AFML-TR-74-208
Part II

ADA040075

WATER-BASE COATINGS

CENTER FOR SURFACE AND COATINGS RESEARCH
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA 18015

AUGUST 1976

TECHNICAL REPORT AFML-TR-74-208, Part II
FINAL REPORT FOR PERIOD FEBRUARY 1975 - NOVEMBER 1975

Approved for public release; distribution unlimited

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

20040301084

NOTICE

This final report was prepared by the Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pennsylvania 18015, under Air Force Contract F33615-75-C-5213, "Exploratory Development of Improved Water Base Coatings", under Project 7340, Task 734007, job order number 73400771. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg as AFML/MBP Project Scientist.

This report has been reviewed by the Office of Information (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This report covers the research work during the period 17 February 1975 to 15 November 1975.

This technical report has been reviewed and is approved for publication.

Harold Rosenberg
HAROLD ROSENBERG
Project Scientist

FOR THE COMMANDER
R. L. Van Deusen
R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

AIR FORCE - 26 APRIL 77 - 125

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
AFML-TR-74-208, Part II

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Water-Base Coatings

5. TYPE OF REPORT & PERIOD COVERED
Final Report
17 February 1975-15 Nov. 1975

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) Yung-Nien Chou; Leslie M. Confer; Ken Earhart; Mohamed S. El-Aasser; Joseph D. Hoffman; John A. Manson; Subodh C. Misra; Gary W. Poehlein; Joseph P. Scolere; John W. Vanderhoff

8. CONTRACT OR GRANT NUMBER(s)
F33615-75-C-5213

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Lehigh University
Bethlehem, Pennsylvania 18015

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Program Element 62102F
Project 7340, Task 734007
Work Unit 73400771

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Materials Laboratory (MBP)
Air Force Systems Command
Wright-Patterson Air Force Base, OH 45433

12. REPORT DATE
August 1976

13. NUMBER OF PAGES
66

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Epoxy
Emulsion
Coatings
Resins
Polyurethane

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this work was to develop water-based analogs of existing solvent-based epoxy primer and polyurethane topcoat systems. The approach was to prepare separate aqueous emulsions of epoxy resin and curing agent that could be mixed just before application and isocyanate prepolymer adducts that could be emulsified without reaction with water. Solvent-free, stable emulsions of epoxy resins with average particle diameter of 0.2μm and below were prepared using the

(continued)

Block 20.

anionic sodium lauryl sulfate-cetyl alcohol or the cationic hexadecyltrimethylammonium bromide-cetyl alcohol combinations as emulsifier. Also, cationic emulsions were prepared from the curing agent. The emulsification of these epoxy resins and curing agents was improved by the substitution of n-decane for the cetyl alcohol in the mixed emulsifier. In order to increase the curing rate of the epoxy films at room temperature, some chemical additives were incorporated either in the epoxy resin or the curing agent prepolymer prior to the emulsification process. The solvent-stripped cationic epoxy resin and curing agent emulsions were mixed in various proportions and cured at room temperature, or 55°C. A mechanism was established for the curing of emulsion-cast epoxy-curing agent films by determining the morphological properties and the dynamic mechanical properties of these films. The results demonstrated that the diffusion of the curing agent molecules into the epoxy resin particles is controlled by the degree of interfacial crosslinking which takes place between the coalesced epoxy resin and curing agent particles.

Some preliminary work was carried out on the formulation of epoxy emulsion primer using aqueous dispersion of zinc chromate. The mixtures showed signs of flocculation to varying degrees. Slight improvement was obtained by the substitution of nonionic emulsifier for part of the cationic emulsifier used in the system.

The present work on the preparation of polyurethane emulsions concentrated on the optimization of the fully-cured polyurethane system. The present work varied the proportions of compounds used to react with the isocyanate groups in the prepolymer as well as the proportions of the reactive monomers. Also n-decane was used instead of cetyl alcohol in the mixed emulsifier combination. These variations gave emulsions with smaller average droplet size than our earlier work, and therefore a more stable emulsion. Also, improvements in film properties were obtained with these variations.

PREFACE

The Lehigh director was Dr. John W. Vanderhoff, Professor of Chemistry and Associate Director-Coatings, Center for Surface and Coatings Research. The faculty associates were: Dr. John A. Manson, Professor of Chemistry and Director, Polymer Laboratory, Materials Research Center; Dr. Gary W. Poehlein, Associate Professor of Chemical Engineering and Staff Member, Center for Surface and Coatings Research; Dr. Mohamed S. El-Aasser, Assistant Professor of Chemical Engineering and Staff Member, Center for Surface and Coatings Research. Also contributing to the project were research associates Ken Earhart, Center for Surface and Coatings Research, and Dr. Joseph D. Hoffman; and graduate students Yung-Nien Chou, Leslie M. Confer, Subodh Misra, and Joseph P. Scolere, Department of Chemical Engineering.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

LIST OF ILLUSTRATIONS (continued)

LIST OF ILLUSTRATIONS (continued)

LIST OF TABLES

SECTION I

SUMMARY

A. General

The purpose of this work was to develop water-based analogs of the solvent-based epoxy primer (1) and polyurethane topcoat (2) presently used by the Air Force. The general approach was to prepare aqueous emulsions of these systems: (i) separate emulsions of epoxy resin and curing agent prepolymers that could be mixed just before application; and (ii) isocyanate prepolymer adducts that could be emulsified without reaction with water.

The unique approach to the emulsification was the use of the mixed emulsifier combination shown earlier (3) to give aqueous styrene emulsions with average droplet sizes as small as 0.2μm. The smallest average droplet size produced by conventional emulsification methods is about 1μm. Droplets of this size settle or cream rapidly so that the shelf-stability of commercial polymer emulsions produced by emulsification is usually not competitive with that of latexes prepared by emulsion polymerization, which have average particle sizes in the range 0.1-0.3μm. This new mixed emulsifier combination gave emulsion droplets of about the same size as the latex particles produced by emulsion polymerization (3).

The first part of this work (4) applied this emulsification approach to the preparation of epoxy resin and curing agent emulsions as well as to fully-cured and air-drying polyurethane systems. The present work extended these earlier results in an effort to develop practical primer and topcoat formulations.

B. Epoxy Emulsion Systems

The earlier part of this work (4) concentrated on the preparation of epoxy resin and curing agent emulsions using the mixed emulsifier combination, particularly the Epon 1001-Versamid 115 system deduced to be that used in the present Air Force system (1). Stable emulsions of Epon 1001 and Epon 828 about 0.2μm average size were prepared using the sodium lauryl sulfate-cetyl alcohol combination and simple stirring, followed by ultrasonic irradiation or homogenization. Similar emulsions of the cationic Versamid 115 could not be prepared using the anionic emulsification system. Therefore, an analogous cationic system, using the hexadecyltrimethylammonium bromide-cetyl alcohol combination, was developed. This combination was used to prepare stable translucent emulsions of Versamid 115, which appeared more solubilized than emulsified, as well as stable cationic emulsions of Epon 1001 and Epon 828. Both anionic and cationic emulsions were prepared of the Genamid 250 curing agent.

Hard, transparent films were formed when the mixed epoxy resin-curing agent emulsions were dried at room temperature or 50°C, but about 30 days at room temperature were required to give the same properties obtained by curing for a few hours at 50°C. A preliminary evaluation showed that the properties of the emulsion-cast films were equivalent to those of the solvent-cast films. The optimum epoxy resin-curing agent ratios were 2:1 for the Epon 1001-Versamid 115 and Epon 1001-Genamid 250 systems, and 1:2 for the Epon 828-Versamid 115 system.

The recommendations for future work included the modification of the Epon 1001-Versamid 115 and other systems to increase the curing rate at room temperature, more thorough characterization of the morphological and dynamic-mechanical properties of the films, and, finally, formulation of an epoxy emulsion primer.

In the present work, three approaches were used to increase the curing rate: (i) the incorporation of Bisphenol A or resorcinol in the epoxy resin emulsion to accelerate the epoxy-amine reaction during curing (5); (ii) the incorporation of Dion Polymercaptan DPM-3-800-LC (reported to cure epoxy systems rapidly in presence of amines) into the Versamid 115 emulsions; (iii) pre-curing of the epoxy resin in the emulsion state to decrease the proportion of the reaction that must be accomplished in the dried film.

The emulsification of the Epon 1001-Bisphenol A or Epon 1001-resorcinol mixtures was accomplished without difficulty although the particle droplet size was somewhat larger. Similarly, the addition of Dion DPM-3-800-LC to the Versamid 115 also gave stable emulsions, but of larger droplet size. The pre-curing of the Epon 1001 emulsion by adding part of the Versamid 115 emulsion also increased the average droplet size, but in this case by forming clusters of very small Versamid 115 droplets around the larger Epon 1001 droplets.

The emulsification of these epoxy resin and curing agents was improved by the substitution of n-decane for the cetyl alcohol in the mixed emulsifier combination; this gave a slightly smaller average droplet size and a more stable emulsion. Stable emulsions of Epon 1001, Epon 828, and Versamid 115 was prepared using the hexadecyltrimethylammonium bromide-n-decane combination.

Versamid 100 was substituted successfully for the Versamid 115 curing agent; stable cationic emulsions of Versamid 100 were prepared in concentrations up to 38%, while the Versamid 115 emulsions were limited to concentrations of 11% or less because of their high viscosity.

For formulation with pigment dispersions, the emulsions of Epon 1001, Epon 828, Versamid 115, and Versamid 100 were prepared using the (Span 80-Tween 80)-hexadecyltrimethylammonium bromide-n-decane combination, the nonionic Span 80-Tween 80 combination being added to improve the emulsion stability when mixed with the pigment dispersion.

C. Morphological and Dynamic-Mechanical Properties of Epoxy Resin Films

The morphological and dynamic-mechanical properties were determined for the following epoxy resin-curing agent systems: (i) Epon 1001-Versamid 115; (ii) Epon 1001-Versamid 115 heated to 55°C for 30 minutes; (iii) (Epon 1001-Bisphenol A)-Versamid 115; (iv) Epon 1001-(Versamid 115-Dion DPM-3-800-LC); (v) solvent-cast Epon 1001-Versamid 115.

The morphological properties of these films aged at room temperature were determined by: (i) transmission electron microscopy of surface replicas and microtomed sections; (ii) scanning electron microscopy of fracture cross-sections. The degree of crosslinking and extent of cure were determined by solvent extraction and differential scanning calorimetry of the aged films. The dynamic-mechanical properties were determined by the log modulus-temperature variation.

The results of these determinations demonstrated that the emulsion-cast Epon 1001-Versamid 115 system cured first at the interface between the coalesced epoxy resin and curing agent particles to produce an interfacial layer of higher T_g, which hindered the diffusion of the curing agent into the epoxy resin particle. In the Epon 1001-Versamid 115 system heated to 55° C, this tendency was accentuated, and in the (Epon 1001-Bisphenol A)-Versamid 115 and Epon 1001-(Versamid 115-Dion DPM-3-800-LC) systems, it was observed in the extreme, i. e., these samples showed both low swelling in solvent but high concentrations of extracted polymer. The solvent-cast Epon 1001-Versamid 115 system was cured uniformly because the epoxy resins and curing agent molecules are mixed on a molecular scale.

D. Formulation of Epoxy Primers

Unpigmented films of the Epon 1001-Versamid 115 system prepared with the hexadecyltrimethylammonium bromide-cetyl alcohol combination were cloudy and poorly adherent to glass. The cloudiness and poor adhesion were attributed to the incompatible cetyl alcohol. Films of the same system prepared substituting n-decane for the cetyl alcohol showed better clarity and adhesion.

Aqueous dispersion of zinc chromate were prepared using the hexadecyltrimethylammonium bromide-n-decane combination and mixed with Epon 1001 and Versamid 115 emulsions prepared with the same system. All the mixtures showed signs of flocculation to varying degrees.

Better results were obtained using the (Span 80-Tween 80)-hexadecyltrimethylammonium bromide-n-decane combination for both the zinc chromate dispersions, and Epon 1001 and Versamid 115 emulsions. Also, better results were obtained by substituting Versamid 100 emulsions for the Versamid 115 emulsions.

Despite these improvements, flocculation was still observed to varying degrees when the pigment dispersion was mixed with the epoxy resin emulsion or when the curing agent emulsion was added to this mixture.

E. Preparation of Polyurethane Emulsions

The first part of this work (4) concerned the development of two types of polyurethane emulsions: fully-cured and air-drying. The fully-cured type was prepared by reacting an isocyanate-containing prepolymer (e.g., Desmodur N-100) with a mixture of a hydroxyalkyl methacrylate (e.g., hydroxypropyl methacrylate) and a monohydric alcohol (e.g., n-butanol) using dibutyltin dilaurate catalyst; this adduct was then dissolved in a reactive diluent (e.g., a n-butyl acrylate-isobutyl methacrylate mixture), emulsified in water using the sodium lauryl sulfate-cetyl alcohol mixture, and polymerized using persulfate-ion initiator. The air-drying type was prepared by reacting an isocyanate-containing prepolymer (e.g., Desmodur N-100) with alkyl alcohol, often in combination with a hydroxyalkyl methacrylate (e.g., hydroxypropyl methacrylate), using dibutyltin dilaurate catalyst; this adduct was then mixed with a polyester prepolymer (e.g., Multron R-16 or Paraplex P-44A) and a methyl ketone-cobalt naphthenate catalyst mixture and emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination.

The recommendations for future work included optimization of the reactant proportions for both types of vehicles and their evaluation as vehicles for aircraft topcoats.

The present work concentrated on the optimization of the fully-cured polyurethane system because it required less development than the air-drying type. The film properties can be varied by the type of isocyanate-containing prepolymer, the composition and proportions of the hydroxyalkyl methacrylate-monohydric alcohol mixture, and the composition and proportions of the reactive diluent mixture. The present work varied the proportions of the hydroxypropyl methacrylate-n-butanol and n-butyl acrylate-isobutyl methacrylate mixtures, as well as substituting small amounts of other monomers for the various vinyl monomer components. Improvements in film properties were obtained with these variations.

The emulsification of the fully-cured polyurethane in reactive diluent solution was also improved by the substitution of n-decane for the cetyl alcohol in the mixed emulsifier combination; this gave a slightly smaller average droplet size as well as a decrease in the large particle-size "tail", and therefore a more stable emulsion.

F. Mechanism of the Emulsification Process

The ionic emulsifier-fatty alcohol and ionic emulsifier-n-alkane combinations have been demonstrated to be effective in preparing 0.2-µm size polymer emulsions, but little is known of the mechanism of the emulsification process.

Preliminary experiments were carried out to determine this mechanism by measuring the variation of conductance of emulsifier solutions upon the addition of benzene to form a small-particle-size emulsion. The conductance of this system is a function of the size and size distribution of the emulsion droplets, the dissociation constants and orientation at the oil-water interface of the emulsifier molecules, and the presence or absence of polar or apolar molecules in combination with the emulsifiers. More work is needed to determine the mechanism, but these preliminary experiments on the hexadecyltrimethylammonium bromide-cetyl alcohol and hexadecyltrimethylammonium bromide-n-decane combinations show that their mechanisms of emulsification are different.

SECTION II

INTRODUCTION

A. Statement of the Problem

The problem is to convert the solvent-based epoxy-polyamide primer (1) and aliphatic isocyanate polyurethane topcoat (2) presently used by the Air Force to water-based systems of equivalent performance. The purpose is to reduce or eliminate the potential toxicity and hazards inherent in the storage and use of these solvent-based coatings.

To accomplish this, the hydrophobic prepolymers must be dissolved or dispersed in water by emulsification or emulsion polymerization coatings must be demonstrated to be equivalent to their solvent-based predecessors in ease of application and final film properties.

B. Water-Based Coatings Systems

Water-based polymer vehicles suitable for the formulation of coatings can be divided into three types, according to the state of subdivision of the polymer: 1. polymer dispersions or latexes; 2. polymer solutions; 3. dispersions of water-solubilized polymer.

The polymer dispersions or latexes comprise essentially unswollen microscopic or submicroscopic polymer spheres colloidally dispersed in water; their viscosities are only slightly greater than that of water and are independent of the molecular weight of the polymer. Polymer solutions comprise molecular dispersions of polymer molecules; their viscosities are relatively high and increase strongly with increasing polymer concentration and molecular weight. The state of subdivision of water-solubilized-polymer dispersions lies between that of the latex polymers and the solution polymers, i. e., between the colloidal and molecular sizes; for example, a latex containing carboxyl groups is prepared at low pH and then neutralized to solubilize these groups, to give a dispersion of partially-disintegrated latex particles and solution polymers.

Water-based polymers can also be classified as "water-dispersible" or "water-reducible." The term "water-reducible" is applied to polymer dispersions or solutions which are prepared in organic solvent media, but which can be diluted with water without separation into two phases. The term "water-dispersible" is applied to dispersions and solutions which contain no organic solvent and can be diluted indefinitely with water.

a. Polymer Dispersions or Latexes

Polymer dispersions or latexes comprise colloidally-dispersed microscopic or submicroscopic polymer spheres. These latexes prepared by emulsion polymerization usually have average particle diameters in the range 0.1-0.3μm and contain emulsifier and residual electrolyte (initiator and buffer residues). Upon drying, the dispersions or latexes form continuous films in which the individual polymer spheres coalesce and lose their identity (5-7).

These polymer dispersions or latexes have several advantages in water-based coating formulations: 1. ease of application by a variety of methods to a variety of substrates; 2. a good balance of properties, including insolubilization after drying; 3. availability in a wide range of molecular weights, to take advantage of the better properties that can be obtained with high-molecular-weight polymers. 4. preparation by either emulsion polymerization (vinyl-addition polymers) or emulsification (step-growth or condensation polymers).

The disadvantages of these dispersions or latexes are: 1. their manufacture and formulation is often complicated by their heterogeneous nature and the need for emulsifiers and thickeners; 2. the formation of continuous films at room temperature is limited to polymers of a given shear modulus (calculated to be about 1600 psi for a particle diameter of 0.1μm(8)); 3. post-stabilization is often required to obtain the requisite freeze-thaw, electrolyte, and mechanical stability; 4. high-gloss coatings are difficult to formulate.

Despite their inherent complexities of manufacture and formulation, however, the polymer dispersions or latexes enjoy a very large market, due primarily to extensive industrial research and development efforts in latex paints, paper coatings, textile sizings, foam, and carpet backing.

b. Polymer Solutions

Polymer solutions dry by evaporation of water to form a continuous film of polymer, in a manner analogous to polymer solutions in organic solvents.

These water-based polymer solutions have several advantages in coatings formulations: 1. ease and simplicity of formulation, characteristic of organic solvent-based systems; 2. ability to form continuous films analogous to these formed by organic solvent-based polymer systems; 3. ability to bind pigment particles well; 4. ease of formulation into high-gloss coatings; 5. ease of application by spraying or dipping, using various types of equipment; 6. excellent shelf stability and freeze-thaw resistance.

Their disadvantages are: 1. only a few commercial systems (e.g., acrylic resins) are available; 2. after application, the polymer must somehow be insolubilized; 3. the drying rates are slower than for organic solvent-based polymer solutions and water-based latexes, sometimes by an order of magnitude; 4. heat is often required to accomplish the drying and insolubilization; 5. polymer solutions are restricted to low polymer concentrations and molecular weights because of the strong increase in solution viscosity with both these parameters.

Most commercial coatings formulated using water-based polymer solutions must be baked to obtain high-gloss enamel-like coatings.

c. Water-Solubilized-Polymer Dispersions

Water-solubilized-polymer dispersions have properties intermediate between those of the water-based polymer dispersions or latexes and polymer solutions. Often, they represent a useful compromise which combines some of the advantages of both types.

C. Epoxy Resin Systems

Epoxy resins can be cured by standard anhydride or amine catalysts, but their use is precluded in aqueous systems because of their reaction with water. However, weaker catalysts such as polyamides and first-stage epoxide-polyamide condensates can be used in aqueous systems. Many of these curing agents must be emulsified to be incorporated into aqueous systems, and therefore most of the aqueous epoxy resin systems described in the literature are blends, especially epoxy resin-polyamide blends, rather than the epoxy resins alone. The preparation of these earlier systems has already been reviewed (4) and will not be discussed further here.

Developmental samples of microscopic-size epoxy resin emulsions are offered by several companies, but their curing rates and film properties are generally not equivalent to those of the solvent-based systems.

In the first part of this work (4), the sodium lauryl sulfate-cetyl alcohol mixed emulsifier combination was applied to the preparation of epoxy resin and curing agent emulsions. Epoxy resins such as Epon 1001 and Epon 828 were emulsified to 0.2-μm diameter droplets without difficulty, but Versamid 115 curing agent could not be emulsified because of its cationic nature. Therefore, an analogous hexadecyltrimethylammonium bromide-cetyl alcohol mixed emulsifier combination was developed and applied successfully to the preparation of Versamid 115, Epon 1001, and Epon 828 emulsions. Another curing agent, Genamid 250, was emulsified using both the anionic and cationic mixed emulsifier combinations.

Preliminary evaluations of these epoxy resin and curing agent emulsions established optimum ratios of 2:1 for the Epon 1001-Versamid 115 and Epon 1001-Genamid 250 systems and 1:2 for the Epon 282-Versamid 115 system. Films of the optimum ratios generally displayed properties equivalent to those of solvent-cast films, but cured more slowly, e.g., 30 days at room temperature or several hours at 50° C were required to attain the same properties displayed by the solvent-cast film in 7 days. This difference in curing rates is expected because of the particulate mixture of the emulsion-cast films compared with the molecular mixture of the solvent-cast films. Nevertheless, the epoxy emulsion systems must have competitive curing rates in order to replace the solvent-based epoxy systems.

D. Polyurethane Systems

Polyurethane technology is based upon the reaction of isocyanate groups with groups containing an active hydrogen, e.g., primary amines, primary alcohols, water, secondary and tertiary amines, other urethanes, carboxyl acids, or carboxylic acid amines. Usually, a prepolymer is formed by reaction of difunctional isocyanates with difunctional or polyfunctional compounds containing active hydrogens (e.g., polyols) and cured in situ to give a polymer with the desired properties. Control of the curing reaction is accomplished in several ways (9): 1. by forming a stable isocyanate adduct with a blocking agent, which is later decomposed by heating; 2. by using atmospheric moisture to cure an isocyanate-terminated prepolymer; 3. by using a two-component system (diisocyanate plus polyol) which is mixed together just prior to application.

Aliphatic diisocyanates (e.g., 1, 6-hexamethylene diisocyanate) produce coatings with better resistance to discoloration, hydrolysis, and heat degradation than the aromatic diisocyanates (10, 11). The di- and polyhydroxyl components include hydroxyl-terminated polyesters, castor oil and its transesterification derivatives, transesterified drying oils, polyether diols and polyols, and hydroxyl-terminated hydrocarbon polymers. The properties of the cured polyurethanes may be varied by modification of the structure of the polyhydroxyl component. For example, linear or slightly branched hydroxyl-terminated polyester prepolymers give elastic coatings of high elongation and good low-temperature flexibility, but of relatively poor chemical resistance; more highly branched polyester prepolymers give relatively rigid films (more highly crosslinked) with excellent chemical resistance, good hardness, and low elongation.

These reactive organic solvent-based polyurethane systems have been adapted to water-based systems. Water-based polyurethane dispersions have been developed for textile finishes, binders for non-woven fabrics, finishes for natural and synthetic leather, fabric coatings, beater addition in paper manufacture, exterior primers for wood, and impregnation of leather (12). The various approaches to the preparation of polyurethane dispersions was reviewed earlier (4) and will not be discussed further here.

Water reacts with the isocyanate group to produce carbamic acids and eventually diamines, but this reaction does not prevent the preparation of polyurethane dispersions. The diamines formed react with the isocyanate group to form a polysubstituted urea, and such chain extension is considered desirable in some cases (9). In the reaction of the isocyanate-prepolymer with an alkyl diethanolamine (13), the slow reaction with water gives a further chain extension. Solvent resistance can be improved by using a trifunctional ethanolamine to promote crosslinking.

Reaction of the isocyanate group with water can be hindered or prevented by "blocking" the isocyanate group and then later heating the coating to split off the blocking compound and reform the reactive isocyanate group. The blocking reaction is an equilibrium reaction which is reversed at higher temperature (14). The temperature of dissociation depends upon the chemical nature of the groups adjacent to the urethane linkage, e.g., diaryl urethans are stable up to about 120° C, and n-alkyl urethans up to about 250° C (15). Dissociation of blocked 1, 6-hexamethylene diisocyanate occurs at temperatures of 120-140° C for such blocking agents as m-nitrophenol, p-chlorophenol, hydrogen cyanide, and ethyl malonate (16). Deblocking at lower temperatures can be catalyzed by tertiary amine salts or organic acids (17) and dibutyltin dicarboxylates (18).

Developmental samples of polyurethane emulsions are offered by several companies, but their film properties are generally not equivalent to those of the solvent-based systems.

In the first part of this work (4), a fully-cured polyurethane system was developed. An isocyanate-containing prepolymer, (e.g., Desmodur N-100) was reacted with a mixture of a hydroxyalkyl methacrylate (e.g., hydroxypropyl methacrylate) and a monohydric alcohol (e.g., *n*-butanol) rising dibutyltin diluent (e.g., a *n*-butyl acrylate-isobutyl methacrylate mixture), and the resulting solution was emulsified in water rising the sodium lauryl sulfate-cetyl alcohol combination and polymerized using persulfate-ion initiator. The product was a film-forming polyurethane dispersion of about 0.2μm average diameter, which dried to form a tough, elastic, hazy film.

Preliminary evaluation of these films showed that they comprised two interpenetrating networks, one the isocyanate-containing prepolymer-hydroxyalkyl methacrylate adduct and the other a copolymer of the reactive diluent with the hydroxyalkyl methacrylate. This system has potential for a variety of coating applications as the film properties can be modified by variation of the isocyanate-containing prepolymer, composition and proportion of the hydroxyalkyl methacrylate-monohydric alcohol mixture, and composition of the reactive diluent mixture. Films ranging from soft and elastic to hard and tough can be prepared.

SECTION III

GENERAL APPROACH

EMULSIFICATION USING THE MIXED EMULSIFIER COMBINATION

A. Effect of Emulsion Droplet Size

The preparation of aqueous epoxy resin and polyurethane emulsion systems has been described in the literature, and developmental samples of such emulsions have been offered by several companies. Most of these commercial emulsions, however, do not display film properties equivalent to those of the corresponding solvent-based systems. There are three main reasons for these differences in properties: 1. the large particle size of these emulsions adversely affects their stability, particularly shelf stability; 2. the combination of large particle size and relatively high polymer shear modulus makes for marginal film-formation and poor film properties; 3. it is difficult to develop a practical post-curing aqueous emulsion system comparable to the curing of prepolymer molecules in the solvent-based systems.

The emulsification of an oil in water by mechanical shear gives an average emulsion droplet size of 1 μm in exceptional circumstances and 2-3 μm in more usual cases. These emulsions have broad particle-size distributions so that an emulsion with an average droplet size of 1 μm will contain particles as small as 0.5 μm. In comparison, most commercial latexes sold for coatings applications have average particle diameters in the range 0.1-0.3 μm, about five-fold smaller.

1. Correlation of Particle Size and Shelf Stability

The five-fold difference in particle size between latexes prepared by emulsion polymerization (0.1-0.3 μm) and the smallest droplet sizes that can be prepared by emulsification (1 μm)is a critical one. For example, a monodisperse polystyrene latex of 1 μm diameter will settle out upon standing within 1-3 months, while monodisperse polystyrene latex of 0.2 μm diameter will never settle at all (19). This experimental observation is supported by a comparison of the calculated rate of sedimentation with the criterion for settling.

The rate of sedimentation of spherical particles according to Stoke's law is:

$$\text{rate of sedimentation} = (D^2/18\eta)\,(d_p - d_m)g \qquad (1)$$

where D is the particle diameter, η the viscosity of the medium, d_p and d_m the densities of the particles and the medium, respectively, and g the gravitational constant.

The tendency for colloidal particles to settle upon standing is offset by their Brownian motion and the convection currents arising from small temperature gradients in the sample. The Brownian motion, which results from the unbalanced collisions of solvent molecules with the colloidal particles, is more intensive, the smaller the particle size. The convection currents, of course, depend upon the sample size and storage conditions. One criterion proposed for settling is that a particle sedimentation rate of only 1 mm in 24 hours will be offset by the thermal convection and Brownian motion within the sample (20). Substituting this sedimentation rate of equation 1 gives values for the critical particle size for settling. Figure 1 shows the variation of log critical particle size with log density difference between the particles and the medium as a function of viscosity of the medium.

For polystyrene latex particles dispersed in water, the density difference is (1.05-1.00) or 0.05 gm/cc and the viscosity of the medium is about 1 cps; therefore, the critical particle size for settling is 0.65 µm.

This calculated size of 0.65 µm is consistent with experimental observation (19, 21) that 0.8 µm diameter monodisperse polystyrene latex particles settle out within 3-6 months while particles of 0.5 µm diameter or smaller never settle out at all.

Since most of the prepolymers to be emulsified have densities in the range 1.10-1.15 gm/cc, their critical particle sizes for settling are 0.3 µm or smaller. Therefore, it is critical whether the emulsification produces droplets of 1 µm or 0.2 µm diameter.

Some polymers and prepolymers must be diluted with solvents to lower their viscosity sufficiently for emulsification. These solvents are usually stripped from the emulsion after preparation, thus reducing the size of the emulsion droplets. Table I shows the reduction in size of 1 µm diameter polymer emulsion droplets upon removal of the solvent as a function of polymer-solvent ratio.

TABLE I

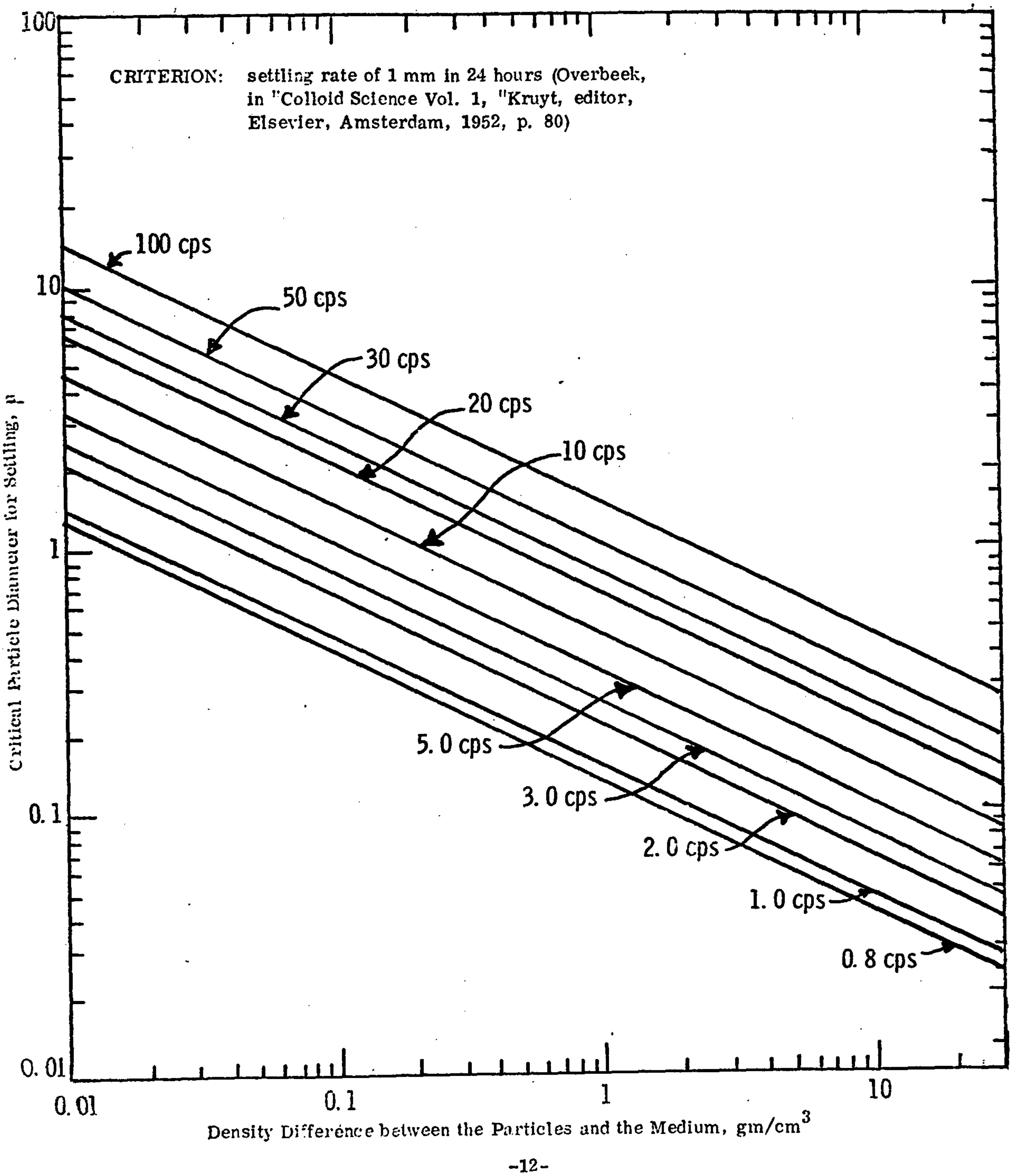
Calculated Decrease in Droplet Size upon Removal of Solvent*

Polymer-Solvent Ratio	Diameter, µm
100:0	1.00
80:20	0.93
60:40	0.84
40:60	0.74
20:80	0.58
10:90	0.46

* assuming equal densities for the polymer and solvent

These calculated values show that there is a substantial reduction in the size of 1 µm polymer emulsion droplets upon solvent-stripping, the reduction being greater, the lower the concentration of polymer; however, the polymer concentration must be impractically low to reduce a 1-µm size droplet to a size smaller than the critical size of about 0.3 µm.

Figure 1: Variation of the Critical Particle Diameter for Settling with Density Difference Between the Particles and the Medium as a Function of Viscosity of the Medium



2. Correlation of Particle Size and Film Formation

The forces exerted on the emulsion or latex particles during drying are those arising from the water-air and polymer-water interfacial tensions (5–7); however, it is the water-air interfacial tension that brings the particles into close contact and initiates the coalescence (5). The maximum shear modulus of a polymer particle that can coalesce upon drying from aqueous dispersion is calculated to be about 1600 psi for a particle diameter of 0.1 μm at 30 dynes/cm surface tension (8). This maximum shear modulus, however, decreases inversely with increasing particle size, i.e., the maximum shear modulus for coalescence for particle diameters of 1 μm and 10 μm are 160 psi and 16 psi, respectively. Thus, the larger the particle size of the dispersion, the softer the polymer must be in order for the particles to coalesce upon drying. If the shear modulus of the polymer is too high for the emulsion particle size, the coalescence will be incomplete and the film properties will be diminished. Thus, it is difficult to prepare epoxy or polyurethane emulsion systems of 2-3 μm diameter that will dry to form hard enamel-like films.

3. Curing of Epoxy and Polyurethane Systems

Many of the good properties of the solvent-based epoxy resin and polyurethane systems can be attributed to the *in situ* curing of the resin prepolymers after application. The prepolymers dissolved in organic solvents are applied to the substrate and, upon evaporation of the solvent, cure to form a three-dimensional polymer network that extends throughout the film and is in intimate contact with the substrate.

In the emulsion systems, the use of solvents is precluded, not because the solvents would not aid in the film formation, but because the principal reason for using aqueous emulsion systems is to avoid solvent emission during drying and curing. The fact that solvents are precluded means that the polymer or prepolymer emulsion particles must conform to the foregoing restrictions without the plasticizing effect of solvents. Thus, the emulsion particles have a higher modulus than the prepolymer solution. Moreover, since the emulsions form a colloidal mixture of the reactive components as compared with the molecular mixture formed by the solvent-based systems, their curing reactions are inevitably slower because of the smaller interfacial area of contact. Of course, the smaller the droplet size of the emulsion, the larger the interfacial area of contact and, hence, the faster the curing rate and the more homogeneous the film.

Thus, the emulsion systems must depend less upon *in situ* curing than the solvent-based systems and therefore the emulsion droplets must have a higher modulus or a greater degree of cure before application.

B. Principles of Emulsification

The emulsifier selected for the preparation of oil-in-water emulsions (22): (i) must reduce the interfacial tension to 5 dynes/cm or less; (ii) must adsorb quickly on the droplet surface and not be displaced when two droplets collide, thus preventing coalescence; (iii) must have a specific molecular structure, with the polar end of the molecule oriented toward the water phase and the non-polar end toward the oil phase; (iv) must be more soluble in the water phase so as to be readily available for adsorption on the oil droplet surfaces; (v) must impart a sufficient electrokinetic potential to the emulsion droplets; (vi) must influence the viscosity of the emulsion; (vii) must work in small concentrations; (viii) should be relatively inexpensive; (ix) should be non-toxic and safe to handle. A wide variety of commercial emulsifiers fulfill these requirements.

