27
6-23-76

UCID- 17116

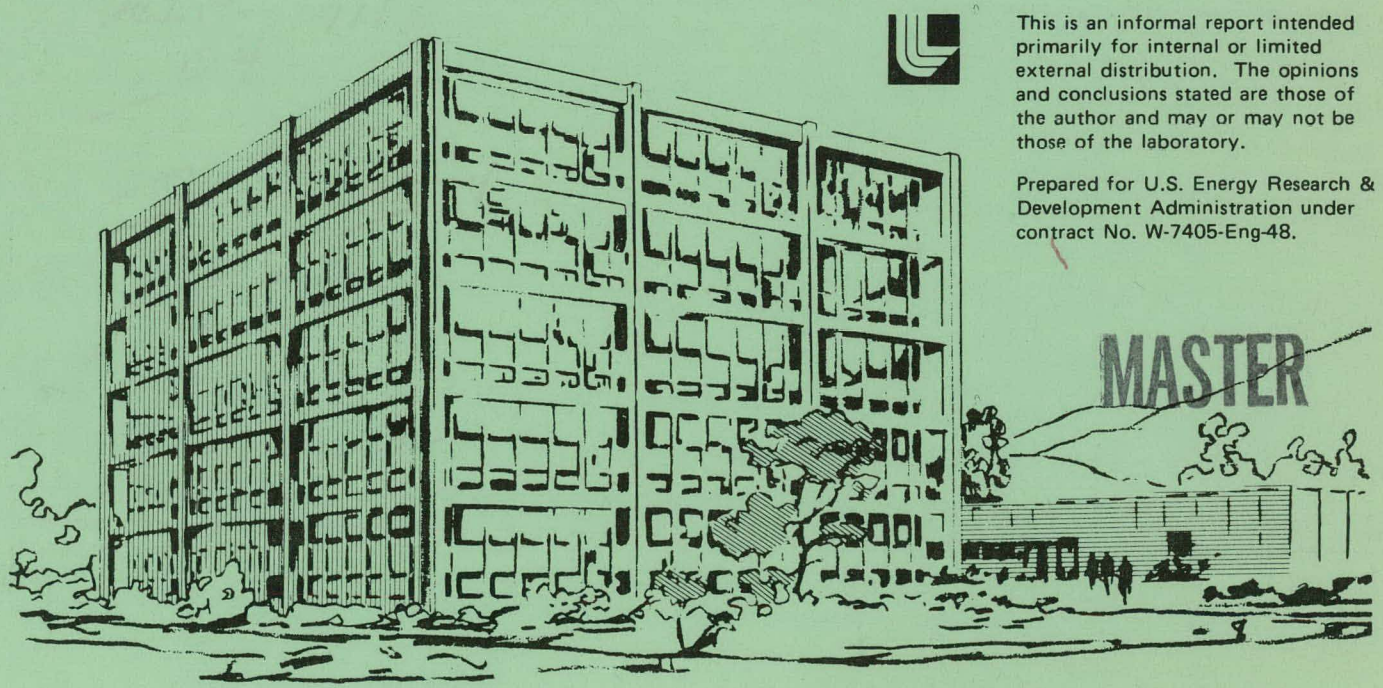
Lawrence Livermore Laboratory

SPECIFICATIONS FOR SEVERAL EPOXY RESINS AND HARDENERS USED IN FILAMENT WINDING

L. S. Penn

H. A. Newey

May 3, 1976



Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

DISCLAIMER

SPECIFICATIONS FOR SEVERAL EPOXY RESINS AND HARDENERS USED IN FILAMENT WINDING

ABSTRACT

We report specifications we developed for several epoxy resins and hardeners used in filament winding. The specifications are concise, aimed at testing convenience, and contain the minimum number of tests necessary to define the material.

INTRODUCTION

We report here specifications we developed for some epoxy resins and curing agents commonly used in filament winding. Many existing specifications are lengthy, complex and contain much irrelevant information. Our purpose is to write concise specifications as convenient as possible to carry out. Our specifications contain the minimum number of tests necessary to define the material for use in filamentary composites.

SPECIFICATION FOR RUBBERIZED EPOXY -- DOW XD7575.02*

General Comments

XD7575.02 is essentially XD7818, reacted with a carboxy-terminated butadiene acrylonitrile copolymer until it contains 10 wt% of this copolymer.

Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 1.

(b) Epoxide equivalent must be between 182 and 192 g/equiv.

(c) Viscosity must be between 11 and 14 Pa·s (110 and 140 P) at 25°C.

(d) Hydrolyzable chlorine content must not exceed 0.20 wt%.

(e) Gel permeation chromatogram must match that shown in Fig. 2.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Determine epoxide equivalent weight by accepted acid titration method such as: American Society of Testing Materials, ASTM D1652-73, or R. R. Jay, *Analytical Chemistry* 34, 667 (1964). Report the average of a minimum of two determinations.

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LVT) viscometer at 25°C using spindle No. 1 and 0.3 rpm spindle speed. See ASTM D2393-68.

(d) Hydrolyzable chlorine content should be determined by mild treatment with alcholic KOH followed by acid titration such as described in ASTM D1726-73. The average of two determinations should be reported.

