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CENTER FOR SURFACE AND COATINGS RESEARCH
LEHIGH UNIVERSITY

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AIR FORCE SYSTEMS COMMAND
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This technical report has been reviewed and is approved for publication.

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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 aqueous emulsions of both epoxy and polyurethane system components using the anionic sodium lauryl sulfate-cetyl alcohol or cationic hexadecyltrimethylammonium bromide-cetyl alcohol combinations as emulsifier.

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Fluid, stable anionic and cationic emulsions of the epoxy resin dissolved in solvents were prepared using the mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization. Electron microscopy of amine-hardened particles showed sizes in the range 0.03-0.3 microns. Both anionic and cationic emulsions of one amide curing agent were prepared, but another was sufficiently cationic to give only cationic emulsions. The solvent-stripped epoxy resin and curing agent emulsions were mixed in various proportions and cured at room temperature or 50°C. The log modulus-temperature variation showed a high degree of cure and the development of a three-dimensional polymer network.

The preparation of polyurethane emulsions is complicated by the reactivity of the isocyanate groups with water. Therefore, the isocyanate prepolymer was pre-reacted to give adducts that were emulsified using the anionic mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization. Both fully-cured and air-drying adducts gave fluid, stable emulsions which dried to tough, flexible films.

FOREWORD

The Lehigh Project 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. Henry Leidheiser, Jr., Professor of Chemistry and Director, Center for Surface and Coatings Research. Also contributing to the project were Postdoctoral Research Associates Dr. Mohamed S. El-Aasser, Center for Surface and Coatings Research, and Dr. Joseph D. Hoffman, Materials Research Center, and Graduate Students Richard C. Stoisits and Charles Kiefer, Department of Chemical Engineering.

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SUMMARY

A. General

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

The unique approach to the emulsification was the use of the mixed emulsifier combination shown earlier (1) to give aqueous styrene emulsions with droplet sizes as small as 0.2μ. At best, the smallest droplet size produced by the conventional emulsification techniques is about 1μ. Droplets of this size settle rapidly, and therefore the stability of commercial polymer emulsions prepared by emulsification often is not competitive with that of latexes prepared by emulsion polymerization, which usually have particle sizes in the range 0.1-0.3μ. This new emulsification technique uses sodium lauryl sulfate-cetyl alcohol combinations to give emulsion droplets of about the same size as latex particles produced by emulsion polymerization.

B. Epoxy Emulsion Systems

Most experiments used the Epon 1001-Versamid 115 epoxy resin-curing agent combination because this combination is deduced to be that used in the present Air Force system (2). Other epoxy resins used included Epon 828 and Component I (commercial epoxy resin now used); other curing agents used included Genamid 250 and Component II (commercial curing agent now used).

The first experiments comprised the emulsification of Epon 1001-phenyl glycidyl ether and Versamid 115-toluene-methyl isobutyl ketone solutions using the sodium lauryl sulfate-cetyl alcohol combination. The Epon 1001 solutions were emulsified with simple stirring to give an emulsion of larger droplet size than was observed earlier for styrene (1). These large droplets were reduced to 0.2-1.0μ diameter (optical microscopy) by ultrasonic irradiation or homogenization of the crude emulsion. The Versamid 115 solution was not emulsified, but instead formed paste-like coagulum with the sodium lauryl sulfate-cetyl alcohol combination, presumably because of flocculation of the anionically-stabilized droplets by the cationic curing agent.

Therefore, the cationic analog of the sodium lauryl sulfate-cetyl alcohol combination -- the hexadecyltrimethylammonium bromide-cetyl alcohol combination -- was applied to the emulsification of both the Versamid 115 and Epon 1001 solutions. This system was shown earlier (3) to give stable cationic emulsions of styrene with droplet sizes as small as 0.2μ (optical microscopy). This cationic mixed emulsifier combination gave stable Epon 1001 and Versamid 115 emulsions with large droplet sizes, which upon ultrasonic irradiation or homogenization were reduced to sizes as small as 0.2μ (optical microscopy).

For the emulsification of Epon 1001 or Epon 828, the recipe should contain at least 1 gm of the 0.33-0.67 hexadecyltrimethylammonium bromide-cetyl alcohol combination in 75 gm water for each 12.5 gm of Epon 1001 or 25 gm of the 50:25:25 Epon 1001-toluene-methyl isobutyl ketone mixture.

Two approaches were investigated to increase the Epon 1001 concentration of these emulsions: (1) emulsification of higher-solids Epon 1001 solutions; (2) removal of the solvents and concentration of the emulsion. Epon 1001-solvent mixtures in proportions as high as 50% gave fluid, stable emulsions, but 71% gave paste-like emulsions; however, both the 50% and 71% emulsions were difficult to handle during the solvent-removal step. Therefore, the emulsification was carried out using 25% Epon 1001-solvent mixture, and the resulting fluid emulsions was subjected to vacuum steam distillation to remove the solvents and concentrate the emulsion to the desired solids content.

The particle size of the Epon 1001 emulsions was determined by transmission electron microscopy after the droplets were hardened in the emulsion state by heating with water-soluble ethylene diamine catalyst. The particles were in the size range 0.03-0.3 μ, attesting to the efficacy of this emulsification technique.

The Versamid 115 curing agent proved difficult to emulsify, even with the cationic mixed emulsifier combination. Stable emulsions of Versamid 115 dissolved in 10:25:25:40 xylene-n-butanol-isopropanol-toluene solvent mixture were formed at low concentrations of the Versamid 115 in the solution (25% instead of 50%) and low oil-water ratios (0.25 instead of 0.50). When these emulsions were subjected to vacuum steam distillation to remove the solvents and concentrate the emulsion, they became viscous and translucent at critical stage, indicating a spontaneous decrease in droplet size. Upon standing for 4-6 weeks, these viscous translucent emulsions slowly reverted to fluid opaque emulsions, indicating an increase in droplet size due to coalescence. These Versamid 115 emulsions were compatible with the Epon 1001 emulsions whether in the viscous, translucent or opaque, fluid form.

Similar results were observed with the Genamid 250 emulsifications, except that the lower viscosity of this curing agent made the emulsification easier and eliminated the need for dilution with solvents. Moreover, anionic emulsions of Genamid 250 could be prepared using the sodium lauryl sulfate-cetyl alcohol combination.

Mixed solvent-free emulsions of the Epon 1001-Versamid 115, Epon 1001-Genamid 250, and Epon 828-Versamid 115 systems were prepared, cast on aluminum alloy panels, and cured at room temperature or in an air oven. For comparison, films of the solvent-based Epon 828-Versamid 115 and Component I-Component II commercial systems were also prepared and cured under similar conditions. The emulsion systems formed transparent films, indicating that the epoxy resin droplets had coalesced with the curing agent droplets. Higher curing temperatures gave faster rates of cure, e.g., about 30 days at room temperature was needed to give the same properties obtained in a few hours at 50°C; however, the final film properties were comparable. 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. Measurements of the log modulus-temperature variations showed that the emulsion-cast films had cured to a three-dimensional polymer network as expected, and that these films were neither better nor worse than the corresponding solvent-cast films.

The following emulsion samples were submitted to the Air Force for evaluation: 25.3% cationic Epon 1001; 24.6% anionic Epon 1001; 22.5% cationic Epon 828; 7.1% cationic Versamid 115; 34.1% cationic Genamid 250; 33.6% anionic Genamid 250.

C. Polyurethane Emulsion Systems

The present Air Force topcoat system (4) is deduced to be a solvent-based mixture of Desmodur N-100 isocyanate prepolymer and Multron E-380 polyester prepolymer. To prepare a water-based analog of this system requires that the isocyanate groups of the Desmodur N-100 be reacted before emulsification because these groups react readily with water. These isocyanate groups can be reacted with a wide variety of hydroxyl-containing compounds using dibutyltin dilaurate catalyst. Since it is the Multron E-380 rather than the Desmodur N-100 that imparts the flexibility to the topcoat film, the hydroxyl-containing compound reacted with the Desmodur N-100 must also fulfill this function.

Desmodur N-100 adducts of varying composition were emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and simple stirring, followed by ultrasonic irradiation or homogenization, to give stable emulsions with droplet sizes of about 0.2μ (optical microscopy). Stable emulsions were prepared of two different types: (1) fully-cured systems; (2) air-drying systems.

To prepare fully-cured polyurethane emulsions, Desmodur N-100 was reacted with hydroxypropyl methacrylate and 1-butanol modifier in butyl acrylate-isobutyl methacrylate reactive diluent mixture using dibutyltin dilaurate catalyst. This adduct was emulsified in water using the anionic mixed emulsifier combination, and its residual vinyl groups were polymerized using persulfate-ion initiator to form a stable emulsion. The emulsion must be added continuously to the persulfate-initiated polymerization; batch polymerization gives excessive coagulum.

The particle size of these emulsions was determined by transmission electron microscopy using the cold stage to prevent deformation of the particles. The particles were in the size range 0.03-0.4μ, attesting to the efficacy of the emulsification process.

In the best cases, the fully-cured polyurethane emulsions dried to form glossy, tough, flexible films. Preliminary measurements of the log modulus-temperature variation showed results typical of a flexible coating film. Moreover, the films showed sound-deadening properties.

Two fully-cured polyurethane emulsions prepared with slightly different butyl acrylate-isobutyl methacrylate ratios (hence, with slightly different flexibilities) were submitted to the Air Force for evaluation.

To prepare air-drying polyurethane emulsions, Desmodur N-100 was reacted with allyl alcohol to form an allyl carbamate derivative that can be air-dried using cobalt naphthenate catalyst. These Desmodur N-100 adducts were prepared, often in combination with a hydroxyalkyl methacrylate, using dibutyltin dilaurate catalyst; then a polyester prepolymer (e.g., Multron R-16 or Paraplex P-444A) was added and the mixture was emulsified in water using the anionic mixed emulsifier combination to form an emulsion that, when dried overnight with cobalt naphthenate catalyst, formed a glossy, tough, flexible film.

The use of Multron R-16 as the polyester prepolymer gave glossy, tough, flexible films that aged well; however, the viscosity of the adduct was too high for easy emulsification, and the alterations in the recipe to make lower-viscosity adducts resulted in incompatible products. The use of Paraplex-444A gave adducts of low-enough viscosity for easy emulsification, and the film properties were initially very good; however, they deteriorated rapidly upon ageing. The best results were obtained using a mixture of Multron R-16 and Paraplex P-444A.

The compositions containing Paraplex P-444A unsaturated polyester prepolymer or other vinyl groups introduced in a different manner can be cured in air using the methyl ethyl ketone peroxide-cobalt naphthenate combination.

Various other adducts were also investigated, e.g., Desmodur N-100 adducts with glycidol and adducts prepared from the 1,6-hexamethylene diisocyanate percursor of Desmodur N-100. Many of these other adducts gave interesting properties, but none are satisfactory for the topcoat application at this stage of development.

SECTION II

INTRODUCTION

A. Statement of the Problem

The problem is to adapt the solvent-based epoxy-polyamide primer (2) and aliphatic isocyanate polyurethane topcoat (4) presently used by the Air Force to a water-based system 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, emulsion polymerization, or some other means, and the resulting water-based coatings must be demonstrated to be equivalent to their solvent-based predecessors in ease of application and final film properties.

B. Water-Base Coatings Systems

Water-based polymer systems suitable for the formulations 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 are comprised of 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 are comprised of molecular disperions of polymer molecules; their viscosities are relatively great and increase sharply 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 alkali-soluble carboxyl groups is prepared at low pH, then the pH is increased so as to solubilize these groups and 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 those polymer dispersions or solutions which contain some organic solvent, but of such type and concentration as to allow dilution with water without separation into two phases. The term "water-dispersible" is applied to those dispersions and solutions which contain no organic solvent and can be diluted indefinitely with water.

a. Polymer Dispersions or Latexes

Polymer dispersions or latexes are comprised of colloidally-dispersed microscopic or submicroscopic polymer spheres, often of 0.1-0.3μ diameter for latexes prepared by emulsion polymerization. These latexes 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 dispersions or latexes have several advantages in water-base 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 improvements in physical and chemical 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 0.1μ (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, these dispersions or latexes enjoy a very large market, due primarily to the extensive industrial research and development effort in paints, paper coatings, textile sizings, 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 those 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 using such standard catalysts as anhydrides or amines, but the use of these 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 condensates 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.

There are two approaches to the emulsification of the epoxy resin component: 1. direct reaction of epichlorohydrin with a bisphenol in the presence of an emulsifier and a water-miscible solvent (9); 2. emulsification of an epoxy resin-amine curing agent mixture, e.g., an epoxy resin with an excess of aliphatic amine dispersed by an organic acid (10), an epoxy resin with a polyamine curing agent emulsified with an alkylphenol polyglycol ether (11), and an epoxy resin with a phenol-polyamine condensate emulsified with ethylene oxide-propylene oxide condensates (12).

The polyamides formed by reaction of a diamine and a dibasic acid may also be emulsified in water using acrylamide-acrylic acid copolymers (13-15), cationic low-molecular-weight polyamides with surplus amine functionality (16), and, for a mixed hexamethylenediamine adipate-hexamethylenediamine sebacate polyamide with an epichlorohydrin-bisphenol A condensate, sodium lauryl sulfate and polyvinyl alcohol (17). The stability of the aqueous polyamide dispersions is improved by addition of a low-molecular weight epoxy resin which is soluble in hot amyl alcohol (18).

Polyamide-epoxy resin dispersions may be prepared by adding acetic acid to an amine-terminated polyamide, then emulsifying the solution to form a cationic emulsion in which the epoxy resin can be emulsified (19), or by dissolving a polyamide in toluene-isopropanol solution and an epoxy resin in toluene-methyl ethyl ketone solution, then emulsifying the mixed solutions (20).

Two-component systems with greatly decreased concentrations of solvents are prepared by combining an aliphatic epoxide-bisphenol A prepolymer with a 70% polyamide solution, which self-emulsifies both the polyamide and epoxy resin prepolymers (16).

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.

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, carboxylic acids, or carboxylic acid amides. 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 (21): 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 (22, 23). 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 polyurethane 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 (24).

Several approaches have been used to prepare water-based polyurethane dispersions: 1. reaction of an isocyanate-terminated prepolymer with a blocking agent (e.g., methyl ethyl ketoxime), followed by addition of a curing agent (e.g., N, N, N', N'-tetrakis(2-hydroxypropyl)ethylene diamine) and emulsification in water using various emulsifiers (25); 2. addition of an alkyl diethanolamine or water-soluble diamine to a prepolymer prepared from a diisocyanate and hydroxyl-terminated polyester or polyether prepolymer, followed by emulsification (often spontaneous) in 3% acetic acid to form a cationic emulsion (26); 3. direct emulsification of the diisocyanate-polyol prepolymer (practicable only for short shelf life and prepolymers of lesser reactivity) (27); 4. reaction of an isocyanate-terminated prepolymer with a hydroxyl-containing vinyl monomer (e.g., propylene glycol monoacrylate), followed by emulsification in water and polymerization of the vinyl groups in the usual manner (28).

Water reacts with the isocyanate group to produce carbamic acids and eventually diamines. It is interesting, however, that this reaction does not prevent the preparation and application of polyurethane dispersions. The diamines formed can react with the isocyanate group to form a polysubstituted urea, and such chain extension by reaction with water is considered desirable in some cases (21). In the reaction of the isocyanate-prepolymer with an alkyl diethanolamine (26), 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 (29). The temperature of dissociation depends upon the chemical nature of the groups adjacent to the urethane linkage, e.g., diaryl urethanes are stable up to about 120°C, and n-alkyl urethanes up to about 250°C (30). 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 (31). Deblocking at lower temperatures can be catalyzed by tertiary amine salts of organic acids (32) and dibutyltin dicarboxylates (33).

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.

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 are available from several companies. In most cases, however, these commercial emulsions do not display properties comparable 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 *in situ* 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 1μ in exceptional circumstances and 2-3μ in more usual cases. These emulsions have broad particle-size distributions so that an emulsion with an average droplet size of 1μ will contain particles as small as 0.5μ. In comparison, most commercial latexes sold for coatings applications have average particle diameters in the range 0.1-0.3μ.

1. Correlation of Particle Size and Shelf Stability

The five-fold difference in particle size between latexes prepared by emulsion polymerization (0.1-0.3μ) and the smallest droplet sizes that can be prepared by emulsification (1μ) is a critical one. For example, a monodisperse polystyrene latex of 1μ diameter will settle out upon standing within 1-3 months, while monodisperse polystyrene latex of 0.2μ diameter will never settle at all (34). This experimental result 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 sedimentation rate of 1 mm in 24 hours will be offset by the thermal convection and Brownian motion within the sample (35). Substituting this sedimentation rate in equation 1 gives the following values for the largest particle sizes that will not settle out upon standing.

Table I. Critical Particle Size for Settling upon Standing
(density of medium 1.00 gm/cm^3)

Particle Density, gm/cm^3	Viscosity of Medium, cps	Particle Diameter, μ
1.01	1.0	1.46
1.02	1.0	1.03
1.03	1.0	0.84
1.05	1.0	0.65
1.10	1.0	0.46
1.15	1.0	0.38
1.20	1.0	0.33
1.30	1.0	0.27
1.50	1.0	0.21
2.00	1.0	0.15
3.00	1.0	0.10
1.05	0.895*	0.62
1.05	1.0	0.65
1.05	2.0	0.92
1.05	5.0	1.46
1.05	10.0	2.06
1.10	0.895*	0.44
1.10	1.0	0.46
1.10	2.0	0.65
1.10	5.0	1.03
1.10	10.0	1.46
1.15	0.895*	0.36
1.15	1.0	0.38
1.15	2.0	0.53
1.15	5.0	0.84
1.15	10.0	1.19

* viscosity of water at 25° C

For polystyrene, which has a density of 1.05 gm/cm^3, the largest particle size that will not settle upon standing is 0.65μ, assuming the viscosity of the medium is 1 cps, in good agreement with the experimental results.

Since most of the prepolymers to be emulsified have densities in the range 1.10-1.15 gm/cm^3, it is critical whether the emulsification produces droplets of 1μ or 0.2μ diameter.

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 of its aqueous dispersion is calculated to be about 1600 psi for a particle diameter of 0.1μ 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 1μ and 10μ 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 particle coalescence will be incomplete and the film properties will be diminished. Thus, it is difficult to prepare epoxy or polyurethane emulsion systems of 2-3μ diameter that will dry to form hard enamel-like films.

3. In Situ 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, as the solvent evaporates, the curing reaction forms 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 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-solvent mixture. 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 extent of cure before application.

B. Principles of Emulsification

The desirable properties of an emulsifier to be used for emulsification of an oil in water are as follows (36):

(i) It must reduce the interfacial tension to about 5 dynes/cm or less;

(ii) It must adsorb quickly on the droplet surface and not be displaced when two droplets collide, thus preventing coalescence;

(iii) It 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) It must be more soluble in the water phase so as to be readily available for adsorption on the oil droplet surfaces;

(v) It must impart a sufficient electrokinetic potential to the emulsion droplets;

(vi) It must influence the viscosity of the emulsion;

(vii) It must work in small concentrations;

(viii) It should be relatively inexpensive;

(ix) It 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 (37). 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, as would be expected 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

To solve this problem, it is necessary to prepare 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 1μ using practical concentrations of emulsifier. However, it was shown recently (1) that anionic emulsions of styrene in water with droplet sizes as small as 0.2μ can be prepared using the sodium lauryl sulfate-cetyl alcohol mixed emulsifier combination. Analogous cationic emulsions with similar droplet sizes can be prepared using the hexadecyltrimethylammonium bromide-cetyl alcohol combination (3). In both cases, the total concentration of the mixed emulsifier combination is 1-2% or less.

It is not known precisely how these mixed emulsifier combinations fit the foregoing criteria for efficient oil-in-water emulsification. However, the success of this system in producing these very small emulsion droplet sizes suggests that it does fulfill these criteria and that it is worthy of further investigation as a means to prepare prepolymer emulsions of similarly small droplet size.

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: (1) Component I is a high-molecular weight epoxy resin prepolymer dissolved in solvents and containing dispersed pigments; (2) 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 425-550 (2). The solvent mixture is reported (2) to be a 46.7:53.3 toluene-methyl isobutyl ketone mixture. The total non-volatile content (prepolymer plus pigment) is 60-62% (2).

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 (2). 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 (2).

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 polymer 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 is to develop a water-based analog of the epoxy resin-curing agent system presently used by the Air Force. The general approach is to prepare separate emulsions of the 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 (55)) 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 of its dependence upon the area of contact between the two phases (which 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 (for the reasons discussed in 5. a. 3.).

These separate emulsions must remain stable indefinitely upon standing, yet upon mixing and drying cure to form a three-dimensional polymer network. In principle, a mixed emulsion comprised of separate stable droplets of epoxy resin and curing agent could be stored indefinitely without pre-curing provided that: (1) all of the reactive components of the epoxy resin and the curing agent are completely insoluble in water; (2) 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 between unlike droplets leading to flocculation and coalescence 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 is based on the earlier development of the mixed emulsifier system (1) which gives styrene emulsion droplets of about 0.2μ 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, if successful, would yield emulsion droplets sufficiently small to remain stable without settling indefinitely upon standing.

Three 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.
3. Component I (Naval Air Development Center) - a commercial sample used for the primer application reputed to be Epon 1001 dissolved in solvents.

Three 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. Genamid 250 (General Mills Chemical Company, Inc.) - a low-viscosity (5-10 poise Brookfield at 25° C) amine adduct with an amine value of 450.
3. Component II (Naval Air Development Center) - a commercial sample used for the primer application reputed to be Versamid 115 dissolved in solvents.

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

B. Experimental Details and Discussion

1. Experimental Details

The emulsification technique was essentially the same as that used earlier for the preparation of styrene monomer emulsions (1). Typically, 0.40-0.80 gm of the sodium lauryl sulfate-cetyl 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 for 30 minutes to form a crude emulsion. Since the prepolymers or prepolymer solutions were much more viscous than styrene monomer, this emulsification by simple stirring produced microscopic-size droplets rather than the submicroscopic-size droplets produced in the styrene emulsifications. Therefore, the crude emulsions were subjected to ultrasonic irradiation or homogenization to reduce the microscopic-size droplets to the submicroscopic-size range.

Figure 1 shows the Model W-350 Sonifier Cell Disruptor (Heat System-Ultrasonics, Inc.) used to subject the crude emulsions to ultrasonic irradiation. The 110-volt AC line voltage is converted to electrical energy with a frequency above the audible range (20 kilohertz). The sonic convertor transforms this energy into mechanical energy at the same frequency, which in turn is transmitted through the 0.75-inch horn tip into the liquid being treated. The ultrasonic waves cause cavitation in the liquid, producing a tearing action at any phase boundaries within the system.

Figure 2 shows the Manton-Gaulin Model 15M-8TA Laboratory Homogenizer and Submicron Disperser (Manton-Gaulin Company) used to homogenize the crude emulsions. The crude emulsion is forced through a small orifice at pressures up to 8000 psi; the rapid increase in velocity between the valve stem and seat causes cavitation of the liquid and the formation of bubbles; the collapse of these bubbles sets the valve stem into vibration at high frequencies (20-50 kilocycles/sec), which breaks the emulsion droplets down to a smaller size. The homogenized emulsion can be recycled through the orifice by using the 3-way valve to direct it back to the supply tank.

In this work, the Sonifier Cell-Disruptor and the Manton-Gaulin Homogenizer were used in a complementary manner, the former for small laboratory samples and the latter for larger-size samples.

2. Epoxy Resin Emulsions

a. Preliminary Experiments

The first experiments used Epon 828 and Epon 1001 epoxy resins. Since Epon 828 is a viscous liquid and Epon 1001 is a solid at room temperature, both resins must be dissolved in a solvent to produce solutions of low-enough viscosity for efficient emulsification. The first solvent tried was the reactive diluent phenyl glycidyl ether, which presumably would react with the epoxy resin during curing and therefore would not need to be removed after emulsification. The 50:50 Epon 828-phenyl glycidyl ether

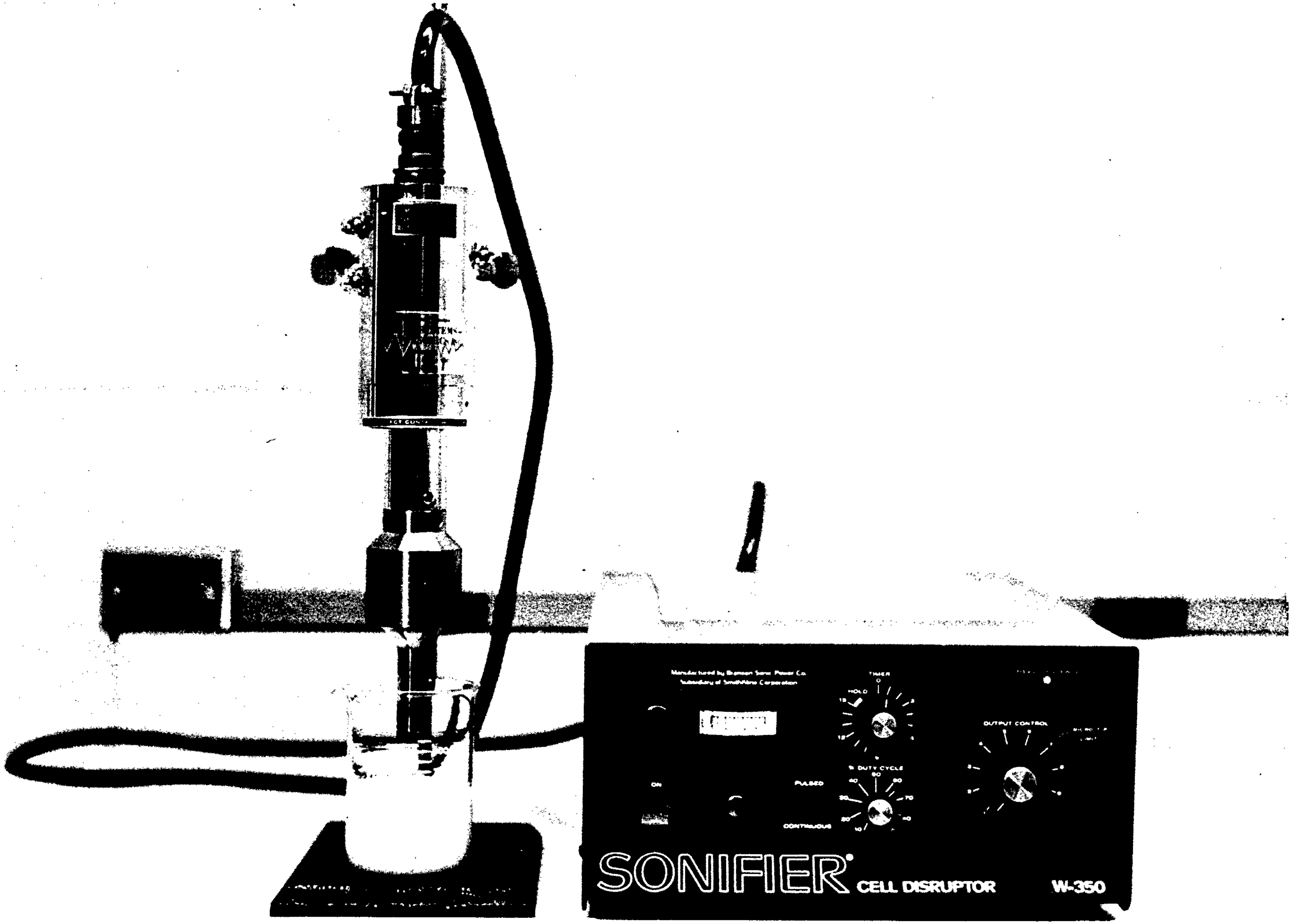

Figure 1. Model W-350 Sonifier Cell Disruptor (Heat System-Ultrasonics, Inc.) used to subject epoxy resin and polyurethane emulsion systems to ultrasonic irradiation.

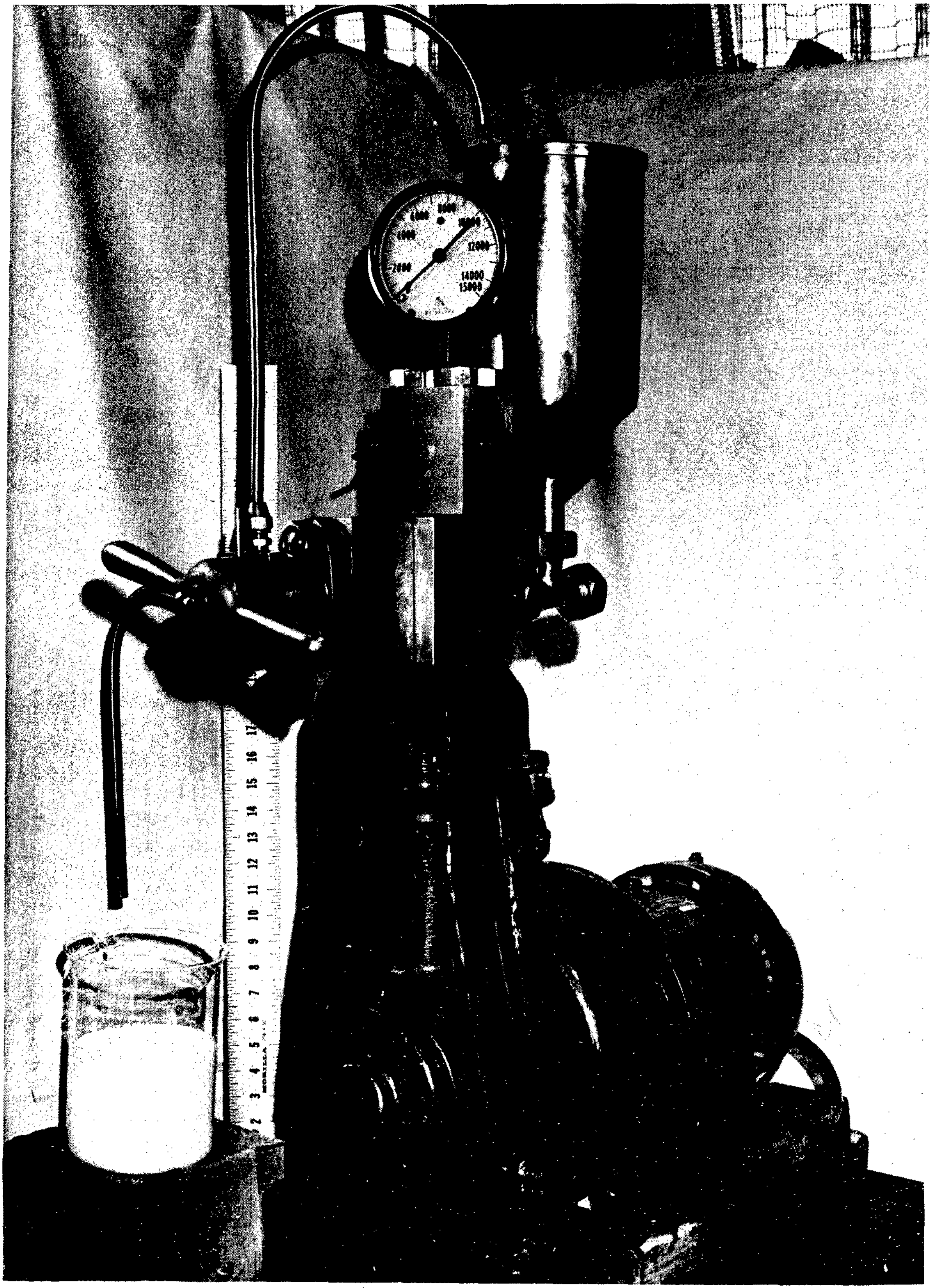

Figure 2. Model 15M-8TA Laboratory Homogenizer and Submicron Disperser (Manton-Gaulin Co.) used to homogenize the epoxy resin and polyurethane emulsion systems.

mixture was emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination to give an emulsion of large droplet size and poor stability. Figure 3 shows an optical photomicrograph of this emulsion. Ultrasonic irradiation while this crude emulsion was still hot gave a stable emulsion with droplet sizes smaller than 2μ (Figure 4). Similar results were observed with the 68:32 and 75:25 Epon 828-phenyl glycidyl ether mixtures as well as with the 25:75 Epon 1001-phenyl glycidyl ether mixture. Figures 5, 6, and 7 show respectively optical photomicrographs of the crude emulsions prepared from these three mixtures. Figure 8 shows the same emulsion of Figure 5 after ultrasonic irradiation at room temperature; Figures 9 and 10 show the same emulsions of Figure 6 and 7 after ultrasonic irradiation while still hot. In all three cases, the ultrasonic irradiation decreased the emulsion droplet sizes significantly. Moreover, the ultrasonically-irradiated emulsions showed no increase in droplet size upon standing at room temperature for extended periods of time, an indication of good stability.

As will be described later, the attempts to emulsify the Versamid 115 polyamide curing agent prepolymer using the sodium lauryl sulfate-cetyl alcohol combination gave pastes rather than emulsions, presumably because of flocculation of the positively-charged polyamide prepolymer by the negatively-charged sodium lauryl sulfate. This explanation was confirmed by the fact that substitution of the cationic hexadecyltrimethylammonium bromide for the sodium lauryl sulfate in the mixed emulsifier system gave stable cationic emulsions of Versamid 115. This cationic emulsifier had earlier been found (3) to function similarly to sodium lauryl sulfate in combination with cetyl alcohol in the preparation of stable cationic polystyrene latexes. Since only cationic emulsions of Versamid 115 could be prepared, the same hexadecyltrimethylammonium bromide-cetyl alcohol combination was used to prepare cationic emulsions of the epoxy resins.

