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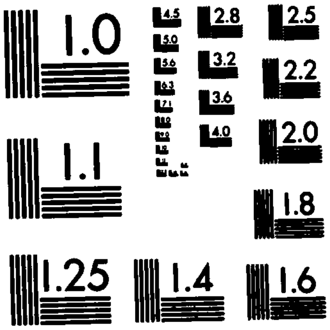

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Properties of Polyester Resins for Fiberglass Reinforced Soil Surfacings

by
A. L. Woodman
and
D. W. Moore
Research Department

NOVEMBER 1982

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

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Naval Weapons Center

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FOREWORD

The testing of polyester resins, to be used for a fiberglass reinforced plastic soil surfacing material program, was authorized by Marine Corps RDT&E Work Directive No. C0079, Program Element 62706N, and was carried out between November 1980 and August 1982. This is a final report describing the testing of the polyester resins.

This report was reviewed for technical accuracy by Eugene C. Martin.

Approved by
E. B. ROYCE, *Head*
Research Department
25 October 1982

Under authority of
J. J. LAHR
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Commander

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(U) *Properties of Polyester Resins for Fiberglass Reinforced Plastic Soil Surfacings*, by A. L. Woodman and D. W. Moore. China Lake, Calif., Naval Weapons Center, November 1982. 44 pp. (NWC TP 6406, publication UNCLASSIFIED.)

(U) A Marine Corps chemical formulation developed for the construction of fiberglass reinforced plastic soil surfacings consists of a polyester resin, a catalyst, and a promoter solution. The baseline properties of the currently used polyester resin, a sole source item, were measured. Two other resins were then obtained for evaluation as possible alternates to the original resin. Even though there are significant chemical differences, both resins appear to be acceptable for this application. One resin has somewhat longer gel times than desired, but this could possibly be remedied by lowering the inhibitor content slightly. Preparation of test pads would be the next step in the resin evaluation.

CONTENTS

ACKNOWLEDGMENT

The authors would like to acknowledge the support and encouragement given during this program by Mr. M. C. Hironaka of the Naval Civil Engineering Laboratory, Port Hueneme, California.

INTRODUCTION

A fiberglass reinforced plastic (FRP) soil surfacing material has been developed by the Naval Civil Engineering Laboratory (NCEL), Port Hueneme, California, to fulfill a need of the Marine Corps for a composite system which will withstand vehicular and aircraft traffic.[1,2] This system is comprised of a fiberglass matting which is spread on the ground, then sprayed with a catalyzed polyester resin which cures to form a tough, semi-flexible surface.

In addition, this FRP is being considered for making rapid runway repairs. For this purpose, large composite patches could be manufactured and stockpiled or the patches could be prepared in place.

At the present time, the resin is a sole source item designated as RS50338 by PPG Industries, Inc. (PPG). It is quite feasible that the manufacture of this resin could be discontinued or that in time of emergency the resin could be in short supply. Thus, an attempt is now being made to acquire alternate sources of suitable resins. More favorable resin prices probably would result from having several acceptable resin suppliers.

The polymer system consists of a polyester resin, a peroxide catalyst (cumene hydroperoxide, CHP), and a two-part, premixed promoter solution. The promoter consists of equal parts of N,N-dimethyl-p-toluidine and a xylene solution of vanadium trineodecanoate. The ratio of promoter to catalyst is maintained at a constant ratio of 1:4.[1] The amount of catalyst and promoter added to the resin is adjusted for various temperature conditions to give gel times in the range of 10-20 minutes.

In addition to the above requirements for the polymer system, the components should have a minimum shelf life of 5 years, and the flexural

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[1] Civil Engineering Laboratory. *Improved Chemicals for Fiberglass Reinforced Plastic Soil Surfacings - Field Evaluation*, by M. C. Hironaka. Port Hueneme, Calif., CEL, September 1978. 25 pp. (TN No. N-1527, publication UNCLASSIFIED.)

[2] Dow Chemical USA. *Fabrication of Fiberglass Reinforced Plastic Surfacing Under Wet Conditions*, by T. J. West. Walnut Creek, Calif., Dow Chemical USA, September 1978. 69 pp. (CR78.018, publication UNCLASSIFIED.)

strength of the cured laminate must be a minimum of 28,000 psi.[2] The resin system must be usable over the temperature range of 4.4-49°C (40-120°F) and must cure properly even in the presence of water. Moreover, the resin viscosity can only be a maximum of 1,600 centipoise (cp) which is the upper limit of material that can be pumped through the spray equipment being used by the Marine Corps.[1]

In this program, baseline properties were obtained for the resin received from PPG. These data were then used to formulate specifications which were submitted to nine polyester resin manufacturers (Appendix A). Two of these suppliers responded with resin samples for testing. This report gives the results of the original baseline property testing and the testing of the two candidate resins.