(e) Gel permeation chromatography. Material dissolved in the chromatographic eluent tetrahydrofuran is injected into a gel permeation chromatograph containing columns in series of crosslinked polystyrene. Columns, 1.22 m × 9.53 mm o.d. each, should consist of four nominal 60 Å STYRAGEL plus one 350 Å and one 50 Å STYRAGEL or equivalent in resolving ability. Eluted components are detected by a differential refractive index-type detector and the concentration of eluted solute is to be plotted against elution volume. Later runs should be done at the same instrument setting for ease of comparison.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

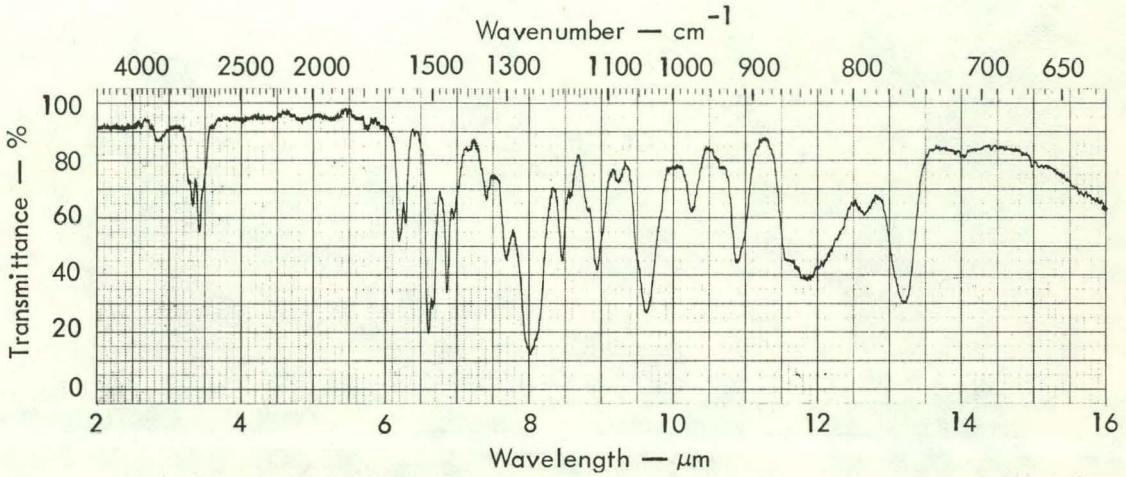


Fig. 1. Standard infrared absorption curve for rubberized epoxy-Dow XD7575.02.

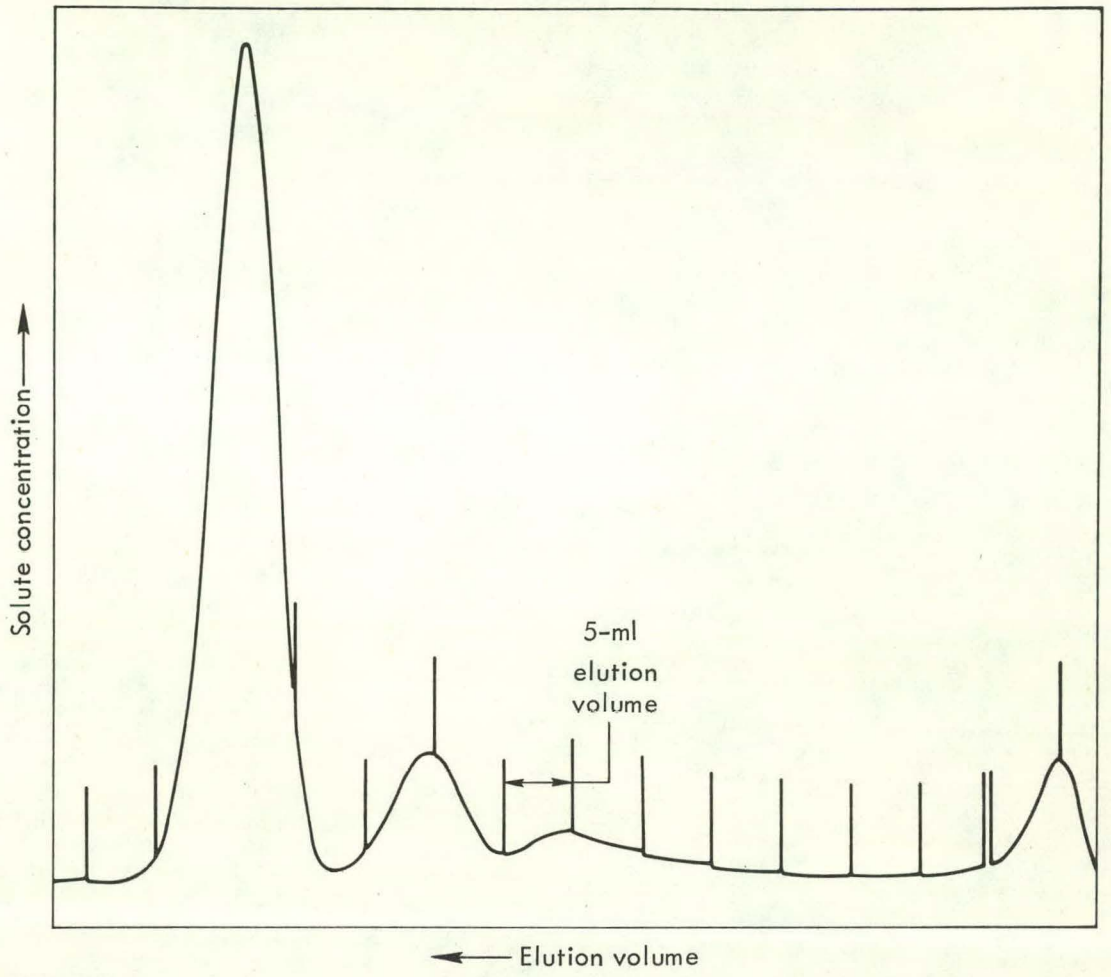
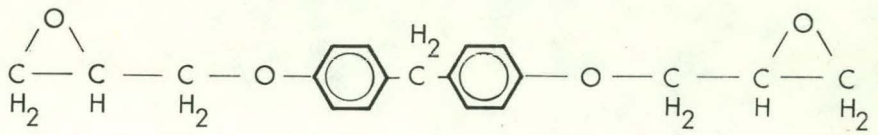


Fig. 2. Standard gel permeation chromatogram for rubberized epoxy-Dow XD7575.02.