Since the 25:75 Epon 1001-phenyl glycidyl ether mixture is a high-viscosity liquid, another solvent system was required which would allow preparation of Epon 1001 solutions of higher solids and lower viscosity. The 50:50 toluene-methyl isobutyl ketone solvent mixture was found to be a suitable choice. The 50:25:25 Epon 1001-toluene-methyl isobutyl ketone mixture was emulsified using the hexadecyltrimethylammonium bromide-cetyl alcohol combination to produce an emulsion droplet size of 1μ or smaller after one pass through the Manton-Gaulin Homogenizer (Figure 11) and an even smaller droplet size after three passes (Figure 12). Thus, homogenization of the crude emulsion in the Manton-Gaulin Homogenizer produced droplet sizes at least equivalent to those produced using ultrasonic irradiation.

The investigations conducted to determine the conditions required for the preparation of stable solvent-free epoxy resin emulsions can be divided into three main areas: (1) the determination of the optimum hexadecyltrimethylammonium bromide-cetyl alcohol ratio and concentration; (2) the removal of solvents from the latex and the concentration to higher solids; (3) the determination of the emulsion droplet size.

b. Determination of the Optimum Hexadecyltrimethylammonium Bromide-Cetyl Alcohol Ratio and Concentration

The effect of the hexadecyltrimethylammonium bromide-cetyl alcohol ratio and concentration on the emulsification of 25 gm of the 50:25:25 Epon 1001-toluene-methyl

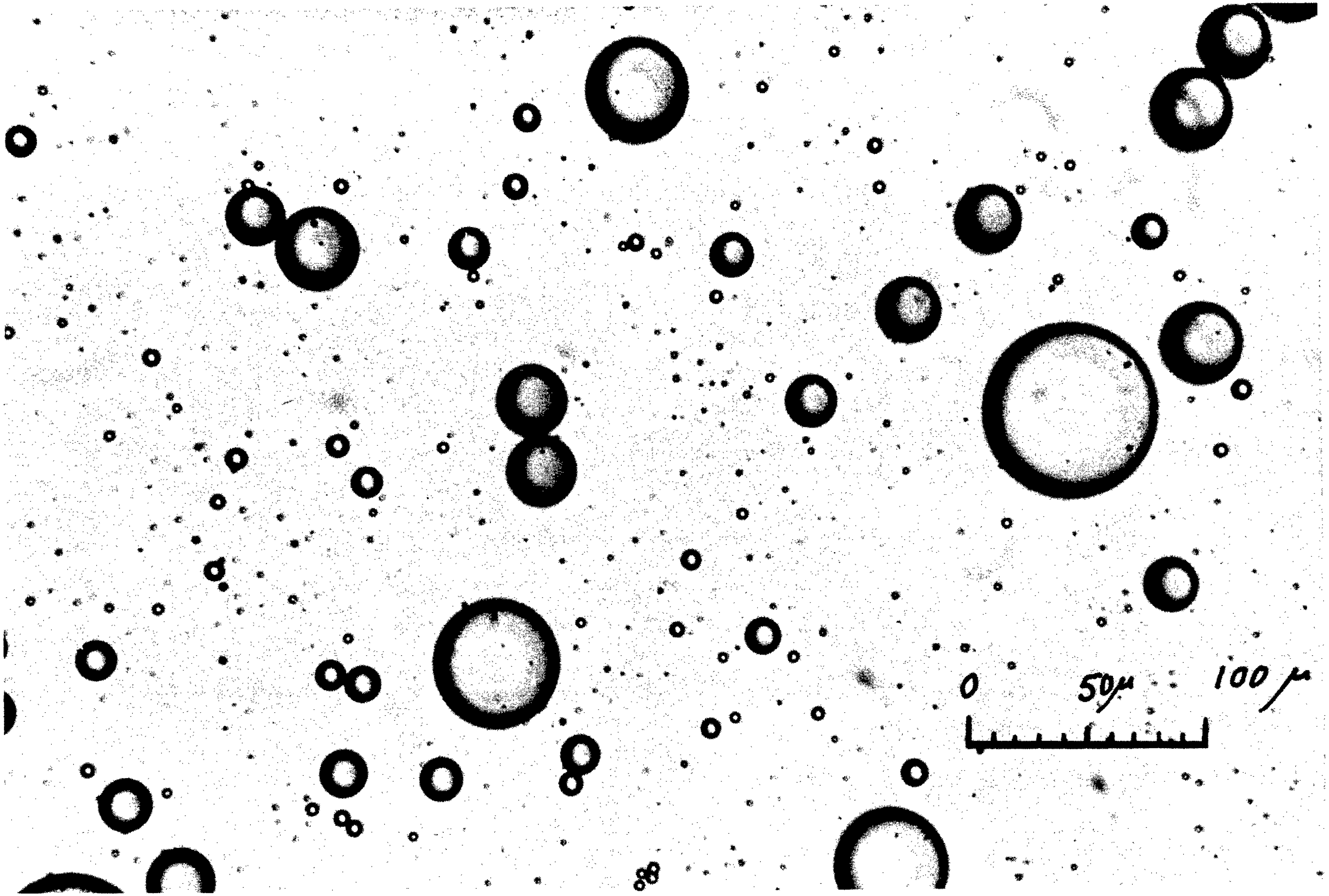

Figure 3. Optical photomicrograph of an emulsion of 50:50 Epon 828-phenyl glycidyl ether mixture prepared with simple stirring, after standing for 3 days.

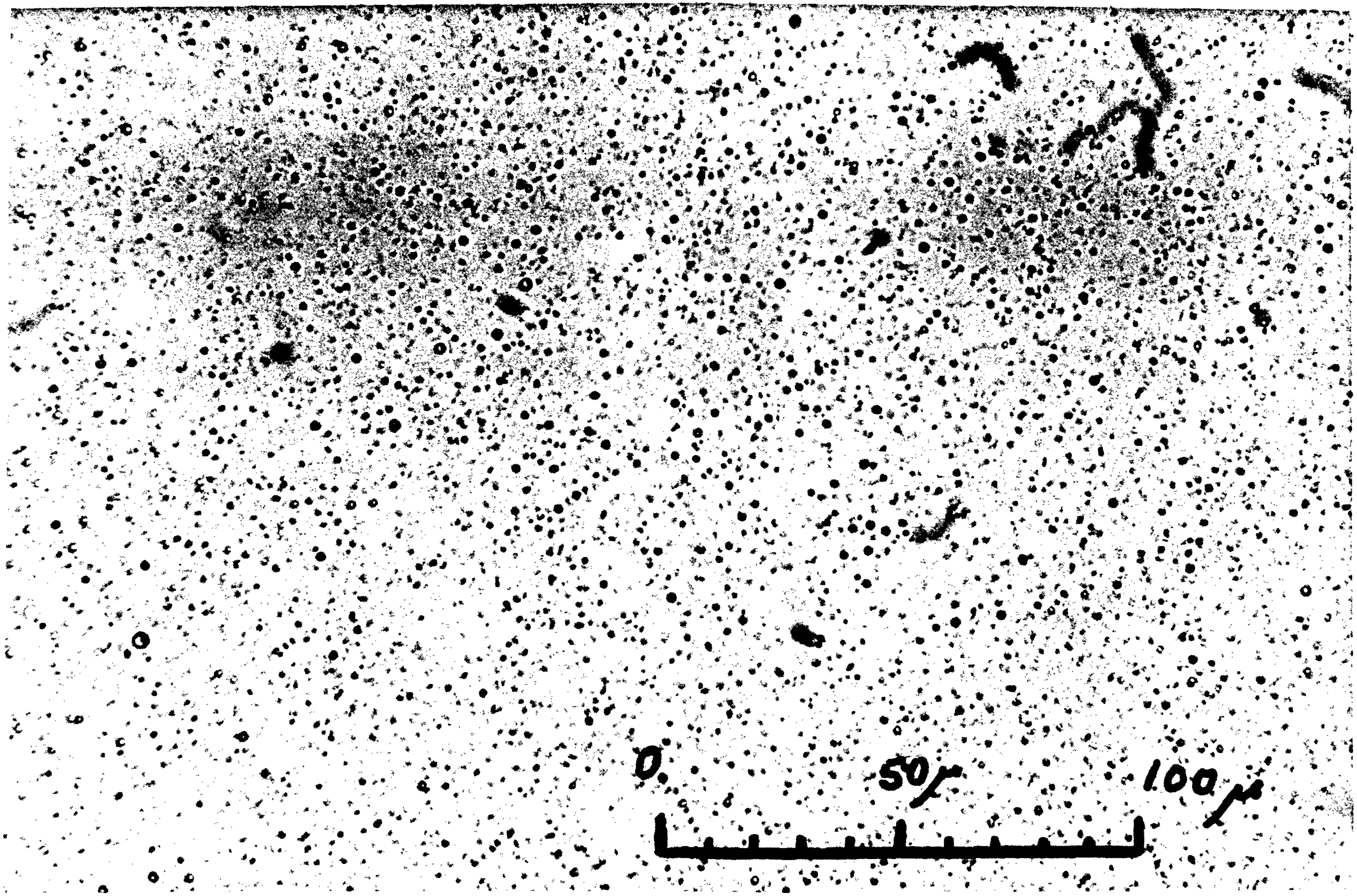

Figure 4. Optical photomicrograph of an emulsion of 50:50 Epon 828-phenyl glycidyl ether mixture prepared with ultrasonic irradiation, followed by standing for 3 days.

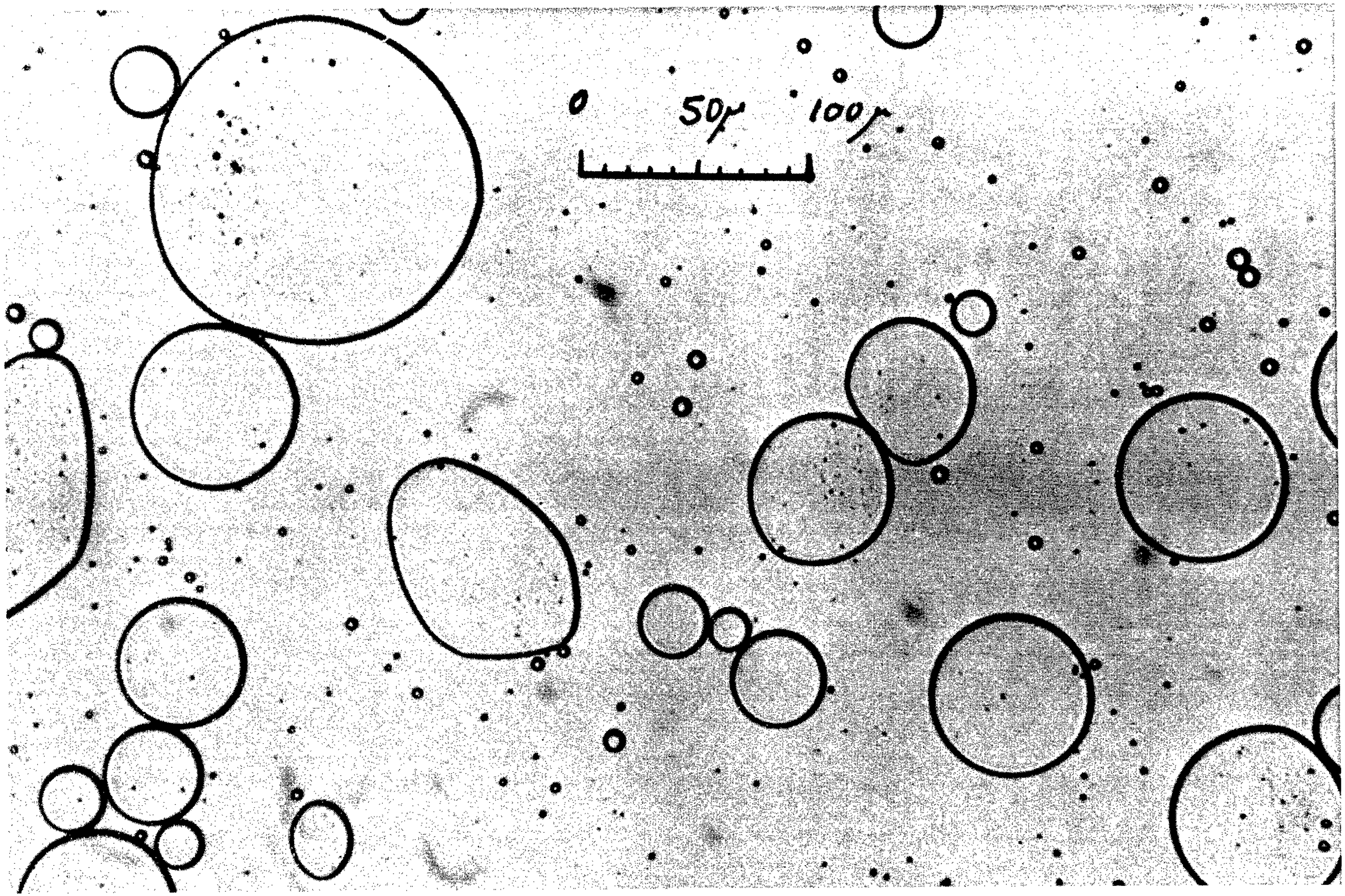

Figure 5. Optical photomicrograph of an emulsion of 68:32 Epon 828-phenyl glycidyl ether mixture prepared with simple stirring, after standing for 6 days.

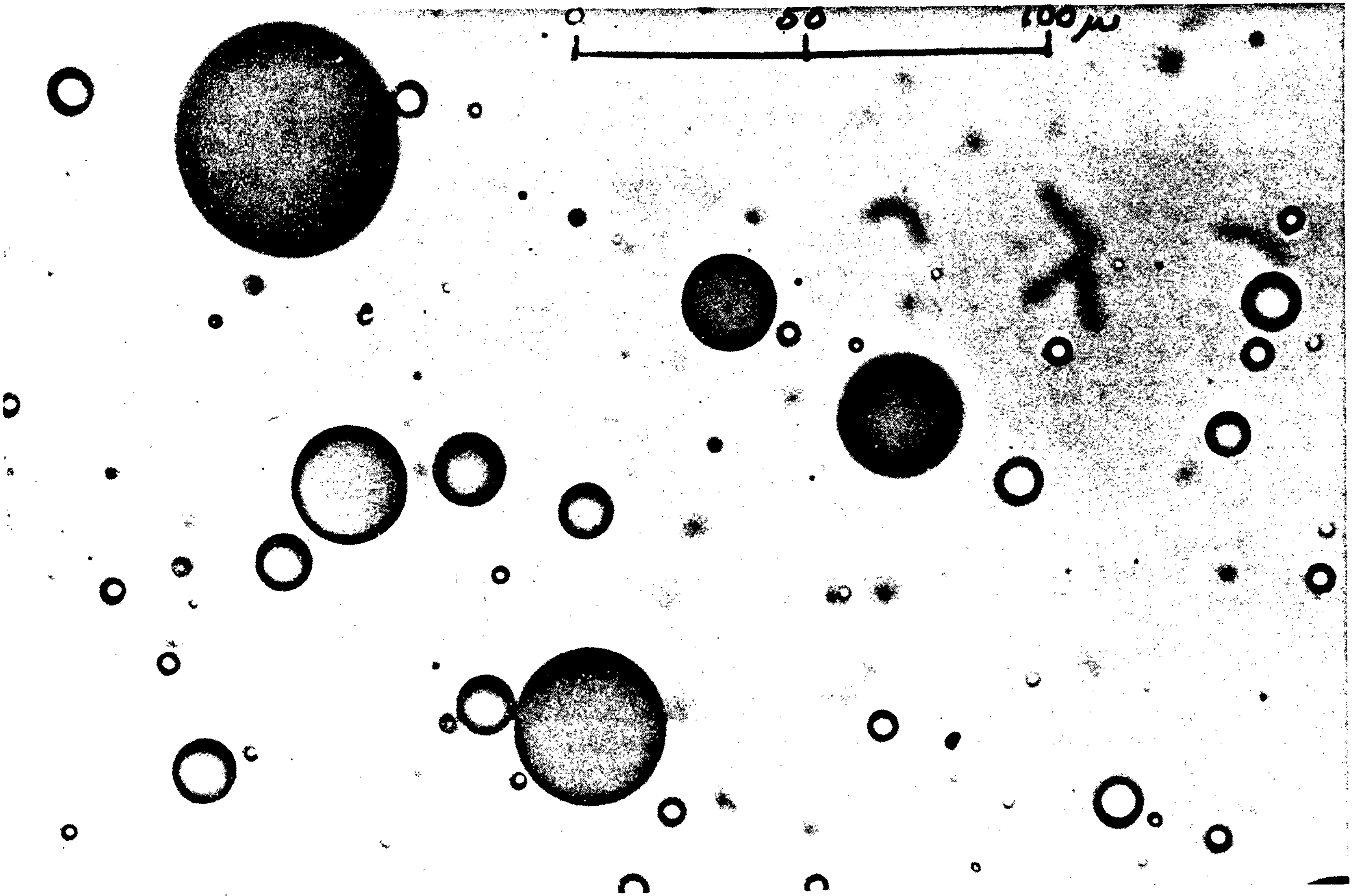

Figure 6. Optical photomicrograph of an emulsion of 75:25 Epon 828-phenyl glycidyl ether mixture prepared with simple stirring, after standing for 1 day.

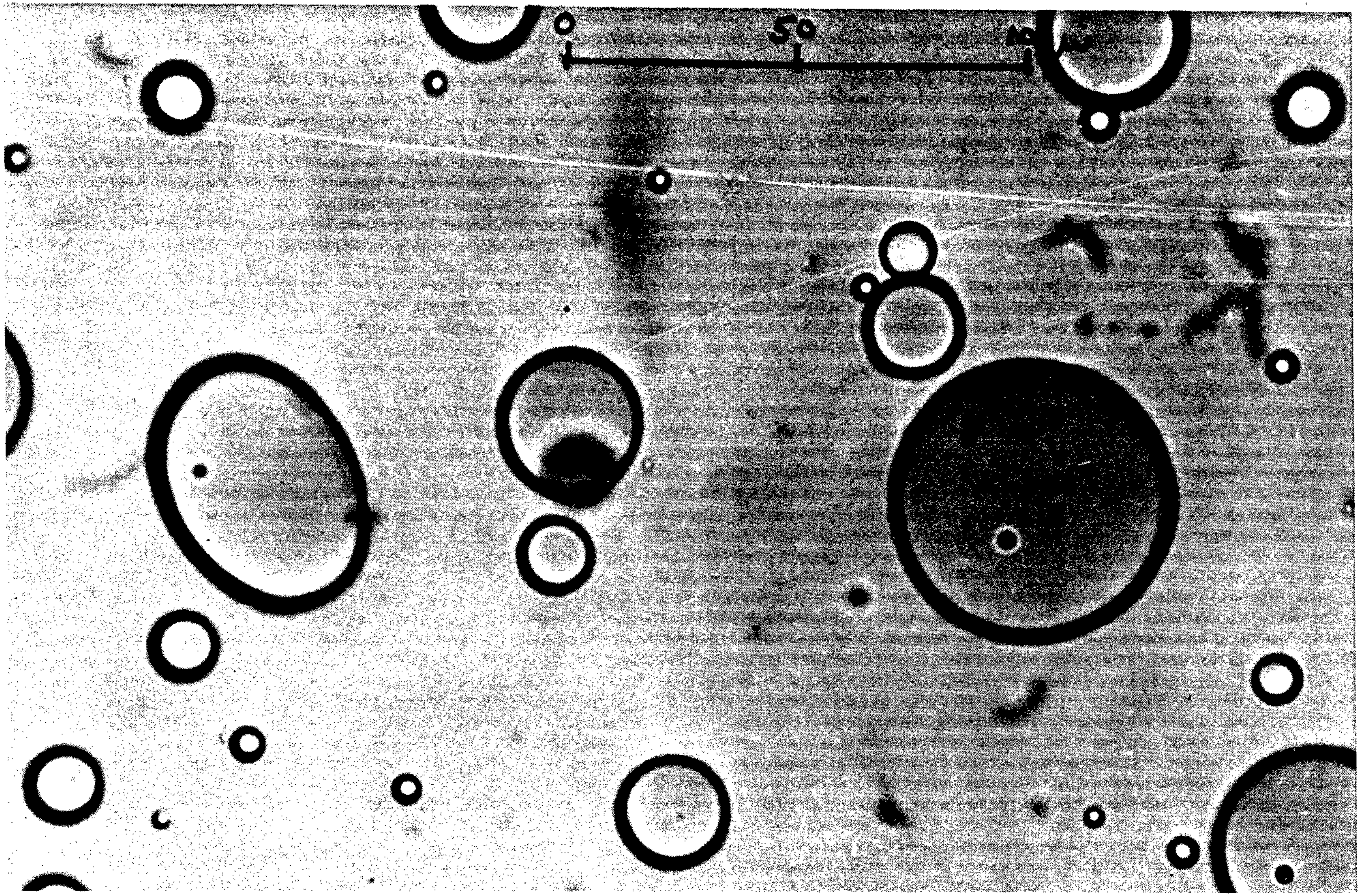

Figure 7. Optical Photomicrograph of an emulsion of 25:75 Epon 1001-phenyl glycidyl ether mixture prepared with simple stirring, after standing for 6 days.

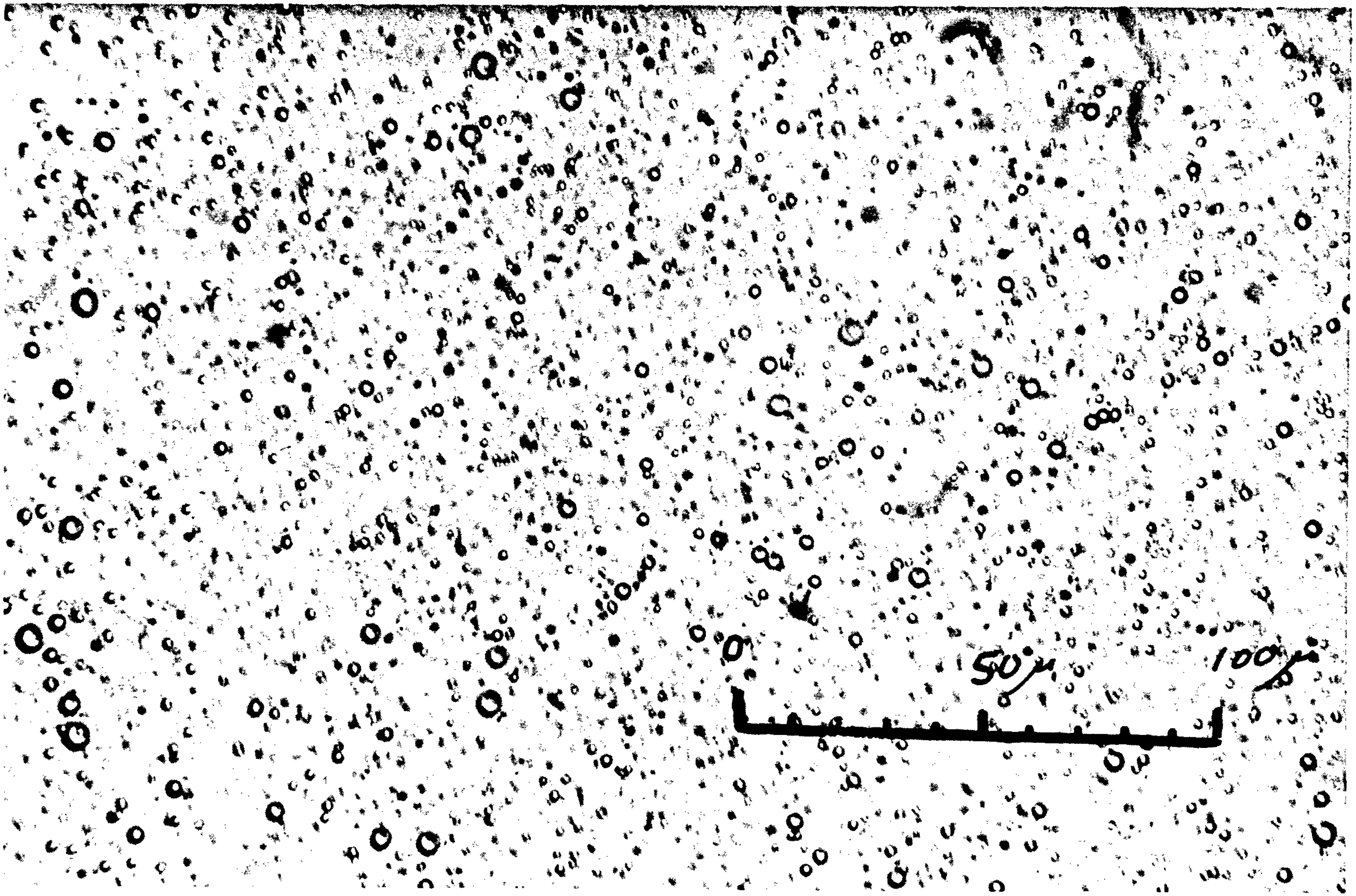

Figure 8. Optical photomicrograph of an emulsion of 68:32 Epon 828-phenyl glycidyl ether mixture after room-temperature ultrasonic irradiation at 3 days, followed by standing for another 3 days.

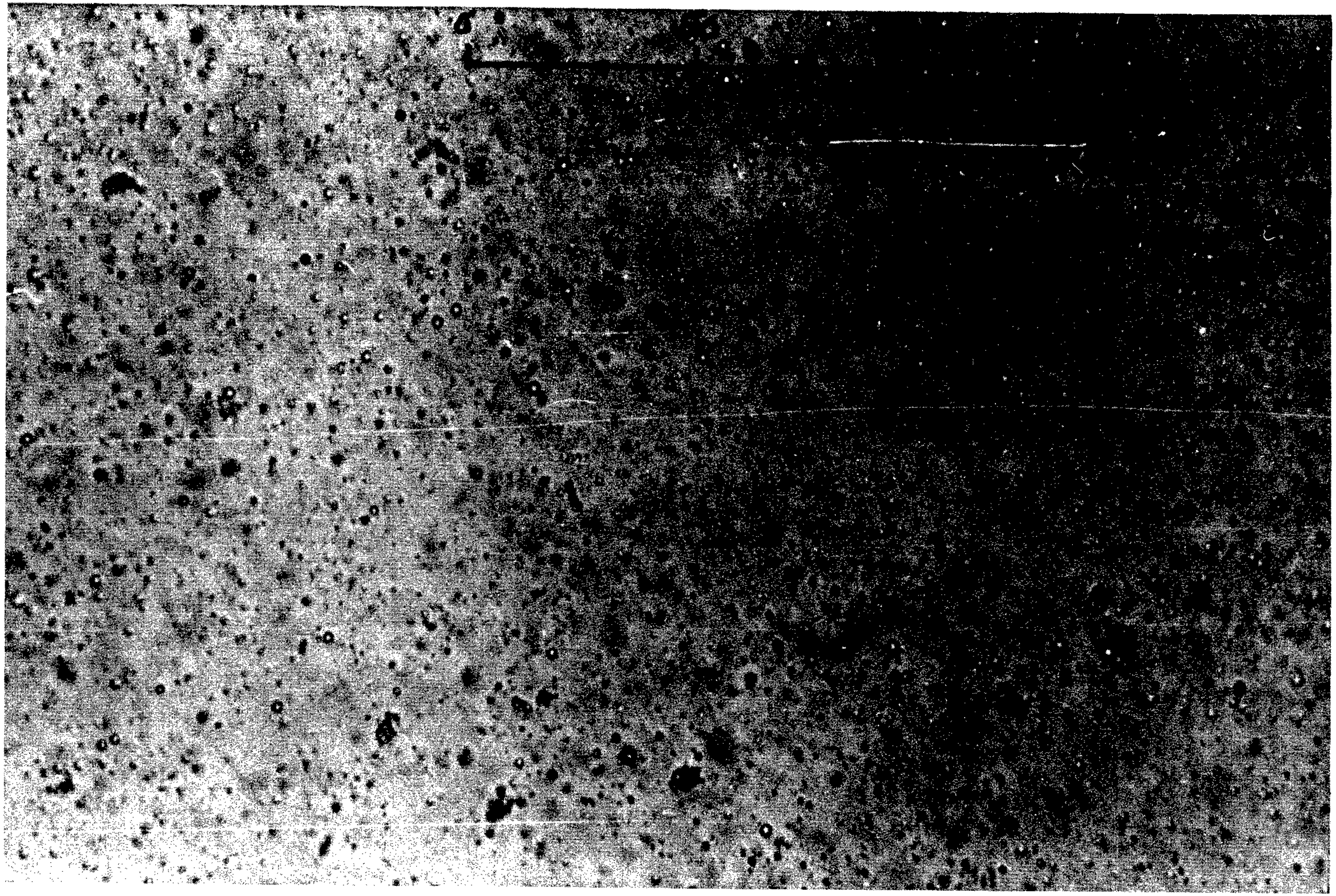

Figure 9. Optical photomicrograph of an emulsion of 75:25 Epon 828-phenyl glycidyl ether mixture prepared with ultrasonic irradiation, after standing for 6 days.

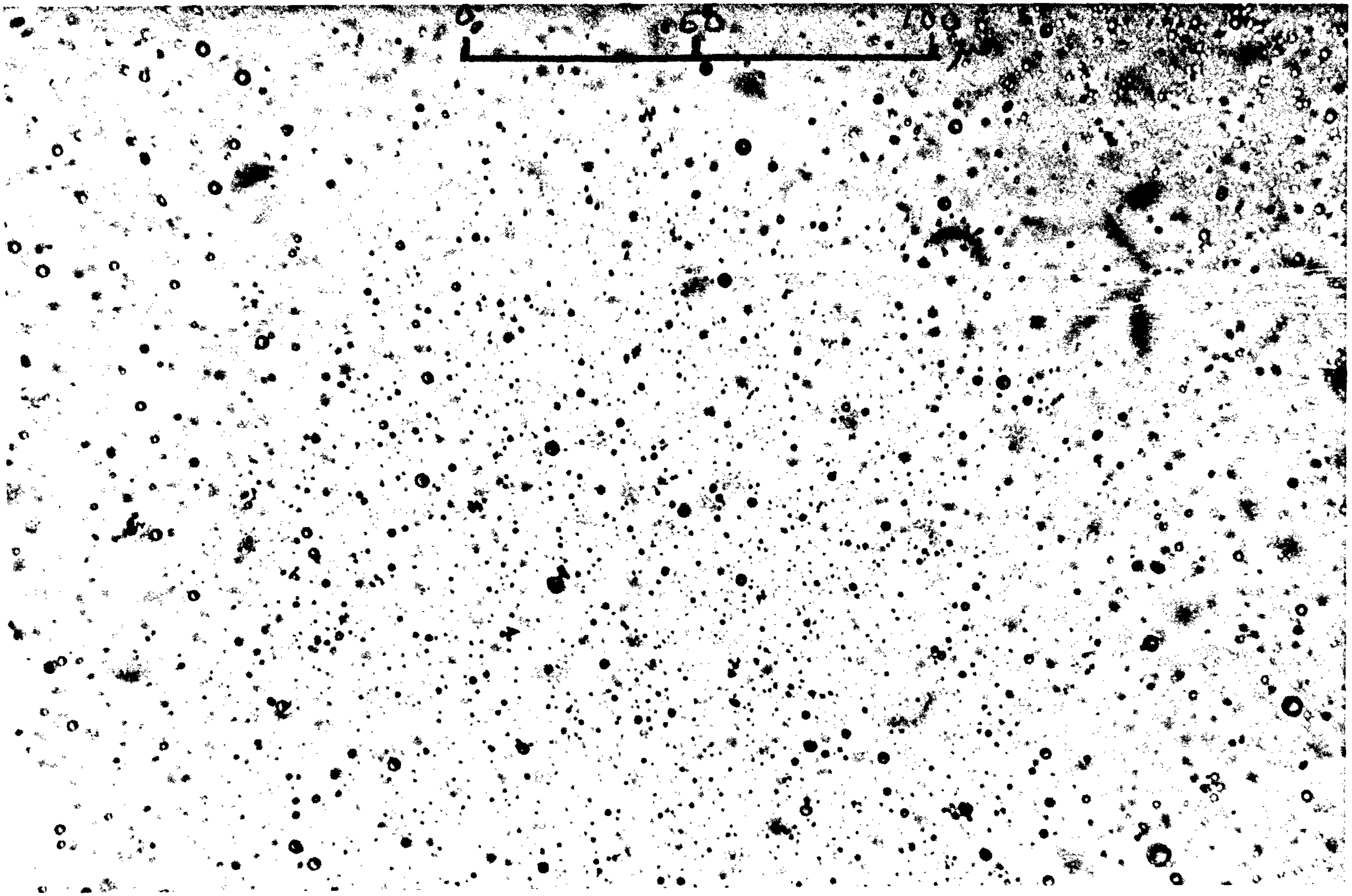

Figure 10. Optical photomicrograph of an emulsion of 25:75 Epon 1001-phenyl glycidyl ether mixture prepared with ultrasonic irradiation, after standing for 6 days.

