Report No. FHWA/RD-81/149

PREPARATION OF AN EPOXY THERMOPLASTIC TRAFFIC MARKING MATERIAL ON A COMMERCIAL SCALE

DECEMBER 1981
FINAL REPORT

Prepared for
FEDERAL HIGHWAY ADMINISTRATION
OFFICE OF ENGINEERING AND
HIGHWAY OPERATIONS RESEARCH
AND DEVELOPMENT

FOREWORD

The Federal Highway Administration (FHWA) of the U.S. Department of Transportation has been instrumental with its support and participation in the development of an epoxy thermoplastic (ETP) highway striping material. This material (ETP) has proven to be extremely durable in field tests in either a white or yellow formulation.

The FHWA staff and contracted personnel developed and tested a variety of ETP formulations on a small scale culminating in the selection of a particular formulation for scale-up. Other results of the work were the establishing of a method of applying ETP to pavements and the developing of specifications and test methods for purchasing. After the foregoing preliminaries, it remained for the FHWA to scale-up to commercial production the selected formulation without compromising the application characteristics or excellent durability found in the field trials. In this quest the FHWA initiated contract research culminating with this report.

This report is of interest to traffic paint technologists and others concerned with pavement striping.

Richard E. Hay, Director,
Office of Engineering and Highway
Operations Research and Development

NOTICE

Technical Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
FHWA/RD-81/149		

4. Title and Subtitle	5. Report Date
PREPARATION OF AN EPOXY THERMOPLASTIC TRAFFIC MARKING MATERIAL ON A COMMERCIAL SCALE	December 1981
	6. Performing Organization Code
7. Author(s) S.W. Osborn, G. Colburn, P. [illegible], J.M. Good	8. Performing Organization Report No. 03G-C5347-01F
9. Performing Organization Name and Address The Franklin Research Center Division of The Franklin Institute 20th and Race Streets Philadelphia, PA 19103	10. Work Unit No. (TRAIS) FCP No. 31I2-293
	11. Contract or Grant No. DTFH61-80-C00041
12. Sponsoring Agency Name and Address U. S. Department of Transportation Federal Highway Administration Washington, D. C. 20590	13. Type of Report and Period Covered Final Report
	14. Sponsoring Agency Code M/0809

15. Supplementary Notes

FHWA Contract Manager: Dr. Lloyd Smith (HRS-23)

FHWA Implementation Manager: Mr. Charles Niessner (HDV-22)

16. Abstract

An Epoxy Thermoplastic (ETP) Pavement Marking Material has been manufactured on both pilot and semi-commercial scales using formulations provided by the Federal Highway Administration project monitors. A total of 3752 gallons (14,260 liters) of two white formulations and 250 gallons (950 liters) of a yellow formulation were prepared using standard batch mixing techniques. To minimize hot mixing time for the epoxy resins, solid components were preheated prior to addition to each batch. The product was cast into open-top silicone coated fiber boxes containing approximately 2 gallons (7.6 liters) each for shipment.

Physical and chemical properties of the ETP materials were measured and found to fall within anticipated limits except for product viscosities, which were in some instances higher than expected.

Present pigments used for the yellow formulation must be handled with all due attention to current industrial hygiene standards.

Using the manufacturing process described herein, including the batch time-cycles described, no difficulty in the manufacture of ETP materials by simple mixing procedures is anticipated.

17. Key Words	18. Distribution Statement
Epoxy Thermoplastic Pavement Marking Material, Pavement Marking, Manufacture of, Properties of	No original distribution by the sponsoring agency. This document is available to the public only through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	55	

PREFACE

This study was conducted for the Federal Highway Administration, U. S. Department of Transportation, Materials Division, Office of Research, under Contract No. DTFH61-80-C00041, by the Engineering and Sciences Department of the Franklin Research Center, Philadelphia, Pa. (FRC).

The work was conducted in Philadelphia and West Chester, Pa. during the period of March 1980 to September 1981.

Principal Investigator for this project was Stephen W. Osborn (FRC), with the assistance of FRC staff members, Mr. Grove Colburn, Joanne M. Good, and Patricia A. Landau.

Principal Subcontractor for the plant scale mixing and packaging operation was Bonded Products, Incorporated, West Chester, Pennsylvania, Mr. Edward M. Hillbush, Jr., President. Mr. Edward M. Hillbush, III supervised the manufacturing trials for Bonded Products.

METRIC CONVERSION FACTORS

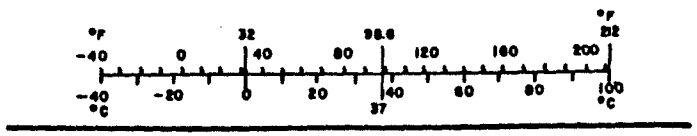
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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1. BACKGROUND AND OBJECTIVES

During the period of 1973-79, The Federal Highway Administration (FHWA) of the U. S. Department of Transportation supported and participated in the development of an Epoxy Thermoplastic (ETP) highway striping material through its contract, DOT-FH-11-8124, with the Southwest Research Institute.

The new material consists of two uncrosslinked epoxy resins, filler, pigment, and glass beads for reflectivity. The formulation contains no solvents. It is sprayed directly from a hot melt and dries to a tack-free consistency in 3-5 seconds. ETP has proven in field tests to be extremely durable, easy to apply (with proper equipment) and capable of both white and yellow formulation.

Because it requires neither evaporative drying or curing, ETP can be applied at low ambient temperatures, thereby extending the striping season, an important consideration especially in northern areas.

In preliminary tests, ETP has proven to be far more durable than traffic paint by virtue of its retention of physical properties and adhesion to paving substrates. These properties are the result of the high mechanical strength and toughness of epoxy polymers, the presence of chemically reactive bond sites in the finished products, and the fact that the material remains thermoplastic in use so that damage is, to some extent at least, self healing.

Having developed and tested a variety of ETP formulations on a small scale[1,2], selected a particular formulation for scale up, and established the method of applying ETP to pavements[3], and having developed specifications and test methods for purchasing, it remained to establish the best method of manufacture and packaging of ETP on a commercial scale for large scale field trials.

2. LABORATORY SCALE MIXING AND TESTING

The ETP formulation developed by FHWA and its contractors utilizes two commercial epoxy resins of the same approximate chemical composition which differ from each other in molecular weight and as a result, in physical properties. Specifically a high molecular weight solid resin is blended with a lower molecular weight liquid resin, together with the pigment and fillers. The final blend ratio determines the softening point of the product.

Approximately 4000 gallons (15,200 liters) of ETP were made during this study, 250 gallons (950 liters) of yellow and the rest white.

Laboratory mixes, as well as the initial production batches (50 gallon, 190 liter scale) were made using formulation A (Table 2-1). During this time period, two ETP formulations were undergoing field evaluation, and it was discovered that formulation A was a composite of the two field formulations. At this point, the rest of the white ETP was prepared using formulation B. Approximately 350 gallons (1,330 liters) were produced using formulation A and shipped to FHWA. The ETP corresponding to formulation B was shipped to various states for testing and evaluation.

Finally, as an addendum to the contract, 250 gallons (950 liters) of yellow ETP was produced in 50 gallon (190 liter) batches for demonstration purposes. The yellow formulation (C) was approved and provided by the Project Monitor.

Table 2-1

FORMULATION OF EPOXY THERMOPLASTIC (ETP) PAVEMENT MARKING MATERIAL

Material	Formulation (pbw)		
	A	B	C
Solid Epoxy Resin[1.]	30.0	30.0	30.0
Liquid Epoxy Resin[2.]	20.0	20.0	20.0
Calcium Carbonate ($CaCO_3$)[3.]	15.0	10.0	10.0
Titania (TiO_2) rutile, pigment grade[4.]	15.0	10.0	-
Lead chromate encapulated, pigment grade[5.]	-	-	9.26
Glass Beads, premix grade[6.]	16.0	14.0	14.0
Total	96.0	84.0	83.26

1. Araldite 7097 (Ciba-Geigy Corp.), or equivalent
2. Araldite 6010 (Ciba-Geigy Corp.), or equivalent
3. Camelwite, (H. T. Campbell & Sons) or equivalent
4. Rutile, R-900 (E.I. DuPont Co.) or equivalent
5. Lead Chromate, KY-795-D, pigment, grade, encapsulated (E.I. DuPont Co.)
6. Cataphote, Pavement Marking Beads, Premix Grade (Ferro Corp, Jackson, Miss. or equivalent.

2.1 LABORATORY MIXING STUDIES

A number of laboratory mixes were made to establish a practical procedure for large batch mixing operations. Batch sizes for these studies were approxmately one gallon (2.8 liters). In these studies, the liquid resin (Araldite 6010) was used as the mixing base and the order of adding solid ingredients was varied.

For rapid mixing, it was expedient to preheat the filler, pigment, and glass beads. Therefore, the choices centered on whether the solid resin (Araldite 7097), which cannot be preheated, should be charged before or after the other solids.

It quickly became apparent that charging the solid resin was the slowest step in the cycle because that resin was required to melt into the mixture before it blended.

The lowest possible blend temperature was desirable as well, to avoid further polymerization (viscosity buildup) or even charring of the resin.

For laboratory batches, a blend temperature of 125°C (257°F) was found to be adequate. Later, in 350 gallon (1330 liter) scale, a minimum batch temperature of 138-150°C (280-302°F) was required to insure complete and efficient mixing.

At all temperatures from 125-155°C (257-311°F) it was found that addition of solid resin to liquid resin before adding other solids resulted in an appreciably shorter batch cycle and permitted better mixing of ingredients.

Accordingly, the mixing cycle established for scale-up was:

1. Araldite 6010 (liquid resin) preheated to 150°C (302°F)
2. Araldite 7097 (solid resin) - slowly
3. $CaCO_3$ - preheated to 120°C (248°F)
4. TiO_2 - preheated to 120°C (248°F)
5. Reflective Glass Beads - preheated to 120°C (248°F).

When this procedure was used a smooth, lump-free mix was obtained within a few minutes, even at 120°C (248°F).

2.2 LABORATORY TESTING

The following laboratory tests were established for ETP, based upon those initially used in developing the formulation:

- Specific gravity, pycnometer method, AASHTO T-250-74 (ASTM D-153, Method A)
- Softening Point, ring and ball method, AASHTO T-250-74 (ASTM D-36, part 7)
- Daylight Reflectance, AASHTO T-250-74 (ASTM E-97)
- Yellowness Index, AASHTO T-250-74 (ASTM E-97)
- Epoxide Equivalent, ASTM, D 1652-72
- % Inorganic Solids, by extraction, FHWA Procedure
- No-Track Time, seconds, FHWA procedure.