SPECIFICATION FOR DOW XD7818

General Comments

XD7818 is a liquid resin that is mainly the diglycidyl ether of bisphenol F.



Small amounts of other isomers present inhibit the crystallization of this compound at room temperature. If the material is stored for a long time at low temperatures, crystallization can occur. If this happens, the material should be warmed to 50°C until all crystals melt and the material should be mixed until homogeneous before using or testing.

Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 3.

(b) Epoxide equivalent must be between 158 and 165 g/equiv.

(c) Viscosity must be between 2.5 and 3.4 Pa·s (25 and 34 P) at 25°C.

(d) Hydrolyzable chlorine content must not exceed 0.15 wt%.

(e) Water content must not exceed 0.20 wt%.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Determine epoxide equivalent weight by accepted acid titration method such as: ASTM D1652-73 or R. R. Jay, *Analytical Chemistry* 34, 667 (1964). Report the average of a minimum of two determinations.

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LVT) viscometer at 25°C using spindle No. 1 and 0.6 rpm spindle speed. See ASTM D2393-68.

(d) Hydrolyzable chlorine content should be determined by mild treatment with alcholic KOH followed by acid titration such as described in ASTM D1726-73. The average of two determinations should be reported.

(e) Water content should be determined by titrating with Karl Fischer reagent (which is a scavenger for water). This method is described in ASTM E203-64. Special commercial apparatus may also be used. The average of two determinations shall be reported.

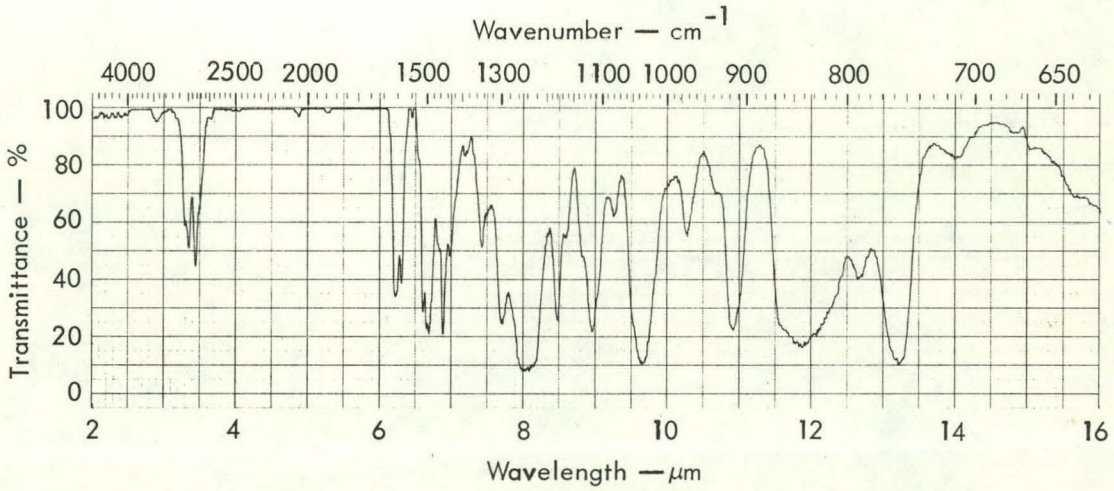


Fig. 3. Standard infrared absorption curve for Dow XD7818.

SPECIFICATION FOR UNIROYAL TONOX 60-40

General Comments

Tonox 60-40 is approximately 60% crude methylenedianiline (the crude product from the reaction of formaldehyde and aniline) and 40% m-phenylenediamine.

Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 4.

(b) Titratable nitrogen must be between 12.85 and 13.50 meq/g.

(c) Water content must be below 0.40 wt%.

(d) Gel permeation chromatogram must match that shown in Fig. 5.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Determine titratable nitrogen by an accepted acid titration method such as given by J. S. Fritz, *Analytical Chemistry* 22, 1028 (1950).

(c) Water content should be determined by titration with Karl Fischer reagent. This method is described in ASTM E203-64. Special commercial apparatus may also be used. The average of two determinations shall be reported.

(d) Gel Permeation Chromatography. Material dissolved in the chromatographic eluent tetrahydrofuran is injected into a gel permeation chromatography containing columns in series of crosslinked polystyrene. Columns, 1.22 m × 9.53 mm o.d. each, should consist of four nominal 60 Å STYRAGEL plus one 350 Å and one 50 Å STYRAGEL or equivalent in resolving ability. Eluted components are detected by a differential refractive index-type detector and the concentration of eluted solute is to be plotted against elution volume. Later runs should be done at the same instrument setting for ease of comparison.