In recent years, much work has been done on the quantitative correlation of the parameters of the emulsification process with the emulsion droplet size produced (23). For emulsions prepared by simple stirring, the droplet size usually decreases with increasing speed and diameter of the stirrer and decreasing diameter of the emulsification vessel (because these variations increase the intensity of agitation). The droplet size also decreases with increasing difference in density between the oil and water phase (because of the different velocities imparted to the fluids) and with decreasing oil-water interfacial tension.

Apart from these factors, the viscosities of the oil and water phases play only minor roles. The temperature has only an indirect effect and that only because of the variation of viscosity, emulsifier adsorption, and interfacial tension with temperature.

C. Emulsification Using the Mixed Emulsifier Combination

This problem requires the preparation of aqueous epoxy resin and polyurethane emulsions of much smaller droplet size than have been prepared before. Generally, it has not been possible to prepare such emulsions with average droplet sizes smaller than about 1 µm using practical concentrations of emulsifier. However, it was shown (3) that anionic emulsions of styrene in water with droplet sizes as small as 0.2 µm can be prepared using the sodium lauryl sulfate-cetyl alcohol mixed emulsifier combination. The first part of this work (4) showed that this mixed emulsifier combination can be used to prepare epoxy resin emulsions of 0.2 µm average diameter and that analogous cationic emulsions with similar droplet sizes can be prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination. In both cases, the total concentration of the mixed emulsifier combination is 1-2% or less.

These mixed emulsifier combinations meet the foregoing criteria for efficient oil-in-water emulsification as shown by their success in producing these very small emulsion droplet sizes.

SECTION IV

PREPARATION AND EVALUATION OF EPOXY EMULSION SYSTEMS

A. Introduction

1. Present System

The epoxy resin primer presently used by the Air Force is a two-component solvent-based system: (i) Component I is a high-molecular weight epoxy resin prepolymer dissolved in solvents and containing dispersed pigments; (ii) Component II is a polyamide curing agent prepolymer dissolved in solvents.

Component I is comprised of a 22.8:37.8:39.4 epoxy resin prepolymer-pigment-solvent mixture. The epoxy resin prepolymer is deduced to be Epon 1001 (Shell Chemical Company) from the required epoxide equivalent (the weight of resin in gm that contains one gram-equivalent of epoxide groups) of 450-550 (1). The solvent mixture is reported (1) to be a 46.7:53.3 toluene-methyl isobutyl ketone mixture. The total non-volatile content (prepolymer plus pigment) is 60-62% (1).

Component II is comprised of an 18.7% solution of polyamide curing agent prepolymer in a 9.9:25.2:25.2:39:7 xylene-n-butanol-isopropanol-toluene mixture (1). The polyamide curing agent prepolymer is deduced to be Versamid 115 (General Mills Chemical Company, Inc.) from the required amine value (the weight of potassium hydroxide in mg that is equivalent to the amine content of one gram of sample) of 230-246 and viscosity of 31-38 poise at 75° C (1).

Equal volumes of Components I and II are mixed and, if necessary, diluted with a 50:50 toluene-methyl isobutyl ketone solvent mixture (up to 0.88 parts solvent/part mixture) to facilitate application by spraying. After application, the two prepolymers are brought into intimate contact by evaporation of the solvents, and the polyamide curing agent prepolymer catalyzes the crosslinking reaction of the epoxy resin prepolymer to form a three-dimensional high-molecular-weight network. The drying time is 30 minutes for the "set-to-touch" and 7 hours for the "dry-hard" conditions.

2. Preparation of Epoxy Emulsion Systems - General Approach

The purpose of this work was to develop a water-based analog of the epoxy resin-curing agent system presently used by the Air Force. The general approach was to prepare separate emulsions of two components, mix these emulsions in the appropriate proportions, and cast a film from the mixed emulsion. Upon drying, the emulsion droplets of epoxy resin and curing agent coalesce to form a continuous film of randomly-mixed deformed spheres. The curing reaction begins at the epoxy resin-curing agent interface and proceeds by the mutual interdiffusion of polymer chain ends across this interface (the "autohesion" process postulated by Voyutskii (22) to form a three-dimensional polymer network. Thus, the emulsion system forms a colloidal mixture of the two components of dimensions equal to the size of the emulsion droplets, in contrast to the molecular mixture formed by the solvent-based system.

The initial rate of curing should be slower for the emulsion system than for the solvent-based system because the area of contact between the two phases is orders of magnitude smaller for the emulsion system. Moreover, as the curing proceeds to completion, the rate should at all times be slower for the emulsion system (4).

These separate emulsions must remain stable indefinitely upon standing, yet upon mixing and drying cure to form a three-dimensional polymer network. In principal, a mixed emulsion comprised of stable, discrete droplets of epoxy resin and curing agent could be stored indefinitely without pre-curing provided that: (i) all of the reactive components of the epoxy resin and the curing agent are completely insoluble in water; (ii) no flocculation and coalescence of the droplets occurs upon standing. However, any components of the curing agent leached from the droplets would soon diffuse through the aqueous phase to the epoxy resin droplets and initiate the curing reaction. Moreover, any collisions leading to flocculation and coalescence of unlike droplets would also initiate the curing reaction. Nevertheless, a practical one-package epoxy emulsion system could be developed if these requirements were met.

The experimental approach to prepare stable emulsions of the epoxy resin and curing agent prepolymers was based on the earlier development of the mixed emulsifier system (3) which gives styrene emulsion droplets of about 0.2 μm diameter, about 5 times smaller than the smallest oil-in-water droplets prepared in the usual manner. The application of this mixed emulsifier system to the emulsification of the epoxy resin and curing agent prepolymers gave emulsions of droplet size sufficiently small to remain stable indefinitely without settling.

The first part of this work (4) demonstrated that anionic and cationic solvent-free emulsion of epoxy resins and curing agents with average droplet sizes of 0.2 μm or smaller can be prepared using mixed ionic emulsifier-fatty alcohol combinations. Furthermore, mixtures of these emulsions can be cured at room temperature to give films of satisfactory properties, but 30 days were required to give properties obtained by heating the emulsion films for a few hours at 50° C or by curing the solvent-based films for about one week at room temperature. This slower curing rate of the emulsion films is expected because the curing of the mixed emulsions is initiated at the interfaces between coalesced droplets of epoxy resin and curing agent, while with the solvent-based system, the curing is initiated at molecular interfaces.

In the present work, two approaches were used to modify the epoxy resin-curing agent system to obtain faster curing rates: 1. add some compound to the epoxy resin or curing agent emulsion that would accelerate the epoxy-amine reaction when the two emulsions are mixed; 2. use a partially-cured epoxy resin emulsion, to decrease the extent of cure required after drying.

For the first approach, a mercaptan-terminated liquid polymer of high viscosity (15,000 cps), was used in combination with the polyamide curing agent. This polymercaptan is reported to cure epoxy systems rapidly in combination with selected amines.

One example of the second approach, was the addition of phenolic hydroxyl compounds to the epoxy resin to accelerate the epoxy-amine reaction during curing. It has been reported that traces of bisphenol A (4, 4'-isopropylidene diphenyl) or resorcinol (m-dihydroxybenzene) form hydrogen bonds between the epoxy and the phenolic hydroxyl groups, thus assisting in the opening of the epoxy ring structure in the presence of amine curing agents. Consequently, the phenolic hydroxy compounds do not become an integral part of the epoxy-amine network formed by curing and their presence does not affect the final properties of the cured epoxy resin.

Another example of the second approach was the pre-curing of the epoxy resin in the emulsion state by adding part of the curing agent before or during emulsification; the partially-cured emulsion was mixed with the rest of the curing agent (emulsion) before application as a film.

B. Experimental Results and Discussion

1. Experimental Details

Two epoxy resin prepolymers were used in the emulsification experiments:

1. Epon 828 (Shell Chemical Company) - a pourable liquid at room temperature (110-150 poise viscosity at 25° C) with an epoxide equivalent of 185-192.
2. Epon 1001 (Shell Chemical Company) - a solid resin at room temperature (but which softens at slightly higher temperatures) with an epoxide equivalent of 450-550.

Two curing agent prepolymers were also used in the emulsification experiments;

1. Versamid 115 (General Mills Chemical Company, Inc.) - a high-viscosity (31-38 poise Brookfield at 75° C) condensation product of a polyamine and a dibasic acid with an amine value of 230-246.

2. Versamid 100 (General Mills Chemical Company, Inc.) - a condensation product of a polyamine and a dibasic acid with an amine value of 90.

All ingredients were used as received without further purification (except as described later).

The emulsification technique was essentially the same as that used ealier for the preparation of styrene monomer emulsions (3). Typically, about 1 gm of this ionic emulsifier-fatty alcohol combination were dissolved in 75.0 gm deionized water by heating for 30 minutes at 63° C in a stirred 300-ml glass flask. Then the prepolymer or prepolymer solution was added, and the mixture was stirred under the same conditions to form a crude emulsion. Since the prepolymer or prepolymer solutions are much more viscous than styrene monomer, this emulsification by simple stirring produces microscopic-size droplets rather than the submicroscopic-size droplets produced in the styrene emulsifications. Therefore, the crude emulsions were subjected to ultrasonic irradiation (Model W-350 Sonifier Cell-Disruptor) or homogenization (Manton-Gaulin Model 15M-8TA Laboratory Homogenizer and Submicron Disperser) to reduce the microscopic-size droplets to the submicroscopic-size range

Other experimental details are given in the following sections.

2. Epoxy Resin Emulsions

The first part of this work (4) demonstrated that stable cationic solvent-free emulsions of Epon 1001, Epon 828, and Versamid 115 with average droplet sizes of 0.2 µm or smaller could be prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination. Furthermore, mixtures of the Epon 1001 and Versamid 115 emulsions could be cured at room temperature to give films of satisfactory properties, but 30 days were required to give properties obtained by heating the emulsion films for a few hours at 50°C or by curing the corresponding solvent-based films for about one week at room temperature. This slower curing rate of the emulsion films is expected because the curing of the mixed emulsions is initiated at the interfaces between coalesced droplets of epoxy resin and curing agent, while with the solvent-based system, the curing is initiated at molecular interfaces.

Two approaches were used to modify the Epon 1001-Versamid 115 system to obtain faster curing rates: 1. compounds were added to the epoxy resin or curing agent emulsion that would accelerate the epoxy-amine reaction when the two emulsions were mixed; 2. the epoxy resin emulsion was partially cured to decrease the extent of cure required after drying.

One example of the second is to add phenolic hydroxyl compounds to the epoxy resin to accelerate the epoxy-amine reaction during curing. It was reported (25) that traces of bisphenol A (4,4'-isopropylidene diphenyl) or resorcinol (m-dihydroxybenzene) form hydrogen bonds between the epoxy and the phenolic hydroxyl groups, thus assisting in the opening of the epoxy ring structure in the presence of amine curing agents. Consequently, the phenolic hydroxyl compound does not become an integral part of the epoxy-amine network formed by curing; however, it was also demonstrated that traces of bisphenol A or resorcinol do not affect the final properties of the cured epoxy resin.

The proportion of bisphenol A or resorcinol must be selected with care, however, because an excess of hydroxyl groups causes polymerization of the epoxy resin through epoxy-epoxy linkages and thus increases the epoxy equivalent weight (the weight of resin in grams that contains one gram-equivalent of unreacted epoxy).

The procedure used was to dissolve the mixture of bisphenol A (4% based on epoxy resin) and epoxy resin in the solvent mixture, emulsify the solution, and remove the solvent. Thus, 100 gm of a 50:2:25:25 Epon 828-bisphenol A-toluene-methyl isobutyl ketone mixture was emulsified in 100 gm water using 1.4-2.8 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give a stable emulsion. Other emulsifications were carried out, in which varying amounts of bisphenol A and resorcinol were used to pre-catalyze Epon 828 and 1001. For example, 100 gm of 25:37.5:37.5:1 Epon 1001-toluene-methyl isobutyl ketone-resorcinol mixture was emulsified in 100 gm of water using 0.7-1.4 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give a stable emulsion. Similar emulsions were prepared substituting bisphenol A for the resorcinol and Epon 828 for the Epon 1001 (with resorcinol). These were subjected to vacuum steam distillation to remove the solvent and to increase the total solids content to about 25%, and were evaluated in comparison with the corresponding emulsions prepared without resorcinol or bisphenol A.

3. Curing Agent Emulsions

For the first approach, Dion Polymercaptan DPM-3-LC (Diamond Shamrock Chemical Co.), a mercaptan-terminated liquid polymer of high viscosity (15,000 cps), was used in combination with the Versamid 115. This polymercaptan was reported to cure epoxy systems rapidly in combination with selected amines.

Thus, 25 gm of 25:12.5:7:17.5:17.5:28 Versamid 115-Dion DPM (3-800-LC)-xylene-n-butanol-isopropanol-toluene mixture was emulsified in 75 gm of water using 0.4-0.8 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give a stable emulsion. Other emulsifications were carried out using different proportions of Versamid 115 and Dion DPM-3-800-LC as well as other fast curing agents. For example, 25 gm of a 15:15:7:17.5:17.5:28 Versamid 115-Dion DPM-(3-800LC)-xylene-n-butanol-isopropanol-toluene mixture was emulsified in 75 gm of water using 0.2-0.4 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give a stable emulsion. The emulsions were subjected to vacuum steam distillation to remove the solvent without complication and were evaluated in comparison with the corresponding emulsions prepared without the Dion DPM-3-800LC.

4. The Hexadecyltrimethylammoinum Bromide-n-Decane Combination

Recently Ugelstad et. al. (26) described the preparation of styrene monomer emulsions using the sodium lauryl sulfate-hexadecane combination in place of the sodium lauryl sulfate-cetyl alcohol combination; the emulsions obtained with hexadecane were even more stable than those prepared with cetyl alcohol.

This finding was applied to the emulsification of polymer solutions, by trying a series of n-alkane hydrocarbons in place of the cetyl alcohol. Preliminary experiments substituting n-decane for cetyl alcohol gave more stable emulsions; these emulsions did not contain the usual large particle-size "tail" found in the corresponding emulsions prepared with cetyl alcohol. These new results should give important advantages in formulation stability and shelf stability.

The first experiment was carried out by eliminating cetyl alcohol from one of the earlier recipes and adding 1% n-decane to the polymer solution prior to the emulsification process. Thus, 125 gm of 25:37.5:37.5:1.25 Epon 1001-toluene-methyl isobutyl ketone-n-decane mixture was emulsified in 375 gm water using 2.5 gm of hexadecyltrimethylammonium bromide and the Manton-Gaulin Submicron Disperser, to give a stable emulsion. In a second experiment, the emulsification of Epon 1001 solution with higher solids content (40%) was carried out using half of the emulsifier used in the above experiment (based on polymer). Thus, 125 gm of 40:30:30:1.25 Epon 1001-toluene-methyl isobutyl ketone-n-decane mixture was emulsified in 375 gm of water using 2 gm of hexadecyltrimethylammonium bromide and the Manton-Gaulin Submicron Disperser to give a stable emulsion. The emulsion was then subjected to vacuum steam distillation to remove the solvent and the transmission electron microscope and the cold stage (4). Figure 2 shows that the particle size of this Epon 1001 emulsion prepared using n-decane is comparable with those prepared with cetyl alcohol, with all particles of 0.4 μm diameter or smaller. However, the properties of the films cast from this emulsion were superior to those prepared with cetyl alcohol (see Section VI).

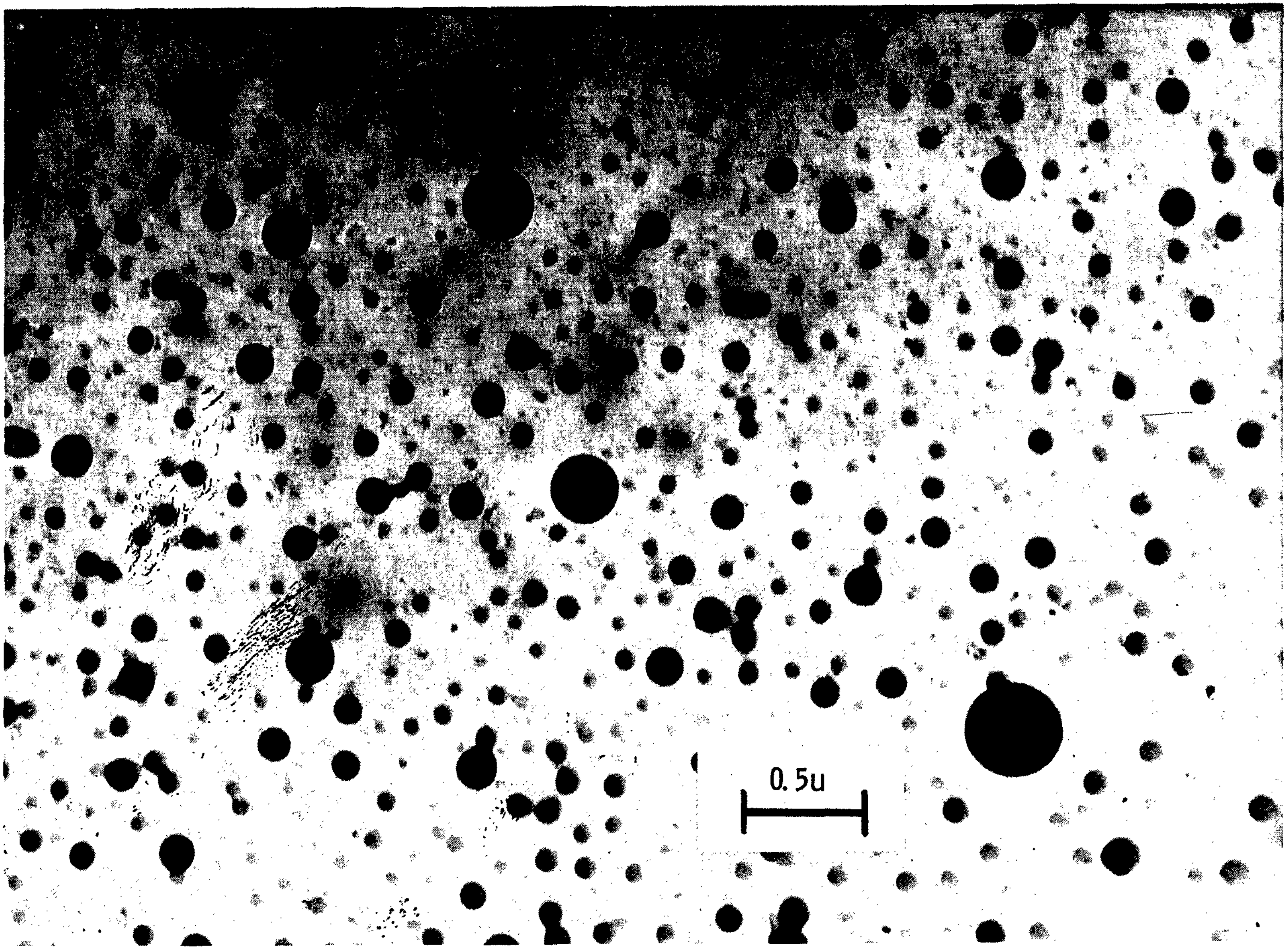


Figure 2. Transmission electron micrograph of diluted dispersion of Epon 1001 emulsion prepared with the hexadecyltrimethylammonium bromide-*n*-decane combination.

The above emulsification recipe was repeated using 4% resorcinol based on the weight of the Epon resin to also give a stable emulsion.

In all these cases, the increase of the solids content of the emulsion to about 40% did not affect the stability of the emulsion, but increased the viscosity of the emulsion so that films could be cast more easily.

Versamid 100 curing agent was also emulsified, to replace Versamid 115 in the Epon 1001-Versamid 115 system; the purpose was to maintain more flexibility in the film during curing, which might insure better internal curing of the Epon 1001 particles. Versamid 100 with an amine value of 90 compared to 240 for Versamid 115 would have to be used in larger quantities to cure the same quantity of Epon 1001. Since both curing agents are liquids at room temperature, the greater amount of Versamid 100 should give a film of lower viscosity upon drying, which should favor more intimate contact between the particles of Epon 1001 and curing agent. Thus, 100 gm of 40:30:30:1 Versamid 100-toluene-methyl isobutyl ketone-n-decane mixture was emulsified in 300 gm of water using 1.6 gm hexadecyltrimethylammonium bromide and the Manton-Gaulin Submicron Disperser. The resulting emulsion was stable, even after removal of the solvents and concentration to 41% solids. Moreover, it was opaque and not translucent as were the Versamid 115 emulsions, indicating that they comprised emulsified rather than solubilized polymer.

The reduction of the amount of the hexadecyltrimethylammonium bromide used in the emulsification gave some flocculation upon mixing with the Epon 1001 emulsion prior to film-casting. This problem was corrected by post-stabilizing the two emulsions with nonionic emulsifier before mixing (see Section IV. B. 7).

In the first part of this work (4), the only emulsifier that would emulsify Versamid 115 satisfactorily was the hexadecyltrimethyl bromide-cetyl alcohol combination. Even so, the stability of these emulsions was sometimes insufficient. Therefore, attempts were made to develop other emulsifying agents that would work in this application. These attempts comprised the determination of the optimum HLB (hydrophile-lipophile balance) required to emulsify this curing agent. The emulsifiers used were the Triton series (Rohm & Haas Co.) and the Span-Tween series (I. C. I. America). The Triton series comprised octylphenol-polyoxyethylene adducts of varying polyoxyethylene chain length. The Span series comprised partial esters of fatty acids and sorbitol; the Tween series comprised polyoxyethylene adducts of the Span series, to give higher HLB's than the corresponding Span's. In each series, emulsifiers with widely different HLB's were mixed to form an intermediate HLB, and the efficiency of the mixture was tested in emulsification.

Also tried were cationic emulsifiers, e.g., the Primonix series (Rohm & Haas Company) which comprised long-chain aliphatic amine-polyoxyethylene addic adducts. Other cationic emulsifiers tried included several mopholinium sulfates and phosphoric acid-polyoxyethylene adducts. None of these cationic emulsifiers was found to be as effective as the hexadecyltrimethylammonium bromide in emulsifying a 40:30:30 Versamid 115-toluene-methyl isobutyl ketone solution; thus, these attempts were discontinued (however, these cationic emulsifiers may be more successful in emulsifying Versamid 100, which is not as water-soluble as Versamid 115).

Emulsions for pigmentation studies were prepared using the Span 80-Tween 80 (HLB 12) mixture. Thus, 200 gm of a 40:30:30:2 Epon 1001-toluene-methyl isobutyl ketone-n-decane or Versamid 115-toluene-methyl isobutyl ketone-n-decane mixture were emulsified in 600 gm water using 4.8 gm of hexadecyltrimethylammonium bromide and 1.6 gm of the Span 80-Tween 80 (HLB 12) combination. The emulsifiers were added to the water in a 1-liter flask and heated to 60° C; the polymer solution was then added with stirring over a 30-minute period and stirred for an additional 30 minutes to form the crude emulsion. The crude emulsions were then subjected to ultrasonic irradiation and homogenization in the Manton-Gaulin Submicron Disperser at 6000 psi. The homogenized emulsions were subjected to vacuum-steam distillation at 40° C in the Buchler Flash-Evaporator, using a drop of Nopco 1719-B Anti-Foam when foaming was observed. The concentration was stopped when the Epon 1001 emulsions reached 35-40% solids and the Versamid 115 emulsions, 11% solids (because of their high viscosity).

5. Pre-Curing of the Epoxy Resin Emulsion

The other approach used for the preparation of the partially-cured epoxy resin emulsions is to mix a portion of the stoichiometric amount of the curing agent with the epoxy resin solution. The mixture is then emulsified and the solvents removed as usual. The balance of the curing agent is added as an emulsion to the partially-cured emulsion prior to film casting.

A preliminary experiment was carried out to investigate the possibility of emulsifying an Epon 1001-Versamid 115-solvent mixture. Thus, 100 gm of 20:20:30:30:1 Epon 1001-Versamid 115-toluene-methyl isobutyl ketone-n-decane mixture was emulsified in 300 gm water using 1.6 gm hexadecyltrimethylammonium bromide and the Manton Gaulin Submicron Disperser. The solvents were removed from the emulsion by vacuum steam distillation, to give a stable emulsion.

The foregoing emulsion contained twice the stoichiometric amount of the Versamid 115 required for curing the epoxide groups in the Epon 1001. Other emulsifications were carried out using smaller proportions of Versamid 100 or Versamid 115 relative to the Epon 1001. Thus, 200 gm of 8:32:30:30:1 Versamid 115 (or Versamid 100)-Epon 1001-toluene-methyl isobutyl ketone-n-decane mixture was emulsified using 3.2 gm of hexadecyltrimethylammonium bromide and the Manton Gaulin Submicron Disperser. In both cases, the emulsions were stable and were subjected to vacuum steam distillation to remove the solvents and increase the solid contents to about 40%.

Other partially-cured Epon 1001 emulsions with various degrees of pre-curing was prepared. Thus, 200 gm of 30:10:30:30:1 Epon 1001-Versamid 100-toluene-methyl isobutyl ketone-n-decane mixture was emulsified in 300 gm water using 1.6 gm hexadecyltrimethylammonium bromide and the Manton-Gaulin Submicron Disperser. The resulting emulsion (C-12) which comprised a 3:1 Epon 1001-Versamid 100 ratio was subjected to vacuum steam distillation to remove the solvents and increase the total solids content to about 40%. Other emulsifications were carried out to prepare Epon 1001 emulsions with various degrees of pre-curing, e.g., with 8:1 (C-13) and 10:1 (C-14) Epon 1001-Versamid 115 ratios.

Emulsions C-11 to C-14 were prepared by using 4% hexadecyltrimethylammonium bromide (based on polymer) in the presence of n-decane. Another emulsion (C-17) comprising an 8:1 Epon 1001-Versamid 115 ratio was prepared using 6% hexadecyltrimethylammonium bromide in the presence of n-decane.

Films were cast from mixtures of these partially-cured epoxy emulsions and the appropriate amounts of the curing agent emulsions, dried, and evaluated, (see Section C).

6. Addition of Phenyl Glydicyl Ether Reactive Diluent

Phenyl glycidyl ether was used as a reactive diluent in the curing of the mixed Epon 1001-Versamid 115 emulsions. The phenyl glycidyl ether would decrease the viscosity of the Epon 1001 during curing and would become an integral part of the crosslinked polymer network. Thus, 1 gm of n-decane was added to 50 gm of phenyl glycidyl ether, and the solution was emulsified in 71 gm water using 5 gm of the Span 80-Tween 80 (HLB 14) emulsifier mixture and ultrasonic irradiation.

Films cast immediately after mixing of the Epon 1001-Versamid 115-phenyl glycidyl ether emulsion mixture were cloudy, tacky, and heterogeneous; however, if the emulsion mixture was allowed to stand for 20 hours at room temperature before film-casting, the films were non-tacky and less cloudy. The pre-curing that occurred in the emulsion state apparetnly increased the compatibility of the three components, to give a more homogeneous film.

Another approach tried was to pre-react the phenyl glycidyl ether with the Versamid 115 in solution, emulsify the adduct, and use this emulsion to cure the Epon 1001 emulsions. In this case, the phenyl glycidyl ether would increase the "aromaticity" of the Versamid 115 and thus increase its compatibility with the Epon 1001. Thus, 15.28 gm of phenyl glycidyl ether and 3.0 gm of n-decane were added to 133 gm of a 40:30:30 Versamid-toluene-methyl isobutyl ketone solution, and the mixture was heated for 90 minutes at 60° C. Complete reaction of the phenyl glycidyl ether and Versamid 115 would increase the equivalent weight of Versamid 115 from 236 to 623 (which is the equivalent weight of Versamid 100). This phenyl glycidyl ether-Versamid 115 adduct (102 gm containing 2% n-decane) was emulsified in 300 gm water using 3.2 gm of hexadecyltrimethylammonium bromide and 1.05 gm of the Span 80-Tween 80 (HLB 12) mixture and the Manton-Gaulin Submicron Disperser. The emulsion was subjected to vacuum-steam distillation to remove the solvents and increase the solids content to 40%. The resulting stable emulsion dried to a hard, glossy film.

7. Evaluation of Epoxy Resin-Curing Agent Films

It was suggested that the emulsification of the epoxy resin and the storage of the emulsions might change the epoxy value of the resin by hydrolysis of the epoxide groups to hydroxyls. Consequently, the number of epoxide groups in an Epon 1001 emulsion which was prepared a year ago was determined by titration with hydrobromic acid in glacial acetic acid according to the ASTM method D 1652-73. The results of two titrations gave an average epoxy value of 551 compared with 500 for the unemulsified Epon 1001. The manufacturer's specification for the epoxy value of solid Epon 1001 is 450-550. These results indicate that the emulsification of Epon 1001 and the storage of the emulsion results in a negligible degree of hydrolysis of epoxide groups to hydroxyls and, for all practical purposes, the emulsion can be considered as chemically stable.

Experiments were carried out to evaluate the various epoxy resin and curing agent emulsions and also to improve the film evaluation process by development of improved methods for determining the solids contents of the emulsions and for thickening them before casting into films.

For the evaluation of emulsions prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination, an emulsion of Versamid 115 was mixed in stoichiometric proportions with various Epon 1001 and Epon 828 emulsions, cast into films on glass substrates, and dried at room temperature. With the Epon 1001, 96:4 Epon 1001-bisphenol A, Epon 828, and 96:4 Epon 828-bisphenol A emulsion systems, all films were hazy and flat (i. e., showed no gloss), and showed poor adhesion to the substrate. Moreover, the solids contents of the emulsions were too low for easy preparation of the films.

To determine if the cetyl alcohol or hexadecyltrimethylammonium bromide components of the emulsifier system were responsible for the poor adhesion, these components were added separately to the corresponding solvent-cast epoxy resin-curing agent films. Standard solutions were prepared: (i) 75% Epon 1001 in toluene; (ii) 85% Epon 828 in toluene (iii) 70% Versamid 115 in xylene. These were combined in the stoichiometric proportions 2.12:1 Epon 1001-Versamid 115 and 0.81:1 Epon 828-Versamid 115. These mixtures cast on glass formed hard, clear, tough films with good adhesion. However, it was necessary to allow the Epon 828-Versamid 115 mixture to react in solution for four hours before the films were cast.

To determine the effect of cetyl alcohol and hexadecyltrimethylammonium bromide on the film properties, 12% (based on polymer) of a 1:2 hexadecyltrimethylammonium bromide-cetyl alcohol mixture was added to the Epon 1001-Versamid 115 solution and the mixture was cast into a film. The cetyl alcohol was soluble in this mixture, but ultrasonic irradiation was required to disperse the hexadecyltrimethylammonium bromide. The mixture dried to form a clear, hard film that showed poor adhesion to the glass substrate. Therefore, it was concluded that the cetyl alcohol has a deleterious effect on the film properties and should be replaced.

Since n-decane was a satisfactory substitute for the cetyl alcohol, the emulsions of Epon 1001, Epon 828, and Versamid 115 prepared with this system were evaluated. In addition, emulsions of Versamid 100 were also prepared and evaluated, to determine if the lower-viscosity film would enhance the curing rate (the stoichiometric proportions are 0.80:1 Epon 1001-Versamid 100 as compared with 2.12:1 Epon 1001-Versamid 115). Mixtures of these emulsions prepared with n-decane gave hard, clear films that showed good adhesion to the glass substrates. Moreover, the n-decane system allowed preparation of Epon 1001 emulsions of 42.8% concentration in comparison with the 22.8% concentration with the cetyl alcohol system, which made for easier film-casting after mixing with the translucent, barely-pourable Versamid 115 emulsion of 11.8% solids concentration.

The emulsions prepared using lower concentrations of the hexadecyltrimethylammonium bromide-n-decane system showed some signs of flocculation when emulsions were mixed.

Since these emulsifier proportions were advantageous for emulsion preparation, various post-stabilizers were added to the emulsions before mixing to prevent this flocculation. To determine the appropriate HLB (hydrophile-lipophile balance) value for the Epon 1001 emulsions, mixtures of Triton X-35 (HLB 7.8) and Triton X-405 (HLB 17.9) were used to emulsify a 65% solution of Epon 1001 in toluene. The preliminary results indicated that an HLB vlaue of 14 was optimum. Similar experiments carried out with a 40% Epon 1001 solution in 50:50 toluene-methyl isobutyl ketone mixture gave the same results. Therefore, this Triton X-35-Triton X-405 emulsifier mixture was used as a post-stabilizer.

The films cast a room temperature from mixtures of 0.81:1 Epon 1001-Versamid 100 emulsions were compared with films prepared from 2.12:1 Epon 1001 and Versamid 115 emulsions. Both types of films were clear upon drying, but after ageing the films cured with Versamid 100 were more flexible and showed poorer adhesion to the glass substrate compared to the films cured with Versamid 115. This difference in properties is due to the smaller proportion of reacted epoxide groups in the film cured with Versamid 100 compared with the films cured with Versamid 115. However, since flexibility is imparted to the film by Versamid 100, a mixture of Versamid 115 and Versamid 100 may represent a good compromise.

Partially-cured Epon 1001 emulsions were mixed with the stoichiometric amounts to attain Versamid 115 or Versamid 100 emulsions. Films were cast from these mixtures on glass substrates, dried at room temperature and evaluated. An opaque film was obtained when the partially-cured Epon 1001 emulsion (4:1 Epon 1001-Versamid 115 ratio) was mixed with the remainder of the Versamid 115 emulsion and dried. However, when Versamid 100 emulsions were used with the same partially-cured Epon 1001 emulsion, a transparent film was obtained upon drying. These results crosslinked to the extent that they maintained their identity (did not coalesce) upon curing with the Versamid 115 emulsion. The corresponding experiments with Versamid 100 (which has a smaller amine value than Versamid 115) used a larger quantity, which apparently filled the interstices between the crosslinked particles and improved clarity of the dried films.

Partially-cured Epon 1001 emulsions with a smaller degree of crosslinking gave transparent films upon drying. Thus, partially-cured Epon emulsions prepared from 8:1 and 10:1 Epon 1001-Versamid 115 ratios gave transparent films when post-cured with the appropriate amount of either Versamid 115 or Versamid 100 emulsion. Also, partially-cured epoxy emulsions prepared from 3:1 Epon 1001-Versamid 100 ratios gave transparent films upon curing with the appropriate amount of either Versamid 115 or Versamid 100 emulsion.

Some flocculation was observed upon mixing the partially-cured Epon 1001 emulsions with the curing agent emulsions. The emulsifier content in these systems were 4% hexadecyltrimethylammonium bromide based on polymer. The degree of flocculation was decreased when the percentage of the emulsifier was raised to 6 or 8%.

Films were cast from 2:1 ratios of mixed Epon 1001-Versamid 115 emulsions which had been heated for 15, 30, 60 or 90 minutes at 50° C, to pre-cure the Epon 1001 in the emulsion state. These films were compared with those cast without the pre-curing. Generally, the films cast from the pre-cured emulsions dried to the touch more rapidly than did those from the control films. Moreover, the longer the pre-curing time, the shorter was the time required for drying-to-touch. The films developed cracks during drying, with the cracking tendency increasing with increasing pre-curing time. Probably, the pre-curing increased the viscosity and decreased the elongation of the Epon 1001 particles so that the inevitable shrinkage upon drying produced stresses that were relieved by cracking.

Other evaluation tests are described in Sections V and VI.

8. One-Quart Mixed Epoxy Resin-Curing Agent Emulsion Samples for Evaluation

The following emulsion samples were prepared using the hexadecyltrimethylammonium bromide-n-decane combination and simple stirring, followed by homogenization and vacuum steam distillation to remove the solvents and concentrate the emulsions. The emulsion samples were submitted to the Air Force for evaluation for the primer application. The sample sizes are sufficient to provide several one-quart samples of the mixed epoxy resin-curing agent emulsions.

a. Epoxy Resin Emulsions

(i) 29.4% solids Epon 1001 emulsion (LB-C-29)
(ii) 35.1% solids Epon 828 emulsion (LB-C-32)

b. Curing Agent Emulsions

(i) 35.6 % solids Versamid 100 emulsion (LB-C-25)
(ii) 9.97% solids Versamid 115 emulsion (LB-C-26-2)

SECTION V

MORPHOLOGY AND PROPERTIES OF EPOXY RESIN FILMS

A. Sample Composition

The morphological and mechanical properties of the epoxy resin films were studied using several methods: 1. transmission electron microscopy of film surface replicas, microtomed sections, and dispersions of the polymer emulsions; 2. Rheovibron Elastoviscosimeter measurement of the modulus-temperature variation; 3. determination of the proportion of crosslinked polymer in the films by solvent extraction; 4. scanning electron microscopy of the films before and after solvent extraction; 5. determination of the reaction isotherms of cured films using differential scanning calorimetry (DCS).