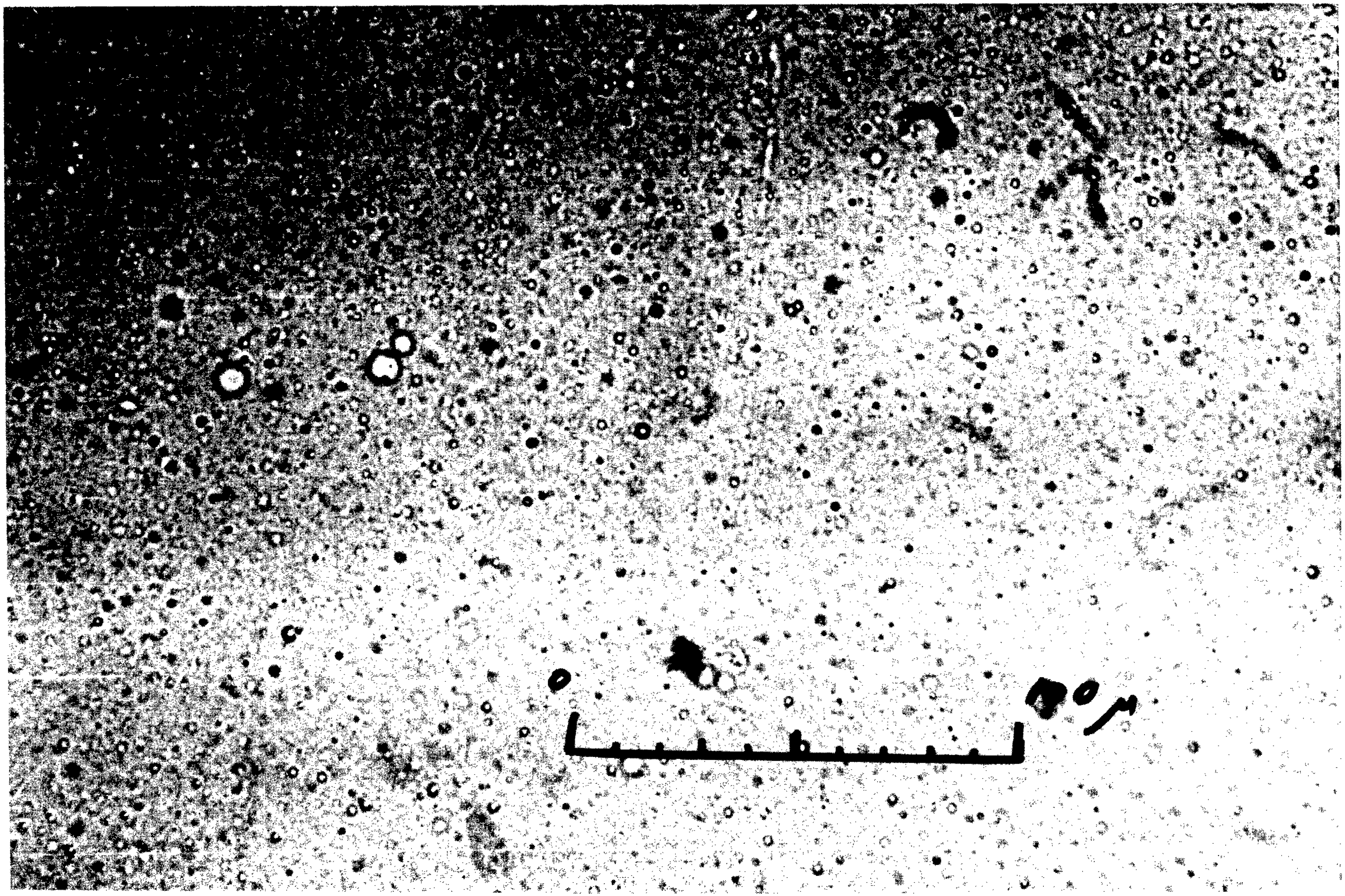

Figure 11. Optical photomicrograph of an emulsion of 50:25:25 Epon 1001-toluene-methyl isobutyl ketone mixture prepared with one passage through the Manton-Gaulin Homogenizer.

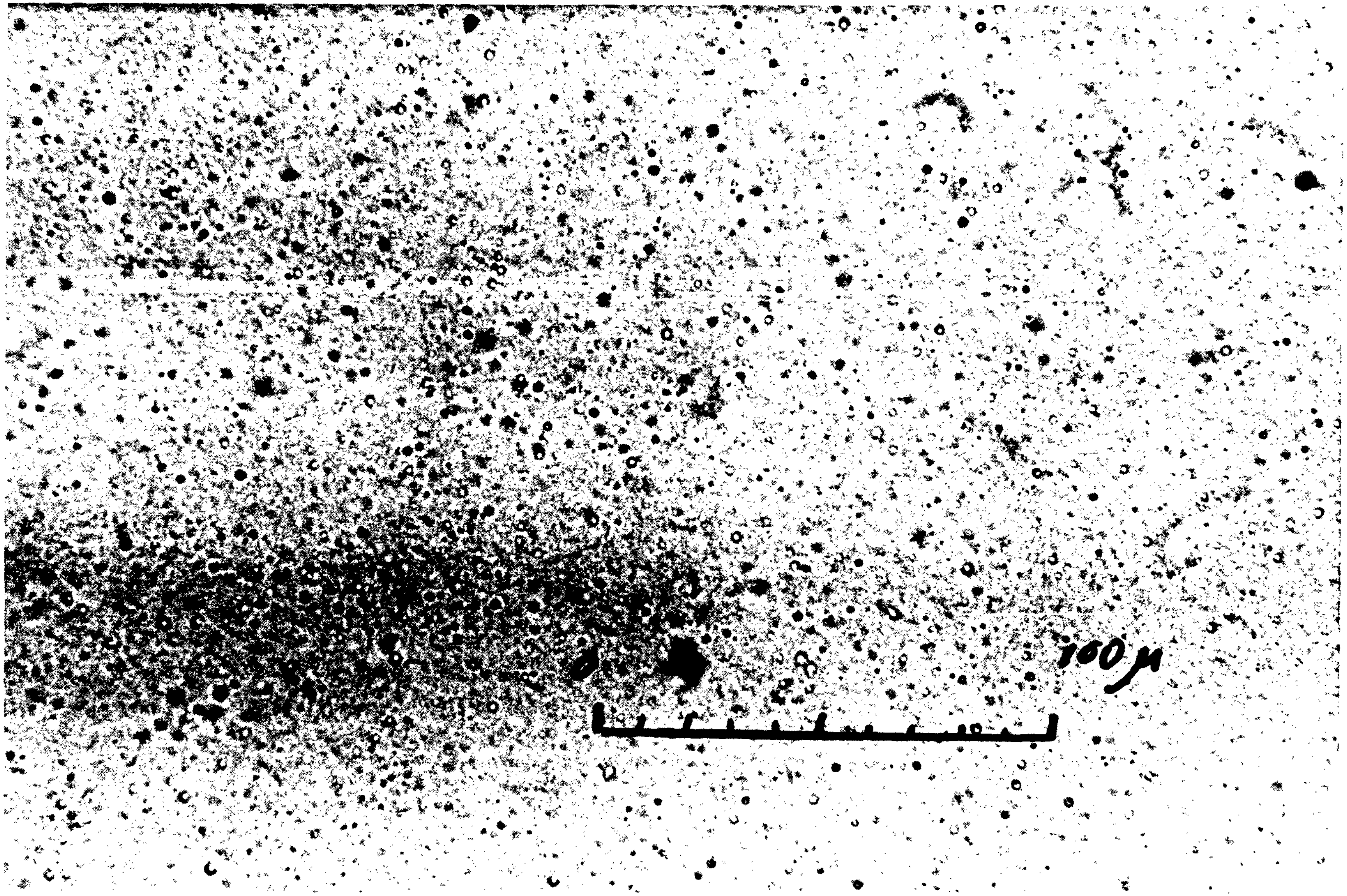

Figure 12. Optical photomicrograph of an emulsion of 50:25:25 Epon 1001-toluene-methyl isobutyl ketone mixture prepared with three passages through the Manton-Gaulin Homogenizer.

isobutyl ketone mixture in 75 gm water at 60° C using simple stirring followed by ultrasonic irradiation has been determined. Stable emulsions were prepared using 0.40-1.60, 0.40-1.20, 0.40-0.80, 0.33-0.67, 0.50-0.50, 0.67-0.33, or 0.77-0.25 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination, but not with 0.17-0.33, 0.25-0.75, or 0.20-0.80 gm of the same combination. These results, as well as an optical-microscopic examination of the emulsion droplet sizes at various ageing times (56), show that the emulsification recipe of the 50:25:25 Epon 1001-toluene-methyl isobutyl ketone mixture should contain at least 0.33-0.67 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination for each 12.5 gm of Epon 1001 (or each 25.0 gm of the 50:50 Epon 1001-solvent mixture).

c. Removal of Solvents and Concentration of Epoxy Resin Emulsions

The foregoing experiments produced emulsions that contained 12.5% Epon 1001 or 25.0% Epon 1001-solvent mixture. This concentration of epoxy resin is too low for practical coating applications; moreover, a concentration of solvent equal to that of the epoxy resin would have a deleterious effect on the coating film properties. Therefore, two approaches were investigated to increase the concentration of Epon 1001 and remove the solvent: (i) emulsification of high-solids Epon 1001 solutions; (ii) concentration of low-solids emulsions during removal of the solvents.

(i) Emulsification of High-Solids Epon 1001 Emulsions

This approach comprised increasing the Epon 1001 concentration in the 50:50 toluene-methyl isobutyl ketone solvent mixture close to the solubility limit of about 71% and emulsifying the high-viscosity solution thus produced. For example, 53 gm of a 71.0:14.5:14.5 Epon 1001-toluene-methyl isobutyl ketone mixture was emulsified in 49 gm water using 0.67-1.33 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give an emulsion containing 37% Epon 1001 or 50% Epon 1001-solvent mixture. The average droplet size of this emulsion (Figure 13) was slightly larger than that of the best earlier emulsions, presumably because of the lower emulsifier-Epon 1001 ratio (1:18.8) as compared with the optimum value of 1:12.5 reported earlier (57).

To further increase the Epon 1001 concentration by increasing the oil-water ratio, 72 gm of a 70:15:15 Epon 1001-toluene-methyl isobutyl ketone mixture was emulsified in 28 gm water using 1.33-2.67 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation, to give a paste-like emulsion containing 50.4% Epon 1001 or 72% Epon 1001-solvent mixture. This emulsion was comprised of very fine droplets (Figure 14), and it could be diluted with water to form a lower-viscosity emulsion, confirming that it was an oil-in-water type.

The density of the 70:15:15 Epon 1001-toluene-methyl isobutyl ketone mixture is 1.066 gm/cm^3, and therefore the volume fraction of the Epon 1001-solvent phase in the foregoing emulsion was 0.71, close to the theoretical value of 0.74 for rhombohedrally-packed monodisperse spheres in contact with one another. Thus, the Epon 1001-solvent droplets in this emulsion were probably almost touching one another, with

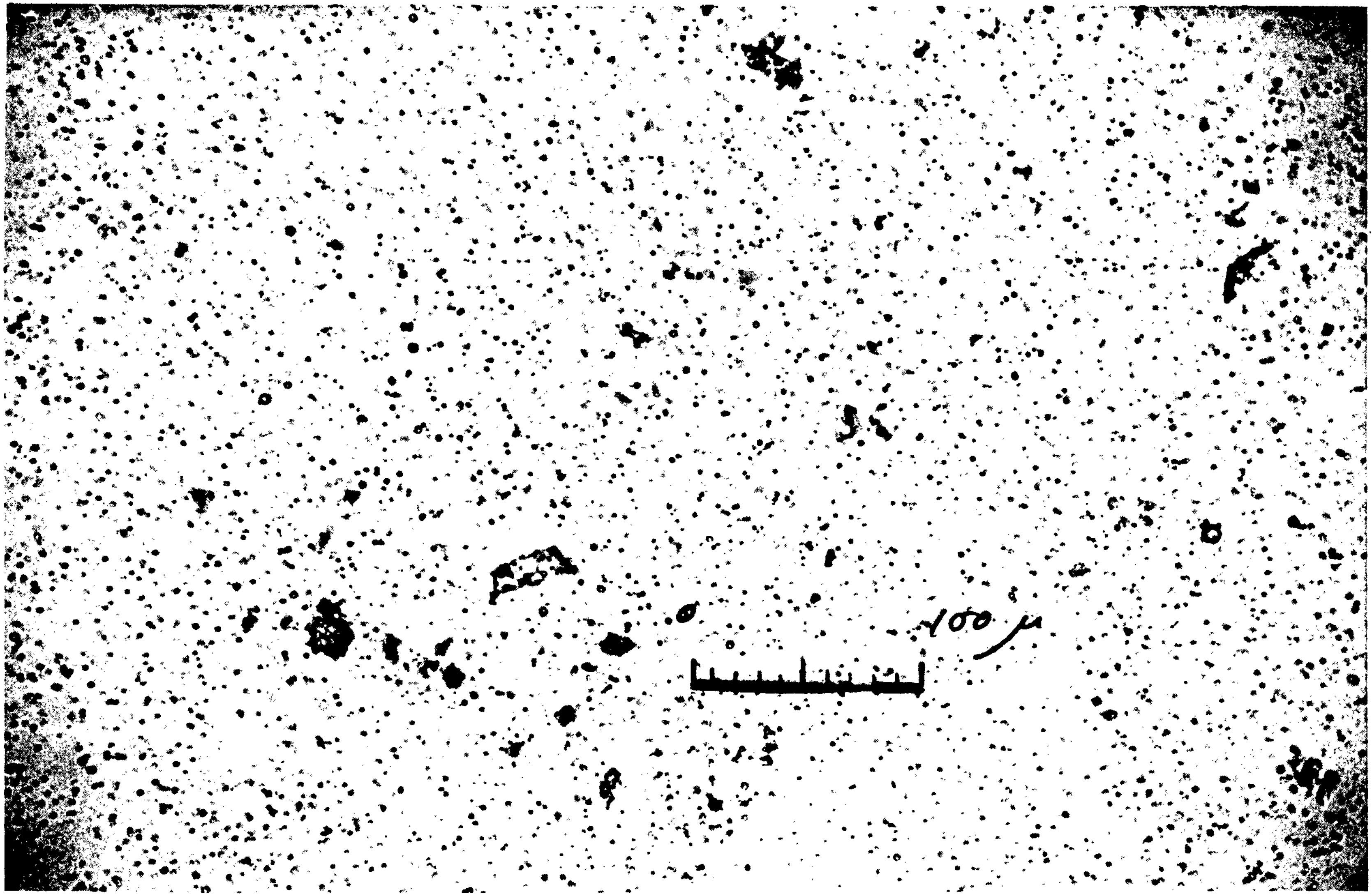

Figure 13. Optical photomicrograph of an emulsion (0.50 volume fraction dispersed phase) of the 71:14.5:14.5 Epon 1001-toluene-methyl isobutyl ketone mixture prepared using ultrasonic irradiation, after standing for 2 hours.

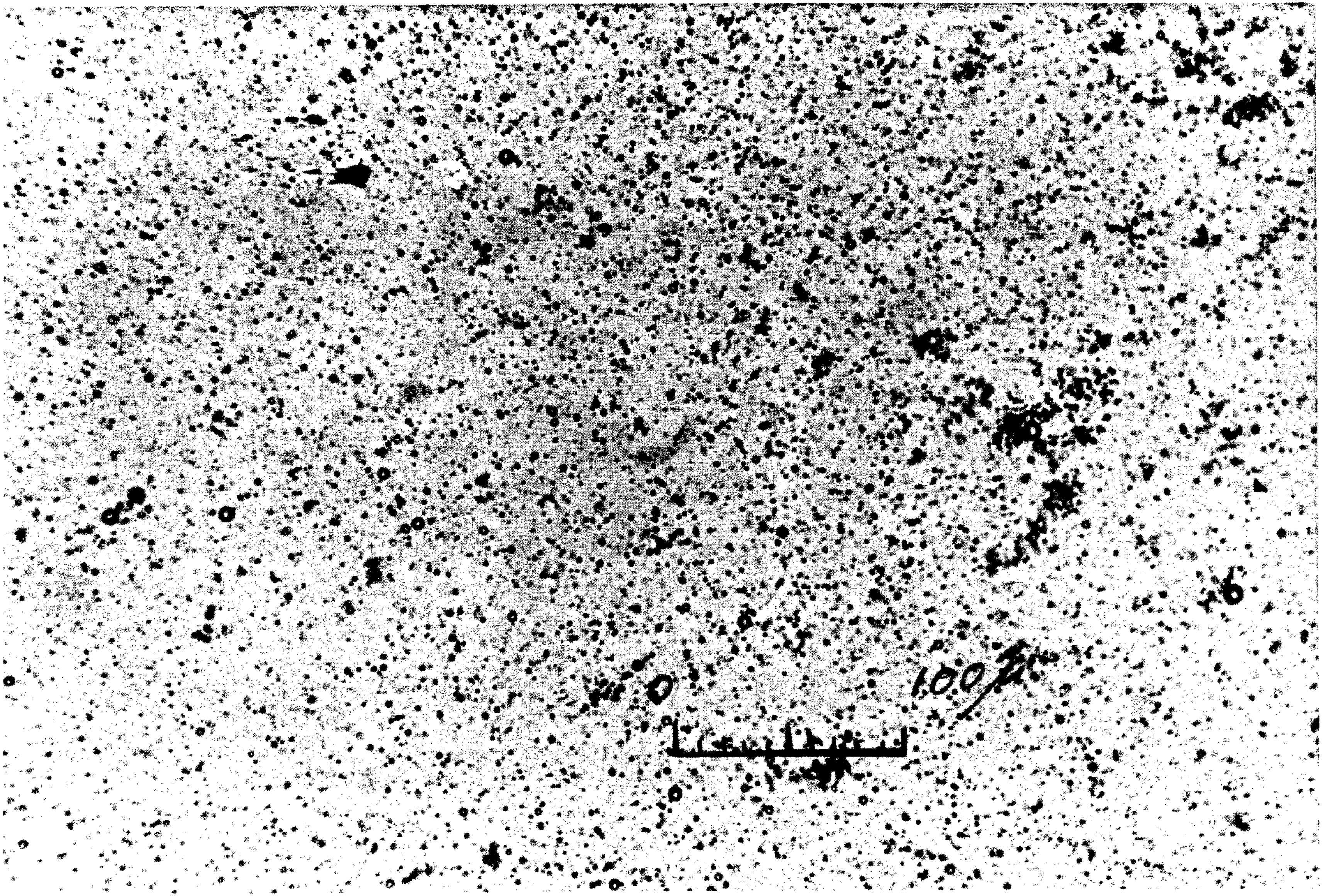

Figure 14. Optical photomicrograph of an emulsion (0.71 volume fraction dispersed phase) of the 70:15:15 Epon 1001-toluene-methyl isobutyl ketone prepared using ultrasonic irradiation, after standing for 1 day.

the water filling the interstices between them. Such an emulsion would be expected to be of high viscosity or paste-like.

Thus, 50% Epon 1001-solvent mixture gave a fluid emulsion, but 71% gave a paste. To repeat the preparation of the fluid emulsion on a larger scale, 265 gm of the 70:15:15 Epon 1001-toluene-methyl isobutyl ketone mixture was emulsified in 245 gm of water using 5.0-10.0 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization. The average droplet size of this emulsion was slightly smaller than that of the corresponding emulsion produced using ultrasonic irradiation (compare Figures 15 and 16 with Figure 13), presumably because of the use of the optimum emulsifier-Epon 1001 ratio in this latter case.

The attempts to remove the solvents from these high-solids Epon 1001 emulsions by vacuum steam distillation in the Buchler Flash Evaporator were generally not successful: the Epon 1001 content was increased to too-high a level by the evaporation of water, and the emulsion droplets either flocculated and coalesced or dried out, to form a film of resin over the inside surface of the flask. Thus, this approach to produce a high-solids Epon 1001 emulsion is practical only if the solvent does not have to be removed before use.

(ii) Concentration of Low-Solids Emulsions During Removal of Solvents

The current industrial practice is to remove residual monomer from emulsion-polymerized latexes by sparging the latex with steam to give a two-layer distillate of water and monomer. Often, the volume of water that must be distilled to remove the monomer from a latex polymerized to about 95% conversion is equal to the volume of the latex. The high temperature (100°C or higher) and the sparging action of the steam often have an adverse effect on the latex stability, so that additional emulsifier must be added to prevent flocculation. Moreover, the latex is usually diluted slightly during the steam distillation.

These difficulties may be lessened or avoided by carrying out the steam distillation at reduced pressure and temperature. This milder vacuum steam distillation has less adverse effect on the latex stability; moreover, the latex can be concentrated during this process, particularly if some of the water in the latex is used to generate the steam.

Vacuum steam distillation was used to remove the residual solvent and concentrate the epoxy resin emulsions prepared by emulsification. To prepare a low-solids Epon 1001 emulsion, 125 gm of a 25.0:37.5:37.5 Epon 1001-toluene-methyl isobutyl ketone mixture was emulsified in 375 gm water using 0.78-1.73 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization, to give an emulsion containing 6.25% Epon 1001 or 25% Epon 1001-solvent mixture. This emulsion, which was stable and of small droplet size (Figure 17), was vacuum steam-distilled at 200 mm Hg pressure and 45°C in the Buchler Flash Evaporator without complication, and the resulting solvent-free Epon 1001 emulsion, when concentrated to 25% solids, was stable and of small droplet size (Figure 18).

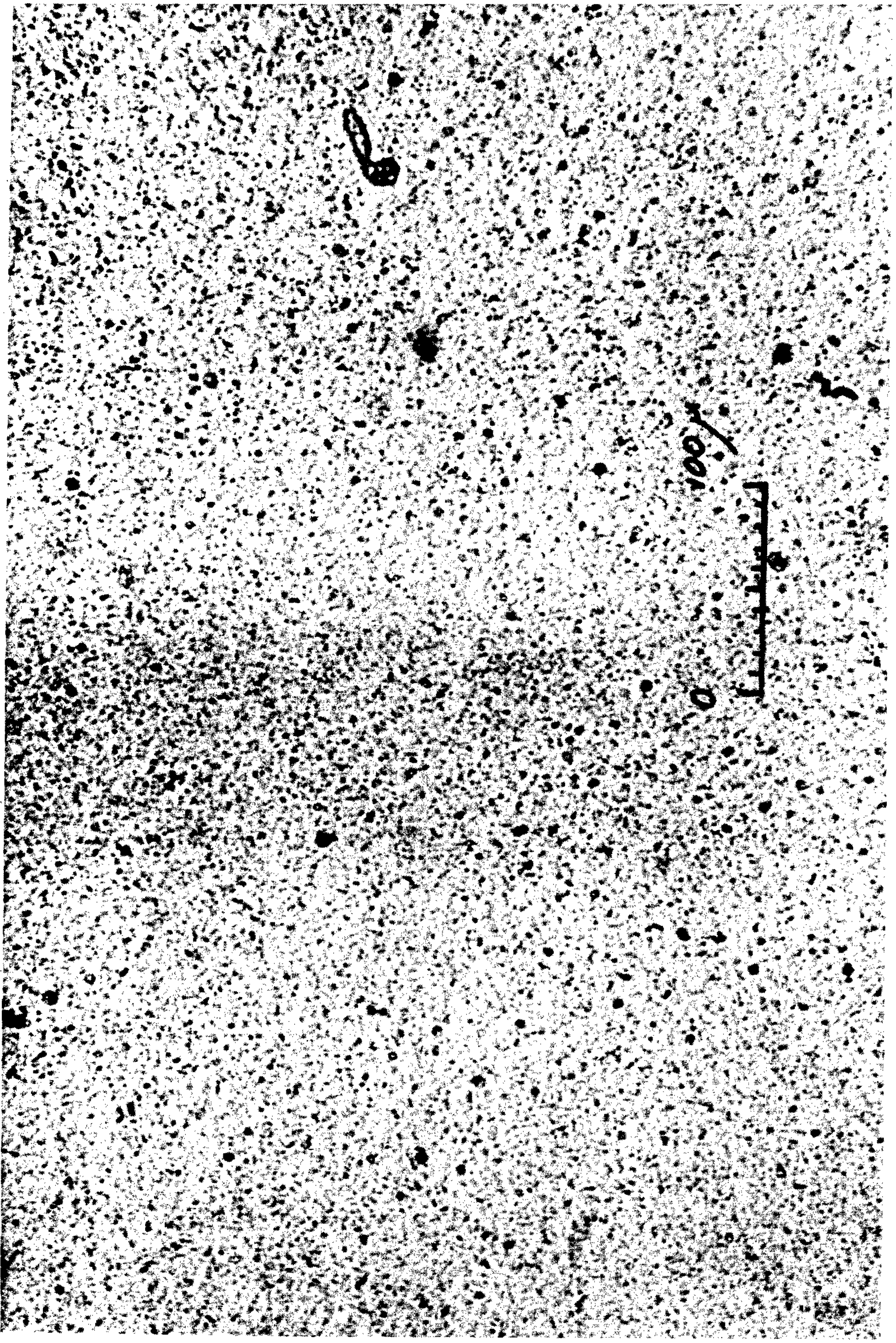

Figure 15. Optical photomicrograph of a 50% emulsion of the 70:15:15 Epon 1001-toluene-methyl isobutyl ketone mixture prepared using the Manton-Gaulin Homogenizer, after standing for 3 days.

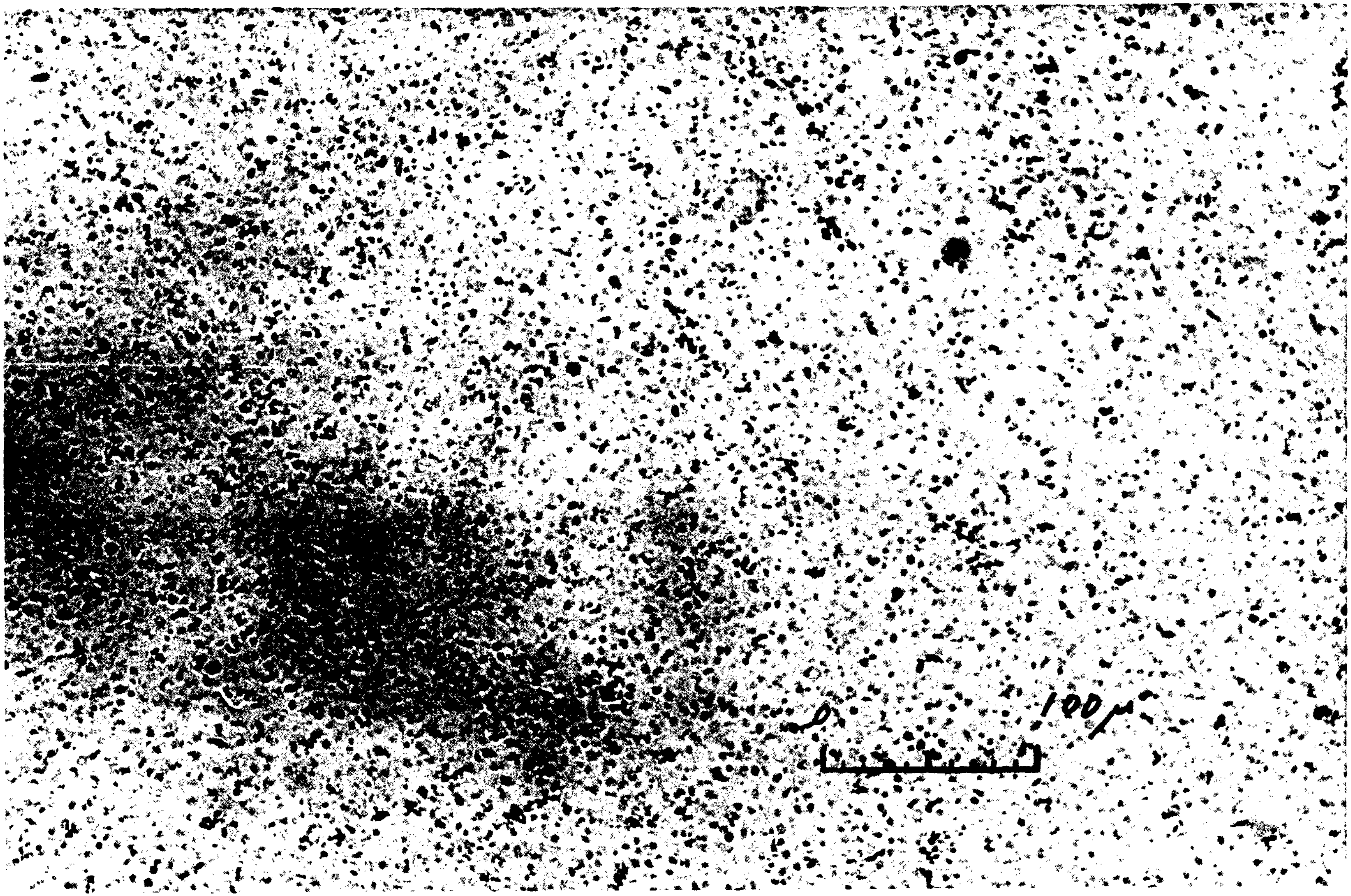

Figure 16. Optical photomicrograph of the same emulsion (Figure 15) of the 70:15:15 Epon 1001-toluene-methyl isobutyl ketone mixture prepared using the Manton-Gaulin Homogenizer, but after standing for 11 days.

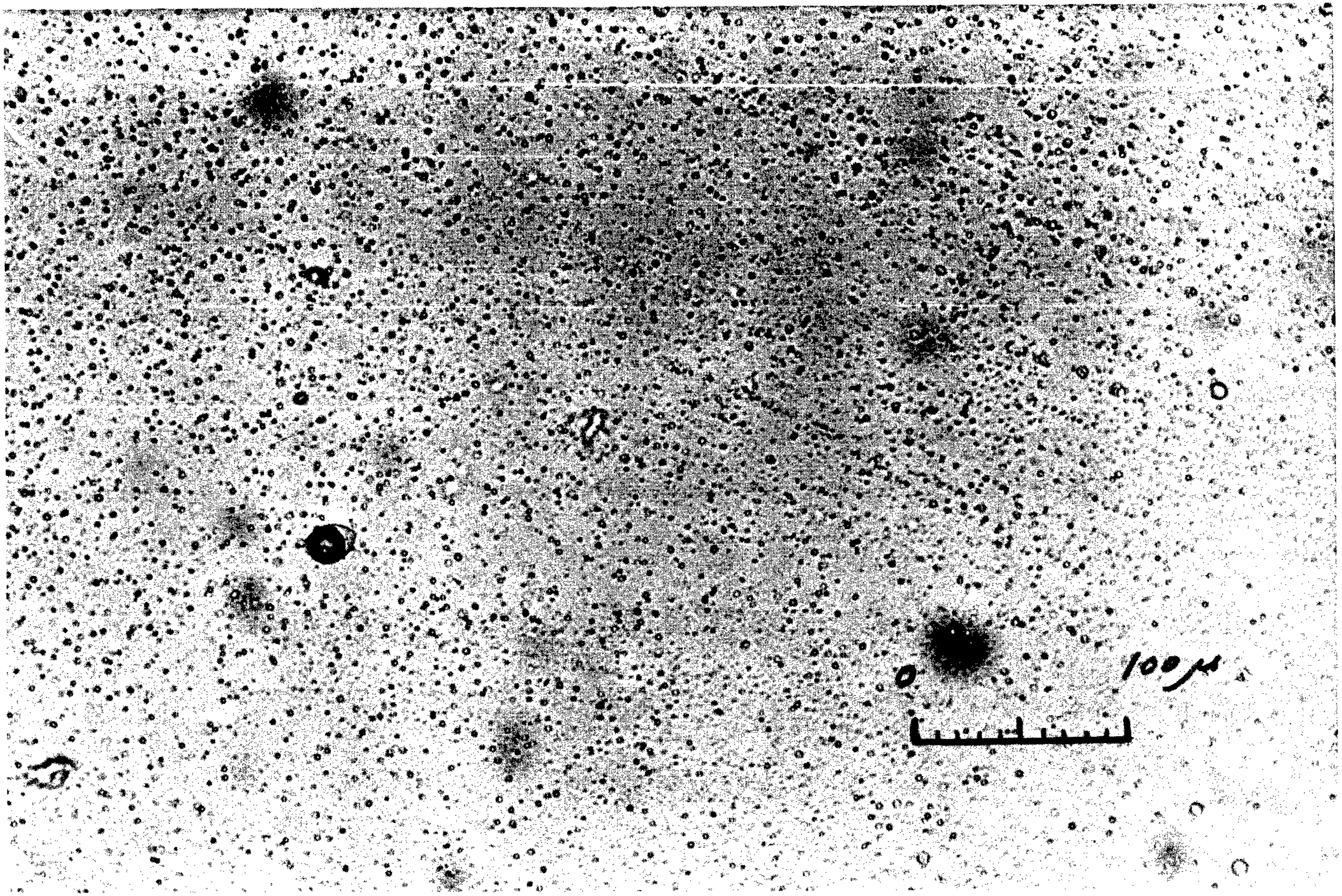

Figure 17. Optical photomicrograph of a 25% emulsion of the 25.0:37.5:37.5 Epon 1001-toluene-methyl isobutyl ketone mixture prepared using the Manton-Gaulin Homogenizer, after standing for 1 day.