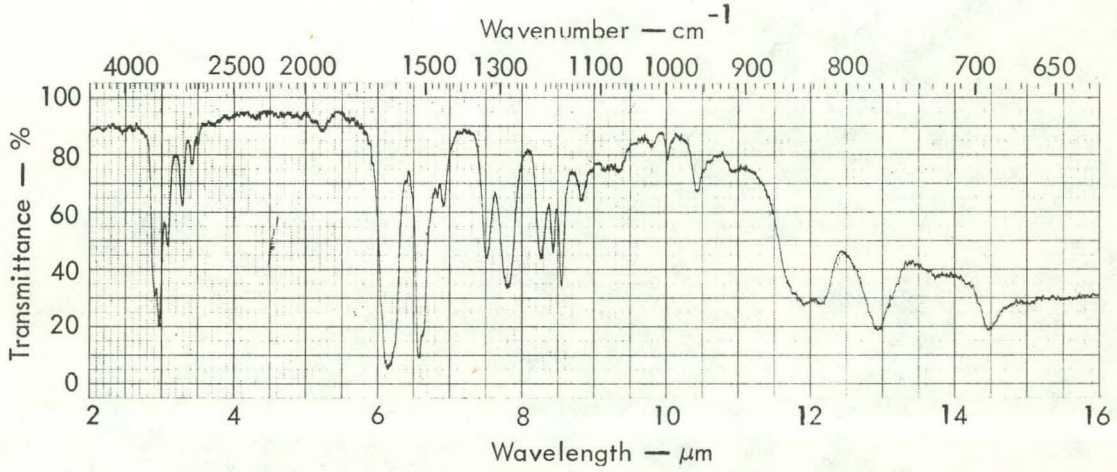


Fig. 4. Standard infrared absorption curve for UniRoyal TONOX 60-40.

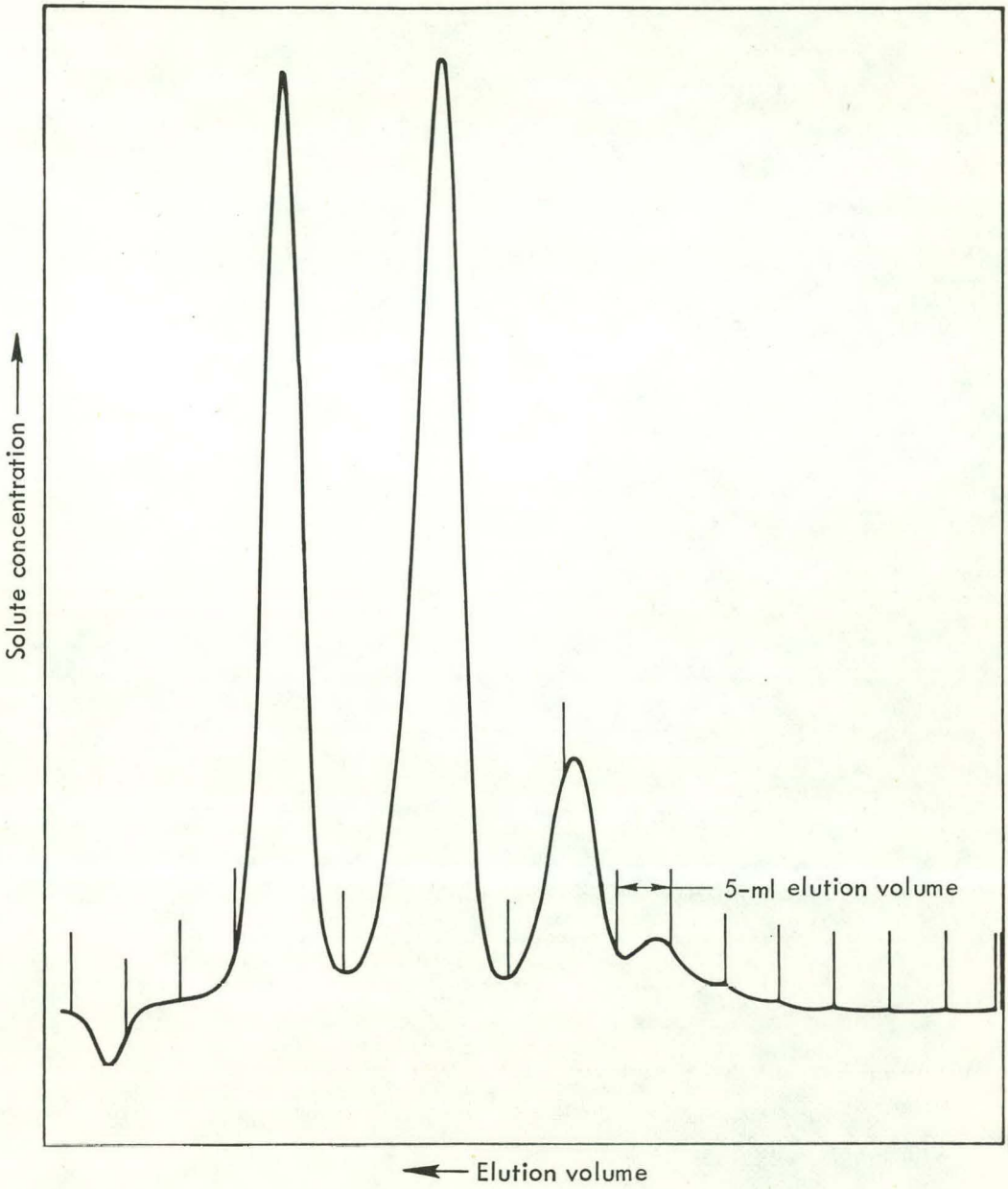
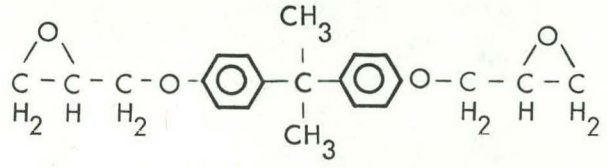


Fig. 5. Standard gel permeation chromatogram for Uniroy TONOX 60-40.