The epoxy resin emulsions were prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination: one comprised Epon 1001 (SR-1) and the other a 96:4 Epon 1001-bisphenol A mixture (JS-3). The curing agent emulsions were also prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination: one comprised Versamid 115 (SR-3) and the other 2:1 Versamid 115-Dion DPM-3-800-LC mixture (YV-4). The following stoichiometric combinations were evaluated.

Combination	Composition
I	Epon 1001-Versamid 115
II	Epon 1001-Versamid 115 heated for 15 min at 55°C
III	(Epon 1001-bisphenol A)-Versamid 115
IV	Epon 1001-(Versamid 115-Dion DPM-3-800-LC)
V	Epon 1001-Versamid 115 cast from organic solvent

B. Transmission Electron Microscopy of Film Replicas and Dispersions

It was shown earlier (27, 28) that dry, transparent, apparently continuous latex films show deformed-particle contours which slowly disappear upon ageing at room temperature; during this process, any substances that are incompatible with the polymer (e.g., emulsifier or electrolyte) are exuded from the film. This process, which is called "further, gradual coalescence", is attributed to "autohesion" (24)--the mutual interdiffusion of free polymer chain ends across the particle-particle interface--and can be correlated with a significant improvement in film properties.

The curing of an epoxy resin-curing agent film comprises three steps: (i) physical contact between epoxy resin and curing agent particles by coalescence during film formation; (ii) reaction between the epoxy resin and curing agent to form a crosslinked polymer network at the interface between these particles;(iii) further curing of the epoxy resin by diffusion of the curing agent molecules through this crosslinked interfacial layer. Since the diffusion rate of a molecular substance through a polymer decreases drastically with an increase in the second-order transition temperature T_g of the polymer, the formation of a crosslinked interfacial layer between the coalesced epoxy resin and curing agent particles would slow the diffusion and, hence, the overall rate of curing.

To determine if these epoxy resin-curing agent films show further, gradual coalescence, samples of Combinations I-IV were dried on glass microscope slides and allowed to age at room conditions (20° C, 50% RH). Two-step carbon-platinum replicas were made at various ageing times in the following way. A drop of 10% aqueous polyvinyl alcohol solution was applied to the film and allowed to dry for 3 hours at room temperature; it was then stripped off, replicated by evaporation of carbon under vacuum (3×10^{-5} torr), and shadowed with platinum. The polyvinyl alcohol replicas were dissolved by immersion in water, and the carbon-platinum replicas were picked up on electron microscope specimen substrates, dried, and examined in the electron microscope. In several cases, no particle contours were seen. Therefore, the films were immersed in methanol for about 30 seconds to dissolve any emulsifier that was on the film surface and reveal the particle contours obscured by this emulsifier layer. Generally, the ageing experiments were continued for 33-45 days.

Figures 3-6 show the replicas of Combinations I-IV, respectively, as a function of ageing time. The Epon 1001-Versamid 115 combination (Figure 3) showed little or no evidence of particle contours for times of 7 hr - 45 days although some replicas (not shown) had a rougher surface than those shown in Figure 3. The Epon 1001-Versamid 115-heated-at-55° C combination (Figure 4) showed distinct particle contours at 7 hr and 15 hr (not shown), which disappeared by 1.5 days; the replica at 6.25 days (not shown) showed some particle contours, indicating that the rate of disappearance was not uniform throughout the film. The most distinct particle contours were those of the (Epon 1001-bisphenol A)-Versamid 115 combination (Figure 5), which persisted with only slight change up to 45 days. The Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination (Figure 6) showed particle contours at 7 hr, which disappeared by 15 hr; at later times, the films were smooth, but showed particles of material that appeared crystalline in nature, similar to the exuded emulsifier films observed earlier (28, 29).

In comparison, Figure 7 shows replicas of a film cast from an Epon 1001 emulsion (SR-1). The film showed distinct particle contours at 7 hr, which disappeared by 15 hr; after 6.25 days, the film surface appeared crystalline, as would be expected for Epon 1001.

Since the hexadecyltrimethylammonium bromide-cetyl alcohol combination is soluble in methanol, the films were immersed in this solvent for 30 seconds, dried, and replicated. The methanol should dissolve any surface layer of emulsifier, revealing the contours of the polymer film underneath.

In most cases, this methanol washing or "etching" had little effect on the morphology of the film. Figure 8 shows that the morphology of the Epon 1001-Versamid 115 film appeared much the same after the methanol washing. Similarly, Figure 9 shows that the appearance was also much the same for the Epon 1001-Versamid 115-heated-to-55° C combination. The (Epon 1001-bisphenol A)-Versamid 115 films swelled slightly in methanol; Figure 10 shows that the particle contours were similar to those of the unwashed film but were slightly less distinct, as would be expected if the film were swelled slightly by the solvent. In contrast, Figure 11 shows that the methanol washing removed the crystalline patches from the

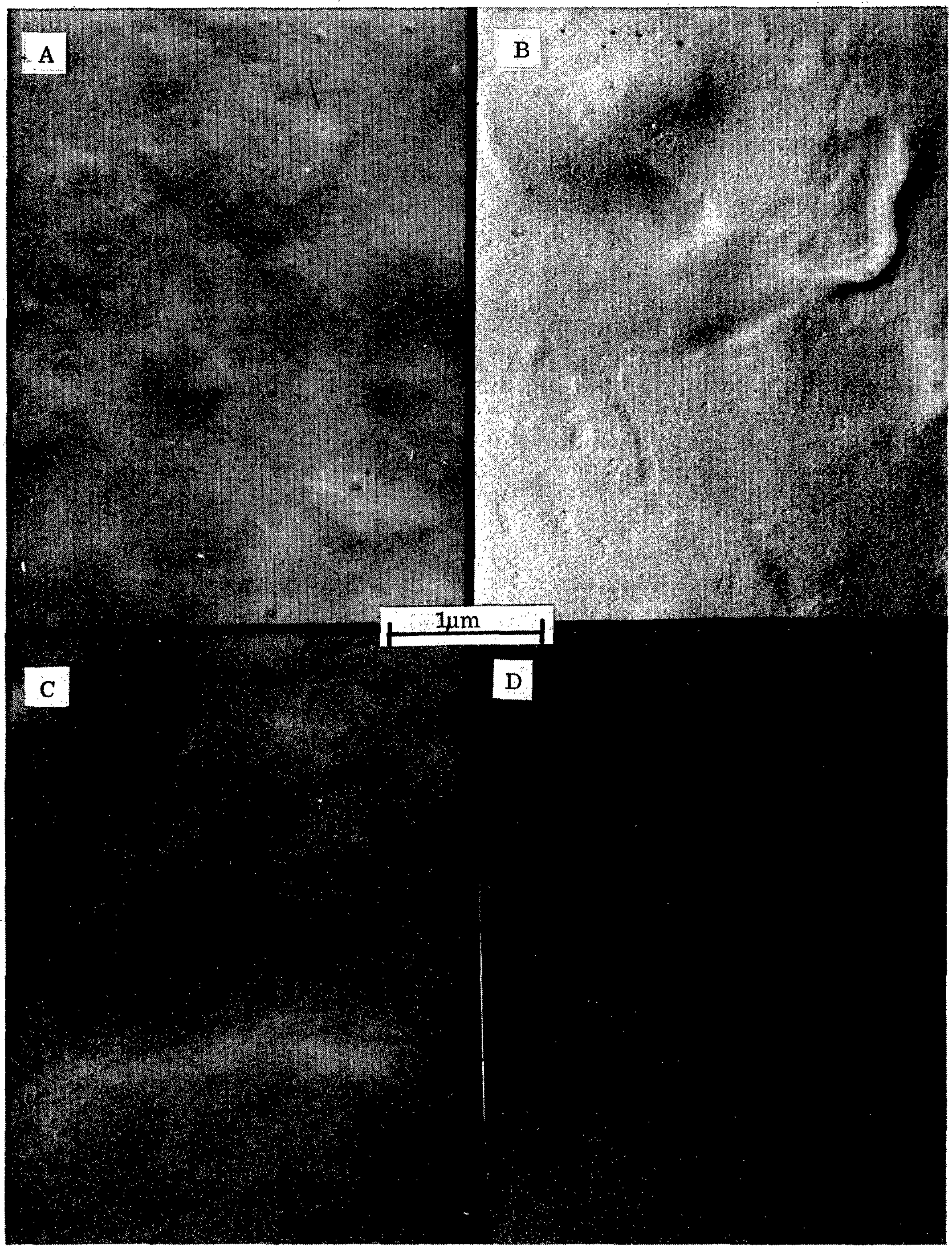


Figure 3. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115 films aged at room temperature: A. 7 hours; B. 1.5 days; C. 11.5 days; D. 45 days.

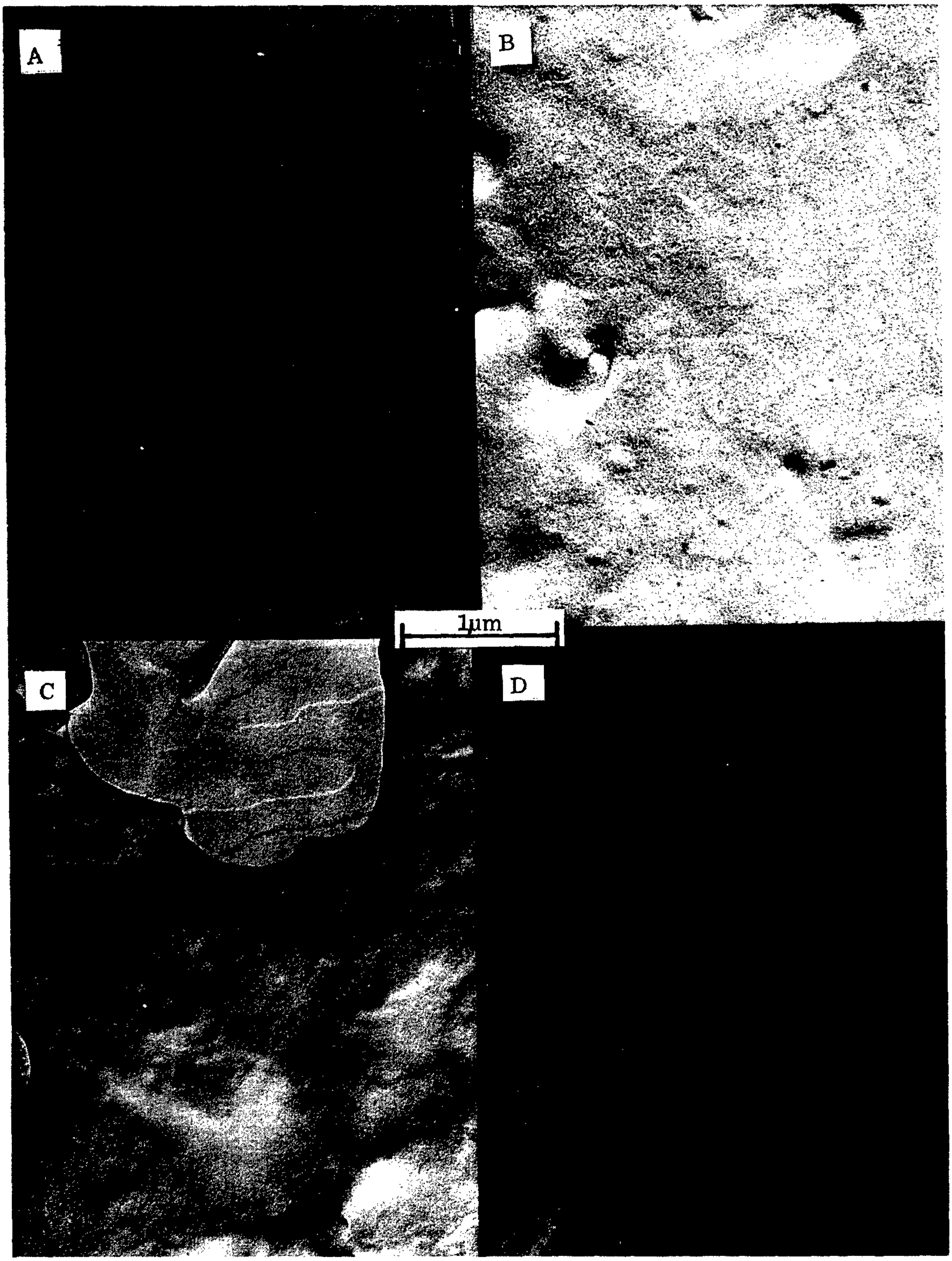


Figure 4. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115-heated-to-55° C films aged at room temperature: A. 7 hours; B. 1.5 days; C. 11.5 days; D. 45 days.

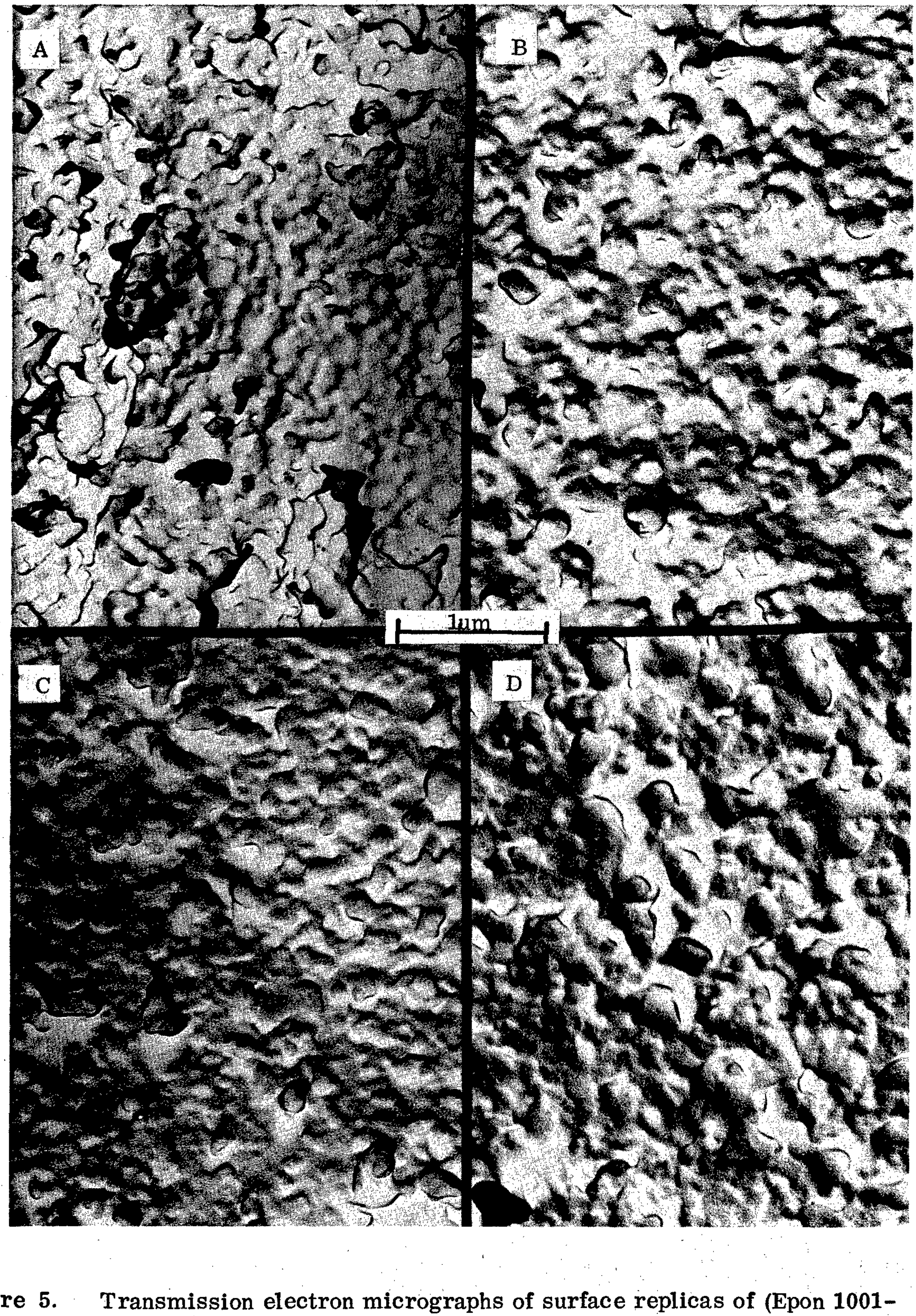


Figure 5. Transmission electron micrographs of surface replicas of (Epon 1001-bisphenol A)- Versamid 115 films aged at room temperature: A. 7 hours; B. 1.5 days; C. 11.5 days; D. 45 days.

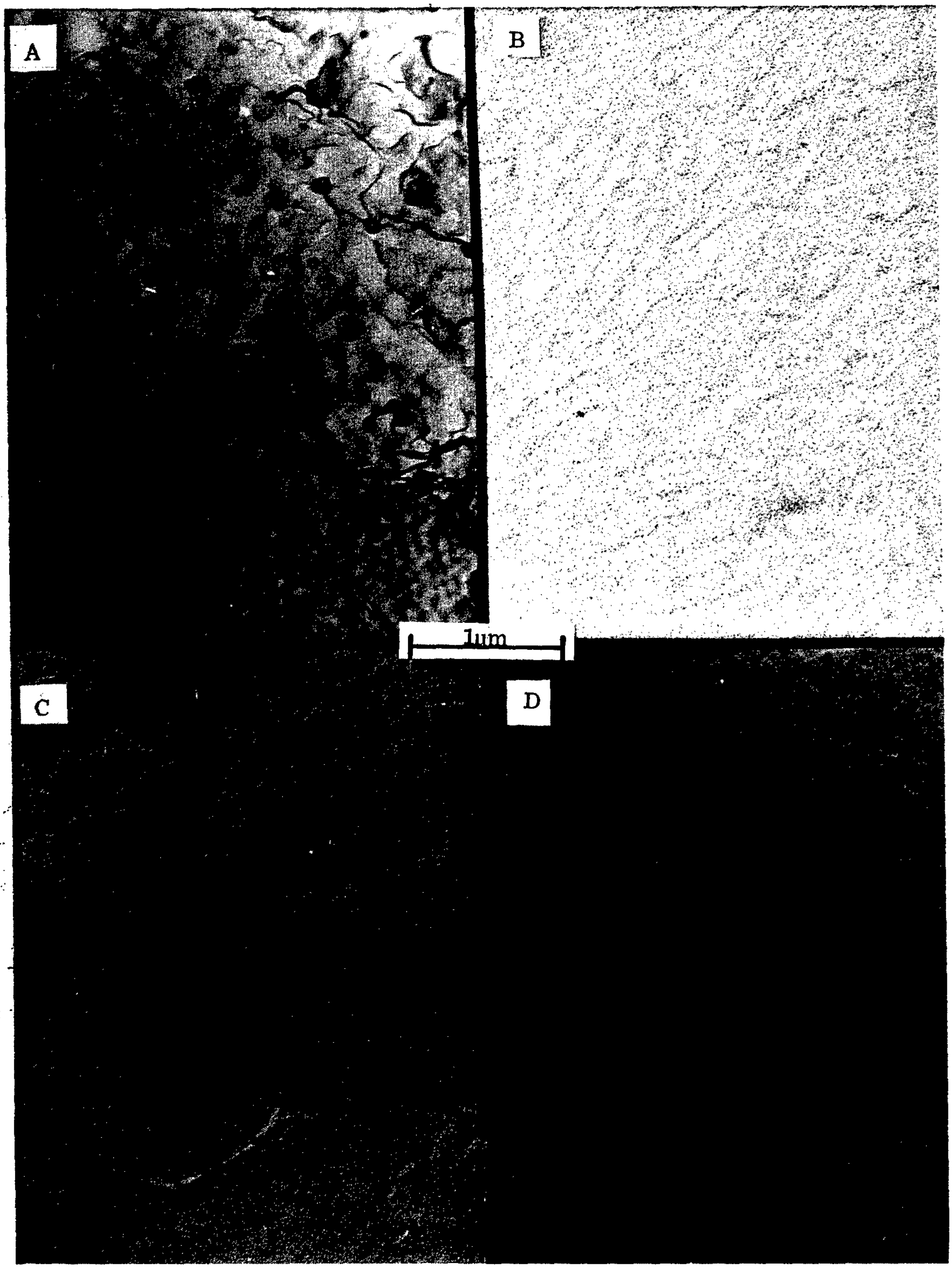


Figure 6. Transmission electron micrographs of surface replicas of Epon 1001-(Versamid 115-Dion DPM-3-800-LC) films aged at room temperaure: A. 7 hours; B. 1.5 days; C. 11.5 days; D. 45 days.

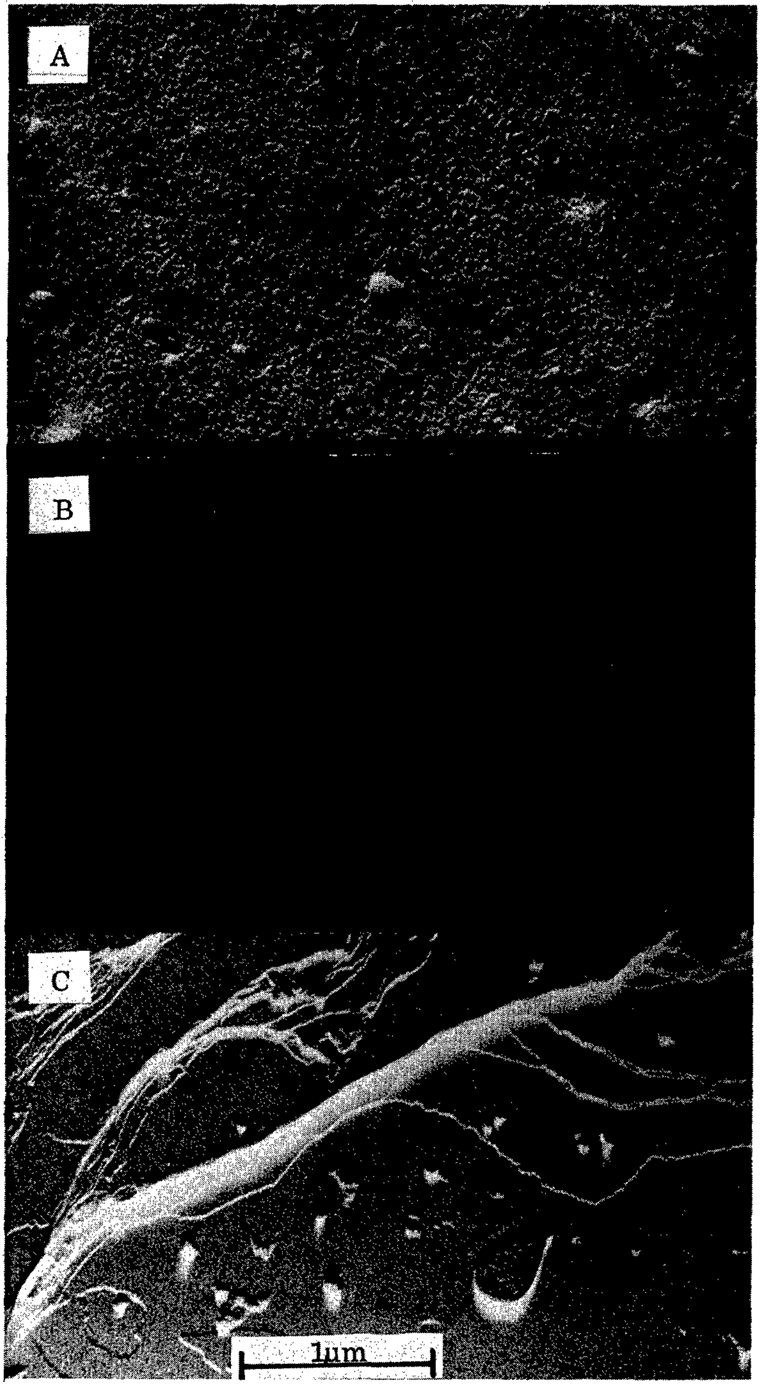


Figure 7. Transmission electron micrographs of surface replicas of an Epon 1001 emulsion film aged: A. 7 hours; B. 15 hours; C. 6.3 days.

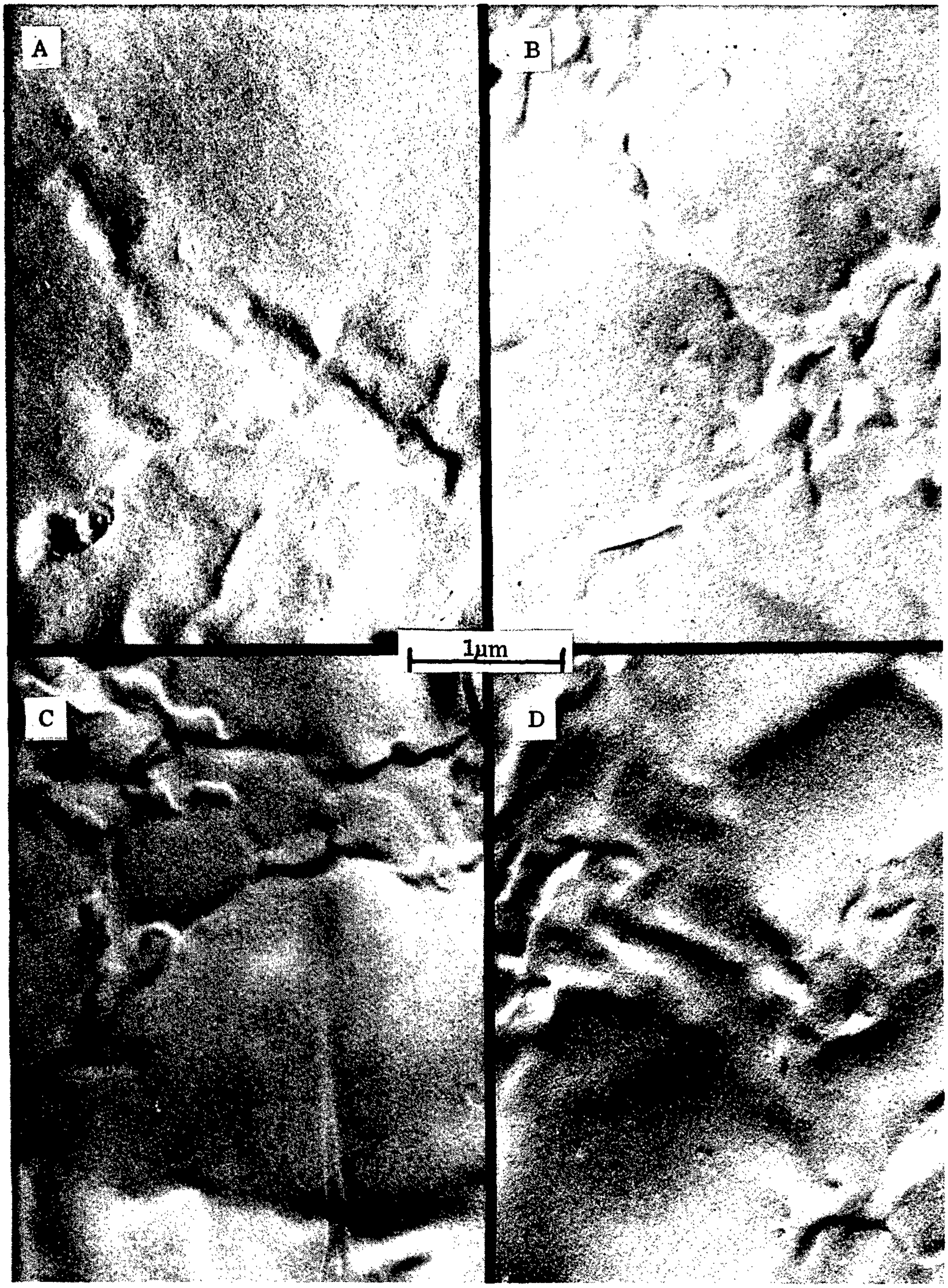


Figure 8. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115 films immersed in methanol after ageing at room temperature: A. 1.5 days; B. 4.5 days; C. 11.5 days; D. 16.5 days.

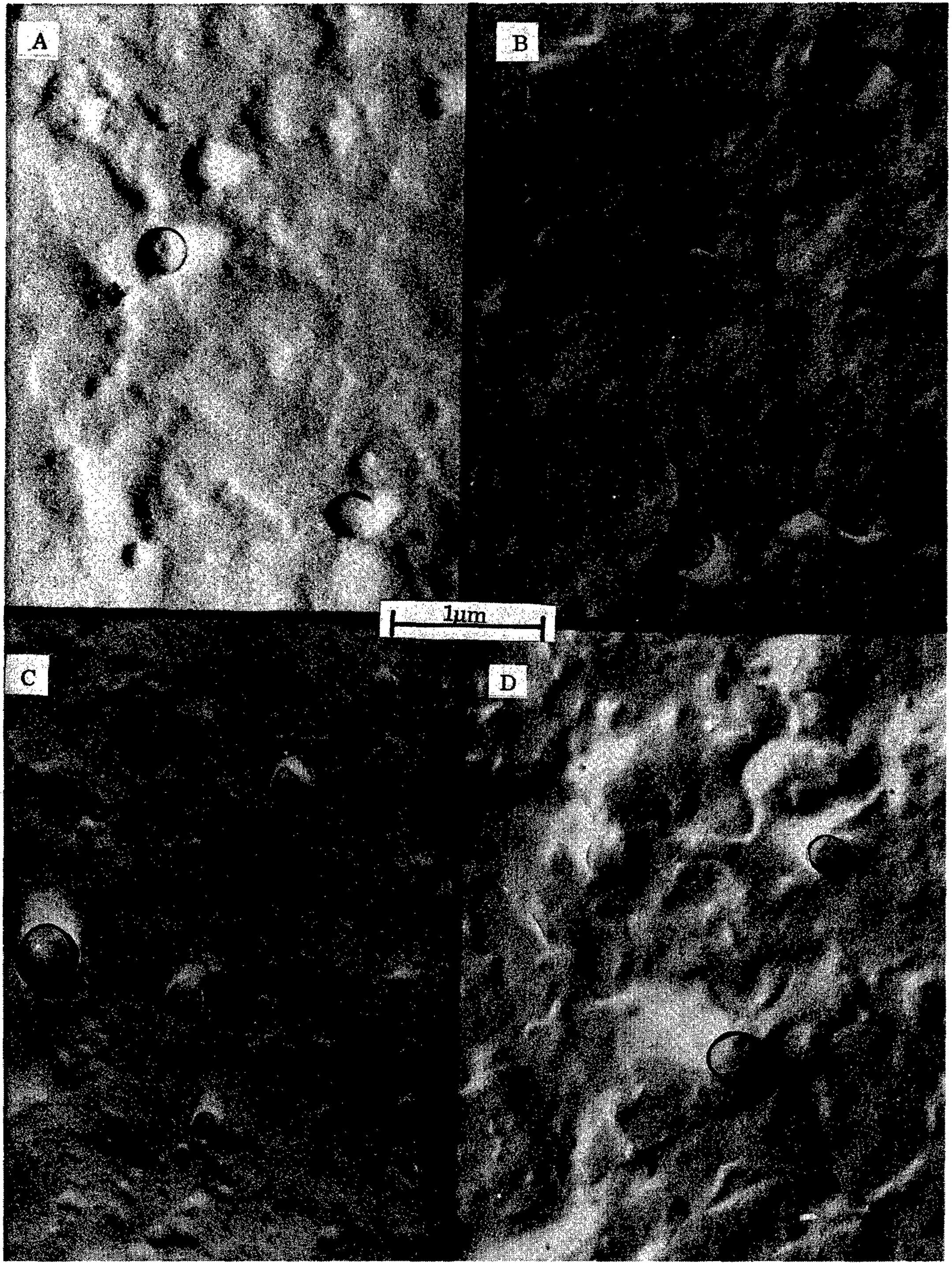


Figure 9. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115-heated-to-55° C films immersed in methanol after ageing at room temperature: A. 1.5 days; B. 4.5 days; C. 11.5 days; D. 16.5 days.

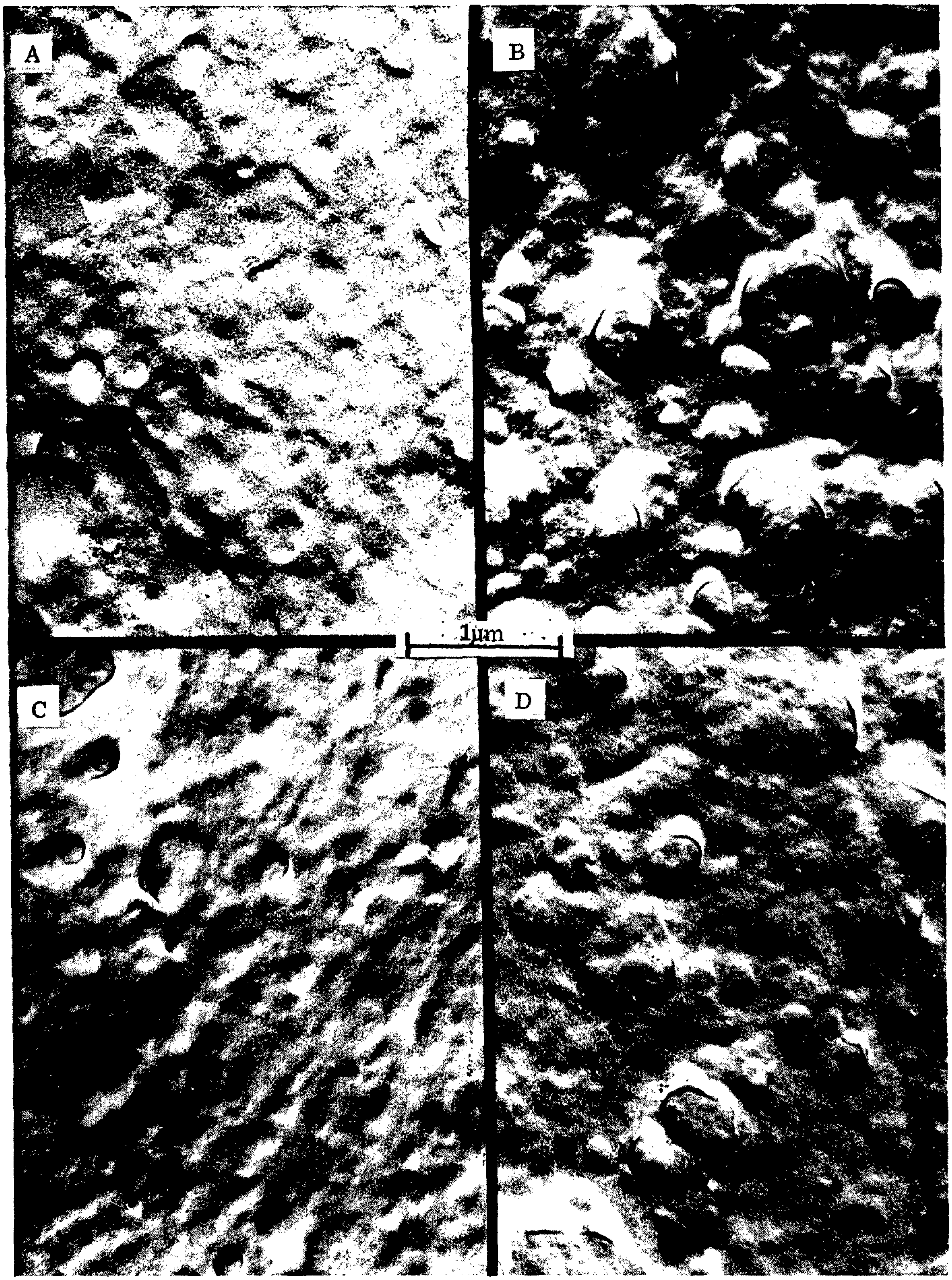


Figure 10. Transmission electron micrographs of surface replicas of (Epon 1001-bisphenol A)-Versamid 115 films immersed in methanol after ageing at room temperature: A. 1.5 days; B. 4.5 days; C. 11.5 days; D. 16.5 days.

