

TABLE 2.

RELATIVE FILM PROPERTIES OF COATINGS

	Solution Vinyls	PVC Dispersion Vinyls	Thermosetting Epoxies	Polyesters	Oleoresins	Phenolics	Acrylics
Fabrication							
Single draw	Exc.	Exc.	Exc.	Exc.	Fair	Fair	Good-Exc.
Double draw	Exc.	Exc.	Good	Good	Poor	V. poor	Poor-Fair
Food sterilization resistance (250°F)	Poor	Exc.	Exc.	Exc.			

Exc. = Excellent

failure. To assure ourselves that these observations were based on sound technical facts, we ran some scratch tests and coefficient of friction values on a number of coatings at 250°F. These results are shown in Table 3 and clearly demonstrate the superiority of a thermoset epoxy to the PVC dispersions.

Having decided that the thermosetting epoxy coatings are best for use on the exterior of the container, we had to determine what level of internal lubricant was optimum for fabrication. We advocate the use of an external lubricant prior to fabrication of the container, but we also recognize that a small amount of lubricant incorporated into the coating (an internal lube) facilitates good fabrication. Typical data showing the effect of lube level are shown in Table 4. Note that the optimum range is 0.25 to 0.75% based on the coating solids. Our experience is that this level is generally sufficient for most coatings. One thing we do want to point out is that we have never been successful in adding a sufficient amount of internal lube so that external lubrication can be eliminated in severe fabrications such as the draw-redraw or triple draw can. Also, at levels of 3-5% lubricant, the coatings begin to take on the characteristics of the lubricant and become soft and cheesy.

Although the PVC dispersions are not hard enough to take the scuffing on the exterior of the container, they are preferred compositions for the interior. Since there is no universal preference for color of the interior coating, we have found it necessary to formulate gold, buff, white and aluminum pigmented coatings. We as formulators have no particular preference for color. We recognize both advantages and disadvantages to a particular color. For example, white will hide any variations in the appearance of the metal surface and have a nice clean look, but if that white shows appreciable variation in color due to film thickness or bake variations or if it absorbs any colorant from the food, it will have less chance of being a successful coating.

Because the levels of colorant may vary, we experience slightly different properties among different colors depending upon coating weight. Some general guidelines are shown in Table 5. Note that the gold and the aluminum coatings generally have good performance in the 6-8 mg/sq. in. range, while the buff and white coatings generally require 8-10 mg/sq. in. for good performance.

Having established that PVC dispersions appear to be best for the interior of the container and the

TABLE 3.

HOT MAR RESISTANCE OF EXTERIOR COATINGS

All measurements made at 250°F.

	Epoxy A	Epoxy B	PVC Dispersion F
Scratch Resistance	Good	Good	Poor
Pencil Hardness	2H	F	HB
Coefficient of Friction	0.2-0.25	0.2	0.35

TABLE 4.

EFFECT OF LUBRICANT LEVEL
ON
COEFFICIENT OF FRICTION AND FABRICATION

Coating: Colorless Epoxy C

Internal Lube Level (%)	COF	Fabrication
0	0.45	Poor - even when using external lube
0.25 - 0.75	0.2	Optimum range for good fabrication using external lube
0.75 - 3.0	--	No advantage over lower level
>3	--	Film is cheesy

TABLE 5.

EFFECT OF LINING COATING WEIGHT
ON
CONTAINER PERFORMANCE

PVC Dispersion Vehicle

	Container Performance*		
Pigmentation:	Gold	Buff or White	Aluminum
Coating Weight (mg/sq in)			
4 ± 1	Marginal	Poor	Marginal
6 ± 1	Acceptable	Marginal	Acceptable
8 ± 1	Preferred	Acceptable	Preferred
10 ± 1	--	Preferred	--

*Rating scale:

Preferred: Will hold most foods.

Acceptable: Will hold only mildly corrosive foods.

Marginal: Will hold some foods, but at this film weight, is on border of good continuity.

Poor: Coating too porous to hold a liquid.

thermosetting epoxy best for the exterior, our next task was to assure ourselves the coatings selected were, in the terms of the can industry, "compatible." In other words, could one coating be applied to one side of the plate and the other coating to the other side. We do not have problems when sheets are coated, since the epoxy is normally applied and baked first and then, the vinyl dispersion is applied and baked. The epoxies generally have sufficient latitude to maintain their properties even after a double bake. However, when coil stock is coated, the coatings are applied in tandem and given one bake, and it is essential that the epoxy coating get its full cure without overbaking the vinyl dispersion. The matching of cure rates has been one of our most difficult problems, and the problem becomes progressively more difficult as the bake time gets shorter and shorter.

In the development of coatings for tinplate and TFS containers, we have been successful in matching the interior and exterior formulations as shown on Table 6. Here we show that, although we have two PVC dispersions which cure at different temperatures on coil bake cycles, one epoxy can be used with both dispersions.

One question that is asked repeatedly is whether coated tinplate can be heated above the reflow point of tin and still give satisfactory performance. Our experience is that temperatures above the reflow point of tin have no effect on the coating if that temperature is needed to cure the coating. We do recognize that if the metal is not quenched immediately on exit from the oven, the tin will crystallize in a matte appearance rather than the shiny appearance normally associated with tin. Actually, slow cooling generally gives a mottled, varied appearance to the sheet. As to whether the heating of the tinplate affects the basic corrosion resistance of the tin, this is a question which needs to be answered by the metallurgists. Our best input is that there is no effect on corrosion resistance under normal coating and baking conditions. For those operations where someone feels they cannot go above the reflow point of tin, they would have to use the coating designated "PVC Dispersion G" in Table 6. If metal temperature is not a real factor, either of the dispersions listed in the table could be used.

The final consideration must be whether the container will hold the product. In Table 7 we have listed typical products and typical results. While we feel that most products can be packed in lined, draw-

TABLE 6.

EQUIVALENT BAKE CYCLES

	Time		Temperature (°F)	
	Total	At Peak	Air	Peak Metal
PVC Dispersion G	10 min	7.5 min	400	400
	25 sec	10 sec	650-675	435
PVC Dispersion H	10 min	7.5 min	400	400
	25 sec	10 sec	700-725	500
Epoxy C	10 min	7.5 min	400	400
	25 sec	10 sec	650-675	435
	25 sec	10 sec	700-725	500

TABLE 7.

PERFORMANCE OF COATED CANS

Coating: PVC Dispersion
Can: Draw/Redraw

Substrate:	Tinplate	TFS (chrome coated steel)
Food		
Low acid	OK	OK
High acid		
Fruits	OK	OK
Vegetables	OK	OK
Pickles	OK	Fails
High sulfur products		
Meats; beans	Some staining	OK*
Milk products	OK	OK
Products in brine	OK	OK

*Unless draw is so severe that appreciable cracking of chrome layer occurs redraw cans, we do recognize the true limitations in Table 7. No organic coating is completely impervious to the sulfur compounds produced during the processing of meats, beans, peas and so forth. Consequently, some metal staining may appear with some products. This is generally not objectionable unless the appearance of the container is changed drastically or if the failure is so severe that the integrity of the coating is reduced to the point where it permits metal ion transfer to the product. One other observation we have made is that the TFS chrome-coated steel is not satisfactory for products with high acetic acid content. Fortunately, not many food products fall into this category.

Conclusion

Coatings suitable for use on tinplate and TFS (chrome-coated steel) for making draw-redraw food containers have been developed. Cans are in commercial production with a limited number of products. We predict that this market will expand rapidly in the next few years as more experience is gained.

RECEIVED MAY 31, 1978.

6

Photocurable Epoxide Coatings for Metal Containers

DENNIS KESTER and W. A. TARWID
American Can Company, 433 N. Northwest Hwy., Barrington, IL 60010

The curing of coatings by ultraviolet radiation offers several significant advantages when compared to thermally cured solvent and waterborne materials. Radiation curing units consume less energy and require less floor space than gas-fired ovens. Furthermore, UV cured coatings contain little or no solvent and therefore significantly reduce pollution.

Ultraviolet radiation curable epoxide coating formulations contain a blend of epoxide monomers and oligomers and a photosensitive diazonium salt. When exposed to ultraviolet radiation, photodecomposition of the diazonium salt occurs releasing a Lewis acid as shown in Figure 1(1,2,3). When thermally decomposed, this reaction is known as the Schiemann reaction(4). Among the Lewis acids that may be generated by this reaction are boron trifluoride (BF_3), pentafluorophosphate (PF_5), antimony pentafluoride (SbF_5), and antimony pentachloride ($SbCl_5$). Once generated, the Lewis acid complexes with the oxirane oxygen causing opening of the epoxide ring and thereby generating cationic polymerization of the blend as shown in Figure 2.

An advantage of this system over the free radical initiated systems is that cationic polymerization is not inhibited by oxygen. A disadvantage is that the cationic polymerization is inhibited whenever the epoxide blends are exposed to materials containing substances which can act as Lewis bases, e.g., nitrogen containing molecules.

By properly blending epoxide monomers and oligomers, UV cured coatings with a wide variety of properties can be prepared. Coatings possessing good film

0-8412-0446-2/78/47-078-038$05.00/0

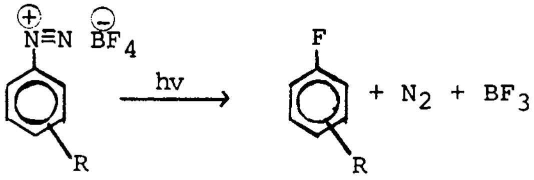


Figure 1. Photodecomposition of diazonium salt

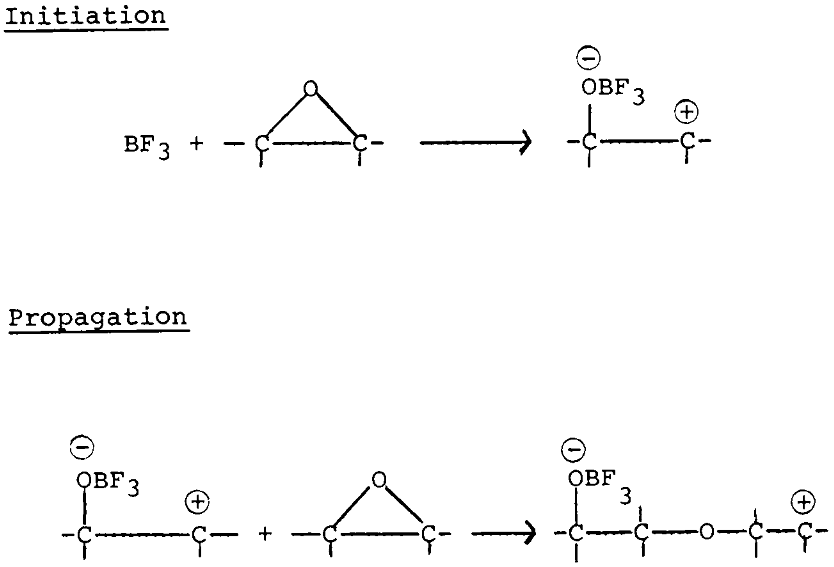


Figure 2. Polymerization

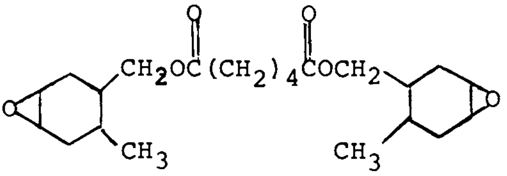
integrity, adhesion, flexibility, hardness, chemical resistance, and toughness are needed for end varnishes where flat metal plate is coated and then formed. Additional properties such as gloss retention and mobility are needed for overprint varnishes for container labels. With the large number of epoxide resins available, these properties may be achieved by proper blending.

Three epoxide monomers and one epoxide oligomer are shown in Figure 3. Table I lists a series of measurements which were made on formulations using these materials. These measurements were obtained on prebaked tin free steel plate with several different formulations in order to illustrate the property versatility of UV curable epoxide coatings.

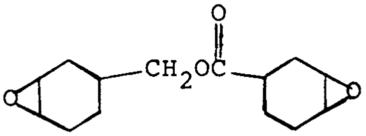
Table II illustrates how different ratios of two epoxide monomers, i.e., CY-179 and RD-2, affect film properties. It might be expected that the higher the epoxide value, the faster the blend would cure or become tack free. However, as shown in Table II, the epoxide values for formulations A through E are the same and formulation B cures the fastest. It is not completely understood why formulation B cures the fastest, however, it may be related to the fact that formulation B has a higher cycloaliphatic epoxide value than formulations C, D and E. Cycloaliphatic epoxides tend to be more reactive than glycidyl epoxides. By this argument, formulation A would be expected to cure the fastest, i.e., highest cycloaliphatic epoxide value; however, it has the highest viscosity. Cure rate tends to decrease at high viscosity values ($>$300 cps at 25°C). It can be seen that there has to be a formulating trade-off between viscosity and cycloaliphatic epoxide values.

The data shown in Table II illustrate that a wide range of softening points may be obtained with differing resin ratios. It can also be seen that the softening point almost always increases when the UV cured film is given a thermal treatment. This is probably the result of further polymerization and the possible volatilization of unreacted low molecular weight materials present in the film.

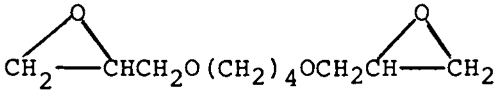
The adhesion grades shown in Table II indicate no definite trend with cure rate, softening points, etc. However, the thermal postbake always improves the adhesion properties of the films. Again, this is



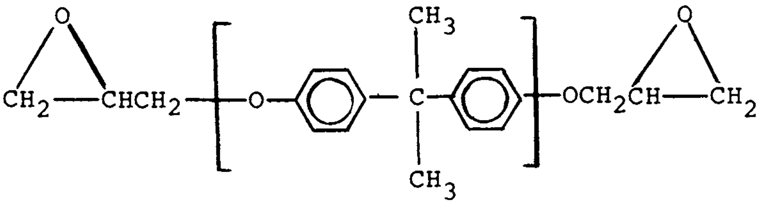
CY-178 (Ciba Products Co.)



CY-179 (Ciba Products Co.)



RD-2 (Ciba Products Co.)



Araldite 6004 (Ciba Products Co.)

Figure 3. Structures of material used in blends

TABLE I.

PARAMETERS AND PHYSICAL PROPERTY MEASUREMENTS

1. Tack Free Time - Number of seconds until tack free after exposure to two 170 watts/inch UV lamps at a belt speed of 110 feet/min.
2. Viscosity - cps at 25°C.
3. Epoxide Value - 100/epoxide equivalent weight
4. Cycloaliphatic Epoxide Value - 100/cycloaliphatic epoxide eq. weight
5. Softening Point - Determined by Perkin Elmer thermomechanical analyzer after UV exposure
6. Softening Point After Thermal Postbake - Determined after UV exposure and a thermal postbake of 380°F. for 9 minutes.
7. Adhesion - Coating is scribed with an "x" and tested with #610 Scotch Tape. Number represents relative amount of loss (0 = no loss and 10 = 100% loss).
8. Adhesion After Thermal Postbake - Same test as No. 7 after UV cured coating has been postbaked at 380°F. for 9 min.
9. Pasteurization Adhesion - Same test as No. 7 after UV cured coating is exposed to 160°F. water for 20 minutes.
10. Pasteurization Adhesion After Postbake - Same test as No. 8 after coating is exposed to 160°F. water for 20 minutes.
11. Reverse Impact Resistance - 30 inch-pounds - The number represents the relative amount of metal exposed after impact (0 = no metal exposure and 10 = 100% metal exposure).
12. Reverse Impact Resistance After Postbake - Same test as No. 11 after UV cured coating has been postbaked at 380°F. for 9 minutes.
13. Wedge-Bend - 30 inch-pounds - The number represents the relative amount of metal exposed after impact.
14. Wedge-Bend After Postbake - Same test as No. 13 after UV cured coating has been postbaked at 380°F. for 9 minutes.

TABLE II.

PROPERTIES OF CY-179 AND RD-2 BLENDS[1]

Formulation		A	B	C	D	E
CY-179		100	75	50	25	0
RD-2		0	25	50	75	100
Properties[2]						
Tack Free Time	-	8	1	2	6	125
Viscosity - CPS @ 25°C.	-	346	100	47	25	24
Epoxide Value	-	0.71	0.71	0.72	0.72	0.72
Cycloaliphatic Epoxide Value	-	0.71	0.53	0.36	0.18	0.00
Softening Point	-	64	74	44	8	8
Softening Point After Postbake	-	74	89	56	12	10
Adhesion	-	0	8	3	5	4
Adhesion After Postbake	-	0	0	1	1	1
Pasteurization Adhesion	-	1	10	10	10	6
Pasteurization Adhesion After Postbake	-	0	2	7	7	1
Reverse Impact Resistance	-	10	3	9	9	10
Reverse Impact Resistance After Postbake	-	10	3	5	9	6
Wedge Bend	-	8	5	7	9	8
Wedge Bend After Postbake	-	9	6	5	8	7

[1] The percent of photoinitiator and surfactants is the same for all formulations.

[2] Explanations of property measurements given in Table I

probably the result of further reactions in the UV cured films and the volatilization of the unreacted materials from the film. Even though pasteurization adversely affected most of the formulations, postbaking the films also improved adhesion after pasteurization.

Wide variations were also observed with the reverse impact and wedge bend tests. For these tests, postbaking the UV cured film usually does not significantly improve film properties.

Table III shows the effect of different ratios of CY-179 and CY-178 on film properties. For these two monomers, the epoxide values and the cyloaliphatic epoxide values are identical. It can be seen that the cure rate decreases as the viscosity increases and as the epoxide values decrease. The softening points of these formulations again usually increased after postbake. The adhesion of formulations A, F, G, H and I is quite good, both before and after pasteurization. This is probably because both of these molecules are quite polar. As shown in Table II, only formulation A had good adhesive properties. When successive amounts of the relatively non-polar RD-2 was added to CY-179, the adhesive properties of the coatings were adversely affected.

Table IV shows the effect of different ratios of CY-179 and Araldite 6004 on film properties. It can be seen that Araldite 6004 cures very slowly because of its low epoxide value and high viscosity. The trends indicate that increasing amounts of Araldite 6004 decrease the adhesive properties of the film and generally increase flexibility and impact resistance.

Although only four epoxide materials and thirteen formulations were investigated, this study illustrates the parameters and formulating trade-offs that must be considered when blending ultraviolet cured epoxide coatings. As with any relatively new technology, these experiments indicate that much is not understood. For example, it is not really known how these monomers and oligomers copolymerize or which materials prefer to homopolymerize and which prefer to copolymerize. These questions will ultimately have to be answered in order to fully utilize these systems. However, coatings formulated using this chemistry are now being used commercially. As pollution regulations and energy costs increase, these types of

TABLE III.

PROPERTIES OF CY-179 AND CY-178 BLENDS[1]

Formulation	A	F	G	H	I
CY-179	100	75	50	25	0
CY-178	0	25	50	75	100
Properties[2]					
Tack Free Time	8	12	22	19	19
Viscosity - CPS @ 25°C.	346	392	465	545	685
Epoxide Value	0.71	0.65	0.59	0.53	0.47
Cycloaliphatic Epoxide Value	0.71	0.65	0.59	0.53	0.47
Softening Point	64	32	20	47	28
Softening Point After Postbake	74	52	35	47	29
Adhesion	0	0	0	0	0
Adhesion After Postbake	0	0	0	0	0
Pasteurization Adhesion	1	0	1	1	0
Pasteurization Adhesion After Postbake	0	0	0	1	0
Reverse Impact Resistance	10	4	1	2	1
Reverse Impact Resistance After Postbake	10	9	9	2	1
Wedge Bend	8	7	2	3	1
Wedge Bend After Postbake	9	9	8	1	1

[1] The percent of photoinitiator and surfactants is the same for all formulations.

[2] Explanations of property measurements given in Table I.

TABLE IV.