SPECIFICATION FOR DOW DER 332

General Comments

DER 332 is almost pure diglycidylether of bisphenol A.



It has a tendency to crystallize so before use or testing it should be warmed to 50°C until all crystals melt and then brought back to room temperature. It is a supercooled liquid at room temperature.

Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 6.

(b) Epoxide equivalent must be between 172 and 178 g/equiv.

(c) Viscosity must be between 4.0 and 6.1 Pa•s (40 and 61 P) at 25°C.

(d) Hydrolyzable chlorine content must not exceed 0.10 wt%.

(e) Water content must not exceed 0.20 wt%.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Determine epoxide equivalent weight by accepted acid titration method such as: ASTM D1652-73 or R. R. Jay, *Analytical Chemistry* 34, 667 (1964).

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LVT) viscometer at 25°C using spindle No. 1 and 3 rpm spindle speed. See ASTM D2393-68.

(d) Hydrolyzable chlorine content should be determined by mild treatment with alcholic KOH followed by acid titration such as described in ASTM D1726-73. The average of two determinations should be reported.

(e) Water content should be determined by titrating with Karl Fischer reagent (which is a scavenger for water). This method is described in ASTM E203-64. Special commercial apparatus may also be used. The average of two determinations should be reported.

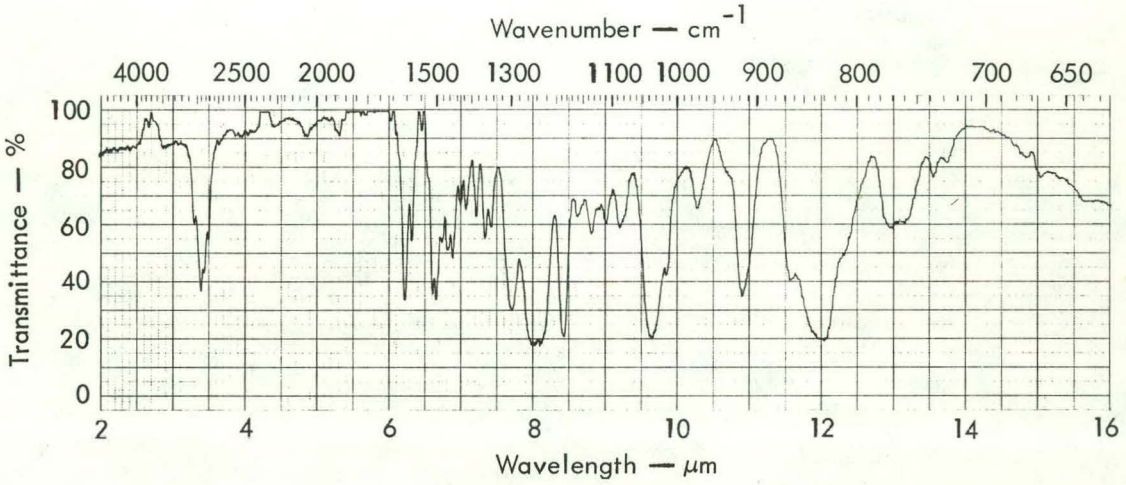
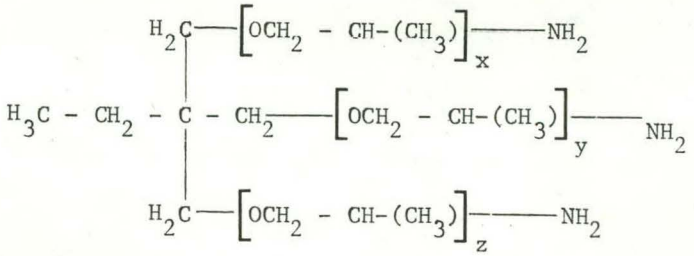


Fig. 6. Standard infrared absorption curve for Dow DER 332.

SPECIFICATION FOR JEFFAMINE T-403 FROM JEFFERSON CHEMICAL

General Comments

Jeffamine T-403 is a liquid with the following chemical structure:



where x + y + z approximately equal 5.3.

Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 7.

(b) Total amine content must be between 6.35 and 6.55 meq/g.

(c) Primary amine content must between 6.10 and 6.45 meq/g.

(d) Viscosity must be between 0.072 and 0.080 Pa•s (0.72 and 0.80 P) at 25°C.

(e) Water content must be below 0.30 %

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Total amine and primary amine should be determined by titrating the total amine, determining the amount of secondary plus tertiary amine present, and calculating the primary amine by difference. The method used can be that described in S. Siggia, J. G. Hanna, and I. R. Kervenski, *Analytical Chemistry* 22, 1295 (1950), or in C. D. Wagner, R. H. Prown, and E. D. Peters, *J. Am. Chem. Soc.* 69, 2609 (1947).

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LV) viscometer at 25°C using No. 1 spindle and 60 rpm spindle speed. See ASTM D2393-68.

(d) Water content should be determined by titrating with Karl Fischer reagent. This method is described in ASTM E203-64. Note that the method as ordinarily run does not work on strongly basic amines, such as Jeffamine T-403. See Note 9 (ASTM E203-64) that recommends using methanol-salicylic acid as a solvent when running water content of amines.