EXPERIMENTAL

MATERIALS

The resin used for the baseline property measurements was obtained from PPG Industries, Inc., Pittsburgh, Pennsylvania, in July, 1981, and was labeled RS50338, Batch 45419. The sample used in this study was part of a 10,000 lb order obtained by NCEL. RS50338 contains the PPG resin, Selectron SR3704, plus 400 ppm of 2,4-dinitrophenol and 200 ppm of p-toluhydroquinone. The large amounts of inhibitors are present to increase the resin shelf life to 5 years.[3]

Two resin samples were received later in the program for comparison with the PPG resin. One was obtained from Freeman Chemical Corp., Port Washington, Wisconsin, and was labeled Developmental Stypol XP40-A273-89/Batch A307-55. The other, which came from Reichhold Chemicals, Inc., Azusa, California, was called AZ-7809-Polylite, F3, T-42, RED.

Cumene hydroperoxide (CHP) (technical grade) was obtained from Thalco Corp., Los Angeles, California, in April 1981.

N,N-Dimethyl-p-toluidine (DMT) (technical grade) was purchased from RSA Corp., Ardsley, New York, in 1981.

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[3] Dow Chemical Company. *Improved Chemical Components for Formulating Fiberglass-Reinforced Plastic Soil Surfacing*, by S. S. Drake, H. E. Filter, and D. L. Stevens. Midland, Mich., Dow Chemical Company, May 1977. 49 pp. (CR77.0017, publication UNCLASSIFIED.)

Vanadium trineodecanoate solution was made at the Naval Ordnance Station, Indian Head, Maryland, under contract to NCEL by the method developed at the Naval Weapons Center.[4]

The fiberglass mat, Fabmat C-4020, is manufactured by Fiberglass Industries and was obtained from NCEL.

The promoter solution, consisting of a 1:1 (by weight or volume) mixture of DMT and vanadium trineodecanoate solution, was prepared at various times as needed throughout the program. There is no apparent short-term storage problem with the mixture.

TEST PROCEDURES

Viscosity

A Haake Rotovisco was used with the MV-I system over a shear rate range of 8-1370 sec^{-1}. There was some indication of a slight dependence of viscosity on shear rate, but the viscosities over the whole shear rate range were averaged.

Gel Time and Time to Maximum Temperature

The only difference in the gel time procedure used in this program and that previously described in detail[4] is that a new Tecam gelation timer which reads to 0.1 minute was employed. Briefly, a 100 g sample of resin was used with various amounts of promoter and catalyst. The ratio of catalyst to promoter was always maintained at 4:1 (by weight) however. A period of one minute elapsed between addition of the CHP and the start of the gel timer; this one minute has not been added to the gel time or time to maximum temperature.

The time to maximum temperature was measured at the same time as the gel time. A thermocouple immersed in the resin mixture was used to monitor the temperature changes. Generally, the time to maximum temperature was 1.5-1.9 times the gel time.

Hardness of Polymer Samples

A Barcol Hardness Tester was used to obtain the hardness of each of the polymer samples obtained from the gel time experiments and of the laminates. Since most of the gel time polymers were highly fractured,

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[4] Naval Weapons Center. *Vanadium Trineodecanoate Promoter for Fiberglass-Polyester Soil Surfacings*, by A. L. Woodman and others. China Lake, Calif., NWC, June 1980. 26 pp. (NWC TP 6184, publication UNCLASSIFIED.)

reliable values were difficult to obtain. However, the hardness values did not vary appreciably except for the polymers from Freeman Chemical Corp. which gave generally slightly lower values.

Density

Resin densities at 30°C (86°F) were obtained with a 10 ml pycnometer. The densities of the PPG resin over the temperature range of 0-50°C (32-122°F) were then determined with a dilatometer.

Accelerated Shelf Life

The room temperature shelf life of each resin was determined by following the viscosity increase of resin samples at various elevated temperatures. Samples of resin (50-55 ml) were stored in 2-oz bottles in an oven for varying periods of time, after which the resin viscosity was determined at 25°C (77°F). Since a resin with a viscosity greater than about 1,600 cp is not acceptable and since this resin system must be usable at temperatures down to 4.4°C (40°F), the shelf life was defined as the number of hours to reach 1,600 cp at 4.4°C. This corresponds to about 350 cp at 25°C for the PPG and Reichhold resins and about 300 cp for the Freeman resin.

Preparation and Flexural Strength of Laminates

Two-ply laminates were prepared by the procedure previously given in detail[4] to provide samples for flexural strength determinations. The laminates were either 23x30 cm (9x12 in) or 20x23 cm (8x9 in) with two layers of fiberglass mat, Fabmat C-4020.