PROPERTIES OF CY-179 AND 6004 BLENDS[1]

Formulation	A	J	K	L	M
CY-179	100	75	50	25	0
6004	0	25	50	75	100
Properties[2]					
Tack Free Time	8	12	9	11	120
Viscosity - CPS @ 25°C.	346	1187	3000	5500	6000
Epoxide Value	0.71	0.67	0.62	0.58	0.53
Cycloalipatic Epoxide Value	0.71	0.53	0.36	0.18	0.00
Softening Point	64	56	57	55	52
Softening Point After Postbake	74	62	65	72	75
Adhesion	0	0	1	5	0
Adhesion After Postbake	0	0	0	1	0
Pasteurization Adhesion	1	1	2	10	10
Pasteurization Adhesion After Postbake	0	0	1	0	0
Reverse Impact Resistance	10	10	9	4	1
Reverse Impact Resistance After Postbake	10	8	3	3	2
Wedge Bend	8	10	8	7	3
Wedge Bend After Postbake	9	8	6	6	4

[1] The percent of photoinitiator and surfactants is the same for all formulations.

[2] Explanations of property measurements given in Table I.

materials will necessarily occupy a more prominent position among container coatings.

References:

(1) S. I. Schlesinger, U.S. Patent 3,708,296

(2) J. J. Licari and P. C. Crepeau, U.S. Patent 3,205,157

(3) E. Fischer, U.S. Patent 3,236,784

(4) For review, see Roe, Org. Reactions 5, 193-228 (1949)

RECEIVED MAY 22, 1978.

7

High Solids Thermally Cured Systems Now, Forthcoming, and Future

ROBERT W. JAMES, PAUL F. WESTFALL, K. L. PIERCE, and H. J. WRIGHT
Cook Paint and Varnish Co., P. O. Box 389, Kansas City, MO 64141

This delivery will concentrate on 80% volume or higher solids, thermally cured systems and the position such coatings possess at the present, and will possess in the future, relative to the three "E"'s--environment, energy, and economics.

High solids coatings are not novel--only the application of such systems to the container industry is relatively new.

State and Federal environmental protection agencies thrust high solid systems to application reality faster than expected; however, regardless of regulations, economics would have forced the change. Conventional 30-60% solid coatings, in addition to being inefficient in the use of raw materials, are rapidly becoming too costly, due to the spiraling price of solvent.

ENVIRONMENT:

At the present point in time, billions of three-piece sanitary food cans have been commercially produced, beginning in August 1973, utilizing high solids coatings. High solids materials have been used as both interior and exterior protective coatings.

The coating material, similar to an oleo resinous system, has a minimum 80% volume solids at a bake temperature of 10 minutes at 400°F. The coating contains approximately 15% by weight volatile exempt solvent. The system fulfills Ringleman II opacity requirements and, obviously, meet F.D.A. needs.

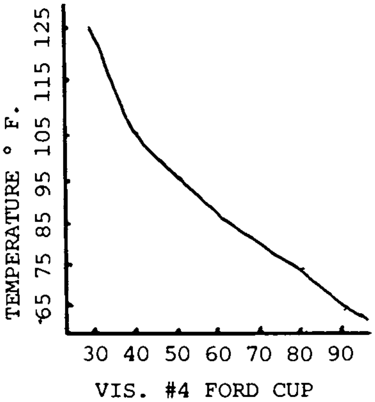
Application problems associated with the above and similar high solid systems have been primarily substrate wetting.

Plate wetting problems may be decreased or eliminated by the use of special flow agents, firm appli-

0-8412-0446-2/78/47-078-048$05.00/0

cation rolls, and heating the coating during roll-coat application. The use of 45-55 durometer application rolls permits the coater operator to apply pressure to the substrate sheet without undue distortion of plate margins. Controlled heating of the coating to 100-120°F. regulates viscosity as well as promoting substrate wetting and minimizes film weight variation.

High solids systems vary widely in viscosity response to heating. The following chart demonstrates the viscosity response of a typical high solids oleo resinous system to heat.



Development problems pertaining to high solids coatings have been discovering cure compositions which exhibit reasonable three to four per cent fuming factors at designed bake schedules. This has been particularly true of melamine of urea curing agents, and tends to be a problem with any condensation reaction which emit a by-product other than carbon dioxide or water. Fuming factors may be governed to an extent by controlled molecular weight distribution, stage baking and reduced baking temperatures.

Fuming factors are not always objectionable or unwanted. Volatilation of unreacted monomer or low molecular weight polymers is desirable and essential to eliminate the possibility of these products being extracted into the food. Extraction into the food product could jeopardize F.D.A. status and possibly cause "off flavor" to the pack media. Volatilization of these undesirables is one advantage thermally-cured coatings display over "cold cure" ultra violet light, electron beam, etc., curing systems that utilize reactive solvents or low molecular weight polymers.

The objective of high solids application is to reduce solvent emission. The following chart demonstrates the relationship between volume solids and surface coated per pound of solvent released. The enamel in the chart is formulated with a 1 to 1 by weight pigment-binder ratio.

HIGH SOLIDS COATINGS

SQUARE FEET OF SURFACE COATED
PER POUND OF SOLVENT RELEASED

% VOLUME SOLIDS	% WT. GAL.	WT. GAL.	SQ. FT. COVERAGE .2 MIL DRY FILM	LBS. OF SOLVENT PER GAL. OF PAINT	SURFACE COATED PER POUND SOLVENT RELEASED
0	0	7.52	0	7.52	0
10	15.6	8.03	800	6.76	110
20	29.4	8.53	1600	6.01	235
30	42.7	9.02	2400	5.26	455
40	52.7	9.53	3200	4.51	710
50	62.5	10.04	4000	3.76	1065
60	71.5	10.54	4800	3.00	1600
70	79.6	11.05	5600	2.25	2485
80	87.0	11.55	6400	1.50	4265
90	93.8	12.05	7200	.75	9600
100	100.0	12.55	8000	0	00

1:1 Wt./Pigment Binder Ratio

Chart #3 demonstrates a commercially available compliance high solids clear and a compliance water-based coating. The water-based coating contains 20% exempt solvent in the volatile.

HIGH SOLIDS VS. WATER

	VOL. SOLIDS	WT. GAL.	SQ. FT. COVERAGE PER .2 MIL FILM	SURFACE COATED PER LB. OF SOLVENT RELEASED
H.S.	80	7.98	6400	4010
Water	26.75	8.46	2140	1686

Clear unpigmented process coatings

Another way of comparing pollution efficiency is pounds of solids vs. pounds of solvent per gallon of coating.

POUNDS OF SOLIDS VS. POUNDS OF SOLVENT
CONTAINED IN ONE GALLON OF COATING

	LBS. OF SOLIDS	LBS. OF SOLVENT	RATIO
High Solids	6.72	1.26	5.34:1
Water	2.49	1.19	2.09:1

Water-based contains 20% exempt solution volatile

New developments are now being introduced to the sanitary coating market which exhibits lower fuming factors, lower bake schedule, and compliance with Ringleman I opacity requirements.

Future coatings will quite possibly be higher than 80% volume solids working toward the goal of 100% volume solids. Possibly two-package system with greatly reduced cure response which approach zero emission.

ENERGY

High volume solids exempt solvent systems allow manufacturers to comply with E.P.A. regulations in certain georgraphical areas without incineration. This fact leads to substantial energy savings over conventional solvent system which must be incinerated.

Two-component high solids systems, requiring shorter bake cycle at low temperature will reduce energy consumption drastically.

ECONOMICS

In general, high solids systems of comparable types display equal to lower applied costs than conventional or water-based coatings due to the following factors:

1. Less manufacturing expense per pound of solids.
2. Less warehouse expense.
3. Lower energy expense.
4. No reduction solvent.
5. Lower shipping costs.

SUMMARY:

High solids coatings are being consumed in large quantities in geographical areas required to meet E.P.A. regulations. High solids systems are economical, energy saving, and can be applied with existing equipment. Future developments pointed toward higher than 80% volume solids and lower cure temperatures will make high solids even more attractive.

RECEIVED MAY 22, 1978.

Automated Dynamic Mechanical Testing: Application to Thermoset and Coatings Research and Development

MARK B. ROLLER
Edison Laboratory, Mobil Chemical Co., Edison, NJ 08817

JOHN K. GILLHAM
Polymer Materials Program, Department of Chemical Engineering,
Princeton University, Princeton, NJ 08540

The freely oscillating torsion pendulum and the vibrating reed are the simplest and yet accurate means for measuring dynamic mechanical properties of solid polymers; Nielsen used both as early as 1950 (1). In 1970, ASTM issued the full standard D-2236-70, "Dynamic Mechanical Properties of Plastics by Means of a Torsional Pendulum." Table I summarizes the literature with respect to important events concerning Dynamic Mechanical Testing (DMT) and its use in the thermoset and coatings industries.

In 1974 Gillham comprehensively reviewed (2) 12 years of development and application of Torsional Braid Analysis (TBA), which utilizes a polymer-impregnated glass braid as a specimen in a torsion pendulum. An automated (temperature controlled, signal initiated, data reduction with immediate time plotting) torsion pendulum system was introduced. This reduction in manual labor made DMT an attractive tool for industrial research and development.

In 1976 and in early 1977, three other events occurred which were crucial to the acceptance of DMT to industrial research. First, in March 1976, at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Blaine and Woo reported (3) a Dynamic Mechanical Analysis attachment to du Pont's thermal analysis system. In it, a specimen is subjected to cyclic strain under forced resonance maintained at constant amplitude. The energy input required to maintain amplitude is a measure of mechanical loss; the natural frequency is a measure of modulus. Loss and frequency are recorded continuously. This instrument will expose DMT to a large number of chemically oriented personnel.

The second event was the report at the San Francisco ACS meeting by Kenyon, et al. of an automated system providing control and data reduction for the Rheovibron (4), in which the specimen is tested under forced tensile oscillation at definite frequencies. Commercial availability will make the Rheovibron more amenable to the requirements of industrial research.

The third event was the report by Davis and Macosko (5), of a forced torsion pendulum with automatic data reduction. This is

0-8412-0446-2/78/47-078-053$09.25/0

Table I.- Development of Dynamic Mechanical Testing in Thermoset and Coatings R & D

Reference	(Yr.)	Author(s)	COMMENTS
1	(1950)	Nielsen	Torsion Pendulum (TP) and Vibrating Reed.
16,17	(1958)	Inoue and Kobataka	Coated Al Foil in TP. Reported equations for properties of coatings from composite specimens and corrections for effect of load.
18	(1959)	Yoshino and Takayanagi	"Rheovibron". E' and tanδ of free films measured under forced oscillation in tension. semi-automatic.
19	(1962)	Lewis and Gillham	"Torsional Braid Analysis" (TBA). Impregnated braid as specimen in TP.
20	(1962)	Zorll	TP. Reported equations for G' and tanδ of coating from coated foil.
21	(1965)	Hansen	TP. Investigation of plasticizers and diffusion of solvents in polymer specimens.
22	(1966)	Myers et al.	"Attneuated Reflection Pulses" (ARP). Drying of Film on a quartz crystal monitored using ultrasonic technique.
23	(1969)	Bender	Counter-balanced TP with free paint film: Correlation with chipping behavior.
24	(1970)	Takahashi et al.	Rheovibron. Cure of oil-modified phenolic resin.
25	(1971)	Myers	Review: "Relaxations during the formation of films". Reference to TBA and ARP.
26	(1971)	Kollinsky and Markert	TP. Double Tgs reveal phase separation in random copolymerization.
7	(1971)	Gillham and Roller	TP. Effect of cure and environment. Comparison of TP & TBA data. Non-drag transducer.
27	(1972)	Naganuma et al.	"Dynamic Spring Analysis" (DSA). Coated spring used as specimen in rheovibron for study of cure.
12	(1973)	Babayevsky and Gillham	Generalization of three regions of temperature for curing behavior, determined by the relative times for gelation and vitrification (using TBA).
28	(1973)	Massa	Rheovibron. Mathematical analysis to account for system and specimen compliance and inertial effects.
29	(1973)	Ikeda	*Progress in Organic Coatings*: 1st review on dynamic viscoelasticity of coating films. Reference to TP, vibrating reed, flexural vibration of freely suspended plate, and rheovibron.
10	(1973)	Heijboer	Molecular assignments for transitions < Tg. Developed method for determining frequency dependence of these transitions from single frequency measurements.
2	(1974)	Gillham	Totally Automated Torsion Pendulum.
30	(1975)	Shibayama	*Progress in Organic Coatings*: 2nd review.
31	(1975)	Massa et al.	Torsion pendulum considered more sensitive than rheovibron at low loss levels.
32	(1976)	Seefired and Koleske	Applications of "Blotter" (impregnated cellulose specimen, for TP) and TP techniques.
33	(1976)	Ginsberg et al.	Compared blotter TP technique with impregnated nylon fabric in rheovibron to study cure.
3	(1976)	Blaine and Woo	"Dynamic Mechanical Analyzer" (DMA): Addition to Dupont's thermal analysis equipment. Totally automated; specimen under cyclic out-of-plane strain in forced resonance.
4	(1976)	Kenyon et al.	Totally automated rheovibron.
5	(1977)	Davis and Macosko	Automated forced TP. Free TP provides higher resolution than forced TP at low loss.
13	(1977)	Gillham et al.	Control of morphology and properties by gelation in two-phase reactive crosslinking systems (rubber-modified epoxies) [using TBA].
39	(1978)	Gillham	Established equivalence of $T_{\ell\ell}'$ and t_{gel} as determining limit of processibility of thermoplastics and thermosets [using TBA].

compatible with the Rheometrics Mechanical Spectrometer, which has been widely used to study fluid state viscoelasticity.

In the last three years, the methods of DMT, that have been for more than 25 years either tools of basic research or academic curiosity, have come of age. Introduction of at least four distinct systems of automatic experimental control, data analysis, and display (2,3,4,5) have made DMT a viable industrial tool akin to Gel Permeation Chromatography, Infrared Analysis, Nuclear Magnetic Resonance, and Thermal Analysis, in terms of the requirements of human attention and intervention.

The available DMT systems require specimens that are large relative to those which are normally encountered in more familiar thermoanalytical polymer characterization techniques. This, together with the low thermal conductivity of polymers, necessitates either slow (maximum 1-2°C/min) or stepwise heating and cooling. Thermal lag problems can be monitored and the correct heating rates chosen by determining physical transitions, both while cooling and heating.

The immediate future will provide great advances in applications of DMT, understanding of thermomechanical spectra, and cross correlation with other properties of bulk polymers.

Reported here are examples of the authors' experiences using one of these techniques, TBA, to provide insight into the behavior of thermosets and coatings. TBA and other techniques using supported specimens (16,17,20,22,27,32-38) are uniquely suited for the study of network-forming polymer systems. The ability to study the systems before, during, and after cure on one specimen provides an efficient means to determine an unambiguous history of the transformation from tractable prepolymers to intractable, but useful products. The present article is an expansion of a recent report which appeared in the Journal of Coatings Technology (40).

EXPERIMENTAL

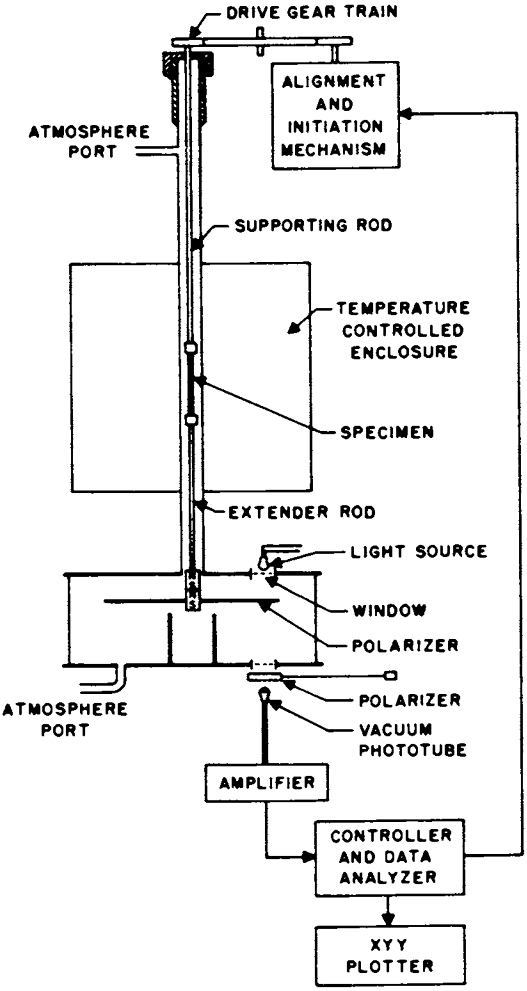
An automated, free-hanging, freely decaying torsion pendulum has been developed which permits monitoring of the changes which occur throughout cure and through load-limiting transitions (2). There are several distinguishing characteristics of a free-hanging, freely decaying torsion pendulum. These include:(1) accurate measurement of low loss at low frequency--the state of the art of electronic data collection and analysis in forced systems has less resolution of phase angle, δ, between stress and strain than in freely decaying systems (5,31);(2) unlike forced oscillating systems a free-hanging one tends to be self-aligning (under the influence of gravity); (3) similarly, free-hanging systems maintain a constant load on the specimen without requiring adjustment for thermal expansion; and (4) the major limitation of resonance systems lies in the difficulty in obtaining the frequency dependence of relaxations. The method of Heijboer (10) provides an estimate, in many cases, of this dependence from single frequency measurements.

The specimen is made by impregnating a glass fiber braid with the reactive system. The specimen can be cured externally or in the apparatus. The pendulum is intermittently set into oscillation to generate a series of freely damped waves. The frequency of operation is about 1 Hz. The character of each of these waves changes throughout cure to provide a monitor of change. Similarly, the dynamic mechanical spectra of a "cured" polymer are provided by the changing character of the waves as a function of temperature. Changes observed in the thermomechanical spectra upon further heating of a "cured" polymer can be related to cure level and/or degradation.

The two mechanical functions, rigidity and damping, are obtained from the frequency and decay constants which characterize each wave. The experiment provides plots of relative rigidity ($1/P^2$, where P is the period in seconds) and logarithmic decrement [$\Delta = \ln(A_i/A_{i+1})$, where A_i is the amplitude of the ith oscillation of a freely damped wave]. The relative rigidity is directly proportional to the in-phase or elastic portion of the shear modulus (G'), the logarithmic decrement is directly proportional to the ratio of the out-of-phase or viscous portion of the shear modulus (G") to G'. [$\Delta \simeq \pi G''/G' = \pi \tan\delta$.] G' and G" are material parameters of the specimen which characterize the storage and loss of mechanical energy on cyclic deformation; quantitative values may be obtained by using dimensions of the specimen.

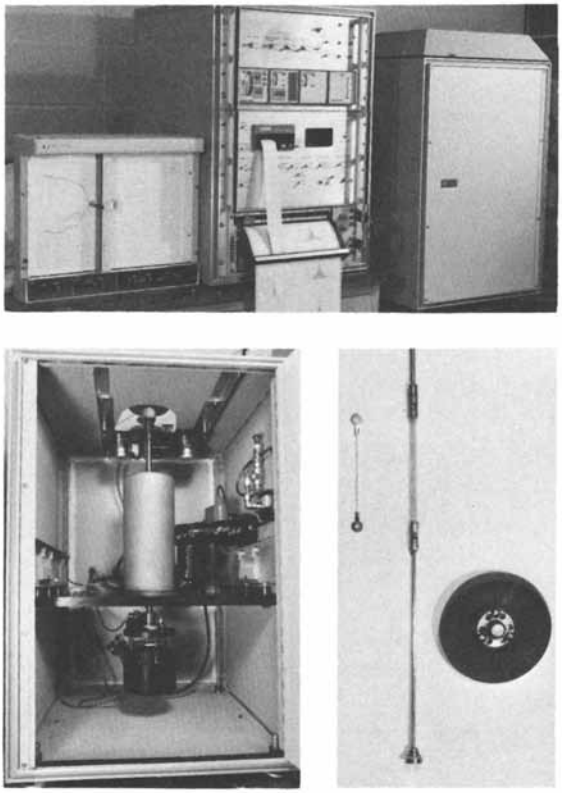
A schematic diagram of the automated pendulum is shown in Figure 1. The photograph (Figure 2) shows the pendulum [enclosed in a cabinet, top right; cabinet door open, bottom left] and the major components of the assembly. An analog computer [top center] is used for automatic control of the experiment and data reduction. A printer and digital panel meter provide numerical values of the temperature (mV) or lapsed time (sec), logarithmic decrement (Δ) and period (P, sec) of each damped wave [top center]. A monitoring strip-chart two-pen recorder provides a continuous record of the waves and temperature (mV) [below computer]. A temperature controller/programmer (range: -195°C to 450°C, rate of change of temperature 0°C to ± 5°C/min) is shown above the computer.