The method of testing was based upon a "Draft Specification for ETP Pavement Marking Material", dated 6/26/80 as developed by the office of Research, Federal Highway Administration, and made available by the Project Monitor. (The draft specification was ultimately issued as Report No. FHWA/RD-80/069 (reference 2)).

The detailed sampling and test procedure as used in this project is given in Appendix A.

3. ETP MANUFACTURE - SCALE-UP IN COMMERCIAL PRODUCTION EQUIPMENT

A tentative ETP Manufacturing Process, developed from laboratory information was scaled up in two stages using commercial raw materials.

Raw Materials Specifications are given in Appendix B.

3.1 STAGE 1 - SCALE UP TO 50 GALLON LOTS

Based upon laboratory mixing data with production raw materials, it became apparent that, using the procedure described in Section 2, no further milling or extrusion was required to prepare a smooth product capable of hot spray application.

Accordingly, a 50 gallon (190 liters) pilot production vessel was set up as shown in Figure 3-1 using a heated, Schedule 304-stainless steel drum fitted with an agitator, feed hopper, and 1-1/4" (31.75 mm) drain valve. Reactants were charged by weight in the order shown.

Charge:	pbw	Charge Wt. (lbs)	(kg)
Araldite 6010 (Resin A)	20	104.16	42.34
Araldite 7097 (Resin B)	30	156.25	71.02
Camelwite ($CaCO_3$	15	78.12	35.51
A-900 (TiO_2	15	78.12	35.51
Glass beads	16	83.33	37.88
Losses (avg. 6%)		30 lbs.	sampling and material loss
Recover: Total	96	470 lbs.	
Gallons (25°C		39.16 gallons (148.8 liters)	

The pigment, fillers, and glass beads, in their shipping containers were heated overnight in an industrial electric oven to 121°C (250°F).

Resin A was charged from a weighed drum and heated with continuous agitation to 150°C (302°F). Resin B was added slowly and steadily during one hour, at a rate slow enough to avoid lump formation as the resins melted together. (Lump formation can easily result in high local viscosities with subsequent stalling of the agitator and/or scorching of the resin at the reactor walls.)

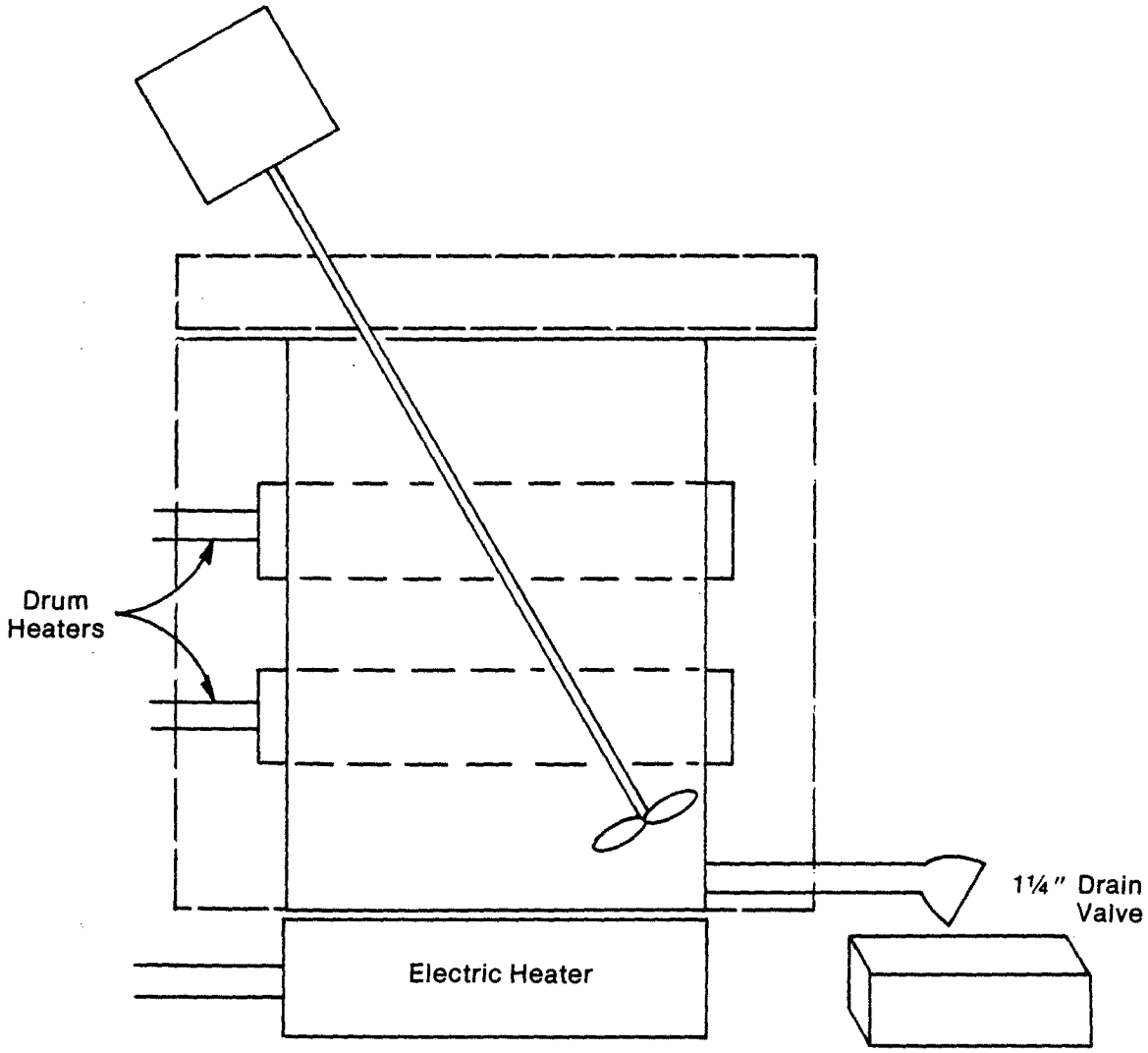

Figure 3-1.

50 GALLON PILOT PRODUCTION

EQUIPMENT SET-UP

With both resins charged, the batch temperature was brought back to 280-300°F, and Camelwite (at 121°C, 250°F) was added slowly during 20 minutes, followed by A-900 TiO_2 (at 121°C) during about 10 minutes. The batch was held at 150°C with efficient stirring for 30-40 minutes until inspection of the mix showed no visual signs of lump formation when tested with a stainless steel spatula.

During the mix, a portion of the batch was removed via the bottom valve and returned to the reactor to insure complete mixing of ingredients.

After 30 minutes, glass beads were added over a period of about 10 minutes and the batch was stirred for an additional 10 minutes.

The product was cast into open-top fiber boxes, 8"x8"x16", (20x20x41 cm) coated on the inside surface with a solid silicone coating, in quantities of 22-25 lbs (10-12 kg. approx. 2.0 gallons, 7.6 liters)/box).

Boxes were weighed, covered with a silicone coated release paper to keep out dust, and allowed to cool overnight on wooden shipping pallets.

Eight batches were made by this procedure, for a total product weight of 4200 lbs. (1909 kg) or 351 gallons (1334 liter). All of these batches were prepared using formulation A.

Material prepared from the earlier batches was palletized, covered with protective fiberboard, and shipped to the attention of the Project Monitor at the FHWA Laboratories.

3.2 SCALE-UP TO 350-GALLON (1330 LITER) BATCH SIZE

During pilot production at the 50-gallon level (190 liter), a 500 gallon (1900 liter) fiberglass-polyester production mixing tank was set up as shown in Figure 3-2.

The insulated, fiberglass tank was equipped with a 5 HP (3.728 KW) propeller type agitator fitted with 3 flights of blades to insure complete mixing.

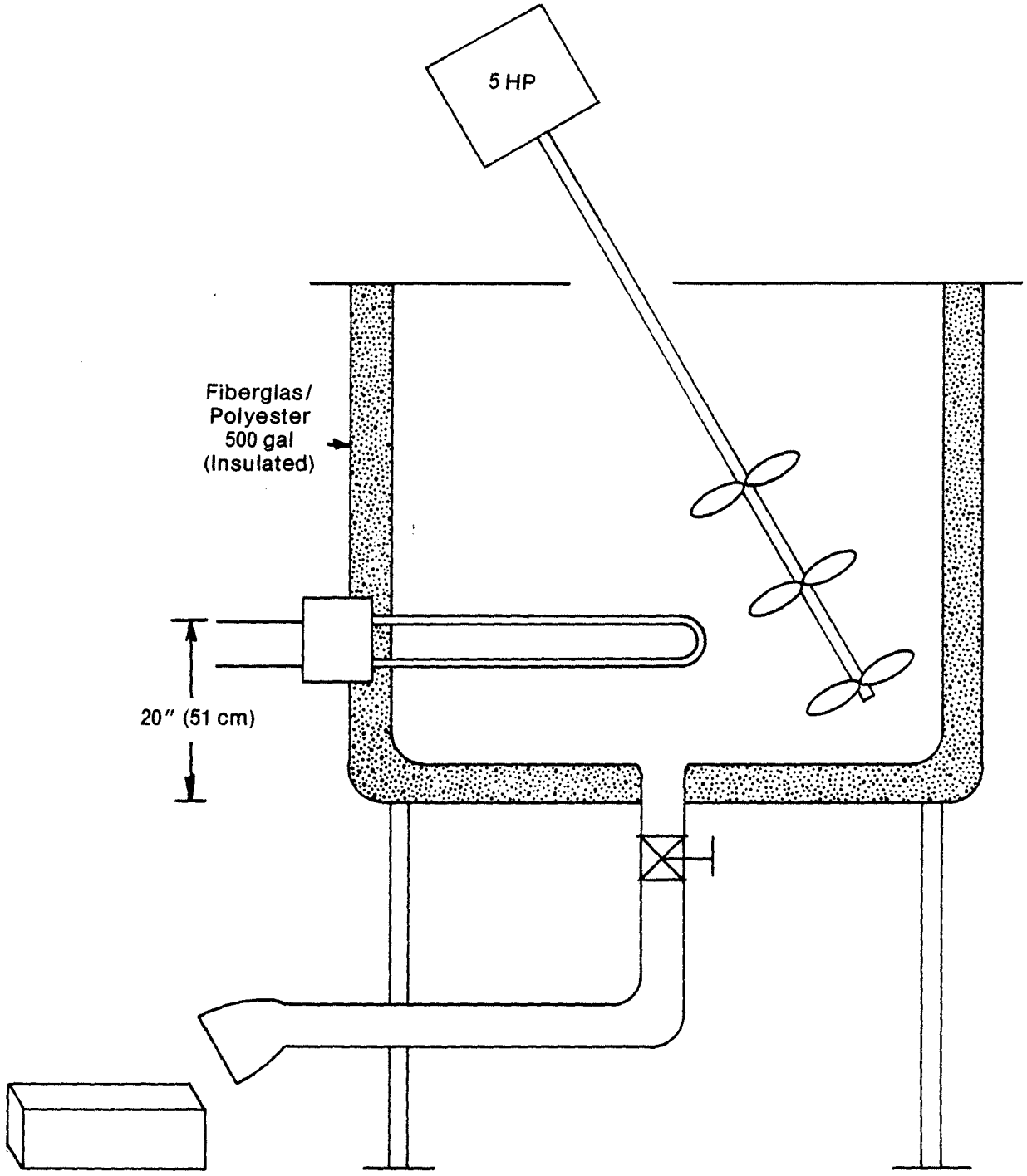

Figure 3-2.