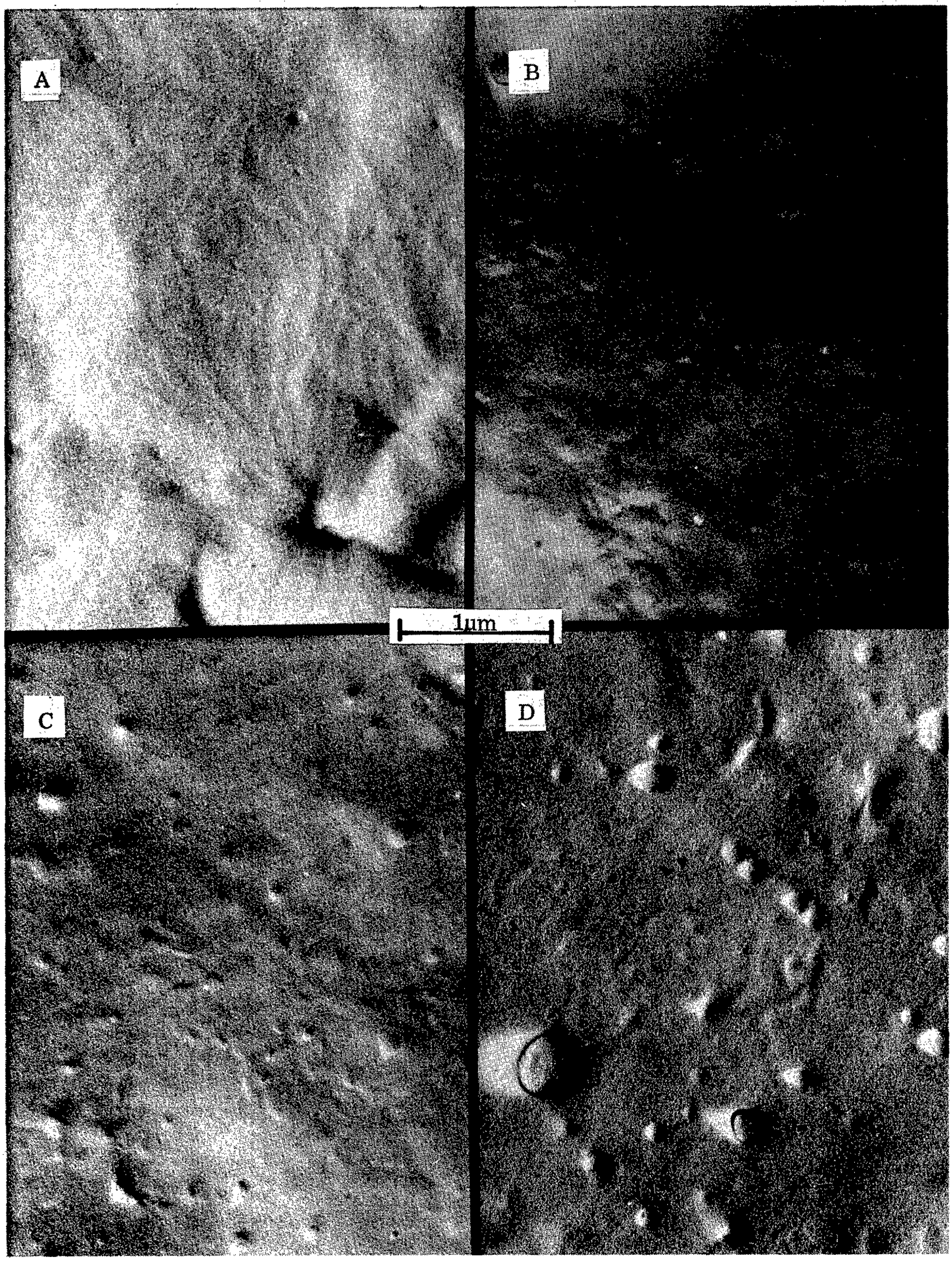


Figure 11. Transmission electron micrographs of surface replicas of Epon 1001-(Versamid 115-Dion DPM-3-800-LC) films immersed in methanol after ageing at room temperature: A. 1.5 days; B. 4.5 days; C. 11.5 days; D. 16.5 days.

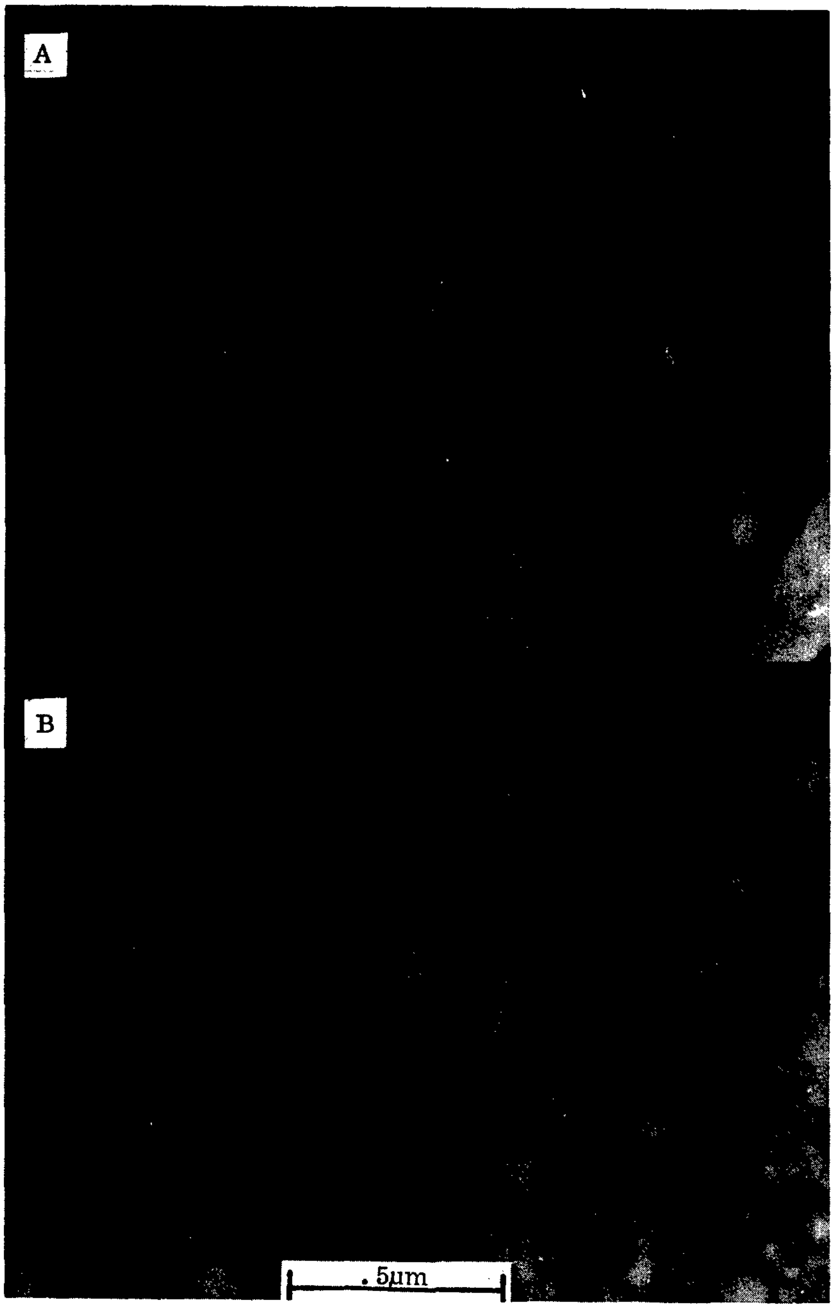


Figure 12. Transmission electron micrographs of microtomed sections of epoxy emulsion films stained with oxmium tetroxide: A. Epon 1001-Versamid 115 combination; B. Epon 1001-Versamid 115-heated-to-55° C combination.

Epon 1001-(Versamid 115-Dion DPM-3-800-LC) films, except for the 1.5-day sample (Figure 11-A) which still showed traces of these patches.

These films were also examined by electron microscopy of the microtomed sections. Small portions of the films of the Epon 1001-Versamid 115 and Epon 1001-Versamid 115-heated to 55° C combinations were exposed to osmium tetroxide vapors for 4 days. The osmium tetroxide adds to residual double bonds of the polymer and gives a dark electron-opaque appearance that is readily visible in the electron microscope; this staining procedure was developed for the visualization of butadiene units in butadiene-containing polymers (30). Since Versamid 115 has residual double bonds in its structure and Epon 1001 does not, the dark electron-opaque areas of the electron micrograph should denote regions rich in Versamid 115 (the residual unsaturation is not involved in the curing reaction and therefore should still remain in cured films).

Microtomed sections of these films (60 nm thickness) were cut using the Ultra-Microtome, mounted on electron microscope specimen substrates, and examined in the electron microscope. Figure 12 shows typical results for the foregoing combinations. The Epon 1001-Versamid 115-heated-to-55° C combination (Figure 12-B) shows lighter spherical Epon 1001-rich particles (distorted slightly by the microtoming) embedded in a darker Versamid 115-rich matrix. The dark vs. light disparity indicates that the curing has not proceeded to the stage where the film is uniform in composition. In comparison, the standard Epon 1001-Versamid 115 combination (Figure 12-A) shows larger regions of lighter Epon 1001-rich material containing a few dark streaks of Versamid 115-rich material as well as the spherical Epon 1001-rich particles dispersed in a Versamid 115-rich matrix. These larger regions are attributed to the curing that obliterates particle boundaries and renders the film more homogeneous. Thus, the Epon 1001 particles in the standard system coalesce to a greater extent when the film is first formed, giving uniform regions of coalesced Epon 1001 particles containing interspersed Versamid 115, while the Epon 1001 particles of the sample heated for 15 minutes at 55° C are pre-cured to the extent that they maintain their integrity and appear as single discrete particles in the final cured film.

The curing of the Epon 1001-Versamid emulsion mixtures was investigated further using emulsions prepared with the hexadecyltrimethylammonium bromide-n-decane combination: Epon 1001 (JS-8) and Versamid 115 (C-7). A film was cast from the stoichiometric Epon 1001-Versamid 115 emulsion mixture and replicated at various times. The remaining mixture was stored in a closed container for one week at room temperature. If the Epon 1001 and Versamid 115 emulsion droplets were stable, and if those prepolymers were completely insoluble in water, such mixed emulsions should remain stable indefinitely without curing. However, this sample showed a visible decrease in viscosity, indicating an increase in particle size. A film was cast from this one-week-old emulsion mixture and replicated at various ageing times. The particle contours in the film prepared from the fresh mixture of the Epon 1001-Versamid 115 emulsions (Figure 13), dissappeared gradually, and by 15 days the film morphology was similar to the other Epon 1001-Versamid 115 system (Figure 3). Figure 14 shows that particle contours were observed at all ageing times up to 33 days in the film cast from the one-week-old emulsion mixture, indicating that the one-week's ageing in the emulsion state increased the viscosity of the particles to the point where further, gradual coalescence no longer occurred.

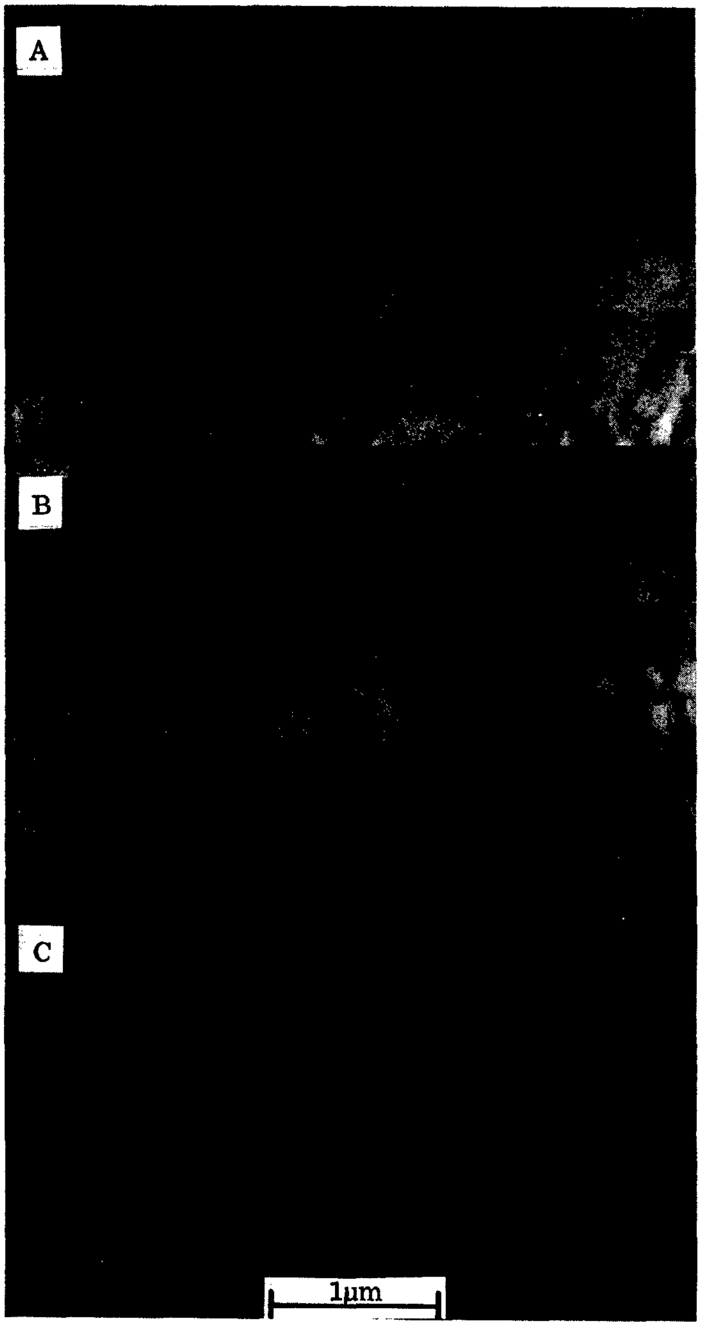


Figure 13. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115 (hexadecyltrimethylammonium bromide-n-decane combination) films aged at room temperature: A. 15 hours; B. 7.5 days; C. 15.5 days.

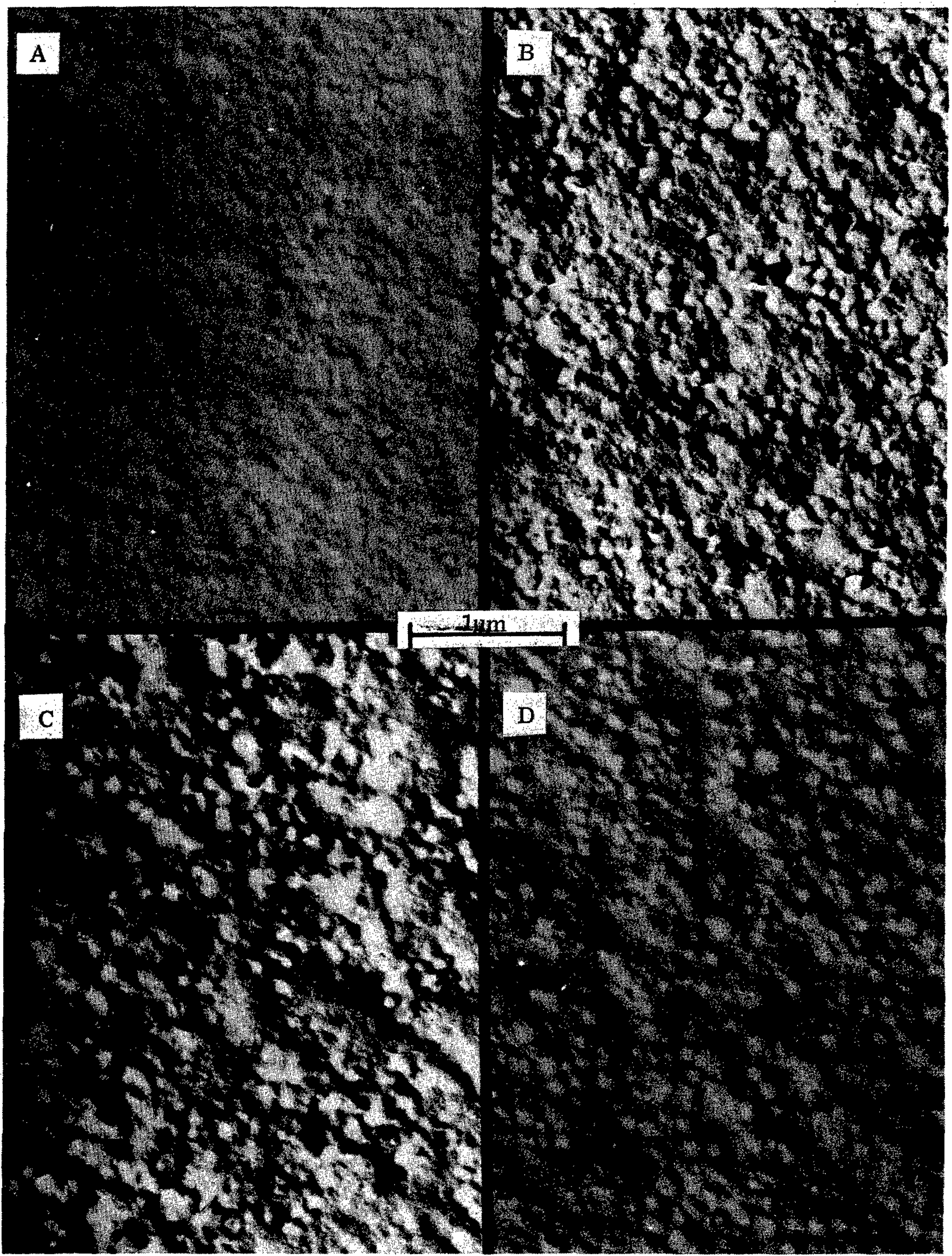


Figure 14. Transmission electron micrographs of surface replicas of Epon 1001-Versamid 115 (hexadecyltrimethylammonium bromide-n-decane combination) films cast after the mixed emulsions were aged at room temperature for one week, aged at room temperature: A. 15 hours; B. 7 days; C. 15 days; D. 33 days.

This curing in the emulsion state was investigated by transmission electron microscopy of diluted dispersions. The mixed emulsions were diluted to about 10 ppm, and a drop of the dispersion was placed on a specimen substrate, frozen, and placed on the cold stage in the electron microscope; the water was then sublimed off while keeping the sample frozen, to prevent the distortion of the particles that occurs when the aqueous dispersion is dried. Figure 15-A shows that the particles of the Epon 1001 emulsions (SR-1) without curing agent are separate and discrete, and range in size from 20 to 200 nm. The corresponding electron micrograph of Versamid 115 emulsion (SR-3) (Figure 15-B) shows discrete 20-30nm particles connected with strands of amorphous polymer or coalesced particles of even smaller size; the decrease in opacity and increase in viscosity of Versamid 115 emulsions after preparation indicates that the dispersed polymer undergoes solubilization. Figure 16-A shows the mixed emulsions after 30 minutes at room temperature; the Versamid 115 particles have clustered around the Epon 1001 particles, forming agglomerates of several Epon 1001 particles held together with the Versamid 115 particles. Figures 16-B and 16-C show the effect of heating the mixed emulsions for 15 minutes at 55° C and 80° C, respectively. Both show similar agglomeration, with that of the 80° C sample being more extensive. Similar agglomeration was observed for the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination; Figure 17 shows that the Epon 1001 particles were agglomerated with amorphous Versamid 115 after 30 minutes at room temperature.

Thus, these results indicate that, immediately upon mixing, the Versamid 115 particles agglomerate with the Epon 1001 particles, leading to a premature curing reaction in the emulsion state. This premature curing is confirmed by the fact that a skin begins to form on the surface as soon as the emulsions were mixed. Also, when the mixed emulsions were placed on the pan of the differential scanning calorimeter (DSC), the recorder indicated that the reaction started immediately, while the water was still evaporating from the emulsion, before the particles had coalesced.

C. Dynamic-Mechanical Properties

The specimen preparation was similar to that used in the first part of this work (4). The mixed emulsions were allowed to stand for 15-20 minutes to allow entrapped air bubbles to escape and then were cast on a glass slide in an aluminum-foil tray with 4-6-mm-high sides to keep the mixed emulsions on the slide. Before film casting, the slide was sprayed with Epoxy Parafilm mold release to facilitate the removal of the cured film. After the film had been cured as desired, the aluminum sides were peeled off, and the film was separated from the slide using a razor blade. Test specimens 1-2 cm long and 0. 14 cm wide were cut from this 0. 04-cm thick film.

The heights of the aluminum sides were varied to obtain films of different thickness. The morphology of these films cast in the aluminum-foil "molds" was invariably different from that of films cast on glass slides without any retaining boundaries. Figure 18 shows optical photomicrographs of the surfaces of these two different types of films. The film cast in the aluminum-foil "mold" shows patches of light-colored material dispersed in a matrix of darker material (Figure 18-A), while that cast without restraining boundaries showed an even gradation from a light-colored center to a dark-colored periphery (Figure 18-B).

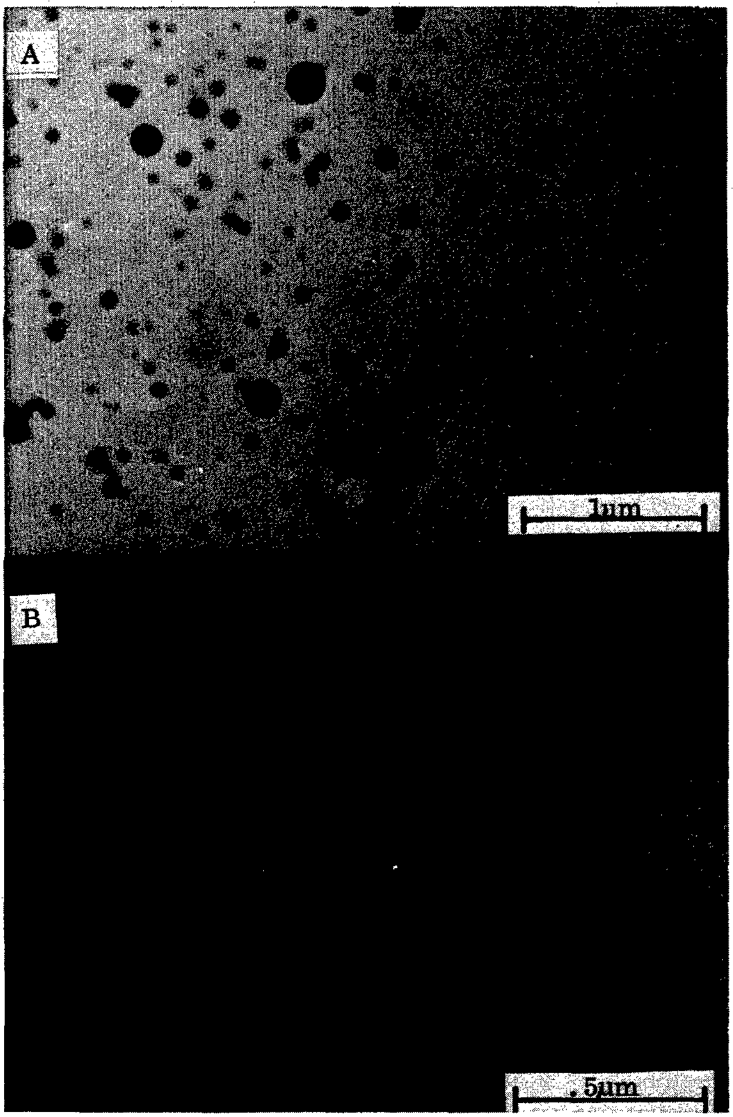


Figure 15. Transmission electron micrographs of diluted dispersions of: A. Epon 1001 emulsion; B. Versamid 115 emulsion.

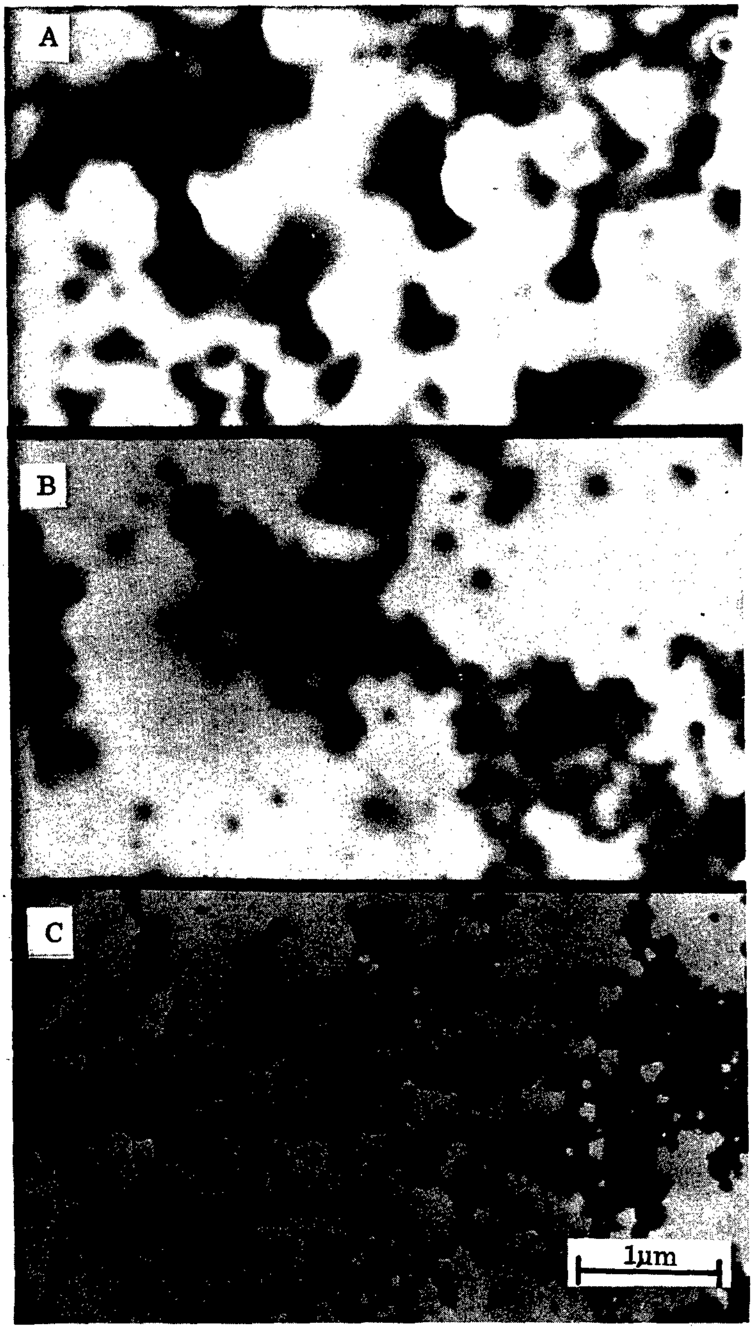


Figure 16. Transmission electron micrographs of diluted dispersions of the Epon 1001-Versamid 115 combination aged: A. 30 minutes at room temperature; B. 15 minutes at 55° C; C. 15 minutes at 80° C.

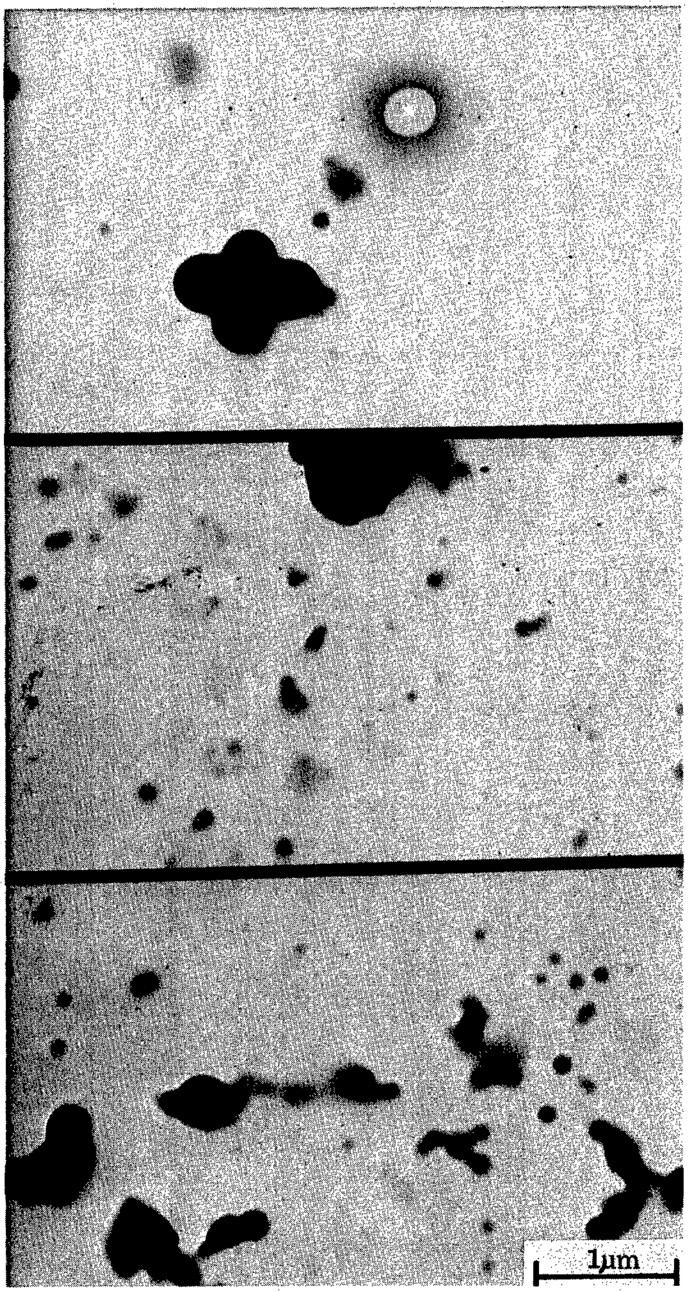


Figure 17. Transmission on electron micrographs of diluted dispersions of Epon 1001-(Versamid 115-Dion DPM-3-800-LC) aged 30 minutes at room temperature.

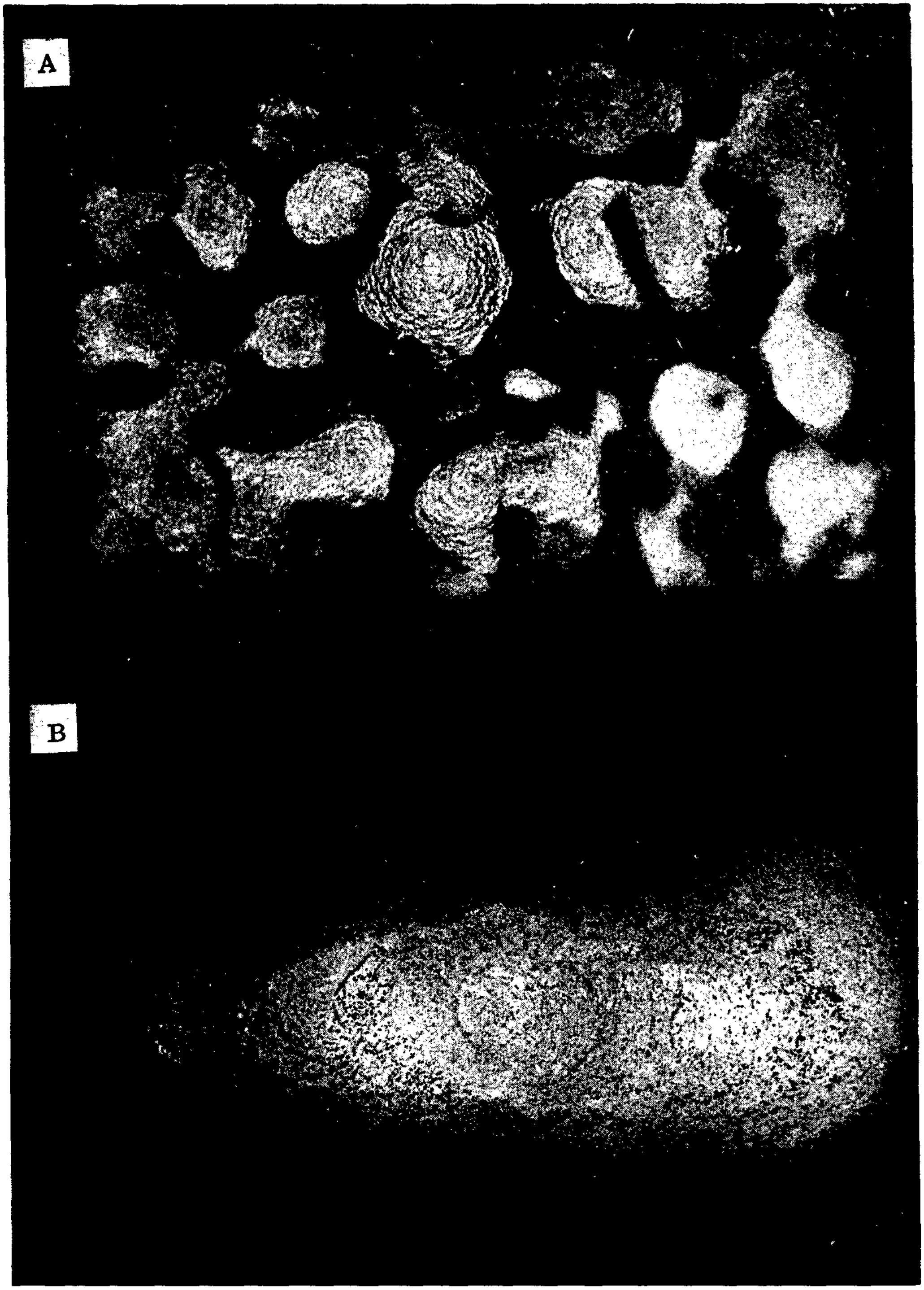


Figure 18. Optical photomicrographs of 0.04-cm thick films of the Epon 1001-Versamid 115 combination; A. cast in aluminum-foil "molds"; B. cast without restraining boundaries.

The films cast in the aluminum-foil "molds" adhered to the glass slide at the lighter patches, even though the glass slides had been sprayed with mold release compound before film casting.

Figure 19 shows scanning electron micrographs of the lighter and darker patches of the film shown in Figure 18-A. The lighter patches were very porous (Figure 19-A) while the darker regions (Figure 19-B) were less porous. Immersing the film in methanol removed the porous material from the light patches, leaving a rough, non-porous film which showed the contours of individual particles (Figure 19-C). The darker patches appeared much the same after immersion in methanol except that the edges of the pores were slightly rounded as would be expected if the methanol swelled the film slightly (Figure 19-D).

This difference in morphology can be explained in two different ways: (i) the light patches are the emulsifiers present in the mixed emulsion which are exuded from the film as it cures; (ii) the light patches are regions rich in Epon 1001 particles and the darker patches regions rich in Versamid 115 particles. The first explanation is consistent with the surface morphology of the light patches (Figure 19-A), but is inconsistent with the observation that the adhesion to the glass slide was greater in the lighter patches; emulsifiers do not give good adhesion to glass. In comparison, a region rich in Epon 1001 particles would give better adhesion to glass than a region rich in Versamid 115 particles. The non-uniform distribution of the Epon 1001 and Versamid 115 particles is consistent with the convection often observed in the drying of relatively thick films. The distribution of the white patches of Figure 18-A is similar to the results of Bénard's classical experiments (31) in which the film dried uniformly until it reached a critical stage, whereupon it broke up into many small convection cells each convection cell showed a distribution of particles after drying, with the larger or heavier particles concentrated in the center of the cell. The distribution of light patches in Figure 18-B is similar to expected from the earlier observation (32) that unrestrained latex films dried in air on glass microscope slides formed a single Bénard convection cell. The dynamic-mechanical properties of the epoxy resin-curing agent films were measured after ageing for 45 days at room temperature using the Rheovibron Elastoviscosimeter (Toyo Instruments Measuring Co., Ltd.) in the temperature range -25 to 110° C. The specimens were measured once, then were cooled and measured again, to determine if any further curing occurred during the measurement cycle. Figures 20-23 show the results for the Epon 1001-Versamid 115, Epon 1001-Versamid 115-heated-at-55° C, (Epon 1001-bisphenol A)-Versamid 115, and Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combinations. For comparison, Figure 24 shows the results for the Epon 1001-Versamid 115 combination cast from organic solvent. The data are expressed as the variation of log elastic modulus $\underline{E}'$ and log loss modulus $\underline{E}''$ with temperature.