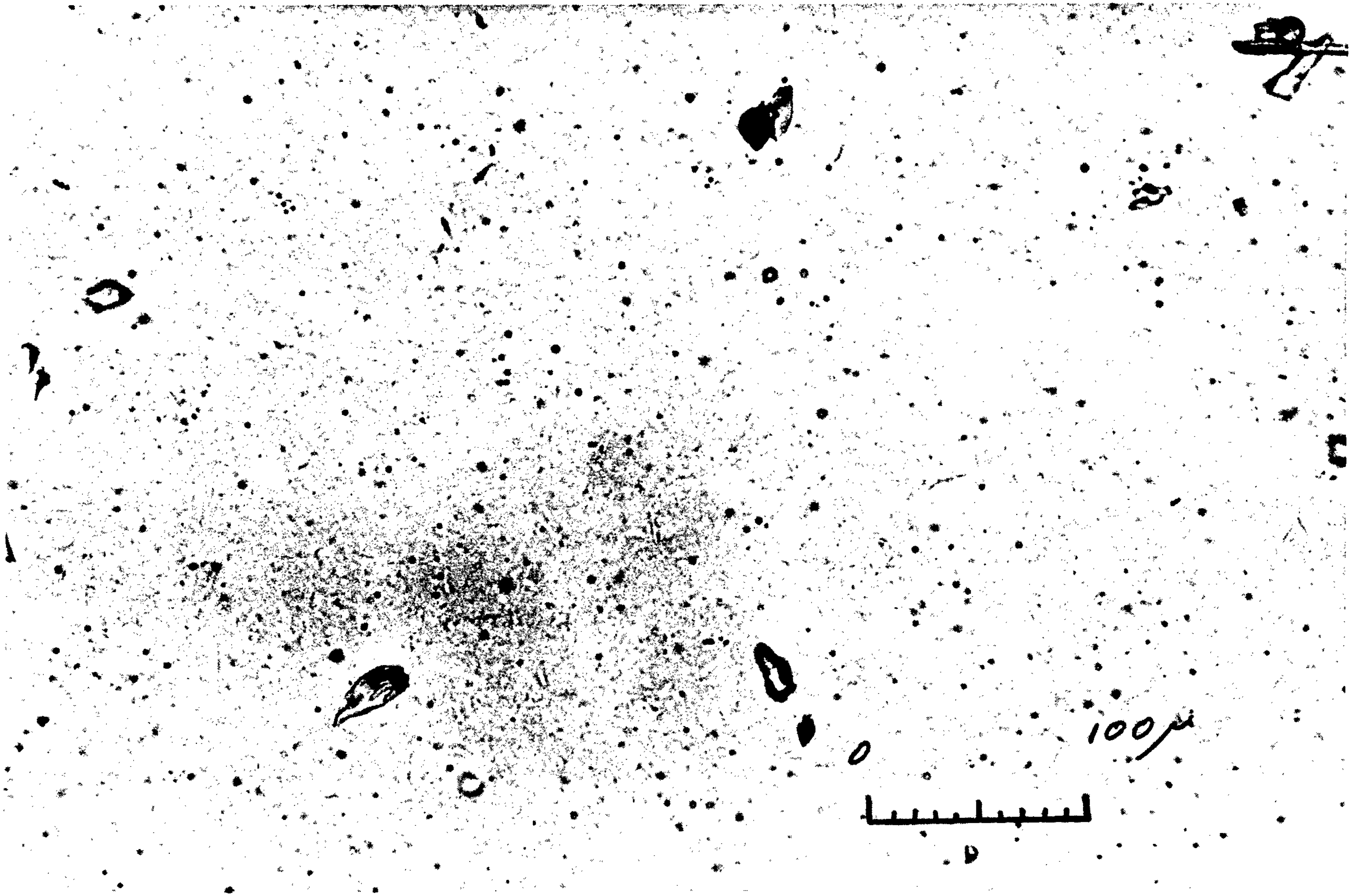

Figure 18. Optical photomicrograph of the same emulsion (Figure 17) of the 25.0:37.5:37.5 Epon 1001-toluene-methyl isobutyl ketone mixture, but after removal of the solvents and concentration to 25% solids, after standing for 1 day.

Vacuum steam distillation was also used to remove the solvents from an Epon 828-toluene-methyl isobutyl ketone emulsion prepared in the same manner. In this case, too, the solvent-free emulsion was stable and of small droplet size (Figure 20), fully comparable to the same emulsion before vacuum steam distillation and concentration (Figure 19).

d. Determination of the Emulsion Droplet Size

The droplet size distributions of these epoxy resin emulsions were examined routinely using dark-field phase-contrast optical microscopy, which distinguishes emulsion droplets as small as 0.2μ in diameter. The optical photomicrographs, such as those shown in this report, were made with conventional optics, which distinguishes emulsion droplets as small as 0.5μ. The results reported in the foregoing sections show that the emulsification of Epon 1001-solvent mixtures using the hexadecyltrimethylammonium bromide-cetyl alcohol combination along with ultrasonic irradiation or homogenization produces emulsions with droplet sizes in the range 1.0-0.2μ, close to the limit of resolution of the optical microscope. These results suggest that some emulsion droplets may be smaller than this 0.2μ lower limit of observation, and, consequently, a more definitive method is needed to differentiate between the different emulsion samples.

One approach to develop a more definitive method is to cure the Epon 1001 droplets in the emulsion state and examine the dried emulsion by electron microscopy. To examine a polymer latex, a sample is diluted to 10-20 ppm polymer, and a drop is dried on a specimen substrate and examined under vacuum in the electron microscope. This procedure is satisfactory to determine the particle size of non-film-forming latexes because their particles deform only negligibly upon drying. Particles of film-forming latexes deform and coalesce with the substrate upon drying, and their images in the electron microscope are larger than the original diameter of the undeformed spheres. Those film-forming latex polymers that contain residual double bonds (e.g., styrene-butadiene copolymers) can be hardened for electron microscopy by addition of bromine (58-61) or osmium tetroxide (62), while those copolymers that predominantly crosslink (rather than degrade) upon exposure to high-energy irradiation (e.g., polyvinyl acetate) can be hardened by that method (61). In addition, the particle size of all film-forming latexes can be determined from the images of the deformed spheres assuming their configuration is that of a spherical segment or an oblate spheroid (63). Only this last tedious and time-consuming method is applicable to the Epon 1001 emulsions.

The most direct approach to determine the particle-size distribution of the Epon 1001 emulsions is to remove the solvent and harden the particles so that they will not deform upon drying. The solvent can be removed by vacuum steam distillation as described in the foregoing section, and in principle the epoxy resin droplets can be hardened by curing with an aqueous amine.

Preliminary experiments in which aqueous diethylene triamine was added to an Epon 1001 emulsion gave a continuous film of epoxy resin on the specimen substrate rather than individually-dispersed spheres.

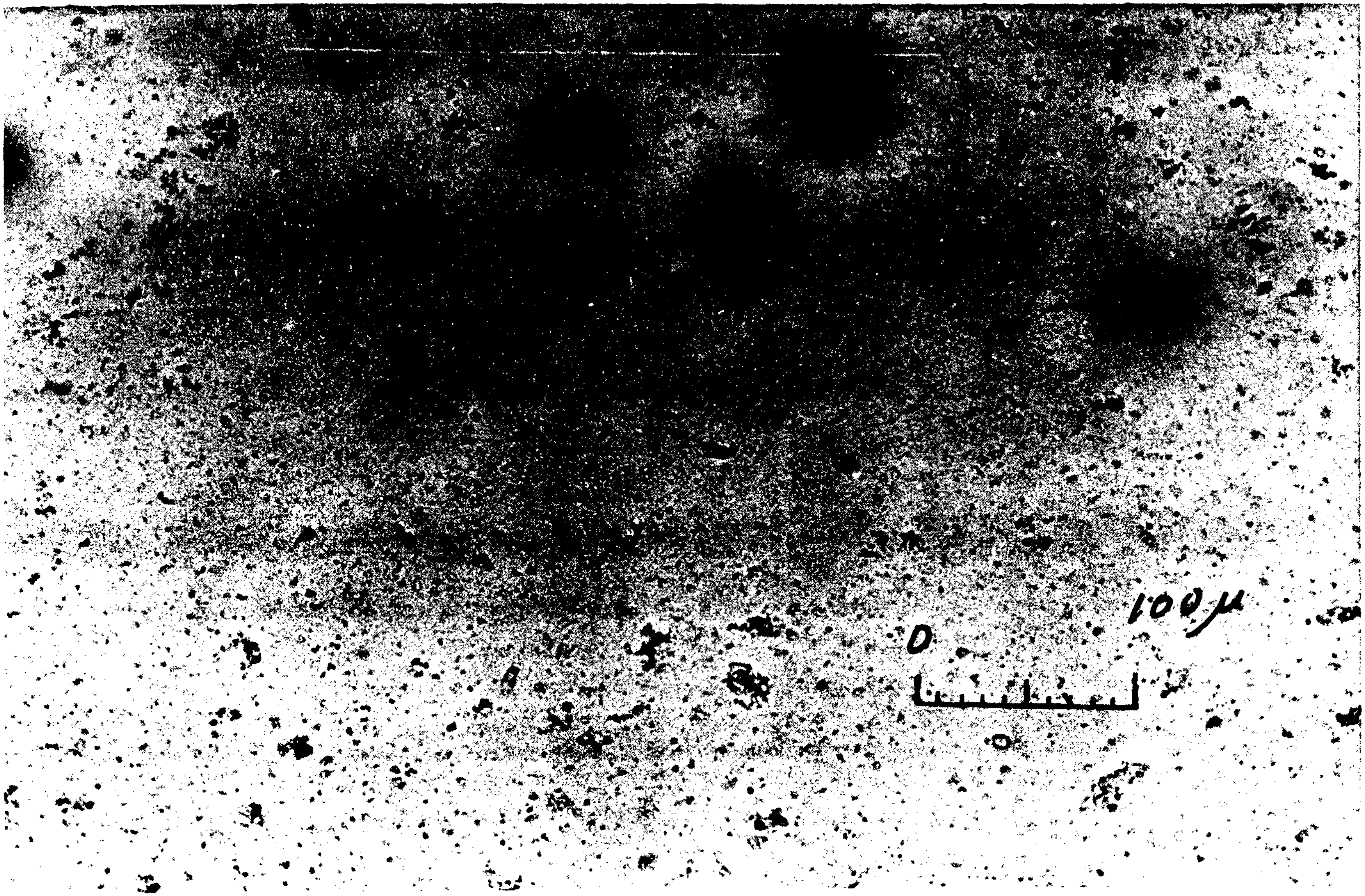

Figure 19. Optical photomicrograph of an emulsion of the 70:15:15 Epon 828-toluene-methyl isobutyl ketone mixture prepared using the Manton-Gaulin Homogenizer, after standing for 6 days.

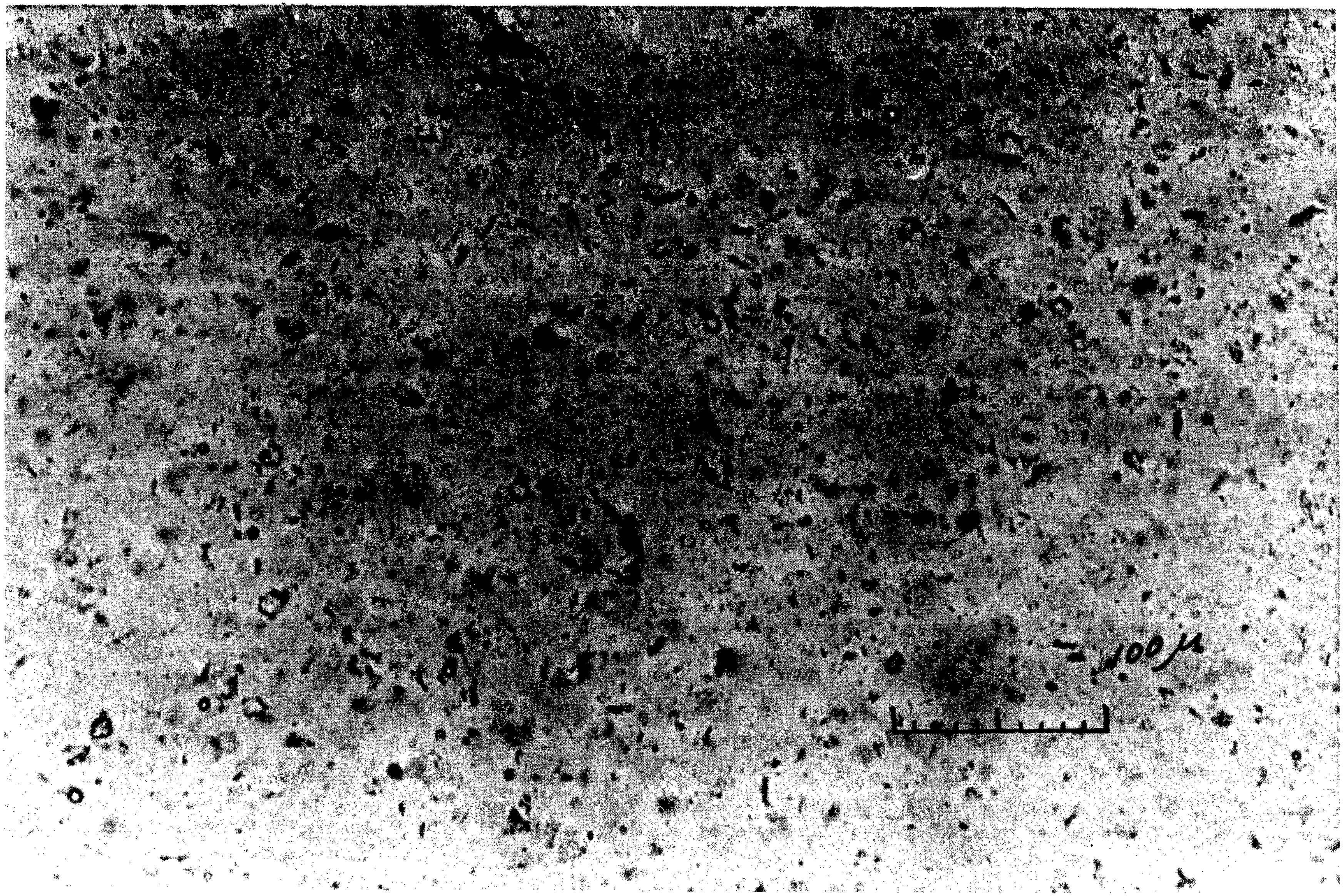

Figure 20. Optical photomicrograph of the same emulsion (Figure 19) of the 70:15:15 Epon 828-toluene-methyl isobutyl ketone mixture, but after removal of the solvents, after standing for 1 day.

In another experiment, a solvent-stripped Epon 1001 emulsion was diluted with distilled water, mixed with a few drops of 20% aqueous ethylene diamine, and heated for 16 hours at 60° C. An electron microscope specimen was prepared by drying one or two drops of the sample mixture on a carbon substrate supported by a copper mesh and shadowing obliquely by evaporation of platinum metal under vacuum. Examination of this specimen in the transmission electron microscope showed discrete Epon 1001 spheres of 300-2000A. diameter (Figure 21), which appeared from the length of their shadows to be coalesced with the substrate only slightly if at all.

In comparison, a sample of the same emulsion prepared in the same manner except that the ethylene-diamine hardening was omitted showed particles that had deformed and coalesced with the substrate (Figure 22).

Figure 21 shows that the smallest emulsion droplets produced using the mixed emulsifier combination was about 300A., considerably smaller than the lower limit of 0.2μ or 2000A. observable by optical microscopy.

3. Curing Agent Emulsions

Most of the work was done on the emulsification of Versamid 115 curing agent, but other commercial curing agents were also tried.

a. Versamid 115 Emulsions

The first experiments comprised the emulsification of a 70:30 Versamid 115-xylene mixture using the sodium lauryl sulfate-cetyl alcohol combination and simple stirring. These experiments produced paste-like coagulum rather than fluid emulsions, presumably because of flocculation of the positively-charged polyamide prepolymer by the negatively-charged sodium lauryl sulfate. Therefore, the emulsification was repeated, substituting the cationic hexadecyltrimethylammonium bromide for the sodium lauryl sulfate in the mixed emulsifier combination. This cationic emulsifier had earlier been found (3) to function analogously to sodium lauryl sulfate in combination with cetyl alcohol in the preparation of stable cationic polystyrene latexes. The emulsification of Versamid 115 using the hexadecyltrimethylammonium bromide-cetyl alcohol combination and simple stirring produced a fluid cationic emulsion with most droplets in the size range 0.5-1.0μ, but with a few as large as 50μ (Figure 23). This emulsion remained stable for only one day, after which it separated into two phases. Ultrasonic irradiation of this emulsion while still hot gave a slightly smaller droplet size (Figure 24) and consequently a slight improvement in shelf stability.

The Component II curing agent (obtained from Naval Air Development Center) is reputed to be an 18.7% solution of Versamid 115 in a 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture prepared according to MIL-P-23377C. This Component II curing agent was emulsified in water using the hexadecyltrimethylammonium bromide-cetyl alcohol combination and ultrasonic irradiation to produce an emulsion of small droplet size (Figure 25). A similar emulsion prepared using homogenization was of even smaller droplet size (Figure 26). This latter emulsion showed no signs of separation after standing for 60 days, although its droplet size after 30 days (Figure 27) was slightly larger than that of the freshly-prepared emulsion (Figure 26).

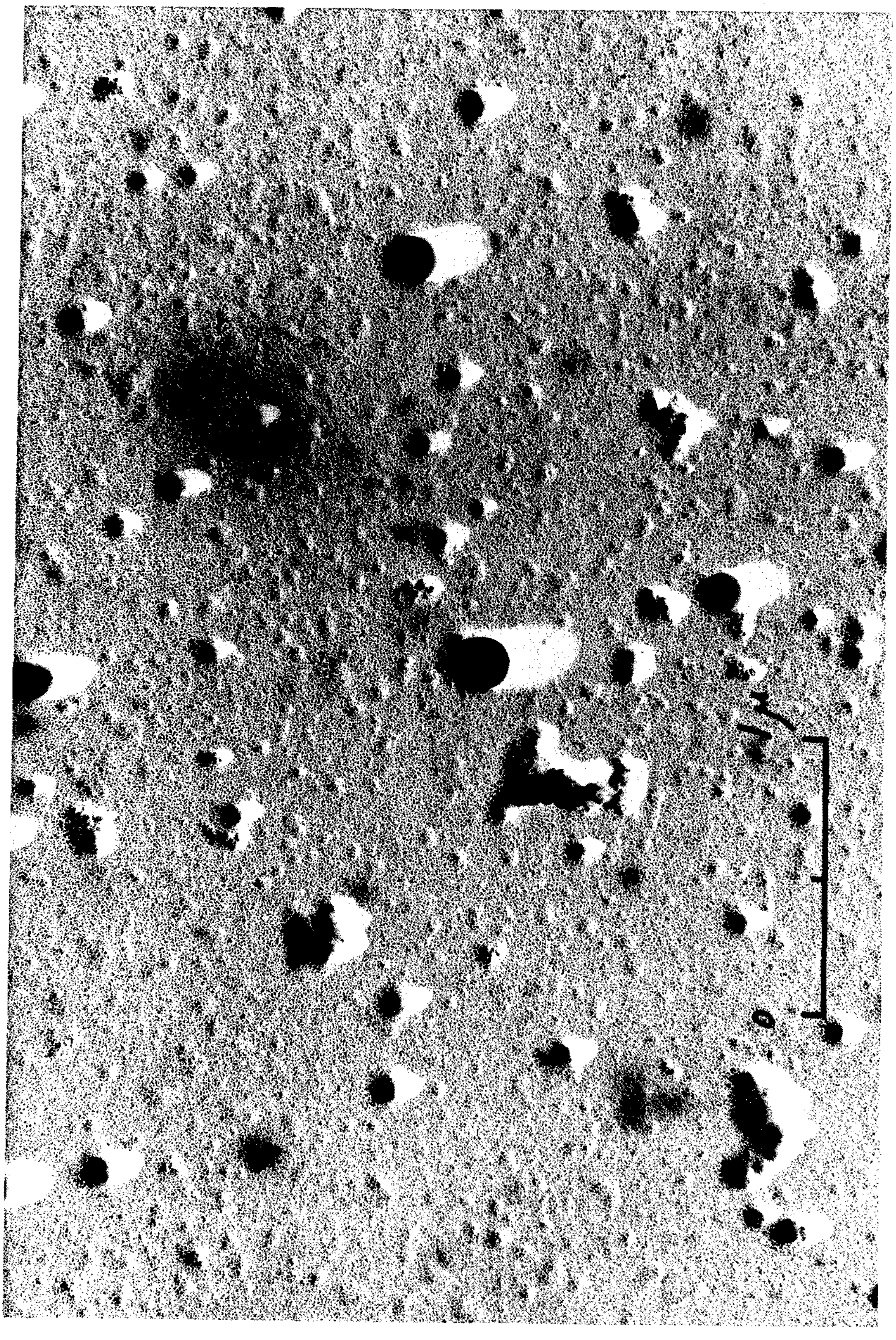

Figure 21. Electron micrograph of a dispersion of solvent-stripped Epon 1001 emulsion (Figure 18), cured with ethylene diamine and shadowed with platinum.

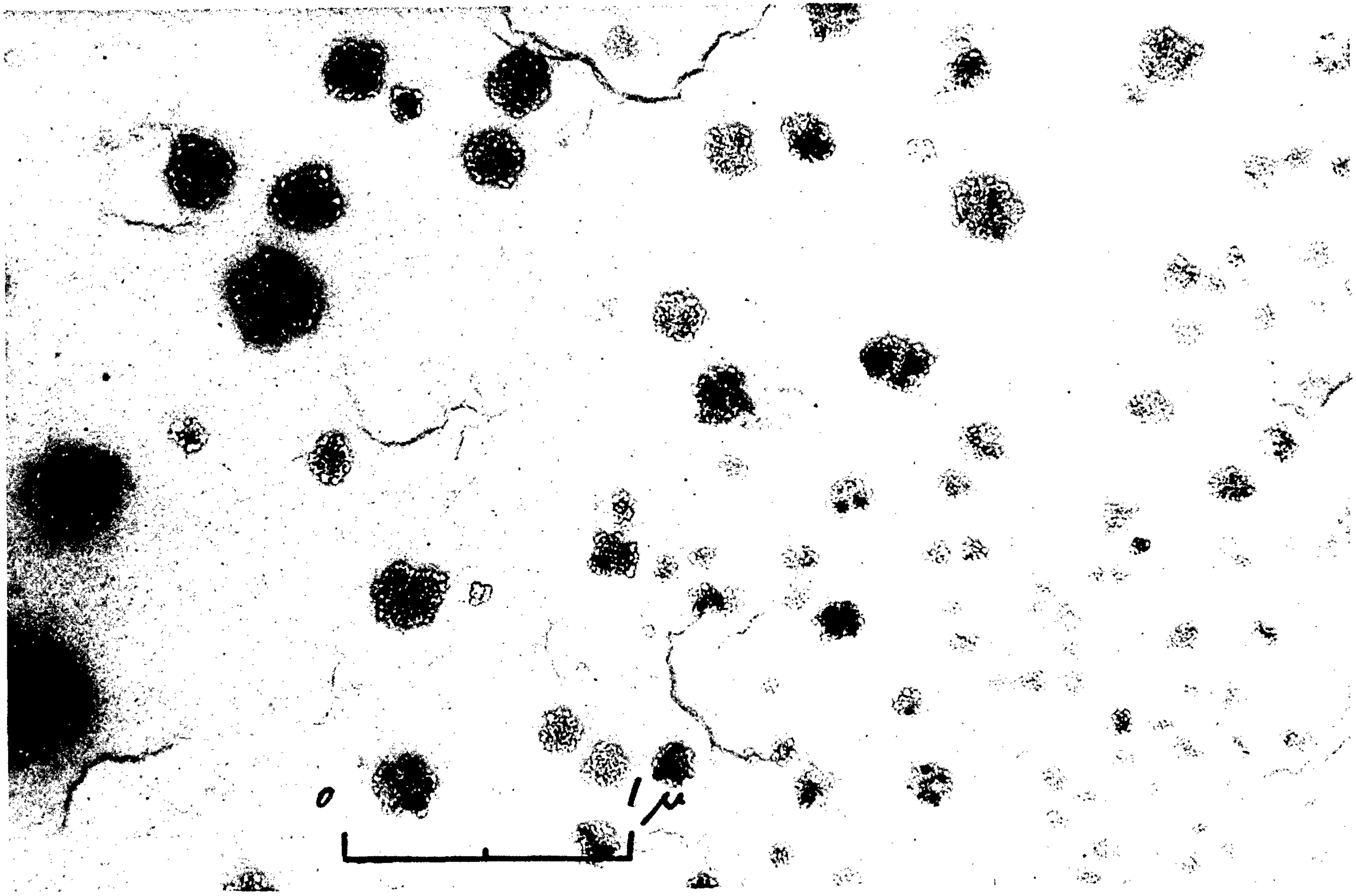

Figure 22. Electron micrograph of a platinum-shadowed dispersion of the same solvent-stripped Epon 1001 emulsion (Figure 18), before curing with ethylene diamine.

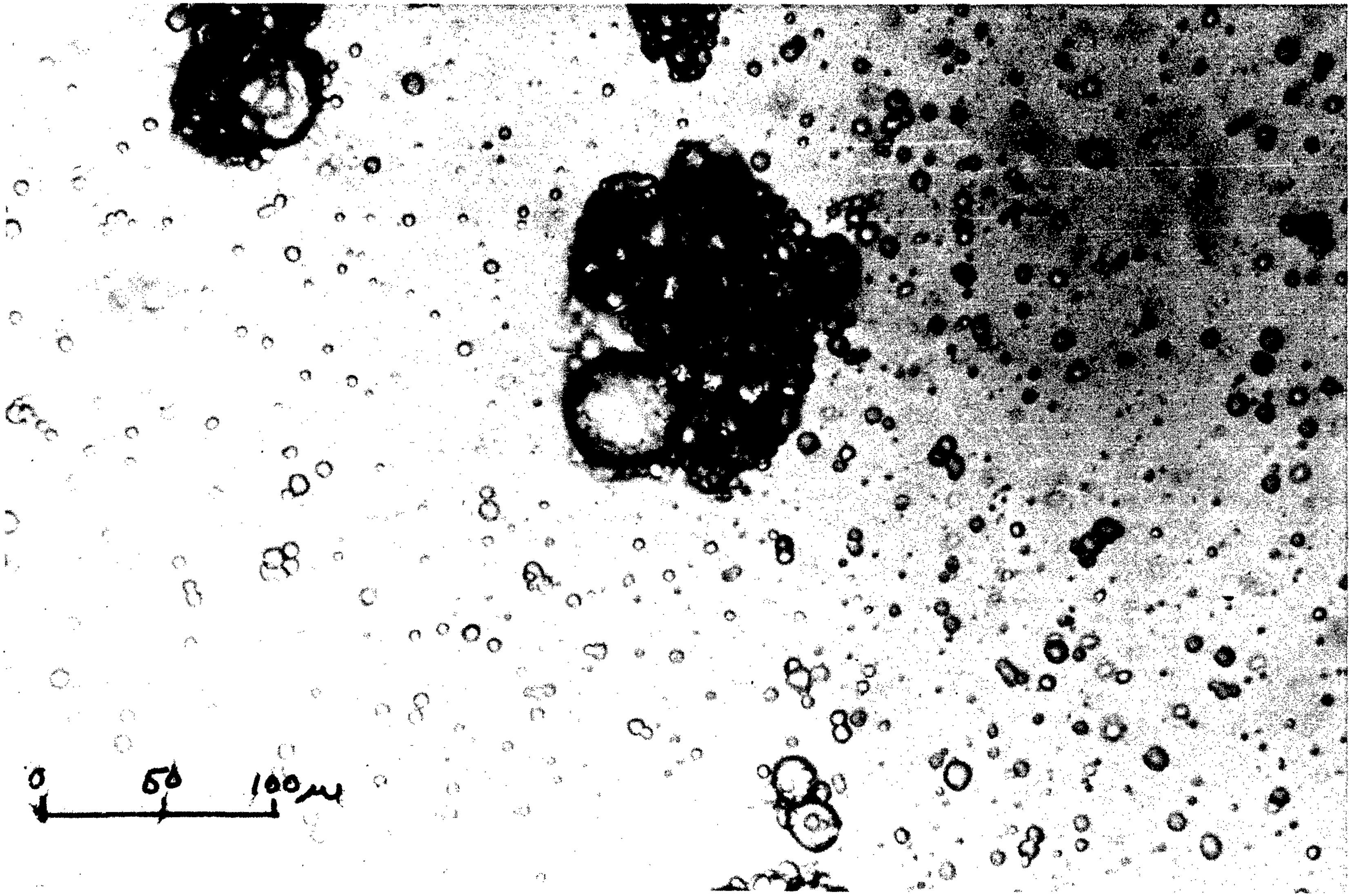

Figure 23. Optical photomicrograph of an emulsion of 70:30 Versamid 115-xylene mixture prepared with simple stirring, after standing for 2 hours.

Figure 24. Optical photomicrograph of an emulsion of 70:30 Versamid 115-xylene mixture prepared with ultrasonic irradiation, after standing for 2 hours.

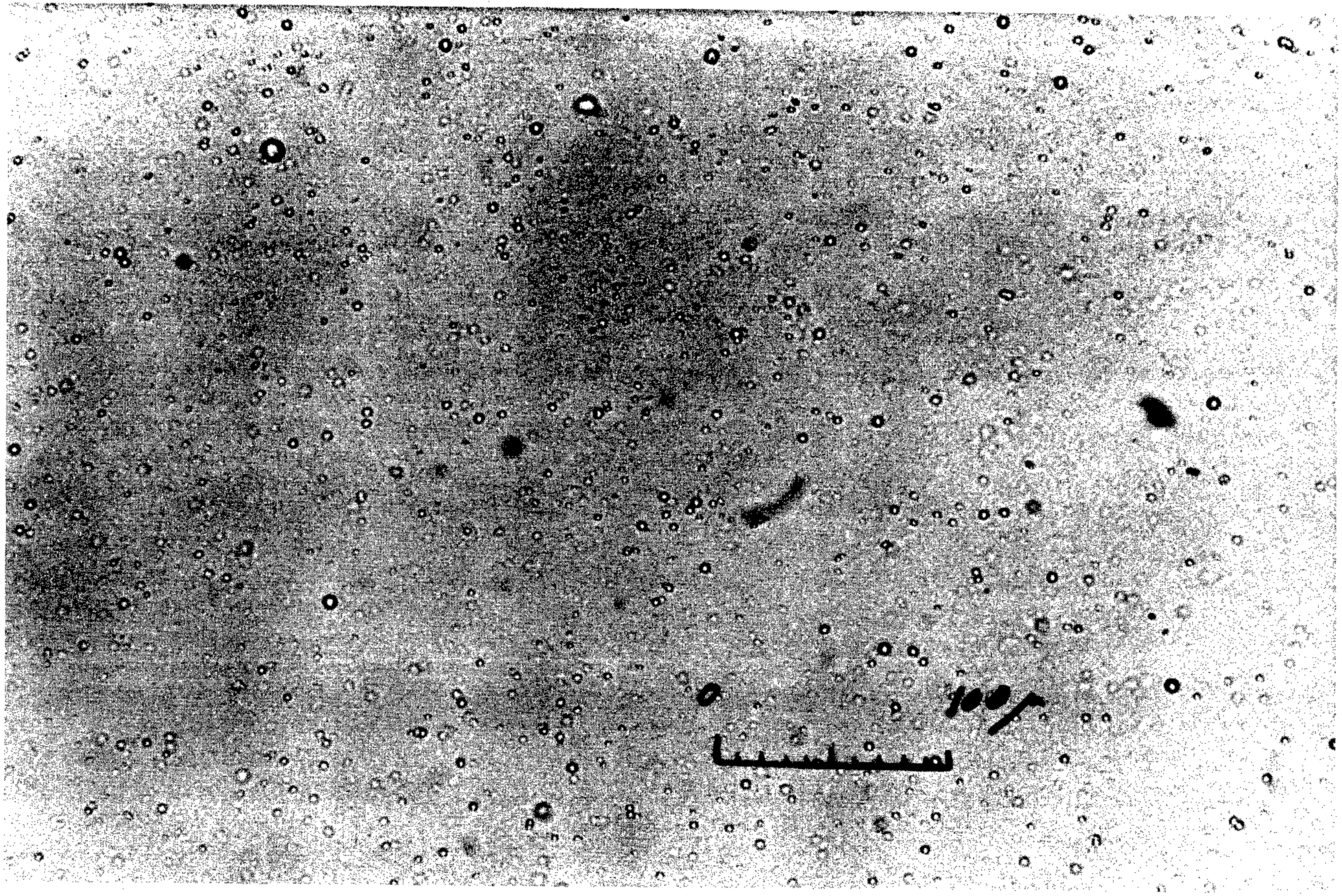

Figure 25. Optical photomicrograph of an emulsion of Component II curing agent prepared with ultrasonic irradiation, after standing for 5 days.