In order to simulate adverse weather conditions, laminates were also prepared starting with fiberglass mats saturated with water. The catalyzed and promoted resin was added and rolled in as before. Laminates made under wet conditions were milky white in appearance in contrast to the transparent yellow-brown color of the polymer cured under dry conditions.

Flexural strengths were determined according to ASTM D790-71 using a 3-point bend apparatus in an Instron testing machine. Specimens were 13 mm wide by 127 mm long by 6 mm thick (0.5x5x0.25 inch), and the supports were 86 mm (3.4 inches) apart. The strips were always tested with the woven side of the mat down. Each flexural strength is the average of 6-9 determinations.

Determination of Styrene Monomer Concentration

Nuclear magnetic resonance (NMR) spectroscopy was used to estimate the concentration of unpolymerized styrene monomer in each resin formulation. Both proton and carbon-13 spectra provided a straightforward means for identifying the monomer and determining its concentration relative to other components of the resin. A Varian XL-100-15 NMR spectrometer equipped with a Nicolet TT-100 Fourier transform data system was used at 100.1 or 25.1 MHz for the two nuclei.

Figure 1 is a typical proton NMR spectrum of RS50338. It shows the characteristic signals of aromatic, olefinic, and aliphatic protons which are present in the unpolymerized mixture. The integrated area under each peak is a direct measure of the relative concentration of the corresponding proton species. The integral of the pair of doublets at 5.70 δ which arise from one of the vinyl group protons was taken to be proportional to the styrene monomer concentration. A standard addition technique is used to determine the actual styrene concentration.

The carbon-13 spectrum of the same material (Figure 2) requires a larger sample and a longer data-averaging time, but it yields more sharply resolved spectra including signals of nonprotonated carbon atoms, thus providing a more detailed picture of the molecular structures present. In order to estimate monomer concentration, a similar standard-addition method is used and results are comparable. The integral value of the vinylic methylene carbon is measured relative to the methyl carbon of the ester. (Subsequent measurements on formulations using different types of unsaturated esters required selection of a different reference peak.)

The detailed procedures are given in Appendix B.

RESULTS AND DISCUSSION

As mentioned previously, all of the testing of the PPG resin was carried out to obtain baseline properties. The two resins from other manufacturers were then obtained and evaluated to determine whether they perform at least as well as the PPG resin. The most critical areas for soil surfacing applications are the gel times as a function of CHP concentration and temperature, viscosity, shelf life, and the flexural strength of the laminates. Other properties were measured also in order to better characterize the resins.

The gel time as a function of amount of CHP added was measured over the temperature range of 0-50°C. Results for the three resins at 0, 25, and 50°C are shown in Figure 3. In addition, these results and additional ones for RS50338 at 10°C (50°F) and 38°C (100°F) are shown in Table 1; the gel times for each individual sample are shown in Appendix C. We