ETP BATCH PRODUCTION EQUIPMENT

The vessel was electrically heated by means of a 40 Kw bayonette heater placed horizontally 20 in. (51 cm) above the bottom valve of the tank.

A 1-1/2" (38.0 mm) positive cut-off valve ("molasses cut-off valve") was connected to the bottom outlet to facilitate casting of the product. For casting, 2 gallon (7.6 liter) fiberboard, open top, silicone lined boxes were again used.

3.2.1 Formulation - 350 gallon (1330 liter) scale, Formulation B

The formulation for 350 gallon (1330 liter) production batches was modified at the direction of the Project Monitor (Formulation C, Table 2-1) as follows (nominal 350 gal. (1330 liter) batch).

Batch A-10

Charge:	pbw	Charge Wt. (lbs)	(kg)
A-6010 (Resin A)	20	1056 lbs	480
A-7097 (Resin B)	30	1584	720
Camelwite ($CaCO_3$)	10	528	240
A-900 (TiO_2)	10	528	240
Glass beads	14	739	335.9
Losses: Ave. 5%		222 lbs (sampling/vessel losses)	100.9
Recover	84		
Pounds		4213 pounds	(1915 kg)
Gallons of Product		351 gallons	(1334 liters)

Eleven batches of Formulation B (A-1 through A-11) were prepared at gradually increasing batch sizes. Because of uncertainty in the efficiency of agitation, the earlier batch were made just large enough to immerse the heating element. Later batches were increased in size to 350 gallons (1330 liters). Total production of this formulation was 3400 gallons (12,920 liters).

3.3 PROCESS IN DETAIL

All raw materials were preweighed. Filler, pigment, and beads were preheated in their weigh containers to 121°C (250°F).

Resin A (liquid) was charged to the reactor and heated, with continuous agitation, to 150°C (302°F). Resin B (solid) was added slowly and continuously during 1-1/2 hours, during which time the temperature was held at 140°C $\pm$ 10°C. Considerable foaming was observed during addition of the solid epoxy resin and the apparent batch volume increased by approximately 30% during solid resin addition.

Camelwite, preheated to 121°C, was added slowly and continuously during about 20 minutes. The Camelwite ($CaCO_3$) acted as a gas entrainer and defoamer and the foam which had been previously observed was quickly eliminated.

Titanium dioxide (A-900, preheated to 121°C) was added slowly and continuously during 20-25 minutes. No further foaming was observed.

Finally, the glass beads were added during 20 minutes and the batch was stirred continuously for an additional 30 minutes.

Periodically during the mix, a 5 gallon quantity of product was withdrawn from the bottom valve and returned to the reactor to insure complete mixing.

The ETP was then cast into 2 gallon (7.6 liter) boxes (approx. 25 lbs/box 11 kg/box) and allowed to cool overnight before packaging for shipment. Power to the bayonet heater was cut off before casting to prevent scorching of the resin.

Three samples of each batch were collected as the material was cast. The sample were taken at the 1st quarter, 2nd quarter, and 3rd quarter of the casting cycle.

For continuous production, the liquid resin (A6010) for the following batch was immediately charged to the warm reactor and allowed to stand overnight at 50-60°C to prevent solidification of residual ETP on the reactor walls.

3.4 CLEANOUT OF EQUIPMENT

Following the last batch of each series, but not more often than about once in 10-15 batches, the reaction equipment was cleaned by rinsing it thoroughly and then soaking out the reactor and piping with warm toluene. Approximately 100 gallons of toluene was used for the cleanout, and the solvent was thoroughly drained to permit complete removal of the resins and solids from the reaction equipment.

The wash solvent, which could be distilled and reused if desired, was, for the purposes of these runs, discarded.

3.5 BATCH TEST DATA

Three hundred fifty gallons (1330 liters) of white formulation A (Table 2-1), made in the eight "50 gallon" (190 liter) batches, where packaged and shipped to the FHWA laboratories without further testing.

Samples of the remaining 11 lot samples of white formulation B (representing 3401 total gallons) (12,924 liters) were tested completely by the procedures given in Section 2 (and Appendix A).

A table of physical and chemistry properties tentatively proposed for ETP Pavement Marking Materials is given in Table 3-1.

The complete data summary for production lots A-1 through A-22 is given in Table 3-2.

A comparison of Table 3-2 with 3-1 indicates that much of the data falls within the expected range. Viscosities among the eleven lots were found to be higher than expected and subject to considerable variability.

For example, at 205°C (400°F) the average measured viscosity of lots A-1 to A-11 was 828 cps (with a standard deviation of 106 cps) as compared with an expected average of 625 cps. All samples fell, however, within the acceptable range of 470-1070 cps. It must be remembered that the tentatively proposed specifications are for samples prepared in the laboratory using different temperature conditions and shorter times. This could explain the higher average viscosities obtained from production lots.

Table 3-1
SUGGESTED PROPERTY RANGES FOR ETP PAVEMENT MARKING MATERIALS
FHWA/RD-80/069

Property	White Formulation 60/40 Value	White Formulation High Limit	White Formulation Low Limit	Yellow Formulation 60/40 Value	Yellow Formulation High Limit	Yellow Formulation Low Limit
Viscosity[1] at 204°C (cps)	625	1070	470	813	1450	522
Softening Point (°C)[2]	74	84	62	77	83	72
Reflectance (percent of MgO standard)[3]	77	-	73	47	-	44
% Organic Material	65.6	66.0	65.0	60.5	61.0	60.0
Epoxide Equivalent	454	468	448	464	488	447

1 Viscosity is given in centipoises (cps) measured with the Brookfield Thermosel Viscometer at 20 rpm to convert to Pa.5 multiply by 10^{-3}
2 Measured by ASTM D-36
3 Measured with Gardner reflectance meter
4 Measured by ASTM D-1652

Batch Number	Viscosity cps				Soft Pt. °C	Sp. Gr. 25°C	Inorg. %	Epoxy Content	Daylight Refl.	Yellow Index	Heat Aged Visc. cps				No. Track sec	Batch Weight	Gal.
	205°C		232°C								205°C		232°C				
	20 rpm	10	20	10							20	10	20	10			
A-1	800	925	518	600	79.9	1.444	39.82	465.8	83.8	1.89 0.48 0.12	3794	4650	2231	2862	30	2796	233
A-2	843	950	600	615	77.9	1.394	38.63	443.2	89.75	1.30	2994	2975	1481	1625	45	3072	256
A-3	706	787	500	456	79.0	1.460	41.62	468.2	88.5	0.86	2694	3150	1550	1900	45	3852	321
A-4	747	919	469	543	78.8	1.432	40.05	424.9	89.1	2.27	3388	4162	2169	2975		3720	310
A-5	750	850	438	462	72.4	1.426	38.1%	469.7	89.9	-1.54	1875	2050	925	1125	60	3636	303
A-6	747	862	556	612	76.9	1.374	34.9%	454.9	88.0	1.49	2838	3238	1538	1725	75	3684	307
A-7	925	1125	547	588	73.9	1.452	35.9%	443.4	84.2	2.22	2462	2762	1381	1575	90	4092	341
A-8	681	731	578	625	72.6	1.446	41.8%	520.7	85.6	2.06	2694	3075	1525	1788	60	3792	316
A-9	875	912	569	594	73.9	1.424	44.0	415.9	88.2	-1.50	2438	2738	1431	1600	60	3744	312
A-10	969	1025	669	675	74.5	1.442	43.1	560.4	87.2	0.53	3938	4388	2206	2638	75	4164	347
A-11	903	900	612	625	74.1	1.428	43.0	448.0	89.0	0.37	4112	4675	2262	2825	75	4260	355
REPEAT A-10	981	1062	638	688				559.2			4044	4712	2281	2800			
REPEAT A-11	912.5	988	620	638				481.8			2362	2612	1356	1512			
TOTALS																40812	3401
Average	828	923	560	597	75.8	1.429	40.1	471.9			3150	3611	1778	2156			
Std. Dev.	106	114	74	78	2.68	0.027	3.0	57.4			899	1126	527	755			

Table 3-2

Data Summary. Production Lots A-1 through A-11 Formulation B

After four hours at 245°C, the conditions specified in the Test Protocol, the average viscosity for the eleven batches (205°C) increased to 3150 cps with a standard deviation of 899 cps. The heat-aged viscosity data imply a finite pot-life for hot spray application and suggest that, in practice, it may be desirable to empty the applicator tank completely at each usage to avoid the necessity to remelt unused product.

Heat-aged viscosities were considerably higher than original viscosities.

3.6 MANUFACTURE OF YELLOW ETP

Two hundred fifty gallons of yellow ETP (Formulation D Table 2-1) was prepared in a total of 6 batches using the 50 gallon reactor.

The formulation was:

Change (in order given)	pbw	Typical Batch lbs. (kg)	Total lbs. (kg)
Araldite-6010 (liquid)	20	165	919
Araldite-7097 (solid)	30	247	1379
Camelwite	10	82.4	460
Lead chromate, encapsulated, pigment grade (Krolor KY795D)	9.26	76.3	426
Glass Beads	14	115.3	643
Total:	83.26	686.0	3827
Losses: (Ave. 6.2%)		42	237
Recover: lbs. (kg)		644 lbs.	3590
gallons (liters)		45.0	251

The manufacturing process was the same as that used for the white formulation in the 50 gallon (190 liter) reactor (Section 3-1).

The liquid resin was added to the reactor and heated to 150°C (302°F). The solid resin was then added during approximately one hour while the batch temperature was held between 137 and 150°C (280-300°F). Camelwite, preheated to 121°C (250°F), was added during 20 minutes, followed by lead chromate, also preheated, during 10 minutes.

The batch was held at 150°C (302°F) for 30-40 minutes with continuous rapid stirring. Preheated glass beads were added and the batch was stirred for an additional 10 minutes.

The product was cast into silicone coated, open-top, fiber boxes 8"x8"x 16" (20x20x41 cm), covered with silicone release paper, and the boxes were cooled overnight on wooden shipping pallets.

Samples were taken at the midpoint of the casting cycle. The physical properties are given in Table 3-3.