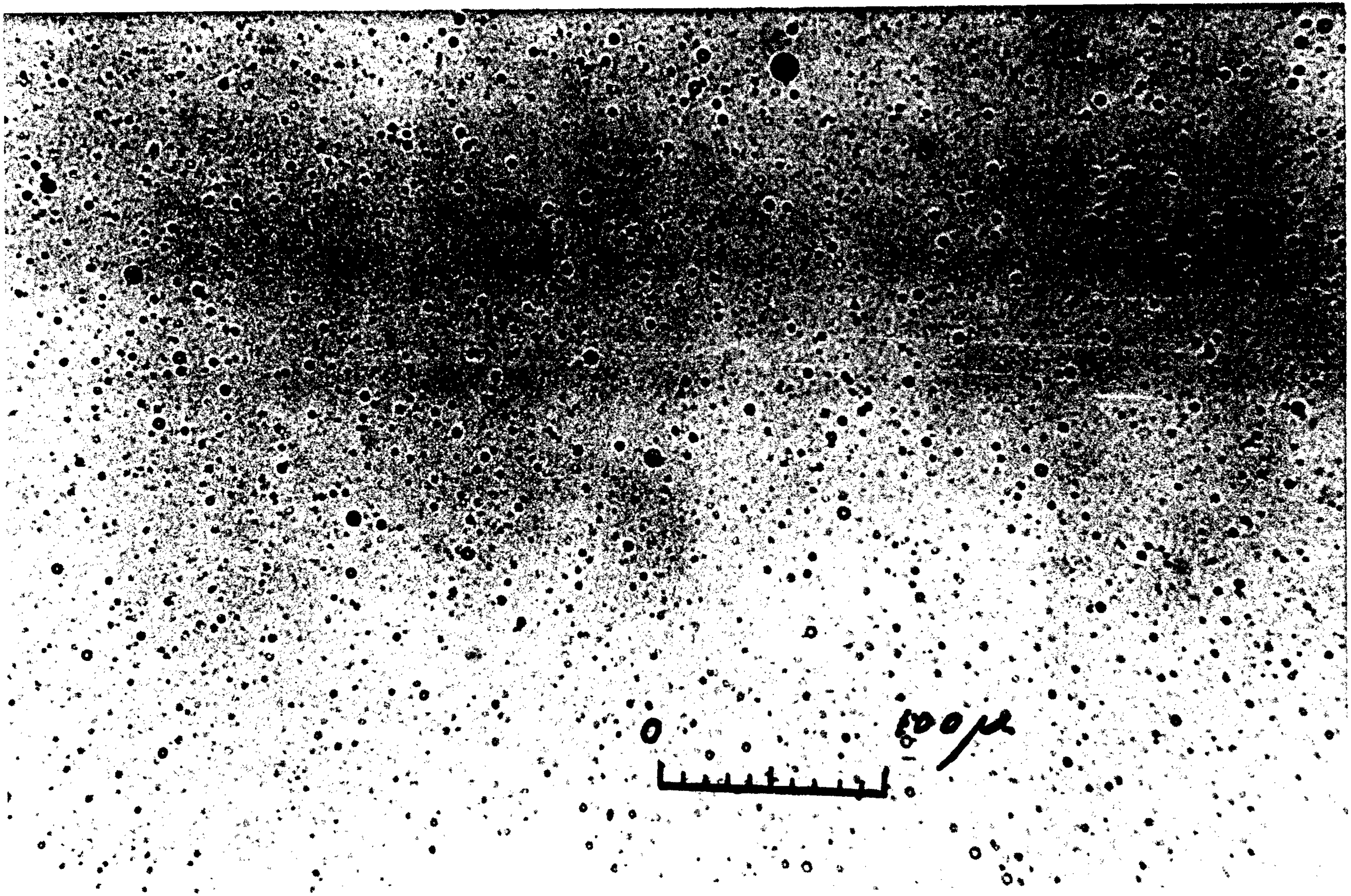

Figure 26. Optical photomicrograph of an emulsion of Component II curing agent prepared using the Manton-Gaulin Homogenizer, after standing for 2 days.

Figure 27. Optical photomicrograph of the same emulsion of Component II curing agent prepared using the Manton-Gaulin Homogenizer, after standing for 30 days.

To corroborate the composition inferred for Component II from MIL-P-23377C and to test the emulsification of higher concentrations of curing agent, 125 gm of an 80% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture was emulsified in 375 gm water using 2.0-4.0 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization to give an emulsion of slightly larger droplet size (Figure 28) than the corresponding Component II emulsion (Figure 26). After standing for one week, this emulsion showed signs of separation, and the droplet size had increased significantly (Figure 29).

A similar emulsification using 2.7-5.4 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization produced an emulsion that remained stable upon standing for three weeks, after which an oil layer appeared on the top. Figure 30 shows this emulsion after standing for one day, and Figure 31, after standing for one week; the gradual increase in droplet size upon standing can easily be seen.

Thus, the emulsions prepared from the high-concentration Versamid 115 solutions have only a three-week shelf stability, whereas the emulsions of Component II curing agent (reputed to be a low-concentration Versamid 115 solution) were still stable after standing for 60 days. This suggests that the stability of the Versamid 115 emulsions might be improved by emulsifying a lower-concentration (and, hence, a lower-viscosity) solution to give an emulsion of small droplet size that could be solvent-stripped and concentrated by vacuum steam distillation.

b. Removal of Solvents and Concentration of the Versamid 115 Emulsions

A lower-concentration Versamid 115 emulsion was prepared by emulsifying 125 gm of a 25% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture in 375 gm water using 2.7-5.4 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization to give an emulsion that was relatively stable and of small droplet size, similar to those prepared from Epon 1001 and Epon 828. When this emulsion was subjected to vacuum steam distillation in the Buchler Flash Evaporator, however, it became viscous and turned translucent and yellowish at a critical point, indicating a sudden decrease in droplet size. When this viscous, translucent emulsion was diluted with water, it turned cloudy, indicating an increase in droplet size (thus precluding examination of the phenomenon by electron microscopy, light scattering, or any other method that involves dilution of the emulsion).

This increase in viscosity and decrease in opacity during vacuum steam distillation could have resulted from three possible causes: (1) the spontaneous breakdown of the already-small emulsion droplets to an even smaller size (less than 0.1μ diameter) in the presence of high emulsifier concentrations; (2) the spontaneous solubilization of the Versamid 115 curing agent, or some water-soluble component thereof, in a solution of high emulsifier concentration; (3) the spontaneous inversion of the oil-in-water emulsion to a water-in-oil type.

To investigate the possibility of spontaneous breakdown of the emulsion droplets or solubilization of the prepolymer molecules in solutions of high emulsifier concentra-

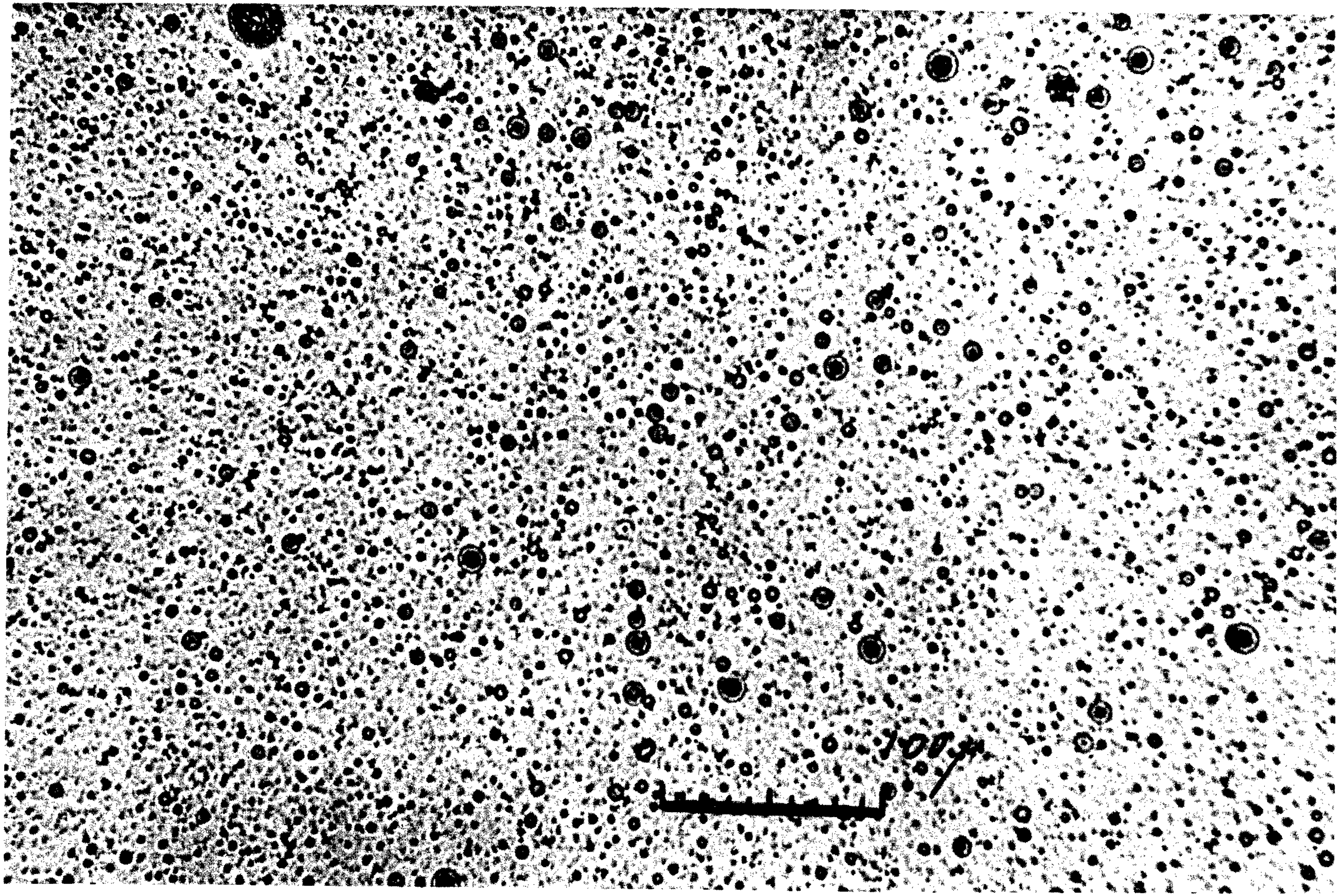

Figure 28. Optical photomicrograph of an emulsion of the 80:2:5:5:8 Versamid 115-xylene-n-butanol-isopropanol-toluene mixture prepared using the Manton-Gaulin Homogenizer, after standing for 1 day.

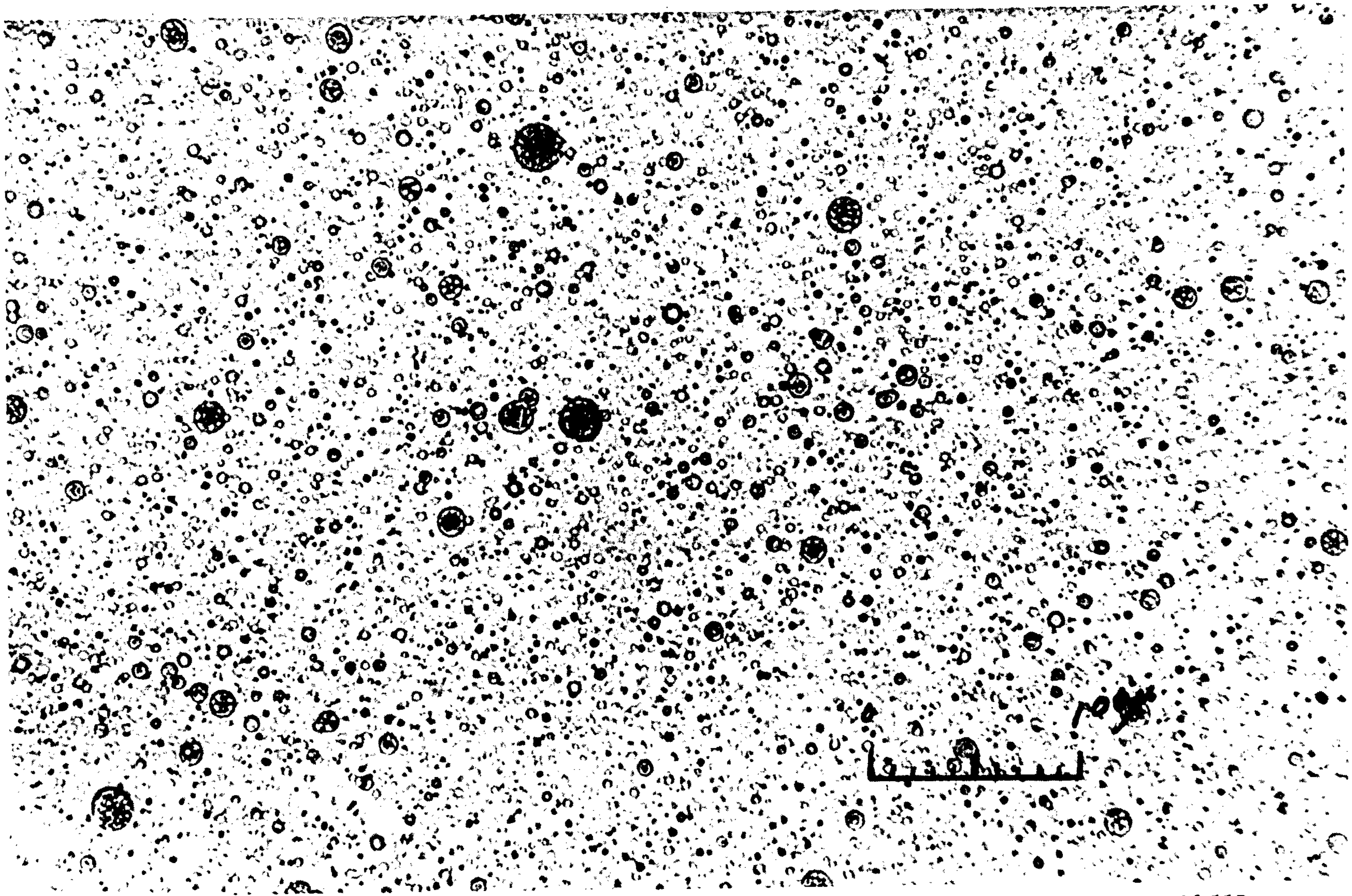

Figure 29. Optical photomicrograph of the same emulsion (Figure 28) of the 80:2:5:5:8 Versamid 115-xylene-n-butanol-isopropanol-toluene mixture prepared using the Manton-Gaulin Homogenizer, after standing for 7 days.

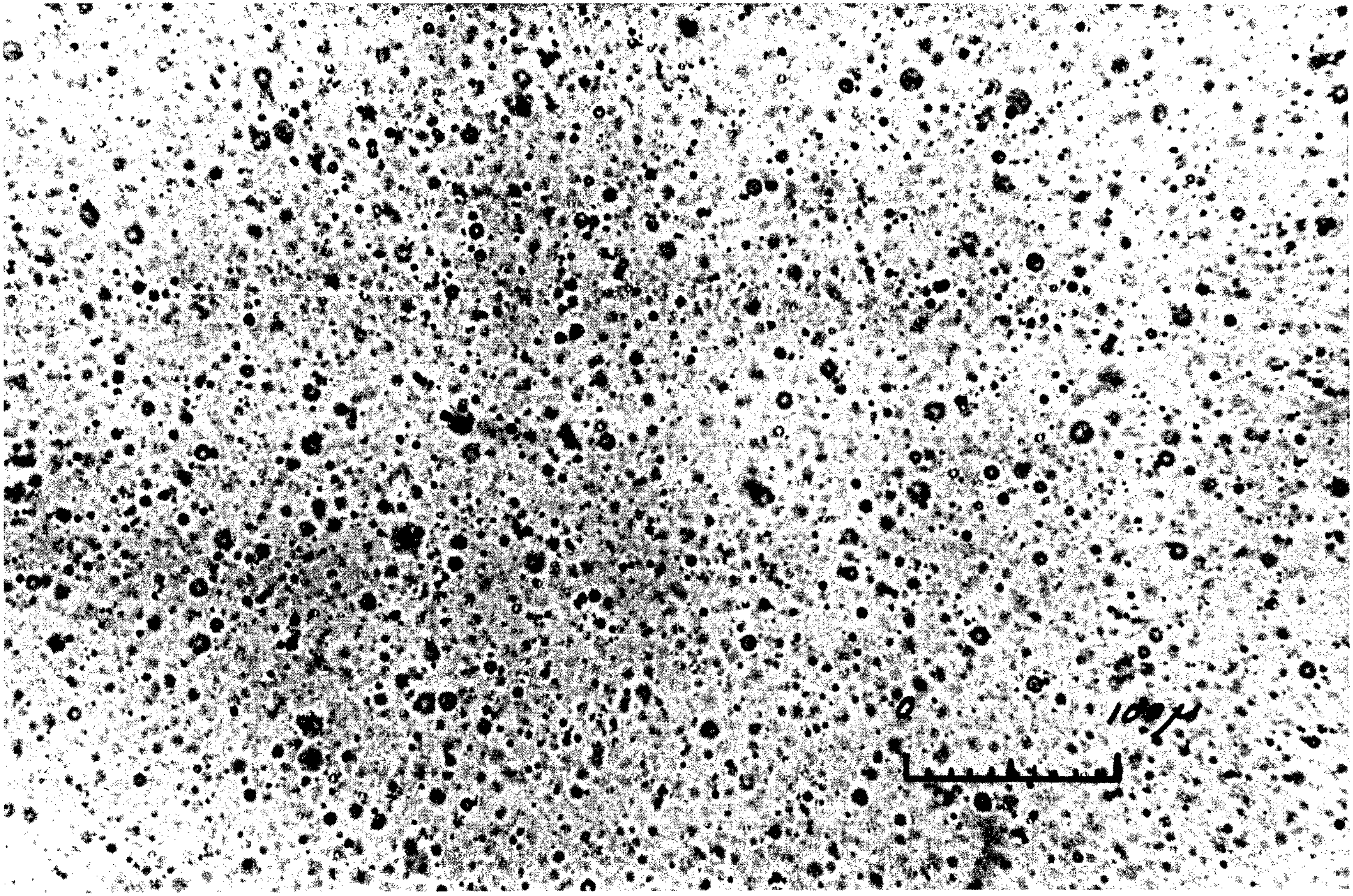

Figure 30. Optical photomicrograph of an emulsion of the 80:2:5:5:8 Versamid 115-xylene-n-butanol-isopropanol-toluene mixture prepared using a higher concentration of mixed emulsifier and the Manton-Gaulin Homogenizer, after standing for 1 day.

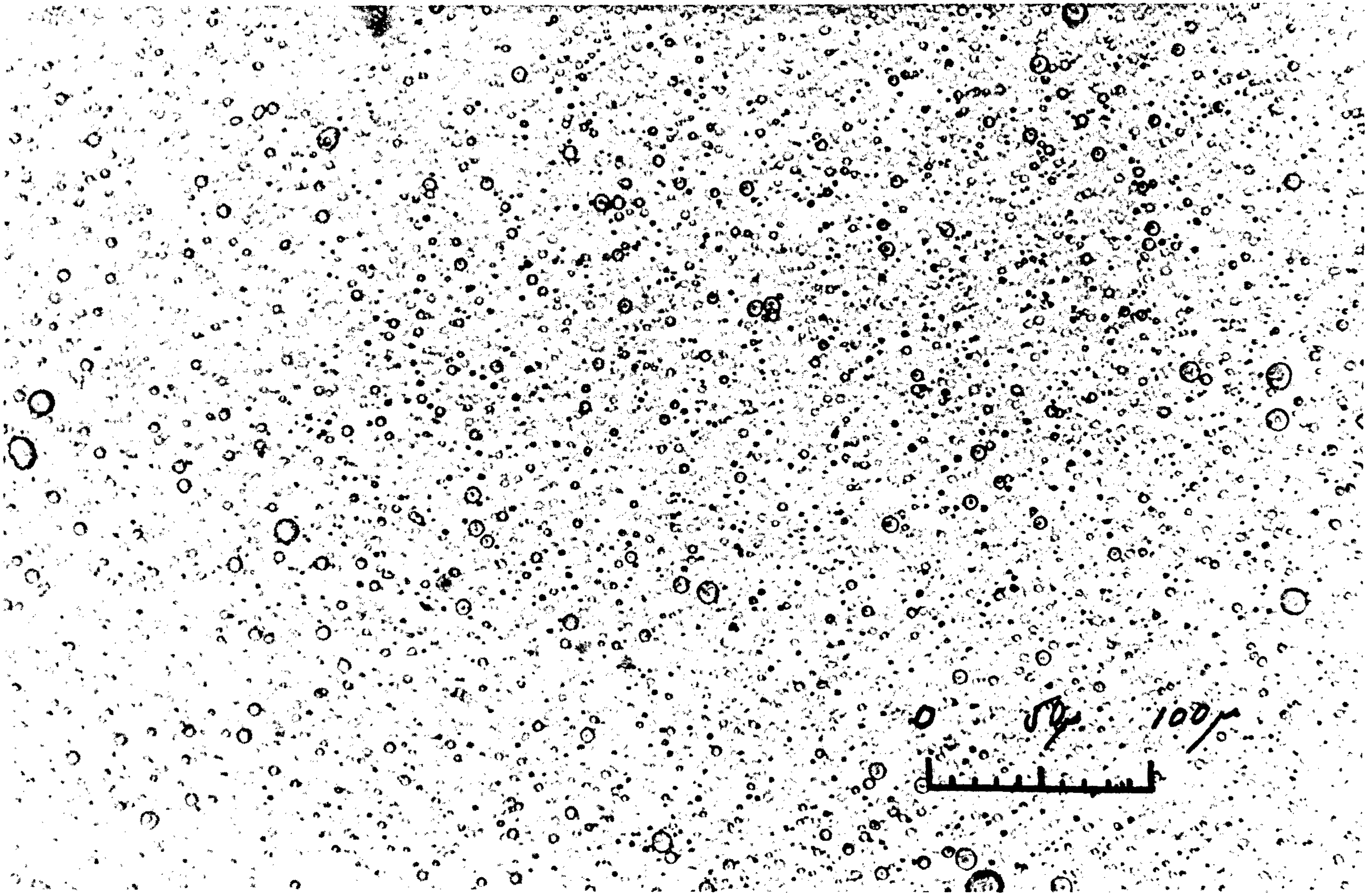

Figure 31. Optical photomicrograph of the same emulsion (Figure 30) of the 80:2:5:5:8 Versamid 115-xylene-n-butanol-isopropanol-toluene mixture prepared using a higher concentration of mixed emulsifier and the Manton-Gaulin Homogenizer, after standing for 7 days.

tion, emulsifications were carried out at lower emulsifier concentrations: 125 gm of a 25% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture was emulsified in 375 gm water using 1.04-2.08 or 0.73-1.46 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol combination and homogenization. Both emulsions were stable and of small droplet size. Upon vacuum steam distillation, both became viscous and translucent in the same manner as the emulsion prepared with a higher emulsifier concentration. Thus, the increase in viscosity and decrease in opacity were not avoided by reducing the emulsifier concentration almost four-fold.

To investigate the possibility that part of the Versamid 115 curing agent can be dissolved, Versamid 115-solvent mixtures were leached repeatedly with water to remove any water-soluble components. When these water-leached Versamid 115 solutions were emulsified and subjected to vacuum steam distillation in the same manner as before, they also became viscous and translucent, indicating that the solubilization or dissolution of water-soluble components of Versamid 115 was not responsible for this phenomenon.

To investigate the possibility of inversion of the oil-in-water emulsion to a water-in-oil type, several samples of the viscous, translucent emulsions were diluted indefinitely with water without forming two separate phases, but not with oil (the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture), indicating that no inversion had occurred.

Meanwhile, upon standing for 6 weeks, these viscous, translucent solvent-free Versamid 115 emulsions slowly reverted to opaque emulsions of low viscosity. This latter transformation suggests that the increase in viscosity and decrease in opacity at a critical point during the removal of solvents by vacuum steam distillation was due to the spontaneous formation of microemulsion droplets, which slowly coalesced upon ageing to form larger-but-still-submicroscopic droplets. To prove this hypothesis would require accurate measurements of the droplet size at different times in the solvent removal process; thus far, a satisfactory method to do this has not been worked out. Fortunately, as will be shown in the following section, the Versamid 115 emulsions, whether viscous and translucent or fluid and opaque, can be used in mixture with the epoxy resin emulsions without complication.

Similar results were observed with the Component II curing agent, i.e., the emulsions became viscous and translucent during removal of the solvents and then later became opaque and fluid again.

c. Genamid 250 Emulsions

Several attempts were made to emulsify Genamid 250 (General Mills Co.), which is described as a water-emulsifiable resinous amine adduct of very low viscosity (5-10 poise Brookfield at 25° C). Thus, 25 gm Genamid 250 was emulsified in 75 gm water using 0.8-1.6 gm of the hexadecyltrimethylammonium bromide-cetyl alcohol or sodium lauryl sulfate-cetyl alcohol combinations, along with ultrasonic irradiation. Both emulsifications produced a paste-like emulsion that could be diluted indefinitely with water, indicating that it was an oil-in-water rather than a water-in-oil type. A similar emulsification omitting the emulsifier altogether also produced a paste-like emulsion that could be diluted indefinitely with water. The fact that this curing agent emulsifies easily using either the cationic or anionic mixed emulsifier combination, as well as with no added emulsifier at all, suggests that it contains a significant proportion of nonionic emulsifier, either as an additive or as part of the prepolymer molecule. Moreover, its emulsification is enhanced by its low viscosity.

4. Evaluation of Epoxy Resin-Curing Agent Films

To evaluate their performance in coating films, the foregoing epoxy resin and curing agent emulsions were mixed in varying proportions, and drawdowns of the mixed emulsions were made on aluminum alloy panels (2024-T3 Fed. QQA-250/5) and cured, either at room temperature or in an oven at elevated temperatures. Films were made of the mixed Epon 1001-Versamid 115 (K-9/K-10; R-77/K-10; R-77/R-89), Epon 1001-Genamid 250 (R-77/R-84; R-77/R-85), and Epon 828-Versamid 115 (R-74/K-10; R-75/K-10) systems. The two paste-like Genamid 250 emulsions were diluted to 4.4% solids before mixing with the Epon 1001 emulsion, which was also diluted to the concentration.

For comparison, films were made of the mixed Epon 828-Versamid 115 (E-1/V-1) and Component I-Component II (M-I/M-II) solvent-based systems and cured under the same conditions.

The following emulsions and solutions were used in this evaluation.

K-9	37.5% cationic Epon 1001 emulsion (Figures 15 and 16) prepared from the 70% solution of Epon 1001 in 50:50 toluene-methyl isobutyl ketone mixture diluted to 20.0% Epon 1001.
K-10	20% cationic Versamid 115 emulsion (Figures 30 and 31) prepared from the 80% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture.
R-74	26.8% cationic Epon 828 emulsion (Figure 19) prepared from the 70% solution of Epon 828 in the 50:50 toluene-methyl isobutyl ketone mixture.
R-75	25.2% cationic Epon 828 emulsion (Figure 20) prepared by steam-stripping the foregoing R-74 emulsion.
R-77	25% cationic Epon 1001 emulsion (Figure 18) prepared by steam-stripping the emulsion prepared from the 25% solution of Epon 1001 in the 50:50 toluene-methyl isobutyl ketone mixture.
R-84	25% Genamid 250 emulsion prepared without solvents or emulsifiers.
R-85	25% cationic Genamid 250 emulsion prepared without solvents.

R-89 5.5% cationic Versamid 115 emulsion prepared by steam-stripping the emulsion prepared from the 25% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture.

E-1 20% solution of Epon 828 in the 50:50 toluene-methyl isobutyl ketone mixture.

V-1 20% solution of Versamid 115 in the 10:25:25:40 xylene-n-butanol-isopropanol-toluene mixture.

M-I Military Component I (36.6% epoxy resin).

M-II Military Component II (18.7% polyamide curing agent resin).

Table II gives the results of a preliminary evaluation of both the emulsion-cast and solvent-cast films prepared using different epoxy resin-curing agent proportions and cured at different temperatures.

The following conclusions can be drawn from the results of Table II.

(i) Transparent films were obtained from the mixed epoxy resin-curing agent emulsions, even at room temperature, indicating that the epoxy resin droplets coalesce with the curing agent droplets.

(ii) Of the emulsion-cast films, those cured at the higher temperatures generally displayed better film properties than those cured at room temperature; however, several room-temperature-cured films cast from the steam-stripped emulsions using the optimum epoxy-resin-curing agent ratio displayed good properties, and those cured at room temperature for longer times (36 days) were almost equivalent or, in some cases, slightly superior to those cured at the higher temperatures.

(iii) The optimum epoxy resin-curing agent ratio was 2:1 for the Epon 1001-Versamid 115 system (K-9/K-10; R-77/K-10; R-77/R-89), 2:1 for the Epon 1001-Genamid 250 system (R-77/R-84; R-77/R-85), and 1:2 for the Epon 828-Versamid 115 system (R-74/K-10; R-75/K-10).

(iv) The film properties of the Epon 1001-Versamid 115 system were slightly better than those of the Epon 828-Versamid 115 system and equivalent to those of the Epon 1001-Genamid 250 system.

(v) Of the solvent-cast films, the properties of the Component I-Component II system (M-I/M-II) were slightly better than those of the Epon 828-Versamid 115 system (E-1/V-1).

(vi) The properties of the best emulsion-cast films were equivalent to those of the best solvent-cast films.

5. Dynamic-Mechanical Spectroscopy of Epon 1001-Versamid 115 Films

a. Mechanical Properties

In coating development work, it is useful to know whether the experimental films have properties comparable to those presently-available. If the coating is formed by

Table II. Properties of Emulsion-Cast and Solvent-Cast Epoxy Resin-Curing Agent Films

Composition	Curing Temperature, °C	Film Evaluation		
		Appearance*	Hardness**	Adhesion***
2:1 K-9/K-10	22	3	5	2
2:1 K-9/K-10	40	3	5	4
1:1 K-9/K-10	22	3	5	2
1:1 K-9/K-10	40	2	5	3
1:2 K-9/K-10	22	1	1	2
1:2 K/9-K-10	40	2	3	3
2:1 R-77/K-10	22	3	5	3
2:1 R-77/K-10	40	4	5	5
1:1 R-77/K-10	22	3	5	2
1:1 R-77/K-10	40	4	5	3
1:2 R-77/K-10	22	4	2	2
1:2 R-77/K-10	40	4	3	2
4:1 R-77/R-89	22 (10 days)	4	4	2
4:1 R-77/R-89	22 (36 days)	4	5	3
4:1 R-77/R-89	50	5	5	3
2:1 R-77/R-89	22 (10 days)	4	4	2
2:1 R-77/R-89	22 (36 days)	4	5	3
2:1 R-77/R-89	50	5	5	4
1:1 R-77/R-89	22 (10 days)	4	3	1
1:1 R-77/R-89	22 (36 days)	5	5	2
1:1 R-77/R-89	50	5	3	2
1:2 R-77/R-89	22 (10 days)	4	2	1
1:2 R-77/R-89	22 (36 days)	5	5	2
1:2 R-77/R-89	50	4	2	2
2:1 R-77/R-84	22	2	5	3
2:1 R-77/R-84	55	5	5	5
1:1 R-77/R-84	22	4	5	2
1:1 R-77/R-84	55	5	4	4
1:2 R-77/R-84	22	5	3	1
1:2 R-77/R-84	55	5	2	1
2:1 R-77/R-85	22	2	5	3
2:1 R-77/R-85	55	4	5	5
1:1 R-77/R-85	22	4	5	2
1:1 R-77/R-85	55	5	5	5
1:2 R-77/R-85	22	5	2	3
1:2 R-77/R-85	55	5	2	3

Table II (continued)

Composition	Curing Temperature, °C	Film Evaluation		
		Appearance*	Hardness**	Adhesion***
2:1 R-74/K-10	22	4	5	3
2:1 R-74/K-10	40	4	5	5
1:1 R-74/K-10	22	5	5	3
1:1 R-74/K-10	40	5	5	5
1:2 R-74/K-10	22	5	5	4
1:2 R-74/K-10	40	5	5	5
2:1 R-75/K-10	22	2	5	2
2:1 R-75/K-10	40	2	5	5
1:1 R-75/K-10	22	1	5	1
1:1 R-75/K-10	40	1	5	5
1:2 R-75/K-10	22	4	5	3
1:2 R-75/K-10	40	3	5	5
2:1 E-1/V-1	22	5	5	5
2:1 E-1/V-1	40	5	5	5
1:1 E-1/V-1	22	5	4	4
1:1 E-1/V-1	40	5	5	4
1:2 E-1/V-1	22	5	3	4
1:2 E-1/V-1	40	5	4	4
2:1 M-I/M-II	22	5	5	5
2:1 M-I/M-II	40	5	5	5
1:1 M-I/M-II	22	5	3	4
1:1 M-I/M-II	40	5	5	5
1:2 M-I/M-II	22	5	3	4
1:2 M-I/M-II	40	5	5	5

Key to film evaluation ratings: the higher the number, the better the film.