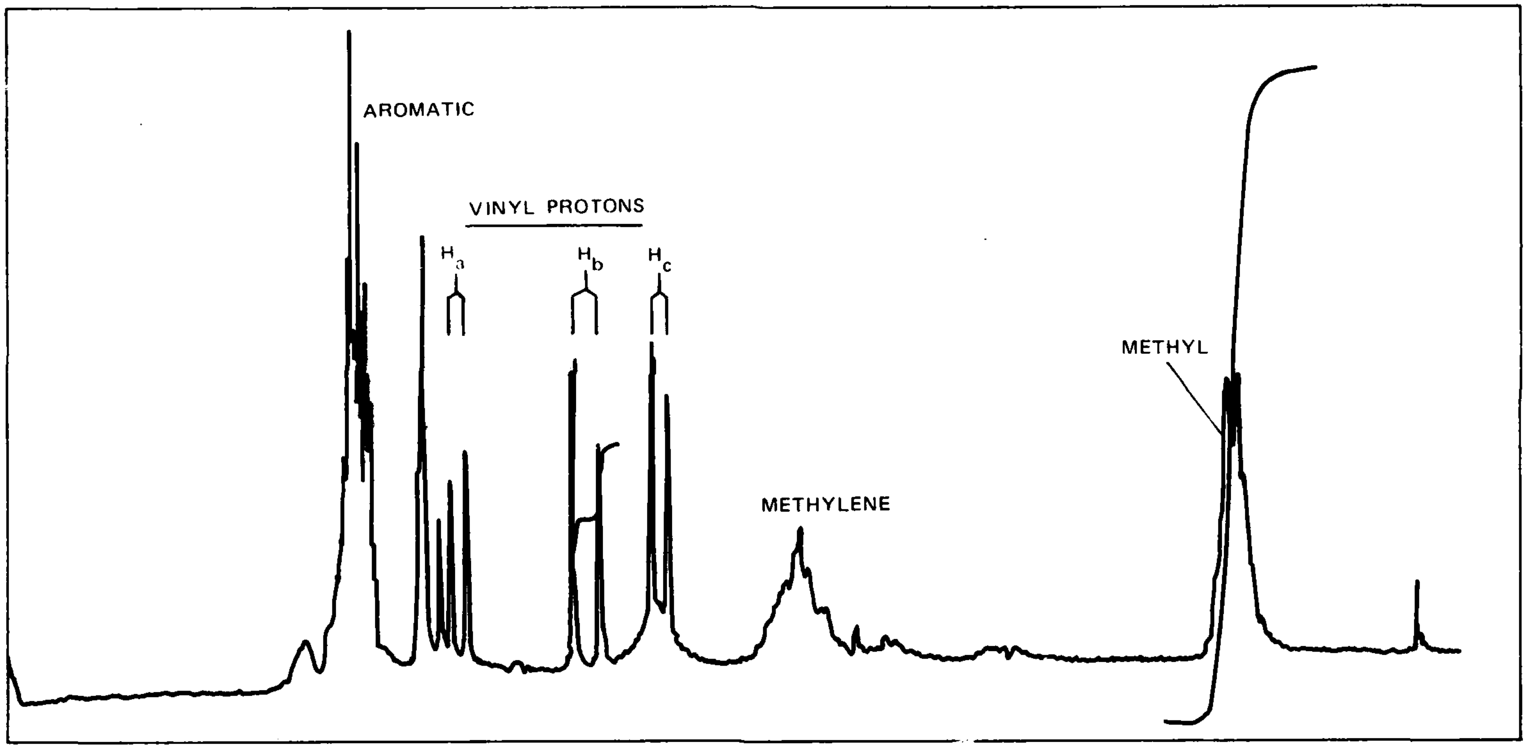

FIGURE 1. NMR Proton Spectrum of PPG Resin.