The Epon 1001-Versamid 115 combination (Figure 20) underwent further curing during the measurement cycle as shown by the divergence of the elastic modulus curves for the two runs. This is confirmed by the fact that the loss modulus curve of the first run shows a single peak, while that of the second run shows two peaks. Similar results were obtained for the Epon 1001-Versamid 115-heated-at-55° C combination (Figure 21), except that the divergence between the two elastic modulus curves was not as great and the first loss modulus curve even showed two peaks; these results are consistent with a higher degree of curing. The (Epon 1001-bisphenol A)-Versamid 115 combination (Figure 22) showed an elastic modulus curve similar to that of the Epon 1001-Versamid 115 combination,

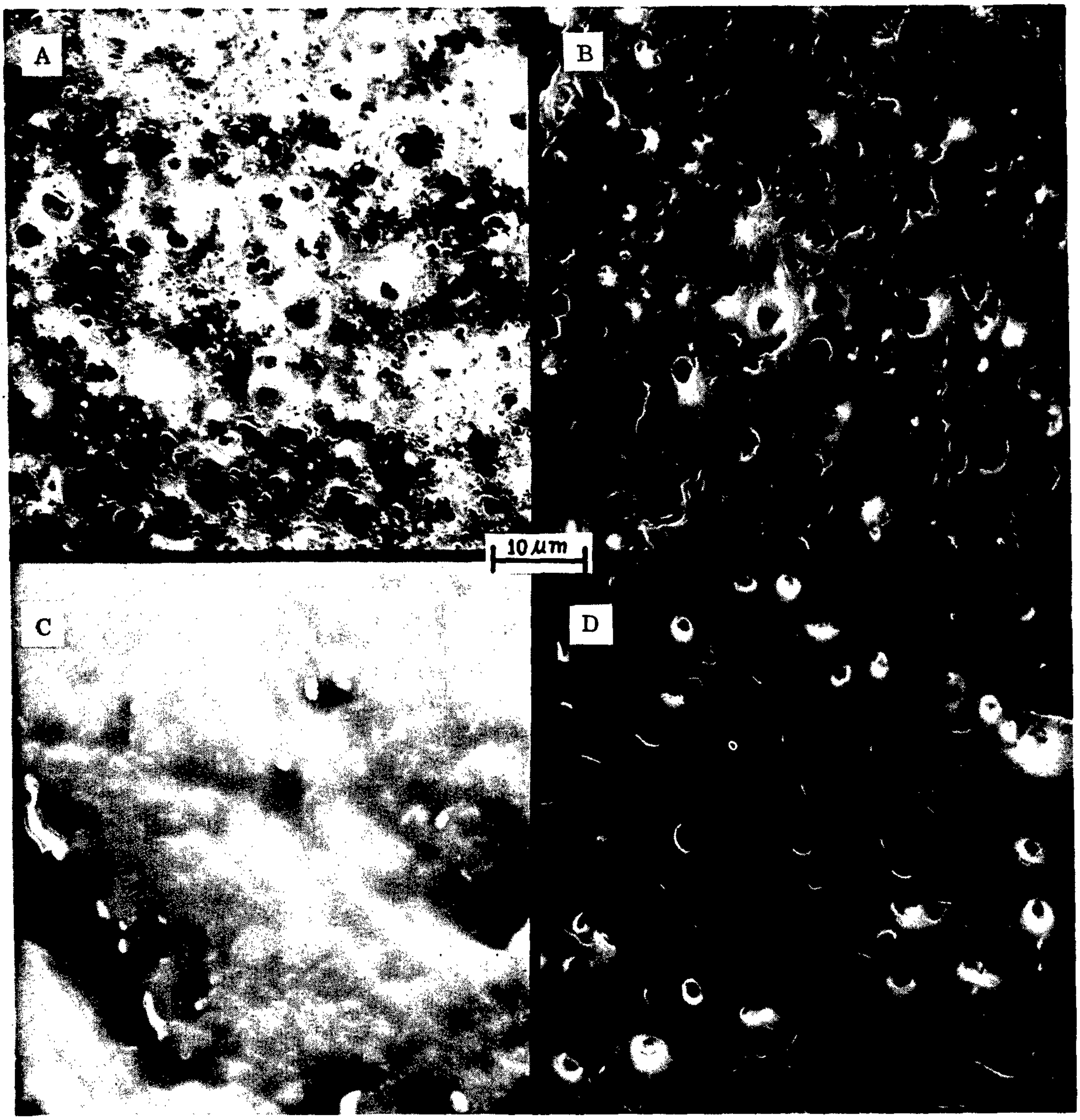


Figure 19. Scanning electron micrographs of the Epon 1001-Versamid 115 film shown in Figure 18-A: A. lighter region; B. darker region; C. lighter region after immersing in methanol; D. darker region after immersing in methanol.

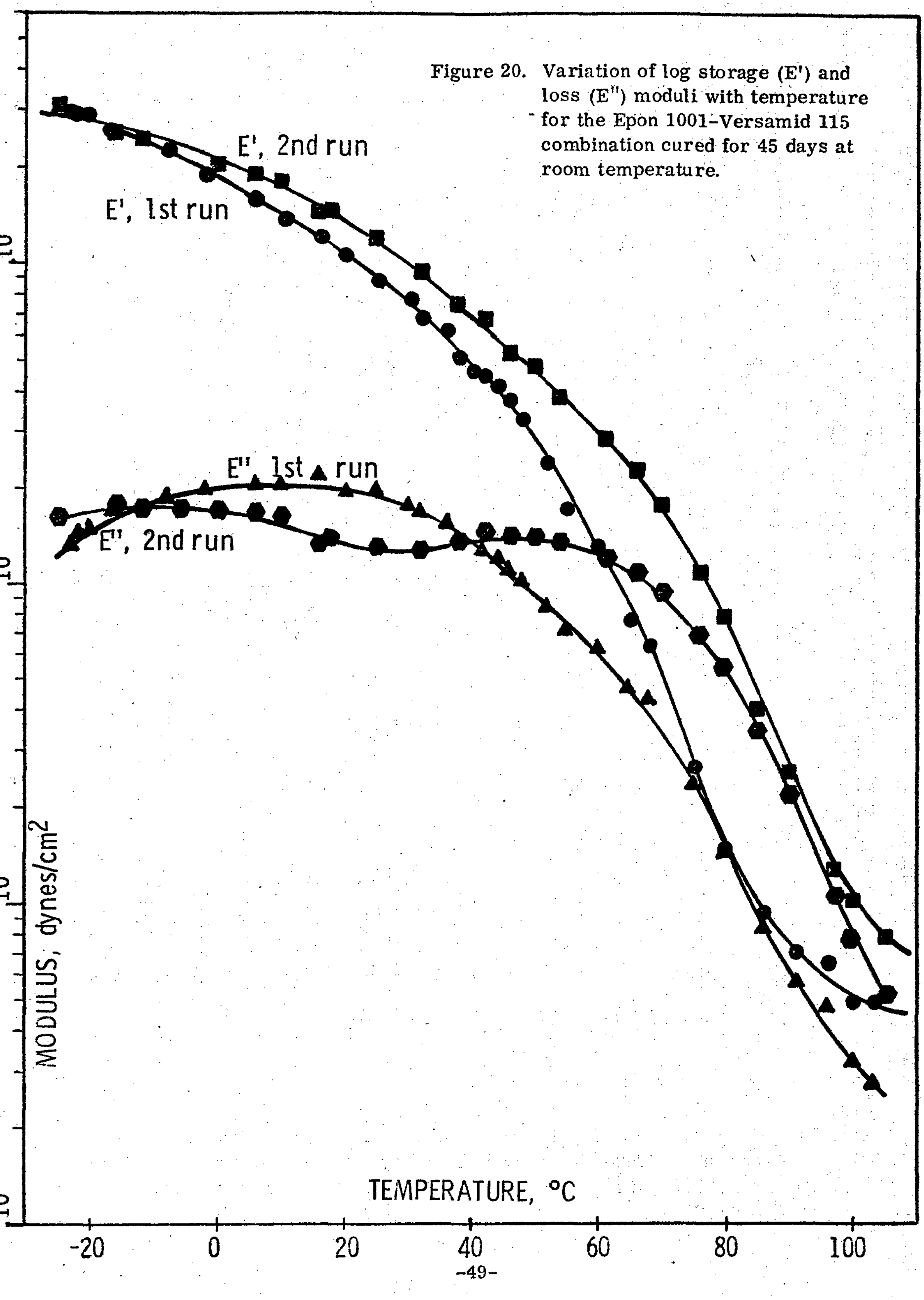


Figure 20. Variation of log storage (E') and loss (E") moduli with temperature for the Epon 1001-Versamid 115 combination cured for 45 days at room temperature.

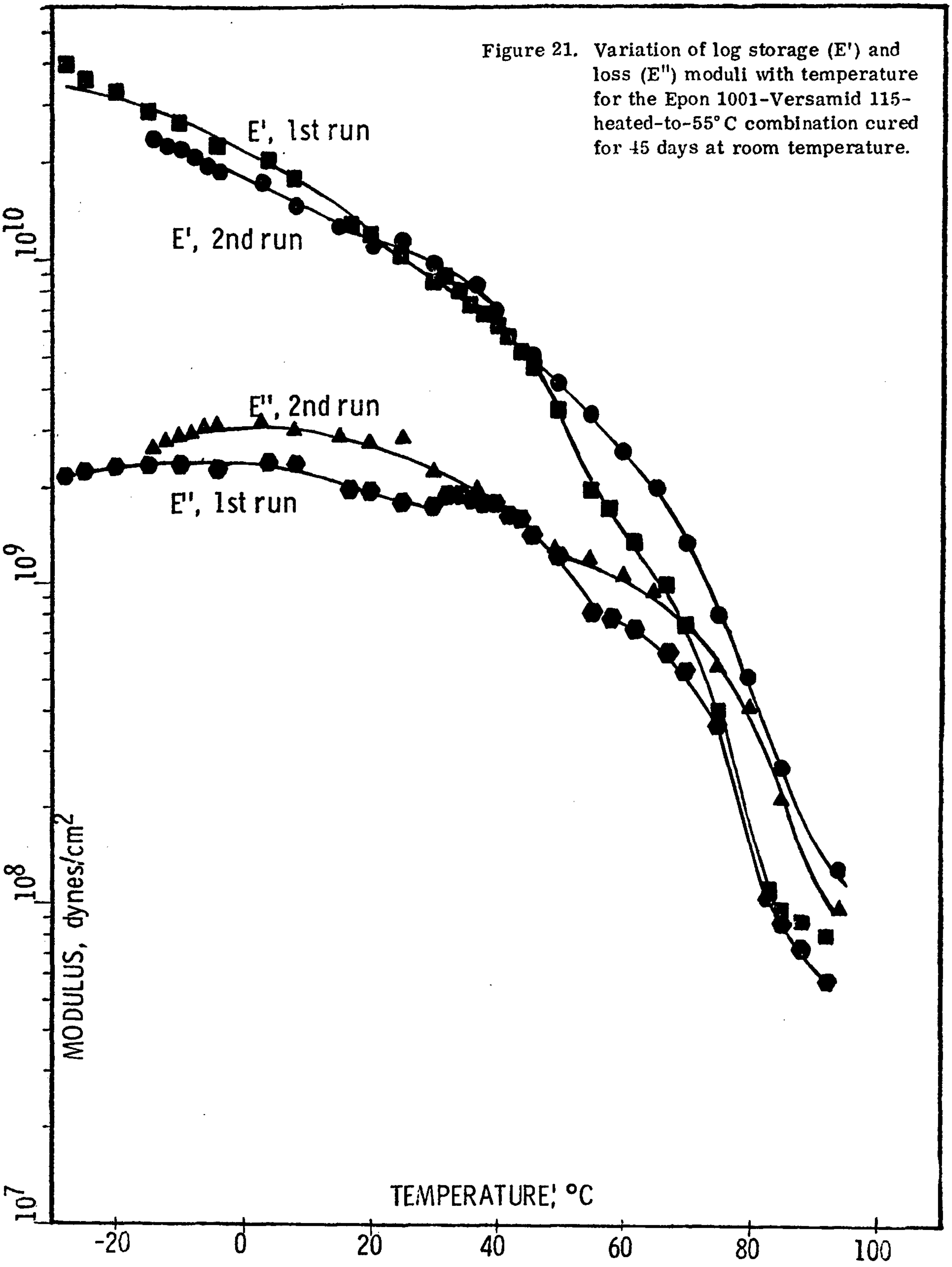


Figure 21. Variation of log storage (E') and loss (E") moduli with temperature for the Epon 1001-Versamid 115-heated-to-55° C combination cured for 45 days at room temperature.

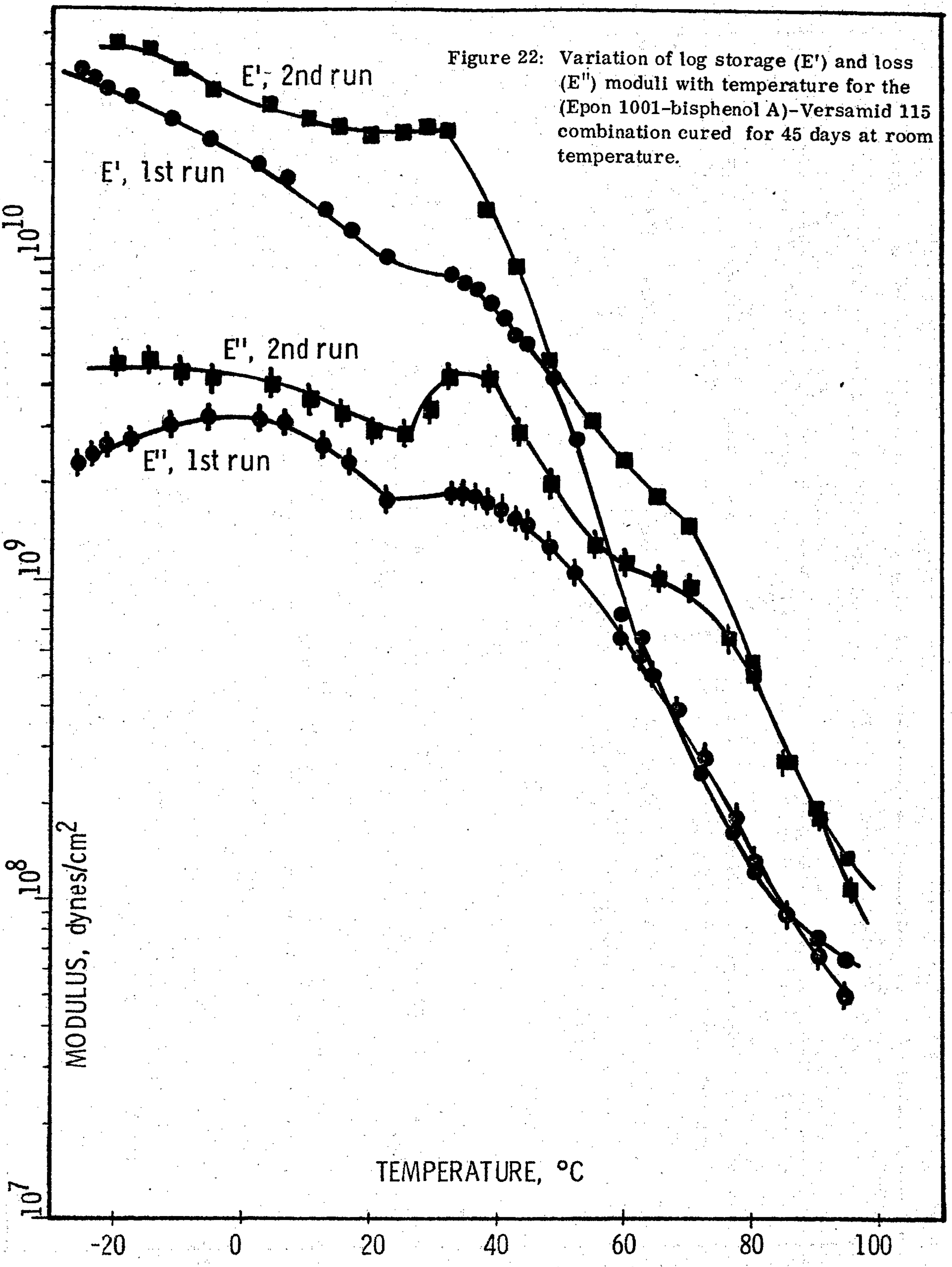


Figure 22: Variation of log storage (E') and loss (E") moduli with temperature for the (Epon 1001-bisphenol A)-Versamid 115 combination cured for 45 days at room temperature.

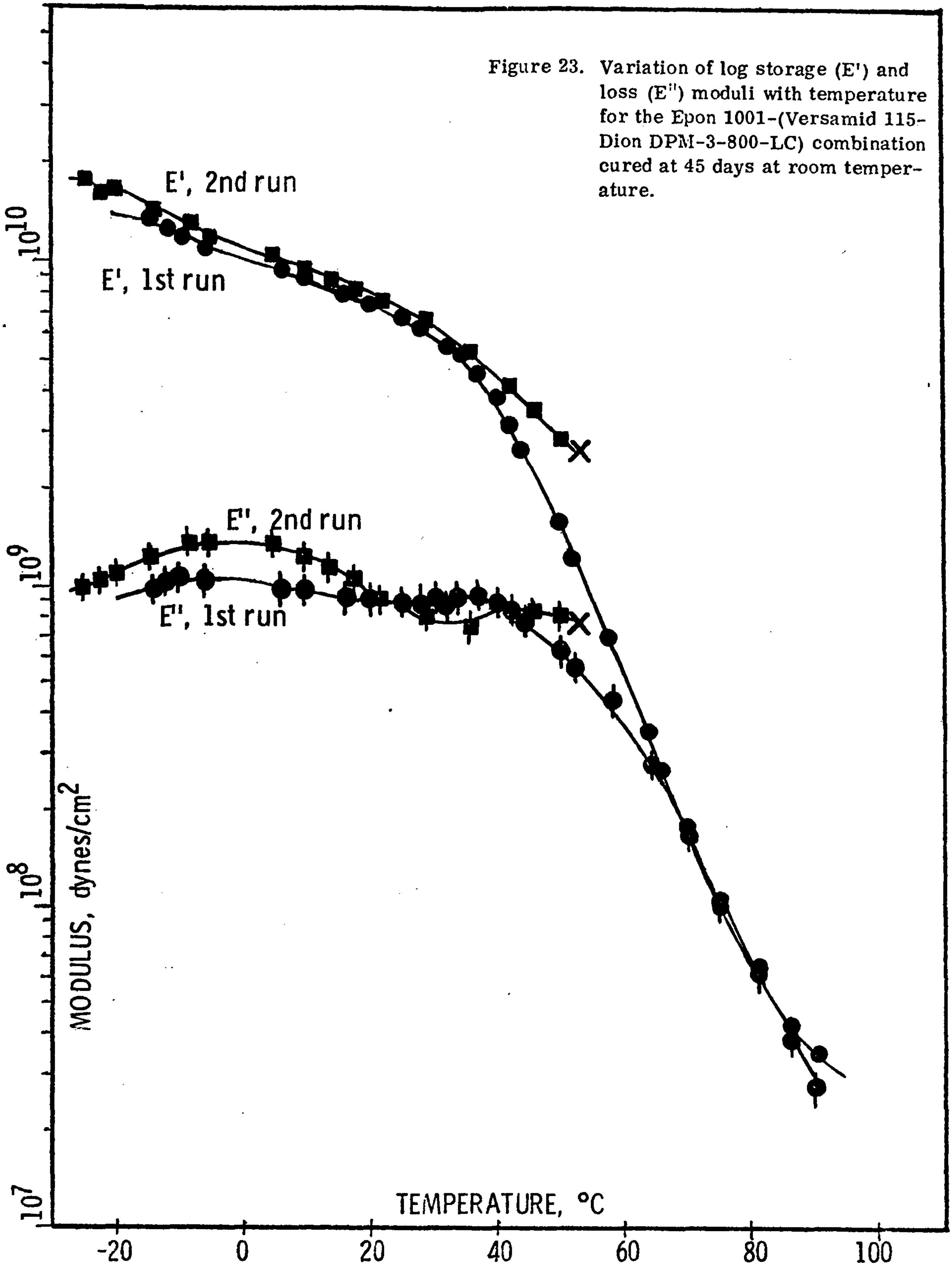


Figure 23. Variation of log storage (E') and loss (E") moduli with temperature for the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination cured at 45 days at room temperature.

but the second run gave a curve of high modulus with a pronounced peak at about 25° C; the loss moduli were also greater, even for the first run, and both curves showed two peaks; that for the second run showed a sharp second peak corresponding to the 25° C peak of the elastic modulus curve. The Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination (Figure 23) displayed a lower elastic modulus than the Epon 1001-Versamid 115 combination; some divergence between the curves was observed, but the sample broke at about 50° C in the second run; both loss modulus curves showed two peaks, but that of the second run were more accentuated.

In comparison, the Epon 1001-Versamid 115-cast-from-solvent combination (Figure 24) showed a distinctly different elastic modulus curve, which decreased only slightly in the temperature range -25° C to 50° C; the loss modulus curve showed a corresponding sharp single peak corresponding to the inflection point of the elastic modulus curve; the second run gave a slightly higher elastic modulus and correspondingly higher loss modulus, but this specimen broke at 50° C.

Table II summarizes the values for the glassy and rubbery moduli, E_g, and E_r, as well as for T_g.

TABLE II

Dynamic-Mechanical Properties of Epoxy Resin Films

	E_g, x10^{-10}, dynes/cm^2		E_r, x10^{-7}, dynes/cm^2		T_g, °C	
Combination	1st Run	2nd Run	1st Run	2nd Run	1st Run	2nd Run
I	3	3	4.9	7.9	10	-6, 50
II	3	4	7	8.5	-3, 33, 63	3, 65
III	4	5	6.3	8.5	-3, 34	-8, 34, 68
IV	2	2	3	--	0, 36	0, 45
V	3	4	14	--	63	--

These values emphasize the difference between the emulsion-cast and solvent-cast films.

D. Degree of Crosslinking by Solvent Extraction

Experiments were carried out to determine the proportion of crosslinked polymer in these epoxy resin films. In principle, such a determination could be carried out by extracting the soluble polymer with some suitable solvent, leaving the crosslinked polymer to be determined gravimetrically. In practice, however, the swelling of the film by the solvent would increase the rate of diffusion of the unreacted curing agent and epoxy resin prepolymers and thus increase the degree of crosslinking while the determination is being made. This further curing can be avoided by extracting the films at a low temperature, e.g., -20° C At this low temperature, the curing reaction is too slow for any appreciable curing to occur during the extraction.

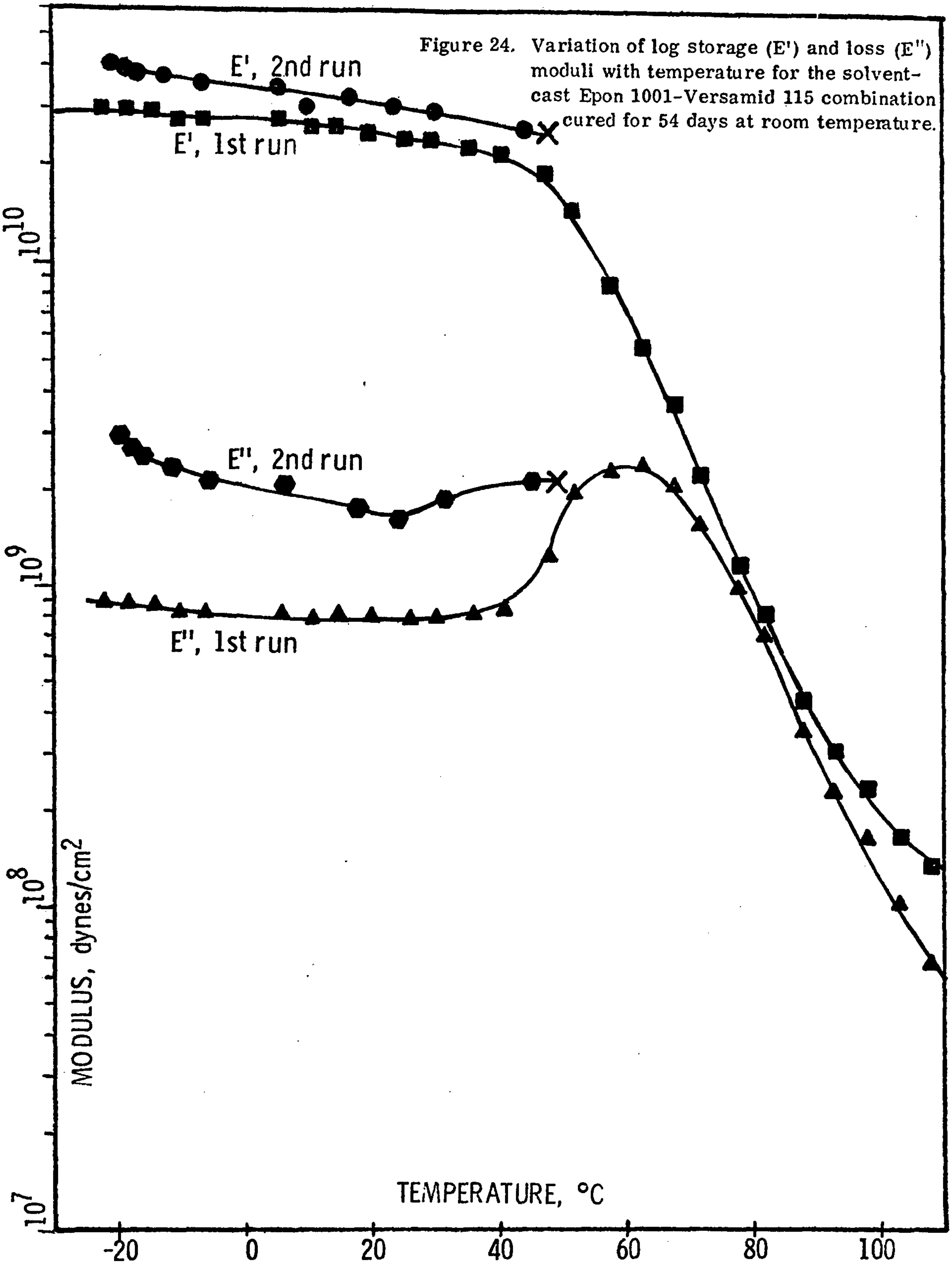


Figure 24. Variation of log storage (E') and loss (E") moduli with temperature for the solvent-cast Epon 1001-Versamid 115 combination cured for 54 days at room temperature.

Duplicate samples of films of Combinations I-V were extracted at -20° C in a relatively large volume of 1:1 toluene-methyl isobutyl ketone mixture. The film samples were immersed in the solvent for two days and then dried, weighed, and immersed in fresh solvent. This process was repeated until two consecutive weights were constant within experimental error. Usually, 15 days extraction were required to reach constant weight.

Table III gives the results of these extractions.

TABLE III

Extraction of Epoxy Resin Films with Toluene-Methyl Isobutyl Ketone Mixture

Combination	Initial Weight, gm	Swollen Weight, gm	Extracted Weight, gm	Percent Extracted	Percent Swelling
I	0.01130	0.01197	0.00987	12.66	21.88
	0.01760	0.01851	0.01522	13.52	21.62
			averages:	13.19	21.45
II	0.00984	0.00999	0.00872	11.38	14.56
	0.00910	0.00939	0.00815	10.44	15.20
			averages:	10.91	14.88
III	0.02346	0.02331	0.02010	14.32	15.97
	0.02552	0.02500	0.02175	14.77	14.94
			averages:	14.54	15.46
IV	0.01285	0.01090	0.00970	24.51	12.37
	0.02229	0.01891	0.01708	23.37	10.71
			averages:	23.94	11.54
V	0.04634	0.04608	0.04580	1.17	0.61
	0.04658	0.04625	0.04600	1.25	0.54
			averages:	1.21	0.58

For the Epon 1001-Versamid 115 combination, 13.2% of the polymer was extractable and the extent of swelling was 21.5%. In comparison, the Epon 1001-Versamid 115-heated-to-55° C combination showed a smaller portion of extractable polymer (10.9%) and a lower degree of swelling (14.9%), demonstrating that the pre-curing gave a higher degree and density of crosslinking. The (Epon 1001-bisphenol A)-Versamid 115 combination gave a higher percent extractable polymer (14.5%) and a lower degree of swelling (15.5%) than the control, indicating that the bisphenol A increases the crosslink density, but leaves more polymer uncrosslinked. Similarly, the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination gave an even higher percent extractable polymer (23.9%) and an even lower degree of swelling (11.5%). In contrast, the solvent-cast Epon 1001-Versamid 115 combination showed a very small proportion of extractable polymer (1.2%) and a very low degree of swelling (0.58%).

Thus, the solvent-cast Epon 1001-Versamid 115 combination gave a higher degree of crosslinking than the same conbination cast from emulsions. Pre-curing the mixed emulsions before casting the film increased the degree of crosslinking somewhat, but not to the level of the solvent-cast film. Moreover, the use of materials such as bisphenol A and Dion DPM-3-800-LC to increase the rate of the curing reaction evidently gave such a rapid crosslinking reaction at the interface between the deformed epoxy resin and curing agent particles that the further diffusion of the reactants was hindered, leaving the epoxy resin in the particle interior uncrosslinked.

E. Scanning Electron Microscopy of Film Surfaces and Fracture Cross-Sections

Scanning electron microscopy was used to determine the morphology of the films before and after solvent extraction. Examinations were made of the film surfaces and cross-sections fractured at liquid-nitrogen and room temperatures. For examination of the film surfaces, a portion of the film was mounted on a specimen stub, coated with a thin film of evaporated carbon, and examined in the scanning electron microscope. For the fracture cross-sections, portions of the films were fractured at liquid-nitrogen or room temperature and examined in a similar manner.

Figures 25-29 show the film surfaces of Combinations I-V, respectively, at two different magnifications. For the Epon 1001-Versamid 115 combination (Figure 25), the film surfaces were not smooth, but instead showed "pock marks" or depressions; there was little difference before and after solvent extraction, but the solvent-extracted sample showed a slightly greater surface porosity, consistent with the removal of 13.2% polymer. The Epon-1001-Versamid 115-heated-at-55° C combination (Figure 26) before solvent extraction showed a smoother surface with little evidence of "pock marks"; after solvent extraction, however, the "pock marks" appeared and the surface became roughened, consistent with the removal of 10.9% polymer. The (Epon 1001-bisphenol A)-Versamid 115 combination (Figure 27) showed many "pock marks" before extraction; these were deepened and accentuated by solvent extraction, consistent with the removal of a relatively large proportion (14.5%) of polymer. The Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination (Figure 28) showed clusters of large uncoalesced spheres embedded in a continuous film with some "pock marks", crevices, and fissures; these large spheres were removed by the solvent extraction, leaving many more "pock marks" and craters in the surface, consistent with the very high proportion (23.9%) of extractable polymer. These large particles are probably Epon 1001 particles, similar to those shown in the electron micrographs (Figure 17) and optical photomicrographs; apparently, the addition of Dion DPM-3-800-LC to the Versamid 115 increases the size of some of the emulsion droplets of the mixture to an extent where coalescence does not occur.

In comparison, the surface of the solvent-cast Epon 1001-Versamid 115 combination (Figure 29) was relatively smooth with no "pock marks", although there was some reticulated surface structure. The appearance of this film was changed but little by solvent extraction, consistent with the removal of only 1.21% polymer.

Figures 30-34 show the cross-section of films of Combinations I-V, respectively, fractured at liquid-nitrogen and room temperatures, before and after solvent extraction.

Figure 25. Scanning electron micrographs of the surfaces of Epon 1001-Versamid 115 films: A & B. control; C & D. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

Figure 26 Scanning electron micrographs of the surfaces of Epon 1001-Versamid 115-heated-to-55° C films: A. & B. control; C. & D. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

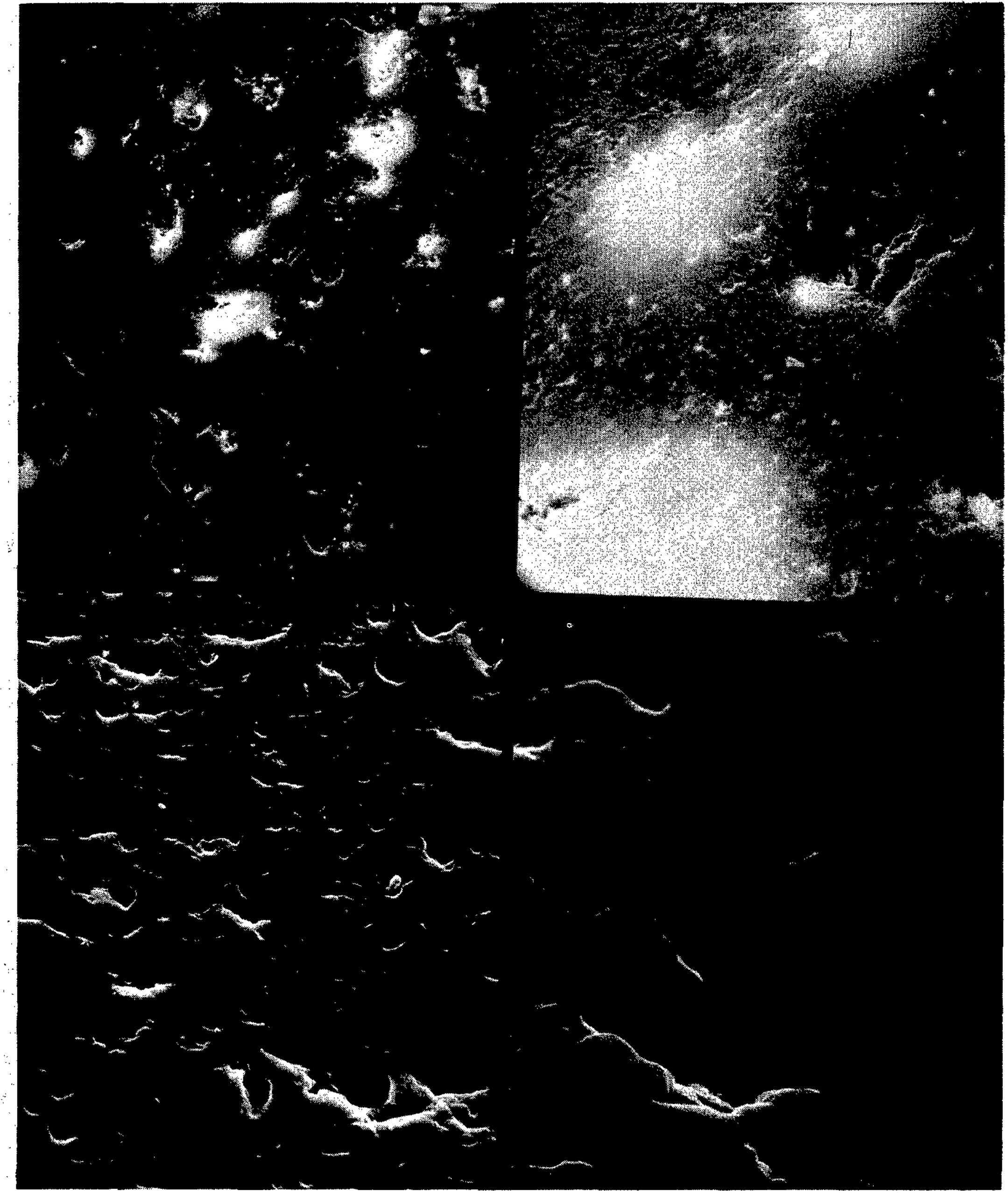


Figure 27. Scanning of electron micrographs of the surfaces of (Epon 1001-bisphenol A)-Versamid 115 films: A & B control; C & D extracted with 1:1 toluene-methyl isobutyl ketone mixture.