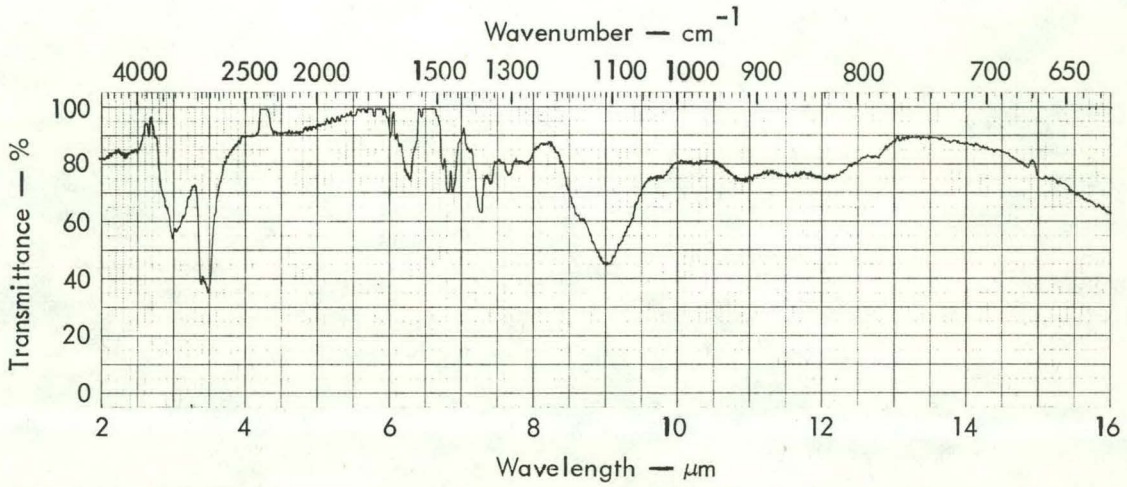
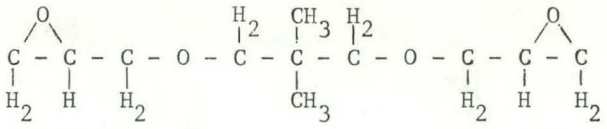


Fig. 7. Standard infrared absorption curve for JFFAMINE T-403.

SPECIFICATION FOR DOW XD7114

General Comments

XD7114 is mainly the diglycidyl ether of neopentylglycol:



Requirements

The materials must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 8.

(b) Epoxide equivalent must be between 145 and 160 g/equiv.

(c) Viscosity must be between 0.012 and 0.030 Pa•s (12 and 30 cP) at 25°C.

(d) Hydrolyzable chlorine content must not exceed 0.50 wt%.

(e) Gas chromatogram should match that shown in Fig. 9; it is especially important that the peak area should show at least 45% one component.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectrum.

(b) Determine epoxide equivalent weight by accepted acid titration method such as: ASTM D1652-73 or R. R. Jay, *Analytical Chemistry* 34, 667 (1964). Report average of a minimum of two determinations.

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LVT) viscometer at 25°C using No. 1 spindle and 60 rpm spindle speed. See ASTM D2393-68.

(d) Hydrolyzable chlorine content should be determined by mild treatment with alcoholic KOH followed by acid titration such as described in ASTM D1726-73. The average of two determinations should be reported.

(e) Gas Chromatography. Inject material into a gas chromotograph column, 1 m × 3.2 mm, containing 10% SP 2100* on 100/120 mesh Supelcoport. A temperature schedule of 100°-200°C at 10°C/min, then 200°-325°C at 15°C/min, gives good results. The gas-eluted components are detected by flame ionization and the amount of eluted solute is plotted against time. Later determinations should be done at the same instrument settings for ease of comparison.

*SP 2100 is a silicone-phase high-temperature partitioning fluid.

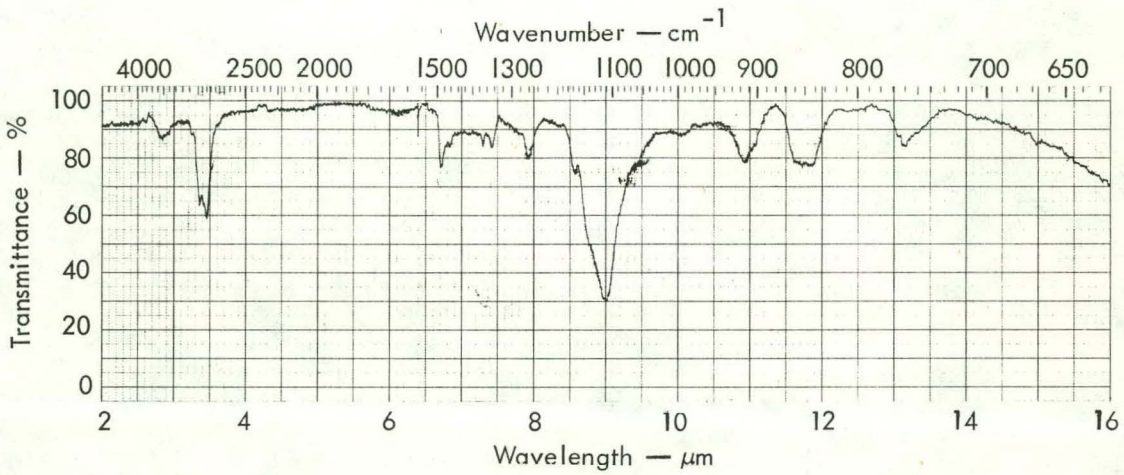


Fig. 8. Standard infrared absorption curve for Dow XD7114.