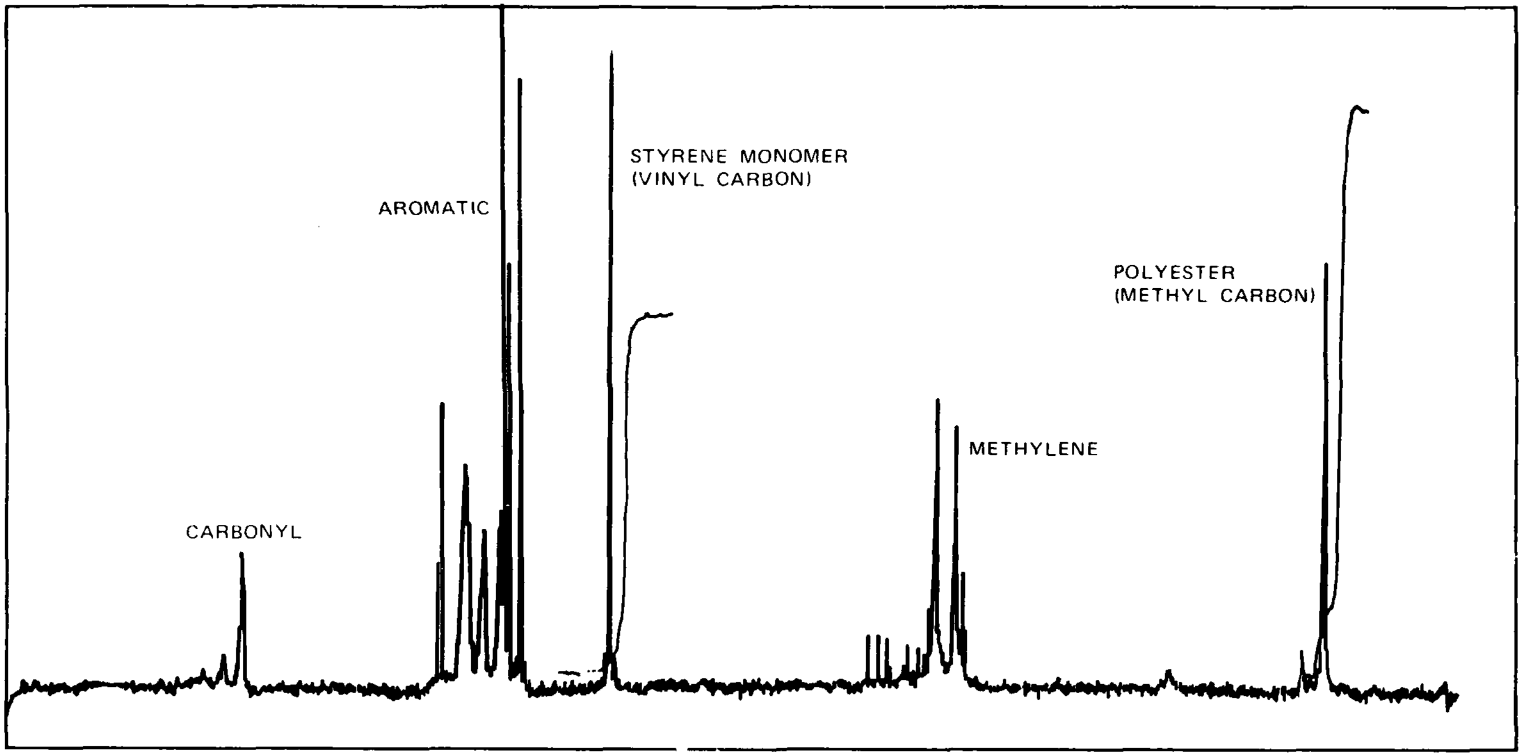

FIGURE 2. NMR Carbon-13 Spectrum of PPG Resin.

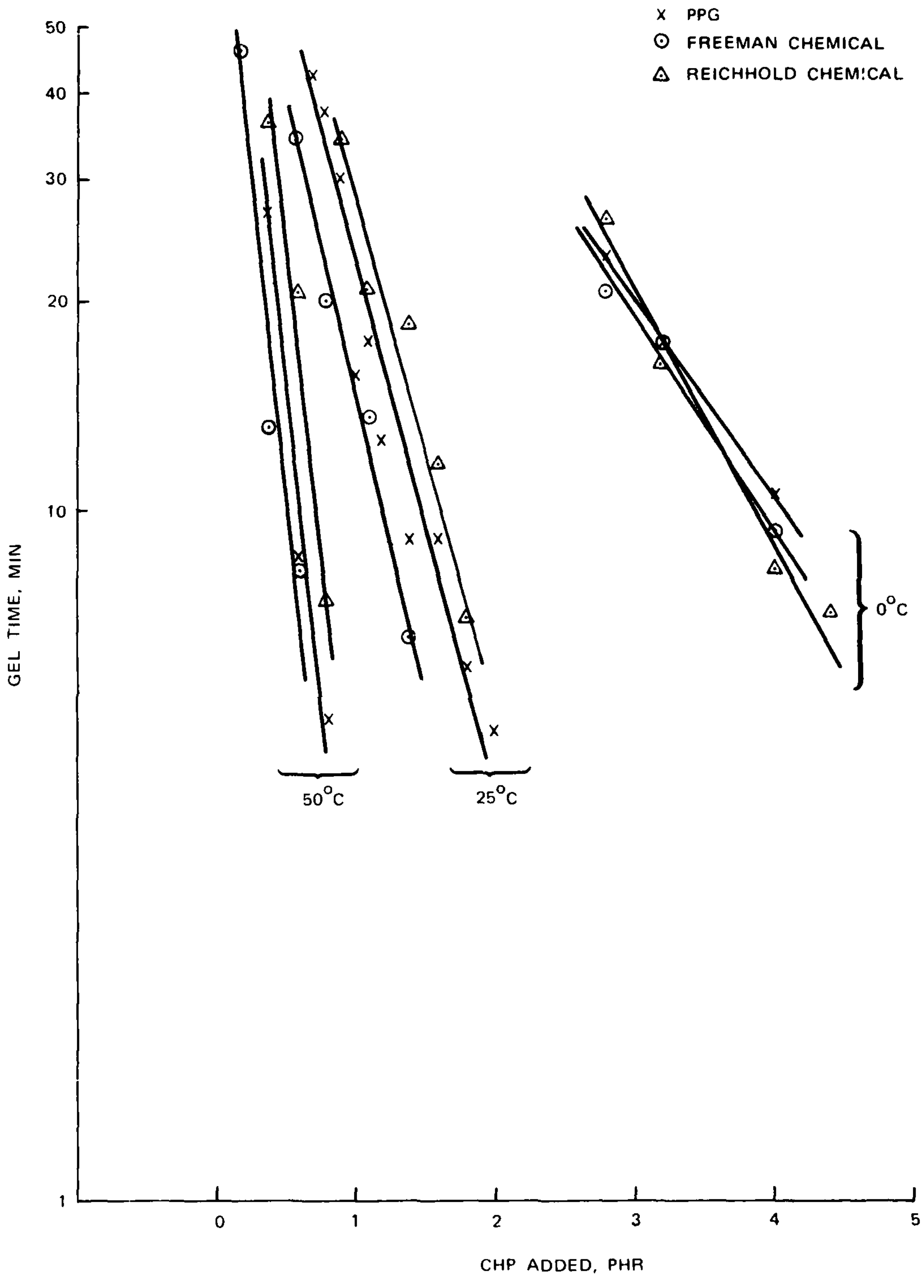

FIGURE 3. Gel Time vs. CHP Added at Various Temperatures for Polyester Resins.

TABLE 1. Gel Time-CHP Relationships at Various Temperatures for Polyester Resins.