As in the case of the white formulations (A and B), the physical properties of the yellow formulation were generally those expected from the specifications except for viscosities, which were generally scattered and slightly higher than expected.

Heat aged viscosities, reflectance, and no-track time were not measured for the yellow formulations.

Once again, the higher viscosities are believed to be the result of longer batch cyles than those used in the laboratory.

The lead chromate pigment was found to mix evenly and quickly. However, dusting of the pigment was difficult to control and respirators, as well as disposable outer garments and shoe coverings were used to avoid skin contact during processing.

SUMMARY OF PHYSICAL PROPERTIES

BATCH NO.	VISCOSITY, CPS 204°C 20rpm	VISCOSITY, CPS 204°C 10rpm	VISCOSITY, CPS 232°C 20rpm	VISCOSITY, CPS 232°C 10rpm	SOFTENING POINT, °C	REFLECTANCE	SPECIFIC GRAVITY	HEAT AGED VISCOSITIES
Y-1	1356	1380	1022	1040	79	Not Measured	1.561	Not Measured
Y-2	1110	1140	925	960	77		1.543	
Y-3	985	1005	842	860	77		1.526	
Y-4	1250	1272	1075	1095	78		1.517	
Y-5	1070	1092	945	960	76		1.523	
Y-6	1282	1302	1120	1145	79		1.549	

Table 3-3

Data Summary - Production Lots Y-1 through Y-6

Formulation C

4. ETP PACKAGING

A variety of packaging methods were considered for ETP. It was recognized immediately that for a thermoplastic product, cold-flow would present a problem for any kind of pelletized or flake formulation.

Efforts to overcome the natural tack of the 60/40 formulation (Formulation B) through use of a powder such as talc, or a lubricant (mineral oil) proved to be unsuccessful.

Efforts to make pellets "self skinning" by treating the surface with ammonia and amines were similarly unsuccessful because the resulting "skins" could not be reworked into the pellets again upon melting.

Accordingly, bulk casting was selected as the packaging method.

Fiberboard, open-top boxes 8x8x16" (20x20x40 cm), coated on the inside with a silicone release agent were found to be particularly successful.

The containers used held approx. 2 gallons (7.6 liters) (liquid measure) or 25 lbs. (11 kg) of ETP. After cooling overnight, the resulting blocks of solid product were palletized onto wooden pallets containing approximately 200 gallons (760 liters)/pallet (2400 lbs) (1100 kg) and covered with protective fiberboard for shipment.

The boxes for casting and shipment of ETP were manufactured and produced by:

The Franklin Container Corporation
7900 Tabor Avenue
Philadelphia, Pa. 19111
215/742-6600

The covered boxes used were without cover. However, an improved box with integral cover is also available at this time which can be flattened and returned for re-use.

The boxes can be manufactured in any dimension, including 2x16x32" (5.2x41.6x83.2 cm), similar to the boxes in which other hot melt products are shipped.

The covered boxes are manufactured by:

The Menasha Corporation
P. O. Box 367
Neenah, Wisconsin
414/722-4251

5. SAFETY AND HANDLING PROCEDURES

ETP Pavement Marking Materials are prepared by a hot blending operation using preheated ingredients.

Care must be taken to insure that ingredients, or the product, do not cause burns.

Full face protection and gauntlet protective gloves must be worn by operators in the mixing operations.

Because of the temperatures involved the mixing area including the reaction vessel and casting area must be well ventilated at all times.

An emergency procedure, including first aid, and rapid medical attention must be made available in the event of burns.

Yellow Formulation

The formulation of yellow ETP presents a special problem because of the toxicity of the yellow pigment.

Lead chromate encapsulated with silica is used to minimize dusting. In addition, this material must be handled in a separate, ventilated facility with OSHA-approved dust filters to prevent escape of pigment. Operators within the area must wear approved respirators, and the manufacturing area must not be used for other operations.

To avoid contamination of other areas, protective shoe covering and outer garments should be worn in the work area, and removed in an approved decontamination facility.

Further safety information on the use of lead chromate pigments is available from the U.S. manufacturers of these materials,

E. I. DuPont de Nemours, Inc. (KY-795 D)

Ciba-Geigy Corp., Ardsley, NY (Rampart S4075).

6. SUMMARY AND CONCLUSIONS

An Epoxy Thermoplastic (ETP) Pavement Marking Material has been manufactured on both pilot and semi-commercial scales using formulations provided by the Federal Highway Administration project monitors. A total of 3752 gallons (14,260 liters) of two white formulations and 250 gallons (950 liters) of a yellow formulation were prepared using standard batch mixing techniques. To minimize hot mixing time for the epoxy resins, solid components were preheated prior to addition to each batch. The product was cast into open-top silicone coated fiber boxes containing approximately 2 gallons (7.6 liters) each for shipment.

Physical and chemical properties of th ETP materials were measured and found to fall within anticipated limits except for product viscosities, which were in some instances higher than expected.

Present pigments used for the yellow formulation must be handled with all due attention to current industrial hygiene standards.

Using the manufacturing process described herein, including the batch time-cycles described, no difficulty in the manufacture of ETP materials by simple mixing procedures is anticipated.

APPENDIX A

TEST PROCEDURES - ETP PAVEMENT MARKING MATERIALS

For use in FRC Project No. 03G-C5347-01

June 30, 1980

Test Procedures - ETP Pavement Marking Materials

ref: FHWA-DOT Draft Specific. Dated 6/26/80, resulting in Report No.
FHWA/RD-80/009 (December 1980)

Formulation

The product shall be prepared from:

30 pbw	Araldite 7097 (Ciba-Geigy Corp)
20 pbw	Araldite 6010 (Ciba-Geigy Corp)
10 pbw	Calcium Carbonate-Camelwite (H. T. Campbell Sons' Co.)
10 pbw	TiO_2 TiPure R-900 (DuPont)
	or
9.26 pbw	Silica encapsulated lead chromate (DuPont)
14 pbw	premix glass beads (Cataphote Div.,-Ferro Corp)

Sampling Procedure - As each batch of ETP is cast into 25 lb. (11 kg) containers, collect 3 1 pint samples at intervals of about 1/4, 1/2, 3/4 of the casting procedure. Cool and send samples to the lab. for analysis.

1. Procedure for Sample Preparation

Equipment

Hot oil bath set at 225°C (437°F)
Oven set at 219°C (425°F)
Paint Film Applicator - Boston-Bradley or equivalent set at 20 mils
Glass Plates 4x4 in (approx)
Draw Down Holder for Glass Plates
Brookfield Viscosity Chambers (10 ml size, two required per test)
Softening Point - ring and ball apparatus, (2 rings required)
100 ml beaker for heat stability samples
tared 400 ml beaker (weigh to 3 or 4 decimals)
25 ml pycnometer

Procedure

1. Heat the sample (approx. 350 g) in 400 ml beaker in an oven set at 219°C until the sample is completely melted.
Place 3 glass plates 4"x4" in the oven and allow these to equilibrate also.
When the sample is completely melted, transfer it to the hot oil bath at 225°C until the sample temperature reaches 219°C (425°F).

2. Remove the sample from the bath, wipe any oil from the bottom, and pour 2 viscosity samples, filling the tubes 3/4 full (10 ml tubes).
Note: Stir the sample with thermometer just before pouring to assure representative samples.

3. Return the sample to the oil bath and reheat to 219°C. Pour sample into 2 softening point rings. Make sure there are no air bubbles and that an excess is poured into each ring. Set rings aside to cool.

4. Fill the pyconometer bulb approximately half full of sample and set it aside to cool.

5. Retrieve the glass plates from the oven one at a time and place them on the draw-down holder with the applicator (set at 20 mils) in place.
   Immediately pour ETP on each plate and slowly draw down a coating on each plate. The coating procedure, including pouring, should take about 5-20 seconds/plate.
   (If "No Track Time" is run, a third plate may be drawn, see Sect. 7.)

6. Pour about 50 ml of sample into a 100 ml. beaker for use in heat stability testing.

7. Pour about 5 g of sample into a weighed 400 ml beaker. Cool and reweigh the beaker to get an accurate sample weight (at least 3 decimals).
   The entire sample preparation procedure should take about 20 min.

Ref: AASHTO T-250
ASTM-D-153

2. Test for Specific Gravity*

1. Standardize the pycnometer by filling it with freshly boiled distilled water at 23-24°C. Place the filled pycnometer in a 25°C water bath and allow the temperature to rise to 25 ± 0.5°C. Dry the outside and weight the pycnometer to 4 decimal places. Record for permanent use. (C)

2. Empty the pycnometer, clean, dry and reweigh it. Record for permanent use. (E)

3. Fill the pycnometer approximately 1/3 full of molten ETP taking care to keep bubbles from forming. (Pour slowly at about 225°C.) Cool and weigh the pycnometer and sample. (A)

4. With the sample cooled just below 25°C, fill the pycnometer with freshly boiled distilled water at 23-24°C and equilibrate the entire pycnometer-sample-water in the constant temperature batch at 25 ± 0.5°C. Dry the pycnometer and weigh.(F)

Calculation:

$$\text{Sp gr. } 25°C = \frac{S}{S + C - F}$$

where S = weight of sample(A-E)
C = weight of pycnometer and water
F = weight of pycnometer and sample and water

* Run all samples in Duplicate!

Ref: AASHTO T-53

3. Softening Point

Samples prepared as described in 1-3.

The brass rings are placed on a heat resistant surface (transite, asbestos board, Teflon, etc) and an excess of material is poured into the ring. After cooling, the samples are leveled with a wide spatula or putty knife heated in a burner flame. Place brass test balls in bath also - but not on the rings.

1. Assemble the rings, thermometer and ball guides in the apparatus and fill it with 4 in. of ethylene glycol.

   Cool the apparatus to 5 ± 1°C in an ice bath for 15 minutes. (Caution! do not get ice or water into the glycol bath.

2. Heat the bath from below with a Bunsen Burner at a rate of 5 ± 05° min.
   (Note! a preset Hotplate can be used for heating, in which case the hotplate setting is recorded for reuse. Always use the same hotplates.)

   Reject any determination where the rate of use does not fall within the use range after 3 min.

3. Record the temperature for each ball at the instant the material surrounding the ball touches the bottom plate.

   Report to the nearest 0.5°C the average of the two duplicate values. (Duplicate values should not differ by more than 2°C.)

ref. FHWA Lab. Oral
Communications 6/26/80
Draft proposed spec.

4. % Inorganic Solids by Extraction

The sample preparation is described in 1-7 (5 g. of sample in a weighed 400 ml beaker).