An XY plotter plots, immediately after computation, the relative rigidity ($1/P^2$) and logarithmic decrement versus temperature (mV) or log time (sec) [top left]. Switches permit selection of options which include ON, OFF or REVERSE of temperature programming at upper and lower set points and selection of temperature or time as the running variable [top center]. Specimens, such as impregnated braid and film, are shown at bottom right. A film is shown assembled with lower and upper extention rods ready for lowering into the apparatus. The polarizer disk of the transducer is also shown [bottom right]. Dimensions of specimens are selected so as to provide periods of oscillation in the range 0.25 to 15 seconds.



AIChE Journal

Figure 1. Automated TBA torsion pendulum (schematic) (2)



American Chemical Society, Preprints

Figure 2. Automated torsion pendulum (13)

A key factor in the instrumentation was the development of a non-drag optical transducer which produces an electrical response that varies linearly with angular displacement (7). As mentioned above, this was implemented by the use of a two-polarizer light attenuation system. A polarizer disc is employed as the inertial member and a second stationary polarizer is positioned, in the path of a light beam, in front of a linear-with-intensity vacuum photo tube (Figure 1).

Light transmission through two polarizers is a $\cos^2$ function of angular displacement. Over a useful range symetrical about the 45° position, the transmission function approaches a straight line. The polarizer system is also insensitive to lateral oscillations (7). As the properties of the specimen change, twisting may cause the transducer to drift out of this linear range. The automation system described below is designed to compensate for this.

The sequence of events of the automated torsion pendulum is as follows: Strip-Chart Recorder monitor (Figure 3, Top): I) Previous wave decays, drift detected and correction begins. II) Polarizers correctly positioned. III) Wave initiating sequence begins. IV) Free oscillations begin. V) AB, first peak-to-peak amplitude less than initial boundary amplitude is measured. VI) CD, first peak-to-peak amplitude <1/2 AB is measured. VII) Time interval between peaks B and D is measured. VIII) No drift correction required, wave initiating sequence re-starts. Controller/ Data Analyzer loop (Figure 3, Bottom): 1) Polarizers positioned. 2) Wave initiated. 3) Peak-to-peak amplitude, AB, measured. 4) Peak-to-peak amplitude, CD, measured. 5) Period (sec.) printed, log $1/P^2$ plotted. 6) Logarithmic decrement (Δ) printed and log Δ plotted. 7) Temperature (millivolts) or Time (seconds) printed and plotted (choice of log time or linear time).

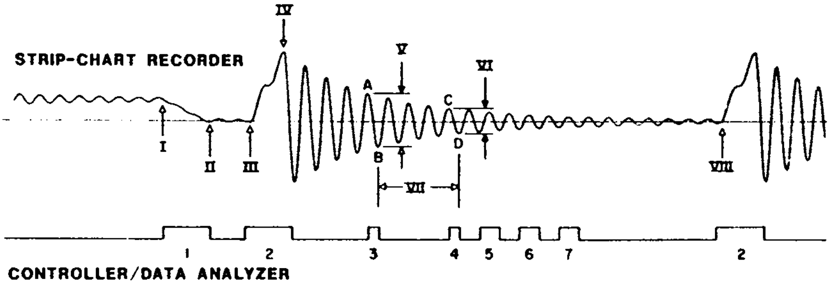
The quality of the data (see figures with "as plotted" data) is matched by the system's ease of operation. No alignments or adjustments of the specimen are necessary after the simple specimen preparation and mounting procedures. Other features include the control of temperature (0.2°C) and atmosphere (vacuum, inert and reactive gases, and water vapor). An on-line hygrometer can be used to continuously monitor the water vapor content of the atmosphere from <20 to 20,000 ppm H_2O.

This adaptation of the torsion pendulum approach for characterizing small quantities of supported polymer has been developed under the name "torsional braid analysis (TBA)" (2). The automated system is available from Plastics Analysis Instruments, Inc.

EXAMPLES OF DYNAMIC MECHANICAL ANALYSIS

Influence of Water Vapor on Dynamic Mechanical Spectra

The effect of controlled levels of water vapor in the atmos-



AIChE Journal

Figure 3. Controller/data analyzer sequence (2)

phere on a cured rubber-modified epoxy system has been reported (6). Figure 4 compares a spectrum of a dry specimen in a dry atmosphere and the same specimen after conditioning at 15°C and 2800 ppm moisture (27% RH) for more than eight hours. The conditioned material displayed a water transition ("T_{H_2O}") at ∿ -80°C, in addition to the Tg (-47°C) of the rubber and the secondary transition (-140°C) of the epoxy. Plasticization by water reduced the Tg of the epoxy to 25°C from 37°C. The original spectrum was regenerated on redrying. Temperatures of such water-induced transitions depend on chemical composition (6,7,8). This example demonstrates the necessity for control of the environment when using DMT techniques, especially with polar polymers which constitute most thermoset formulations.

Comparison of Chemically Similar Coatings

In the coatings industry it is often necessary to compare different coatings of similar chemistry. The left sides of Figures 5-8 are spectra of crosslinkable water-dispersed acrylic resins (A, B, C and C2). Specimens were prepared by heating impregnated braids at 191°C (375°F) for 2 min in a forced air oven under 15g tension (the weight of the inertial mass of the pendulum). They were then subjected to the thermal treatment 120°C → 0°C → 204°C (400°F) → 0°C and simultaneous DMT in the TBA apparatus.

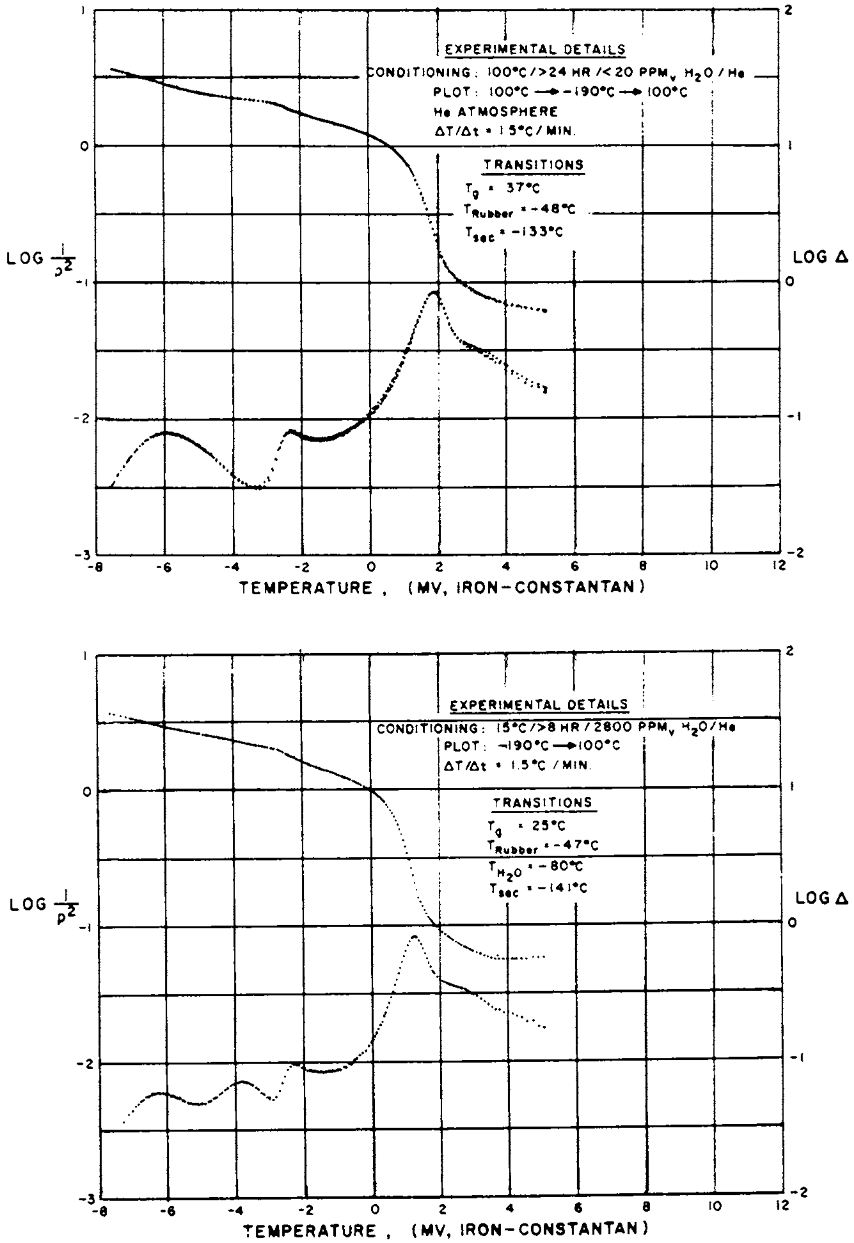
During the first cool/heat cycle, coatings A, C and C2 had spectra with Tg values at 78.5, 112 and 101°C; B displayed two loss peaks, T_{g1} at 100°C and T_{g2} at 17°C. On heating to 204°C, A and C2 increased their levels of cure with Tgs being raised to 83°C and 112°C. In contrast, the main Tg values of B and C were unchanged, although T_{g2} of B increased to 24 from 17°C which was accompanied by an increase in the level of damping between T_{g1} and T_{g2}. The thermomechanical fingerprints of these coatings reveal differences due to cure, post-cure, and phase distribution (B is probably two-phased).

The data at the right of Figures 5-8 were generated from uncured specimens cycled between 20 and 145°C at 1.5°C/min. These simple experiments yield information on the kinetics of cure. The Tg after each cycle to 145°C shown in Figure 9 provides a measure of the energy input required to attain a given Tg. More definitive approaches to kinetics are discussed below.

It is of interest to note that C and C2 were assumed to differ only in the solids level required for different methods of application. It was found that although they had the same ultimate glass transition temperatures, C2 cured more slowly.

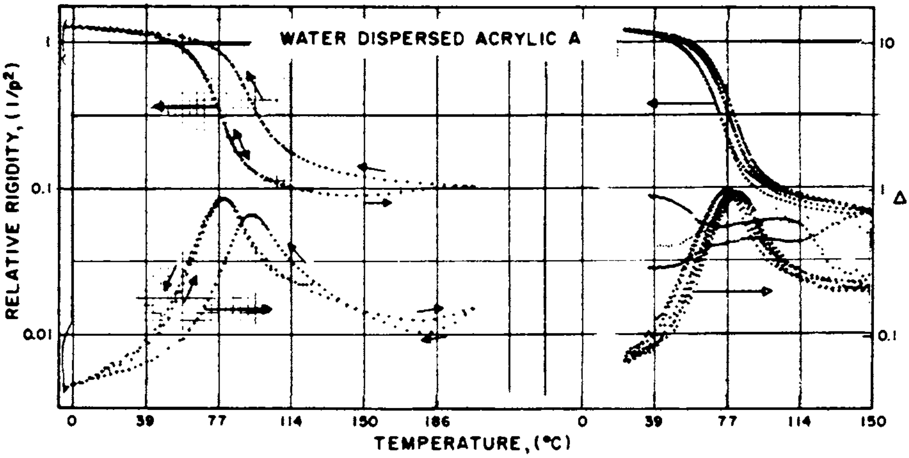
Accelerated-Aged Vs. Room Temperature-Aged Unreacted Prepolymers

The supported specimens used in TBA permit study of uncured



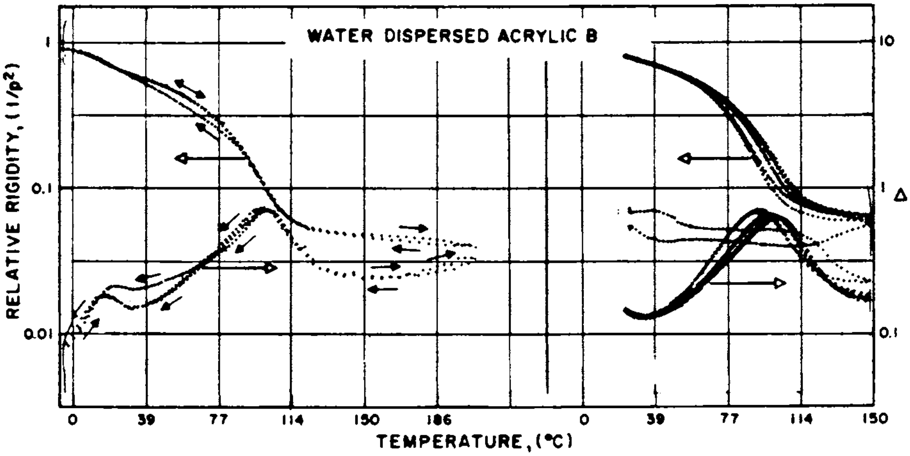
American Chemical Society, Preprints

Figure 4. Effect of environment on the dynamic mechanical spectra of a cured epoxy/rubber system. The temperature scale (MV) corresponds to that in Figure 12 (°C). Bottom plot after conditioning in a humid atmosphere (13).



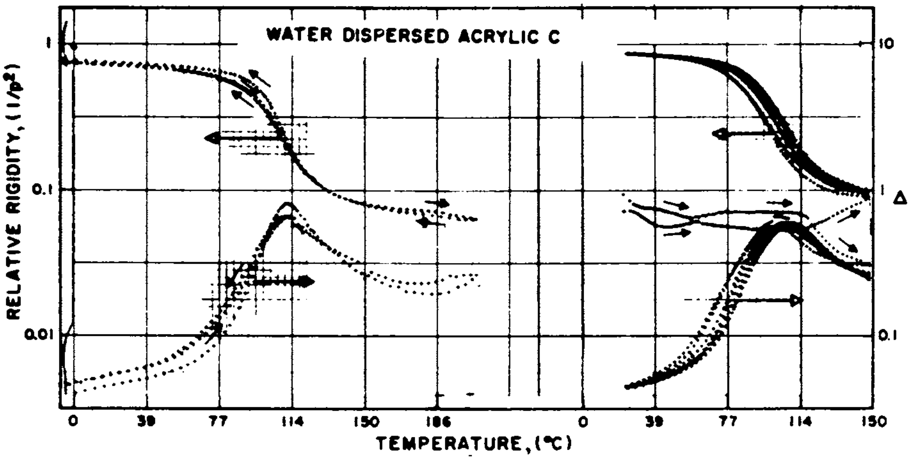
Journal of Coatings Technology

Figure 5. Water-dispersed Acrylic A. Left side: dynamic mechanical spectra 120°C → 0°C → 200°C → 0°C at 2°C/ min in He of specimen cured 2 min in forced-air oven at 191°C. Right side: wet coating cycled from RT ⟷ 145°C, spectra generated during cycling (40)



Journal of Applied Polymer Science

Figure 6. Water-dispersed Acrylic B. Left side: dynamic mechanical spectra 120°C → 0°C → 200°C → 0°C at 2°C/min in He of specimen cured 2 min in forced-air oven at 191°C. Right side: wet coating cycled from RT ⟷ 145°C, spectra generated during cycling (12).



Journal of Coatings Technology

Figure 7. Water-dispersed Acrylic C. Left side: dynamic mechanical spectra 120°C → 0°C → 200°C → 0°C at 2°C/min in He of specimen cured 2 min in forced-air oven at 191°C. Right side: wet coating cycled from RT ⟷ 145°C, spectra generated during cycling (40).

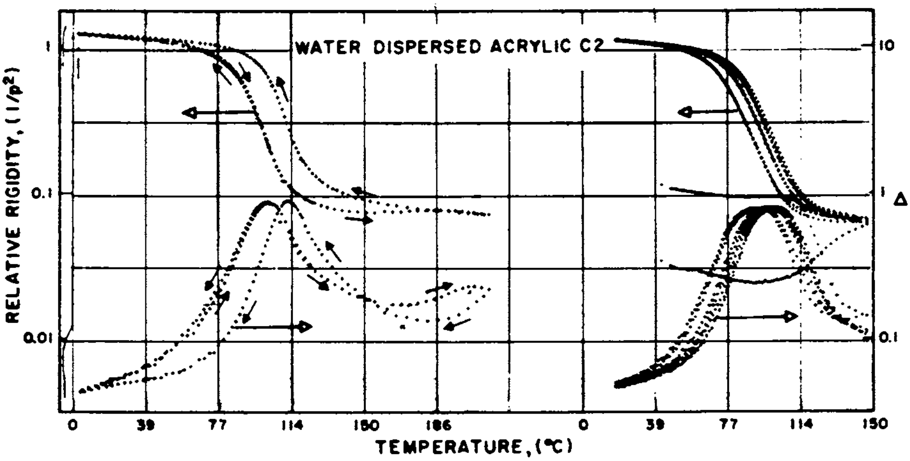


Figure 8. Water-dispersed Acrylic C2. Left side: dynamic mechanical spectra 120°C → 0°C → 200°C → 0°C at 2°C/min in He of specimen cured 2 min in forced-air oven at 191°C. Right side: wet coating cycled from RT ⟷ 145°C, spectra generated during cycling.

In Modern Container Coatings; Strand, R.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

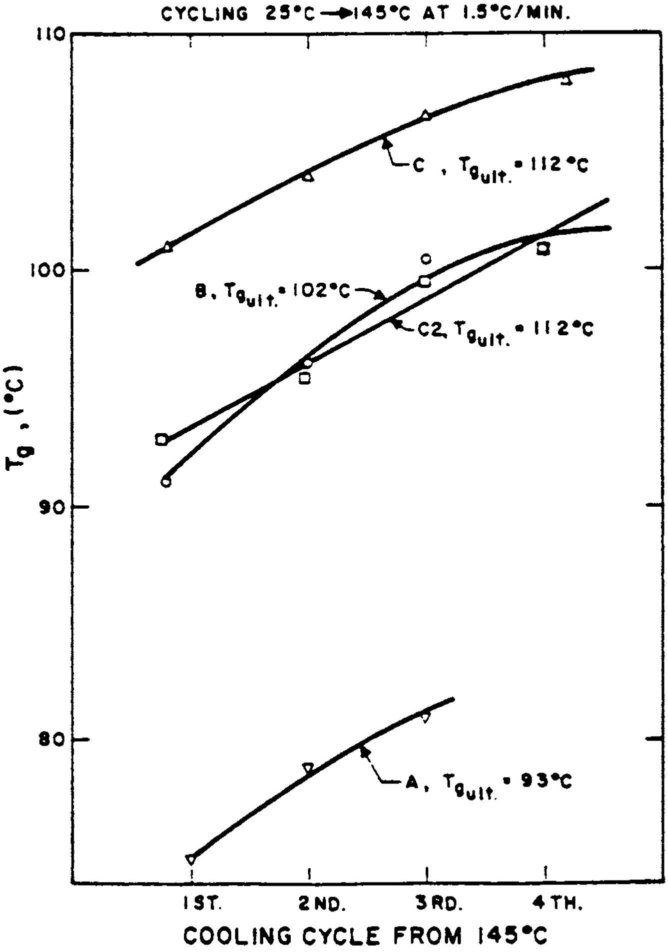


Figure 9. Plot of T_g *vs. number of cycles to 145°C for Acrylics A, B, C, and C2*

coatings. Spectra of two specimens of the same water-based coating formulation are presented in Figures 10 and 11: one after aging in the container for two months at room temperature (RT), the other after aging in the container for two months at 49°C (HT). The HT aging resulted in cured coatings with serious increases in water sensitivity (blushing) and decreases in MEK resistance. Spectra on the left are from specimens dried side-by-side (10-20 mm Hg) for three days to remove water and solvent. Data were then obtained during the cycle: 50°C → -190°C → 50°C. Spectra on the right were obtained after curing the same specimens in the TBA apparatus at 176°C for 5 min.