*Appearance - arbitrary scale of 1-5, with 1 = opaque and 5 = transparent.

**Hardness or degree of cure as determined by finger tack test - arbitrary scale of 1-5, with 1 = sticky and 5 = non-tacky, hard.

***Adhesion as determined by scratching with a needle - arbitrary scale of 1-5, with 1 = needle point penetrating to the substrate, some residue left on needle, and 5 = needle point barely scratches the surface, no residue left on needle.

the in situ curing of a thermosetting resin, it is also useful to know how the curing reaction affects the mechanical properties of the film and the nature of the crosslinked network (64-73). Moreover, if the film contains pigments or fillers and is cast on a substrate, it is useful to know the effect of the interactions between the polymeric binder, the substrate, and the dispersed pigments or fillers.

One of the most practical yet fundamental methods for characterization of polymer networks is the modulus-temperature variation (74), i. e., measurements of the shear modulus G or Young's modulus E ($E \sim 3G$) in tension or torsion as a function of temperature. The modulus (or stiffness), defined as the stress-strain ratio, is measured at a specified time because of the well-known time-dependency of polymer properties. The measurements may be made statically (e.g., with a torsional pendulum) or dynamically (i. e., with cyclic loading). The dynamic tests (dynamic-mechanical spectroscopy) yield more information because the complex modulus E* thus determined can be subdivided into two components E' and E'' according to:

$$E^* = E' + i\,E'' \qquad (2)$$

where i is $\sqrt{-1}$, E' the storage modulus (i. e., a measure of the energy stored elastically or the stiffness) and E'' the loss modulus (i. e., a measure of the energy dissipated as heat through viscous mechanisms). The combined effects of the two modulii on damping may be expressed as:

$$\tan\,\delta = E''/E' \qquad (3)$$

in which $\tan\,\delta$ is a measure of energy dissipation analogous to the power factor in alternating electrical circuits.

The experimental variation of E' and E'' with temperature gives several different types of information:

1. The fact that an experimental film can survive the test without breaking is in itself evidence that it is comprised of a high polymer with at least a minimum level of "guts."
2. The values of the moduli E and E' determine whether a given thermoplastic polymer is glassy, leathery, or rubbery (74). For example, E is about 10^{10} dynes/cm^2 for a glassy polymer, 10^8-10^{10} dynes/cm^2 for a leathery polymer, and about 10^8 dynes/cm^2 for a rubbery polymer. In general, higher values of E are correlated with hardness and high strength, and lower values with flexibility and, to a certain extent, toughness (see Figure 32).
3. The foregoing relationships do not necessarily apply to a crosslinked polymer network, e.g., a cured thermosetting resin film cannot undergo viscous flow at elevated temperatures and, hence, its values of E and E' in the rubbery region will be greater than those of the corresponding thermoplastic polymers. For a crosslinked network in the rubbery state, the values of E and E' are measures of the tightness of the polymer network, which may be characterized by the average molecular weight between crosslinks M_c (Figure 33). For the

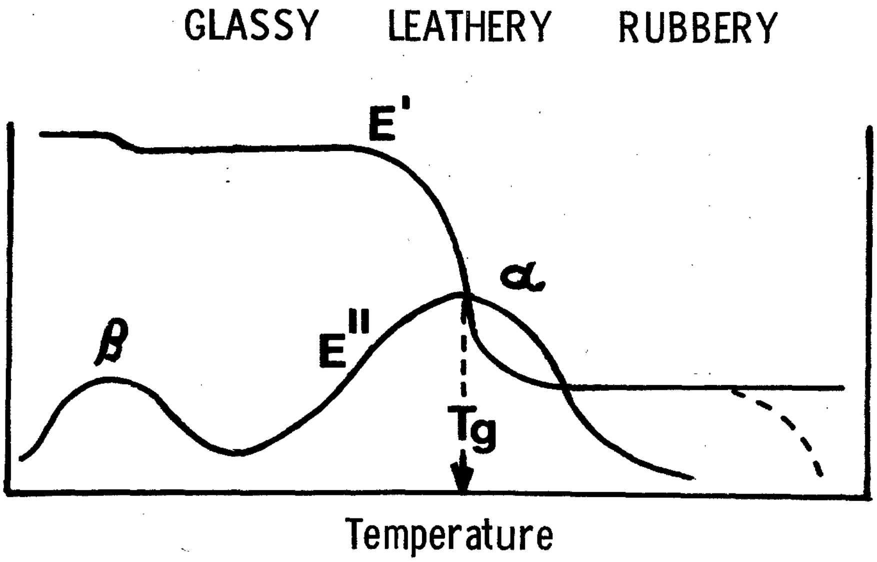

Figure 32. Typical log modulus-temperature variation for a homogeneous crosslinked polymer for the case, $T_g = T_\alpha$, the temperature of the highest-transition observed. E' is the storage modulus (a measure of stiffness) and E'' the loss modulus (a measure of damping and energy dissipation). The dotted line indicates the onset of viscous flow, which is possible only in the absence of crosslinking.

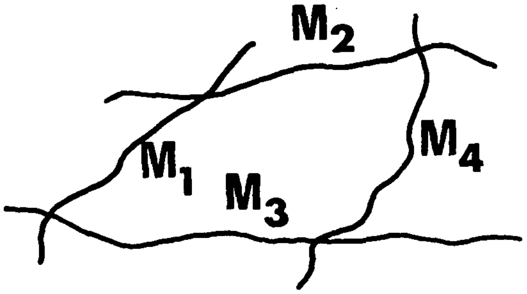

Figure 33. Schematic representation of a crosslinked polymer network. The tightness of the network is controlled by the average molecular weight between crosslinks M_c, in this case the average of M_1, M_2, M_3, M_4, etc.

epoxy resin systems used here (i. e., with $E' \sim 10^8$ dynes/cm^2 -- in the rubbery range -- and with rather large values of M_c), the values of M_c can be estimated from the following equation (64):

$$E' = 3\, d\, R\, T/M_c \tag{4}$$

where d is the polymer density, R the gas constant, and T the temperature. This equation, which is analogous to the well-known equation of state for gases PV = nRT, allows the comparison of experimental values of M_c with predicted values based on reactant structures as well as the determination of the completeness of cure. The value of M_c is also related to toughness, the maximum toughness correlating with intermediate values of M_c.

4. The engineering-use temperatures of a polymer are determined by its transitions, e.g., the glass-to-rubber transition at temperature T_g. These transitions are also important in curing reactions because the rate of curing at a given temperature T_c slows down when the T_g of the growing network approaches T_c. The nature of the transition is also related to the polymer composition and behavior, e.g., a broad glass-to-rubber transition (in terms of E' and E'') is indicative of phase separation or incompatibility and is often correlated with toughness (74), as is the second damping peak β (75, 76). For a thermosetting resin at different stages of cure, small peaks in the modulus-temperature variation near T_c are indicative of gelation or incomplete curing (65, 66).

Thus, the modulus-temperature variation is useful in characterizing such thermosetting resins as epoxy resins, both as films and as adhesives (64-73). Regrettably, most earlier studies of curing lack the useful information derived from these modulus-temperature variations. However, since an understanding of the basic curing reactions is, in our opinion, the most direct route to the optimization of the system, the modulus-temperature variation was determined, at least in a preliminary way, for the Epon 1001-Versamid 115 emulsion system.

b. Preparation and Measurement of the Films

Solvent-free epoxy resin and curing agent emulsions were mixed in the desired proportions and allowed to stand for 15-20 minutes to allow entrapped air bubbles to rise to the surface. Then, a film of the mixed emulsions was cast on a glass slide placed in an aluminum tray with 4-6-mm high edges to keep the emulsion on the slide. Before film-casting, the glass slide was sprayed with Epoxy Parafilm mold release agent to facilitate the removal of the cured film. After casting, the film was cured in an air oven at 50°C. Then, the aluminum sides were peeled off, and the film was removed from the slide with a razor blade. Test specimens 1-2 cm long and 0.14 cm wide were cut from this 0.04-cm thick film.

Measurements of the storage modulus E' and loss modulus E'' of the films were carried out using the Rheovibron Elastoviscosimeter (Toyo Measuring Instruments Company, Ltd.) shown in Figure 34. This instrument gives a direct reading of the dynamic force applied to the sample and the tangent of the angle (tan δ) between the

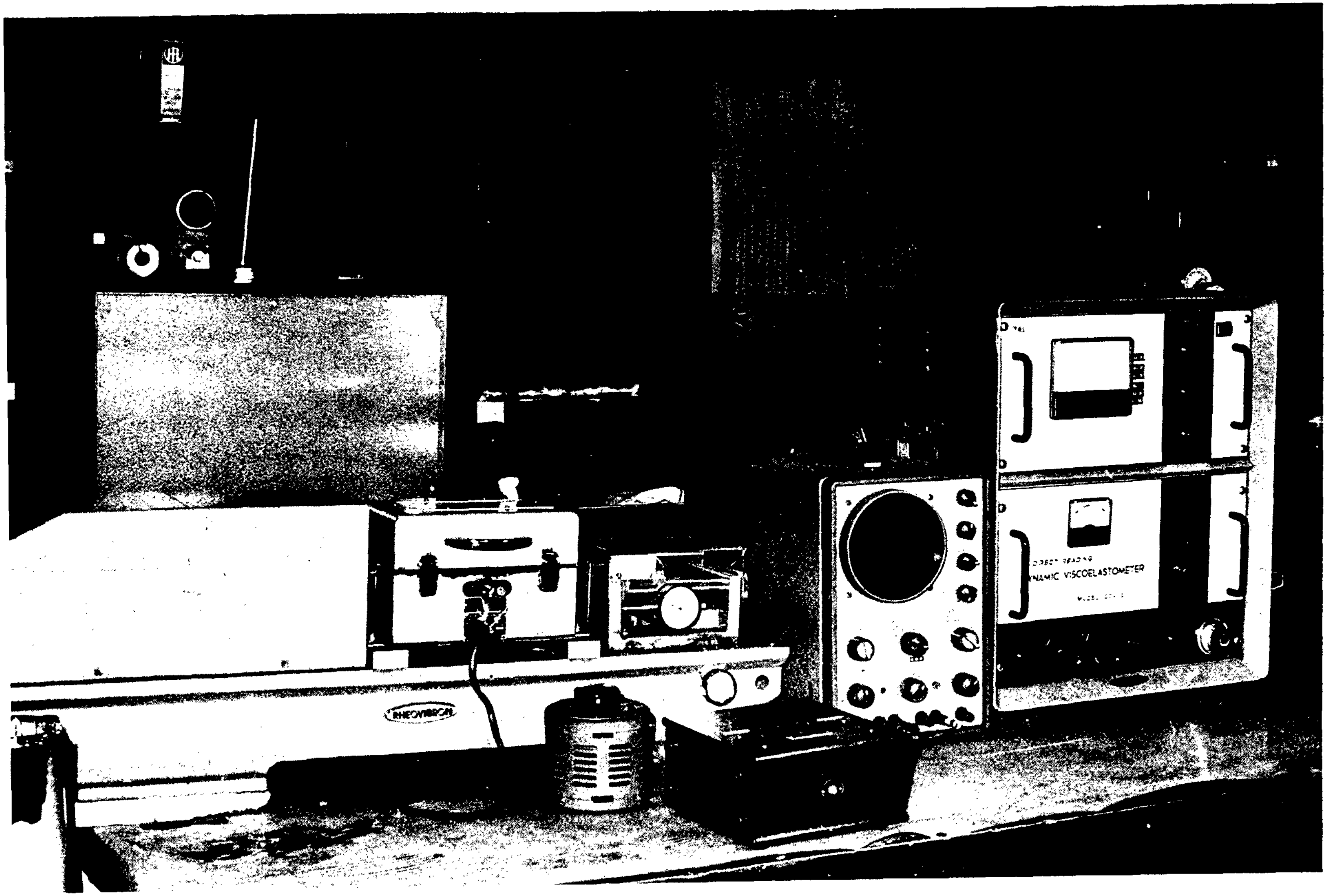

Figure 34. The Rheovibron Elastoviscosimeter. The film specimen is gripped in a chamber controlled at the desired temperature and vibrated at the desired frequency. The values of E' and E'' are calculated from the strain, the applied force, and the phase angle between them.

applied sinusoidal stress and the strain generated at the other end of the sample. The composite modulus, and therefore the storage and loss moduli, are calculated using a formula supplied by the manufacturer.

c. Modulus-Temperature Variation of the Epon 1001-Versamid 115 Films

Figures 35 and 36 show the variation of log storage and loss moduli with temperature for films of the emulsion-cast 5:2, 5:1, and 2:1 Epon 1001-Versamid 115 combinations. For comparison, the corresponding variation is shown for the solvent cast 1:1 Epon 828-Versamid 140 combination. These few preliminary data are not sufficient to completely describe the Epon 1001-Versamid 115 film properties; however, a number of interesting observations follow:

1. The log moduli-temperature curves of the emulsion-cast films generally resembled those of ordinary polymers up to about 90° C, i. e., the curing of the film had proceeded sufficiently to develop the desired "guts." Moreover, the curves provided numerical values to corroborate the visual observations, namely, that the properties of the emulsion-cast Epon 1001-Versamid 115 films are neither better nor worse than those of the solvent-cast Epon 828-Versamid 140 film, but simply different, as are those of other epoxy systems (65, 66, 71-73). Also, as discussed in 3, these curves suggest that further curing occurred during testing at temperatures above T_c (50° C).
2. The glassy modulus was more than twice as great for the film of the 5:1 Epon 1001-Versamid 115 ratio than for that of the 5:2 ratio; moreover, these values were typical of those of epoxy resins. Also, the glass-to-rubber transition was broader for the Epon 1001-Versamid 115 films than for the Epon 828-Versamid 140 film, reflecting a greater heterogeneity of composition (65-67, 77) and probably increased toughness. It was not possible to extend the measurements of the Epon 1001-Versamid 115 films into the rubbery region because the specimens failed (at the grips); however, their rubbery moduli would be expected to be lower than that of the Epon 828-Versamid 140 film because the lower epoxide content of Epon 1001 should yield a lower value of M_c and, hence, a more flexible polymer.
3. With increasing temperature, the log moduli-temperature variation of the Epon 1001-Versamid 115 films showed two peaks at temperatures T_α and T_β. These transitions may be attributed to gelation, incomplete curing, or phase separation. The second peak (actually a "shoulder" on the curve) occurred near T_c (50° C), suggesting that, as expected, a pseudo-cure was attained at 50° C, but that further curing took place at high temperature. This is supported by the fact that the two peaks for the 2:1 Epon 1001-Versamid 115 film (Figure 36) became one after the film was heated through the programmed cycle to 90° C.
4. At temperatures above 90° C, the moduli of the emulsion-cast films dropped off monotonically to rupture, instead of leveling out to a rubbery region as expected. This may be attributed to incompleteness of cure and network development or, alternatively, to flaws in the film specimens (because of failure at the grips).

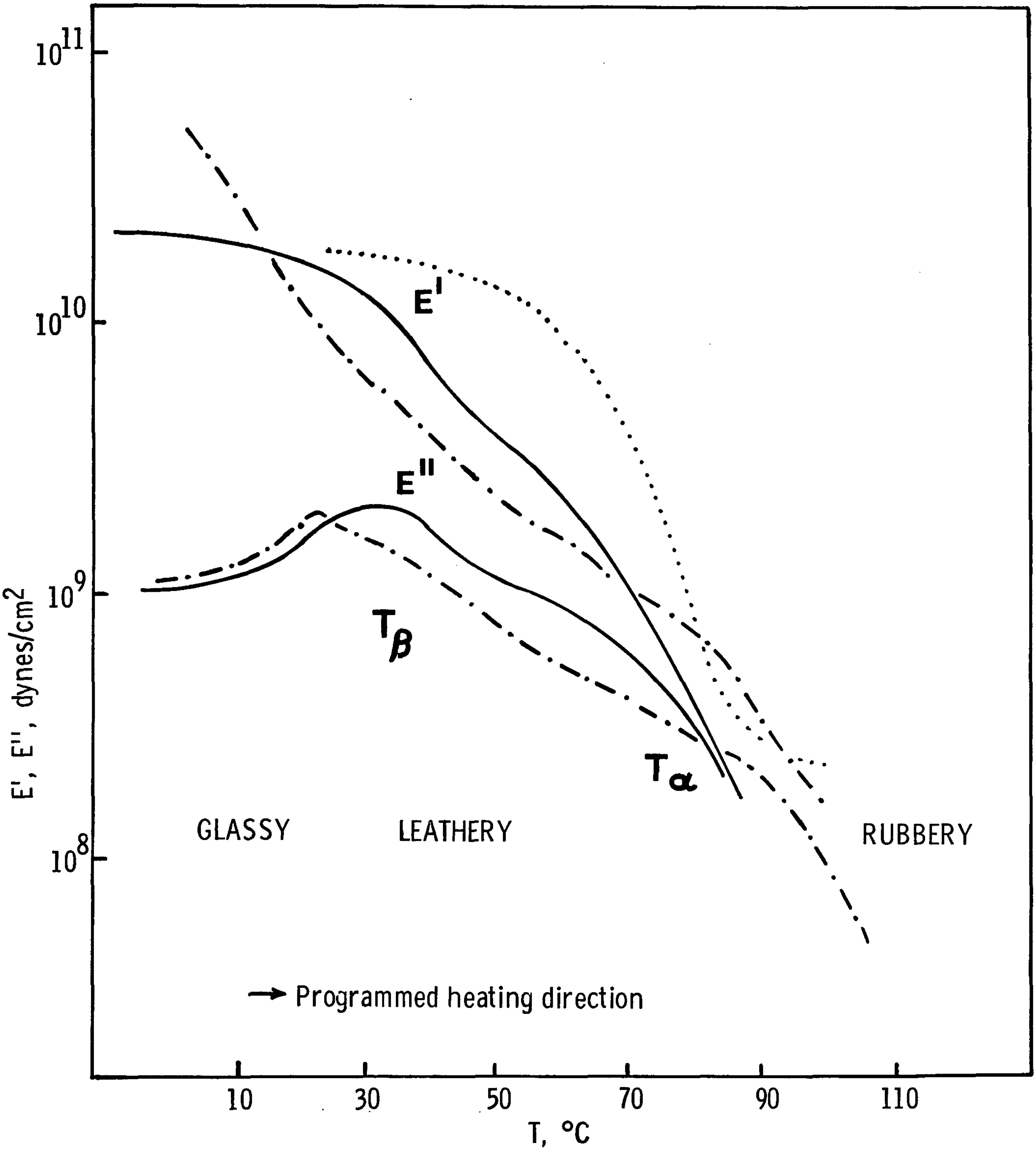

Figure 35. Variation of log modulus with temperature for emulsion-cast films of the 5:2 and 5:1 ratios of the Epon 1001-Versamid 115 combinations cured at 50°C: (——) 5:2 ratio; (—•—) 5:1 ratio; (·····) solvent-cast 1:1 Epon 828-Versamid 140 ratio included for comparison.

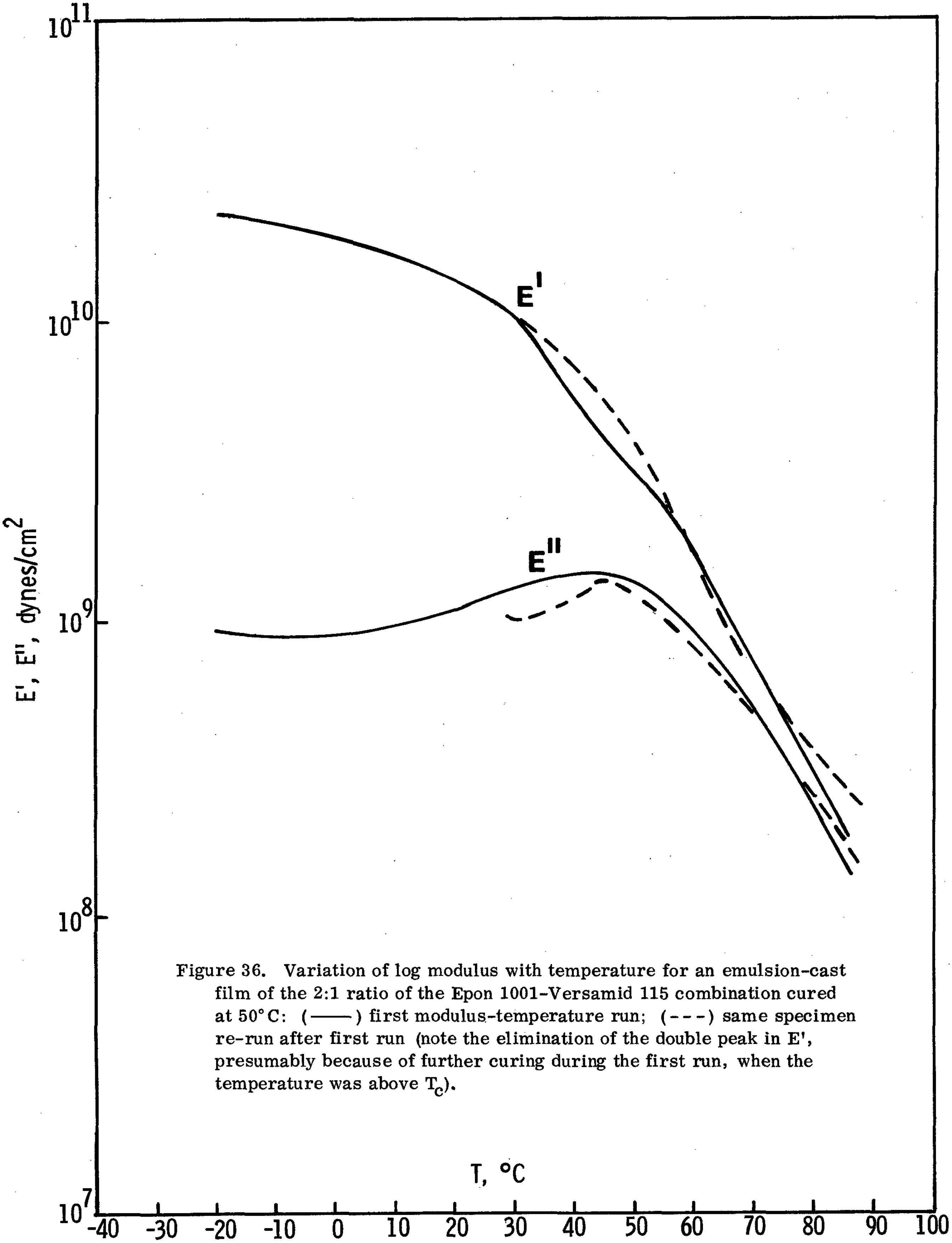

Figure 36. Variation of log modulus with temperature for an emulsion-cast film of the 2:1 ratio of the Epon 1001-Versamid 115 combination cured at 50° C: (——) first modulus-temperature run; (- - -) same specimen re-run after first run (note the elimination of the double peak in E', presumably because of further curing during the first run, when the temperature was above T_c).

In summary, these preliminary results show that the modulus-temperature variation can be used to characterize a given thermosetting emulsion system. Systematic measurements of samples prepared with different experimental variations and comparison with reference systems would lead quickly to the optimization of cure rate and film properties. This approach would be complemented by experiments using torsional braid analysis, in which a coating is applied to a glass braid and its rate of cure is monitored as a function of time and temperature.

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

The following samples were prepared using the mixed emulsifier combination and simple stirring, followed by homogenization, and sent to the Air Force Materials Laboratory for evaluation for the primer application. The sample sizes were sufficient to provide several one-quart samples of the mixed epoxy resin-curing agent emulsions.

A. Epoxy Resin Emulsions

1. 25.3% cationic Epon 1001 emulsion
2. 24.6% anionic Epon 1001 emulsion
3. 22.5% cationic Epon 828 emulsion

B. Curing Agent Emulsions

1. 7.12% cationic Versamid 115 emulsion
2. 34.1% cationic Genamid 250 emulsion
3. 33.6% anionic Genamid 250 emulsion

SECTION V

PREPARATION AND EVALUATION OF POLYURETHANE EMULSION SYSTEMS

A. Introduction

1. Present System

The polyurethane topcoat presently used by the Air Force (4) is a two-component solvent-based system: (1) Component I is a hydroxyl-terminated polyester prepolymer dissolved in solvents and containing dispersed pigments; (2) Component II is an aliphatic isocyanate prepolymer dissolved in solvents. Component I contains a small amount of dibutyltin dilaurate as catalyst for the isocyanate-hydroxyl curing reaction. Components I and II 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 (in our opinion, it is questionable whether such precise control can be maintained, since the hydroxyl number of the polyester prepolymer varies from batch to batch, and the differences in the storage history of the isocyanate prepolymer may introduce different concentrations of water).

The pot life of the mixed Components I and II 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 in Component II 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 in Component I is Multron R-221-75 (formerly E-380 and so designated in this report; 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 Components I and II 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.

2. 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 pre-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-reaction 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 following hydroxyl-containing materials were used to form adducts with the Desmodur N-100 isocyanate prepolymer:

1. hydroxyethyl and hydroxypropyl methacrylates (Rohm & Haas Company)
2. hydroxyalkyl methacrylate-polyester prepolymer mixtures
3. hydroxyalkyl methacrylate-monohydric alcohol mixtures
4. polyester prepolymer-monohydric alcohol mixtures
5. hydroxyalkyl methacrylate-methyl ricinoleate mixtures
6. glycidol (2,3-epoxy-1-propanol; Eastman Kodak Company)
7. hydroxyalkyl methacrylate-allyl alcohol mixtures
8. hydroxyalkyl methacrylate-allyl alcohol-polyester prepolymer mixtures
9. allyl alcohol (Eastman Kodak Company)

The following monomers were used as reactive diluents for the foregoing isocyanate prepolymer adducts:

1. methyl methacrylate (Rohm & Haas Company)
2. butyl acrylate (Rohm & Haas Company)
3. isobutyl methacrylate (Rohm & Haas Company)
4. acrylonitrile (Eastman Kodak Company)
5. diethyl fumarate (Eastman Kodak Company)
6. 1,4-butanediol diglycidyl ether (Eastman Kodak Company).

The following polyester prepolymers were reacted with the foregoing isocyanate prepolymer adducts:

1. Multron E-380 hydroxyl-terminated polyester prepolymer
2. Multron R-16 hydroxyl-terminated polyester prepolymer (hydroxyl number 44; Mobay Chemical Company)
3. Paraplex P-444A (75:25 unsaturated polyester prepolymer-methyl methacrylate mixture; Rohm & Haas Company)
4. Polypropylene Glycol 425 (molecular weight 425; J. T. Baker Company).

All ingredients were used as received without further purification.

B. Experimental Details and Discussion

1. Experimental Details

When expressed in convenient laboratory quantities, the 29:71:0.072 Desmodur N-100-Multron E-380-dibutyltin dilaurate mixture deduced from the equi-volume mixture of Components I and II amounts to 8.10 gm Desmodur N-100, 19.64 gm Multron E-380, and 0.02 gm dibutyltin dilaurate. These quantities were mixed together in Pyrex glass beakers and allowed to stand at room temperature for 24 hours to form the adduct.

The adducts were emulsified in water using the same procedure developed earlier for styrene monomer (1) and the epoxy emulsion systems. Typically, 0.40-0.80 gm of the sodium lauryl sulfate-cetyl alcohol combination was dissolved in 75 gm water by stirring for 30 minutes at 63°C in a 250 ml Erlenmeyer flask. Then, 25 gm of the adduct was added, and the stirring was continued for another 30 minutes at the same temperature to form a crude emulsion, which was subjected to ultrasonic irradiation or homogenization to form an emulsion of small droplet size.

While still hot, these emulsions were transferred to 12-oz glass bottles fitted with screw caps containing self-sealing gaskets ("sandwich" of B. F. Goodrich W-7 butyl rubber and W-9 50:50 PVC-SBR mixture). The atmosphere of the bottles was flushed with nitrogen by inserting two hypodermic needles through the gasket, one connected to the nitrogen supply and the other providing the outlet. The potassium persulfate initiator (0.25 gm) and sodium bicarbonate buffer (0.25 gm) dissolved in 10 ml water were then injected through the gasket, and the bottle was rotated end-over-end in a thermostated bath at 60°C.

Other polymerizations were carried out in which the adduct emulsion was added continuously to the polymerization medium. Sodium lauryl sulfate (0.80 gm), cetyl alcohol (0.40 gm), and sodium bicarbonate (0.25 gm), along with 50-200 gm deionized water were added to a one-liter four-neck flask equipped with a Teflon-paddle stirrer, condenser, addition funnel, and nitrogen inlet and stirred at 300 rpm for 30 minutes at 63° C; during this time, the mixture was sparged with oxygen-free nitrogen. Potassium persulfate initiator (0.25 gm) was then added through the nitrogen inlet, and the stirring rate was reduced to 60 rpm. After 10 minutes, the dropwise addition of the adduct emulsion was begun; typically, the rate of addition was such that 3-4 hours were required to complete the addition of the emulsion. After the addition of the emulsion was completed, the stirring rate was reduced further to 40 rpm, and the polymerization was continued for another 4 hours at the same temperature under nitrogen atmosphere.

2. Preliminary Experiments

a. Gel Time of the Isocyanate Prepolymer-Polyester Prepolymer Adduct

The purpose of this work was to determine the gel time of the isocyanate prepolymer-polyester prepolymer mixture used in the present solvent-based topcoat and, also, the feasibility of direct emulsification of this adduct. The gel time for a mixture of 8.1 gm Desmodur N-100 and 19.6 gm Multron E-380 at room temperature was 3-4 hours with 0.02 gm dibutyltin dilaurate catalyst and about 24 hours without catalyst. The optimum time for emulsification was determined to be 2 hours after addition of the catalyst; at longer times, the viscosity of the mixture was too great for easy emulsification. The emulsions prepared at this optimum time dried to form a residue comprised partly of a friable, white powder and partly of a transparent film. Further experiments failed to produce a satisfactory film; it was not possible to control the extent of the reaction between the two prepolymers precisely enough to give a continuous film with the desired properties.

b. Addition of Monohydric Alcohols to the Isocyanate Prepolymer-Polyester Prepolymer Mixture

The purpose of this work was to delay or prevent gelling by introducing monohydric alcohols to compete with the hydroxyl groups of the polyester prepolymer in the reaction with the isocyanate prepolymer. Monohydric alcohols such as methanol, ethanol, and isopropanol were added in 10.0 ml quantities to a mixture of 8.1 gm Desmodur N-100, 19.6 gm Multron E-380, and 0.02 gm dibutyltin dilaurate catalyst. In all three experiments, gelling did not occur, although the viscosity increased upon standing, indicating that some reaction between the two prepolymers had occurred. Trimethylolpropane trimethacrylate (2.0 gm) was added to each sample, and the resulting mixtures were emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation, and then polymerized in capped bottles at 60°C using persulfate-ion initiator. It was hoped that the sulfate ion-radicals generated by decomposition of the persulfate ion would abstract a hydrogen from both the blocked isocyanate and hydroxyl-terminated polyester prepolymers and initiate a free radical that would then add to the trimethylolpropane trimethacrylate, thus crosslinking the two prepolymers. No evidence of such reaction was found; the polymerization produced lumps of coagulum that were softer than expected had extensive crosslinking occurred (later it was found that polymerization of similar adduct emulsions in capped bottles almost always produced excessive coagulum and that this coagulum could be avoided by continuous addition of the adduct emulsion; however, these observations should not change the conclusions of these experiments).

3. Modification of the Isocyanate Prepolymer-Polyester Prepolymer System

a. Isocyanate Prepolymer-Hydroxyalkyl Methacrylate Adducts

One approach to the preparation of polyurethane emulsion systems is to block the isocyanate groups of the isocyanate prepolymer by reaction with a hydroxyalkyl methacrylate, dissolve the isocyanate prepolymer-hydroxyalkyl methacrylate adduct in a vinyl monomer (reactive diluent), emulsify the adduct solution in water, and copolymerize the vinyl groups of the hydroxyalkyl methacrylate and the reactive diluent to produce a fully-cured polyurethane emulsion.

Several adducts of Desmodur N-100 and hydroxyethyl methacrylate were prepared using dibutyltin dilaurate catalyst and were found to be soluble in various acrylate and methacrylate esters. These solutions were emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation to give stable emulsions. However, emulsion polymerization at 60° C using persulfate-ion initiator produced a single lump of coagulum instead of a fluid, stable latex.

When first observed, this formation of coagulum was attributed to two possible reasons: (1) hydrolysis of the adduct during polymerization and the subsequent reaction of the reformed isocyanate groups with water; (2) coagulation of the polymerizing emulsion droplets at an early stage of polymerization.

The hydrolysis of the urethane linkage during emulsion polymerization was suggested by a report (78) that hydrolysis had been observed in solvent-cast polyurethane films under conditions of high temperature and high humidity. However, no evidence was found that such hydrolysis occurs in these emulsion systems. Moreover, the adducts formed by reaction of the isocyanate prepolymer with excess methanol, ethanol, or isopropanol showed no evidence of hydrolysis under similar conditions.