4.1 Solvent Extraction Mixture

(by volume) (ppv)

Diethyl ether	10 pts.
Toluene	6 pts.
Methanol	4
Acetone	1

4.2 Procedure

Weigh the sample (5 g) in the 400 ml beaker and dissolve sample in 250 ml of the solvent mixture. Centrifuge the mixture at 20,000 rpm for 15 min. and carefully decant the supernatant solution into a round-bottomed flask (1 l.). Wash the inorganic residue with 2 50 portions of solvent, centrifuge each time, and combine the washes with the supernatant.

Wash the inorganic residue with 20 ml of acetone, centrifuge and discard the wash. Weigh and record the residue weight.

Evaporate the extract to dryness using a rotary flash vacuum adapter at 55-60°C. Do not overheat! Save for epoxy tests.

$$\% \text{ inorganic solids} = \frac{\text{wt. of residue}}{\text{wt sample \& beaker}} \times 100$$

Ref: ASTM-D1652

5. Epoxide Equivalent (of Organic Portion)

Using the resin (organic extract) obtained in section 4, evaporate the last traces of solvent, in a vacuum oven at 60°C overnight.

Accurately weigh (3) 1 g. samples of the organic residue into a 125 ml Erlenmeyer flask. Dissolve the sample in 25 ml of chlorobenzene and place a Teflon stirring bar in the solution. Include a 4th sample of chlorobenzene (no epoxy) as a blank.

Add 4-6 drops of crystal violet indicator solution (0.1% crystal violet in glacial acetic acid) and attach the flask to the buret using a rubber stopper.

Titrate the sample with standardized 0.1N HBr in glacial acetic acid (see Note) to a blue green end point which persists for at least 30 seconds.

Note: Prepare and standardize HBr solution containing approx. 8 g HBr/liter of glacial acetic acid by titrating against 0.4 g of potassium acid phthalate (accurately weighed) in 10 ml of glacial acetic acid.

Calculations:

Normality HBr

$$N = \frac{W \times 1000}{204.2\ H}$$

where W = wt. potassium acid phthalate (g.)
H = ml of HBr solution

$$\text{epoxy content} = \frac{N\ (V-B)}{10\ S} \quad \text{(g. eq./100 g. resin)}$$

N = Normality of HBr solution
V = ml HBr used to titrate sample
B = ml HBr used for blank
S = wt of sample (g)

6. Infrared Spectrum (of Organic Portion)

Place approx. 5 mg of the organic residue from 4 on a sodium chloride IR plate. Sandwich this sample between a second sodium chloride plate so that a thin coating (about 5 ml) exists between the plates. (The plates may have to be warmed to about 30°C to soften the sample into place.

Mount the sample in the instrument and position the pen at 90-95 percent transmittance at 2100-2200 cm^{-1} by adjusting the 100 percent potentiometer.

Examine the spectrum at 1240 cm^{-1}. If the tip of the peak at 1240 cm^{-1} is between 10 and 25% transmittance, proceed to run the spectrum between 4000-650 cm^{-1}. If the 1240 cm^{-1} peak extend to lower transmittance, repeat using a thinner sample.

Compare spectrum with a reference resin spectrum.

ref: FHWA lab. -
Mr. Brian Choller
private communication
6/25/80

7. No Track Time

When "no track time" is measured, a third glass plate is coated at the time of sample preparation and the test is run immediately.

The glass plate is preheated in the oven at 219°C. The plate is placed on the draw-down holder and a 20 mil film is drawn (within 5-20 seconds).

After 15 seconds (following draw-down) the plate is placed on the included base of the test roller and the roller is allowed to roll across the plate. If a mark appears on the plate, or there is paint pickup on the roller the test is repeated at 15 second intervals until no mark is observed.

Under these conditions, a "no track time" of 1 min or less is considered acceptable.

Ref: AASHTO T-250
ASTM E-97

8. Daylight Reflectance and Yellowness Index

Instrument: Photovolt, Model 670 Photometer

Using the glass plates prepared in Part 1, operate the reflectance meter according to manufacturers instructions:

1. adjust meter (if necessary) to zero.

2. turn on power (power switch only) and, with zero suppressor fully off (clockwise until it locks) and sensitivity controls fully clockwise set meter to zero.

3. turn on the lamp switch and allow the phototube to warm up for 30 min.

4. insert the green tristimulus color filter and standardize the meter using the test plate.

5. record the green (daylight) reflectance of each sample.

6. insert the blue tristimulus filter and remeasure all of the plates.

   Note! Use the standard test plate to recalibrate the meter each time the filter is changed.

7. Calculate the yellowness index (YI) from:

   YI = 100 (1-blue/green)

Ref: FHWA Draft Specifica.
of 6/25/80

9. Viscosity Measurement

Instrument: A model RFV Brookfield Thermosel system equipped with stainless steel viscosity chambers, spindle, thermosel heating chamber, SCR control control and Brookfield synchro-electric viscometer.
Spindle No. SC-4-27 is used.

Procedure:

1. Set the heating container to 205°C (400°F). Melt the sample and rotate the spindle at 20 RPM until a constant shear is obtained.

2. Repeat the measurement at 10 RPM.

3. Reset the heating chamber to 232°C (450°F) and repeat the measurements at 20 and 10 RPM, waiting until a constant shear value is obtained.

4. Convert the reading to centipoises (CPS) as in the instrument tables.

If desired -

5. Using a 2nd 50 ml sample heated at 245°C for 4 hours, refill the viscosity measurement cups and redetermine the viscosity as described above.

APPENDIX B

RAW MATERIALS USED IN MAKING ETP PAVEMENT MARKING MATERIALS

Project No. 03G-C5347-01

Araldite 6010 - Ciba-Geigy Corp.

Araldite GT 7079 - Ciba-Geigy Corp.

Camelwite - Calcium Carbonate - Harry T. Campbell Son's Co.

R-900-TiO_2 - DuPont Company

Pavement Marking Beads, Phoenix Grade, Cataphote Division

Fero Corporation

Araldite® 6010

A Medium Viscosity, Unmodified Liquid Epoxy Resin

General

Araldite 6010 is a widely applied general purpose unmodified liquid epoxy resin. Applied in cold or heat cured systems, it has become a standard from which a great number of variations have been developed.

Chemical Description

Araldite 6010 is an unmodified liquid epoxy resin based on bisphenol-A and epichlorohydrin.

Advantages

- Superior mechanical and electrical properties
- Excellent chemical resistance
- Good heat resistance
- Excellent adhesion
- Outstanding versatility
- Easy to cure with a variety of different type hardeners
- Compatible with many different fillers, diluents and accelerators
- FDA regulated

Application Areas

Coatings: Solvent-free high solids coatings, chemical resistant maintenance coatings, marine finishes, tank linings, trade sales paint, pipe coatings, industrial and decorative floorings.
Electrical: Laminating, casting, encapsulating, potting.
Construction: Adhesives, tooling, filament windings.

Typical Properties

Epoxy value, eq/100g	0.52-0.55
Weight per epoxide	182-192
Viscosity @ 25°C(77°F), cP	12,000-16,000
Color, Gardner	2 max.
Weight per gallon, lb	9.6-9.8
Flash point, closed cup °F	490

FDA Status	Araldite 6010 is included in Section 175.300 of Title 21 of the Code of Federal Regulations (21 CFR 175.300) for resinous and polymeric coatings.
Packaging and Storage	Araldite 6010 is supplied in bulk and 500 lb steel drums. This product has a minimum shelf life of 4 years when stored in unopened sealed containers in a dry location at room temperature. Like most liquid epoxy resins, Araldite 6010 may crystallize when stored below room temperature. Heating the resin to 60-70°C (140-160°F), preferably in a water bath, for several hours, will reliquify it and restore its original properties.
Toxicological Information	Araldite 6010 is practically non-toxic on acute exposure (Acute Oral LD^{50} 13,300 mg/kg in rats and Acute Dermal LD^{50} V 6000 mg/kg in rabbits.) However, it is a mild skin and eye irritant as well as a moderate sensitizer.
Handling/Safety Precautions	It is important to avoid contact with eyes, skin and clothing. Use general mechanical ventilation and local exhaust, drawing dust or vapors away from the worker. Wear impervious gloves and splash proof goggles. The use of a NIOSH approved organic vapor respirator is recommended.
First Aid	In case of contact, flush eyes immediately with plenty of water for at least 15 minutes. Call a physician. Flush skin with plenty of water and soap if available. Remove contaminated clothing and wash before reuse. If inhaled, remove to fresh air. Give oxygen and artificial respiration if necessary. If swallowed, give plenty of water to drink and induce vomiting by touching back of throat with finger or blunt instrument.
Important	CIBA-GEIGY warrants that this product conforms to the Chemical Description contained in this brochure. **No other warranties, whether expressed or implied, including warranties of merchantability or of fitness for a particular purpose shall apply to this product.** No statements or recommendations contained herein are to be construed as inducements to infringe any relevant patent, now or hereafter in existence. CIBA-GEIGY neither assumes nor authorizes any representative or other person to assume for it any obligation or liability other than such as is expressly set forth herein. **Under no circumstances shall CIBA-GEIGY be liable for incidental, consequential or other damages arising out of a claim from alleged negligence, breach of warranty, strict liability or any other legal theory, through the use or handling of this product.**

PLASTICS & ADDITIVES DIVISION
CIBA-GEIGY Corporation
Ardsley, New York 10502
(914) 478-3137

CIBA—GEIGY

SAFETY DATA SHEET

The information and recommendations contained herein are based upon data believed to be correct. However, no guarantee or warranty of any kind expressed or implied is made with respect to the information contained herein.

SECTION I.

TRADE NAME	ARALDITE 6010	PRODUCT TYPE	Liquid Epoxy Resin
CHEMICAL FAMILY	Epoxides		

SECTION II. HAZARDOUS INGREDIENTS

INGREDIENT	%	TLV (UNITS)	INGREDIENT	%	TLV (UNITS)

SECTION III. PHYSICAL DATA

BOILING POINT (°F.)		SOLUBILITY IN WATER	Insoluble
MELTING POINT (°F.)		SPECIFIC GRAVITY (H_2O=1) @ 77°F	1.16
VAPOR PRESSURE (mm Hg.)		PERCENT VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (=1)	
APPEARANCE AND ODOR	Clear colorless to light-colored liquid		

SECTION IV. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (°F.) (Method Used)	490 (Pensky-Martens Closed Cup)	FLAMMABLE LIMITS IN AIR	LEL	UEL
EXTINGUISHING MEDIA	Carbon dioxide, foam, dry chemical, water spray.			
SPECIAL FIRE FIGHTING PROCEDURES	Use self-contained breathing apparatus.			
UNUSUAL FIRE AND EXPLOSION HAZARDS	No unusual hazards.			

