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The Dow Chemical Company

SYNTHESIS AND CHARACTERIZATION OF MODEL POLYMERS FOR
USE IN THE INVESTIGATION OF CHAR FORMING HEAT SHIELDS

NUMBER 1

STATUS REPORT

JANUARY 1965

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ELEMENT ONE - EPOXY RESINS

Researchers: R. L. Carlyle
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Problem No.: 7504

January Objectives:

Obtain all starting materials including epoxy novolac resin, Nadic methyl anhydride and necessary catalysts. Begin chemical and physical characterization of the monomers and polymers. Fabricate molds and have first lot of billets ready by the month's end.

Summary:

Large lots of both D.E.N. 438 epoxy novolac resin and Nadic methyl anhydride (NMA) were obtained. Sufficient amounts of DMP-30 and benzyl dimethyl amine catalysts were obtained. The greater part of analytical results on the D.E.N. 438 and NMA have been obtained. Molds were fabricated to mold 1-1/2" by 6" sample billets. Phase I was completed with the molding of D.E.N. 438/NMA billets in the three ratios 1/0.75, 1/0.85, and 1/0.95 equivalents D.E.N. 438 per equivalent NMA. The billets are ready for shipment. Work is progressing on obtaining physical and chemical analytical results to aid in characterizing the cured polymer. General physical properties were obtained on the Phase I billet formulations.

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Discussion:

1. Analytical results were obtained on the monomers as follows:

Analytical Results

	<u>Lot No. 12094</u> <u>D.E.N. 438</u>	<u>Nadic Methyl</u> <u>Anhydride</u>
Percent Epoxide	24.2	--
Gardner Color	1	--
Brookfield Viscosity, 125°F	53,400 cps	--
Ostwald tube Viscosity	50°C - 35,980 cps	15.6°C - 423 cps
Ostwald Tube Viscosity	65°C - 4,570 cps	25°C - 172 cps
Ostwald Tube Viscosity	75°C - 1.630 cps	50°C - 32 cps
Percent Lights	0.2	--
Molecular Weight	680	182 (178 Theor.)
Water, ppm	155	--
Specific Gravity	1.231	--
Durrant Softening Point	31°C	--
Metals		
Iron, ppm	0.3	0.2
Aluminum, ppm	2.0	2.5
Calcium, ppm	11.0	4.0
CHOH		
Carbon, %	73.34	66.54 (Theor. 67.45)
Hydrogen, %	6.30	5.57 (" 5.62)
Oxygen, %	20.34	26.92 (" 26.96)
Nitrogen, %	-	-
Hydrolyzable Chloride, %	0.06	-
Refractive Index	1.5962	1.5045

2. Preparation of Billets and Cured Resin Samples

The following mixing and molding procedure was used:

1. Heat resin to 60°C under nitrogen purge.
2. Add Nadic methyl anhydride and mix 15 minutes.
3. Add Catalyst and mix 30-40 minutes.
4. Deaerate with vacuum for 5 minutes.
5. Pour into mold preheated to 105°C)
6. Cure 4 hours at 105°C) under nitrogen seal
7. Cure 16 hours at 200°C)
8. Cool to room temperature)
9. Remove from molds and store in nitrogen purged triple tight metal cans.

3. Recipes chosen for the first sample series are:

<u>Sample No.</u>	<u>1A</u>	<u>1B</u>	<u>1C</u>
D.E.N. 438 parts by wt.	100	100	100
Nadic methyl anhydride parts by wt.	75	85	95
DMP-30 parts by wt.	1.5	1.5	1.5

4. A partial list of the physical properties measured on these recipes follows:

	1A	1B	1C
Heat distortion temp., °F	360	403	352
Flexural strength, psi	11,500	13,000	15,280
Compressive yield strength, psi	19,630	20,640	20,510
Tensile Strength, psi	3,410	3,960	4,440
Izod impact-ft.-lb./Inch of notch	0.19	0.22	0.19
Rockwell "M" hardness	117	122	123

5. Chemical and physical testing will continue. A more complete list of properties for the three recipes will be forwarded as soon as possible. The anhydride and D.E.N. 438 epoxy resin should be completely characterized by about March 1. Accelerator or catalyst materials will be characterized as time permits.
6. Synthesis studies for the para tertiary butyl adduct of D.E.N. 438 are not yet completed. This work will continue through February.
7. In response to the request for a resume' of the analytical and physical properties tests that will be used for characterization work on this project, the following list is provided:

Analytical results requested on D.E.N. 438

Viscosity curve
 Durran softening point
 Total % OH
 Phenolic OH
 Total chloride
 Inorganic chloride
 % C, H, O, N.
 Quantitative on metals
 Infrared scan

Analytical results requested on Nadic Methyl Anhydride (NMA)

Molecular weight	Free acid	Total chloride
Viscosity curve	Unsaturation	Purity by hydrolysis
Sp. Gr. 25°C	% C, H, O, N	Quantitative on meta.
Water	Inorganic chloride	Infrared scan

Analytical results requested on catalyst

DMP-30	Infrared scan
BDMA	Infrared scan

Analytical results to be requested on catalysts

Water
 Percent lights
 Primary and secondary amines
 Phenol content

Analytical results to be requested on cured resins

Reflectance infrared

Nujol Mull infrared

Infrared on resin cured between salt plates

Mold release penetration into sample

Method: Remove outer 5 mils

Remove 2nd 5 mils

Obtain material from interior of sample

Mold sample without mold release

Compare for fluoride by

Nujol Mull I.R.

Mass spec on pyrolyzed sample

Chemical analysis (probably too

insensitive for low concentrations)

Sol-gel ratio

Peak exotherm during cure

Physical properties of cured resins at room temperature

Tensile strength

Compressive yield strength

Flexural strength

Izod impact

Rockwell hardness

8. The following list shows specific techniques or methods used for some of these tests:

Chemical and Physical Methods

Percent Epoxide	HBr titration method or Pyridine HCl reflux method
Percent Lights	150°C at 10 mm Hg for one hour
Molecular Weight	Ebullioscopic (boiling point in dioxane)
Water	Fischer water titration
Metals	
Iron	Emission spectroscopy
Aluminum	" "
Calcium	" "
CHON	
Carbon	Pregl method
Hydrogen	" "
Oxygen	Modified Unterzaucher Method
Nitrogen	Kjeldahl Method
Hydrolyzable Chloride	Caustic-solvent reflux-AgNO ₃ potentiometric titration

Physical Properties

Heat distortion temperature [*]	ASTM D-648-56 (264 psi)
Flexural Strength	ASTM D-790-58T
Compressive Yield Strength	ASTM D-695-54
Tensile Strength	ASTM D-638-60
Izod Impact	ASTM D-256-56
Rockwell "M" Hardness	ASTM D-785-60

^{*} Recipe used for Heat Distortion Measurement (Standard)

Mixture	D.E.N. 438	-	100 parts
	MDA	-	28 parts
Cure	2 Hours	-	93°C
	4-1/2 Hrs.	-	204°C

MDA = Methylene Dianiline

Heat Distortion Temperature for Lot No. 12094 D.E.N. 438 =
429.8°F

9. As agreed the outer surface of the three samples (six billets) were machined away.

February Objectives:

1. Preparation of 30 to 40 pound/cu.ft. density foams from D.E.N. 438/Nadic methyl anhydride will be examined to determine feasibility.
2. Techniques will be established for conducting sol/gel studies of the cured epoxy systems.

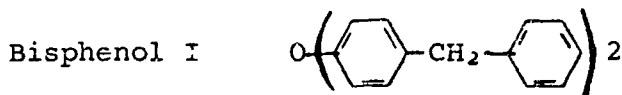
ELEMENT THREE - PHENOLICS

Researchers: L. F. Sonnabend Problem No.: 0299069107
 R. Y. Wen

January Objectives:

1. Preparation of Bisphenol I, a mixture of 2,2'-2,4'- and 4,4'-isomers.

2. Preparation of 2,2'-isomer of Bisphenol I.



Summary:

1. Mixture of isomeric Bisphenol I was prepared from excess phenol and diCMDPO. Work has begun in isolation of the three isomers by thin-layer chromatography.
2. The starting material, ethyl p-hydroxybenzoate, for the synthesis of the 2,2'-isomer of bisphenol I was prepared.

Discussion:

Oda, et al. CA. 60, 11926 c (1964) reported the synthesis of the 4,4'-isomer of Bisphenol I. Attempts will be made to prepare sufficient quantity of this isomer for the synthesis of polymer.

The preparation of finished billets is not scheduled for this phase of the program. As shown in the time schedule contained in the contract proposal, preparation of billets begins after the fourth month, or about the end of April.

February Objectives:

1. Synthesis of 4,4'-isomer of Bisphenol I.
 2. N.M.R. study on isomers isolated by TLC.
 3. Synthesis of methylol derivatives from the 4,4'-isomer and the mixture of Bisphenol I.
-

Schedule:

In response to ARTICLE II - REPORTS, page 3 of Contract NAS7-344, which requires that a schedule of man hours versus time be provided, a revised copy of the man time estimated for the Epoxy Element is attached (see following page).