The Tg value of the dried HT aged specimen was 24°C, that of the dried RT specimen was 17°C. Note that there is a transition (Tsec) in the RT specimen at -73°C in addition to the two in both at -140 and -180°C. These data are taken as evidence of the disappearance upon HT aging of the entity which provided the mechanical loss responsible for the -73°C Tsec transition. The increase in Tg with HT aging is attributed to an increase in molecular weight of the uncured resins.

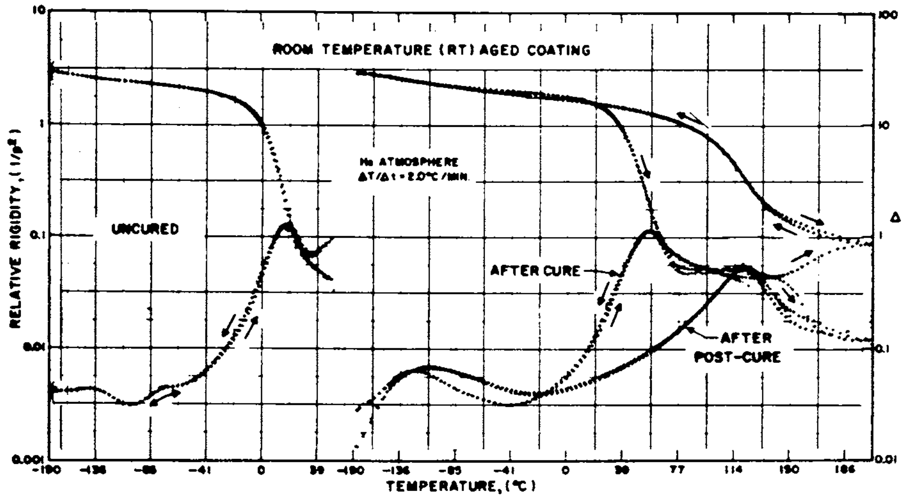
After curing, the spectra are similar with Tg values of 57 and 60°C for both the RT and HT materials. A Tsec transition occurred at -124°C in both. On post curing to 204°C, both RT and HT materials increased their Tg values to 119 and 112°C, respectively. The increases of 60 and 52°C indicate a significant level of under cure. The higher temperature and narrower Tg regions of the RT specimen after the controlled post bake provide evidence of a lower and more uniform molecular weight between crosslinks in the post-baked RT specimen. This concurs with an increase in molecular weight of the resin during aging.

Since these experiments were performed on specimens taken from a single coating's batch, conditioned side by side, conclusions drawn relating the small differences in dynamic mechanical spectra to differences in aging, are considered to be justified.

Fabricable Cured Coatings

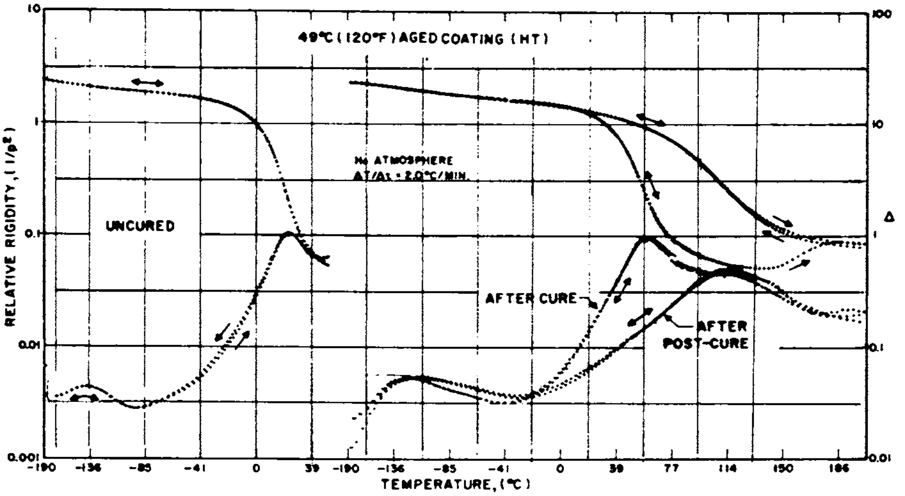
Thermoset coatings for metal substrates to be post-formed are often observed to be hard and glassy, yet ductile materials. The spectra of Figures 12 and 13 were obtained for two varnishes cured 204°C/10 min. Figure 12 is for a conventional commercial epoxy-based coating. Figure 13 is for an experimental coating formulated from lower molecular weight epoxy and crosslinker in an attempt to decrease solvent levels. The wedge bends (ASTM D3281-73) on tinplate were 85 (cracking)/80 (adhesion) and 85/75, respectively. Testing fabricated screw caps and can ends gave the conventional coating a rating of 18 out of 30 (perfect) and 18 out of 20 (perfect), respectively. The experimental coating was rated 9/30 and 0/20.

After cure, the most fabricable (i.e., the conventional) coating had a higher Tg (110 vs. 82°C) than the experimental coating.



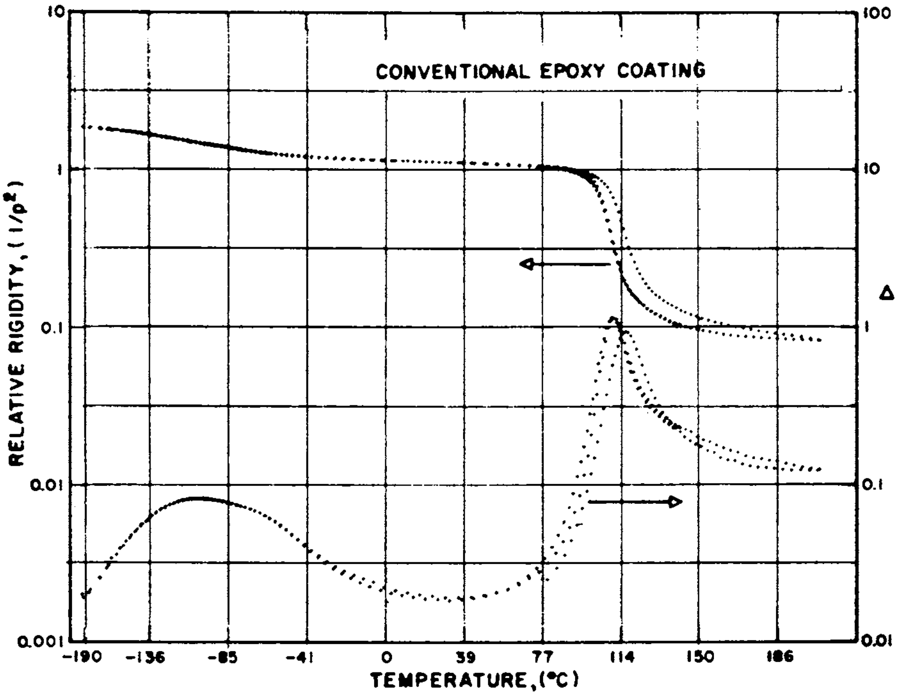
Journal of Coatings Technology

Figure 10. Room temperature-aged coating. Left: dynamic mechanical spectra from RT → −180°C → RT at 2°C/min in He of vacuum-dried specimen. Right: dynamic mechanical spectra, 120°C → −180°C → 204°C → −180°C at 2°C/min of specimen cured in the TBA 5 min at 176°C in air (40).



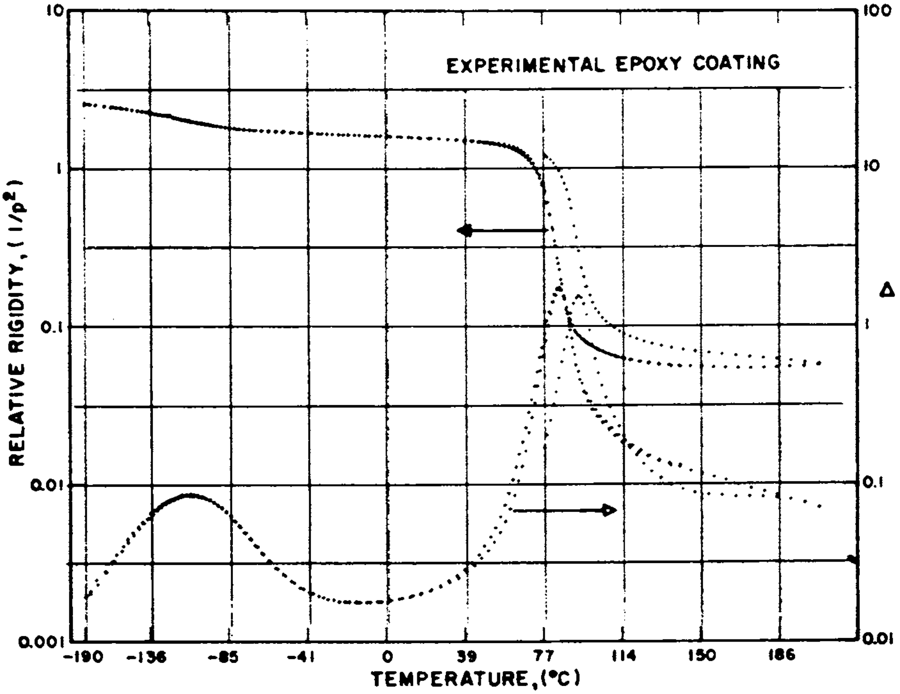
Journal of Coatings Technology

Figure 11. 49°C aged coating. Left: dynamic mechanical spectra from RT → −180°C → RT at 2°C/min in He of vacuum-dried specimen. Right: dynamic mechanical spectra, 120°C → −180°C → 204°C → −180°C at 2°C/min of specimen cured in the TBA 5 min at 176°C in air (40).



Journal of Coatings Technology

Figure 12. Conventional epoxy coating: dynamic mechanical spectra, 120°C → −180°C → 204°C → 77°C at 2°C/min in He of varnish cured 10 min at 204°C (40)



Journal of Coatings Technology

Figure 13. Experimental epoxy coating: dynamic mechanical spectra, 120°C → −180°C → 204°C → 77°C at 2°C/min in He of varnish cured 10 min at 204°C (40)

The similarity in chemistry of the two coatings coupled with the respective Tg values suggests a higher crosslink density for the conventional one. Examination of the T < Tg regions reveals low temperature transitions at -100°C (conventional) and -108°C (experimental) with more skewness in the loss towards higher temperature for the more fabricable coating. The differences in the T_{sec} are inherent in behavior of uncured epoxy resin constitutents. The question arises whether the suitability of coatings for postformable substrates, which is related to impact and adhesion, can be correlated with the shape and temperature of these transitions.

Survey (9) of the literature on impact properties of thermoplastics reveals that materials with low temperature transitions, which are related to polymer backbone motion, generally display higher levels of impact strength than do polymers without such transitions. Furthermore, if the transitions are not due to the presence of a phase-separated rubbery material, the impact resistance peaks at a temperature above Tsec. In contrast, the presence of rubber particles generally results in a step-increase in impact resistance above the Tg of the rubber.

Consider the molecular motion of a polymer backbone at the temperature of Tsec (at impact frequency), where a fraction of the groups responsible for Tsec is moving. On impact, energy can be dissipated by initiating motion of stationary segments. If all of the available groups are moving (T >> Tsec and T < Tg) there is no mechanism (related to Tsec) available to absorb the impact. On the other hand, the presence of a damping peak due to a glass transition (Tg < T) of a separate rubber phase can provide mechanisms for energy dissipation due to flow (uncrosslinked rubber) and/or local stress dissipation (crosslinked rubber).

Application of Heijboer's method (10) for calculating the shift of Tsec with frequency to take Tsec to impact frequencies (10^3 - 10^5 Hz), results in the intensity of the damping of the conventional coating at room temperature being about double that for the experimental coating.

Whether there is a direct correlation between Tsec and fabrication remains to be established by examining further samples of crosslinked systems. Determination of whether the mechanism providing fabricability is related to impact properties, adhesion (11) or a combination of these and other factors, must be left to further studies. [Note that these coatings were also undercured during the initial bakes (see Figures 12 and 13)].

Gelation and Vitrification
As Determinants of Thermoset Material Behavior

The three generalized temperature regions for cure described in the first part of this section stem from examinations of several epoxy systems (2, 12).

The experimental results for the cure of an epoxy system at a series of constant temperatures can be used to obtain the apparent gelation (onset of infinite network formation) time and the vitrification (glass formation) time vs. cure temperature. These transformation times correspond to peaks in the mechanical damping curves; they also correspond to points of inflection in the rigidity curves (see Figure 14). Schematic results for isothermal cure of a typical system relating the time to gelation and the time to vitrification to the temperature of cure are summarized in Figure 15.

It is apparent from Figure 15 that there are three types of behavior depending on the temperature of cure. At high temperatures the liquid gels but does not vitrify. At low temperatures the liquid vitrifies as a result of molecular weight increases and need not gel -- if reactions are quenched at low chemical conversion by vitrification. At intermediate temperatures the liquid first gels and later vitrifies (Figures 14 and 15).

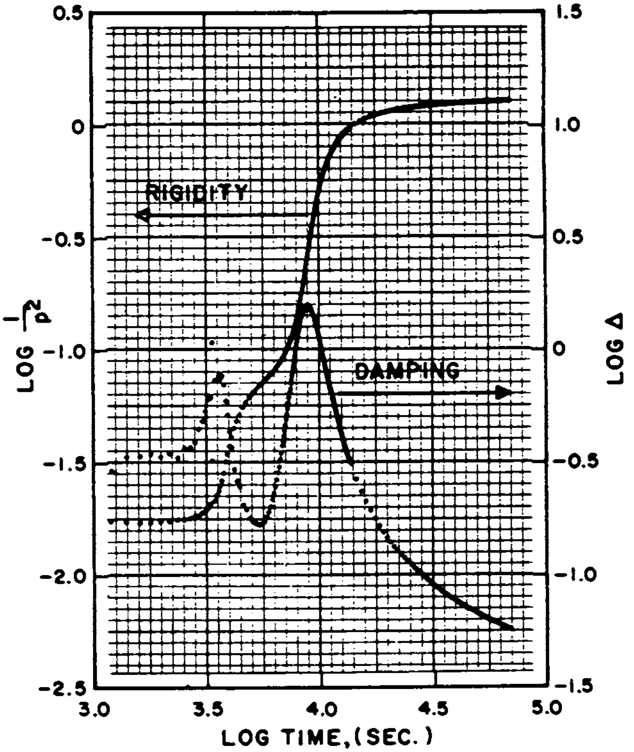
The time to gelation decreases exponentially with temperature since the chemical conversion at the point of gelation is constant. [It follows that a plot of log (time to gelation) vs. 1/T (°K) provides an activation energy which can be used for obtaining gel times at experimentally inaccessible temperatures.] On the other hand, it is noted that the time to vitrify passes through a minimum which occurs at intermediate temperatures of cure. This reflects competition between the increased rate constants for reaction and the increased degree of crosslinking (and, therefore, of reaction) required for vitrification at higher temperatures. The temperature at which gelation and vitrification occur together is defined as T_{gg} (Figure 15).

Vitrification can occur before gelation ($T_{cure} < T_{gg}$) simply by an increase of molecular weight. Gelation occurs without vitrification when cure is performed above the maximum softening point of the system, $T_{g\infty}$ (Figure 15). It is also apparent that if reactions cease at vitrification, the softening temperature (glass transition temperature, Tg) of the system after cure will equal the temperature of cure. The vitrification curve, therefore, gives the time to reach the softening temperature which the system can achieve by curing at T_{cure}. In particular, T_{gg} is the glass transition temperature of the reactive system at its point of gelation.

A diagram, such as Figure 15, summarizes much of the behavior of the thermosetting process and in particular shows that it is characterized by two temperatures, T_{gg} and $T_{g\infty}$. In contrast, thermoplastic materials are characterized only by $T_{g\infty}$ since gelation does not occur in their formation. The temperatures T_{gg} and $T_{g\infty}$ are critical parameters which will vary from system to system.

From the practical point of view, the diagram (Figure 15) explains a number of practices in the field of thermosets. Examples follow:

- Finite vs. infinite shelf-life: If the storage temperature is below T_{gg}, a reactive material will convert to a vitrified solid (prepreg or "B"-stage) which is stable and can be later



Polymer Engineering and Science

Figure 14. Mechanical rigidity and mechanical damping vs. time during cure of an epoxy system at a constant temperature ($T_{gg} < T_{cure} < T_{g\infty}$)*. The first peak in the damping curve represents gelatin, the second vitrification* (43)*.*

"melted" and processed; above T_{gg} the material will have a finite shelf-life since gelation will occur before vitrification.

- Post-cure: If $T_{cure} < T_{g\infty}$ a reactive material will vitrify and full chemical conversion may be prevented; the material will then need to be post-cured above $T_{g\infty}$ for development of ultimate properties. For the manufacture of objects of large size, it is often necessary to go through a two-step process because of the exothermic nature of the reactions.

The process of gelation can act also to arrest the development of morphology, and, therefore, the time to gelation can be used to control mechanical properties. The gelation time can be varied by catalysts and temperature. This is particularly important during the curing of rubber-modified-epoxy systems which often involve change from an initially homogeneous solution to a heterogeneous multiphase morphology (13).

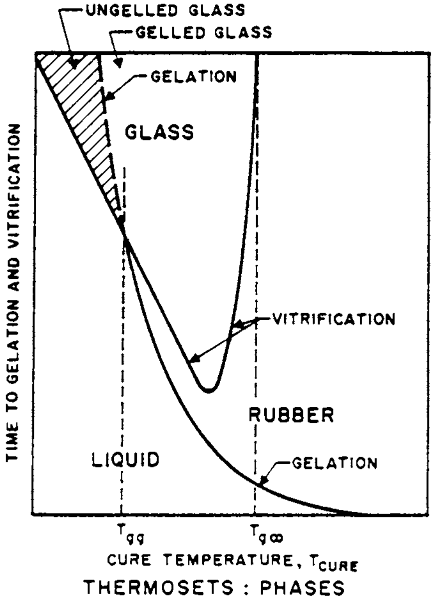
The effect of catalyst level on thermomechanical plots obtained after "complete" cure (170°C/100 min) of a rubber-modified system on glass braid supports is made evident by comparison of Figures 16 and 17. The rubber phase glass transition is most dominant in the sample cured without catalyst (Figure 16). Curing without catalyst at a lower temperature (120°C/16 hr) also leads to a dominant rubber glass transition but, on the basis of the lower glass transition temperature of the epoxy, to inadequate cure. Curing at a lower temperature (120°C/16 hr) with catalyst can give rise to a marked rubber glass transition and yet a cured system (13). These results suggest that the intensity of the rubber transition, the damping level between the transitions, and the size of the rubbery domains depend on the time available for the development of morphology, which is limited by the process of gelation. The higher glass transition temperature of the epoxy for the fully cured sample, cured with long gelation time, suggests more complete separation of the two phases.

The relationship between cure temperature, gelation time, and morphology is summarized schematically in Figure 18, which demonstrates how a single chemical amorphous composition can produce distinctly different morphologies which in turn are responsible for distinctly different macroscopic behavior.

It is noted that, although reaction at lower temperatures will lengthen the time to gel, the increased viscosity at lower temperatures can retard the development of morphology. The effect of temperature on solubility is another complicating factor, increase of which *per se* would inhibit phase separation.