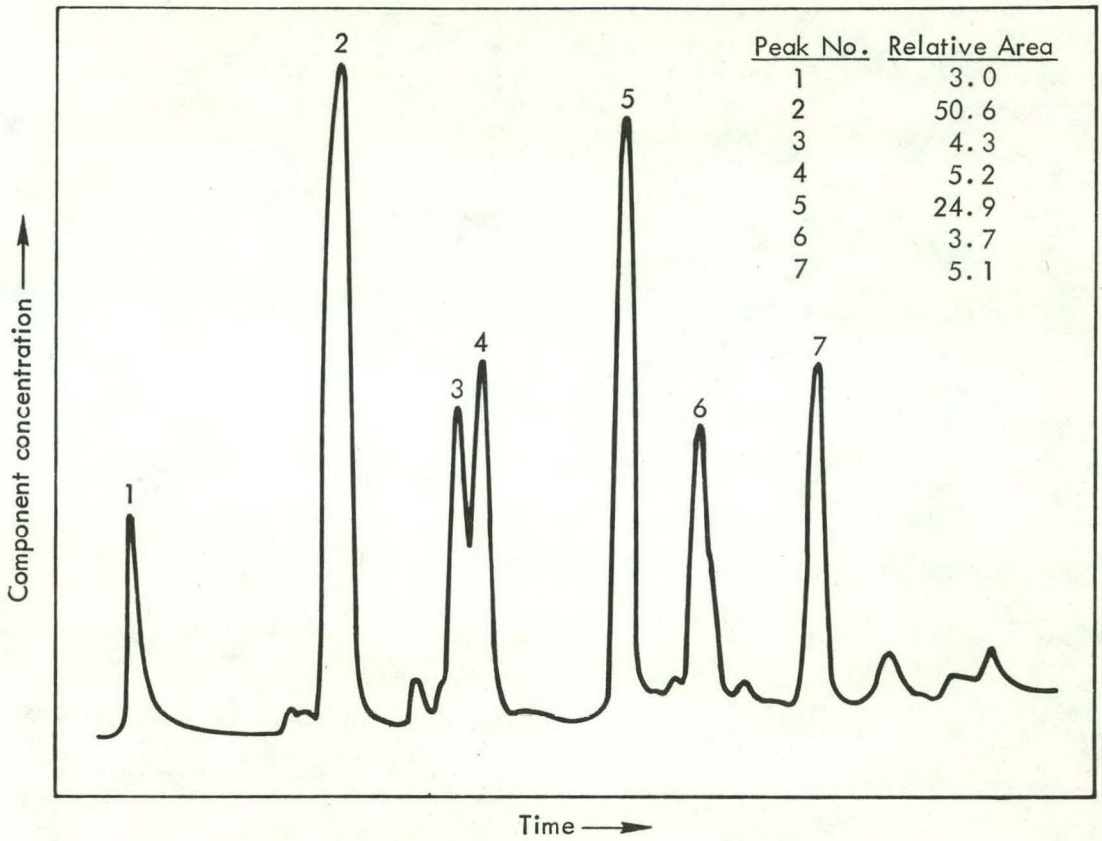
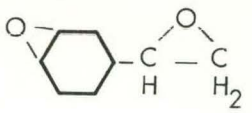


Fig. 9. Standard gas chromatogram for Dow XD7114.

SPECIFICATION FOR UNION CARBIDE ERL 4206

General Comments

ERL4206 is fairly pure vinyl cyclohexene dioxide



Requirements

The material must conform to the following:

(a) The infrared absorption curve must match that shown in Fig. 10.

(b) Epoxide equivalent must be between 70 and 74 g/equiv.

(c) Viscosity must be between 0.010 and 0.016 Pa•s (0.10 and 0.16 P) at 25°C.

(d) Gas chromatogram should match that shown in Fig. 11; it is especially important that the peak area should show at least 93% one component.

Methods for Determining Values

(a) Infrared spectra. Record on any spectrophotometer and compare with known spectra.

(b) Determine epoxide equivalent weight by an accepted acid titration method such as: ASTM D1652-83 or R. R. Jay, *Analytical Chemistry* 34, 667 (1964). Report the average of a minimum of two determinations.

(c) Viscosity should be determined on a rotating spindle (Brookfield Model LVT) viscometer at 25°C using spindle No. 1 and 60 rpm spindle speed. See ASTM D2393-68.

(d) Gas Chromatography. Inject material dissolved in a suitable solvent, such as benzene, into a gas chromatography containing a 15% free fatty acid phase on 60/80 mesh chromosorb W. The gas-eluted components are detected by flame ionization and the amount of eluted solute is plotted against time. A column 1 m × 3.2 mm and a temperature schedule of 75°C to 200°C at 15°C/min resulted in a major peak 94% by area. Later determinations should be done at the same instrument settings for ease of comparison.

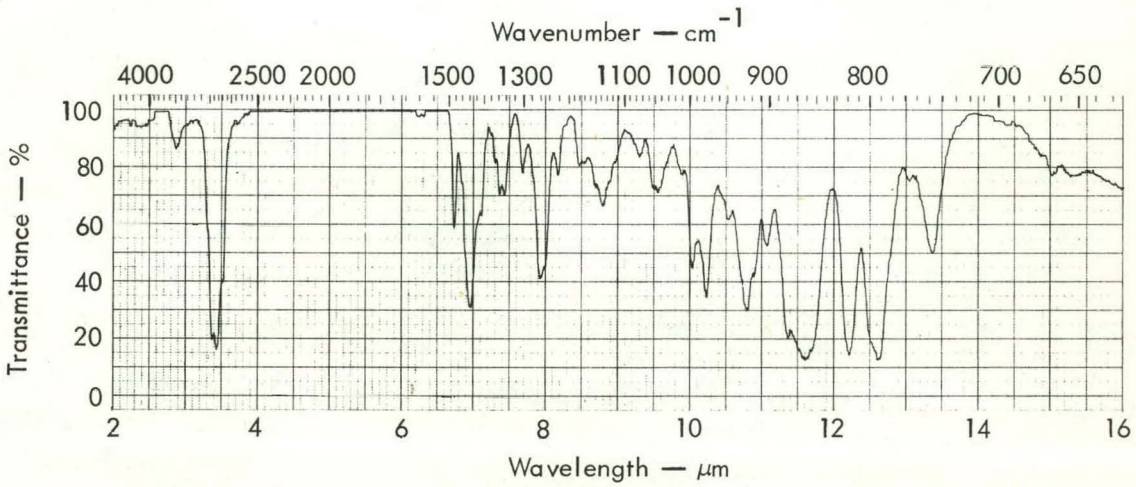


Fig. 10. Standard infrared absorption curve for Union Carbide ERL 4206.