Temp. (°C)	CHP added (phr)*	Promoter added (phr)*	Gel time (min)			Min to maximum temp.		
			PPG	Freeman	Reichhold	PPG	Freeman	Reichhold
0	2.8	0.7	23.0	20.6	26.2	33.5	30.75	41.5
	3.2	0.8	17.3	17.3	16.3	24.0	25.75	24.0
	4.0	1.0	10.4	9.3	8.2	15.75	16.0	13.5
	4.4	1.1	...	...	7.1	...	...	12.25
10	1.6	0.4	37.0	...	...	58.5	...	...
	2.0	0.5	27.6	...	...	42.5	...	...
	2.4	0.6	17.5[a]	...	...	27.6[a]	...	...
	2.8	0.7	9.5[a]	...	...	15.1[a]	...	...
25	0.6	0.15	...	34.1	...	...	55.0	...
	0.7	0.18	42.5	...	...	72.0	...	...
	0.8	0.2	37.7	20.0	...	64.25	32.75	...
	0.9	0.23	30.1	...	34.0	49.0	...	58.75
	1.0	0.25	15.6	...	...	25.0	...	...
	1.1	0.28	16.8[b]	13.6[a]	20.9[c]	26.8[b]	22.5[a]	36.4[c]
	1.2	0.3	12.6	...	...	20.0	...	...
	1.4	0.35	9.1	6.6	18.6[a]	14.5	11.75	31.50[a]
	1.6	0.4	9.1	...	11.5	14.75	...	19.75
	1.8	0.45	5.9	...	7.0	10.0	...	12.0
	2.0	0.5	4.8	...	...	8.0	...	...
38	0.6	0.15	24.3	...	...	43.0	...	...
	0.8	0.2	13.3	...	...	23.0	...	...
	1.2	0.3	5.2	...	...	8.5	...	...
50	0.2	0.05	...	45.9	...	...	83.5	...
	0.4	0.1	27.1[a]	13.2	36.2	50.5[a]	23.0	71.25
	0.6	0.15	8.6	8.2	20.6	16.5	14.75	37.25
	0.8	0.2	5.0	...	7.4	11.5	...	14.0

* Parts per hundred parts resin.

[a] Average of 2.

[b] Average of 11.

[c] Average of 4.

can see from Figure 3 that there is a fair amount of scatter in the data, especially at 25°C. However, it is also obvious that there is quite a broad range in gel times at each CHP concentration for the three resins. The Freeman resin has the shortest gel times while the Reichhold has the longest except at 0°C where the results are mixed.

A number of factors could affect the gel times of the resins. The most important of these are probably the amount and type of inhibitors added to the resin. Additional inhibitors have been added to these resins to increase their shelf life to 5 years or greater. Small differences in inhibitor content could have an appreciable effect on the gel time. Resin impurities and styrene content could also have a sizable effect. In field use, the pump control valve settings can be adjusted to some extent to change the catalyst and promoter feed rates to give the desired gel times.[1]

We considered it important to determine whether there really were major chemical differences between the resins either in styrene monomer concentration or in the polyester polymer itself.

Either proton or carbon-13 NMR spectroscopy provides the quickest and easiest way to estimate the concentration of styrene monomer in polyester resin formulations. At the same time, NMR provides a complete characterization of the major organic components of the mixture and thus a ready means for observing differences between formulations which might influence properties of the finished polymer. NMR is less effective as a means for identifying minor constituents such as inhibitors unless their spectral characteristics are known and the signals are not obscured by those of the main components.

The usefulness of NMR analysis for styrene monomer was first demonstrated with the PPG sample which displayed a relatively simple proton NMR spectrum (Figure 1). A direct comparison of styrene concentration relative to the ester component was facilitated by the presence of separate isolated signals arising from vinyl protons (in the styrene) and methyl protons of the ester. The ratio of the integrated areas of these signals was a direct measure of styrene content requiring only the addition of a known amount of styrene to provide the needed calibration constant. The styrene content was determined to be 43% (by weight) from the proton spectrum and 46% from the carbon-13 spectrum.

Apparently because of the use of a different unsaturated ester by the Freeman Chemical Corp., their formulation yielded quite a different proton spectrum (Figure 4). Although the styrene monomer signals were clearly evident, there was no single methyl signal which could be used for an accurate integral reference. Alternatively, a small amount (<1%) of tetramethylsilane, added normally as a shift reference, was found to be a suitable integral reference, and the same standard addition procedure was used to determine the styrene monomer content which was found to be 30%.

This method was used with satisfactory results in measuring styrene content of the Reichhold sample, which gave a proton NMR spectrum (Figure 5) nearly identical with that of the original PPG resin and a styrene content of 42%.