SECTION V. REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	Storage at elevated temperatures over long periods of time degrades the resin.
INCOMPATIBILITY (Materials to Avoid)	Strong oxidizing agents.		
HAZARDOUS DECOMPOSITION PRODUCTS	Carbon monoxide and/or carbon dioxide.		
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

D-11614 7/75

SECTION VI. HEALTH HAZARD DATA

ORAL: LD_{50}	(rat) 13,300 mg/kg
DERMAL: LD_{50}	(rabbit) >6,000 mg/kg
IRRITATION: SKIN	(rabbit) Mild. SPI CLASS. 2
EYE	(rabbit) Mild.
SENSITIZATION	Moderate sensitizer.
THRESHOLD LIMIT VALUE	
RESPIRATORY	May cause sensitization.
EFFECTS OF OVEREXPOSURE	Possible irritation and sensitization.
EMERGENCY & FIRST AID PROCEDURES:	Call a physician.
INHALATION	Remove to fresh air. Oxygen & artificial respiration, if necessary.
INGESTION	If conscious, give water or milk. Induce vomiting.
SKIN	Remove contaminated clothing. Wash with soap and water.
EYES	Flush with water for at least 15 minutes.
OTHER	

SECTION VII. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Remove all sources of ignition.
Absorb on combustible material for proper disposal.
Flush contaminated areas with water.

WASTE DISPOSAL METHOD

Incineration in accordance with local pollution regulation. and ordinance.

SECTION VIII. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify Type)	NIOSH approved organic vapor respirator recommended.
PROTECTIVE CLOTHING	Impervious gloves.
EYE PROTECTION	Splash-proof goggles.
VENTILATION	General mechanical ventilation and local exhaust.

SECTION IX. SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING, STORING ETC.

WARNING! Causes Irritation
May Cause Sensitization

Avoid contact with eyes, skin and clothing.

Wash thoroughly after handling.

First Aid: In case of contact,

Eyes - Immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

Skin - Flush skin with plenty of water.

Clothing - Wash clothing before reuse.

DATE: Revised 6-12-78

SIGNATURE: K. T. Shen

KTS:cm

Sw 12/79

Araldite® GT 7097

Solid Epoxy Resin

General

Araldite GT 7097 is a solid high melt viscosity epoxy resin designed for high quality industrial coatings and for thick-film powder coatings.

Chemical Description

Araldite GT 7097 is a solid, unmodified epoxy resin based on bisphenol A.

Applications

- Metal decorating finishes
- Can, drum and tank linings
- Application primers and enamels
- Metal furniture finishes
- Primers for practically all types of substrates
- Araldite GT 7097 is successfully used for the production of powder coatings for:
  Coatings of components used in the chemical industry with high chemical and mechanical resistance
  Tube and pipe coatings

Advantages

- Superior flow and wetting properties
- Excellent batch-to-batch uniformity
- Excellent solubility characteristics
- High gloss development with reduced pigment floating and flocculation
- Good chemical, solvent and water resistance
- Outstanding adhesion and flexibility

Typical Properties

Visual appearance	Clear, no contamination
Epoxy value, eq/100g	0.050-0.061
Weight per epoxide	1650-2000
Viscosity, Gardner-Holdt* @ 25°C (77°F)	X-Z
Color, Gardner	3 max
Melting point, Durran's, °C (°F)	113-123 (235-252)
Density, lb/gal, 25°C (77°F)	9.8 average
Bulking value, gal/lb, 25°C (77°F)	0.102
Specific gravity @ 25°C (77°F)	1.18
Flash point (closed cup), °C (°F)	>93 (200°)

* 40% N.V. in Butyl Carbitol

FDA Status	Surface coatings made from Araldite GT 7097 epoxy resin conform to Section 175.300 of Title 21 of the Code of Federal Regulations (21 CFR 175.300).
Packaging and Storage	Araldite GT 7097 is supplied in 50 pound bags. This product has minimum shelf life of four years when stored in a dry place at room temperature. If stored under warmer conditions, sintering may occur.
Toxicological Information	Araldite GT 7097 is non-toxic by ingestion (acute oral LD_{50}, 8720 mg/kg in rats): It is not an eye irritant or a skin sensitizer.
Handling Precautions	• When handling resin, use due care and avoid unnecessary personal contact in accordance with good industrial practice. • In dusty conditions, use general mechanical ventilation and local exhaust, and wear a NIOSH approved dust respirator if necessary. • Use impervious gloves and chemical goggles for special protection.
First Aid	For eye contact, flush eyes immediately with plenty of water for at least 15 minutes. Call a physician. For skin contact, wash skin immediately with plenty of water and soap. If inhaled, remove to fresh air give oxygen or artificial respiration if necessary. If swallowed and if conscious, give plenty of water to drink and induce vomiting by touching back of throat with finger or blunt instrument. Call a physician.
Important	CIBA-GEIGY warrants that this product conforms to the Chemical Description contained in this brochure. **No other warranties, whether expressed or implied, including warranties of merchantability or of fitness for a particular purpose shall apply to this product.** No statements or recommendations contained herein are to be construed as inducements to infringe any relevant patent, now or hereafter in existence. CIBA-GEIGY neither assumes nor authorizes any representative or other person to assume for it any obligation or liability other than such as is expressly set forth herein. **Under no circumstances shall CIBA-GEIGY be liable for incidental, consequential or other damages arising out of a claim from alleged negligence, breach of warranty, strict liability or any other legal theory, through the use or handling of this product.**

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CIBA—GEIGY

SAFETY DATA SHEET

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SECTION I.

TRADE NAME	PRODUCT TYPE
ARALDITE 7097	Solid Epoxy Resin
CHEMICAL FAMILY: Epoxides	

SECTION II. HAZARDOUS INGREDIENTS

INGREDIENT	%	TLV (UNITS)	INGREDIENT	%	TLV (UNITS)

SECTION III. PHYSICAL DATA

BOILING POINT (°F.)		SOLUBILITY IN WATER	Insoluble
MELTING POINT (°F.)	235.4-253.4	SPECIFIC GRAVITY (H_2O=1) @ 77°F	1.18
VAPOR PRESSURE (mm Hg.)		PERCENT VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (=1)	
APPEARANCE AND ODOR	Clear amber-colored solid.		

SECTION IV. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (°F.) (Method Used)	FLAMMABLE LIMITS IN AIR	LEL	UEL
>200°F Pensky-Martens Closed Cup			

EXTINGUISHING MEDIA: Carbon dioxide, dry chemical, foam.

SPECIAL FIRE FIGHTING PROCEDURES: None.

UNUSUAL FIRE AND EXPLOSION HAZARDS: None.

SECTION V. REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	
INCOMPATIBILITY (Materials to Avoid)	Strong oxidizing agents.		
HAZARDOUS DECOMPOSITION PRODUCTS	Carbon monoxide and/or carbon dioxide.		
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

D-11614 7/75

SECTION VI. HEALTH HAZARD DATA

ORAL: LD_{50}	(rat) 8,720 mg/kg
DERMAL: LD_{50}	
IRRITATION: SKIN	Not an irritant. SPI CLASS. 1
EYE	Not an irritant.
SENSITIZATION	Not a sensitizer
THRESHOLD LIMIT VALUE	
RESPIRATORY	
EFFECTS OF OVEREXPOSURE	None expected.
EMERGENCY & FIRST AID PROCEDURES:	
INHALATION	Remove to fresh air.
INGESTION	If conscious, give water or milk and induce vomiting.
SKIN	Wash with soap and water
EYES	Flush with plenty of water.
OTHER	

SECTION VII. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Sweep or scrape into container for proper disposal.

Flush contaminated areas with water.

WASTE DISPOSAL METHOD

Incineration or landfill under approved conditions.

SECTION VIII. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify Type)	Dust respirator. NIOSH approved.
PROTECTIVE CLOTHING	Impervious gloves.
EYE PROTECTION	Splash-proof goggles.
VENTILATION	General mechanical ventilation and local exhaust.

SECTION IX. SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING, STORING ETC.

CAUTION:

In accord with good industrial practice, handle with due care and avoid unnecessary personal contact.

For Manufacturing Use Only.

DATE: 7-1-75 SIGNATURE: _____

CAMELWITE®

Harry T. Campbell Sons, Inc.
Hunt Valley, Maryland

Finer than 44 Microns	—	—	—	99.5
30 Microns	—	—	—	99
25 Microns	—	99.7	99.7	96
20 Microns	—	96	86	83
12 Microns	99.9	90	60	68
10 Microns	95	78	48	62
8 Microns	85	70	40	59
7 Microns	78	65	36	50
5 Microns	67	50	28	42
4 Microns	59	42	20	36
3 Microns	50	33	15	29
2 Microns	36	20	10	22

Specific Gravity	2.70-2.71	2.70-2.71	2.70-2.71	2.70-2.71
One lb. bulk gallons	0.0443	0.0443	0.0443	0.0443
Wt. per Solid Gal. (lbs.)	22.57	22.57	22.57	22.57
pH of Saturated Sol.	9.5	9.5	9.5	9.5
Index of Refraction	1.6	1.6	1.6	1.6
Oil Absorption (cc/100g.) (Approx.)	15	14	10	13
Average Particle Dia. (Micron)	3.0	5.0	11.0	7.0
Particle Range (Micron)	0.3 to 12.0	0.3 to 25.0	0.4 to 25.0	0.3 to 44.0
Dry Brightness (Hunter Refl.) (Min.)	95	93	93	93
Bulk Density (Loose) lbs./cu.ft. (Approx.)	40	50	50	58
Solubility in water (%)	0.08	0.04	0.04	0.03
Mho Hardness	3.0	3.0	3.0	3.0

TITANIUM DIOXIDE*

R-900 (DuPont) or equivalent

Rutile Type

Uses: R-900 is designed for use gloss and semi-gloss enamal paints. It contributes high brightness and a blue-white undertone in paint formulation.