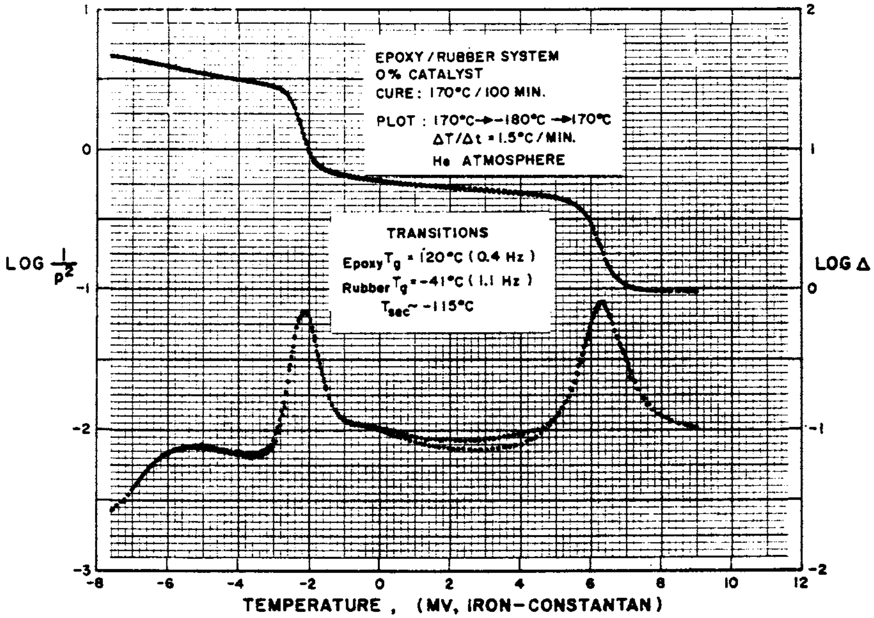
Emulsion Polymers/Gelation Kinetics

This section compares two emulsion polymer-based coating vehicles. Figure 19 is the spectrum of an emulsion polymer cured 191°C/3 min with 20% melamine crosslinker. Figure 20 is the spectrum of a similarly cured commercially available emulsion polymer/melamine crosslinker vehicle. The obvious difference between the



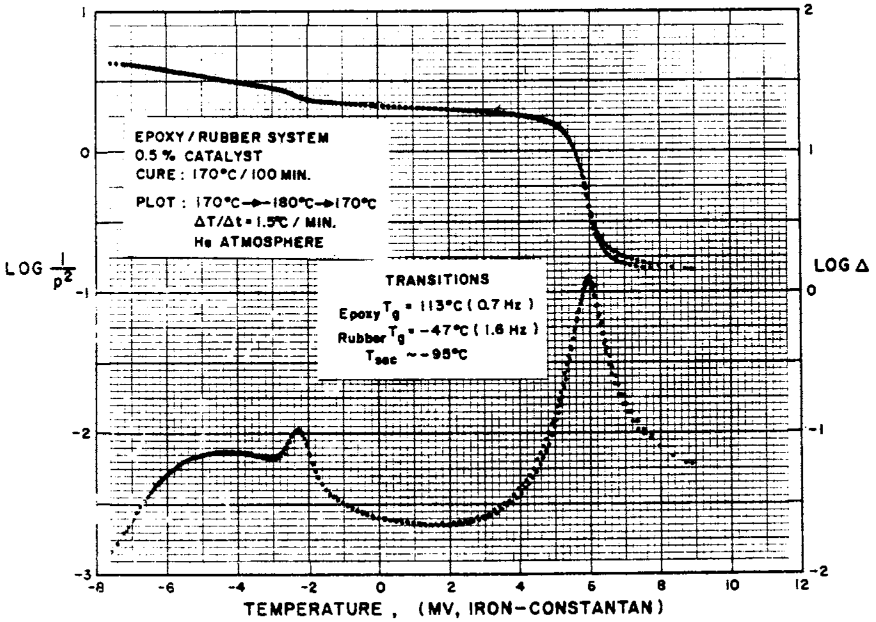
Journal of Coatings Technology

Figure 15. Time to gel and time to vitrify vs. isothermal cure temperature for thermosetting systems (note the two critical temperatures, T_{gg} *and* $T_{g\infty}$*) (40)*



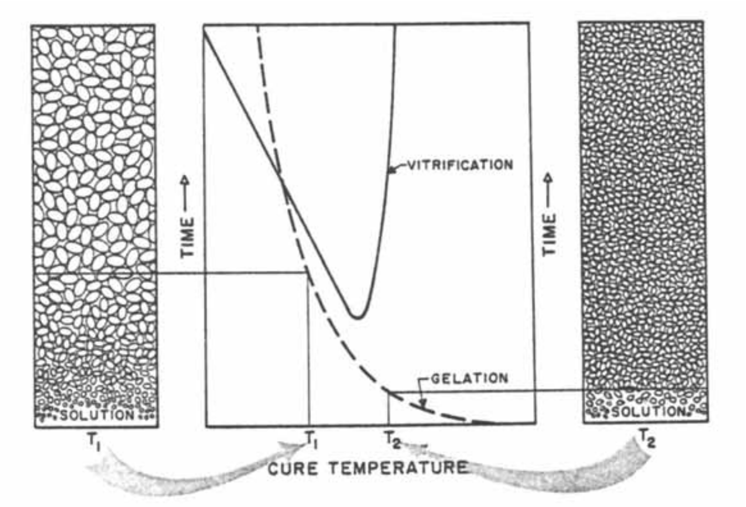
American Chemical Society, Preprints

Figure 16. Effect of catalyst level on the cure of rubber-modified epoxy: dynamic mechanical spectra, 170°C → −180°C → 170°C at 1.5°C/min in He. 0% catalyst. The temperature scale (MV) corresponds to that in Figure 12 (°C) (13).



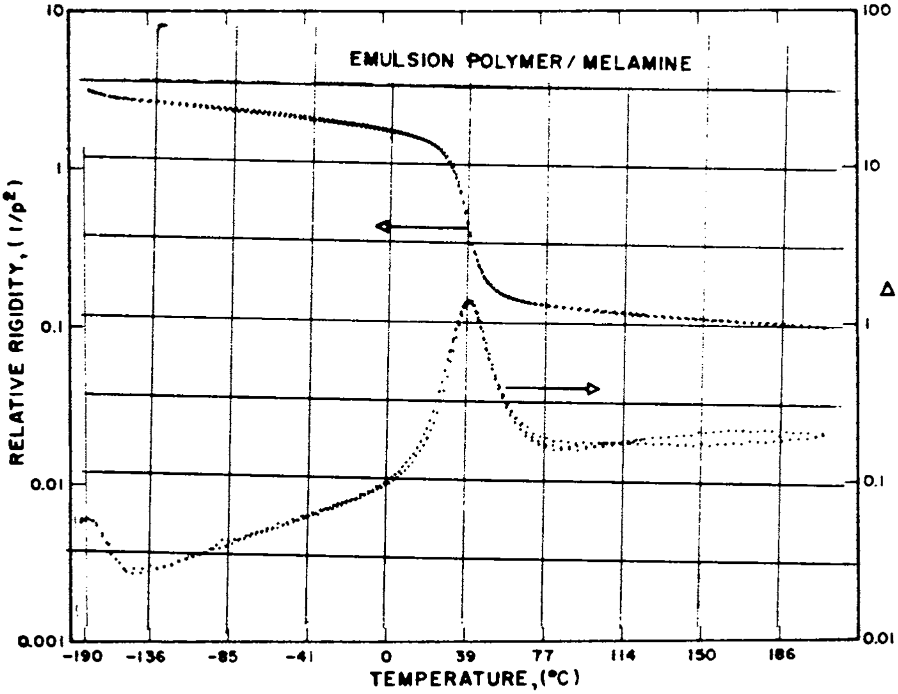
American Chemical Society, Preprints

Figure 17. Effect of catalyst level on the cure of rubber-modified epoxy: dynamic mechanical spectra, 170°C → −180°C → 170°C at 1.5°C/min in He. 0.5% catalyst. The temperature scale (MV) corresponds to that in Figure 12 (°C) (13).



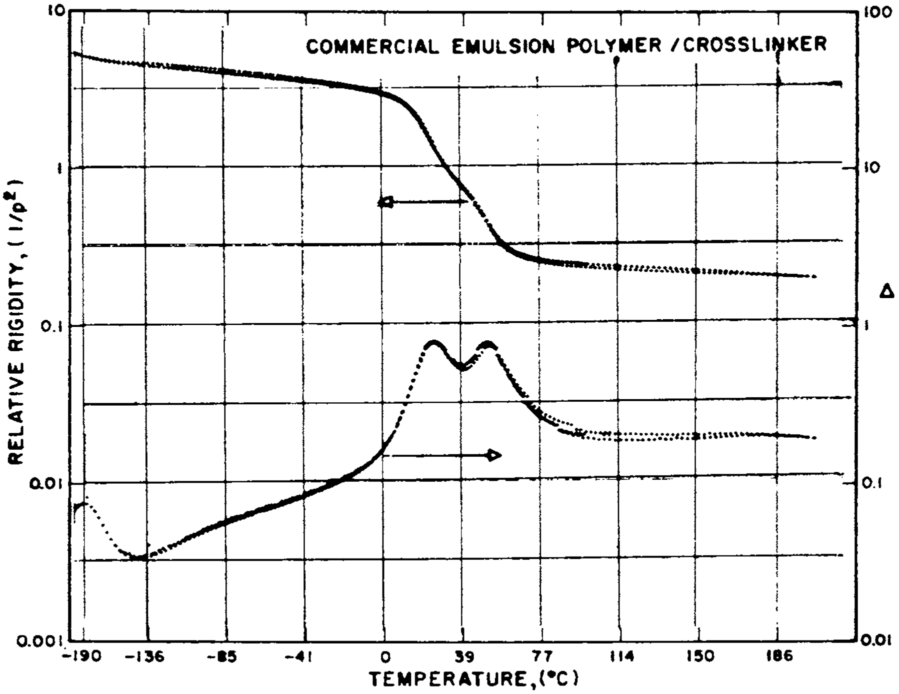
American Chemical Society, Preprints

Figure 18. Development of a two-phase, rubber-modified thermosetting system vs. gelatin time. As polymerization progresses rubber precipitates in domains which grow in size with time. Gelatin is considered to arrest the growth process. Different morphologies result from reaction at different temperatures (e.g., T_1 *and* T_2*) (44).*



Journal of Coatings Technology

Figure 19. Emulsion polymer cured with 20% melamine cross-linker: dynamic mechanical spectra, 120°C → −180°C → 204°C → RT at 2°C/min in He of coating cured 3 min at 191°C (40)



Journal of Coatings Technology

Figure 20. Commercial emulsion polymer/cross-linker: dynamic mechanical spectra, 120° C→ −180°C → 204°C → RT at 2°C/min in He of coating cured 3 min at 191°C (40)

two systems lies in the bimodel glass transition region (Tg = 26 and 52°C) of the commercial product vs. the single Tg (39°C) for the other. This feature has been related to the presence of phase separation (14). Similarities in the low temperature regions and simple calculations of an average Tg (39°C) for equal amounts of the two phases present in the commercial material attest to these two coatings being similar in monomer residue composition.

The technology required to produce this type of behavior via emulsion polymerization concerns itself with the production of core and shell emulsion particles as has been described (14). The technique should provide rubber-modified, impact resistant coatings, wherein the soft phase is totally encased in the hard phase with the domain size defined by the particle. This system, in one coating, would display a combination of impact resistance, hardness, mar resistance, and adhesion.

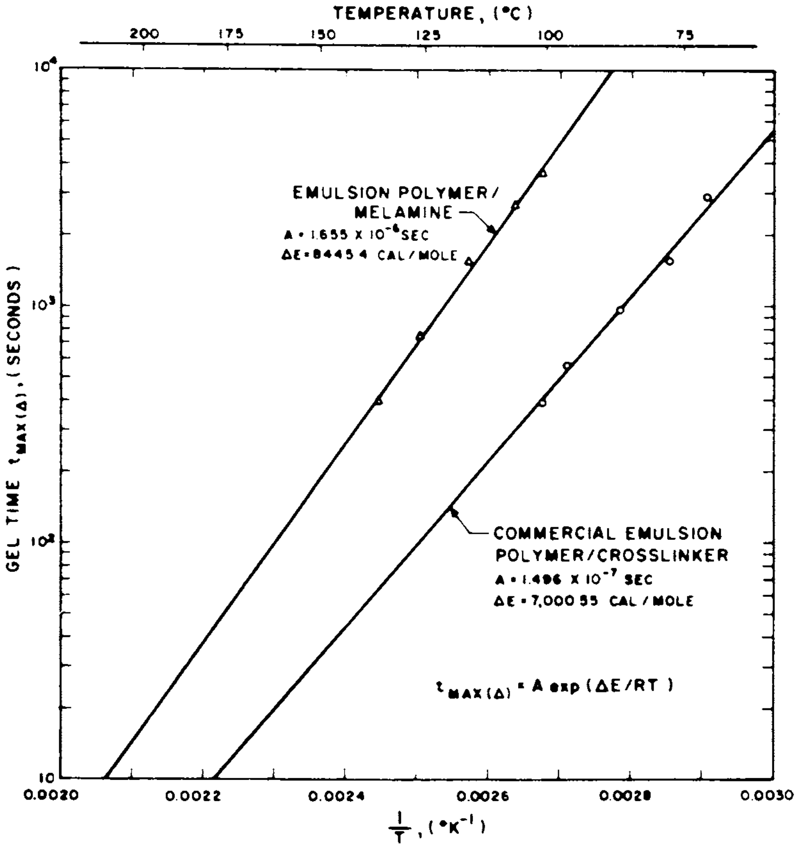
Investigation of the curing history of these two coatings revealed the capability of the commercial product to provide required coating properties at low baking temperatures. This prompted a study of the gelation kinetics of the two systems. Figure 21 shows the Arrhenius straight line plots of log (apparent gel time) vs. 1/T°K for each system. Note that the commercial system gels nearly four times as fast as the other at 204°C and nearly 10 times as fast at 100°C. Whether the source of the higher gelation rate lies in higher functionality of the resins and crosslinkers or more efficient catalyst systems has not been ascertained.

Note that in the case of these two emulsion polymers the mechanical properties do not change after heating to 200°C. Presumably, the room temperature toughness of these materials is related to their low glass transition temperatures. Emulsion polymers develop their final Tg values before crosslinking as a consequence of their very high molecular weights. The relatively light levels of crosslinking introduced to these materials provide required resistance to cold flow and solvents in the vicinity of the glass transition which is close to room temperature.

Comparison of the Effect of Crosslinking Agents

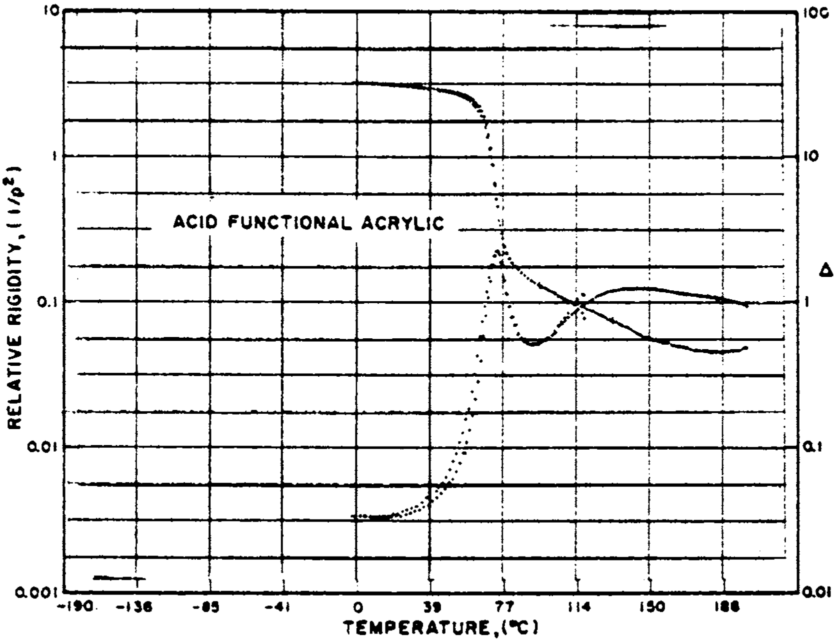
The nature of crosslinkers can drastically affect the properties of cured thermosets. Figures 22-24 are the spectra of an acid functional acrylic prepolymer and the same prepolymer cured with two monomeric hexamethoxymethyl melamine (HMMM)-type crosslinkers at the same concentration. One crosslinker had less than 0.5% free hydroxymethyl and the other had approximately 16% free hydroxymethyl groups. The prepolymer itself displays a Tg of 73°C and evidence of flow through both a reduction in rigidity and a broad damping maximum above 100°C.

The crosslinked systems show distinctly different behavior. The < 0.5% free hydroxymethyl system displays a sharp Tg region centering about 79°C. The rigidity starts to decrease at 69°C and



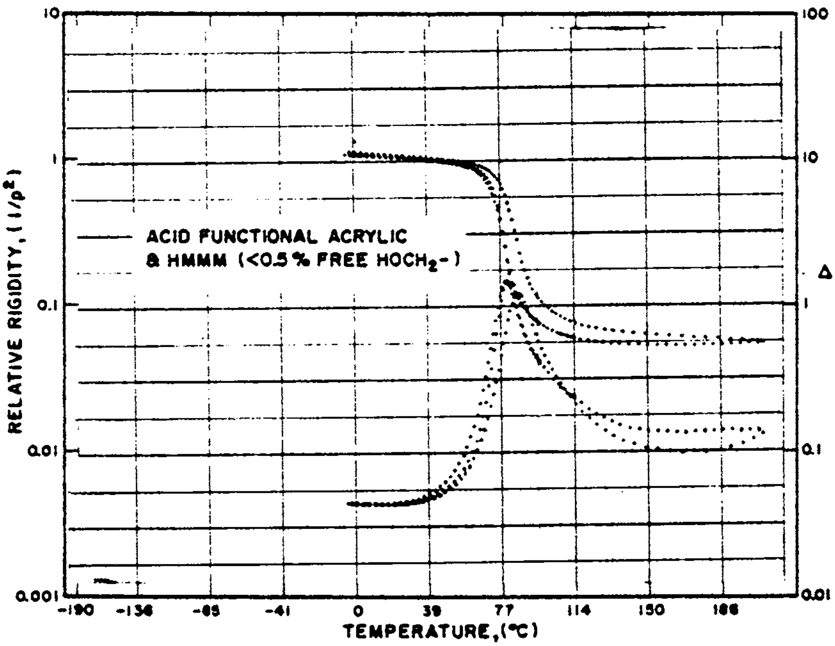
Journal of Coatings Technology

Figure 21. Arrhenius plots of log (gel time) vs. 1/T°K for systems of Figures 19 and 20 (40)



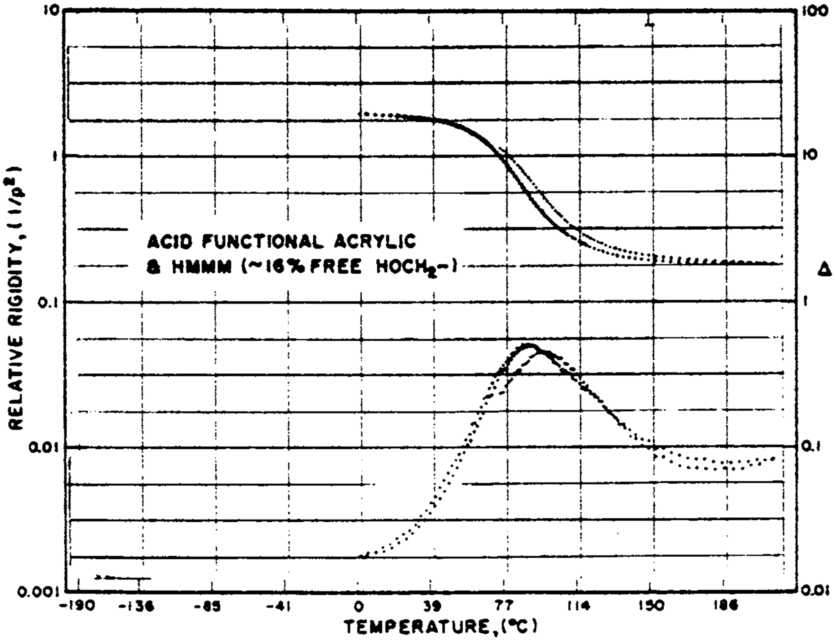
Journal of Coatings Technology

Figure 22. Acid functional acrylic polymer dried from solvent at 204°C for 2 min: dynamic mechanical spectra, 120°C → 0°C → 204°C at 2°C/min in He (40)



Journal of Coatings Technology

Figure 23. Acid functional acrylic polymer and hexamethoxymethylmelamine with < 0.5% free hydroxymethyl; cured 204°C for 2 min: dynamic mechanical spectra, 120°C → 0°C → 204°C → 0°C/min in He (40)



Journal of Coatings Technology

Figure 24. Acid functional acrylic polymer and hexamethoxymethylmelamine with ~ 16% free hydroxymethyl; cured 204°C for 2 min: dynamic mechanical spectra, 120°C → 0°C → 204°C → 77°C at 2°C/min in He (40)

and levels off near 91°C. The ∿16% hydroxymethyl system displays a broad Tg region centering about 87°C. In this case, the rigidity begins to decrease at about 58°C and levels off near 110°C. This behavior bears on the general properties of the final products over a wide temperature range. The broad Tg region of the high hydroxymethyl system presumably arises from the contributions of the competing reactions of the methoxymethyl groups with both acid and hydroxymethyl groups which give rise to molecular heterogeneties.