The more likely reason was the destabilization and coalescence of the emulsion droplets during polymerization. In conventional batch emulsion polymerizations, the stability of the latex during polymerization is often adversely affected by the addition of a difunctional monomer to the monomer mixture, e.g., by adding divinylbenzene to styrene monomer (79). The reason for this destabilization is not well understood, but an increasing sensitivity of the latex to small variations in polymerization conditions (e.g., rate of agitation) and the formation of increasing amounts of coagulum can be correlated with an increasing concentration of the difunctional monomer. In the present work, the Desmodur N-100 molecules are multifunctional in isocyanate groups; therefore, reaction with hydroxyethyl methacrylate gives adducts that are multifunctional in vinyl groups.

Also, the batch emulsion polymerization of acrylate esters often produces substantial amounts of coagulum or coagulated latexes. In these cases, the formation of coagulum can be correlated with the increase in polymerization temperature above the control temperature (79), presumably because of the autoaccelerating polymerization rate of these monomers. The formation of coagulum is often eliminated by the continuous addition of the monomer at a rate equal to or slightly less than the rate of polymerization, thus giving rigorous control of the polymerization temperature. In the present work, the batch emulsion polymerization of the adduct emulsions in capped bottles may have resulted in poor temperature control and the consequent formation of coagulum.

This principle applied to the present work eliminated or substantially reduced the formation of coagulum during polymerization: the continuous addition of the adduct emulsion to a stirred glass polymerization flask gave a fluid, stable latex with little or no coagulum.

The development of the continuous adduct-emulsion addition technique made possible the evaluation of various isocyanate prepolymer-hydroxyalkyl methacrylate adducts. Typically, 8.1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst were mixed with 20-30 gm of a mixture containing varying proportions of hydroxyethyl methacrylate and a reactive diluent (methyl methacrylate, isobutyl methacrylate, butyl acrylate, or acrylonitrile). After 24 hours at room temperature, the adducts were emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation, and the emulsions were polymerized at 60° C using persulfate-ion initiator and a 3-hour emulsion addition time; the total polymerization time was 8 hours.

The films cast from these emulsions displayed varying degrees of hardness, according to the proportion of hydroxyethyl methacrylate and the type and proportion of the reactive diluent. Those emulsions containing more than an equivalent amount of hydroxyethyl methacrylate contained some friable white powder; this was attributed to byproduct polyhydroxyethyl methacrylate formed by polymerization in the aqueous phase (hydroxyethyl methacrylate is soluble in water and is probably distributed between the oil and water phases during polymerization).

Hydroxypropyl methacrylate was substituted for the hydroxyethyl methacrylate to avoid the formation of homopolymer in the aqueous phase (hydroxypropyl methacrylate is not water-soluble). Typically, 8.1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst were mixed with 20 gm of a mixture containing varying proportions of hydroxypropyl methacrylate and reactive diluents (methyl methacrylate or butyl acrylate). Other experiments used 20 gm hydroxypropyl methacrylate alone or a mixture comprised of 5 gm hydroxypropyl methacrylate, 5 gm hydroxyethyl methacrylate, and 12 gm methyl methacrylate. After 24 hours at room temperature, the adducts were emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation, and the emulsions were polymerized at 60° C using the continuous-addition technicque and persulfate-ion initiator. Most polymerizations gave fluid, stable latexes, which upon drying formed opaque, glossy, brittle, non-adherent films.

Table III compares films of different composition, i. e., prepared using hydroxyethyl methacrylate or hydroxypropyl methacrylate, 1-butanol as a monohydric alcohol modifier, and reactive diluents such as butyl acrylate, isobutyl methacrylate, methyl methacrylate, and acrylonitrile. The incorporation of 1-butanol into the adduct improved its compatibility with such flexibilizing monomers as butyl acrylate and isobutyl methacrylate; these adducts appeared to act as plasticizers for the final film (the Desmodur N-100-1-butanol adduct is a clear, very viscous, plasticizer-like material). In addition, the 1-butanol offers a means of controlling the degree of crosslinking in the final film. Films of the Desmodur N-100-hydroxyalkyl methacrylate-1-butanol adducts displayed better properties than those of adducts without the 1-butanol. The use of acrylonitrile as a reactive diluent improved the clarity of the film, but too high a concentration produced a brittle film. The use of methyl methacrylate as a reactive diluent gave similar results. The best properties of this series were obtained with the Desmodur N-100-hydroxypropyl methacrylate-1-butanol adduct prepared using a 50:50 butyl acrylate-isobutyl methacrylate mixture as reactive diluent.

b. Isocyanate Prepolymer-Hydroxyalkyl Methacrylate-Methyl Ricinoleate Adducts

To decrease the vinyl-group multifunctionality of the isocyanate prepolymer-

Table III. Fully-Cured Desmodur N-100-Hydroxyalkyl Methacrylate-1-Butanol Adduct Emulsions

	Adduct (1)			Reactive Diluent (2)				
Experiment	HEMA	HPMA	1-Butanol	nBA	iBMA	MMA	VCN	Film Properties
327	5.0	---	---	18.0	---	---	---	rubbery
339	3.0	---	1.3	8.0	8.0	---	---	slightly rubbery
344	5.0	---	---	16.0	---	---	2.0	slightly "cheesy"
345	5.0	---	---	14.0	---	---	2.0	slightly brittle
346	3.0	---	1.3	16.0	---	---	2.0	slightly "cheesy"
347	3.0	---	1.3	14.0	---	---	4.0	slightly rubbery
350	3.0	---	1.3	10.0	---	6.0	---	slightly rubbery
351	5.0	---	1.3	8.0	---	4.0	4.0	hard, brittle
352	3.0	---	1.3	8.0	---	4.0	4.0	slightly rubbery
353	3.2	---	1.3	12.0	---	---	4.0	"cheesy"
364	---	3.4	1.3	8.0	8.0	---	---	good
366	---	3.4	1.3	6.4	9.6	---	---	good

---

(1) The adducts were prepared by mixing the listed ingredients with 8.1 gm Desmodur N-100 isocyanate prepolymer and 0.25 ml toluene solution containing 0.02 gm dibutyltin dilaurate catalyst and allowing to stand for 48 hours at room temperature (HEMA = hydroxyethyl methacrylate; HPMA = hydroxypropyl methacrylate).

(2) After standing for 48 hours at room temperature, the adducts dissolved in the listed reactive diluent mixtures (nBA = butyl acrylate; iBMA = isobutyl methacrylate; MMA = methyl methacrylate; VCN = acrylonitrile) were emulsified at 60° C using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation; after standing for 24 hours at room temperature, the emulsions were polymerized at 60° C using the continuous addition technique and persulfate-ion initiator.

hydroxyalkyl methacrylate adducts, methyl ricinoleate was substituted for part of the hydroxyalkyl methacrylate. For example, 8.1 gm Desmodur N-100 was mixed with 1.4 gm hydroxyethyl methacrylate (equivalent to 25% of the isocyanate groups) and 0.02 gm dibutyltin dialurate catalyst; the mixture was allowed to stand for 24 hours at room temperature, then 7.6 gm methyl ricinoleate (equivalent to the remaining 75% of the isocyanate groups) was added along with 6.0 gm isobutyl methacrylate as a reactive diluent; a small amount of toluene was also added to reduce the viscosity.

This mixture was emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation to produce an emulsion that remained stable upon standing for one week. This emulsion was then polymerized at 60°C using the continuous-addition technique and persulfate-ion initiator to give a stable latex containing little coagulum; the total polymerization time was 8 hours. When dried at room temperature in an aluminum dish, this latex formed a clear, soft, semi-gloss film that showed good adhesion to the substrate after baking for 16 hours at 60°C. The film was too soft for the topcoat application, but this approach should be investigated further.

c. Isocyanate Prepolymer-Hydroxyalkyl Methacrylate-Polyester Prepolymer Adducts

The methyl ricinoleate in the foregoing experiments was replaced with a polyester prepolymer of lower functionality than the previously-used Multron E-380 (hydroxyl number 105-120). Only 0.5 gm of Multron E-380 was required to gel 8.1 gm Desmodur N-100 isocyanate prepolymer, although the equivalent amount is 19.6 gm. In comparison, 7.0 gm Multron R-16 (hydroxyl number 44) was required to gel the same amount of Desmodur N-100. Also used was Paraplex P-444A unsaturated polyester prepolymer, which is the only commercially-available unsaturated polyester prepolymer that does not contain styrene as the reactive diluent and which is claimed (80) to have "good weathering properties and resistance to discoloration by ultraviolet light."

The first experiments were carried out in bulk to determine the optimum proportions and curing conditions, before attempting to emulsify the adducts in water. For example, 8.1 gm Desmodur N-100 was mixed with 5.0 gm hydroxyethyl methacrylate and 0.02 gm dibutyltin dilaurate catalyst; the mixture was allowed to stand for 24 hours at room temperature, then 15.0 gm Paraplex P-444A was added to give a total of 20.0 gm of ester-containing compounds as compared with the 19.6 gm of Multron E-380 used earlier. This viscous mixture was polymerized for 2 hours at 60°C using 0.5% azobisisobutyronitrile initiator to give a hard, glossy, fairly-tough, light-straw-colored polymer. Although the properties of the polymer were good, the adduct mixture was too viscous to emulsify easily in water.

d. Isocyanate Prepolymer-Glycidol Adducts

The purpose of this work was to prepare a Desmodur N-100-glycidol (2,3-epoxy-1-propanol) adduct by reaction of the isocyanate groups of the prepolymer with the hydroxyl groups of the glycidol, then crosslink a mixture of this adduct and a polyester prepolymer by the polyamide- or polyamine-catalyzed reaction of the oxirane groups of the glycidol with the hydroxyl groups of the polyester prepolymer.

For the first step, Desmodur N-100-glycidol adducts were prepared in 1,4-butanediol diglycidyl ether solution using different proportions of the reactants. Theoretically, 3.5 gm glycidol is equivalent to 8.1 gm Desmodur N-100; however, experimentally, these proportions gel rapidly. The minimum amount of glycidol needed to avoid gelling under these conditions is 6.0 gm, which still gives a very viscous adduct. Larger amounts of glycidol (e.g., 7.0 gm) give lower-viscosity adducts.

The samples containing 6.0 or 7.0 gm glycidol were cured to gels within 3-4 hours by addition of 4 drops ethylene diamine catalyst. However, the corresponding samples in 1,4-butanediol diglycidyl ether solution never hardened, indicating that there was no appreciable reaction between the Desmodur N-100-glycidol adduct and the reactive diluent. Moreover, the formation of the adduct evidently involves side reactions other than the expected reaction between isocyanate groups of the prepolymer and the hydroxyl groups of the glycidol. In any event, this approach was abandoned because of the failure of the compositions to harden.

4. 1,6-Hexamethylene Diisocyanate Derivatives

The work up to this point used the same Desmodur N-100 isocyanate prepolymer used in the present topcoat formulation. The purpose of the following experiments was to prepare adducts from the 1,6-hexamethylene diisocyanate precursor of this isocyanate prepolymer.

a. 1,6-Hexamethylene Diisocyanate-Hydroxyethyl Methacrylate Adducts

In the first experiment, 17.0 gm 1,6-hexamethylene diisocyanate and 26.0 gm hydroxyethyl methacrylate were mixed with 0.02 gm dibutyltin dilaurate catalyst. Upon standing at room temperature for 24 hours, this mixture polymerized to a soft, waxy solid (presumably (2-ethyl methacrylate)-1,6-hexane dicarbamate) that was soluble in hot acrylate and methacrylate esters. This solid (43.0 gm) was dissolved in 25 ml isobutyl methacrylate and allowed to stand at room temperature for 48 hours; then 0.5 gm trimethylolpropane trimethacrylate and 0.5 gm azobisisobutyronitrile initiator were added, and the mixture was polymerized in bulk at 55°C to form a transparent, hard, somewhat-brittle polymer.

A similar preparation in toluene solution followed by precipitation in petroleum ether gave a white powder (presumably the pure adduct). The purpose of the work was to use this adduct as a crosslinking agent (since it contains about 20% isocyanate groups) by dissolving it in various acrylate esters, emulsifying the solutions in water, and polymerizing to form a polymer emulsion. However, the recovered adduct proved to be insoluble in the butyl acrylate and octyl acrylate monomers for which it was intended (monomers which form polymers of low T_g), but could be dissolved at 60°C in 20% concentration in methyl methacrylate or ethyl acrylate and at room temperature in acrylic acid or methacrylic acid. Polymerization of a 20% solution of the adduct in methyl methacrylate-hydroxyethyl methacrylate, methyl methacrylate-methacrylic acid, or ethyl acrylate-methacrylic acid mixtures at 60°C using 0.5% azobisisobutyronitrile initiator gave hard, brittle polymers.

b. 1, 6-Hexamethylene Diisocyanate-Hydroxyethyl Methacrylate-Polypropylene Glycol Adducts

The purpose of this work was to modify the adduct by substituting a flexibilizing polypropylene glycol for part of the hydroxyethyl methacrylate. To give a 1:1 molar ratio of hydroxyl and isocyanate groups, 17.0 gm 1, 6-hexamethylene diisocyanate, 13.0 gm hydroxyethyl methacrylate, and 21.0 gm Polypropylene Glycol 425 were mixed with 0.02 gm dibutyltin dilaurate catalyst. Upon standing for 24 hours at room temperature, this mixture polymerized to form a waxy solid, which, unfortunately, did not dissolve in any of the monomers used as reactive diluents. Therefore, work on this approach was discontinued.

c. 1, 6-Hexamethylene Diisocyanate-Glycidol Adducts

The purpose of this work was to prepare a 1, 6-hexamethylene diisocyanate-glycidol adduct that could be cured using polyamide or polyamine catalysts. In the first experiment, 4.25 gm 1, 6-hexamethylene diisocyanate and 3.70 gm glycidol were mixed with 0.02 gm dibutyltin dilaurate catalyst in 20.0 gm 1, 4-butanediol diglycidyl ether as reactive diluent. The viscosity of the mixture increased slightly, presumably because of the formation of the (2, 3-epoxypropane)-1, 6-hexane carbamate adduct. However, no product could be isolated from the reaction mixture so work on this approach was discontinued.

5. Air-Drying Allyl Alcohol-Containing Systems

a. Substitution of Allyl Alcohol for Hydroxyethyl Methacrylate and Polyester Prepolymers

O'Neill and Brett (81) described the use of allyl alcohol derivatives (i. e., ethers) in the presence of 0.05% cobalt naphthenate catalyst to dry coating films by air oxidation. The chemical reactions of curing were claimed to be analogous but superior to those that take place in the conventional drying-oil films because much less oxygen is required and fewer scission products are produced upon ageing.

These results are not strictly applicable to the present work because the addition of allyl alcohol to the isocyanate group produces a carbamate linkage rather than an allyl ether linkage; however, since the structures are similar, the preparation and evaluation of the isocyanate prepolymer-allyl alcohol adducts were investigated.

A stoichiometric amount of allyl alcohol (2.2 gm) was added to 8.1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst in 5.0 gm methyl methacrylate reactive diluent. The mixture became hot upon stirring (usually the isocyanate prepolymer-hydroxyl compound reaction mixture only becomes warm, indicating that the reaction might have proceeded without addition of catalyst. After 16 hours at room temperature, 12.0 gm Paraplex P-444A unsaturated polyester prepolymer was added to the mixture (the allyl alcohol must be added before the Paraplex P-444A because this unsaturated polyester prepolymer with an acid number of 10 reacts with the isocyanate groups of Desmodur N-100 to release carbon dioxide) along with 0.3 gm 6% cobalt naphthenate (0.05% cobalt based on total organic phase). After 24 hours at room temperature, the mixture cured to a hard, semi-brittle polymer (however, part of the sample which had been poured into a small aluminum dish cured to a flexible film with poor tear strength). The brittleness was attributed to three possible causes: 1. incompleteness of cure resulting in a brittle rather than a tough polymer; 2. the choice of methyl methacrylate as the reactive diluent since polymethyl methacrylate is a hard, brittle polymer with a T_g of 100°C; 3. the choice of the non-flexible Paraplex P-444A as the polyester prepolymer. Table IV summarizes the experiments carried out to distinguish between these possible reasons for the brittleness and to determine the proportions of ingredients needed to produce a tough, flexible film.

To determine if 24 hours at room temperature was sufficient to complete the cure, the proportions of allyl alcohol and hydroxyethyl methacrylate were varied in the preparation of the adduct. The results showed that at least 80% of the isocyanate groups of the Desmodur N-100 must be combined with allyl alcohol to give complete curing in 24 hours at room temperature. Thus, in the foregoing experiment, incompleteness of cure was probably not the cause of the brittle film.

To determine if the choice of methyl methacrylate as the reactive diluent was the cause of the brittleness, butyl acrylate was used in its place: 2.2 gm allyl alcohol was mixed with 8.1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst in 10.0 gm butyl acrylate reactive diluent. After 16 hours at room temperature, 12.0 gm Paraplex P-444A unsaturated polyester prepolymer was added along with 0.05% cobalt drier. Within 24 hours at room temperature, this composition cured to a glossy, semi-brittle film. Brittle films were also obtained in similar experiments using 9.0 gm butyl acrylate, 6.0 gm isobutyl methacrylate, 6.0 gm methyl methacrylate, and 10.0 gm of a 70:30 n-butyl acrylate-styrene mixture, as well as with the 5.0 gm methyl methacrylate reported above. Therefore, the choice of methyl methacrylate as the reactive diluent was not the cause of the brittleness.

To determine if the choice of Paraplex P-444A as the polyester prepolymer was the cause of the brittleness, Multron R-16 hydroxyl-terminated polyester prepolymer was used in its place: 1.2 gm allyl alcohol and 2.5 gm hydroxyethyl methacrylate were mixed with 8,1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst in 6.0 gm isobutyl methacrylate reactive diluent. After 16 hours at room temperature, 7.0 gm Multron R-16 was added along with 0.05% cobalt drier. A film cast from this mixture cured slowly in air to give a glossy film that was still flexible after 10 days. A similar experiment combining 3.5 gm Multron R-16 and 6.0 gm Paraplex P-444A also gave a flexible, tough film. Other experiments using varying proportions of the ingredients, but omitting the Paraplex P-444A, cured very slowly or not at all. Therefore, the choice of Paraplex P-444A as the sole polyester prepolymer was the cause of the brittleness; this brittleness can be ameliorated by substituting Multron R-16 for part of Paraplex P-444A; replacing all of the Paraplex P-444A by Multron R-16 slows the rate of cure significantly.

Table IV. Desmodur N-100-Hydroxyethyl Methacrylate-Allyl Alcohol-Multron R-16 Adducts
(polymerized in bulk using 0.05% cobalt drier)

	Adduct (1)			Reactive Diluent or Polyester Prepolymer (2)					
Experiment	HEMA	AA	R-16	nBA	iBMA	MMA	S	P-444A	Film Properties (3)
165	---	2.2	---	---	---	6.0	---	12.0	hard, brittle
170	1.5	1.2	7.0	---	6.0	---	---	---	flexible, tough
171	2.5	1.2	---	---	6.0	---	---	12.0	brittle
172	---	2.2	---	---	6.0	---	---	12.0	brittle
176 (4)	---	2.2	---	9.0	---	---	---	12.0	brittle, high gloss
181	---	2.2	---	7.0	---	---	3.0	12.0	brittle
187	1.0	1.8	---	7.0	---	---	---	12.0	hard, brittle
190	0.8	1.7	3.5	---	3.0	4.0	1.5	6.0	flexible, tough
191	2.5	1.1	---	---	9.0	---	---	---	did not cure
195	1.5	1.4	7.0	5.0	---	3.0	3.0	---	did not cure
201	1.4	1.3	5.0	---	9.0	4.0	---	---	did not cure
202	1.5	1.3	7.0	---	5.0	4.0	---	---	did not cure
203	1.5	1.3	7.0	5.0	---	4.0	---	---	cures in one week
204	---	2.0	2.0	7.0	---	---	---	10.0	cures in one week
205	---	2.0	3.0	7.0	---	---	---	10.0	brittle
209	---	2.0	2.0	9.0	---	---	---	10.0	brittle

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(1) The adducts were prepared by mixing the listed ingredients with 8.1 gm Desmodur N-100 isocyanate prepolymer and 0.25 ml toluene solution containing 0.02 gm dibutyltin dilaurate catalyst and allowing to stand for 48 hours at room temperature (HEMA = hydroxyethyl methacrylate; AA = allyl alcohol; R-16 = Multron R-16 polyester prepolymer.

(2) After standing for 48 hours at room temperature, the adducts were mixed with the listed ingredients (nBA = butyl acrylate; iBMA = isobutyl methacrylate; MMA = methyl methacrylate; S = styrene; P-444A = Paraplex P-444A unsaturated polyester prepolymer).

(3) The adduct-reactive diluent-polyester prepolymer mixtures were cured overnight in air at room temperature using 0.05% cobalt naphthenate catalyst.

(4) After standing for 48 hours at room temperature, the adduct-reactive diluent-polyester prepolymer mixture was emulsified in water with 0.05% cobalt naphthenate catalyst using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation; the emulsion dried to form a continuous film that became a hard, brittle, glossy film within 48 hours.

b. Methyl Ethyl Ketone Peroxide-Cobalt Naphthenate Curing Agent

The methyl ethyl ketone peroxide-cobalt naphthenate combination is often used to cure unsaturated polyester prepolymers. To evaluate this combination as a curing agent for the adducts prepared in this work, various polymer compositions were prepared and polymerized in bulk. The isocyanate groups of Desmodur N-100 isocyanate prepolymer were reacted with hydroxyethyl methacrylate, hydroxypropyl methacrylate, or a mixture of the two, followed by Paraplex P-444A unsaturated polyester prepolymer. Butyl acrylate, isobutyl methacrylate, or a mixture of the two, was used as the reactive diluent. Typically, 5.5 gm hydroxyethyl methacrylate was added to 8.1 gm Desmodur N-100 and 0.02 gm dibutyltin dilaurate catalyst, followed by 12.0 gm Paraplex P-444A in 10.0 gm butyl acrylate, along with 0.1 gm 60% methyl ethyl ketone peroxide in dimethyl phthalate and 0.1 gm 6% cobalt naphthenate emulsion as curing agent. These compositions were polymerized in bulk at room temperature. The gel times of these compositions can be varied somewhat by varying the amount of curing agent, but the variation is sensitive and difficult to control.

A preliminary evaluation of these bulk polymers showed that those prepared with isobutyl methacrylate alone or isobutyl methacrylate-butyl acrylate mixtures could be cracked when struck with a hammer, while those prepared with butyl acrylate alone could not be cracked when struck. The polymer prepared with isobutyl methacrylate alone had the highest gloss and was the most brittle; that prepared with butyl acrylate alone had the lowest gloss and was the least brittle (although films cast from this composition were glossy and fairly tough). These results are consistent with the properties of the respective homopolymers: polybutyl acrylate is a rubbery polymer with a T_g of -40° C, while polyisobutyl methacrylate is a semi-rigid polymer with a T_g of 50°C.

To further evaluate this methyl ethyl ketone-peroxide-cobalt naphthenate combination, various adducts were prepared, emulsified, and cured. Desmodur N-100 adducts of varying composition were prepared using dibutyltin dilaurate catalyst and allowed to stand for 48 hours at room temperature. These adducts were then emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation. Methyl ethyl ketone peroxide was added in 1% concentration based on organic phase, and 100 drops of each emulsion were placed in a small aluminum dish. Varying amounts (1-10 drops) of a 6% cobalt naphthenate emulsion were stirred into the adduct emulsion, and the mixture was allowed to stand for 16 hours at room temperature. The amounts of cobalt naphthenate were adjusted to give both undercured and overcured films. Most of the adducts air-dried within 16 hours to form tack-free films, provided an adequate amount of cobalt naphthenate was used. About 0.05% cobalt based on total organic phase (8 drops of 6% emulsion) was found to be optimum; lower concentrations gave films that did not cure; higher concentrations cured the films but did not affect the film properties adversely.

Table V lists the compositions used in this study. Most of the cured films could be easily removed from the aluminum dish; none of them were tough, and some were friable. Some films displayed excellent gloss, particularly those prepared from the Desmodur N-100-hydroxyethyl methacrylate adducts. Most of these compositions

Table V. Air-Drying Adduct Emulsion Systems

Experiment	Adduct (1)					Reactive Diluent or Polyester Prepolymer (2)			
	HEMA	HPMA	AA	MeOH	R-16	nBA	iBMA	DEF	P-444A
243	---	11.0	---	---	4.0	16.0	---	---	10.0
250	10.0	---	---	---	---	16.0	---	---	20.0
251	10.0	---	---	---	---	16.0	---	---	24.0
252	---	11.0	---	---	---	16.0	---	---	20.0
263	10.0	---	---	---	---	16.0	---	---	20.0
264	---	11.0	---	---	---	16.0	---	---	20.0
267	10.0	---	---	---	---	16.0	---	---	14.0
271	---	11.0	---	---	---	24.0	---	---	---
272	8.0	---	---	0.8	---	24.0	---	---	---
273	6.0	---	---	0.8	---	24.0	---	---	---
276	---	---	4.4	---	---	16.0	---	---	24.0
278	---	---	2.2	---	5.0	26.0	---	---	---
308	10.0	---	2.2	---	---	20.0	---	---	---
309	---	5.5	2.2	---	---	20.0	---	---	---
312A	3.5	---	2.4	---	10.0	20.0	14.0	14.0	---
312B	3.5	---	2.4	---	10.0	---	16.0	14.0	---
313	4.0	---	2.7	---	10.0	20.0	---	---	---
316	---	---	4.4	---	---	---	---	20.0	20.0
321	6.0	---	1.8	---	---	16.0	---	6.0	---

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(1) The adducts were prepared by mixing the listed ingredients with 16.2 gm Desmodur N-100 isocyanate prepolymer and 0.50 ml toluene solution containing 0.04 gm dibutyltin dilaurate and allowing the mixture to stand for 48 hours at room temperature (HEMA = hydroxyethyl methacrylate; HPMA = hydroxypropyl methacrylate; AA = allyl alcohol; MeOH = methanol; R-16 = Multron R-16 polyester prepolymer).

(2) The reactive diluents and polyester prepolymer were added after the adduct had cured for 24 hours (nBA = butyl acrylate; iBMA = isobutyl methacrylate; DEF = diethyl fumarate; P-444A = Paraplex P-444A unsaturated polyester prepolymer).

(3) The adduct-reactive diluent-polyester prepolymer mixtures along with 1% methyl ethyl ketone peroxide based on organic phase were emulsified using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation; 0.05% cobalt (as a 6% cobalt naphthenate emulsion) was added to the emulsions in aluminum dishes, and the mixture was allowed to dry for 16 hours at room temperature.

used butyl acrylate as the reactive diluent; since this monomer has a boiling point of about 150° C, it must be regarded as relatively volatile and, therefore, the gelling must be accomplished within 12 hours to avoid undue losses by evaporation. The less-volatile diethyl fumarate (see next section) can be used in its place, but not 2-ethylhexyl acrylate because it is not compatible with these adducts.

c. Fumarate Esters as Reactive Diluents

Unsaturated polyester prepolymers often contain as the unsaturated acid component esters of maleic acid or maleic-fumaric acid mixtures. These unsaturated acid esters (e.g., diethyl maleate or diethyl fumarate) do not homopolymerize readily, but do copolymerize with various other monomers (the fumarate esters more readily than the maleate esters). One class of monomers that do copolymerize readily with maleate and fumarate esters is the allyl ethers (82), which also do not homopolymerize readily.

The isocyanate prepolymer-allyl alcohol adducts prepared in this work contain the allyl carbamate linkage, which does not necessarily have the same reactivity in copolymerization as a vinyl ether. Experimentally, an adduct prepared from the stoichiometric amounts of allyl alcohol (2.2 gm) and Desmodur N-100 (8.1 gm) in 10.0 gm diethyl fumarate reactive diluent using 0.02 gm dibutyltin dilaurate catalyst and mixed with 0.1 gm 60% methyl ethyl ketone peroxide in dimethyl phthalate and 0.1 gm 6% cobalt naphthenate showed no signs of curing after several days at room temperature. In comparison, the corresponding adduct prepared by substituting 1.8 gm allyl alcohol and 5.0 gm Multron R-16 polyester prepolymer for the 2.2 gm allyl alcohol used previously cured to a tough, flexible solid in 24 hours at room temperature. However, when this adduct was emulsified using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation, and then cured with the methyl ethyl ketone peroxide-cobalt naphthenate combination, the film properties were poor.

Thus, diethyl fumarate can be considered as a non-volatile reactive diluent (its boiling point is 220° C). However, more work is needed to optimize its proportions in the isocyanate prepolymer-allyl alcohol-Multron R-16 adduct mixtures.

d. Discussion of the Air-Drying Isocyanate Prepolymer-Allyl Alcohol Adduct Systems

In this work, two curing systems have been used with two different types of adducts:

1. Cobalt naphthenate was used to cure the Desmodur N-100 isocyanate prepolymer-allyl alcohol adducts (these adducts contain allyl carbamate groups, which behave similarly to allyl ether groups in promoting the same type of air-drying displayed by drying oils);
2. The methyl ethyl ketone peroxide-cobalt naphthenate combination was used to cure the unsaturated polyester component of the adducts (this system can be used to cure any adduct that contains a substantial proportion of double bonds, e.g., an adduct in which most of the isocyanate groups of Desmodur N-100 are reacted with a hydroxyalkyl methacrylate).

The Desmodur N-100 isocyanate prepolymer and its products formed upon curing are inherently brittle because of the high isocyanate content of the prepolymer. In the presently-used topcoat system, flexibility is imparted to the film by the Multron E-380 polyester prepolymer normally used in combination with the Desmodur N-100. However, Multron E-380 contains 25% ethoxyethyl acetate non-reactive thinner which acts as a plasticizer and, hence, is unsuitable as an ingredient of a water-based system unless this thinner is removed. Therefore, in developing a water-based analog of the presently-used topcoat system, either Multron E-380 or its substitute must impart the flexibility to obtain a tough, flexible film.

The only air-drying allyl alcohol-containing transparent, tough, flexible film prepared to date contained Multron R-16 low-hydroxyl-number polyester prepolymer. A less-than-stoichiometric amount of allyl alcohol (1.2 gm; equivalent to 55% of the isocyanate groups) and 1.5 gm hydroxyethyl methacrylate were added to 8.1 gm Desmodur N-100 along with 6.0 gm isobutyl methacrylate reactive diluent and 0.02 gm dibutyltin dilaurate catalyst. After 16 hours at room temperature, 7.0 gm Multron R-16 was added along with 0.3 gm 6% cobalt naphthenate. Within 24 hours at room temperature, this composition cured to form a transparent, tough, flexible film. Unfortunately, however, this proportion of Multron R-16 increased the viscosity of the composition to such a level that it could not be emulsified. Dilution of the mixture with more isobutyl methacrylate resulted in separation into two phases. Further dilution with a methyl methacrylate solution in toluene gave a lower-viscosity solution that separated into two phases upon emulsification.

Another air-drying allyl alcohol-containing composition (Experiment 176, Table V) which could be emulsified without difficulty, and which formed a transparent, flexible film, unfortunately, embrittled upon ageing. A stoichiometric amount of allyl alcohol (2.2 gm) was added to 8.1 gm Desmodur N-100 along with 10.0 gm butyl acrylate reactive diluent and 0.02 gm dibutyltin dilaurate catalyst. After 16 hours at room temperature, 12.0 gm Paraplex P-444A unsaturated polyester prepolymer was added. This adduct was emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and ultrasonic irradiation to give an emulsion, which upon addition of a cobalt naphthenate emulsion (0.05% cobalt based on total organic phase) dried to form a glossy, flexible film that embrittled upon ageing for two weeks at room temperature. The embrittlement was attributed speculatively to two possible causes: (1) too high a proportion of allyl alcohol in the adduct, which would give excessive crosslinking upon air-drying; (2) the choice of the non-flexible unsaturated Paraplex P-444A as the polyester prepolymer (because of its good weatherability).

Thus, this approach to develop an air-drying allyl alcohol-containing composition must combine the good ageing properties of the Multron R-16 with the easy emulsification and good weatherability of the Paraplex P-444A.

6. One-Quart Polyurethane Emulsion Samples for Evaluation

Two variations of the fully-cured Desmodur N-100-hydroxypropyl methacrylate-1-butanol system were selected for the one-quart samples to be submitted to the Air Force Materials Laboratory for evaluation. The variations are given in Table VI.

Table VI. Fully-Cured Desmodur N-100-Hydroxypropyl Methacrylate-1-Butanol Adducts

	Experiment X364		Experiment X366	
	gm	gm (1)	gm	gm (1)
Desmodur N-100	97.0	8.1	97.0	8.1
hydroxypropyl methacrylate	40.8	3.4	40.8	3.4
1-butanol	15.6	1.3	15.6	1.3
butyl acrylate	108.0	9.0	86.0	7.2
isobutyl methacrylate	108.0	9.0	130.0	10.9
dibutyltin dilaurate	0.25	0.02	0.25	0.02

(1) equivalent standard laboratory recipe

The foregoing mixtures were prepared and allowed to stand for one week at room temperature before emulsification (similar adducts were allowed to stand for 2-30 days before emulsification without apparent effect). Then, 250 gm of the adduct was emulsified at 60°C in 750 gm deionized water containing 4.0-8.0 gm of the sodium lauryl sulfate-cetyl alcohol combination by simple stirring to form a crude emulsion; this crude emulsion was passed through the Manton-Gaulin Homogenizer and Submicron Disperser twice to form a stable emulsion of very small droplet size.