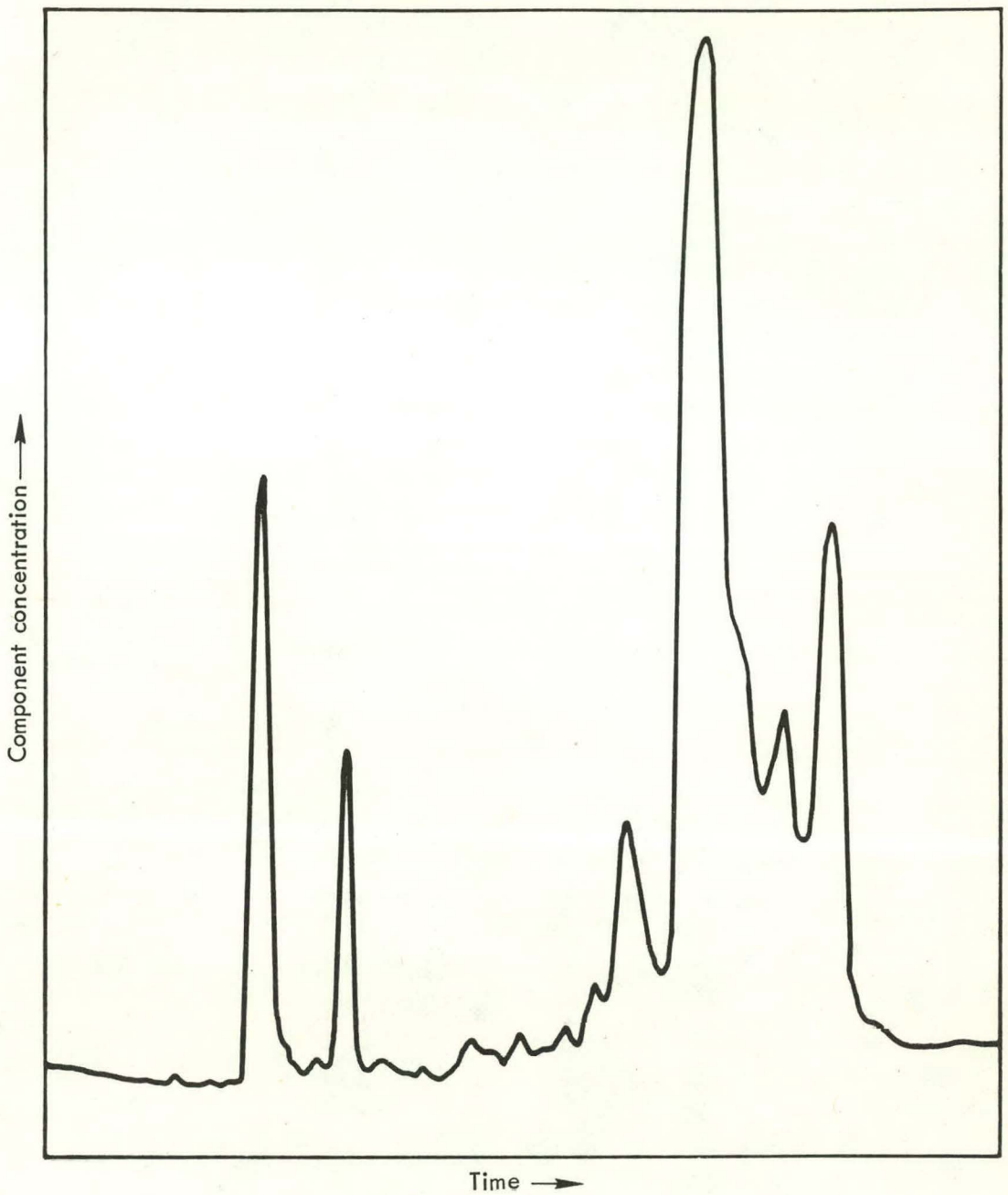


Fig. 11. Standard gas chromatogram for Union Carbide ERL 4206.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $; Microfiche $2.25

Page Range	Domestic Price	Page Range	Domestic Price
001–025	$ 3.50	326–350	10.00
026–050	4.00	351–375	10.50
051–075	4.50	376–400	10.75
076–100	5.00	401–425	11.00
101–125	5.25	426–450	11.75
126–150	5.50	451–475	12.00
151–175	6.00	476–500	12.50
176–200	7.50	501–525	12.75
201–225	7.75	526–550	13.00
226–250	8.00	551–575	13.50
251–275	9.00	576–600	13.75
276–300	9.25	601–up	*
301–325	9.75		

*Add $2.50 for each additional 100 page increment from 601 to 1,000 pages: add $4.50 for each additional 100 page increment over 1,000 pages.

MBB/af

Technical Information Department
LAWRENCE LIVERMORE LABORATORY
University of California | Livermore, California | 94550