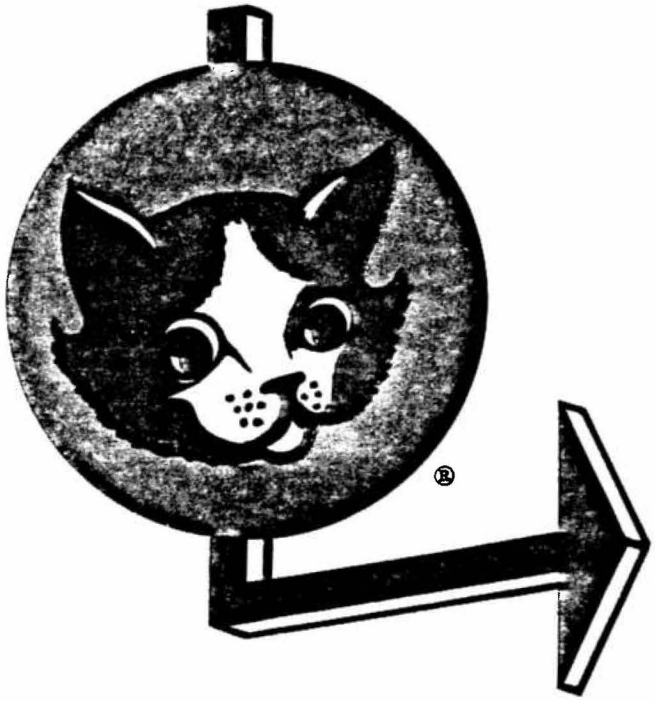
Typical Properties:

Specific Gravity	4.1
Lbs. per (solid Gallon)	34.3
1 lb. bulks (in gallons)	0.0291
TiO_2 %, dry basis, min	93
Oil Absorption, Spatula	19-22 (lb oil/100 lbs. pigment

Specification, ASTM D476, Type II

*E. I. DuPONT deNEMOURS & Co., Inc.
Chemicals, Dyes and Pigments Dept.
1007 Market Street
Wilmington, DE 19898

Information Bulletin Number 101



FOR REFLECTORIZED TRAFFIC MARKINGS

CATAPHOTE

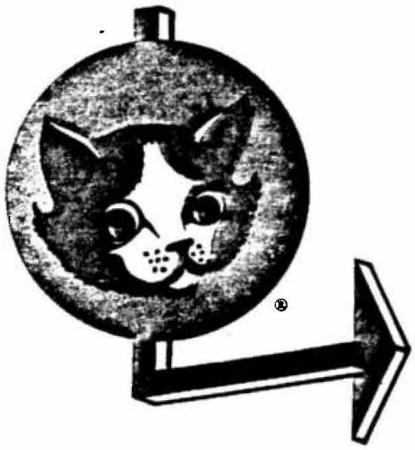
Pavement Marking Beads

Traffic stripes reflectorized with Cataphote glass beads stay brighter to provide that extra margin of nighttime safety. The life of traffic markings is increased as much as 50%. With pavement beads, lines are quicker drying, too.

CATAPHOTE DIVISION ® **FERRO CORPORATION**

(CALL COLLECT)

P. O. BOX 2369 / JACKSON, MISSISSIPPI 39205 PHONE 601-939-4612



CATAPHOTE

GLASS BEADS FOR REFLECTORIZING PAVEMENT MARKINGS.

Why use glass beads?

Increase visibility and safety at night.

Increase marking life by 50%.

Reduce drying time, tracking and traffic tie-ups.

Cataphote Glass Beads add nighttime visibility to traffic markings for increased safety and improved channeling of traffic. In addition to brilliant all-weather reflectance, the tiny beads used with traffic paint add up to 50% extra life to the marking, thus reducing frequency of restriping.

Use of beads with traffic paint also reduces drying time, tracking and traffic tie-ups. Cataphote Glass Beads for reflective pavement marking meet all U. S. Standard specifications.

METHODS OF REFLECTORIZING TRAFFIC MARKINGS

BEADS DROPPED ON PAINT

In drop-on application, wide gradation glass beads are spread on the surface of the wet marking by a bead dispenser attached to the striping machine. Dispensers which are available for all standard striping machines provide even, economical distribution of the beads. The glass beads, graded by U. S. Standard Sieves between 20 and 100 mesh size, penetrate and disperse through the wet paint. The glass spheres, embedded in the paint, act as retro-reflective lens that reflect rays of automobile headlights back to the driver, thus creating highly visible road markings. The larger diameter beads provide immediate nighttime reflectivity. As the paint thickness is reduced by traffic wear, the smaller diameter beads continue to provide reflectivity throughout the life of the line.

BEADS PRE-MIXED IN THE PAINT

Pre-mixed traffic paint, consisting of approximately five pounds of pre-mix type beads, intermixed in each gallon of bead-free paint binder, is applied with an ordinary striping machine.

Within two weeks the thin film of paint covering the top surface of the beads wears off to provide brilliant reflectorization of the marking.

COMBINATION METHOD

You can combine the advantages of both drop-on and pre-mix type Cataphote Glass Beads. Known as "in and on" application, pre-mix beads are applied **in** the paint through the striping machine and, in the same operation, drop-on beads are applied **on** the paint with a bead dispenser.

TYPES OF CATAPHOTE PAVEMENT MARKING BEADS

DROP-ON TRAFFIC BEADS (H-85)

Applied by a bead dispenser on any standard striping machine, crystal-clear Cataphote beads provide immediate reflectance and lower the paint drying time. Usual application is six pounds of Drop-on beads per gallon of paint binder.

Cataphote beads show no tendency toward decomposition and surface etching under atmospheric conditions, dilute acids, or alkalies and paint film constituents.

Refractive index range is between 1.50 and 1.60. Available in Plain or Waterproof* types.

PRE-MIX TRAFFIC BEADS (P-93)

This type of bead is intermixed with the traffic paint binder and applied with regular striping equipment.

About five pounds of P-93 Pre-mix beads are needed per gallon of bead-free paint.

When the thin film of paint covering the uppermost beads wears away (about 10 days depending on traffic), the stripe is reflective and resistant to weather and wear. Index of refraction is between 1.50 and 1.60. . . .there's no change in appearance in the daytime.

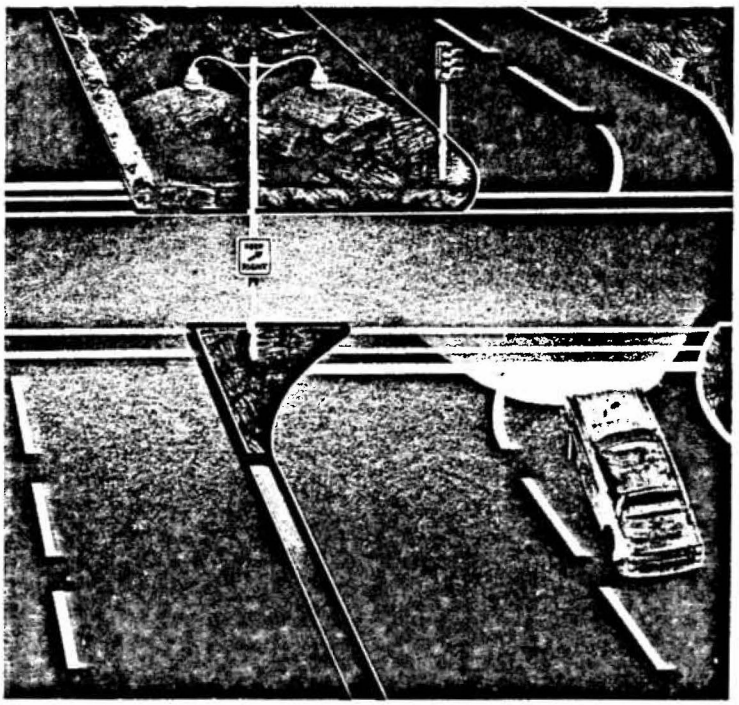
DROP-ON AIRPORT BEADS (FA-85)

Cataphote FA-85 beads are designed for reflectorization of the thicker film thicknesses normally applied to airport runways and taxiways. FA-85 beads are graded between 25 and 45 mesh sizes (U. S. Sieve). Twelve pounds of FA-85 beads are recommended for drop-on application with each gallon of striping paint. This higher application rate provides the increased reflectivity necessary for aircraft landing at night. Refractive index is 1.50. Available in Plain or Waterproof types.

BISYMMETRIC BEADS

These specially coated beads float to their diameter in wet paint lines rather than sinking completely into the paint. As a result, a greater percentage of the spheres are available for immediate reflectorization.

Bisymmetric beads, because of their high concentration in the upper portion of the paint line, provide somewhat reduced reflectivity as the paint line is reduced in thickness by traffic wear.



FEDERAL SPECIFICATION BEADS (TT-B 1325-A)

Federal specifications for pavement marking beads.

Cataphote annually supplies thousands of pounds of beads for usage by the U. S. Government and other agencies requiring federal specification beads:

Type I ..... 1.50 Refractive Index
Type II ..... 1.65 Refractive Index
Type III..... 1.90 Refractive Index

* Waterproof beads have a molecular film (which becomes a permanent part of the bead) applied to the outer surface to prevent clotting or "clumping" before and during bead application. Waterproofing also tends to maintain reflectivity of the beads during wet weather.

SPECIFICATIONS

PAVEMENT MARKING GLASS BEADS TYPE H-85 WP WATERPROOF FOR PAVEMENT MARKING

GENERAL

This specification is intended to cover free flowing glass beads for application on traffic paint for the production of a reflective surface creating night visibility of the painted markings without altering day visibility of the markings.

The beads are manufactured from high grade optical crown glass of a composition designed to be highly resistant to traffic wear and to the effect of weathering.

The spheres are completely waterproofed by application of a molecular film to the outer surfaces of the spheres, which prevents clotting before and during application, and also tends to prevent "blanking out" in wet weather. The film is applied at 400°F. and becomes a permanent part of the sphere itself.

WATERPROOF PAVEMENT BEADS DROP-ON TYPE

SPHERICAL BEAD CONTENT:
The beads contain not less than seventy (70) percent spherical particles on each sieve size and seventy-five (75) percent true spheres overall, when tested with ASTM D-1155-53. They are reasonably free of sharp angular particles showing milkiness or scoring or scratching, the quantity of which does not exceed two (2) percent, and foreign matter, the quantity of which does not exceed nine-tenths (9/10) percent.

REFRACTIVE INDEX:
The beads, when tested by the liquid immersion method at 25°C. show an index of refraction not less than 1.50. The beads do not show any tendency toward decomposition, including surface etching, when exposed to atmospheric conditions, moisture, dilute acids, or alkalies or paint film constituents. The beads are crystal in color and free from all surface film. They are corrected to prevent their imparting any noticeable daytime hue to the paint film.

SIEVE ANALYSIS:
The beads meet the following gradation requirements, when tested in accordance with ASTM Method of Test D 1214-54 "Method of Test for Sieve Analysis of Glass Spheres".

U. S. Standard Sieve		Min.	Max.
Passing #20	Retained #30	10	20
Passing #30	Retained #50	30	75
Passing #50	Retained #80	9	32
Passing #80		0	15

MOISTURE RESISTANCE TEST:
Place a 300-gram portion of the air-dry sample in a 300-ml. Erlenmeyer flask; add 5 drops of water from a pipette calibrated to produce 20 drops per ml. (± drop); stopper the flask immediately and shake the flask and its contents vigorously for at least one minute; remove the stopper and connect the flask mouth-to-mouth to another air-dry flask of the same size in hour-glass fashion, by means of stoppers joined by a short glass tube having an inside diameter of ¼ inch; invert the assembly and observe the flow qualities of the beads.