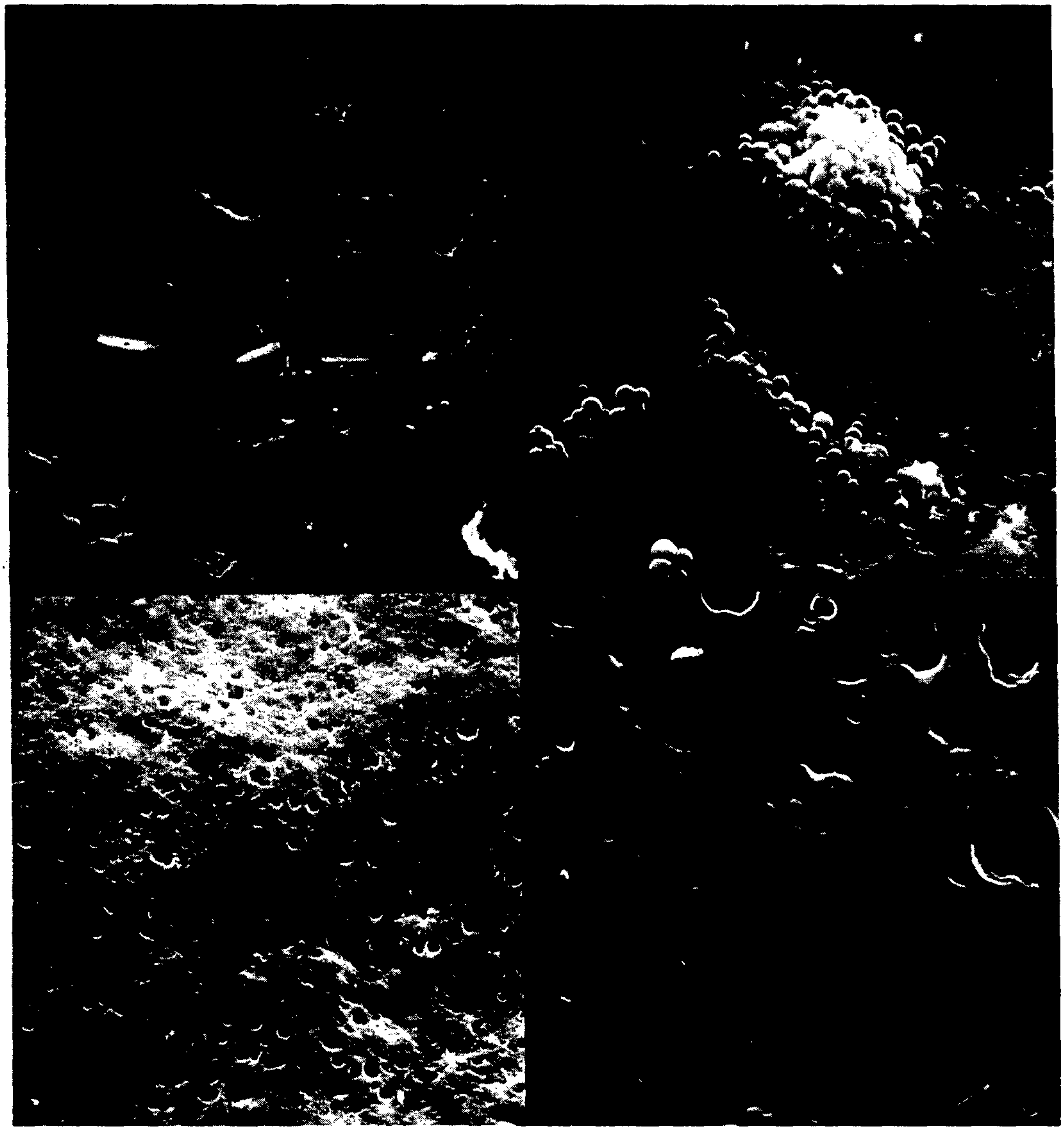


Figure 28. Scanning electron micrographs of the surfaces of Epon 1001-(Versamid 115-Dion DPM-3-800-LC) films: A & B control; C & D extracted with 1:1 toluene-methyl isobutyl ketone mixture.

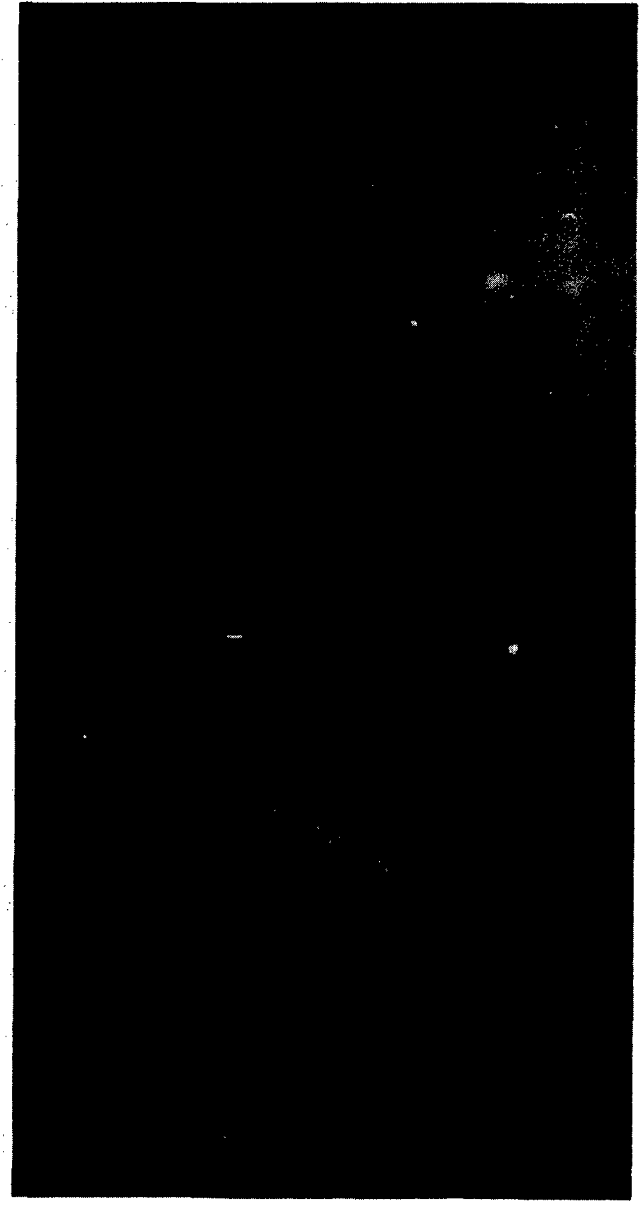


Figure 29. Scanning electron micrographs of the surfaces of solvent-cast Epon 1001-Versamid 115 films: A. control; B. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

The fracture cross-sections of the Epon 1001-Versamid 115 combination (Figure 30) were solid and typical of hard brittle polymers; there was little difference in appearance between films fractured at liquid-nitrogen or room temperatures, before or after solvent extraction. The appearance was similar to that of the solid, non-porous fracture cross-sections of the solvent-cast Epon 1001-Versamid 115 combination (Figure 34); however, the entities of the film exposed by fracture were larger for the solvent-cast than for the emulsion-cast film. For the Epon 1001-Versamid 115-heated-to-55° C combination (Figure 31), the fracture cross-section of the film before solvent extraction appeared much more reticulated, with many asperities and craters, than the film after solvent extraction, which appeared similar to the solvent-cast Epon 1001-Versamid combination (Figure 34). For the (Epon 1001-bisphenol A)-Versamid 115 combination (Figure 32), the cross-section of the film fractured at liquid-nitrogen temperature before solvent extraction was also reticulated, with asperities and craters; after solvent extraction, these asperities had disappeared and the surface was smoother, but still displayed fissures and craters; the fracture of the film at room temperature exposed many large uncoalesced particles, which were evidently poorly adhered to the rest of the film; the cross-section of the solvent-extracted film fractured at room-temperature was much smoother with no evidence of poorly-adhered particles. For the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination (Figure 33), the cross-section of the film fractured at liquid-nitrogen temperature was reticulated, with many asperities and craters; after solvent extraction, these asperities had disappeared and the surface was smooth and solid; the cross-sections of the films fractured at room temperature and liquid-nitrogen temperature were similar in appearance.

F. Differential Scanning Calorimetry of Epoxy Resin Films

The degree of curing of an epoxy resin system can be determined by differential scanning calorimetry (DSC). A small sample of the epoxy resin system and a reference sample are heated at a predetermined rate, and the amount of energy required to keep the temperature of the reference sample the same as that of the epoxy resin sample is a measure of the further curing reactions that occur. This method was applied to the Epon 1001 and Versamid 115 components of the epoxy resin system as well as to the films of Combinations I-V.

Figure 35 shows the DSC scans (scan rate 10° C/min) of the Epon 1001 epoxy resin before emulsification, a film cast from an Epon 1001 emulsion (SR-1), the Versamid 115 curing agents before emulsification, and a film cast from a Versamid 115 emulsion (SR-3).

The Epon 1001 sample showed inflection points corresponding to a second-order transition temperature $\underline{T_g}$ of 22° C and a crystalline melting temperature $\underline{T_m}$ of 76° C. Moreoever, at 147° C it started to degrade, as evidenced by the sharp upturn of the curve. In comparison, the Epon 1001 emulsion film sample (16.47 mg) showed a sharp endothermic peak at 37° C; when the sample was cooled and re-run, a smaller endothermic peak corresponding to $\underline{T_g}$ was observed at 36° C as well as an inflection point corresponding to $\underline{T_m}$ at 97° C. The emulsion film sample showed no signs of degradation at 147° C as did the pure resin, but instead showed a slight exotherm, indicating that some curing had taken place at that temperature. This curing is attributed to the hexadecyltrimethylammonium bromide emulsifier acting as a catalyst. The sharp endothermic peak observed in the first heating of the

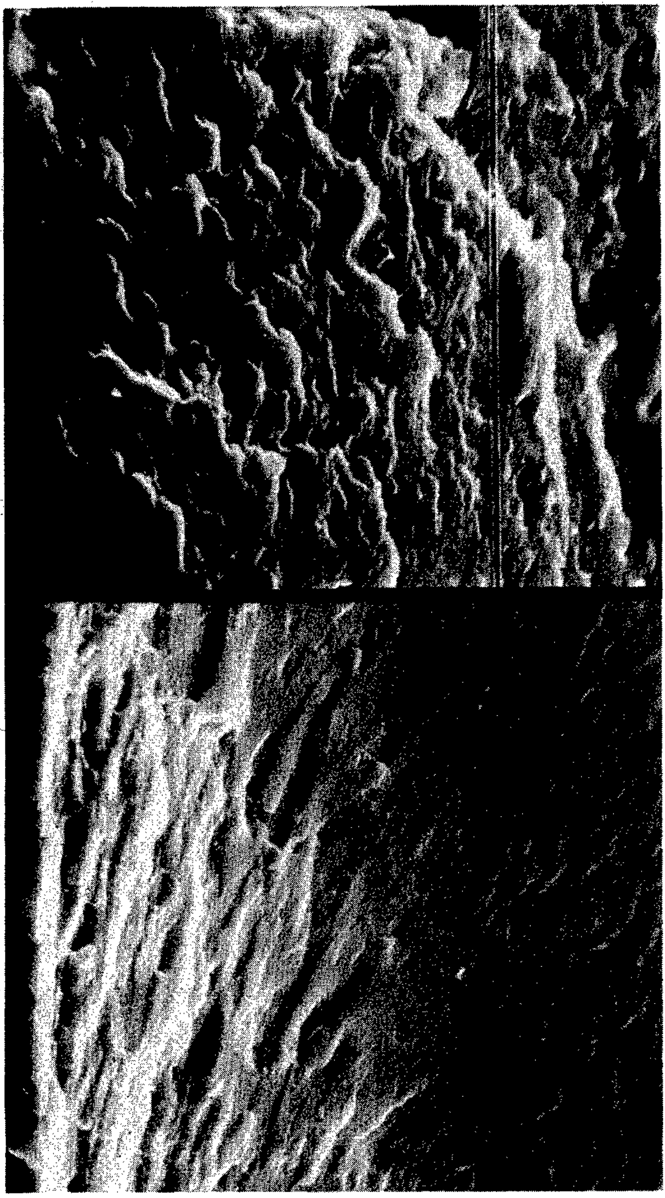


Figure 30. Scanning electron micrographs of fracture cross-sections of Epon 1001-Versamid 115 films: fractured at liquid-nitrogen temperature: A. control; B. Extracted with 1:1 toluene-methyl isobutyl ketone mixture.

Figure 31. Scanning electron micrographs of fracture cross-sections of Epon 1001-Versamid 115-heated-to-55° C films fractured at liquid-nitrogen temperature: A. control; B. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

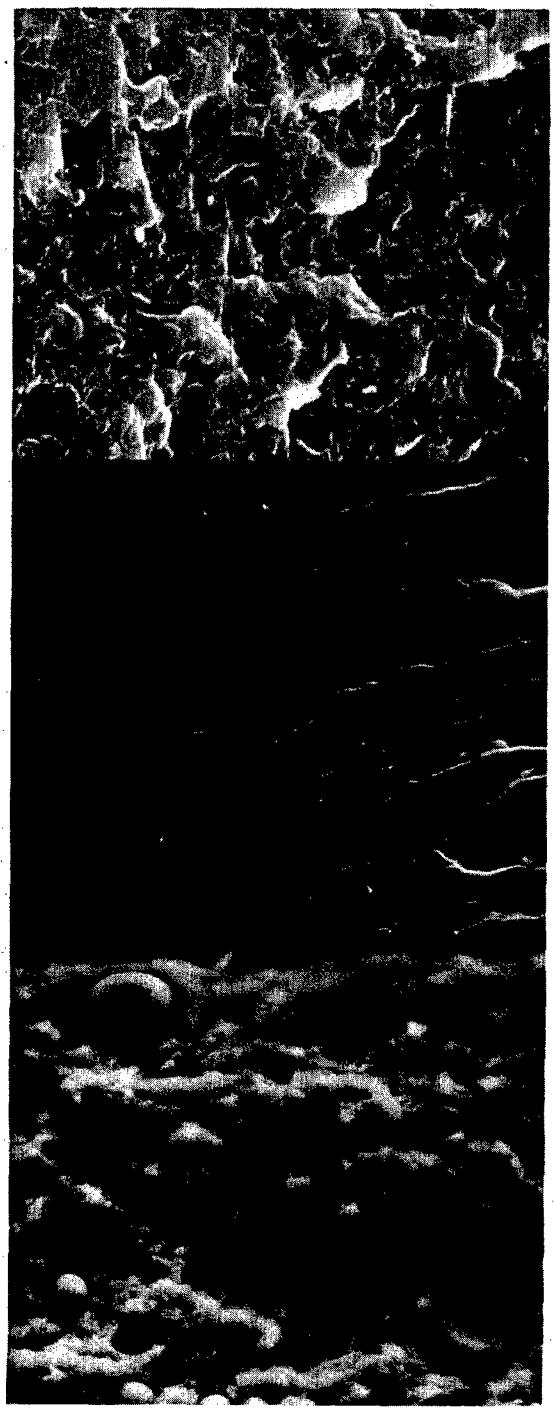


Figure 32. Scanning electron micrographs of fracture cross-sections of (Epon 1001-bisphenol A)-Versamid 115 films: A. control fractured at liquid-nitrogen temperature; B. extracted with 1:1 toluene-methyl isobutyl ketone mixture and fractured at liquid-nitrogen temperature; C. control fractured at room temperature.

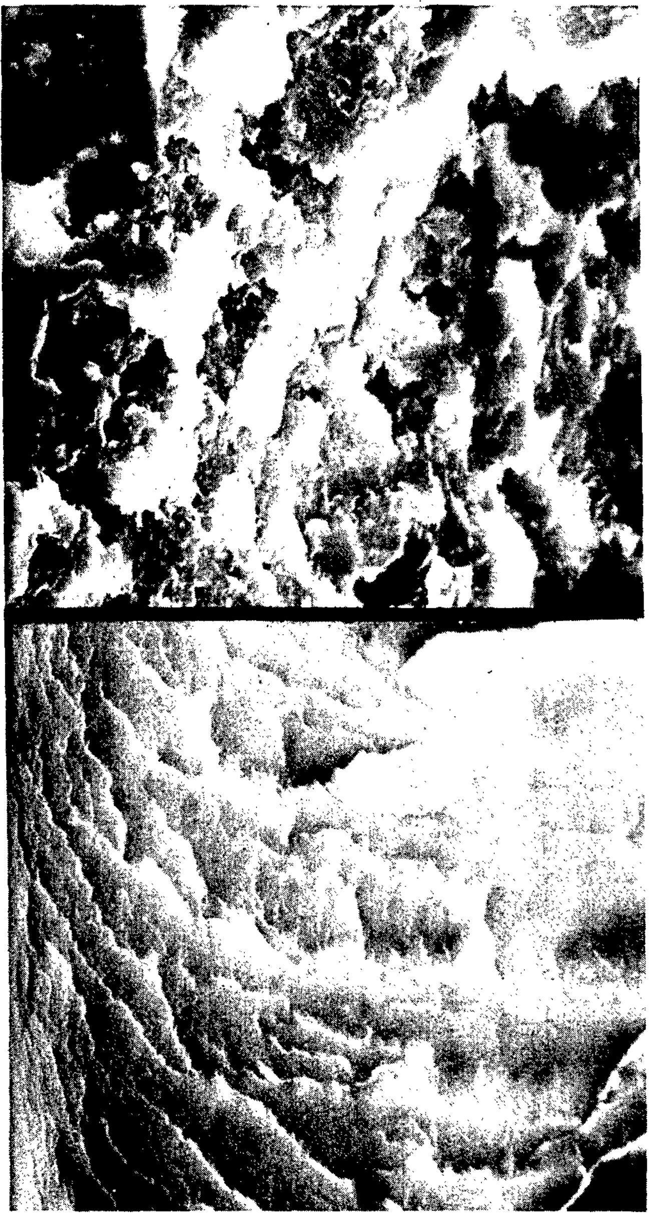


Figure 33. Scanning electron micrographs of fracture cross-sections of Epon 1001-(Versamid 115-Dion DPM-3-800-LC) films fractured at liquid-nitrogen temperature: A. control; B. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

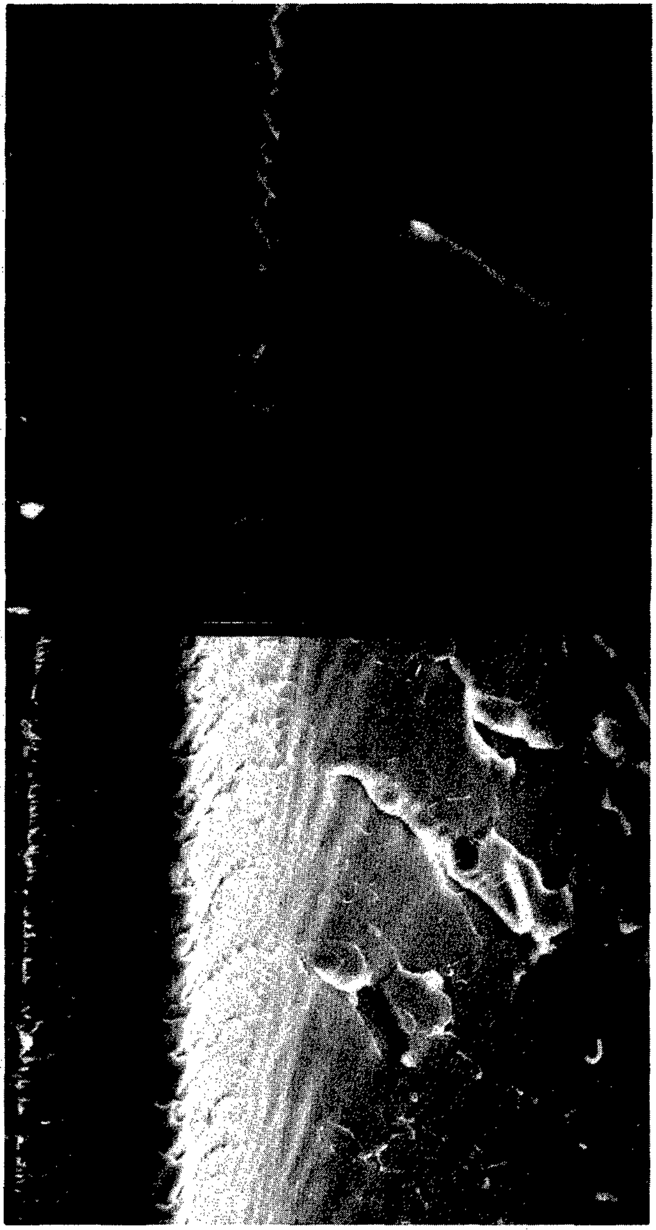


Figure 34. Scanning electron micrographs of fracture cross-sections of solvent-cast Epon 1001-Versamid 115 films fractured at liquid-nitrogen temperature: A. control; B. extracted with 1:1 toluene-methyl isobutyl ketone mixture.

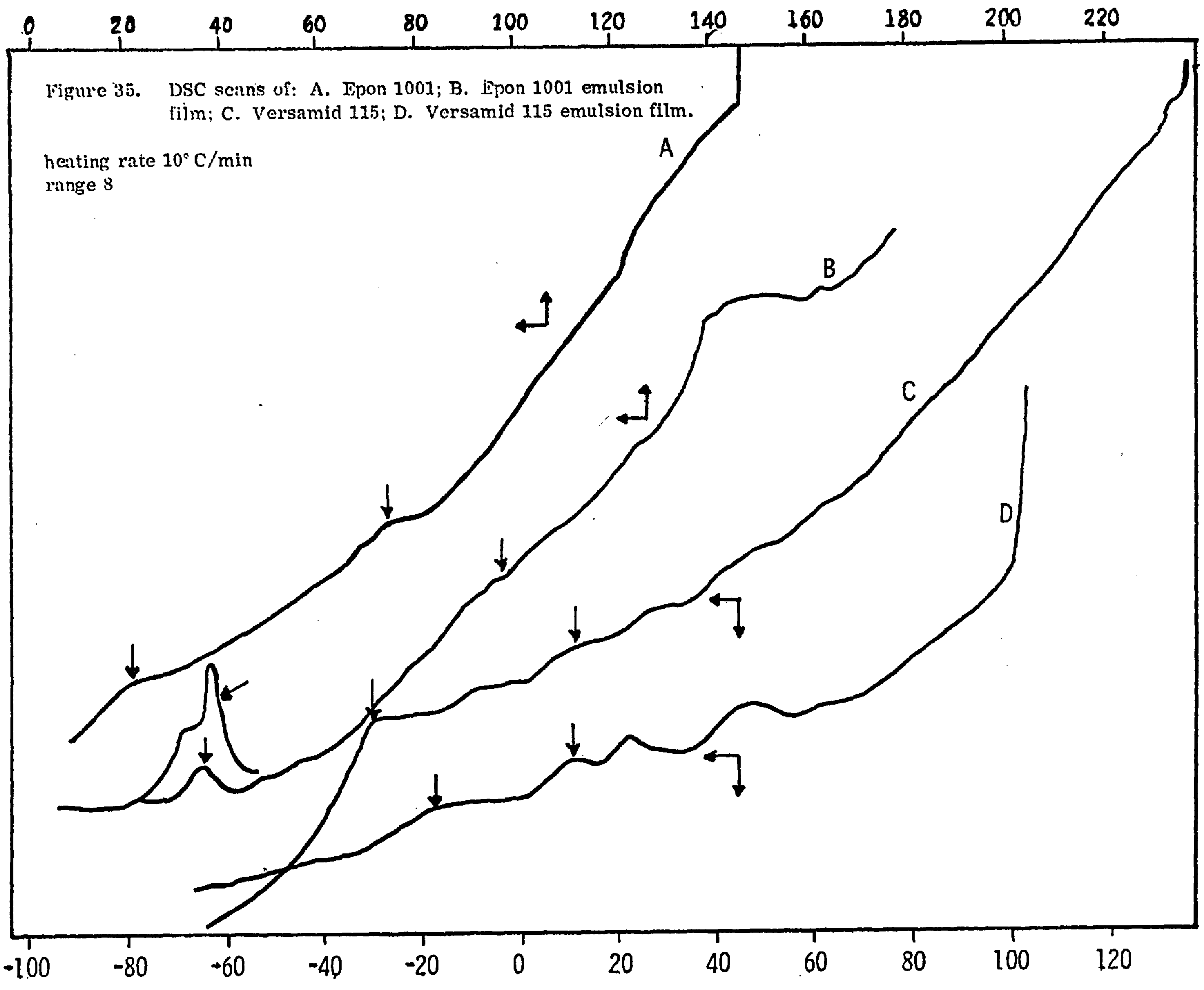


Figure 35. DSC scans of: A. Epon 1001; B. Epon 1001 emulsion film; C. Versamid 115; D. Versamid 115 emulsion film.

heating rate 10° C/min
range 8

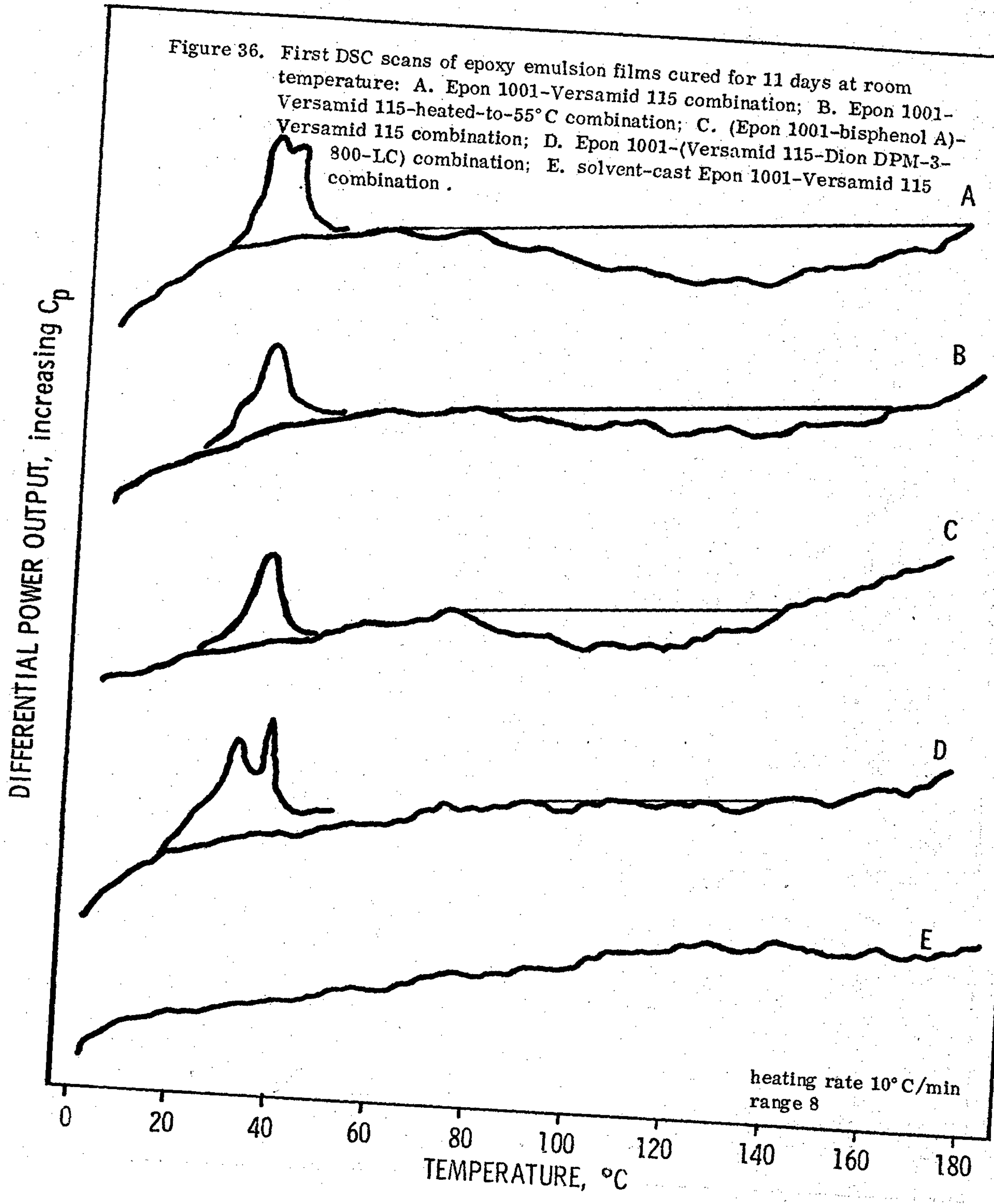


Figure 36. First DSC scans of epoxy emulsion films cured for 11 days at room temperature: A. Epon 1001-Versamid 115 combination; B. Epon 1001-Versamid 115-heated-to-55° C combination; C. (Epon 1001-bisphenol A)-Versamid 115 combination; D. Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination; E. solvent-cast Epon 1001-Versamid 115 combination.

Figure 37. Second DSC scans of epoxy emulsions films cured for 11 days at room temperature: A. Epon 1001-Versamid 115 combination; B. Epon 1001-Versamid 115-heated-to-55° C combination; C. (Epon 1001-bisphenol A)-Versamid 115 combination; D. Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination; E. solvent-cast Epon 1001-Versamid 115 combination.

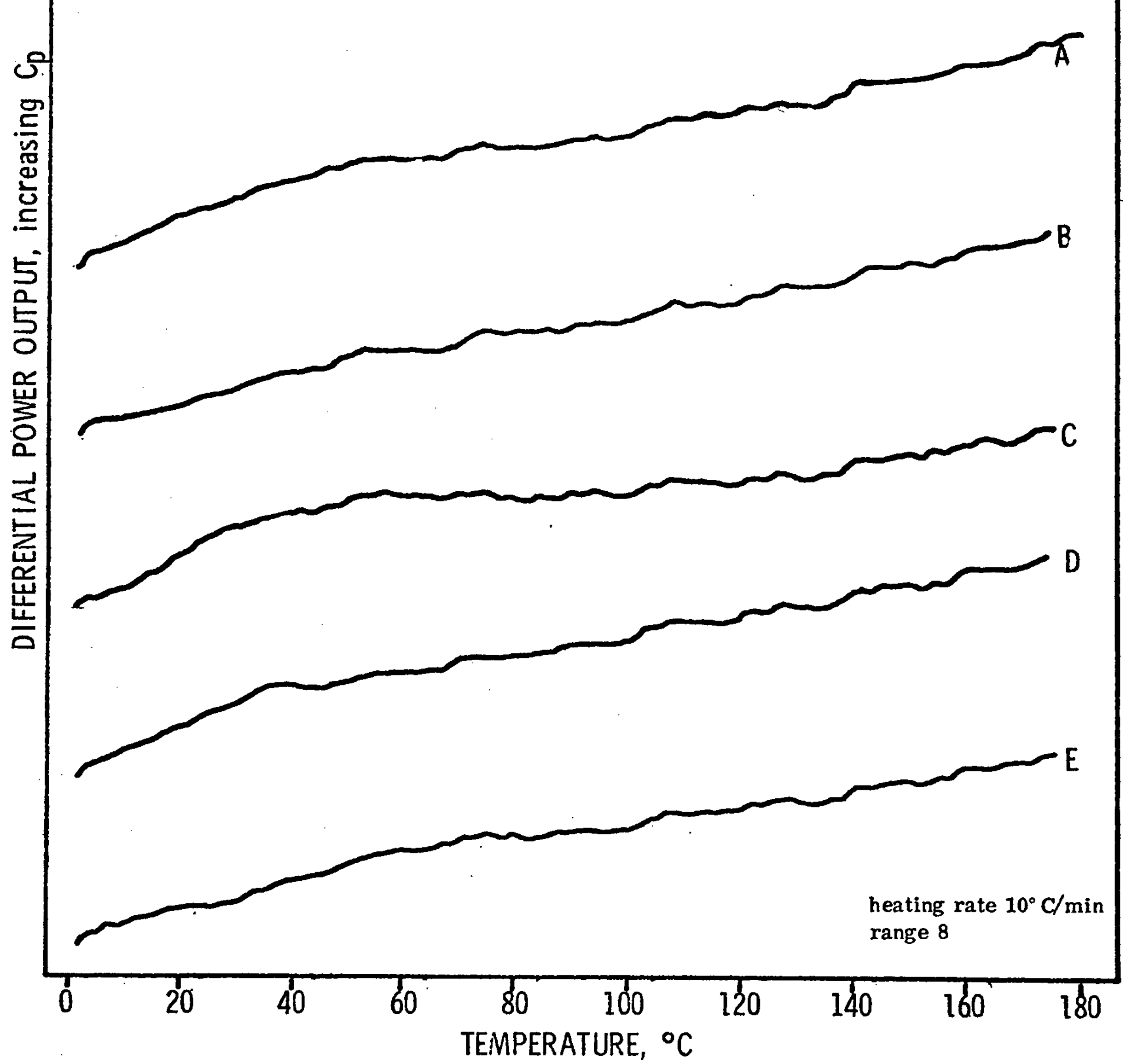


Figure 38. First DSC scans of epoxy emulsion films cured for 50 days at room temperature: A. Epon 1001-Versamid 115 combination; B. Epon 1001-Versamid 115-heated-to-55° C combination; C. (Epon 1001-bisphenol A)-Versamid 115 combination; D. Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination; E. solvent-cast Epon 1001-Versamid 115 combination.

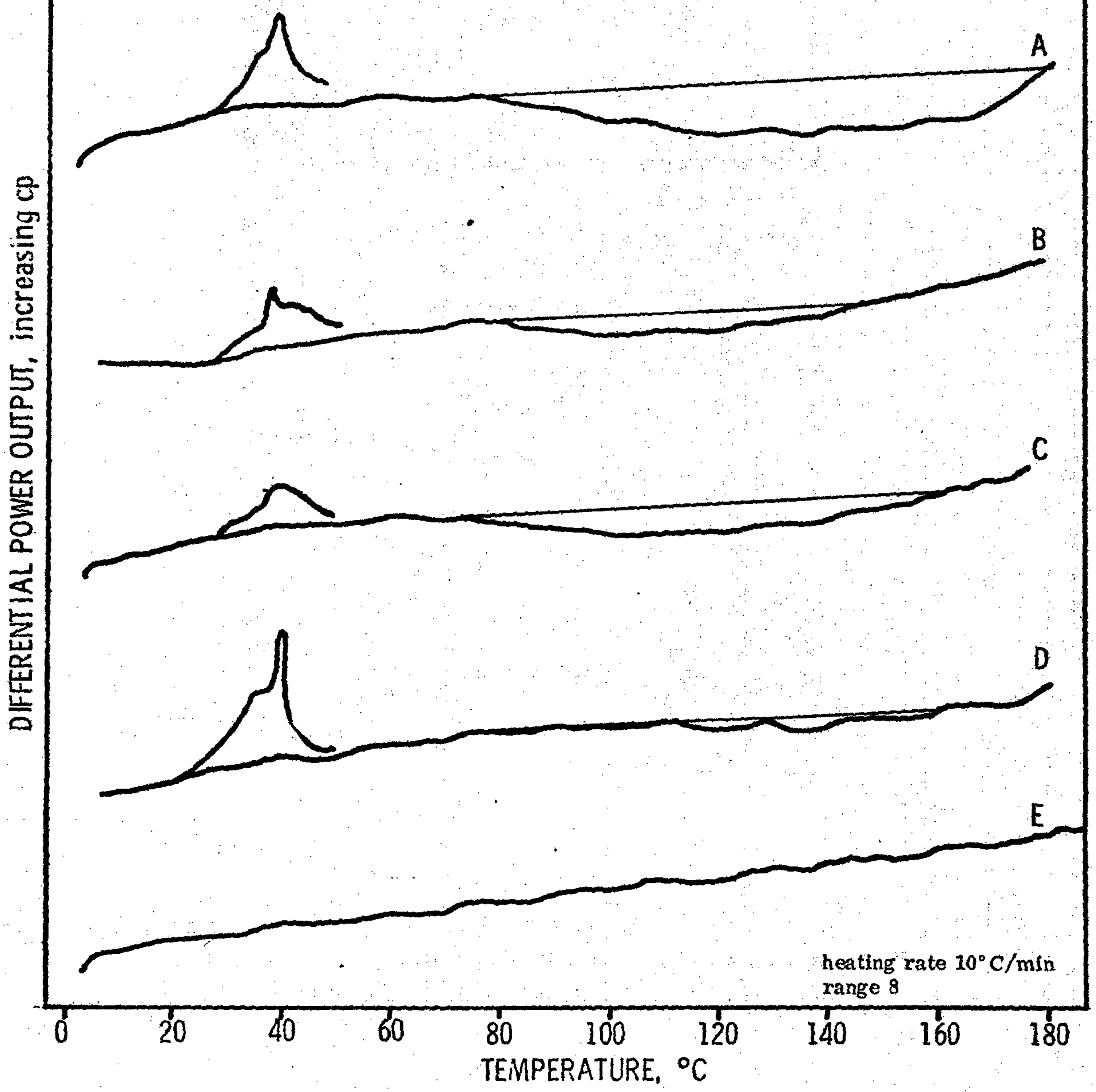
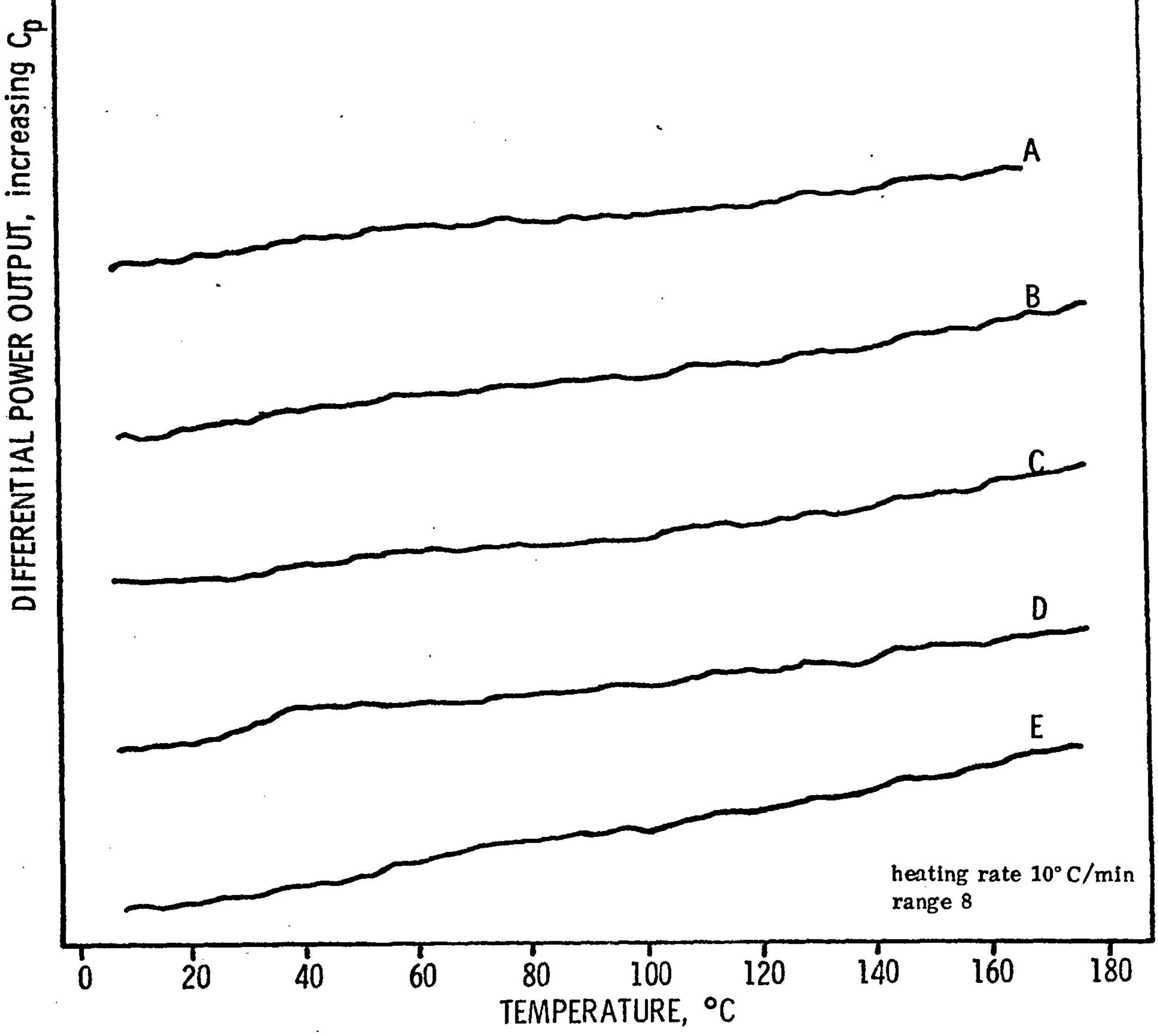


Figure 39. Second DSC scans of epoxy emulsion films cured for 50 days at room temperature: A. Epon 1001-Versamid 115 combination; B. Epon 1001-Versamid 115-heated-to-55° C combination; C. (Epon 1001-bisphenol A)-Versamid 115 combination; D. Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination; E. solvent-cast Epon 1001-Versamid 115 combination.



heating rate 10° C/min
range 8

Epon 1001 emulsion film sample is attributed to residual stresses that are relieved when the film is heated (discussed in more detail below).