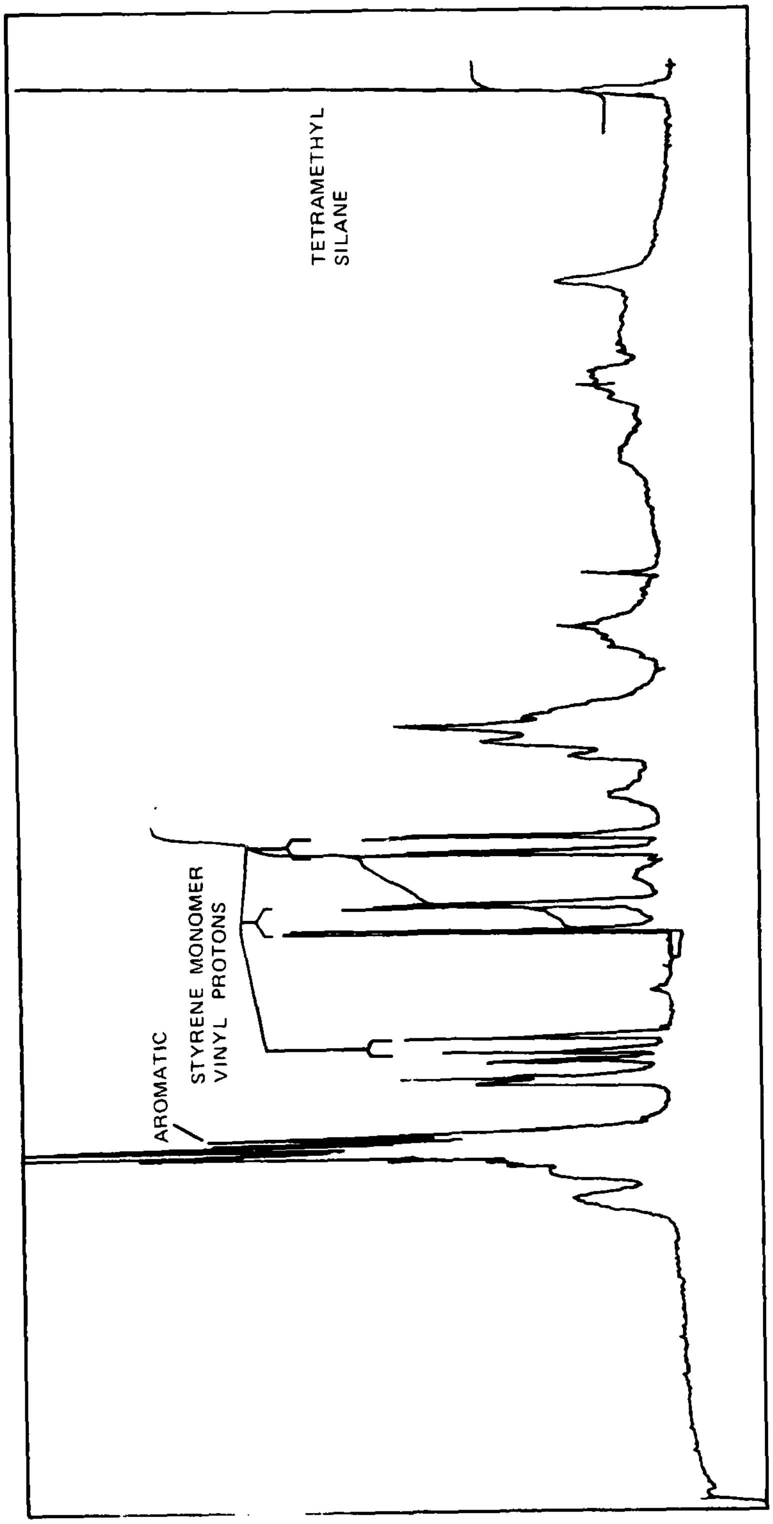

FIGURE 4. NMR Proton Spectrum of Freeman Resin.