The beads shall then flow continuously into the lower flask until the upper flask is emptied. The flask may be gently tapped to initially start the flow of beads, after which the beads shall flow continuously without further agitation.

If, after three trials, the beads fail to flow continuously, the sample shall be reported as not having acceptable flow qualities. A small quantity of beads sticking to the sides of the flask shall not be cause for rejection.

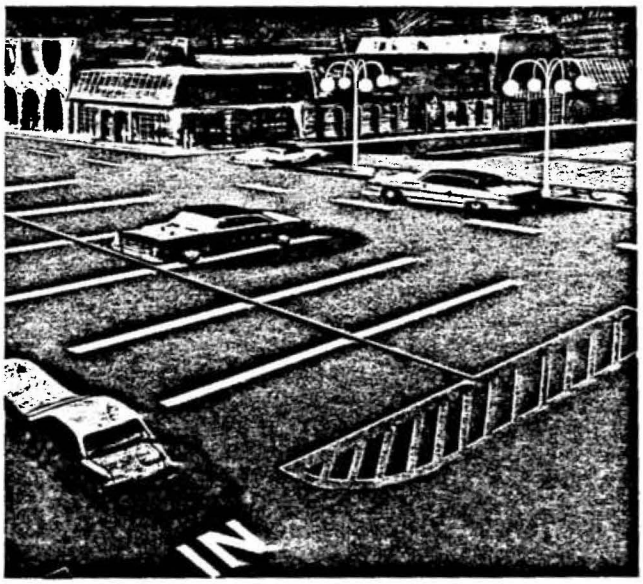
PACKAGING (H-85 WP)

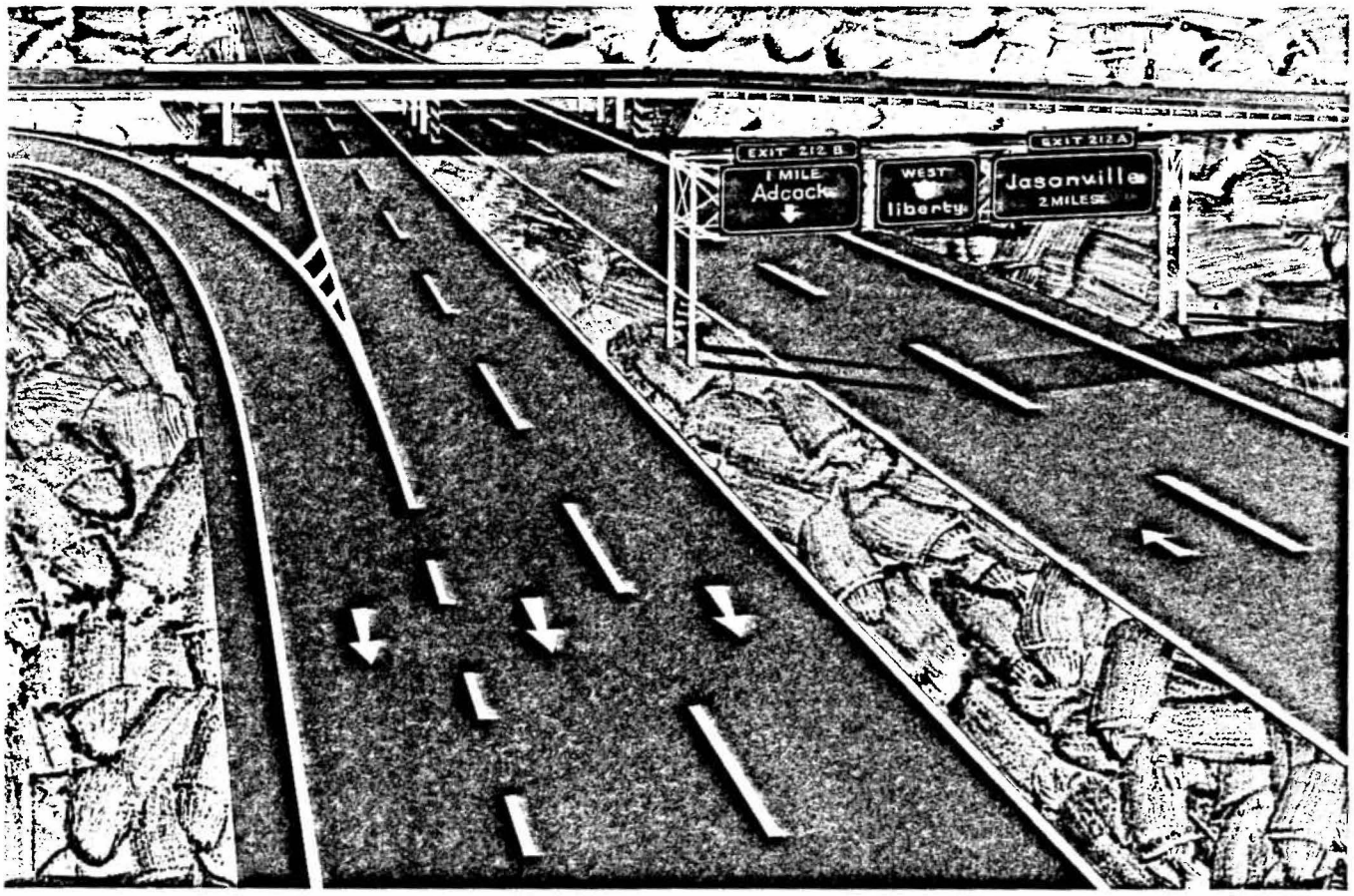
The beads are furnished in clean containers of uniform size. All containers are of the type that the beads will not be lost through normal package failure, and all containers meet I. C. C. requirements for strength and type. All containers, or bags are of the type known as "Moisture-proof."

Cataphote Corporation standard bags are composed of multiple plys of natural kraft paper and asphalt or polyethylene laminations. Other composition bags including burlap are available at premiums varying with composition and/or availability.

SUMMARY

The effectiveness of reflective glass beads is dependent upon both the quality and film thickness of the paint binder. The bead binder must contain a high degree of pigmentation if the bead is to adequately return the true color of the paint. A poorly pigmented paint will appear bleached or less reflective at night. A paint line, for optimum wear and reflectivity, should be at least ten mils thick when dry and should have reflective beads of varying diameters dispersed throughout the film thickness. The various diameter beads, such as Cataphote's H-85 WP, provide not only initial reflectivity but reflectivity through the life of the painted line.





APPENDIX C

TENTATIVE MANUFACTURING PROCESS FOR ETP TRAFFIC MARKING PAINT - WHITE FORMULATION

May 28, 1981

Project No. 03G-C5347-01

MANUFACTURING PROCESS FOR

EPOXY THERMOPLASTIC HIGHWAY MARKING PAINT

WHITE FORMULATION

Prepared for

Lloyd M. Smith, Ph.D.
U. S. Department of Transportation
Federal Highway Administration
Washington, D. C. 20590

Under Contract No. DTDFH 61-80-C00041

Written by: S. W. Osborn

1. EQUIPMENT USED

1. Batch Weighing Scale.

2. Heated blending tank, 500 gallon (1900 liter), stainless steel, jacketed, capable of being heated to 350°F-continuous basis. Five HP (3.728 KW) propeller type agitator fitted with 2 or 3 flights of blades for efficient top to bottom mixing of a viscous product. Closed top. No pressure requirement. (Note 1)

3. Drum hoist for charging the blending tank.

4. Safety equipment, including face masks, thermal protective gloves and protective coveralls for casting the heated ETP product.

Note 1: In these runs, a 500 gallon (1900 liter)Fiberglass/Polyester tank was used with a KW bayonette type electric immersion heater. With efficient mixing, this equipment worked extremely well. However, care must be taken during casting of the product to turn off heater as the batch level drops, and to cast the final 100 gallons (380 liters) quickly before the product cools.

2. RAW MATERIALS

Description	Ref.	Parts by Wt.	Wt. Lbs.(kg)
Charge			
Epoxy Resin, Solid (727.3)	1	60	1600
Epoxy Resin, Liquid (485.0)	2	40	1067
Calcium Carbonate (242.7)	3	20	534
Titanium Dioxide (242.7)	4	20	534
Glass Beads (339.5)	5	28	747
Recover			
ETP Highway Marking Paint, (1936.4 (355 gallons)	6		4260

References

1. Araldite 7097, Ciba Geigy Corp., Ardsley, N. Y.
2. Araldite 6010, Ciba Geigy Corp., Ardsley, N. Y.
3. Camelwite, Harry T. Campbell Sons, Inc., Hunt Valley, Md.
4. Pigment Grade, R-900, E. I. duPont Corp., Wilmington, Del.
5. Premix Grade, Reflective Glass Beads, Cataphote Divison, Ferro Corp., Jackson, Miss.
6. Basis, 95% recovery of product, average, for an 11 batch run. May be slightly higher in a longer production run. Losses include samples for laboratory testing and retention.

3. PROCESS IN DETAIL

1. Pre-weigh all materials.

2. Preheat pigment, filler, glass beads, in bags to 250°F (121°C) in an oven for several hours to minimize batch cooling during the blending operation.

3. Charge liquid epoxy resin and heat the resin, with good agitation to 300°F. ( ).

4. When batch reaches 250°F (121°C), charging of pre-weighted solid epoxy resin can start, charging is continued at a slow rate until charge is complete. Care must be taken to feed the solid resin slowly to avoid viscosity build up, or gelation. Addition of solid requires 1 - 1.5 hrs. After charge is complete, bottom reactor valve is flushed thoroughly to insure complete mixing of resins.

5. Heated calcium carbonate is transferred to a tilting drum hoist and added slowly and steadily to the batch during 20-30 minutes at a rate that allows thorough mixing without formation of lumps. Batch temperature is maintained in the range of 250-300°F (121-148°C).

6. Titanium Dioxide (pigment) is added in the same manner - but more slowly, to avoid formation of lumps. Addition requires 30-50 minutes.

7. Batch is held, with stirring, until it is free of visible lumps. Bottom tank valve is flushed thoroughly to ensure complete mixing.

8. With the batch temperature at 300°F (148°C), charge the glass beads slowly and steadily during 30-35 minutes. Avoid large quantities because of the tendency of beads to settle.

9. Recyle at least 25 gallons (95 liters) of the batch from bottom part and continue to stir until all visible lumps are gone.

10. Cast the batch into 2 gallons (17.6 liters), silicone lined, fiberboard containers (approximately 25 lbs (11.4 kg)/box) and cool under a silicone treated release paper until solid.

11. During the casting process, three samples are taken for viscosity determination. Sample near the beginning, middle and end of the cast. Viscosity of the three samples should agree within 5% when measured at 232°F (111°C), 20 RPM.

12. The liquid epoxy resin for the following batch can be charged to the reactor to initiate the next cycle.