The Versamid 115 emulsion film sample (12.89 mg) showed a small endothermic peak at -18°C corresponding to T_g and a larger endothermic peak at 13°C corresponding to T_m. However, it showed the sharp increase in slope at 100°C indicative of degradation.

The films of Combinations I-V were scanned (Scan rate 10°C/min) after 11 and 50 days ageing at room temperature. Figures 36 and 37 show the first and second scans of the films aged 11 days; Figures 38 and 39 show the first and second scans of those aged 50 days. All first scans of the mixed-emulsion films showed endothermic peaks in the temperature range 21-51°C. At the end of the peak, the samples were cooled and re-run; the re-runs showed no such peaks, nor were these peaks observed in the second scans of these samples (Figures 37 and 39). The solvent-cast Epon 1001-Versamid 115 combination did not show such peaks in any of the scans.

As mentioned before, these endothermic peaks are attributed to residual stresses in the emulsion-cast films that are relieved when the film is heated past 51°C and thus do not appear in the second scans. These stresses probably arise from the coalescence of the emulsion particles to form a continuous film, beginning at the point where the particles come into irreversible contact with one another (0.74 volume fraction for rhombohedrally-packed spheres) and continuing through the coalescence of the spheres to form a continuous film. During this process, the film usually does not retract from its original wet area; the shrinkage that must occur is in the thickness of the film. This uneven shrinkage may set up stresses that are not present in solvent-cast films.

Table IV gives the values of these residual stresses as measured by the area under the peak relative to the re-run of the first scan.

TABLE IV

Residual Stresses in Epoxy Resin Films

Combination	Residual Stress, cal/gm 11 days	50 days ageing	Average
I	22.34	22.02	22.18
II	16.58	18.30	17.44
III	14.93	16.31	15.62
IV	25.00	23.64	24.32
V	0	0	0

These residual stresses do not vary with ageing time; the values at 11 and 50 days ageing were within experimental error and hence are expressed as averages.

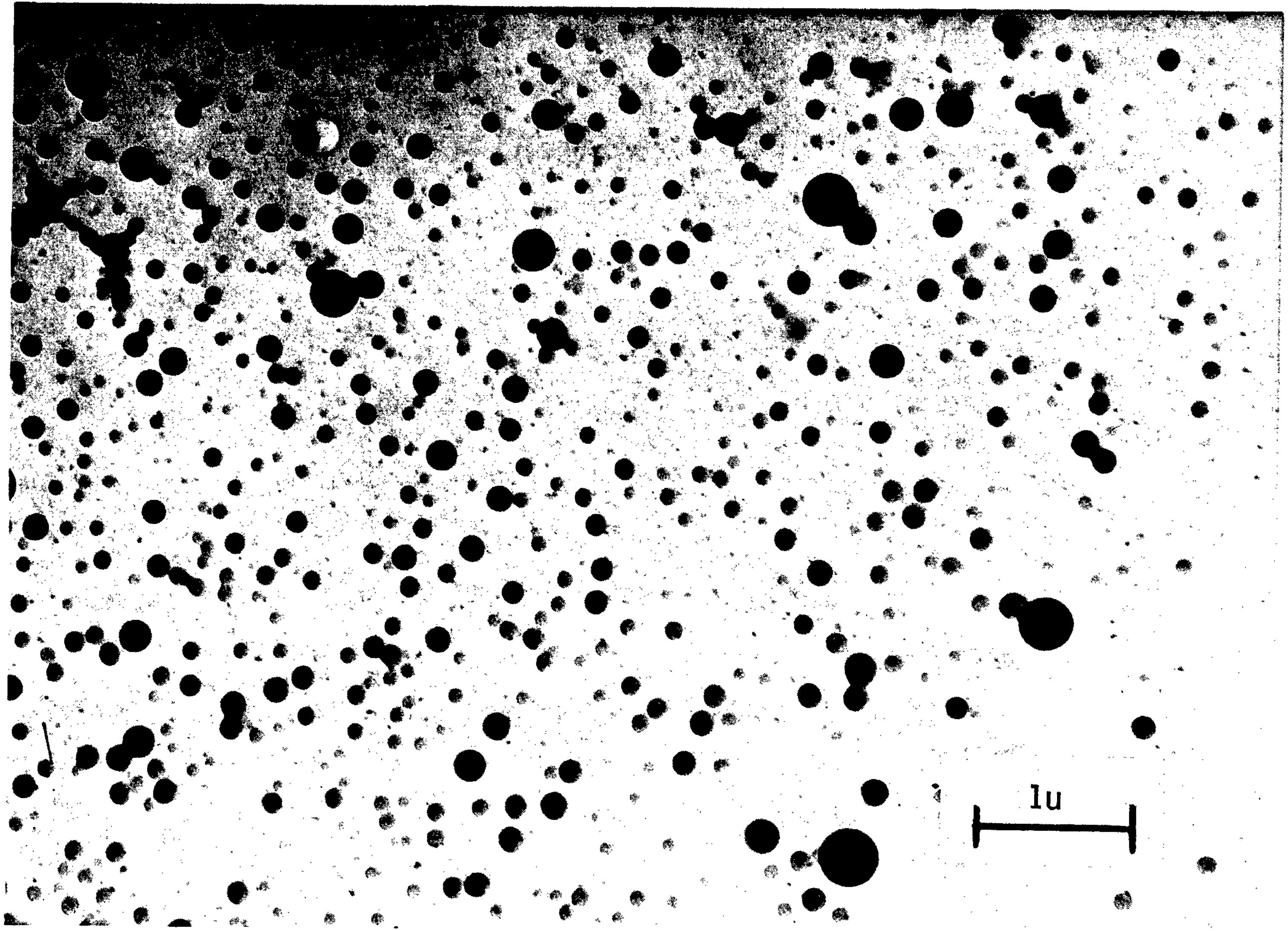


Figure 40. Transmission electron micrograph of a diluted dispersion of Experiment X395 (similar to X364) polyurethane emulsion freeze-dried on a cold stage in the electron microscope.

Figures 36-39 also show that all of the emulsion-cast films displayed exothermic peaks in the re-runs of the first scan. These exothermic peaks are attributed to the further curing of the films that occurs upon heating. These exothermic peaks did not appear in the second scans, indicating that the curing reaction was completed in the first scan or at least that there was no further curing during the second scan. Table V summarizes the heats of reaction of these exothermic peaks as measured by the area between the exothermic peak and a smooth curve drawn assuming no curing had occurred.

TABLE V

Exothermic Heats of Reaction for Epoxy Resin Systems

Combination	Sample Weight, mg		Heat of Reaction, cal/gm	
	11 days	50 days	11 days	50 days
I	19.38	11.06	68.0	126.8
II	19.50	9.74	33.0	37.6
III	19.10	10.26	34.2	54.9
IV	19.10	14.88	8.4	9.5
V	20.19	11.09	0	0

This exothermic heat of reaction is often used to determine the degree of cure of epoxy resin systems: the smaller the exothermic heat of reaction observed when the sample is heated, the greater is the degree of cure of the original sample. According to this principle, the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination showed the greatest degree of cure of the emulsion systems; however, this sample had a relatively large proportion of uncrosslinked polymer (23.9%) as well as a significant degree of swelling (11.5%). This apparent anomaly is attributed to the diffusion control of the curing reaction in emulsion-cast films. During film formation, the epoxy resin particles coalesce with the curing agent particles, and the curing reaction begins at the interface between the deformed particles. The crosslinked polymer formed in this interface by this curing reaction hinders the diffusion of the curing agent molecules into the epoxy resin particles (an increase in T_g of a polymer always decreases its permeability) so that further curing is dependent upon diffusion of the curing agent through this crosslinked layer. When the film is subjected to DSC, the temperature increase gives both a sudden exothermic reaction and an increased rate of diffusion of the curing agent molecules; however, the curing reaction soon becomes diffusion-controlled and for all practical purposes ceases, so that the second scan shows no peaks even though the curing reaction may still be incomplete.

For the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination, the smaller, less numerous Dion DPM-3-800-LC molecules diffuse rapidly to the interface between the epoxy resin and curing agent particles and initiate the curing reaction, which quickly forms a tightly crosslinked network of polymer throughout the interfaces between the coalesced particles. This tightly crosslinked layer hinders the diffusion of the larger, more numerous

Versamid 115 molecules to such an extent that a significant proportion of the Epon 1001 resin in the particle cores remains uncured. Moreover, the clusters of larger-size Epon 1001 particles found in this film (Figure 28) would accentuate the diffusion control of the curing reaction. This explanation is consistent, not only with the exothermic heats of reaction, but also with the solvent extraction and dynamic-mechanical results.

The foregoing explanation can also be applied to the other films. The Epon 1001-Versamid 115 combination showed the greatest exothermic heats of reaction (and hence the smallest degree of cure) of the emulsion-cast film samples; these values probably represent a relatively complete degree of curing. As expected, the Epon 1001-Versamid 115-heated-to-55° C combination showed smaller exothermic heats of reaction (because of the pre-curing in the emulsion state); these values also probably represent a relatively complete degree of curing. The (Epon 1001-bisphenol A)-Versamid 115 combination showed exothermic heats of reaction greater than those of the Epon 1001-Versamid 115-heated-to-55° C combination and less than those of the Epon 1001-Versamid 115 combination. This system is similar to the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination except that it is the bisphenol A that diffuses to the interface and increases the rate of the crosslinking reaction that slows the diffusion of the Versamid 115 molecules. Apparently, this rapid crosslinking reaction is not as effective as in the former case, as this combination displayed a smaller proportion of uncrosslinked polymer (14.5%) and a greater degree of swelling (15.5%). The solvent-cast Epon 1001-Versamid 115 system showed no exothermic heat of reaction as expected, because this system comprises a molecular mixture of the epoxy resin and curing agent molecules; diffusion control is not such an important factor in this curing reaction.

The diffusion control of the curing reaction is confirmed by the greater reaction isotherms of the 50-day-old films. These greater values are attributed to the increased availability of curing agent molecules resulting from diffusion during 50 days ageing relative to those available in 11 days ageing. If the curing reaction were not diffusion-controlled and the reaction exotherms represented its completion during the DSC scan, the reaction exotherms of the 50-day-old samples should be smaller than those of the 11-day-old samples because some curing should have occurred during the 11-50 day interval. That the opposite was observed indicates that the curing observed during the DSC scan involves only those curing agent molecules that have diffused to the epoxy resin molecules, leaving the curing reaction probably still incomplete.

Table VI shows that this increase in the reaction exotherm between 11 and 50 days ageing can be correlated with the degree of swelling of the film during solvent extraction.

TABLE VI

Correlation of Reaction Exotherms with Degree of Swelling

Combination	Percent Increase in Reaction Exotherm Between 11 and 50 days ageing	Percent Swelling
I	86.5	21.5
III	60.6	15.5
II	14.1	14.9
IV	13.5	11.5

This correlation is explained as follows: upon ageing at room temperature, the curing agent molecules slowly diffuse through the crosslinked interfacial layer into the uncrosslinked core of the epoxy resin particles, where they would eventually react; however, when the sample is heated during the DSC scan, these molecules react rapidly and the diffusion flux of curing agent molecules is increased. Thus, the extent of curing that occurs during the DSC scan depends upon the crosslink density of the interfacial layer and the particle size of the epoxy resin particles. Therefore, the lower the crosslink density (as measured by the degree of swelling), the greater the diffusion flux during ageing and hence the greater the increase in extent of reaction between 11 and 50 days ageing.

Table VI shows that the Epon 1001-Versamid 115 combination had the smallest crosslink density and the greatest increase in reaction exotherm between 11 and 50 days ageing, and the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination, the greatest crosslink density and the smallest increase in reaction exotherm. The (Epon 1001-bisphenol A)-Versamid 115 and Epon 1001-Versamid 115-heated-to-55° C combinations had intermediate values of crosslink density and increase in reaction exotherm. The Epon 1001-Versamid 115-heated-to-55° C combination had a higher crosslink density and smaller reaction exotherms as well as a smaller increase between 11 and 50 days ageing than the Epon 1001-Versamid 115 standard. These differences are consistent with the pre-curing of the mixed emulsions before film-casting, which would slow the diffusion of curing agent molecules during ageing at room temperature. For the (Epon 1001-bisphenol A)-Versamid 115 and Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combinations, the more rapid initial curing results in a more tightly crosslinked interfacial layer through which the curing agent molecules must diffuse, and their larger particle size results in a greater distance the curing agent molecules must diffuse into the particle core to completely cure the epoxy resin. The (Epon 1001-bisphenol A)-Versamid 115 combination had a smaller crosslink density, a greater reaction exotherm, and a greater increase between 11 and 50 days ageing than the Epon 1001-(Versamid 115-Dion DPM-3-800-LC) combination, probably because the molecular size of bisphenol A is smaller than that of Dion DPM-3-800-LC and its mechansim of reaction is different.

Table VII shows that there is no simple correlation between the residual stresses of the emulsion films and the crosslink density, percent extractable polymer, heats of reaction, or the increase in heat of reaction between 11 and 50 days ageing.

TABLE VII

Correlation of Residual Stresses of Epoxy Resin Films

Combination	Residual Stress, cal/gm	Percent Swelling	% Polymer Extracted	Heat of Reaction, cal/gm		
				11 days	50 days	% Increase
IV	24.3	11.5	23.9	8.4	9.5	13.5
I	22.2	21.5	13.2	68.0	126.8	86.5
II	17.4	14.9	10.9	33.0	37.6	14.1
III	15.6	15.5	14.5	34.2	54.9	60.7
V	0	0.58	1.21	0	0	--

These residual stresses are probably a complex function of the particle-size distribution of the epoxy resin and curing agent emulsions and hence do not correlate with the other parameters of the film. For the two films prepared from the same emulsions--the Epon 1001-Versamid 115 and Epon 1001-Versamid 115-heated-to-55° C combinations--the residual stress was smaller for the sample that was pre-cured in the emulsion state; this correlated with decreased percent polymer extracted, increased crosslink density, decreased reaction exotherm, and decreased difference in reaction exotherm between 11 and 50 days ageing.

The second DSC scans (Figures 37 and 39) show that all film samples without exception displayed inflection points at 104° and 144° C, which correspond to the degradation temperatures T_d of Versamid 115 (100° C) and Epon 1001 (147° C), respectively. These films also showed other inflection points, which are attributed to the second-order transition temperatures of the crosslinked films. Table VIII compares these second-order transition temperatures determined by DSC with those determined by the Rheovibron Elastoviscosimeter.

TABLE VIII

Second-Order Transition Temperatures of Epoxy Resin Films

	Second-Order Transition Temperatures, °C		
	DSC		Rheovibron
Combination	11 days	50 days	Viscosimeter (2nd run)
I	34, 67	17, 52	-6, 50
II	47, 67	35, 57	3, 65
III	30	33, 50	-8, 34, 68
IV	37	34, 71	0, 45
V	27, 67	53	--

Epon 1001: $T_g = 22$ $T_m = 75$ $T_d = 147$

Versamid 115: $T_g = -26$ $T_m = 29$ $T_d = 100$

The values obtained using the Rheovibron Elastoviscosimeter are lower than those obtained by differential scanning calorimetry. This difference is attributed to the different degrees of curing: it is likely the DSC samples were probably not cured even after 50 days ageing, and the degree of cure of the Rheovibron samples, although high, is not known. Several samples determined by DSC showed second-order transition temperatures close to the T_g value of 22° for Epon 1001 and the T_m value of 29° for Versamid 115, consistent with a proportion of unreacted epoxy resin or curing agent. The solvent-cast Epon 1001-Versamid 115 combination showed two second-order transition temperatures after 11 days ageing (close to the T_g and T_m of Epon 1001), but only a single value after 50 days ageing, indicating that the film was homogeneous at this time.

SECTION VI

FORMULATION OF EPOXY EMULSION PRIMERS

A. Introduction

Preliminary evaluation results were reported earlier (4) for films of mixed epoxy resin-curing agent emulsions. The films were cast on aluminum alloy panels (2024-T3 Fed. QQA-250/5) and cured either at room temperature or in an oven at elevated temperatures. The cured films were rated for "appearance" from opaque to transparent, for "hardness" or degree of cure, and for "adhesion" as determined by scratching with a needle. For the Epon 1001-Versamid 115 system, the 2:1 ratio (based on polymer) gave better results than the 4:1, 1:1, and 1:2 ratios.

In the present work, this evaluation was continued: films were cast from the mixed epoxy resin-curing agent emulsions and evaluated in terms of gloss, hardness, adhesion, and flocculation upon mixing (as evidenced by the presence of visible particles in the film). The formulation of the mixed epoxy resin-curing agent emulsions was altered to give transparent, tough, adherent films. Then, aqueous pigment dispersions were mixed with the mixed emulsions or with the epoxy resin emulsion alone, to formulate a primer. Generally, the mixed emulsions or epoxy resin emulsions showed signs of flocculation upon mixing with the pigment dispersion. This section describes the efforts to avoid this flocculation and develop a satisfactory primer system.

B. Experimental Details

The epoxy resin and curing agent emulsions were mixed in the desired proportions and observed for signs of flocculation. Usually, the emulsions were mixed with a spatula and agitated in a sealed bottle by tumbling end-over-end for 30 minutes at 10 rpm. Films of the mixed emulsions were cast on 9x12x0. 25-inch glass plates, which had been scrubbed thoroughly with Bon Ami, wiped with an acetone-saturated towel, and dried with paper towels. The mixed emulsions were poured on the glass plate and drawn-down with a 2-inch "blade" applicator (Precision Gage & Tool Co.) with eight different gap clearances ranging from 1 to 8 mils. Different gap clearances were used to control the thickness of the dried film; the gap clearance selected (in mils) was equal to 120 divided by the percent solids of the emulsion, e.g., a 3-mil gap clearance was used for an emulsion containing 40% solids.

During drying and curing at room temperature, the films were inspected for: 1. "puddling" - the retraction of the film from its original area to form a smaller film of greater thickness; 2. "fish eyes" - small circular blemishes resulting from imperfect wetting of the substrate by the film; 3. "craters" - resulting from an air bubble forming during drying and then bursting at a stage when the film was no longer fluid; 4. "mud-cracking" - formation of cracks in film during drying; 5. "orange peel" - formation of a film with reticulated surface morphology resembling the orange-skin texture.

After drying, the films were inspected for clarity, gloss, flocculated particles, and "Tyndall scattering", i. e., a bluish-white haze indicative of incipient incompatilibity of one ingredient. The films showed good gloss and clarity with no evidence of flocculated particles, "craters", "fish eyes", or Tyndall scattering were evaluated for hardness using the Sward Rocker Arm.

The morphological and dynamic-mechanical properties of these epoxy resin-curing agent films are described in Section V.

Usually, stoichiometric proportions of the epoxy resin and curing agent were used for the evaluations. For example, Epon 1001 has an epoxide equivalent weight of about 500, and Versamid 115 and Versamid 100 have amine values (expressed as mg KOH/gm) of 238 and 90, respectively, which correspond to amine equivalent weights of 236 and 623. Thus, the stoichiometric proportions would be 2. 12:1 for the Epon 1001-Versamid 115 (close to the 2:1 ratio determined experimentally) and 0. 80:1 for the Epon 1001-Versamid 100 systems.

In some cases, the epoxy resin was pre-cured in the emulsion state: Epon 1001 or Epon 828 was blended with less-than-stoichiometric amounts of Versamid 100 or Versamid 115 before emulsification; this mixture was then emulsified to form a partially-cured epoxy resin emulsion. This partially-cured emulsion was later mixed with the same curing agent emulsion in proportions equivalent to the calculated unreacted epoxide groups.

The pigment composition of the epoxy-polyamide primer presently used (1) was calculated to be:

titanium dioxide	10. 13 parts
strontium chromate	52. 86 parts
magnesium silicate	24. 23 parts
diatomaceous silica	12. 78 parts
total	100. 00 parts

These proportions were used to prepare 200-gm batches of pigment by dry-blending the mixed pigments in glass jars, which were tumbled for 30 minutes at 10 rpm. The pigment-binder ratio of the primer presently used (1) is 51. 78:48. 22. Therefore, 5. 178 gm of pigment mixture was ground in an aqueous solution of wetting agent and mixed with 4. 822 gm of epoxy resin and curing agent in the form of aqueous emulsions. The pigment mixture (5. 178 gm) was placed in a 2-oz glass jar along with 25 gm of 8-12-mesh Ceremedia beads, 3. 20 gm of 10% aqueous Span 80-Tween 80 (HLB 12) mixture, and 2. 10 gm deionized water. The jar was capped and shaken for 10 minutes on a Red Devil paint shaker to disperse the pigment in the aqueous solution of emulsifier. Then, 5. 50 gm of 39. 0%-solids Epon 1001 emulsion (C-29) was added with stirring, followed by 7. 06 gm of 37. 8%-solids Versamid 100 emulsion (C-23), also with stirring. The jar was then tumbled for 10 minutes, and the paint was strained through a tea strainer into a 1-oz bottle for evaluation.

C. Emulsions Prepared with the Hexadecyltrimethylammonium Bromide-Cetyl Alcohol Combination

The first evaluation experiments used the Epon 1001 ( ) and Versamid 115 ( ) emulsions prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination, which proved to be so successful in preparing emulsions of very small droplet size. The Epon 1001 and Versamid 115 emulsions were mixed in stoichiometric proportions and drawn-down on the glass plates using various gap clearances of the applicator. The solids contents of the mixed emulsions were only 20-30%, and their viscosities were too low for easy preparation of films of sufficient thickness.

The Epon 1001 and Epon 828 emulsions were concentrated to 35-40% solids without difficulty, but the translucent Versamid 115 emulsions, which apparently comprise solubilized rather than emulsified polymer, could not be concentrated above 11% solids without increasing their viscosity to the point where they could not easily be mixed with the epoxy resin emulsions.

Films were prepared from the Epon 1001-Versamid 115 and Epon 828-Versamid 115 mixed emulsions. These films were generally cloudy rather than transparent, and their adhesion to the glass substrate was poor. Both the cloudiness and the poor adhesion were traced to the cetyl alcohol, which apparently is incompatible with the cured epoxy resin and was exuded from the film as it cured, to form exudates of a solid, waxy substance. Such exudation of incompatible emulsifiers was observed earlier (27, 28) in studies of the further gradual coalescence of latex films. In these latter cases, the incompatible emulsifier was exuded from the film as the further gradual coalescence proceeded, to form exudates on the surface of the film as well as in the interface between the film and the substrate (28). The formation of such exudates in the present system would not only give cloudy films because of the exudates on the surface, but would also give poor adhesion because of the exudates at the film-substrate interface.

D. Emulsions Prepared with the Hexadecyltrimethylammonium Bromide-n-Decane Combination

When it was found that n-decane could be substituted for the cetyl alcohol in the mixed emulsifier system, emulsions of Epon 1001, Epon 828, Versamid 115, and Versamid 100 were prepared with this new hexadecyltrimethylammonium bromide-n-decane combination. Usually, the concentration of n-decane was 1-2% based on polymer solution (40% polymer). The changeover to this new emulsifier combination required many experiments before transparent, adherent epoxy resin-curing agent films were obtained. These additional experiments included the concentration of the Epon 1001 and Epon 828 emulsions to solids contents high enough so that the mixed-emulsion films would not "puddle" on the glass substrates. Most of the Epon 1001 and Epon 828 emulsions contained 35-40% solids, but some contained higher concentrations. As before, the Versamid 115 emulsions could not be concentrated above 11% solids without increasing their viscosity to the point where they could not be easily mixed with the epoxy resin emulsions. The Versamid 100 emulsions, however, could be prepared in concentrations up to 38% solids.

Films were prepared from the stoichiometric proportions of epoxy resin and curing agent emulsions, and also from the partially-cured epoxy resin emulsions combined with the appropriate amount of curing agent emulsion. Generally, these films showed better clarity and adhesion to the substrate, confirming the deleterious effects of cetyl alcohol.

The Versamid 115 emulsions of about 11% solids were very viscous and could not easily be mixed with the Epon 1001 or Epon 828 emulsions. Also, films cast from the mixed Epon 1001-Versamid 115 emulsions showed visible flocculated particles, probably small, discrete, jelly-like clots of Versamid 115 emulsion that were never properly dispersed in the Epon 1001 emulsion. Moreover, these films were softer than the corresponding films of the mixed Epon 1001-Versamid 100 emulsions.

The best results in terms of film hardness and appearance were obtained with a mixture of Epon 1001 emulsion with a Versamid 100 emulsion or an emulsion of the Versamid 115-phenyl glycidyl ether reaction product of equivalent weight equal to that of Versamid 100. These mixed emulsions gave transparent, adherent films without flocculated particles.

The pre-reaction of the epoxy resin and curing agent emulsions in the emulsion state did not produce the hoped-for faster curing rates. In this case, the epoxy resin emulsion was mixed with a portion of the curing agent emulsion to produce partially-cured epoxy resin particles; this partially-cured emulsion was then mixed with the remainder of the curing agent emulsion and cast into a film. It was hoped that the pre-curing of the epoxy resin emulsion would give a faster-curing, harder film. Actually, the opposite effect was observed because the partially-cured particles were so much larger and more tightly crosslinked than the original epoxy resin particles that surrounding Versamid 100 or Versamid 115 curing agent could not diffuse into the epoxy resin particle sufficiently to crosslink it further.

E. Emulsions Prepared with the Span 80-Tween 80-Hexadecyltrimethylammonium Bromide-n-Decane Combination

The quaternary hexadecyltrimethylammonium bromide is the best cationic emulsifier found to date for emulsifying the epoxy resin and curing agent emulsions. It is a solid at room temperature, however, and is exuded from the epoxy resin-curing agent films to give them a cloudy appearance. Moreover, it may crystallize from aqueous solution at low dilutions.

This tendency to "bloom" or show Tyndall scattering can be avoided by using the 0.28:0.72:3:1 Span 80-Tween 80-hexadecyltrimethylammonium bromide-*n*-decane combination. The 28:72 Span 80-Tween 80 ratio has a HLB of 12 and was developed from Epon 1001 emulsification experiments using various mixtures of Span 80 (HLB 4.3) and Tween 80 (HLB 15); the mixture of HLB 12 gave emulsions of better stability than those of HLB 10 or 14. Epoxy resin and curing agent emulsions prepared with the foregoing 0.28:0.72:3:1 proportions gave transparent, adherent films with no evidence of exudations or flocculated particles. In this respect, it is the best combination found to date. In comparison, the 0.54:1.44:2:1 combination gave emulsions of poorer stability.

F. Combination of the Epoxy Emulsion System with Pigment Dispersions

The present primer (1) comprises an equal-volume mixture of a 22.8:37.8:39.4 Epon 1001-pigment-solvent mixture and a 18.7:81.3 Versamid 115-solvent mixture. The pigment used is the titanium dioxide-strontium chromate-magnesium silicate-diatomaceous silica mixture described earlier. To develop a water-based analog of this primer, the pigment mixture must be dispersed in water and the aqueous dispersion "let down" into the epoxy resin emulsion. The preparation of such an aqueous dispersion is a difficult task because most commercial pigments are treated during manufacture to give surface characteristics suitable for easy dispersion, and heretofore this pigment mixture has been used for organic solvent-based systems.

To find a practical wetting agent for a pigment is a common problem in the paint industry. The powdered pigment is wetted with water to give a dispersion of heavy consistency, and this dispersion is titrated with aqueous solutions of various wetting agents while measuring the viscosity of the dispersion (e.g., with a Stormer or Brookfiled Viscometer) until a low-viscosity dispersion is obtained. This minimum-viscosity point is called the "Fluidity Point" or "FP".

The titration is then continued beyond the Fluidity Point until no flocculation is observed when a drop of pigment dispersion is added to 1 ml of an aqueous ionic-thickener solution (e.g., Acrysol GS, Rohm & Haas Co.) and stirred gently with a glass stirring rod (33). This point at which no flocculation is observed is called the "Concentration Aggregation Point" or "CA". The CA values are often as high as 10 times the FP values, and it is recommended that the proper amount of emulsifier to add to the pigment dispersion is about 3.33 times the FP value (33). Since the Acrysol GS is essentially polyacrylic acid, an anionic polyelectrolyte, it cannot be used to determine the CA value of a cationic pigment dispersion, and to develop suitable cationic polyelectrolytes for this purpose would require considerable experimentation. Therefore, a CA value of 3.33 times the FP value was assumed to be applicable to the present cationic epoxy resin emulsions and was used in the following experiments.

The FP value for a 50-gm sample of zinc chromate pigment dispersed in water was found to be 7.5 ml of 10% aqueous solution of the 0.28:0.72:3 Span 80-Tween 80 hexadecyltrimethylammonium bromide combination. Then, assuming CA = 3.33 FP, 5.178-gm samples of the pigment mixture were mixed with 2.6 ml of the foregoing 10% mixed emulsifier solution and 1 ml water; the resulting pigment dispersion was mixed with the stoichiometric proportions of the Epon 1001 and Versamid 100 emulsions (both prepared with the same emulsifier combination used for the pigment dispersion) to give 4.822 gm epoxy resin-curing agent binder.

When the mixed Epon 1001-Versamid 100 emulsions were added to the pigment dispersion, the sample immediately flocculated. When only the Epon 1001 emulsion was added to the pigment dispersion, the mixture flocculated to a heavy mass; when the Versamid 100 emulsion was added, a large ball of pigment and resin was formed. When all of the nonionic Span 80-Tween 80 mixture was added to the pigment dispersion (instead of part in the pigment dispersion, part in the epoxy resin emulsion, and part in the curing agent emulsion), the system also flocculated.

Since the formulation of the pigment mixture with the same emulsifier system used to prepare the epoxy resin and curing agent emulsions gave flocculated systems, another approach was tried, i.e., to use a nonionic water-soluble polymer as a dispersing and stabilizing agent. Methylcellulose (Dow Methocel HG-1500) was used for this purpose: 5.178 gm pigment was ground in 2.10 ml water, 3.2 ml 10% aqueous 28:72 Span 80-Tween 80 mixture, and 3.2 ml 3% aqueous Methocel, to give a stable dispersion.

When 5.5 gm of the Epon 1001 emulsion was added to this dispersion, it increased in viscosity, but remained stable; however, when 7.06 gm of the Versamid 100 emulsion was added, the system flocculated.

All other attempts to formulate a stable pigment dispersion using the foregoing approaches also produced flocculated or unstable systems.

To check the validity of this system with an anionic latex, 5.178 gm pigment mixture was ground with Ceremedia beads in 2.85 gm water and 3.20 gm 10% aqueous 28:72 Span 80-Tween 80 mixture to produce a stable dispersion, which was then mixed with 8.61 gm Flexbond 315 polyvinyl acetate latex (Air Products & Chemicals Co., Inc.). No flocculation was observed, but the latex film contained many air bubbles or foam. When the dispersion was de-aerated under vacuum, it gave a bubble-free film with good hiding. Thus, the nonionic Span 80-Tween 80 mixture functions as a pigment dispersing agent for anionic systems, but not for cationic systems.

SECTION VII

PREPARATION OF POLYURETHANE EMULSION SYSTEMS

A. Introduction

1. Present System

The polyurethane topcoat presently used by the Air Force (2) is a two-component solvent-based system: (i) a hydroxyl-terminated polyester prepolymer dissolved in solvents and containing dispersed pigments; (ii) an aliphatic isocyanate prepolymer dissolved in solvents. The first component contains a small amount of dibutyltin dialurate as catalyst for the isocyanate-hydroxyl curing reaction. Both components are formulated so that equal volumes are mixed and applied as a coating. The two prepolymers are brought into intimate contact by evaporation of the solvents, and isocyanate groups of one react with the hydroxyl groups of the other to produce a crosslinked polymer film. The isocyanate prepolymer is present in small excess so that the isocyanate groups remaining unreacted after the solvent has evaporated can react with the moisture in the air to produce further crosslinking.

The pot life of the mixed components is 6 hours, and the mixture may be diluted further with solvents to facilitate application by spraying. After application, the drying time is 2 hours for the "set-to-touch" and 6 hours for the "dry-hard" conditions. The isocyanate prepolymer used is Desmodur N-100 (Mobay Chemical Company), a clear, pale-yellow, viscous liquid which is reported to be a "high-molecular-weight biuret of 1,6-hexamethylene diisocyanate containing less than 0.7% 1,6-hexamethylene diisocyanate. The polyester prepolymer used is Multron R-221-75 (formerly E-380; Mobay Chemical Company), a light-yellow, viscous liquid which is reported to be a 75:25 mixture of a short oil-alkyd resin adduct and ethoxyethyl acetate with a hydroxyl number of 105-120.

Equal volumes of the two components give a 29:71:0.072 Desmodur N-100-Multron E-380-dibutyltin dilaurate mixture. Films prepared from these proportions are transparent, tough, and flexible.

B. Preparation of Polyurethane Emulsion Systems - General Approach

The preparation of polyurethane emulsion systems is complicated by the fact that the isocyanate groups react readily with water. Simple emulsification of the two prepolymer components as practiced with the epoxy emulsion systems destroys the reactivity of the isocyanate prepolymer; when mixed with water, Desmodur N-100 reacts rapidly with much foaming. The usual way of avoiding this difficulty is to react the isocyanate groups with other functional groups in organic media, to form an adduct that does not react with water. The general approach of this work is to pre-react the isocyanate groups with a hydroxyl-containing material that contains other functional groups capable of undergoing further reactions (e.g., vinyl groups). This pre-eaction forms adducts containing the urethane linkage which are then emulsified and subjected to further reactions. In most cases, the hydroxyl-containing materials are used in a concentration equivalent to that of the polyester prepolymer normally used.

The first part of this work (4) described the preparation of fully-cured and air-drying polyurethane emulsions.

The fully-cured types were prepared by reacting Desmodur N-100 with a mixture of a hydroxyalkyl methacrylate (e.g., hydroxypropyl methacrylate) and a monohydric alcohol (e.g., 1-butanol) using dibutyltin dilaurate catalyst. This adduct dissolved in a reactive diluent mixture (e.g., a n-butyl acrylate-isobutyl methacrylate mixture) was emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and polymerized using persulfate-ion initiator. These emulsions dried to form glossy, tough, flexible films. The film properties could be varied by the choice of the hydroxyalkyl methacrylate and monohydric alcohol, the hydroxyalkyl methacrylate-monohydric alcohol ratio, and the composition of the reactive diluent mixture.