After heating to 204°C, the Tg of the low hydroxymethyl HMMM increased 6°C to 85°C, whereas the Tg of the 16% hydroxymethyl system increased 7°C to 94°C. This behavior is typical of the response to further heating of most thermosetting materials after their normal industrial cure cycles. In the interest of economy of time industry tends to design its systems to have acceptable properties in an undercured state.

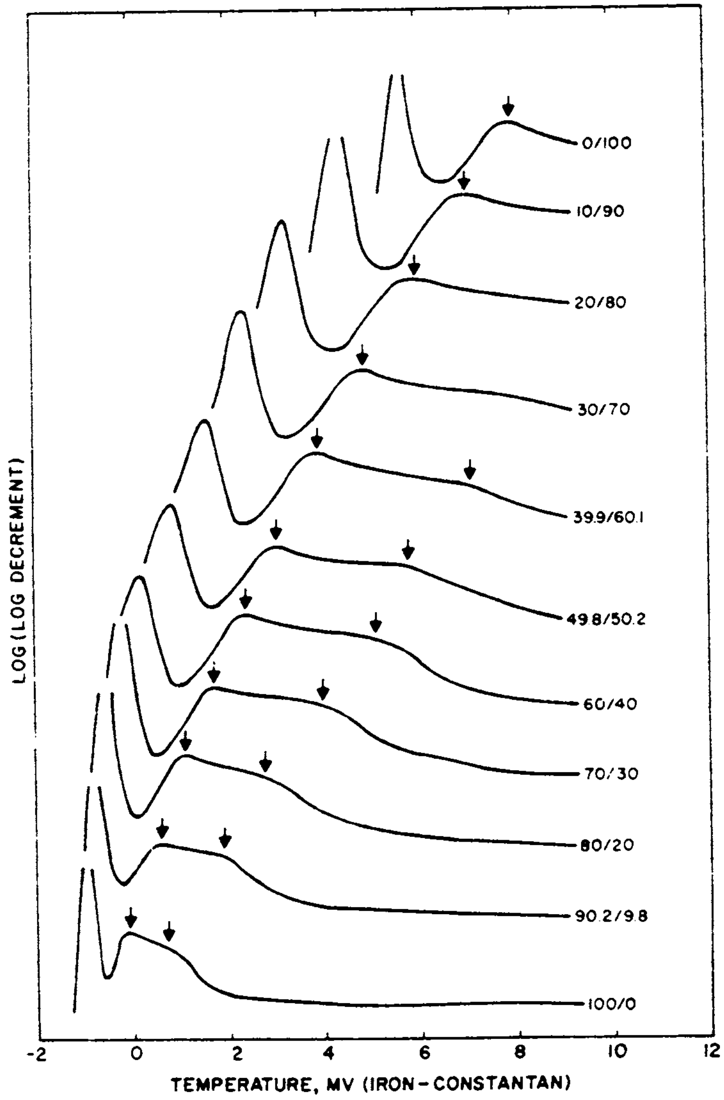
Plasticization

The ability to examine liquids by using supported samples permits study of transitions in the fluid state as well as transformation of liquid to solid. The most complete example of transitions in the fluid state is the plasticization of thermoplastic polystyrene throughout the range of composition (15). Polystyrene ($M_n = 37000$, $M_w/M_n < 1.1$) was homogeneously plasticized with $(C_6H_5OC_6H_4O)_2C_6H_4$ (which is a low molecular weight analogue of polyphenylene oxide).

Dynamic mechanical spectra for the plasticizer/polymer system are displayed in Figure 25. Three transitions are made apparent, i.e., Tg, $T_{\ell\ell}$ and $T_{\ell\ell}'$, all following the relationship $T = {}_AT W_A + {}_BT W_B + K W_A W_B$ where K is an empirical constant, T represents the transition temperature of the mixture (T) and of the constituents (${}_AT$ and ${}_BT$), and W_A and W_B refer to the respective weight fractions of the components. Corresponding transitions have been noted by us in low molecular weight thermosetting prepolymers. These transitions, which relate to flow, bear particularly on processing operations (see below).

Processability - The Significance and Equivalence of $T_{\ell\ell}'$ and t_{gel} (39)

Recent work has shown the coincidence of $T_{\ell\ell}'$ obtained as a function of temperature with the loss peak attributed to gelation (t_{gel} = time of gelation) observed during isothermal cure of a thermosetting system (39). Similarly it has been shown that $T_{\ell\ell}$ corresponds to a second maximum in Δ observed after the "apparent" gel peak and before vitrification. The importance of these loss maxima to thermoset processing is obvious since they occur during the transformation from fluids to intractable products. It follows from the coincidence of the isothermal transi-



Polymer Engineering and Science

Figure 25. TBA. Dynamic mechanical spectra of a plasticized polystyrene: effect of composition (wt % plasticizer/wt % polystyrene). Anionic polystyrene; $M_w/M_n < 1.1$. *Plasticizer:* $(C_6H_5OC_6H_4O)_2$-C_6H_4. *Curves have been displaced vertically by arbitrary amounts for purposes of clarification. The temperature scale (MV) corresponds to the temperature scale demarcations of Figure 12 (°C) where the 0 MV and 0°C are taken as coincident* (15).

tions with $T_{\ell\ell}$ and $T_{\ell\ell}'$ that the latter loss maxima observed in thermoplastics should bear on their processing. It has also been observed that the temperatures for $T_{\ell\ell}$ and $T_{\ell\ell}'$ can be substrate (braid) material and/or geometry dependent (41). Different thermomechanical spectra have been observed after curing isothermally at different temperatures to the peak of the loss maximum which has been used to approximate gelation. It follows that this loss maximum cannot correspond to the theoretical gel point which is defined as an isocompositional state.

It can be demonstrated that if t_{gel} as determined by torsional braid analysis represents an isoviscous state than an Arrhenius plot of log t_{gel} vs. 1/T (°K) will give a straight line over a significant temperature range. This has been done by applying an empirical time-temperature-viscosity model (42) that has been used to predict the change in viscosity of a curing system. This model reduced to isothermal conditions has been used by many workers (42).

The viscosity model is expressed for isothermal curing conditions as follows:

$$\ln \eta(t) = \ln \eta_\infty + \Delta E_\eta/RT + tk_\infty e^{\Delta E_k/RT}$$

where $\eta(t)$ = viscosity of time t (sec)
η_∞ = calculated viscosity of the initial material at T = ∞, cps
T = temperature °K
ΔE_η = Arrhenius activation energy for the viscosity, cal/mole
R = gas constant = 1.987 cal/mole °K
k_∞ = calculated kinetic constant at T = ∞, sec^{-1}
ΔE_k = "apparent" kinetic activation energy, cal/mole.

If a given isoviscosity level is selected and the log of predicted time to that viscosity vs. 1/T (°K) is plotted, the data can be fitted with a straight line. Furthermore, the fit becomes better as the viscosity range traversed (from zero time to the end point) increases. This can be accomplished by choosing a higher cure temperature (lower initial viscosity) or a higher viscosity end point. As the fit improves, the activation energy of log t_{gel} vs. 1/T curve approaches the "apparent" activation energy in the viscosity model.

As the temperature for isothermal cure is reduced, the zero time viscosity approaches the isoviscous level chosen and "t_{gel}" goes to zero. At higher temperatures, "t_{gel}" goes through a maximum and then decreases. It is in this decreasing region where the linear fit holds.

From this analysis, it appears that if t_{gel} is an isoviscous state, linear Arrhenius plots can be obtained. Furthermore if the viscosity level detected for t_{gel} is sufficiently high, it is close enough to the true gel point to be representative. As with all mechanical measurements of gelation, one depends upon a viscosity measurement. Rising bubbles, tack tests and viscosity-time measurements all provide similar approximations. As a matter of fact, the SPI Prepreg Reinforced Plastics Committee Test Method: Prepreg 3 - Measurement of Gel Time of Preimpregnated Inorganic Reinforcements (New York, May, 1960) was found to provide gel times corresponding to 120,000-140,000 cps (42).

SUMMARY

In this paper the history of dynamic mechanical testing and its past relationship to thermoset and coatings research and development is reviewed. With the introduction of several fully automated systems, the study of thermosetting systems by these techniques will greatly increase. Provided are examples of the use of the technique as a tool to help understand the mechanical behavior of thermosetting materials. The examples include effect of environment, comparison of similar materials, cure, aging of prepolymers, correlation with fabrication, monitoring of phase separation, apparent gelation kinetics, and the influence of gelation and vitrification on material properties. The article concludes with recent results which reveal the coincidence of transitions in thermoplastics observed above the glass transition, and in thermosets during the transformation from fluid to intractible solids; these bear on processing.

Now that the difficulties of data reduction have been eliminated, the future applicability of dynamic mechanical techniques depends only upon the ingenuity of research and development personnel.

ACKNOWLEDGMENT

The authors wish to thank the management of Mobil Chemical Co. for permission to publish this paper. Plastics Analysis Consultants Inc., P. O. Box 408, Princeton, New Jersey provided thermomechanical TBA plots.

LITERATURE CITED

(1) Nielsen, L.E., *ASTM Bulletin* No. 165, p. 48, April (1950); *Rev. Sci. Instr.*, 22, 690 (1951).

(2) Gillham, J.K., *A.I.Ch.E. J.*, 20, 1066 (1974).

(3) Blaine, R.L. and Woo, L., *Am. Chem. Soc., Polymer Preprints*, 17(2), 1 (1976).

(4) Kenyon, A.S., Grote, W. A., Wallace, D. A., and Rayford, M. J., *ibid.*, 17(2), 1 (1976). Also *J. Macromol. Sci.-Phys.* B13(4), 553 (1977).

(5) Davis, W.M. and Macosko, C. W., *Polymer Eng. Sci.*, 17(1), 32 (1977).

(6) Gillham, J.K. and McPherson, C.A., *Preprints of 32nd Annual Tech. Conf.*, Reinforced Plastics/Composites Institute, SPI, sect. 9-E (1977).

(7) Gillham, J.K. and Roller, M.B., *Polymer Eng. Sci.*, 11, 295 (1971).

(8) Ozari, Y., Chow, R. H. and Gillham, J.K., *Am. Chem. Soc., Polymer Preprints*, 18(1), 649 (1977).

(9) Roller, M.B., unpublished literature survey.

(10) Heijboer, J., Publication P73/28, of Central Laboratories TNO, Delft, The Netherlands, 1973; also "Secondary Loss Peaks in Glassy Amorphous Polymers," presented at 4th Midland Macromol. Meeting, Midland, Mich. Feb. (1975), *Int. J. Polymer Material.* 6, 11 (1977). See also *Ann. N.Y. Acad. Sci.*, 279, 104 (1976).

(11) Kaelble, D.H., "Physical Chemistry of Adhesion," Wiley Interscience, New York, N.Y. 1971.

(12) Babayevsky, P.G. and Gillham, J.K., *J. Appl. Polymer Sci.*, 17, 2067 (1973).

(13) Gillham, J. K., Glandt, C. A., and McPherson, C. A., *Am. Chem. Soc., Preprints*, Div. Org. Coat. Plastics Chem., 37(1), 195 (1977); also "Chemistry and Properties of Crosslinked Polymers," S.S. Labana, Ed., Academic Press, New York, 1977, p. 491.

(14) Manson, J.A. and Sperling, L.H., "Polymer Blends and Composites," Plenum Press, New York, 1976, Chapters 3, 8 and 13.

(15) Gillham, J. K., Benci, J.A., and Boyer, R.F., *Polymer Eng. Sci.*, 16(5), 357 (1976).

(16) Inoue, Y. and Kobatake, Y., *Kolloid, Z.*, 159(1), 18 (1958).

(17) Inoue, Y. and Kobatake, Y., *ibid.*, 160(1), 44 (1958).

(18) Yoshino, M. and Takayanagi, M., *Zairyo Shiken*, 8, 330 (1959).

(19) Lewis, A. F. and Gillham, J. K., *J. Appl. Polymer Sci.*, 6, 422 (1962).

(20) Zorll, U., *Forschungsber. Landes Nordhein-Westfalen*, No. 1361, Westdeutschen Verlag Omblt, Köln and Opladen (1962).

(21) Hansen, C.M., *Official Digest*, 37(480), 57 (1965).

(22) Myers, R.R., Klimek, J., and Knauss, C.J., *Journal of Paint Technology*, 38(500), 479 (1966).

(23) Bender, H.S., *J. Appl. Polymer Sci.*, 13, 1253 (1969).

(24) Takahashi, Y., Naganuma, S., Onozawa, K., and Kishi, H., *Proc. 5th Inter. Cong. Rheology*, 1968, p. 485 (1970).

(25) Myers, R. R., *J. Polymer Sci.*, Part C 35, 3 (1971).

(26) Kollinsky, F., and Markert, G., "Multicomponent Polymer Systems," *Advances in Chemistry Series*, No. 99, American Chemical Society, Washington, D. C., 1971, p. 175.

(27) Naganuma, S., Sakurai, T., Takahashi, Y., and Takahashi, S., *High Polymer Chemistry (Hobunski Kagaku)*, 29(322), 105, and (327), 519 (1972).

(28) Massa, D. J., *J. Appl. Phys.*, 44, 2595 (1973).

(29) Ikeda, S., *Prog. Org. Coatings*, 1(3), 205 (1972/3).

(30) Shimbayama, K., *ibid.*, 3(3), 245 (1975).

(31) Massa, D. J., Flick, J. R., and Petrie, S.E.B., *Am. Chem. Soc. Preprints*, Div. Org. Coat. Plastic Chem., 35(1), 371 (1975).

(32) Seefried, C.G., Jr. and Koleske, J.V., *J. Testing Eval.*, 4(3), 220 (1976).

(33) Ginsberg, T., Merriam, C.N., and Robeson, L.M., *J. Oil Colour Chemists' Assoc.*, 59, 315 (1976).

(34) Cowie, J.M.G., *Am. Chem. Soc. Preprints*, Div. Org. Coat. Plastic Chem., 38(1), 284 (1978).

(35) Koleske, J.V. and Faucher, J.A., *ibid*, 38(1), 355 (1978).

(36) MacKnight, W.J., Neuman, R.A. and Senich, G.A., *ibid*, 38(1) 360 (1978).

(37) Senich, G. A. and MacKnight, W.J., *ibid*, 38(1), 510 (1978).

(38) Hill, D.R.J., *ibid*, 38(1), 590 (1978).

(39) Gillham, J. K., *Polymer Eng. Sci.*, in press. Also *Amer. Chem. Soc., Preprints*, Div. Org. Coat. Plastic Chem., 38(2), (1978).

(40) Roller, M. B. and Gillham, J. K., *J. Coatings Tech.*, 50, No. 636, 57 (1978).

(41) Schwartz, B., Ph.D. Thesis, Department of Chemical Engineering, Princeton University, 1979.

(42) Roller, M. B., *Polym. Eng. Sci.*, 15, 406 (1975).

(43) Gillham, J. K., Polym. Eng. Sci., 16, 353 (1976).

(44) Gillham, J. K., Am. Chem. Soc., Preprints, Div. Org. Coat. Plastics Chem., 38(1), 221 (1978).

RECEIVED MAY 22, 1978.

9

Application of Electrochemical Techniques to the Evaluation of the Corrosion Barrier Properties of Modern Container Coatings

R. E. BEESE
American Can Co., 433 N. Northwest Highway, Barrington, IL 60010
J. C. ALLMAN
M&T Chemicals, Inc., 26701 Telegraph Rd., Southfield, MI 48076

Introduction:

Testing programs are required to evaluate the performance of materials considered for the development of new containers to preserve and store foods and beverages. Historically, testing was accomplished by packing fabricated containers with a representative product, storing the packed containers, and periodically evaluating to determine container performance. This lengthy procedure limits the number of variables to be considered and causes development delays. Experience has shown that electrochemical techniques can be used to evaluate the corrosion performance of new containers and coating materials. The electrochemical testing program permits one to evaluate a large number of variables in a short time. We have found that electrochemical tests can readily determine container failure caused by metal dissolution or corrosion for variables which perform poorly. In cases where measured corrosion rates are low, test packs are needed to establish whether or not long-term protection is provided.

Application of Electrochemical Technique:

We chose to measure the rate of iron dissolution by the slope-intercept technique identified by Stern(1) and formalized by ASTM(2) rather than the polarization resistance technique(3)

0-8412-0446-2/78/47-078-090$05.00/0

which Kleniewski(4) employed to measure the relative corrosion barrier properties of can coatings. Polarization resistance is inversely proportional to corrosion rate provided the nature of the anodic and cathodic reactions which account for the corrosion process remain constant; however, this is not the case. Makrides(5) solved this problem by measuring an average corrosion rate by weight loss and then calculating an average proportionality constant between polarization resistance and corrosion rate. This procedure is not applicable because the corrosion of iron through can coatings cannot be monitored by weight loss. Mansfeld(6) points out that the IR drop in the potential measuring circuit causes errors in the evaluation of corrosion rate from polarization resistance data. Hausler(7) also discusses further problems associated with this technique.

The slope-intercept technique was chosen because it provides an actual corrosion rate rather than a relative measure of corrosion performance. While problems associated with errors caused by IR drops in the potential measuring circuit are still with us, the data developed in both beer and tomato juice provide reasonable estimates of iron corrosion rate through organic enamel coatings or at discontinuities or fractures in organic enamel coatings on tinplate or electrolytic chromium coated steel(8). Whether the corrosion reaction occurs by ion diffusion through organic enamel coatings generally or through coatings at discrete sites caused by foreign material as indicated by Koehler(9) or through discontinuities such as cracks caused by mechanical damage to the coatings depends on the system under study. Since the slope-intercept technique for measuring corrosion depends only on the anodic and cathodic reactions; i.e., the rate of iron dissolution and hydrogen evolution respectively in air-free systems, the location of the reaction sites is not important.

Two other problems associated with the electrochemical approach to container evaluation need to be recognized. The barrier properties of some coatings diminish because the coatings are degraded by exposure to aggressive media. This was illustrated by Leidheiser(10) in his work with polybutadiene coatings in aerated sodium chloride solutions. Secondly, the metal area at a pore or crack in the coating increases as corrosion proceeds; thus, it is reasonable to expect instantaneous corrosion rates to increase as corrosion proceeds. Test procedures are developed to establish reasonably steady state conditions before making the corrosion rate measurement. For example, corrosion in beer cans can be evaluated after a 15 minute immersion in a 150° F water bath to simulate a pasteurization cycle. Tomato juice cans are permitted to stand two days before evaluating container performance to establish a steady corrosion rate.

Instrumentation and Test Procedure:

Corrosion rate can be estimated from a potentiostatic polarization curve by the slope-intercept technique. The linear portion of the log current-potential plot of a polarization curve; i.e., the Tafel line, is extrapolated to the corrosion potential. The current at the intersection of the Tafel line and the corrosion potential is the rate of the corrosion reaction. Any quality potentiostat can be used to control the potential of a corroding metal sample. The log current-potential relationship is automatically plotted with an X-Y recorder. The potential of the corroding metal is measured with respect to a reference electrode on the Y axis of the recorder. The log of the current flow between an auxiliary platinum electrode and the corroding metal is recorded on the X axis. Examples of cathodic polarization curves are shown in Figure 1.