JOB TITLE

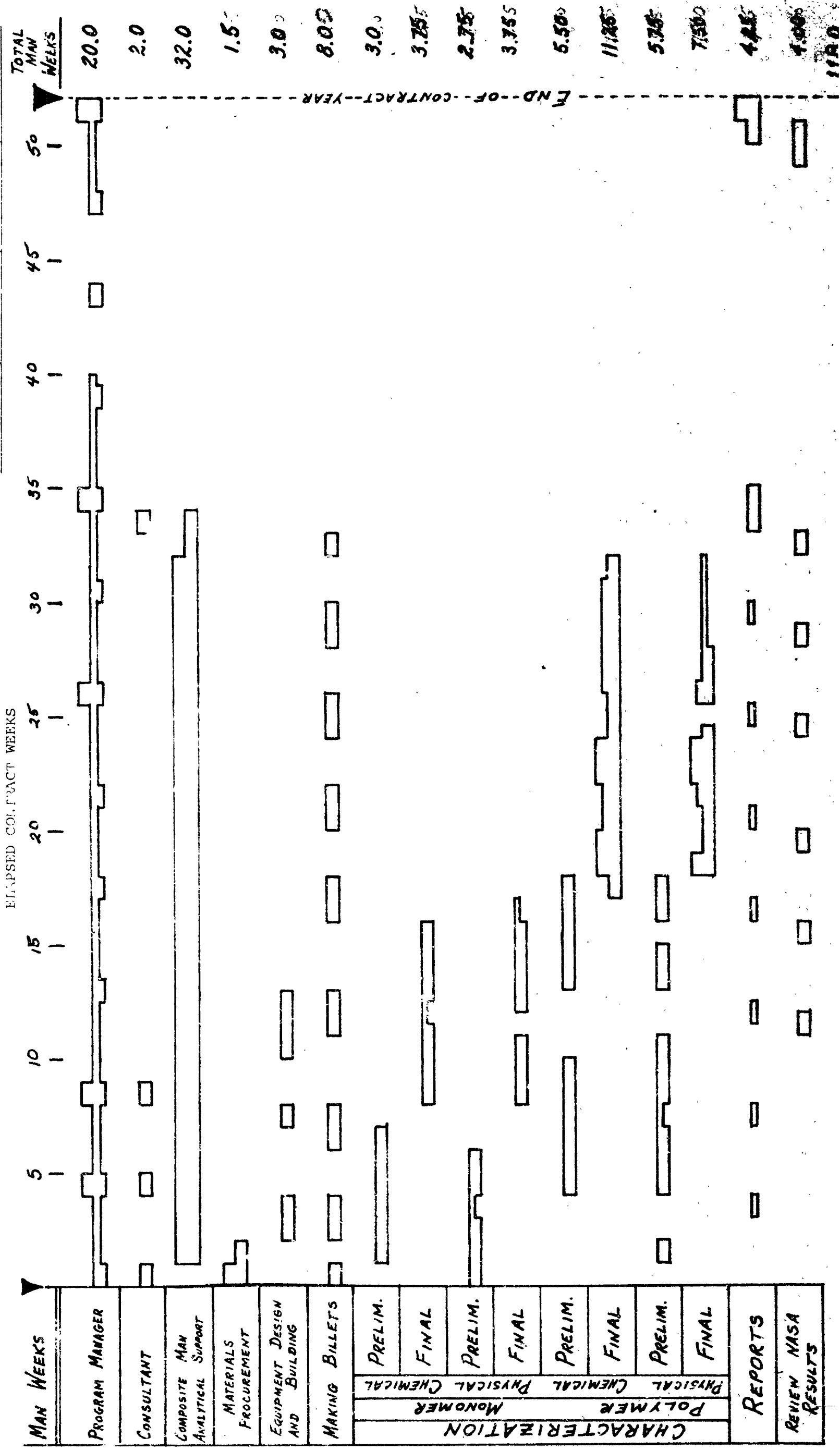
CHAR FORMING HEAT SHIELD POLYMERS

Work done by (or for) (other than technical)

ELEMENT ONE - EPOXY RESINS

CHARGE BY CHECKED APPROVED

7504 E.L.P.



END-OF-CONTRACT-YEAR

The original man time schedule for the Phenolics Element is correct as it was originally submitted when the cross-hatched areas are not counted (see original proposal.)

Respectfully submitted,



Elmer L. Pendleton
Program Manager

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