The air-drying types were prepared by reacting Desmodur N-100 with allyl alcohol, often in combination with a hydroxyalkyl methacrylate (e.g., hydroxypropyl methacrylate), using dibutyltin dilaurate catalyst, followed by a polyester prepolymer (e.g., Multron R-16 or Paraplex P-444A). This adduct was emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination. These emulsions combined with cobalt naphthenate catalyst dried and cured overnight to form glossy, flexible films. The film properties could be varied by the type and concentration of the hydroxyalkyl methacrylate combined with the allyl alcohol, the choice of the polyester prepolymer, and the type and concentration of the catalyst.

1. Preparation of Fully-Cured Polyurethane Emulsions

The samples submitted to the Air Force for evaluation (4) comprised a 63:27:20:0.16 Desmodur N-100-hydroxypropyl methacrylate-butanol-dibutyltin dilaurate adduct dissolved in 42:58 ratio in the n-butyl acrylate-isobutyl methacrylate reactive diluent mixture. The two samples used 50:50 and 40:60 n-butyl acrylate-isobutyl methacrylate mixtures, to give films of slightly different flexibility.

The present work comprised experiments to optimize the proportions of Desmodur N-100, hydroxypropyl methacrylate, n-butyl acrylate, and isobutyl methacrylate, to develop a composition with the desired film properties.

In the samples submitted earlier (4), the Desmodur N-100-reactive diluent ratio was about 1:2. Experiments were carried out in which this ratio was increased from 1:2 to 1:2.2, keeping the same 50:50 proportion of the isocyanate groups reacted with hydroxypropyl methacrylate and 1-butanol. The films of the latter emulsion showed slight improvements in gloss and strength, but were slightly more cloudy. When the Desmodur N-100-reactive diluent ratio was decreased to 1:1.6, considerable coagulum was produced during the polymerization, indicating that the degree of crosslinking was too great. Therefore, the ratio was increased to 1:1.8, which produced a stable latex.

Another series of experiments were carried out using this 1:1.8 Desmodur N-100-reactive diluent mixture, but varying the n-butyl acrylate-isobutyl methacrylate ratio. All of these films were cloudy or opaque and showed poor strength; however, the gloss and adhesion to the aluminum substrate were improved. The films using only n-butyl acrylate were soft and tacky.

Similar experiments were carried out in which the equivalent amount of 1-propanol or 1-hexanol were substituted for the 1-butanol. These films were similar to those described above except that the film strength was even poorer.

In other experiments, an equivalent amount of styrene was substituted for the isobutyl methacrylate in the reactive diluent mixture. This emulsion dried to a glossy, almost transparent film. Also, acrylonitrile was substituted for part of the isobutyl methacrylate. These films showed improved strength, but displayed a faint yellow color.

2. Preparation of Polyurethane Emulsions Using the Sodium Lauryl Sulfate n-Decane Combination

The substitution of n-decane for the cetyl alcohol in the sodium lauryl sulfate-cetyl alcohol combination was also applied to the fully-cured polyurethane emulsions. Using the proportions of Experiment X364, which was submitted for evaluation (4), 8.1 gm Desmodur N-100 was reacted with 3.4 gm hydroxypropyl methacrylate and 1.3 gm 1-butanol using 0.02 gm dibutyltin dilaurate catalyst to form an adduct in 9.0-9.0 gm n-butyl acrylate-isobutyl methacrylate reactive diluent mixture. This solution (36 gm) containing 0.45 gm n-decane was emulsified in 100 gm water containing 0.40 gm sodium lauryl sulfate using ultrasonic irradiation, and the resulting emulsion was added with stirring to 100 gm water containing 0.40 gm sodium lauryl sulfate, 0.25 gm potassium persulfate initiator, and 0.25 gm sodium bicarbonate buffer at 60° C and maintained at that temperature to complete the polymerization. The emulsion (Figure 40) dried to give cloudy films which were more glossy and showed better adhesion to the aluminum substrate than the corresponding films prepared with the cetyl alcohol system.

Larger batches were also prepared. For example, Experiment 422 was used as a basis to prepare a 400-gm batch of emulsion.

TABLE IX

Fully-Cured Polyurethane Emulsions

Ingredient	Expt 422	Expt 422 gm basis*	400-gm batch
Desmodur N-100	10.0 gm	10.0 gm	105.8 gm
Hydroxypropyl Methacrylate (94%)	4.2 ml	4.30 gm	45.5 gm
1-Butanol	1.6 gm	1.60 gm	16.9 gm
n-Butyl Acrylate	9.9 ml	8.85 gm	93.7 gm
Isobutyl Methacrylate	14.8 ml	13.05 gm	138.1 gm
Total		37.80 gm	400.0 gm
Dibutyltin Dilaurate (5%)	0.5 ml	--	5.29 ml

*calculated from the specific gravities

The foregoing ingredients were mixed in a 3-neck flask and allowed to stand under nitrogen for 3 days at room temperature. Then, the solution was heated to 60°C in a water bath over a 90-minute period and was stirred gently at that temperature for 3 hours. Then 4.0 gm n-decane was added to the solution, and it was transferred to an addition funnel. The solution was added from this funnel to 1200 gm of deoxygenated (boiled)-deionized water containing 6.4 gm sodium lauryl sulfate, to form a crude emulsion. This crude emulsion was then subjected to ultrasonic irradiation using the Sonifier and homogenization at 6000 psi using the Manton-Gaulin Submicron Disperser.

This fine-droplet-size emulsion was transferred to an addition funnel and was sparged with nitrogen to remove traces of oxygen. The emulsion was added slowly with slow stirring over a 4-hour period to a glass flask containing 500 gm of deoxygenated (boiled)-deionized water in which were dissolved 4.0 gm potassium persulfate, 4.0 gm sodium bicarbonate, and 2.0 gm sodium lauryl sulfate. The glass flask was equipped with a stirrer, condenser, and apparatus for introducing nitrogen to maintain an inert atmosphere; it was immersed in a constant-temperature bath maintained at 60°C. After all of the emulsion had been added to the flask, the contents were stirred slowly for another 17 hours. Then, 0.5 gm potassium persulfate dissolved in 20.0 gm water was added, and the mixture was stirred slowly for another 3 hours. The emulsion was then cooled, strained through glass wool to remove any coagulum, and transferred to a 2-liter round-bottom flask in two portions, for concentration in the Buchler Flash Evaporator.

Two batches were prepared using the foregoing recipe and procedure. The yield of the first batch was 299 gm solids (of a theoretical 400 gm) recovered as concentrated emulsion; the yield of the second batch, which formed more coagulum, was 295 gm.

Considerable batch-to-batch variation was encountered in the preparation of these polyurethane emulsions. Most of it was attributed to the changes in the Desmodur N-100 supply that occurred upon ageing, even though the samples were stored at -20°C, as the use of fresh ingredients usually eliminated the variation.

3. Air-Drying Polyurethane Emulsions

Little work was done on the air-drying polyurethane emulsions during the present work; however, attempts were made to prepare an unsaturated polyester based on the condensation of diethylene glycol, fumaric acid, and tetrahydrophthalic anhydride in 70% diallyl phthalate solution with one chain end "blocked" with trimethylolpropane diallyl ether. The viscosity of this polyester-diallyl phthalate solution was greater than 1000 stokes, too great for use in the present system. Further experiments to reduce the viscosity of this polyester prepolymer are not yet completed.

C. One-Quart Polyurethane Emulsion Samples for Evaluation

One-quart samples of the fully-cured Desmodur N-100-hydroxypropyl methacrylate-1-butanol emulsion was submitted to the Air Force Materials Laboratory for evaluation. The sample was prepared according to the recipe given under 400-gm batch of Table IX. This polyurethane latex sample with solids content of 40.1% was given the identification number LB-422.

SECTION VIII

MECHANISM OF THE EMULSIFICATION PROCESS

A. Preliminary Experiments

Preliminary experiments were carried out to determine the mechanism by which the hexadecyltrimethylammonium bromide-cetyl alcohol and hexadecyltrimethylammonium bromide-n-decane combinations produce submicroscopic-size emulsion droplets. Benzene was added with stirring to aqueous solution of emulsifier at 62° C, and the conductance of the emulsions was measured as a function of benzene concentration.

Figure 41 shows the variation of conductance of 100 ml water containing 0.60 gm hexadecyltrimethylammonium bromide as a function of added benzene concentration for three different cases: (i) Curve 1, where the water contained only hexadecyltrimethylammonium bromide; (ii) Curve 2, where the water contained 1.20 gm cetyl alcohol in addition to the hexadecyltrimethylammonium bromide; (iii) Curve 3, where the benzene added contained 1% n-decane. The shapes of these three curves are distinctly different; all three are reproducible.

The conductance of these benzene emulsions is a complex function of several parameters, e.g., the droplet size and size distribution, the adsorption isotherm of the emulsifier, (which determines the solute concentration of emulsifier), the surface charge density of the droplets, the orientation of the emulsifier at the oil-water interface, and the presence or absence of polar (cetyl alcohol) or apolar (n-decane) molecules combined with the emulsifier.

The few results shown in Figure 41 are insufficient to yield a definitive interpretation of the action of these mixed emulsifier combinations; however, the results can be interpreted speculatively. For hexadecyltrimethylammonium bromide alone, the sharp decrease in conductance is expected and is similar to results reported earlier for a different ionic emulsifier (34). The emulsification of the benzene should decrease the conductance because a non-conducting substance is interposed between the electrodes, which measure an average of the overall conductance of the material between them. Presumably, the decrease in conductance depends upon the amount of benzene added, the size of the benzene emulsion droplets, and the decrease in aqueous emulsifier concentration due to adsorption on the benzene droplet surfaces. The decrease in conductance is complicated further if the change in aqueous emulsifier concentration passes through the critical micelle concentration.

The results for the hexadecyltrimethylammonium bromide-n-decane combination were similar to those for the hexadecyltrimethylammonium bromide alone, i.e., a sharp decrease in conductance with increasing benzene concentration. The curve for the mixed emulsifier combination fell below that for the emulsifier alone; since the average droplet size is much smaller for the mixed emulsifier system this suggests that the decrease in conductance is greater, the smaller the droplet size; however, the difference is not great, possibly because the n-decane is added with the benzene, so that its concentration

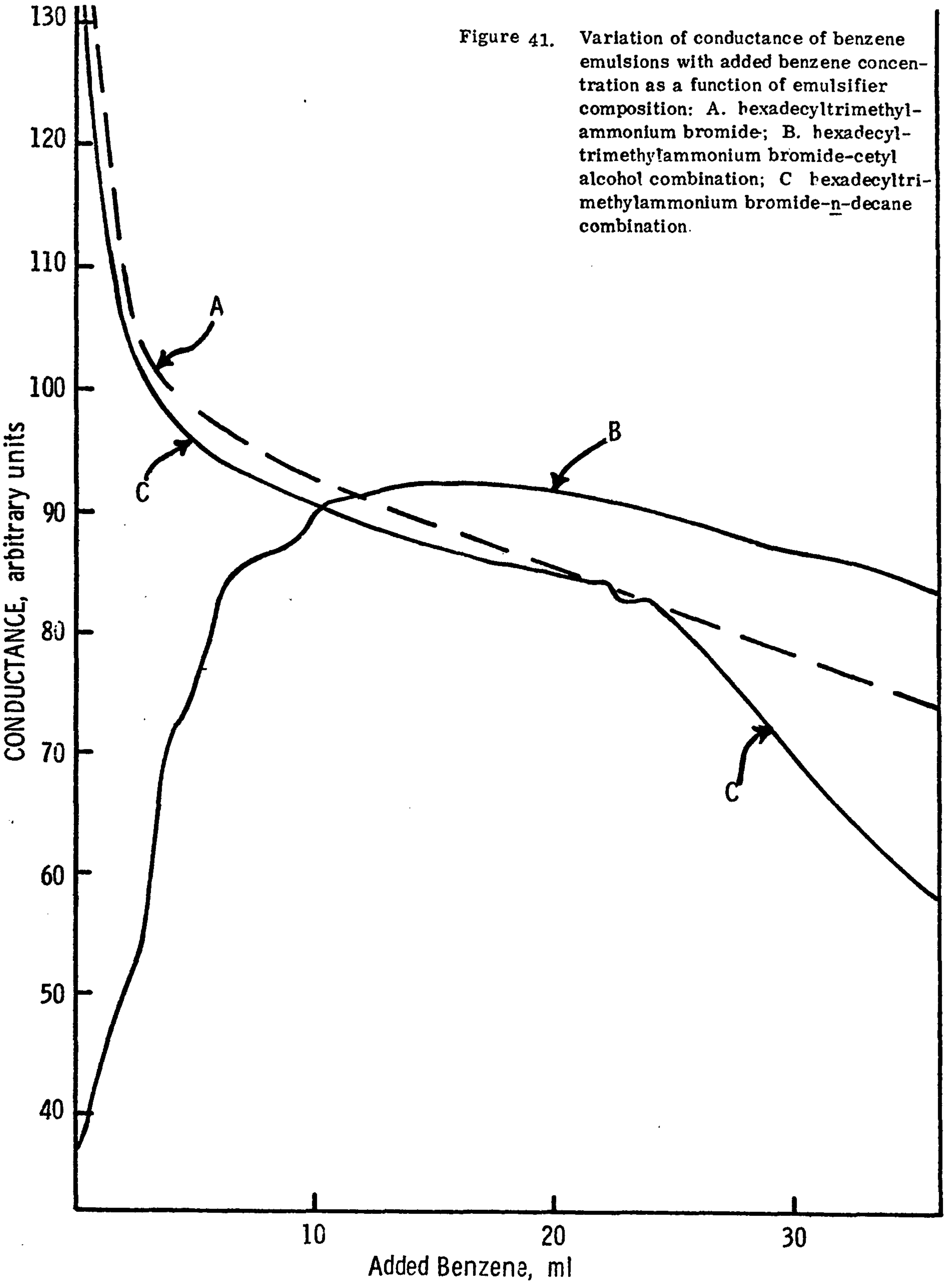


Figure 41. Variation of conductance of benzene emulsions with added benzene concentration as a function of emulsifier composition: A. hexadecyltrimethylammonium bromide; B. hexadecyltrimethylammonium bromide-cetyl alcohol combination; C hexadecyltrimethylammonium bromide-n-decane combination.

varies with the amount of benzene added.

The results for the hexadecyltrimethylammonium bromide-cetyl alcohol combination were distinctly different from those for the two foregoing systems, i.e., the conductance increased with increasing benzene concentration. Such an increase is consistent with an increase in the aqueous hexadecyltrimethylammonium bromide concentration or an increase in the average droplet size. With a given concentration of mixed emulsifier, an increasing concentration of benzene should give an increase in the average droplet size.

More experiments on the effects of temperature, agitation rate, chain length of the polar or apolar molecules, and the ratio of these molecules to the ionic emulsifier must be carried out to determine the mechanism of this emulsification process.

SECTION IX

CONCLUSIONS

A. General Approach

1. The critical size for settling of spherical particles can be calculated from Stokes Law as a function of the difference in density between the particles and the medium, and the viscosity of the medium.

2. The 5-fold decrease in average droplet size (from 1 μm to 0.2 μm) achieved with the mixed emulsifier combinations is sufficient to give epoxy resin and polyurethane emulsions with particle sizes smaller than the critical size for settling.

B. Epoxy Emulsion Systems

1. Stable cationic emulsions of Epon 1001, Epon 828, and Versamid 100 can be prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation or homogenization. These emulsions can be vacuum-steam-distilled to remove the solvents and concentrate the emulsions to 35-40% solids.

2. Stable cationic emulsions of Versamid 115 can be prepared using the foregoing system, but these emulsions quickly become translucent and more viscous, indicating some solubilization of the curing agent. These translucent emulsions can be vacuum-steam-distilled to remove the solvents and excess water; however, the maximum practical solids concentration is about 11% because of the high viscosity.

3. The hexadecyltrimethylammonium bromide-n-decane combination proved to be more effective in emulsification than the hexadecyltrimethylammonium bromide-cetyl alcohol combination; emulsions prepared with the former combination were slightly more stable and lacked the large particle-size "tail".

4. The stoichiometric mixed Epon 1001-Versamid 115 emulsions formed a satisfactory film, but 30 days at room temperature or a few hours at 50°C were required to give the same degree of cure attained in 7 days at room temperature by the solvent-cast Epon 1001-Versamid 115 system.

5. The room-temperature curing rate of the Epon 1001-Versamid 115 emulsion system is too slow to be competitive; therefore, some means must be found to increase its rate of curing.

6. To increase the curing rate, part of the Versamid 115 can be mixed with the Epon 1001 before emulsification to produce partially-cured particles; this emulsion is then mixed with the remaining Versamid 115 in the form of an emulsion; however, the partially-cured epoxy resin particles may be too hard and the concentration of curing agent emulsion too small to form continuous films.

7. To increase the curing rate, the Epon 1001 and Versamid 115 emulsions can be mixed in stoichiometric proportions and allowed to cure for a short time in the emulsion state before casting into a film; this pre-curing gives an increase in the size of the emulsion droplets, apparently by agglomeration of the Versamid 115 droplets with the Epon 1001 droplets.

8. To increase the curing rate, bisphenol A can be mixed with the Epon 1001 or Dion DPM-3-800-LC with the Versamid 115 before emulsification; the emulsions of Epon 1001 and Versamid 115 thus produced can be mixed with the stoichiometric proportions of Versamid 115 or Epon 1001 emulsions.

9. Versamid 100 may be more suitable than Versamid 115 for these emulsions systems because of its lower amine value (90 compared with 238); therefore, its stoichiometric ratio with Epon 1001 is 0.8:1 rather than the 2:1 ratio for the Epon 1001-Versamid 115 system.

C. Morphology and Properties of Epoxy Resin Films

1. The morphology, properties, and degree of cure of an epoxy resin-curing agent film can be determined by a combination of methods: transmission electron microscopy of film surface replicas, microtomed sections, and diluted dispersions; low-temperature solvent extraction of cured films; scanning electron microscopy of the surfaces and fracture cross-sections of solvent-extracted films; modulus-temperature measurements of cured films; differential scanning calorimetry of cured films.

2. In the emulsion-cast films, the curing reaction begins at the interface between the coalesced epoxy resin and curing agent particles and soon forms a crosslinked interfacial polymer network of higher T_g that slows the overall curing rate.

3. In the solvent-cast films, the epoxy resin and curing agent molecules are mixed on a molecular scale and thus cure to form a homogeneous film.

4. The pre-curing by heating the mixed epoxy resin and curing agent emulsions before film-casting gives a short-term increase in curing rate, but gives little long-term increase because the crosslinked interfacial network slows the difussion of curing agent.

5. The addition of bisphenol A to the Epon 1001 or Dion DPM-3-800-LC to the Versamid 115 before emulsification gives a rapid curing rate for a short time, to produce a highly crosslinked interfacial network that hinders the diffusion of curing agent to complete the cure. Thus, these films combine a high crosslink density with a high proportion of extractable polymer.

6. The addition of bisphenol A to the Epon 1001 or Dion DPM-3-800-LC to the Versamid 115 increases the emulsion droplet size, thus accentuating the diffusion control of the curing process.

7. Thus far, no Epon 1001-Versamid 115 emulsion system has given the same curing rate (7 days at room temperature) as the solvent-cast Epon 1001-Versamid 115 system.

D. Formulation of Epoxy Primers

1. The hexadecyltrimethylammonium bromide-cetyl alcohol combination gives epoxy resin and curing agent emulsions of 0.2 μm droplet size, but the cetyl alcohol makes the epoxy resin-curing agent films hazy and gives poor adhesion to glass substrates.

2. The substitution of n-decande for the cetyl alcohol not only gives more stable emulsions, but also gives clear films with good adhesion to glass substrates.

3. Neither the hexadecyltrimethylammonium bromide-cetyl alcohol or hexadecyltrimethylammonium bromide-n-decane combinations make the emulsions stable enough for formulation into paints; instead, their function is to give the small droplet size, and other stabilizers must be added to give the requisite stability for formulation.

4. The nonionic Span 80-Tween 80 (HLB 12) mixture can be used to improve the stability of the epoxy resin and curing agent emulsions.

5. The Span 80-Tween 80-hexadecyltrimethylammonium bromide combination can be used to prepare aqueous dispersions of the strontium chromate-titanium dioxide-magnesium silicate-diatomaceous silica pigment mixture used in the present primer.

6. When this aqueous pigment dispersion was combined with the mixed epoxy resin-curing agent emulsions, some flocculation of the polymer emulsions was observed. This aqueous pigment dispersion was mixed with the epoxy resin emulsion without flocculation, but the addition of the curing agent emulsion gave some flocculation.

7. Because of these flocculation problems, a satisfactory aqueous epoxy emulsion primer has not yet been developed.

8. Improved pigment grinding and emulsion stabilizing systems are needed to prepare an aqueous epoxy emulsion primer.

E. Fully-Cured Polyurethane Emulsions

1. Fully-cured polyurethane emulsions can be prepared by reacting Desmodur N-100 with a hydroxypropyl methacrylate-1-butanol mixture in n-butyl acrylate-isobutyl methacrylate reactive diluent mixture using dibutyltin dilaurate catalyst; this adduct solution is then emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and polymerized using persulfate-ion initiator. These emulsions dry to form tough, glossy films.

2. The film properties of this fully-cured polyurethane system can be varied systematically by varying the hydroxypropyl methacrylate-1-butanol ratio, the adduct-reactive diluent ratio, and the composition of the reactive diluent mixture.

3. The hexadecyltrimethylammonium bromide-n-decane combination gave polyurethane emulsions of better stability than the hexadecyltrimethylammonium bromide-cetyl alcohol combination.

F. Mechanism of the Emulsification Process

1. The mechanism by which these mixed emulsifier combinations give submicroscopic-size emulsion droplets is not known, but preliminary experiments measuring the conductance of benzene emulsions show that the mechanism is different for the hexadecyltrimethylammonium bromide-cetyl alcohol and hexadecyltrimethylammonium bromide-n-decane combinations.

SECTION X

RECOMMENDATIONS FOR FUTURE WORK

A. Epoxy Emulsion Systems

The approach used was to prepare separate emulsions of the epoxy resin and curing agent, mix these emulsions in the desired proportions, and cast a film from the mixture. Solvents were used to reduce the viscosity for emulsification, the solvents were removed and the emulsions were concentrated by vacuum steam distillation.

The emulsification of epoxy resins and curing agents to 0.2μm droplet sizes can be accomplished routinely using mixed emulsifier combinations and simple stirring, followed by ultrasonic irradiation or homogenization. The first part of this work (4) prepared anionic emulsions of Epon 1001 and Epon 828 epoxy resins using the sodium lauryl sulfate-cetyl alcohol combination and cationic emulsions using the hexadecyltrimethylammonium bromide-cetyl alcohol combination. Similarly, anionic and cationic emulsions of Genamid 250 were prepared, but only cationic emulsions of Versamid 115, because of its positive charge. Thus, the development of an emulsion analog of the currently-used solvent-based Epon 1001-Versamid 115 system is restricted to cationic emulsion systems.

The best film properties were obtained with the 2:1 Epon 1001-Versamid 115 and Epon 1001-Genamid 250 ratios and the 1:2 Epon 828-Versamid 115 ratio. However, the curing rate was too slow--30 days at room temperature or a few hours at 50° C were required to give properties equivalent to those obtained in 7 days at room temperature with the solvent-based Epon 1001-Versamid 115 system.

The present work concentrated on the development of the cationic Epon 1001-Versamid 115 emulsion system. In the emulsification, n-decane was substituted for the cetyl alcohol, to give more stable emulsions without the large particle-size "tail". Several approaches were used to increase the room-temperature curing rate: (i) by adding part of the Versamid 115 to the Epon 1001 solution before emulsification, with the remaining Versamid 115 added later in the emulsion form; (ii) by heating the mixed Epon 1001-Versamid 115 emulsions before film-casting; (iii) by adding bisphenol A to the Epon 1001 or Dion DPM-3-800-LC to the Versamid 115 before emulsification. At best, these approaches gave minor increases in the curing rate; at worst, they gave slower curing rates because the rapid curing at the interface between the coalesced particles formed a highly crosslinked interfacial network that slowed the diffusion of curing agent to the core of the epoxy resin particles. Moreover, although an aqueous dispersion of the primer pigment mixture (1) was prepared using a modification of the cationic emulsifier combination, the combination of this pigment dispersion with the mixed epoxy resin-curing agent emulsions flocculated part of the polymer; combination with the epoxy resin emulsion alone produced flocculation when the curing agent emulsion was added.

Therefore, the following recommendations are made for future work with these systems:

1. The use of lower-viscosity epoxy resin and curing agents--Epon 1001 is a solid, and Epon 828, Versamid 115, and Versamid 100 are viscous liquids. The same approaches used to increase the curing rates of solvent systems did not work with the emulsion systems: diffusion control of the curing raction gave incomplete curing or a highly crosslinked interfacial network enveloping partially-cured epoxy resin particles. Therefore, lower-viscosity epoxy resins and curing agents should be tried, so that better mixing would be obtained upon film formation, before the T_g of the crosslinked interfacial network becomes so high as to hinder diffusion of the curing agent.

2. Pre-curing of the Epon 1001 emulsion particles--Pre-curing the mixed Epon 1001-Versamid 115 emulsions or adding part of the Versamid 115 to the Epon 101 before emulsification gave only minor increases in curing rate (but significant differences in film morphology). Therefore, if Epon 1001 is to be used, a more-soluble or smaller-molecular-size curing agent should be used to pre-cure the Epon 1001 particles, e.g., the ethylene diamine used to harden Epon 1001 particles for electron microscopy or other polyamines of low molecular weight. These soluble curing agents should harden the Epon 1001 as completely as desired before mixing with the Versamid 115 emulsion. An alternate approach is to add the ethylene diamine or other polyamine curing agent to the Versamid 115 emulsion, so that it would diffuse into the Epon 1001 particles before the crosslinked interfacial network is formed.

3. Development of an anionic epoxy emulsion system--The cationic system was developed because it was the only approach to an emulsion analog of the Epon 1001-Versamid 115 system currently used (only cationic emulsions of Versamid can be prepared). However, the use of other curing agents, e.g., Genamid 250 or some lower-molecular-weight analog, would allow the development of an anionic system. Most emulsion coatings are anionic, and only a few special cationic systems are used in practical applications. The changeover to an anionic epoxy emulsion system would facilitate the development of a practical primer because the post-stabilization of anionic emulsions and the preparation of anionic pigment dispersions is better worked-out than the corresponding cationic systems.

4. Investigation of pigment surface treatment--Current pigment manufacturing practice is to surface-treat the pigment particles to make it easier to disperse them in a fluid vehicle; however, most commercial pigments (including those used in the present epoxy primer (1)) were manufactured for use in organic solvent-based vehicles and hence their surface characteristics are not suitable for dispersions in aqueous media. Therefore, the surface characteristics of the pigments should be investigated to determine if they are best suited for dispersion in organic or aqueous media. Pigments developed specifically for aqueous dispersions should be used if available; if not, the appropriate surface treatment should be developed for the available pigments.

5. Development of emulsion post-stabilizers--Both cationic and anionic epoxy resin and curing agent emulsions are likely to require post-stabilization for formulation as paints. These post-stabilizers are usually nonionic emulsifiers or ionic-nonionic emulsifier mixtures. This work developed the Span 80-Tween 80 (HLB 12) combination for the cationic epoxy resin and curing agent emulsions; however, the determination

of HLB 12 as the optimum only serves as a basis for selecting post-stabilizers with HLB values in that range. Similar experiments should be carried out for the anionic epoxy resin and curing agent emulsion.

6. Evaluation of the epoxy resin-curing combinations developed according to MIL-C-23377C (1) and selection of the most suitable composition for the aircraft primer application.

B. Polyurethane Emulsion Systems

The direct emulsification approach developed for the epoxy emulsion systems does not work with polyurethane emulsions because the isocyanate groups of the Desmodur N-100 prepolymer react with water. Therefore, it was necessary to pre-react these isocyanate groups before emulsification. Two such approaches were developed: (i) a fully-cured polyurethane emulsion comprising the preparation of a Desmodur N-100-hydroxypropyl methacrylate-1-butanol adduct in n-butyl acrylate-isobutyl methacrylate reactive diluent mixture using dibutyltin dilaurate catalyst, emulsification of this adduct solution in water using the sodium lauryl sulfate-cetyl alcohol combination, and polymerization using persulfate-ion initiator to form an emulsion that dries to a tough, glossy film; (ii) an air-drying polyurethane emulsion comprising the preparation of a Desmodur N-100-allyl alcohol-hydroxypropyl methacrylate adduct in n-butyl acrylate-isobutyl methacrylate reactive diluent mixture using dibutyltin dilaurate catalyst, mixing with a polyester prepolymer, and emulsification in water using the sodium lauryl sulfate-cetyl alcohol combination, to form an emulsion that air-dried upon addition of methyl ethyl ketone-cobalt naphthenate catalyst.

The present work concentrated on the optimization of the fully-cured polyurethane emulsion, e.g., by variation of the Desmodur N-100-reactive diluent ratio and the n-butyl acrylate-isobutyl methacrylate ratio. Moreover, improved emulsion stability was obtained by substitution of n-decane for the cetyl alcohol in the mixed emulsifier combination.

Therefore, the following recommendations are made for future work with this system:

1. Further variation of the parameters of this system--The present system has a high degree of crosslinking of the emulsion particles. Desmodur N-100 is thought to comprise three isocyanate groups per prepolymer molecule, so that the present hydroxypropyl methacrylate-1-butanol ratio would give a certain three-dimensional structure. The hydroxypropyl methacrylate-1-butanol ratio should be decreased so that the Desmodur N-100 would function more as a difunctional rather than a trifunctional prepolymer.

2. Post-stabilization of the fully-cured polyurethane emulsions--Suitable post-stabilizers should be developed by using the Span-Tween or some other suitable series to determine the HLB value needed to stabilize these emulsions for formulation as paints; then, various emulsifiers with HLB values in this range would be selected from those available and tried as post-stabilizers.

3. Development of an anionic aqueous pigment dispersion--Pigments should be selected from those presently used (2), and experiments should be carried out to develop aqueous pigment dispersions suitable for formulation with the polyurethane emulsions. Commercial pigment grinding vehicles would be used (e.g., Jonquil 67, S. C. Johnson Co.) to prepare these pigment dispersions, which would then be "let-down" into the polyurethane emulsions. Alternatively, difunctional isocyanate-containing prepolymers would be reacted so as to introduce carboxyl groups, to prepare a polyurethane-based aqueous grinding vehicle.

4. Evaluation of the polyurethane emulsion systems according to MIL-C-83286A (2) and selection of the most suitable composition for the aircraft topcoat application.

SECTION XI

REFERENCES

1. Military Specification MIL-P-23377C "Primer Coating: Epoxy-Polyamide, Chemical and Solvent Resistant, "August 26, 1969, Amendment I, March 31, 1972.

2. Military Specification MIL-C-83286A "Coating, Urethane, Aliphatic Isocyanate, for Aerospace Applications," October 27, 1972.

3. J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, "Emulsion Polymerization: Initiation of Polymerization in Monomer Droplets," Polymer Letters 11, 503 (1973).

4. M. S. El-Aasser, J. D. Hoffman, C. Kiefer, H. Leidheiser, Jr., J. A. Manson, G. W. Poehlein, R. Stoisits, and J. W. Vanderhoff, "Water-Base Coatings" Technical Report AFML-TR-74-208, Part I, November 1974.

5. J. W. Vanderhoff, H. L. Tarkowski, M. C. Jenkins, and E. B. Bradford, "Theoretical Considerations of the Interfacial Forces Involved in the Coalescence of Latex Particles," J. Macromol. Chem. 1, 361 (1966).

6. J. W. Vanderhoff, "Mechanism of Film Formation of Latices," Brit. Polymer J. 2, 161 (1970).

7. J. W. Vanderhoff, E. B. Bradford, and W. K. Carrington, "The Transport of Water Through Latex Films," J. Polymer Sci.: Sump. No. 41, 155 (1973).

8. G. L. Brown, "Formation of Films from Polymer Dispersions," J. Polymer Sci. 22, 423 (1956).

9. H. Warson, "The Application of Synthetic Resin Emulsions," Ernest Benn, Ltd., London, 1972, p. 269-72.

10. K. Wagner and G. Mennicken, "Aliphatic Isocyanates as Starting Materials for the Preparation of Coatings," F. A. T. I. P. E. C., 6th, Wiesbaden, 1962, p. 289.

11. W. R. Grace & Co., Brit. 1,132,887 (1968); cited in Reference 9, p. 272.

12. Reference 9, p. 272-4.

13. S. P. Suskind, "Polyurethane Latex," J. Appl. Polymer Sci. 9, 2451 (1965).

14. T. Makaiyama and Y. Hoshino, "On the Thermal Dissociation of Organic Compounds. X. The Effects of Solvents (Amines and Fatty Acids) on the Thermal Dissociation of Urethanes," J. Am. Chem. Soc. 78, 1946 (1956).

15. O. Bayer, "Das Diisocyanat-Polyadditions Verfahren, "Carl Hansen Verlag, Munich, a963, p. 12.

16. K. C. Frisch, talk presented at the University of Detroit Polymer Conference Series, "Technology of Organic Coatings," June 4-8, 1973.

17. W. Bunge, K. H. Mielke, and F. Moeller (to Farbenfabriken Bayer Akt.-Ges.), "Masked Polyisocyanate Having Low Cleavage Temperatures, " U.S. 2,886,555 (1959).

18. A. Damusis and K. C. Frisch (to Wyandotte Chemical Corp.), Can. 722,764 (1965); cited in Reference 16, p. 47.

19. J. W. Vanderhoff, H. J. van den Hul, R. J. M. Tausk, and J. Th. G. Overbeek, "Well-Characterized Monodisperse Latexes," in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies," G. Goldfinger, editor, Marcel Dekker, New York, 1970, p. 15.

20. J. Th. G. Overbeek, in "Colloid Science Vol. I," H. R. Kruyt, editor, Elsevier, New York, 1952, p. 80.

21. J. W. Vanderhoff, unpublished research results.

22. R. M. K. Cobb, in "Emulsion Technology," H. Bennett, editor, Chemical Publishing Co., New York, 1946, p. 7-32.

23. E. S. R. Gopal, in "Emulsion Science," P. Sherman, editor, Academic Press, New York, 1968, p. 1-75.

24. S. S. Voyutskii, "Polymer Reviews Vol. 4 Autohesion and Adhesion of High Polymers," Wiley-Interscience, New York, 1963, Chapters I-IV.

25. B. Nagy, Adhesives Age, April, 1967.

26. J. Ugelstad, A. R. M. Azad, R. M. Fitch, "Emulsification and Emulsion Polymerization Using Cationic Surfactants and Long Chain Fatty Alcohols," Abstracts, 169th ACS National Meeting, Philadelphia, April 6-11, 1975, POLY-019.

27. E. B. Bradford and J. W. Vanderhoff, "Morphological Changes in Latex Films," J. Macromol. Chem. 1(2), 335 (1966).

28. E. B. Bradford and J. W. Vanderhoff, "Additional Studies of Morphological Changes in Latex Films," J. Macromol. Sci.-Phys. B6(4), 671 (1972).

29. G. D. McCann, E. B. Bradford, H. J. van den Hul, and J. W. Vanderhoff, "The Effect of Ion Exchange on Latex Stability," "Polymer Colloids," R. M. Fitch, editor, Plenum Press, 1971, p. 29.

30. K. Kato, "Osmium Tetroxide Fixation of Rubber Latices, "J. Electron Microscopy 14, 219 (1965); ibid. Polymer Letters 4, 35 (1966).

31. H. Benard, "Sur les tourbillons cellulaires et la theorie de Rayleigh, " Compt. Rend. 185, 1109 (1927).

32. J. W. Vanderhoff and E. F. Gurnee, "A Motion Picture Investigation of Phenomena in Latex Films, " Tappi 39, 71 (1956).

33. Rohm & Haas Company Bulletin C-271, "Tamol 731 and Tamol 850 Pigment Dispersants for Aqueous Systems, " February, 1969.

34. A. J. Hyde and D. M. Stevenson, "The Effect of Additives in the Properties of Paraffin Chain Electrolyte Solutions: Part V: The Effect of Additives in the Electrical Conductance, " C. R. Congr. Int. Deterg., 5th, Borcelma, Sept. 1968, p. 1107; CA 74, 16257c (1971).

☆ U. S. GOVERNMENT PRINTING OFFICE: 1977 — 757-001/352