Cans or can parts are tested by filling with a representative product and measuring corrosion rate. Beer is the test medium for beer cans. Tomato juice is used as a representative moderately corrosive mildly acid food product. Cans are closed by sealing a lucite fixture to the can or the can part with an O-ring. Cans filled with beer are maintained under a carbon dioxide atmosphere and can be given a simulated pasteurization cycle by immersing the closed filled can in a 150° F water bath for 15 minutes. The can is stored overnight at 80° F before testing. Cans to be tested with tomato juice are maintained under a nitrogen gas atmosphere. They are filled with 190° F tomato juice and stored two days at 80° F before testing.

Corrosion rate is measured by inserting a platinum auxiliary electrode and a saturated calomel reference electrode in a 1% sodium chloride salt bridge into the product through a silicone rubber gromet in the lucite closure. The potentiostat's reference potential is set at a potential a few millivolts anodic to the corrosion potential. The potentiostat's reference potential is then permitted to change in the cathodic direction; i.e., to more negative potentials at a rate of 5 to 6 millivolts per minute to generate the cathodic polarization curve. It is important to polarize at the slow rate to obtain reproducible data. The slow adsorbtion-desorbtion of the corrosion inhibitor systems naturally occurring in beer and tomato juice on the corroding metal probably explains the need for the slow polarization rate.

Application of Polarization Measurements:

The following three examples of iron corrosion through organic enamel can coatings illustrate the various mechanisms by which

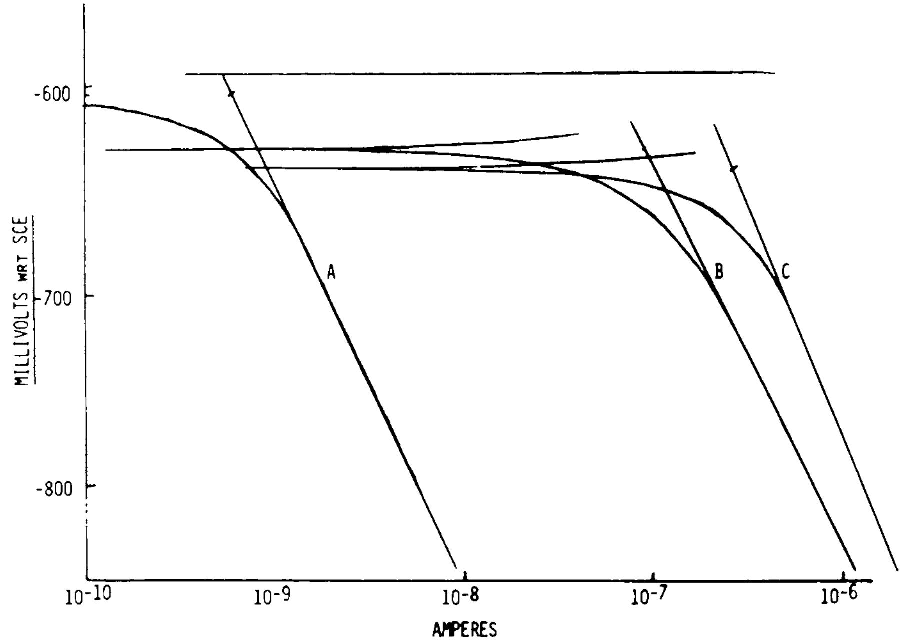


Figure 2. Iron corrosion rate for experimental beer cans in 80°F beer: ○, #1 211 × 413 cemented can; △, #2 211 × 413 cemented can; □, #3 207.5/209 × 504 D&I can; ×, #4 209/211 × 413 D&I can

corrosion can occur through properly applied can coatings:

A. Iron Corrosion Through Breaks in Coatings:

The draw-redraw process for the manufacture of two-piece food cans involves the coating of electrolytic chromium coated steel or tinplate with an organic enamel coating and mechanically forming the coated steel into a cylinder with an integral end. Mechanical damage can occur to the organic coating during the drawing operation. Microscopic tears occur in the vinyl organosol coating used on many draw-redraw cans.

Draw-redraw cans have been evaluated with tomato juice to determine the area of metal exposure through the damage to the organic coating. This testing permits an estimate of the container performance from the rate of iron pickup. Typical polarization curves and corrosion rate data for drawn cans are given in Figure 1 and in Table I. The differences between the containers are related to the area of iron exposed.

It should be pointed out that Table I indicates that the corrosion reaction through a 21 square inch area of vinyl organosol coated steel was very small. Since this coating provides an excellent barrier to corrosion before drawing, one must conclude that the observed corrosion occurs at sites where the organic coating was mechanically damaged by drawing.

B. Iron Corrosion Through a Thick Plastisol:

Experimental easy-open beer ends made from organic enamel coated electrolytic chromium coated steel were made by partially cutting two circular holes through the steel and resealing the partially cut circle with a plastisol film approximately 10 mils thick. The organic enamel coatings on the chromium coated steel provide an excellent barrier to corrosion. The plastisol sealant was designed to fill the crack between the disc and the end and to provide a mechanical seal. The properties of this plastisol are unique. It must provide a gas and liquid seal and still be easily torn so that the container can be opened. The plastisol seal provided an excellent physical barrier; however, beer test packs indicated that this plastisol was a poor barrier to iron corrosion. Reformulation of the plastisol improved its corrosion barrier properties, as indicated in Table II.

This example describes an organic material that originally was formulated with very poor corrosion barrier properties.

TABLE I

Representative Iron Corrosion in Drawn Cans Made From Vinyl Organosol Coated Electrolytic Chromium Coated Steel After Two Days in 80° F Tomato Juice

		Electrochemical Data			
Container Description	Steel Code	Corrosion Potential mV	Tafel Slope V	Corr. Rate µa/Can	Iron Corr. Rate ppm Fe/Yr.
21 square inches of enamel coated steel	A	-594	0.21	0.0006	0.02*
	B	?	∞	<0.0003	<0.01*
404 x 307 cans	A	-616	0.20	0.038	0.46
	B	-623	0.20	0.093	1.13
307 x 406 cans	A	-664	0.26	0.36	5.4
	B	-658	0.26	0.29	4.4

*Calculation based on 307 x 406 can interior surface area and container volume

TABLE II

Rate of Iron Corrosion Through Plastisol on Experimental Steel Easy-Open Ends in 80° F Beer

		Electrochemical Data			
Test Code	Plastisol Description	Corr. Pot. mV	Tafel Slope V	Corr. Rate µa	Rate Iron Pickup ppm Fe/3 Mos.
15-1	Initial formulation	-626	0.54	0.034	0.22
15-13		-609	0.50	0.022	0.14
15-25		-572	0.64	0.028	0.18
21-10	Reformulated Plastisol	-659	0.17	0.00062	0.0040
21-13		-660	0.23	0.00007	0.0004
21-16		-664	0.25	0.00004	0.0003

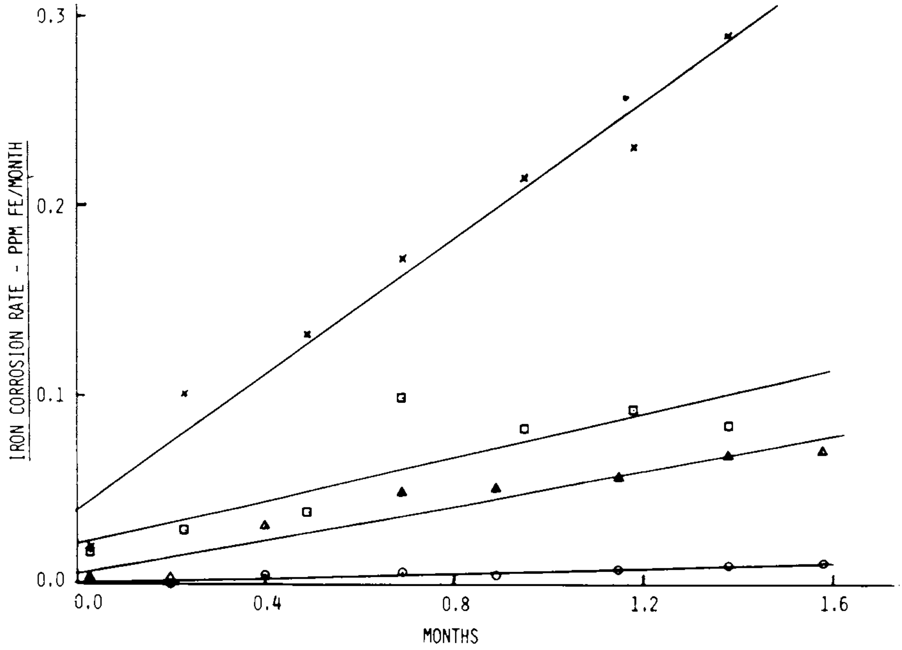


Figure 1. Rate of iron corrosion through vinyl organoso-coated electrolytic chromium-coated steel in drawn cans after 2d with 80°F tomato juice: A, 21 in. 2-coated steel surface; B, 404 × 307 can; C, 307 × 406 can

Diffusion of moisture, ferrous ions, hydrogen ions and hydrogen gas occurred easily. Reformulation improved the barrier properties, as measured by polarization tests and test packs. This electrochemical technique permitted the evaluation of a series of plastisol formulations before one was selected for commercial trials.

C. Iron Corrosion Through Discrete Sites in Coatings

Experimental beer cans were closed, maintained under a carbon dioxide atmosphere, filled with beer, pasteurized, and stored at 80° F. Iron corrosion rates were monitored periodically over a 1.5 month test period. Measured corrosion rates were expressed in terms of ppm iron pickup per month. Typical data are shown in Figure 2. Corrosion rate increases with time. The least square line for each can was calculated. The total iron corrosion was calculated by integrating the least square line from time zero to the time samples were taken for iron analysis. The calculated results from the corrosion rate data are compared to the measured iron pickup in Table III. Excellent agreement was found.

TABLE III

Measured Iron Pickup Compared to Iron Pickup Calculated from Corrosion Rate Measurements

Experimental Beer Cans	Test Period Mo.	Measured Iron Pickup Caused by Corrosion ppm Fe	Iron Pickup Predicted from Polarization Data ppm Fe
#1 211 x 413 Cemented Can	1.6	0.02	0.01
#2 211 x 413 Cemented Can	1.6	0.06	0.07
#3 207.5/209 x 504 D&I Can	1.4	0.11	0.09
#4 209/211 x 413 D&I Can	1.4	0.24	0.24

This case illustrates corrosion through barrier coatings at discrete sites. Initially, the organic coating provides nearly complete protection; however, as time passes, diffusion through the coating at discrete sites permits corrosion. This mechanism is described in detail by Koehler(9).

Conclusion:

The examples cited illustrate the application of electrochemical techniques to the evaluation of corrosion through can coatings. This approach speeds the development of new coating materials and the application of these coatings to new containers.

References:

(1) M. Stern and A. L. Geary, "Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves," Journal of the Electrochemical Society, 104, 56 (1957).

(2) ASTM Designation G3-74, "Standard Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing."

(3) M. Stern, "A Method for Determining Corrosion Rates from Linear Polarization Data," Corrosion 14, 440t, (1958).

(4) A. Kleniewski, "Polarization Resistance Measurements as a Guide to the Performance of Lacquered Tinplate," Br. Corros. J., 10, 91 (1975).

(5) A. C. Makrides, "Corrosion in Dilute Acids Part I A Modified Linear Polarization Technique," Corrosion, 29, 148 (1973).

(6) F. Mansfeld, "The Effect of Uncompensated IR-Drop on Polarization Resistance Measurements," Corrosion, 32, 143 (1976).

(7) R. H. Hausler, "Practical Experiences with Linear Polarization Measurements," Corrosion, 33, 117 (1977).

(8) ASTM Designation A 657-74, "Standard Specification for Steel, Cold-Rolled, Single and Double Reduced Tin Mill Black Plate Electrolytic Chromium Coated."

(9) E. L. Koehler, "The Influence of Contaminants on the Failure of Protective Organic Coatings on Steel," accepted for publication in Corrosion (1977).

(10) H. Leidheiser, Jr., and M. W. Kendig, "The Mechanism of Corrosion of Polybutadiene-Coated Steel in Aerated Sodium Chloride," Corrosion, 32, 69 (1976).

RECEIVED MAY 22, 1978.

10

Detecting, Measuring, and Analyzing Visible Emissions from High Solids Coatings in the Laboratory

P. GANSER and C. W. HEIDEL

The O'Brien Corporation, 450 E. Grand Ave., South San Francisco, CA 94080

INTRODUCTION:

Odors and visible emissions from large users of baking finishes have been a problem for many years and some container plants had installed fume incinerators prior to Rule 66.(1). With the enactment of this rule, Regulation 3 (2) and others which have followed, all California metal decorating lines were forced to install after burners or control devices. These have been expensive to install, run and maintain not to mention the increased drain on our natural gas supply.

National regulations which would have required similar control devices across the country would have been disasterous for the container industry and others. Fortunately, exemptions were provided for water borne and high solids coatings and the coatings industry has aimed its research and development programs toward these technologies. Exempt high solids coatings have been defined as 70, 80 or 95 percent nonvolatile by volume in various regulations (1,2). The coatings industry is attempting to move legislation toward 70 percent which is considered to be the state of the art today.

Early attempts to supply exempt coatings led to many problems such as poor wetting of oily plate, poor flexibility and excessive visible emissions. Most Air Quality Control Regions limit visible emissions to less than No. 1 on the Ringleman scale (3) (20 percent opacity). Stack monitoring devices are not usually available on litho lines and inspectors are usually trained to observe smoke of various degrees of opacity against various sky conditions. If you will, they calibrate their eyes.

As formulators of coatings for the container industry, we felt that a test procedure was required which would allow us to measure quantitatively and analyze the smoke given off during the bake cycle for various coatings if we were to be successful in supplying coatings exempt from incineration. The only test method available at the beginning of our program was a laser system which required about 40 sq. ft. of plate to be baked in

0-8412-0446-2/78/47-078-099$05.00/0

a laboratory oven. A slip stream sampling tube drew off part of the oven exhaust and attenuated it thru a T tube. A laser beam was projected thru the tube and received by a photo cell, the signal was amplified and recorded on a strip chart recorder.

This procedure has been used in several labs with fairly good correlation to production ovens; but it has failed to give correlation in all cases. It was considered too cumbersome and time consuming for our laboratory, as it would be quite difficult to use when many variables were to be checked and the amount of coating and plate used would have been a problem for the coating formulator.

PROCEDURE FOR MEASURING VISIBLE OMISSIONS

In seeking an alternative lab procedure, we contacted Monitor Technology (4) and determined that their Model 160/131 turbidimeter was sensitive enough to measure smoke from a very small area of coating. This instrument was purchased and adapted to what we call the O'Brien/Monitek Method of measuring visible emissions.

The Monitek slip stream turbidimeter was designed originally for liquids. It uses an intense collimated beam of white light passing thru the stream. In using the instrument for air, we had the glass tube used for aqueous measurements removed. The light passing thru the stream is measured by the direct beam detector. The light scattered in a forward direction, by turbidity in the stream, is measured by the scattered beam detector. These signals are ratioed to provide the turbidity measurement. The effects of color and source drift are thereby eliminated, providing an accurate and linear measurement of opacity.

In THE O'BRIEN/MONITEK METHOD we generate smoke by bar coating approximately 20 sq. ins. of coating on a tinplate panel which is cut to fit our oven. The oven is actually a cure hot plate with shims to hold the panel above the hot plate surface, a spring clip to hold the panel in place, a hood to collect vapors and fumes and a tube leading to the Monitek unit. A small tube in the turbidimeter presents the emissions just below the light beam and a larger tube just above the light beam collects the emissions which are drawn off by an air pump. This design should minimize contamination of the optics due to the negative pressure in the light beam area.

The air flow thru the unit is 35 cc. per minute and we have determined that by setting the cure hot plate about 50 degrees F higher than the desired metal temperature, we get approximately 2 minutes come up time and bakes are normally held 8 minutes at the desired metal temperature.

The Monitek unit has scales of 0.5 to 500 ppm. The lowest scale which will measure the emissions without off scale readings is used for each sample. Results are recorded on an integrating strip chart recorder at 300 counts per minute.

The recorder has a zero suppression adjustment which is used to blank out the background air reading.

Tared panels are coated, baked and reweighed to determine total coating weight. The coated area is measured to determine mgs. per sq. in. of dry film.

In our comparison of variables of a particular formulation we use the integrator counts per mg. of dry film based upon the 20 ppm. full scale setting to determine the relative amount of smoke from each variable. Formula I is used to calculate the counts per mg:

$$\text{I.} \quad M = \frac{C \times S}{20 \times W}$$

M = Counts per mg. of dry film - 20 ppm. scale basis
C = Total integrator counts for bake cycle.
S = Full scale ppms. required for on scale readings.
W = Total coating dry film weight in mgs.

If coating of different application weights and bakes are to be compared, we use the counts per square inch of coating as the basis. Formula II is used to convert all data to the 20 ppm. scale basis.

$$\text{II.} \quad I = \frac{C \times S}{20 \times A}$$

I = Counts per sq. in. of coatins - 20 ppm. scale basis
A = Area coated (sq. ins.)

A comparison of some typical coatings is shown in Table I. These results seem to agree well with observed emissions from commercial ovens; but, as stated earlier, no reliable quantitative data has been available from the field to date.

TABLE I

	Dry Film Wt. Mgs./sq. in.	Counts/Mg.	Counts/Sq. In.
Organosol Non Repair	10.0	24.9	249
Acrylic White Enamel	10.0	20.9	209
Oleoresinous Sanitary	4.7	11.6	55
Conventional Alkyd-melamine WI Varnish	3.4	11.8	40
Hi Solids WI Varnish	3.4	3.8	13
Epoxy-Urea Enamel	3.9	2.8	11

PROCEDURE FOR QUALITATIVE ANALYSIS OF EMISSIONS:

Another procedure which we have found useful in formulating in conjunction with the O'Brien Monitek Method is infrared analysis of the emissions from bakes.

The orifice on an 8 mm. x 10 cm. medicine dropper is partially blocked with a "Boileze" boiling stone. Approximately 100 mgs. of Infrared Grade Potassium Bromide is transferred to the prepared dropper, which is then attached to the exhaust line of the "oven". Care must be used to avoid loss of KBr powder by mechanical sifting around the boiling stone. A coated panel is inserted into the baking chamber and the fumes are drawn off thru the line containing the KBr trap. An FMI Laboratory (5) pump has been used successfully in this procedure. It allows the air flow to be regulated to prevent the KBr from being blown from the trap.

At the end of the bake cycle, the pump is stopped and the dropper removed with care to avoid loss of KBr. The KBr is ground in an agate mortar and pestle to reduce particle size, then charged into a Wilks Mini-press. The three release cycle procedure is used to form the pellet. Recent studies have revealed that better results are obtained if the KBr is not ground prior to pressing into a pellet.

After removal of bolts, the pellet is mounted in an infrared spectrophotometer and the scan is run. We use a P.E. 297 (6) and run at X 1, 8 mins. scan time, slit 2 program.

If the spectrum is too weak for interpretation, three modifications of the procedure can be used:

1. If the instrument used is equipped for ordinate expansion, a weak spectrum can be expanded satisfactorily.
2. The KBr trap can be exposed to the vapors of a second panel increasing the amount of vapors trapped which will give a stronger spectrum.
3. The use of Micro KBr accessories will provide good spectra from smaller amounts of vapors on proportionately smaller amounts of KBr. We have used the Harshaw Chemical Company's "Wick Stick" method of processing the vapors into a micro 1 mm by 3 mm pellet. When used with a beam condenser accessory, excellent spectra have been obtained.

Modifications 1 & 3 are preferred to #2 since the latter will frequently present problems due to trapping of atmospheric moisture on the KBr. This causes a very low profile spectrum, the appearance of strong water absorption bands, and other spectral abnormalities. These can be partially avoided by drying the KBr powder after it is placed in the Wilks Mini-press (8) and before it is pressed. This is done by heating for three or more hours at 60 degrees C and 30 inches vacuum, pressing immediately and running the scan. There is always a possibility that part of the condensed vapors will be volatilized with the moisture, so this procedure is the least favored of the three.