The polymerizations were carried out in a stirred 3-liter 4-neck flask under nitrogen atmosphere. Deionized water (600 gm) containing 4.0-8.0 gm of the sodium lauryl sulfate-cetyl alcohol combination and 2.5 gm sodium bicarbonate was added to the flask, and the solution was heated to 60°C. The emulsion (900 gm) was added continuously to the flask over a 5-hour period. During this period, four equal increments of the potassium persulfate initiator (2.5 gm total) were added in aqueous solution, in the beginning and every 100 minutes thereafter. The polymerization was continued for 5 hours after the emulsion addition was complete. The latexes produced were fluid and stable, with solids contents of about 15%.

These dilute latexes, which displayed a noticeable monomer odor, were concentrated by evaporation of water at 50°C and 50mm Hg vacuum in the Buchler Flash Evaporator to a solids contents of about 25%. The concentrated latexes were slightly more viscous than the original latexes, but displayed no monomer odor.

The less-flexible Experiment X366 emulsion was examined by transmission electron microscopy in a manner similar to that used for the epoxy resin emulsions. However, the polyurethane emulsion particles though soft are fully-cured and do not respond to hardening by aqueous amines, bromine, or osmium tetroxide. Therefore, to prevent the deformation of these particles upon drying, a diluted drop of emulsion on a specimen substrate was freeze-dried and placed on the cold stage in the vacuum chamber of the microscope; the water was removed from the specimen by sublimation, and the particles were examined. Figure 37 shows that the particles have deformed only negligibly and that their sizes are in the range 0.03-0.4μ, attesting to the efficacy of the emulsification technique. It should be emphasized, however, that in this case not all of the particle need necessarily have been formed by emulsification; there may have been some nucleation of butyl acrylate-isobutyl methacrylate copolymer particles in the aqueous phase during the persulfate-initiated polymerization. However, this is judged to be minor because of the low solubility in water of butyl acrylate and isobutyl methacrylate.

At the same time, the modulus-temperature variation was determined for a film of the more-flexible Experiment X364 emulsion that had been dried and aged at room temperature. Figure 38 shows the variation of log-modulus with temperature (83). By comparison with the results for films of the epoxy emulsion systems (Figures 35 and 36), the log modulus-temperature variation for this polyurethane emulsion film was typical of a flexible coating film with "guts." Moreover, the curve shows that the curing of the film was complete. Also, it is of interest that the damping was high over a broad range of temperatures, typical of the behavior of a sound-deadening coating (84).

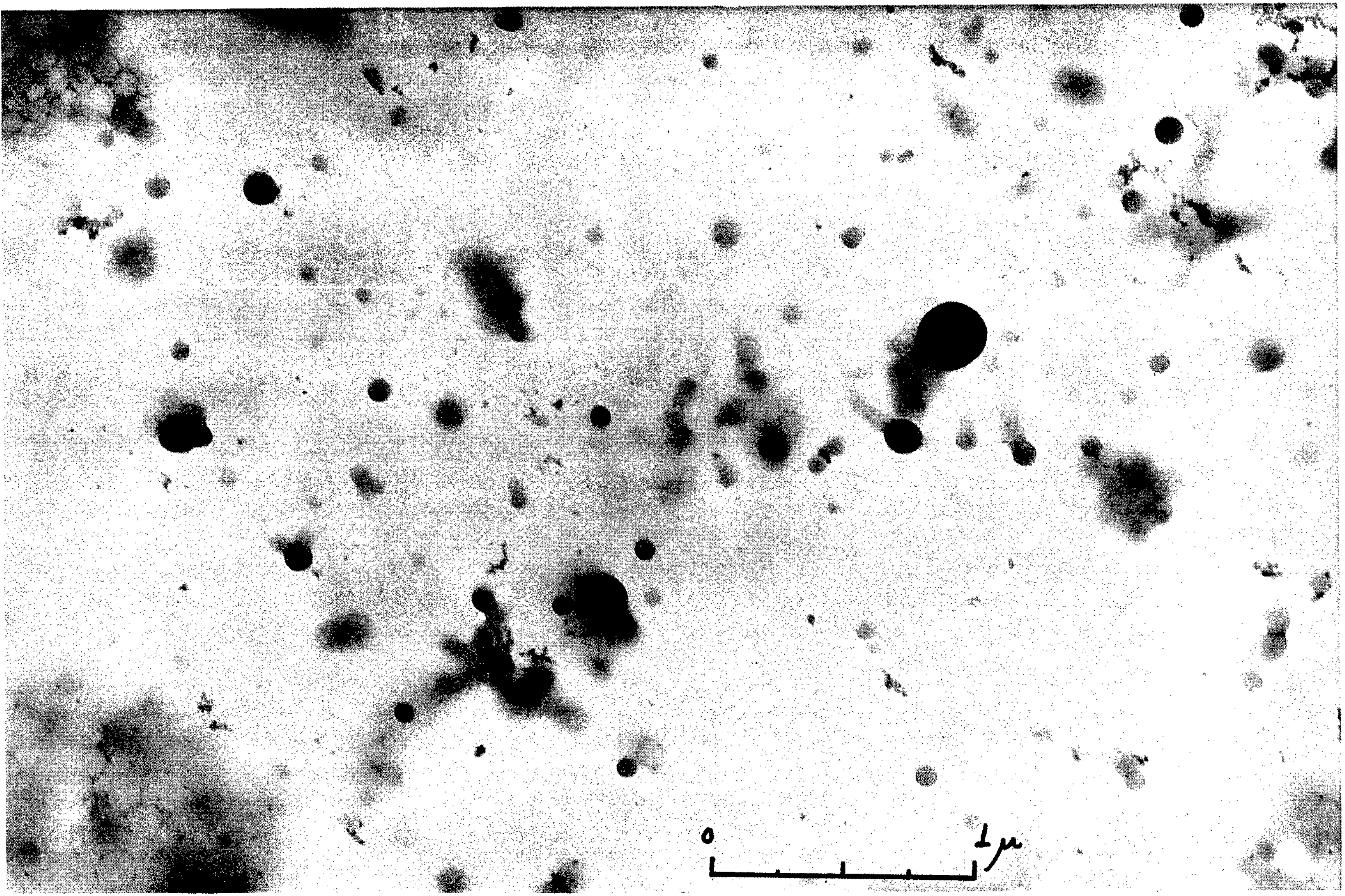

Figure 37. Electron micrograph of a dispersion of Experiment X366 polyurethane emulsion freeze-dried on a cold stage in the electron microscope.

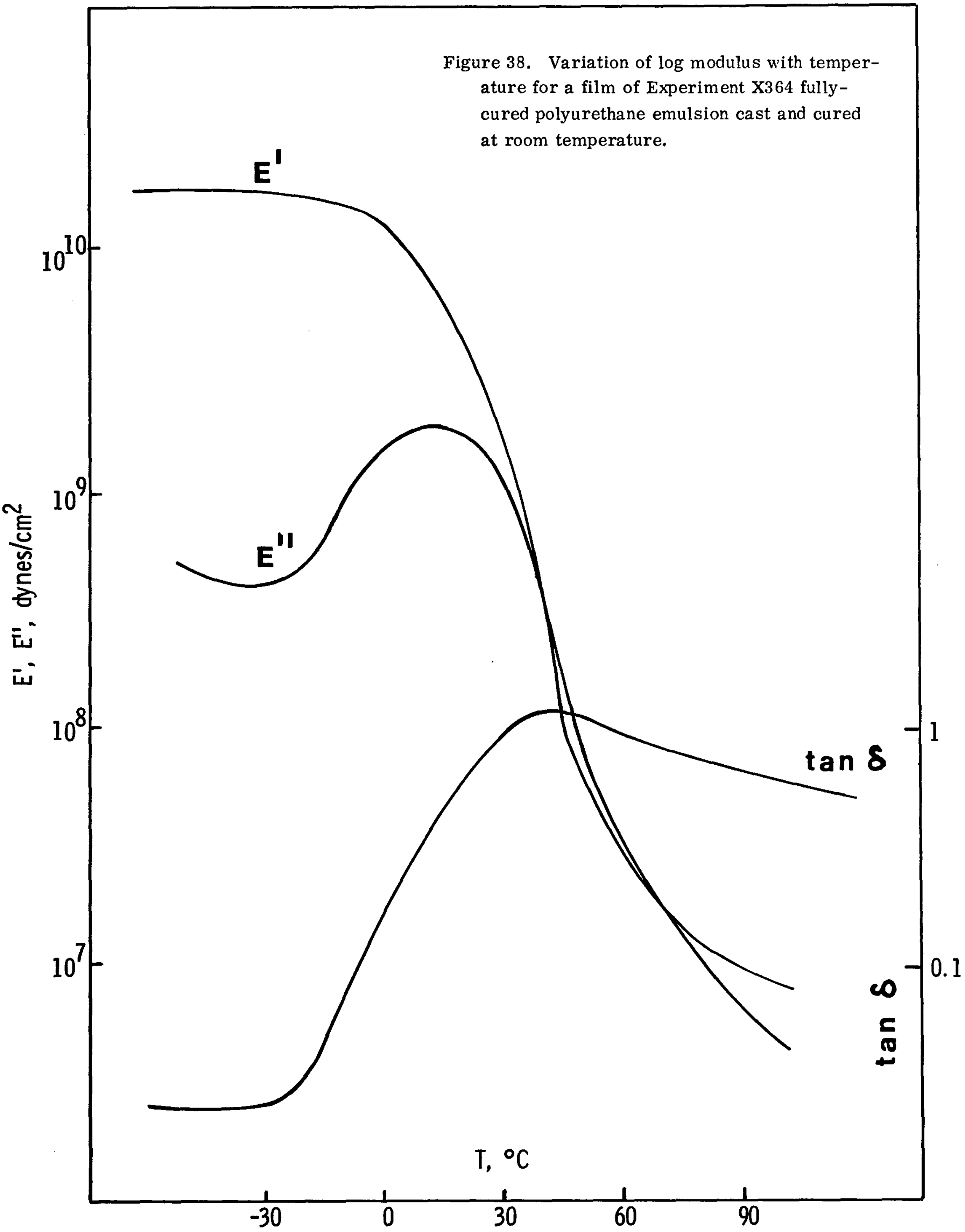

Figure 38. Variation of log modulus with temperature for a film of Experiment X364 fully-cured polyurethane emulsion cast and cured at room temperature.

SECTION VI

CONCLUSIONS

A. Epoxy Emulsion Systems

1. Epoxy Resin Emulsions

a. Stable cationic or anionic emulsions of Epon 828 or Epon 1001 with droplet sizes of about 0.2μ (optical microscopy) can be prepared using the cationic or anionic mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization.

b. The efficiency of emulsification can be increased by using lower-concentration epoxy resin solutions (e.g., 25% instead of 50%) and lower oil-water ratios (e.g., 25:75 instead of 50:50).

c. The recipe for the preparation of cationic 50:50 Epon resin-solvent mixtures should contain at least 1 gm of the 0.33-0.67 hexadecyltrimethylammonium bromide-cetyl alcohol combination for each 25 gm of the Epon resin-solvent mixture.

d. Vacuum steam distillation can be used to remove the solvents and concentrate these Epon resin emulsions to stable high-solids emulsions.

e. The particle-size distribution of the Epon resin emulsions can be determined by transmission electron microscopy after the resin particles have been hardened in the emulsion state using a water-soluble amine catalyst (e.g., the particles of an Epon 1001 emulsion were shown to be in the range 0.03-0.3μ).

2. Curing Agent Emulsions

a. Stable cationic emulsions of Versamid 115 with droplet sizes of 0.2μ (optical microscopy) can be prepared using the cationic mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization; the anionic emulsifications form paste-like coagulum, presumably because of the interaction between the positive Versamid 115 and the negative sodium lauryl sulfate.

b. Vacuum steam distillation can be used to remove the solvents and concentrate these cationic Versamid 115 emulsions; however, the emulsions become viscous and translucent at low solids, but upon standing for 4-6 weeks, revert to the opaque, low-viscosity form; the first transformation is attributed to a spontaneous decrease in particle size and the second, to a spontaneous increase.

c. Stable, paste-like cationic or anionic emulsions of Genamid 250 can be prepared using the cationic or anionic mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization.

3. Epoxy Resin-Curing Agent Films

a. Hard, transparent films were formed when the mixed epoxy resin-curing agent emulsions were dried at room temperature or at 50°C, indicating that coalescence of the two different types of particles had occurred.

b. About 30 days curing at room temperature is required to give the same properties obtained by curing for a few hours at 50°C.

c. The best properties were obtained with the 2:1 Epon 1001-Versamid 115, 2:1 Epon 1001-Genamid 250, and 1:2 Epon 828-Versamid 115 ratios.

d. The log modulus-temperature variation of the cured epoxy resin-curing agent film offers a means to characterize the morphology of the film, the nature of the three-dimensional polymer network, and the extent of cure.

B. Polyurethane Emulsion Systems

1. General

a. To prepare a water-based analog of the present Desmodur N-100-Multron E-380 system, the isocyanate groups of the Desmodur N-100 must be pre-reacted before emulsification because they react readily with water.

b. The isocyanate groups of Desmodur N-100 can be reacted with hydroxyl groups of monohydric alcohol modifiers, hydroxyalkyl methacrylate monomers, allyl alcohol derivatives, and hydroxyl-terminated polyester prepolymers, using dibutyltin dilaurate catalyst.

c. Since it is the Multron E-380 rather than the Desmodur N-100 that imparts the required flexibility to the present system, the compounds reacted with the isocyanate groups must fulfill this function, e.g., 1-butanol and Multron R-16 improve the flexibility while other compounds do not.

d. The Desmodur N-100 adducts can be emulsified in water using the sodium lauryl sulfate-cetyl alcohol combination and simple stirring, followed by ultrasonic irradiation or homogenization, to give stable emulsions with droplet sizes of about 0.2μ (optical microscopy).

e. Stable anionic emulsions of two different types can be prepared: 1. fully-cured systems; 2. air-drying systems.

2. Fully-Cured Polyurethane Emulsion Systems

a. Fully-cured polyurethane emulsions can be prepared by reacting Desmodur N-100 with a hydroxypropyl methacrylate-1-butanol mixture in butyl acrylate-isobutyl methacrylate reactive diluent mixture using dibutyltin dilaurate catalyst; these adducts can then be emulsified in water and polymerized using persulfate-ion initiator to form stable emulsions.

b. In the persulfate-initiated polymerization, the emulsion must be added continuously to the polymerization vessel; batch polymerization produces excessive coagulum.

c. The particle size of these fully-cured emulsions can be determined by transmission electron microscopy using the cold stage to prevent deformation of the particles; typically, the particle sizes are in the range 0.03-0.4μ.

d. In the best cases, these fully-cured polyurethane emulsions can be dried to form glossy, flexible, tough films; the log modulus-temperature variation is typical of flexible coating films and, moreover, indicates damping over a broad temperature range, typical of a sound-deadening coating.

3. Air-Drying Polyurethane Emulsion Systems

a. Air-drying polyurethane emulsions can be prepared by reacting Desmodur N-100 with allyl alcohol, often in combination with a hydroxyalkyl methacrylate, using dibutyltin dilaurate catalyst, followed by a polyester prepolymer (e.g., Multron R-16 or Paraplex P-444A); these adducts can then be emulsified in water to form stable emulsions that with cobalt naphthenate catalyst cure overnight to form a glossy, tough, flexible film.

b. Using Multron R-16 as the polyester prepolymer gives glossy, tough, flexible films that age well; however, the viscosities of the adducts are too great for easy emulsification, and alterations in the recipe to lower the viscosities give incompatible products.

c. Using Paraplex P-444A as the polyester prepolymer gives adducts of low-enough viscosity for easy emulsification, but the films, although initially tough and flexible, deteriorate rapidly upon ageing.

d. The best properties are obtained using a mixture of Multron R-16 and Paraplex P-444A.

e. Compositions containing Paraplex P-444A unsaturated polyester prepolymer (or vinyl groups from other compounds) can be cured at room temperature using the methyl ethyl ketone peroxide-cobalt naphthenate combination.

4. Desmodur N-100-Glycidol Adducts

a. Adducts of Desmodur N-100 and glycidol can be prepared without catalyst, often in combination with monohydric alcohols, hydroxyalkyl methacrylates, and acrylate or methacrylate esters; however, thus far the film properties have not been good enough for the application.

5. 1,6-Hexamethylene Diisocyanate Adducts

a. Adducts can be prepared by substituting for Desmodur N-100 its precursor 1,6-hexamethylene diisocyanate, often in combination with monohydric alcohols, hydroxyalkyl methacrylates, and acrylate or methacrylate esters, using dibutyltin dilaurate catalyst; however, thus far the film properties have not been good enough for the application.

SECTION VII

RECOMMENDATIONS FOR FUTURE WORK

A. Epoxy Emulsion Systems

The approach used in this work was to prepare separate emulsions of the epoxy resin and curing agent prepolymers, mix these emulsions in the appropriate proportions, and cast a film from the mixture. In most cases, solvents were used to reduce the viscosity to a suitable level for emulsification using the mixed emulsifier combination. After emulsification, these solvents were removed by vacuum steam distillation, and the emulsions were concentrated to the desired solids content.

The emulsification of both the epoxy resin and curing agent prepolymers to submicroscopic droplet sizes of about 0.2μ can be accomplished routinely using the mixed emulsifier combination and simple stirring, followed by ultrasonic irradiation or homogenization. Both anionic and cationic emulsions of Epon 1001 and Epon 828 epoxy resins can be prepared, but only cationic emulsions of Versamid 115 and Component II curing agents (because of their positive charge); anionic, cationic, or nonionic emulsions of Genamid 250 curing agent can be prepared.

The best film properties are 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 rate of cure of these systems at room temperature is too slow -- about 30 days is required to obtain properties equivalent to those obtained in a few hours at 50°C.

Therefore, the recommendations for future work are as follows:

1. Investigation of the effect of temperature on the emulsification --- Thus far, the emulsifications have been carried out at 63°C, and the effect of higher temperatures has not yet been investigated; since the viscosity of the prepolymer solutions decreases with increasing temperature, an increase in the emulsification temperature would allow the emulsification of higher-solids solutions.

2. Determination of the mechanical properties of the cured films --- The preliminary measurements of the log modulus-temperature variation demonstrate the value of this technique in characterizing a cured epoxy emulsion system as to its morphology, degree of crosslinking, and extent of cure, and comparing it with standard solvent-based systems.

3. Determination of the rate of cure of different systems using torsional braid analysis --- Thus far, the rate of cure has been determined only by empirical measurements and visual observations; to increase the rate of cure at room temperature requires the ability to measure this rate; this can be done by torsional braid analysis, in which the mechanical properties of a thin coating film deposited on a braided glass rope are measured as a function of time during the curing process.

4. Modification of the present system and investigation of other curing agents --- Other curing agents should be tried to increase the rate of cure at room temperature yet retain the film properties of the Epon 1001-Versamid 115 system; one type is the polysulfides, which should yield varying degrees of flexibility, perhaps to the extent that a lower-molecular-weight epoxy resin could be substituted for the Epon 1001; another approach is to use a partially-cured epoxy resin emulsion to decrease the extent of cure required after drying; a third approach is to introduce fully-cured latex particles, e.g., cationic polystyrene latex particles, which have already been shown to cure epoxy resin emulsions.

5. Evaluation of the various epoxy resin-curing agent emulsion systems according to MIL-P-23377C and selection of the most suitable composition for the aircraft primer application.

B. Polyurethane Emulsion Systems

The direct emulsification approach used successfully with the epoxy emulsion systems does not work with the polyurethane emulsion systems because the isocyanate groups of the prepolymer react with water. Therefore, it is necessary to pre-react these isocyanate groups before emulsification. Many approaches to do this have been tried; of these, two show promise:

1. the fully-cured isocyanate prepolymer-hydroxyalkyl methacrylate-acrylate or methacrylate ester adduct.

2. the air-drying isocyanate prepolymer-allyl alcohol-hydroxyalkyl methacrylate-polyester-acrylate or methacrylate ester adduct.

For the first approach, the isocyanate prepolymer-hydroxyalkyl methacrylate adduct is prepared in an acrylate or methacrylate ester reactive diluent using dibutyltin dilaurate catalyst, emulsified in water using the anionic mixed emulsifier combination, and polymerized using persulfate-ion initiator, to form a fully-cured polyurethane emulsion. In the best cases, these emulsions form glossy, tough, slightly hazy films upon drying. However, the emulsions tend to flocculate during polymerization, although this can be avoided by continuous addition of the emulsion. Moreover, the film properties and morphology are sensitive to the proportions of reactants and the method of preparation.

The recommendations for future work with this first approach are as follows:

1. Optimization of the proportions of reactants and the method of preparation to avoid flocculation during polymerization and obtain the desired film properties.

2. Determination of the mechanical properties and morphology of the dried films by measurement of the log modulus-temperature variation and correlation with the proportions of reactants and method of preparation.

3. Evaluation of the various polyurethane emulsion systems according to MIL-C-83286A and selection of the most suitable composition for the aircraft topcoat application.

For the second approach, the isocyanate prepolymer-allyl alcohol-hydroxyalkyl methacrylate adduct is prepared in an acrylate or methacrylate ester reactive diluent using dibutyltin dilaurate catalyst, mixed with a polyester prepolymer and emulsified using the anionic mixed emulsifier combination and ultrasonic irradiation or homogenization, to form an air-drying emulsion that air-dries upon addition of the methyl ethyl ketone peroxide-cobalt naphthenate catalyst mixture to form a fully-cured film.

The use of Multron R-16 as the polyester prepolymer gives films of good properties that age well, but the viscosity of the adducts is too great for easy emulsification, and the efforts to lower the viscosity give either incompatible products or poorer film properties. In comparison, the use of Paraplex P-444A as the polyester prepolymer gives adducts that emulsify easily, but the initially-good film properties deteriorate rapidly upon ageing.

The recommendations for future work with this second approach are as follows:

1. Optimization of the method of preparation and the proportions of reactants, particularly the polyester prepolymer, to combine the desired film properties with satisfactory rates of air-drying.
2. Measurement of the rate of cure of different variations using torsional braid analysis and correlation of this rate with the proportions of reactants and the method of preparation.
3. Determination of the mechanical properties and morphology of the cured films by measurement of the log modulus-temperature variation and correlation with the rate of cure, proportions of reactants, and method of preparation.
4. Investigation of other adduct types, e.g., isocyanate prepolymer-aldol adducts, the aldehyde groups of which could react with other monomers or prepolymers.
5. Evaluation of the various air-drying polyurethane emulsion systems according to MIL-C-83286A and selection of the most suitable composition for the aircraft topcoat application.

C. Silicone Emulsion Systems

Thus far, this work has concerned only the epoxy resin and polyurethane emulsion systems. Recently, however, the Air Force Materials Laboratory has expressed interest in considering silicone emulsion systems for the aircraft primer and topcoat applications.

Both anionic and cationic dispersions of polysiloxanes can be prepared from hydroxyl-terminated lower-molecular-weight siloxanes under acidic or alkaline conditions by a process analogous to emulsion polymerization (38, 39, 41, 85). The alkaline catalyst is preferred: its concentration is used to control the molecular weight of the polysiloxane. These aqueous dispersions of polysiloxanes dry to form soft continuous films. It has not yet been determined if these films have properties suitable for the aircraft primer and topcoat applications, but it has been suggested (86) that their modulus is too low for these applications.

Another class of silicone-containing coating vehicles is the reaction products of silicones and conventional coating vehicles, e.g., a silicone-alkyd adduct that air-dries to form a superior coating film (86). These adducts are prepared in organic solvents and are not available as water-based emulsions or dispersions; however, they should be amenable to emulsification using the mixed emulsifier combination in the same manner as the epoxy and polyurethane emulsion systems.

The recommendations to initiate work on the silicone emulsion systems are as follows:

1. Determination of the feasibility of using silicone-containing resins for the aircraft primer and topcoat applications by surveying the literature.

2. Evaluation of the aqueous polysiloxane dispersions for their suitability for the aircraft primer and topcoat applications.

3. Preparation of silicone-alkyd resin adducts and their emulsification in water using the mixed emulsifier combination, followed by evaluation of the emulsions for the aircraft primer and topcoat application.

4. Preparation, emulsification, and evaluation of other adducts of silicones and conventional coating vehicles as suggested by the literature survey.

SECTION VIII

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APPENDIX

LITERATURE SURVEY

A. General

Chemical Abstracts was searched systematically for references to aqueous emulsions of polymers that cannot be prepared by emulsion polymerization. Thus far, Volumes 72-79 for the years 1970-73 have been searched, and the references of Volumes 74-77 for the years 1971-72 have been compiled and categorized as follows:

1. polyurethanes
2. epoxy resins
3. polyesters
4. silicones
5. polyolefins
6. elastomers
7. miscellaneous

B. Epoxy Emulsion Systems

In addition to references 9-20 cited in Section II, the following references describe the preparation of epoxy emulsion system components.

1. Epoxy Resin Prepolymers Emulsified Using Various Emulsifiers

a. Fr. 1,597,167 CA 74, 77475u: Bisphenol A-epichlorohydrin resin modified with a C_8-C_{20}-alkyl glycidyl ether emulsified using an alkylphenoxypoly(ethyleneoxy)ethanol.

b. Japan 70 29,240 CA 74, 143256b: Epikote 512 emulsified using sulfonated polystyrene.

c. Japan 70 34,455 CA 75, 37208y: Bisphenol A-epichlorohydrin epoxy resin containing coal or pine tar in xylene solution emulsified using polyvinyl alcohol.

d. U.S.S.R. 293,028 CA 75, 37338r: epoxy resins emulsified using high aliphatic acid esters of monoglycidyl polyethylene glycol ethers.

e. U.S. 3,619,398 CA 76, 73867s: Epon 836 emulsified using 2-(β-dimethylaminoethoxy)-4-methyl-1,3,2-dioxaborinane.

f. Ger. Offen 2,037,523 CA 76, 101337q: Vanoxy 128 emulsified using a mixture of 2-[(nonylphenoxy)pentakis(ethyleneoxy)]ethanol and 2-[(nonylphenoxy)-nonadecakis(ethyleneoxy)]ethanol.

g. Fr. 2,062,608 CA 76, 128170s: methacrylic acid-Bisphenol A polyglycidyl ether copolymer polyester resin containing styrene and treated with maleic anhydrode emulsified using Tergitol XD (nonionic ethylene-propylene oxide-alkanol copolymer).

h. Brit. 1,268,780 CA 77, 20872d: Epoxy 7071 emulsified using N-tallow-N, N, N', N', N'-pentamethyltrimethylene diquaternary ammonium dichloride.

i. Ger. Offen. 2,152,515 CA 77, 63505d: epoxy resin emulsified using a 12-hydroxystearic acid-methacrylic acid-methyl methacrylate copolymer.

j. Japan 71 29,625 CA 77, 76822e: epoxy resin emulsified using a surfactant of HLB 13-18.

k. U.S. 3,694,390 CA 77, 165535f: diethylenetriamine-triethylenetetramine-isophthalic acid-epichlorohydrin copolymer emulsified using aqueous tapioca starch.

2. Epoxy Resin Prepolymers Emulsified Using Aqueous Acid

a. Ger. 1,694,718 CA 77, 153118j: diacetone alcohol-diethanolamine-Bisphenol A glycidyl ether copolymer emulsified by adding acetic acid to pH 7.

3. Curing Agent Prepolymer Emulsified Using Various Emulsifiers

a. Kozh.-Obuv. Prom. 13(10), 52-5 (1971) CA 76, 72899s: polyamides emulsified using aqueous polyacrylamide solutions.

b. Brit. 1,275,389 CA 77, 115418z: polyamide resin prepared from a dimer acid, diethylenetriamine, and triethylenetetramine emulsified using aqueous N-[9(10)-phenylstearyl]-N, N, N', N', N', -pentamethyltrimethylenediammonium dichloride.

4. Glycidyl Methacrylate Copolymers Prepared by Emulsion Polymerization

a. J. Paint Tech. 44(564), 116-23 (1972): emulsion polymerization of glycidyl methacrylate with a wide variety of acrylate and methacrylate esters.

b. Japan 71 27,149 CA 77, 21733w: glycidyl methacrylate-vinyl propionate emulsion copolymers.

5. Epoxidization of Latex Polymers

a. Kauch. Rezina 30(1), 23-5 (1971) CA 74, 77173u: butadiene-styrene, butadiene-acrylonitrile, or polyisoprene latexes epoxidized using aqueous peracetic acid.

C. Polyurethane Emulsion Systems

In addition to references 21-33 cited in Section II, the following references describe the preparation of polyurethane emulsion systems.

1. Diisocyanate-Polyol Adducts with Blocked Isocyanate Groups Emulsified by Stirring into Aqueous Emulsifier Solution

a.	Ger. Offen. 2,004,276	CA 74, 13916f
b.	U.S. 3,539,388	CA 74, 23461t
c.	U.S. 3,542,505	CA 74, 43486h
d.	U.S. 3,551,364	CA 74, 64894e
e.	U.S. 3,565,844	CA 74, 112783s
f.	Japan 71 03,594	CA 74, 126731k
g.	Ger. 1,619,191	CA 75, 37859m
h.	Ger. Offen. 2,048,956	CA 75, 130858v
i.	Japan 71 22,944	CA 76, 15573g
j.	U.S. 3,642,553	CA 76, 142140p
k.	Ger. Offen. 2,035,729	CA 76, 154794t
l.	Ger. Offen. 2,117,395	CA 76, 155045m
m.	Japan 71 38,986	CA 77, 6412x
n.	Ger. Offen. 2,041,550	CA 77, 6563x
o.	Japan 72 00,908	CA 77, 6929w
p.	Japan 72 01,234	CA 77, 6969j
q.	Ger. Offen. 2,146,888	CA 77, 35598t
r.	Ger. Offen. 1,669,346	CA 77, 63385q
s.	Japan 71 42,070	CA 77, 89818h
t.	Fr. 2,087,669	CA 77, 103046p
u.	Japan 72 13,979	CA 77, 153308w
v.	Japan 72 23,904	CA 77, 166304s

2. Diisocyanate-Polyol Adducts Reacted with Amines and Emulsified by Stirring into Aqueous Acid

a.	Ger. Offen. 2,001,971	CA 74, 112796y
b.	Ger. Offen. 1,942,927	CA 74, 126858g
c.	Ger. Offen. 1,954,090	CA 75, 37386e
d.	Ger. Offen. 2,054,467	CA 75, 89389c
e.	Ger. Offen. 1,953,345	CA 75, 98952h
f.	Ger. Offen. 2,053,900	CA 75, 99158r
g.	Ger. Offen. 2,004,130	CA 75, 141552s
h.	Japan 71 27,266	CA 76, 4755s
i.	Ger. Offen. 2,141,807	CA 77, 6940t

D. Silicone Emulsion Systems

Aqueous dispersions or emulsions of silicone polymers can be prepared by a process analogous to emulsion polymerization (38-41) or by emulsification (42-44). In addition, organosilicone-urethane adducts have been prepared (45-54), but not as aqueous emulsions.

The following references to silicone emulsions were found in the Chemical Abstracts search of Volumes 74-77:

1. Coupling Agents for Glass-Fiber Composites

a.	U.S. 3,554,952	CA 74, 64967f
b.	Ger. Offen. 2,032,432	CA 74, 127021r
c.	Ger. Offen. 2,050,466	CA 75, 64841f
d.	Brit. 1,250,194	CA 76, 46957q
e.	U.S. 3,630,825	CA 76, 155062q

2. Textile Finishes - Water Repellency, Wrinkle Resistance

a.	Brit. 1,220,587	CA 74, 100555f
b.	Ger. Offen. 2,047,919	CA 75, 22422q
c.	Brit. 1,241,165	CA 75, 130749k
d.	U.S. 3,619,278	CA 76, 73679g
e.	Text. Chem. Color 4(1), 14 (1972)	CA 76, 114658v
f.	Ger. Offen. 2,157,580	CA 77, 102661y

3. Mold Release Agents

a.	Ger. Offen. 2,014,174	CA 74, 13797t
b.	Ger. Offen. 2,057,121	CA 75, 118900v

4. Coatings - All Types

a.	Ger. Offen. 2,017,022	CA 74, 65750s
b.	Ger. (East) 74,529	CA 74, 143263b
c.	Brit. 1,228,527	CA 75, 21729h
d.	Legka. Prom. (6), 47 (1970)	CA 75, 22532a
e.	J. Paint Tech. 43(558), 49 (1971)	CA 75, 89363q
f.	Ger. Offen. 2,144,972	CA 77, 21737a

5. Binders for Non-Woven Fabrics

a.	Japan 70 33,797	CA 75, 50376w
b.	Brit. 1,257,974	CA 76, 114759d

6. Paper Sizings

a.	Ger. Offen, 2,038,782	CA 74, 113500j

7. Anti-Foaming Agents

    a. Gdansk. Tow. Nauk. Rozpr. Wydz. 3, No. 7, 95 (1970) — CA 75, 132954x

8. Rheology of Silicone Emulsions

    a. J. Colloid Interface Sci. 36, 155 (1971) — CA 76, 49626w

9. Emulsion Polymerization of Permethylcyclosiloxanes

    a. Polymer Preprints 11(2), 995 (1970) — CA 77, 5874n

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