As an example of how these procedures have been used to develop a practical high solids coating, a low molecular weight alkyd was prepared to have a molecular weight of about 1150 (number average), for good gloss, flexibility,low emissions and the lowest viscosity for roll coat application. Blends of the alkyd resin low molecular weight melamine resins were then prepared to give a ratio of 75% alkyd to 25% melamine on a solids basis. Flow additives and solvents were added to give 70% solids by volume.

The first variable used a monomeric methoxy melamine with a molecular weight of about 600. This resin gives the minimum viscosity and might be roll coated at room temperature. It gave a reading 6.32 counts per mg. of dry film. The IR spectrum of the vapors condensed on KBr indicated that the emissions were predominately melamine resin.

A second variable was prepared using a butoxy melamine resin with a molecular weight of about 1200. This coating gave a reading of 3.75 counts per mg. of dry film and the IR spectra was almost entirely free of melamine resin.

In formulating a coating for minimum visible emissions and minimum viscosity which would be applicable at the lowest possible temperature, the O'Brien-Monitek procedure indicated that the low molecular weight melamine should not be used. The butoxy melamine was found to contribute little to visible emissions and was chosen for cross linking the alkyd resin.

A wet ink finishing varnish was formulated with these preferred resins and run commercially without objectionable visible emissions.

CONCLUSIONS: The O'Brien-Monitek system of measuring visible emissions gives the coatings formulator a simple tool for measuring visible emissions of bake finishes quantitatively. Small samples can be used and many variables can be compared in a relatively short period of time. The method can be adapted to trap vapors on KBr and subsequently scanned by IR and identified.

ACKNOWLEDGEMENTS: The authors acknowledge the contributions of colleagues in preparing resins and discussing procedures and results. A special thanks is due to our Technical Director, Mr. R.M. Levine, for his enthusiastic support of this program.

REFERENCES:

1. Rule 66 County of Los Angeles APCD Amended 8/31/71 Currently Rule 442 Southern California APCD.
2. Regulations 3 Bay Area APCD San Francisco, CA.
3. Ringlemann Chart, U.S. Bureau of Mines.
4. Monitor Technology, 630 Price Avenue, Redwood City, CA 94063
5. FMI Model RPD-D Fluid Metering, Inc., Oyster Bay, N. Y.
6. Perkin Elmer Corp., Instrument Div. Norwalk, Conn.
7. Harshaw Chem. Co., Div. Kewauee Oil Co., Crystal & Electronics Prod. Dept. 6801 Cochran Rd., Solon, Ohio 44139.
8. Wilks Scientific Co., P.O. Box 449, So. Norwalk, Conn. 06856.

RECEIVED MAY 22, 1978.

11

Polyethylene Powders for Glass Retentive Beverage Bottle Coatings

S. E. HMIEL

ARCO/Polymers, Inc., Research and Development Dept., Monaca, PA 15061

ARCO/Polymers commercialized SUPER DYLAN® high density polyethylene production (HDPE) via Ziegler catalysts in 1958 and currently operate a 150 million pound plant at Port Arthur, Texas. New production facilities are being constructed for completion in 1978 which will significantly add to present capacity. Ethylene feedstocks are supplied by our Houston and Channelview, Texas, olefin plants. These commitments have established ARCO Polymers as a reliable present and future source for high density polyethylene.

The ARCO polymers polymerization process can be controlled to produce HDPE as a finely divided powder with 20-60 micron average particle diameter. These powders are particularly suitable for use in electrostatic powder spray (EPS) application equipment. SUPER DYLAN powders applied via EPS demonstrated considerable promise for coating glass, metals and other substrates.

In the mid-1970's, the glass container industry had developed lightweight, non-returnable, resealable, family-sized soft drink bottles to compete with the ever increasing threat from cans. However, their increased usage by bottlers was accompanied by increasing consumer complaints due to injuries from glass fragments scattered when filled beverage bottles were accidentally broken. A survey of hospital emergency rooms, National Electronic Injury System (NEIS) by the U. S. Consumer Product Safety Commission (CPSC), Bureau of Epidemiology, confirmed an increase in reported cases and glass beverage bottles were considered for study by the CPSC.

SUPER DYLAN powders, because of their low cost, availability, strength, and chemical resistance, were candidates for glass retentive beverage bottle coatings. ARCO Polymers initiated exploratory programs to establish their feasibility for electrostatic powder spray coating of glass bottles. These studies revealed that application, fusion, and cooling technique development would be required to maximize their performance as glass retentive coatings. The successful

0-8412-0446-2/78/47-078-105$05.00/0

development of a coating process and correlation of powder physical properties vs. coating performance resulted in the development of a medium density ethylene copolymer powder for glass retentive beverage bottle coatings. ARCO Polymers' commitment did not cease with this development and the next generation of ethylene polymers being studied have demonstrated significant improvements in both strength and transparency.

Bottle Coating Requirements

A survey of the glass container industry established the following desired characteristics for coatings and powders:

A. Low Cost - Available In Bulk
B. Total Glass Containment And/Or Low Glass Scatter When Broken
C. Transparent
D. Alkali Resistant
E. Recyclable
F. Pollution Free - Air/Water.

SUPER DYLAN HDPE powders had all these desired characteristics with the exception of transparency.

Polymer Properties Vs. Coatings

The initial program objective was the establishment of a correlation between physical properties and coating performance on non-returnable glass beverage bottles. Melt index and density as illustrated in Figures 1 and 2 would influence coating performance. Our HDPE powders, 0.940-0.960 density, produced coatings with varying degrees of opaqueness and, therefore, low melt index powders would be more desirable to minimize haze or cloud in the coatings. However, a compromise in melt index, i.e., 3.0 was necessary to achieve acceptable coating smoothness and fragment retention.

TABLE I
POLYMER AND COATING PROPERTIES

	Sample No.			
Property	1	2	3	4
Powder				
Density(1), g/cc	0.952	0.953	0.958	0.955
Melt Index(2), g/10 Min.	3.0	6.0	16.0	26.0
Coating				
Transparency, %(3)	75	<70	<70	<65
Glass Retention, Wt. % (4) (5)	98	86	95	95

(1) ASTM D1505
(2) ASTM 1238
(3) Light Transmission
(4) Thickness >10 Mils, Wt. % Retained Within 3 Foot Diameter Drop Zone
(5) Bare Glass 30-50%

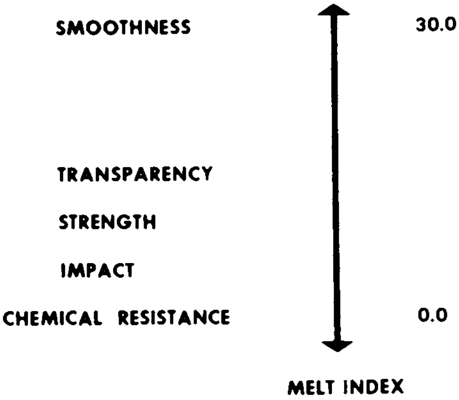


Figure 1. Polymer properties vs. coating performance—melt index

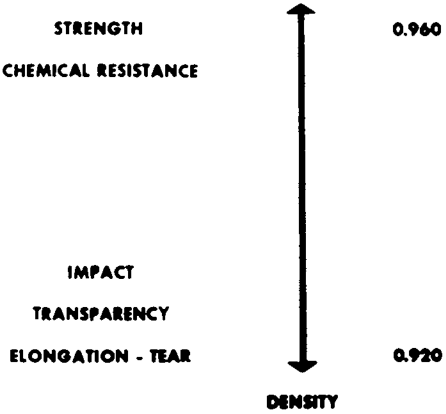


Figure 2. Polymer properties vs. coating performance—density

Coating Process

Electrostatic powder spray coating technology was in it's infancy and although more advanced for metal substrates, coating glass bottles required considerable process development to achieve uniform and reproducible coatings. Electrostatic powder spray, dust collection, heating, and cooling equipment were installed in our Powder Laboratory and processing studies initiated.

A. Powder Application

A Model 720 GEMA EPS gun was used to manually apply powder to the rotating glass bottle. Since glass is an insulator, it was necessary to increase the conductivity of the glass by preheating. The rotation, grounding via metal holder chuck, and bottle surface temperature control (150-175°C.) measured via infrared pyrometry resulted in uniform powder deposition and coating thickness control. This procedure was sufficiently flexible and permitted selective powder deposition to more critical areas if desired (Figure 3).

B. Fusion

The powder applied to the heated bottle would partially fuse and further post heating was required to achieve continuity and melt "flow out." Smooth and continuous coatings were obtained with final melt temperatures of 200-215°C. with forced air or infrared heating equipment (Figure 4).

C. Cooling

HDPE coated bottles cooled gradually in air or with fans were somewhat opaque or translucent.

A "water quench" cooling procedure was developed to maximize coating transparency. This procedure was as follows:

1. Molten coatings were fan cooled to a temperature slightly above the 130°C. crystalline melting point, i.e., 145°C. (Figure 5).
2. Water was directed downward onto the rotating bottle slightly below the finish onto the shoulder for 10-20 seconds (Figure 6).

The coatings provided an insulation barrier and minimized thermal shock of the glass. Once the coating crystallized, the coated bottles could be handled mechanically without damage. This water quenching procedure formed smaller crystals than those obtained by slower annealing rates, in effect, lowered the density, and improved both transparency and strength.

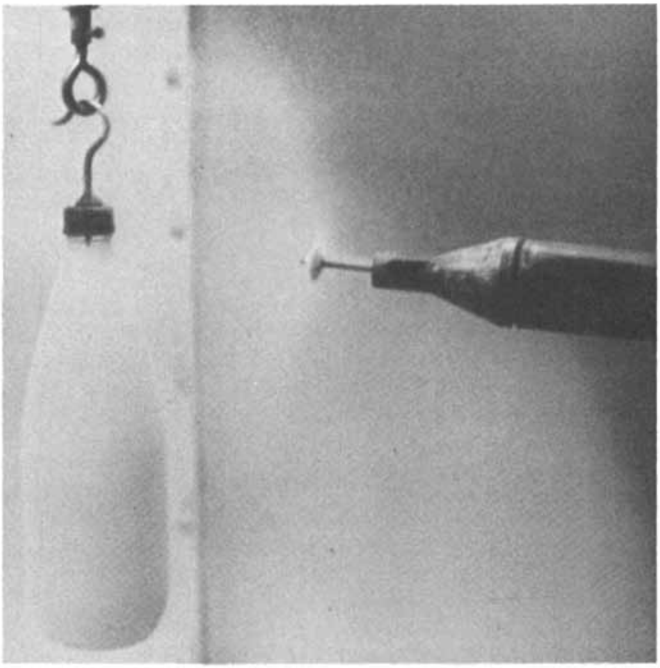


Figure 3. Powder application—electrostatic powder spray

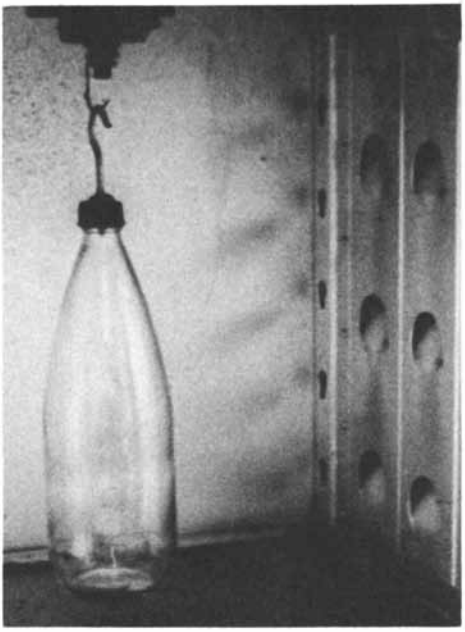


Figure 4. Powder fusion—melt transparency

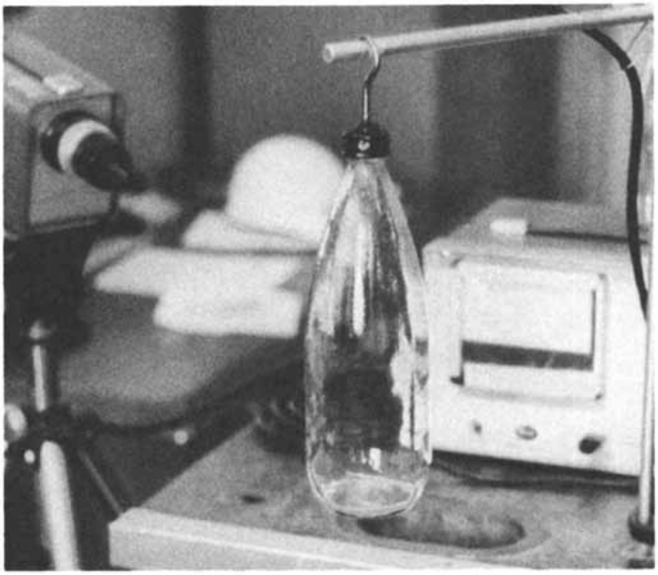


Figure 5. Melt temperature via IR—air cooling

Figure 6. Water cooling-coated bottle—transparency

Coated Bottle Performance

The coating-cooling process developed for HDPE coated beverage bottles demonstrated improved strength and transparency. However, there was concern that heating and shock cooling might induce undetectable stresses or strains in the glass which might rupture under pressure on filling lines or in storage. Normally, glass beverage bottles will withstand thermal shock differentials up to 38°C. (100°F.); our water quench procedure had a differential of 65-100°C. American Glass Research (AGR), a leader in glass technology, was commissioned to study the effects of this cooling procedure on glass bottle strength. They tested the coated bottles for internal burst (pressure ram), thermal shock, lubricity, and other quality tests. AGR reported:

> "Coated ware (bottles) had higher internal burst strengths and maintained this advantage even if scratched or abused when compared to bare glass."

Our coating-cooling process did not adversely affect glass bottle strength characteristics and coated bottles appeared safer even with minor flaws which might not be detected during manufacture.

Cooperative glass retention studies of pressurized bottles were also made with several glass companies. The following procedure was used in our laboratory studies:

A. Dilute acid solution was charged to the bottles, volume adjusted, sodium bicarbonate added, and sealed. An internal pressure of 60 PSI was generated overnight at 72°F.

B. Bottles were dropped from 48" horizontally to impact on their sidewalls on an 18" x 18" x 2" reinforced concrete slab with a 12" x 12" x 1/4" steel plate imbedded in the surface. This slab was centered in a three (3) foot diameter circle.

C. Glass scattered beyond the circumference of the circle was collected and weighed.

D. Glass retention was expressed as wt. % glass retained within the three foot circle.

Transparency was determined by the transmission of a monochromatic light beam through a water filled bottle and measuring the transmitted light with a photo light meter.

Polyethylene Fragment Retentive Coatings

HDPE powders were selected to provide a range of density (0.940-0.960) and melt index (0.2-30.0) to establish a correlation between polymer properties and coated bottle performance. The powders shown in Table I were the more promising of the many powders tested in this preliminary testing program. Coating thickness $>$10 mils did contain fragments within the impact zone. However, transparency was not acceptable and the economics with >10 mil coatings were borderline. To meet program objectives, 6-8 mil coatings would be required and low melt index - lower density powders were the obvious targets.

Several medium density ethylene copolymers produced via our versatile polymerization process exhibited significantly improved transparency and strength with excellent glass retention at nominal 6 mil coating thickness. SDP-531, a medium density ethylene copolymer, was successfully produced meeting the targeted physical properties: 0.935 density and 5-6 melt index. Beverage bottle coatings obtained with SDP-531 exhibited excellent glass retention, strength, and acceptable transparency: contact clarity with beverage was exceptionally good (Figure 7) and Tables II and III.

TABLE II
MEDIUM DENSITY POLYETHYLENE
POLYMER PROPERTIES

Property	Test Method	SDP-531
Density, g/cc	ASTM-D1505	0.935
Melt Index, g/10 Min.	ASTM-1238	5.5
Melting Point, °C.	DSC(1)	122

(1) Differential Scanning Calorimeter, DSC-1B, Perkin-Elmer Corporation.

TABLE III
MEDIUM DENSITY POLYETHYLENE
GLASS BOTTLE COATING PROPERTIES

Thickness, Mils	5.5
Glass Retention, Wt.(1) %	98.0
Transparency (2), %	91.0
Appearance	Very Slight Haze
Coating Elongation (3), %	800
Coating Tensile Strength (3), PSI	3500

(1) Wt. % Retained Within 3' Drop Zone.
(2) Light Transmission, Water Filled Bottle.
(3) ASTM D-638, Type IV Modified.

SDP-531 was extensively evaluated in laboratories and on pilot coating lines with the following results:

A. Glass Retention - >95% @ 5.5 Mils
B. Transparency - >90% Light Transmission
C. Alkali Resistance 5% Caustic @ 80°C - No Change in Strength or Appearance After 16 Hours Immersion

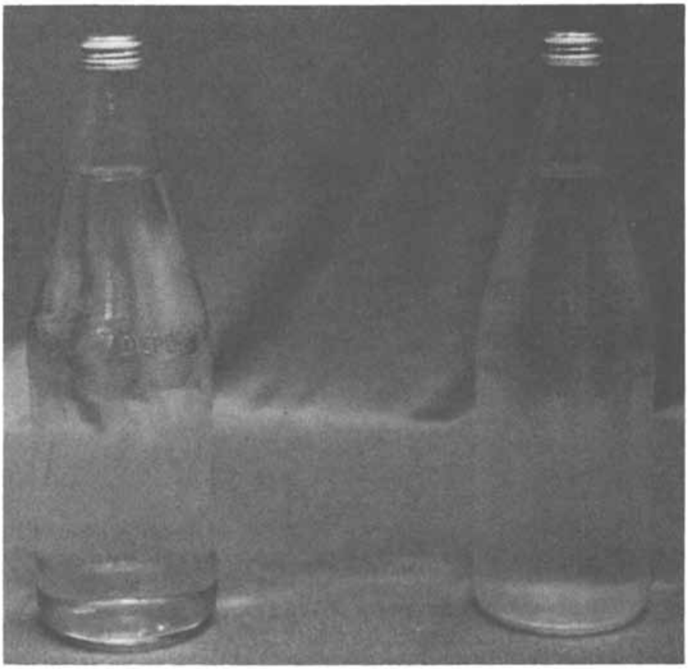


Figure 7. Super Dylan SDP–531-coated glass beverage bottle—water cooling (left) vs. air cooling (right)

D. Heat Resistance - No Change in Strength or Appearance After 4 Hours @ 98°C. In Water
E. U. V. Stability - 1000 Hours Fadeometer Exposure.

NR glass beverage bottles have hot-cold end surface treatments to improve on-line handling and scratch resistance. Studies were made varying these treatments as well as using bare (pristine) glass to determine their effects. SDP-531 coatings performed comparably regardless of surface treatment.

Production Coating and Market Trials

A successful production trial on a commercial coating line was made and the coated beverage bottles exhibited performance characteristics comparable to laboratory and pilot line coated ware. Normal production rates were obtained with our recommended coating and cooling process. These bottles were filled on a commercial bottling line and successfully marketed. The contact clarity of filled bottles was acceptable to bottling and marketing personnel.

Returnable Beverage Bottles

Glass returnable bottles are designed to withstand normal abuse repeatedly through the washing, filling, and consumer use cycle. The excellent alkali resistance of SDP-531 coatings suggested possible use on returnable bottles with corresponding reduction in glass weight. Both lightweight NR's and returnable bottles were coated and tested on a commercial soft drink bottling line. The bottles were washed in a two-stage caustic washer, filled with carbonated beverage, capped, and distributed to selected users. These coated bottles remained intact and functional through nine complete cycles before a mechanical malfunction terminated the test. These preliminary results suggest that lighter weight coated glass bottles for limited trip returnables are a near-future possibility.

Conclusion

A medium density ethylene copolymer powder was successfully developed and scaled up in production equipment for fragment retentive non-returnable beverage bottle coatings with acceptable transparency. This R&D program established a correlation between polymer properties and coating performance; developed procedures to maximize strength and transparency by water quenching molten coatings and successfully applied these coating-cooling procedures on a commercial coating line. Current studies with our versatile polymerization process are designed to further refine these "ethylene" powders for even better performance as economical, fragment retentive beverage bottle coatings with glass-like transparency.

RECEIVED MAY 31, 1978.

INDEX