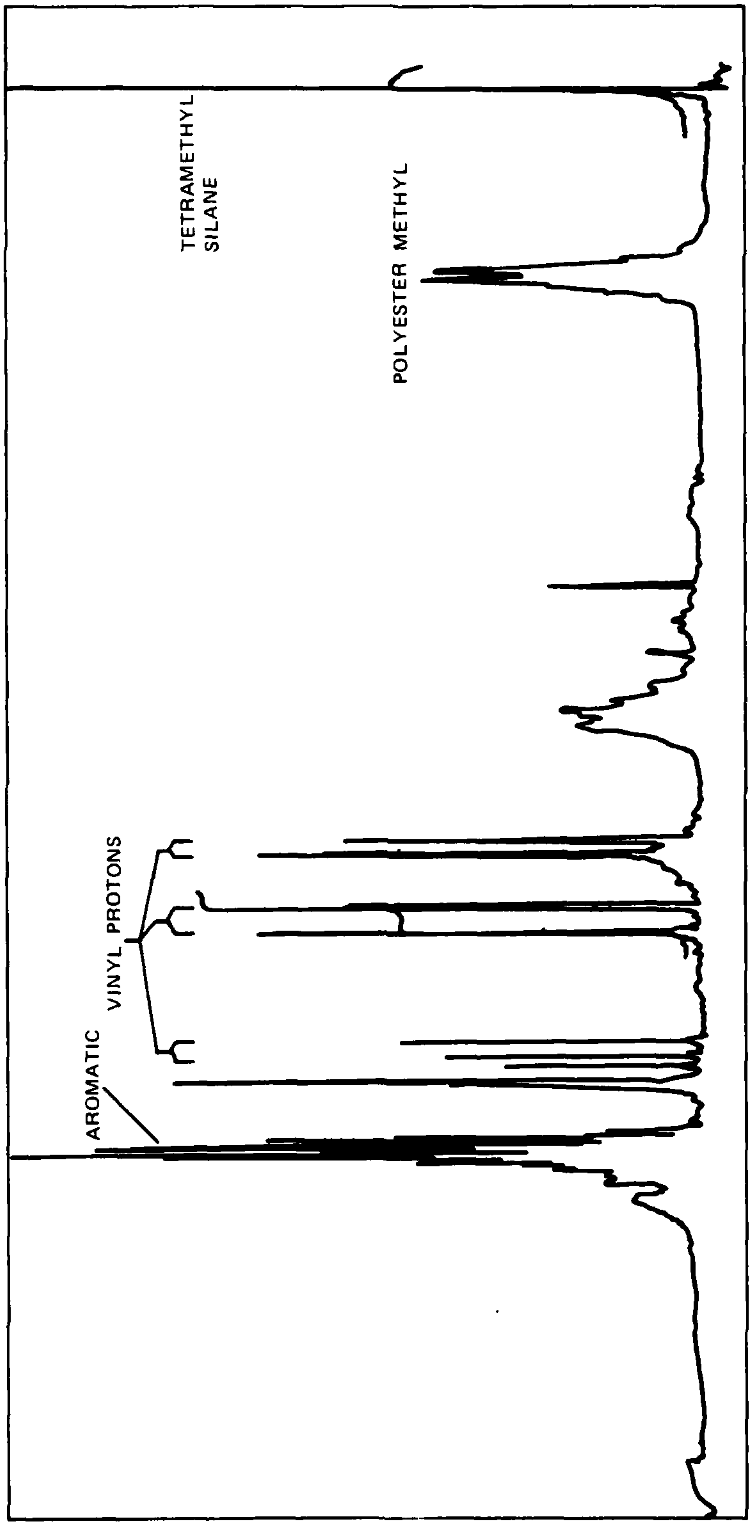

FIGURE 5. NMR Proton Spectrum of Reichhold Resin.

The accuracy with which the styrene monomer can be determined is nominally within 2% in the range of 20-50% by weight which is normally found in polyester resins. Greater accuracy can be achieved by replication and averaging of results and by using longer signal-averaging times for each determination.

Several other qualitative differences can also be seen between the Freeman resin and the other two resins. The color is much darker brown compared to the pale yellow of the PPG and Reichhold resins. During the cure of the Freeman resin, the color changes from brown to almost black and then back to dark brown. The exotherm obtained with the Freeman resin is much less, probably because of the lower styrene content, and the gel time samples are not fractured like the samples made with the other two resins.

Because of the large differences seen in the Freeman resin, a few experiments were carried out to ascertain whether mixing the Freeman resin with either of the other two resins would have a deleterious effect on the gel time. Thus, gel times were measured on mixtures of PPG and Freeman resins in ratios ranging from 3:1 to 1:3. There was no compatibility problem, and the gel times were well within the range expected.

Figure 6 and Table 2 show the viscosities of the three resins as a function of temperature. The PPG and Reichhold resins have similar viscosities over the whole temperature range of 0-50°C. Comparable viscosities are seen for the Freeman resin at the higher temperatures but become significantly higher at the low temperatures.

TABLE 2. Temperature-Viscosity Data for Polyester Resins.

Temp. °C	Viscosity (cp)		
	PPG	Freeman	Reichhold
0	1,370.0	1,717.0	1,293.0
10	598.9	657.7	557.7
20	281.1	286.2	260.1
25	200.9	195.6	183.3
30	149.0	146.0	132.5
40	86.9	79.7	78.2
50	55.7	54.8	55.5

Since we felt that this higher viscosity at low temperature might affect the shelf life of the resin, the viscosities of samples of resins which had undergone accelerated aging were measured both at 25° and at 4.4°C (40°F). A PPG sample with a viscosity of 341 cp at 25°C was found

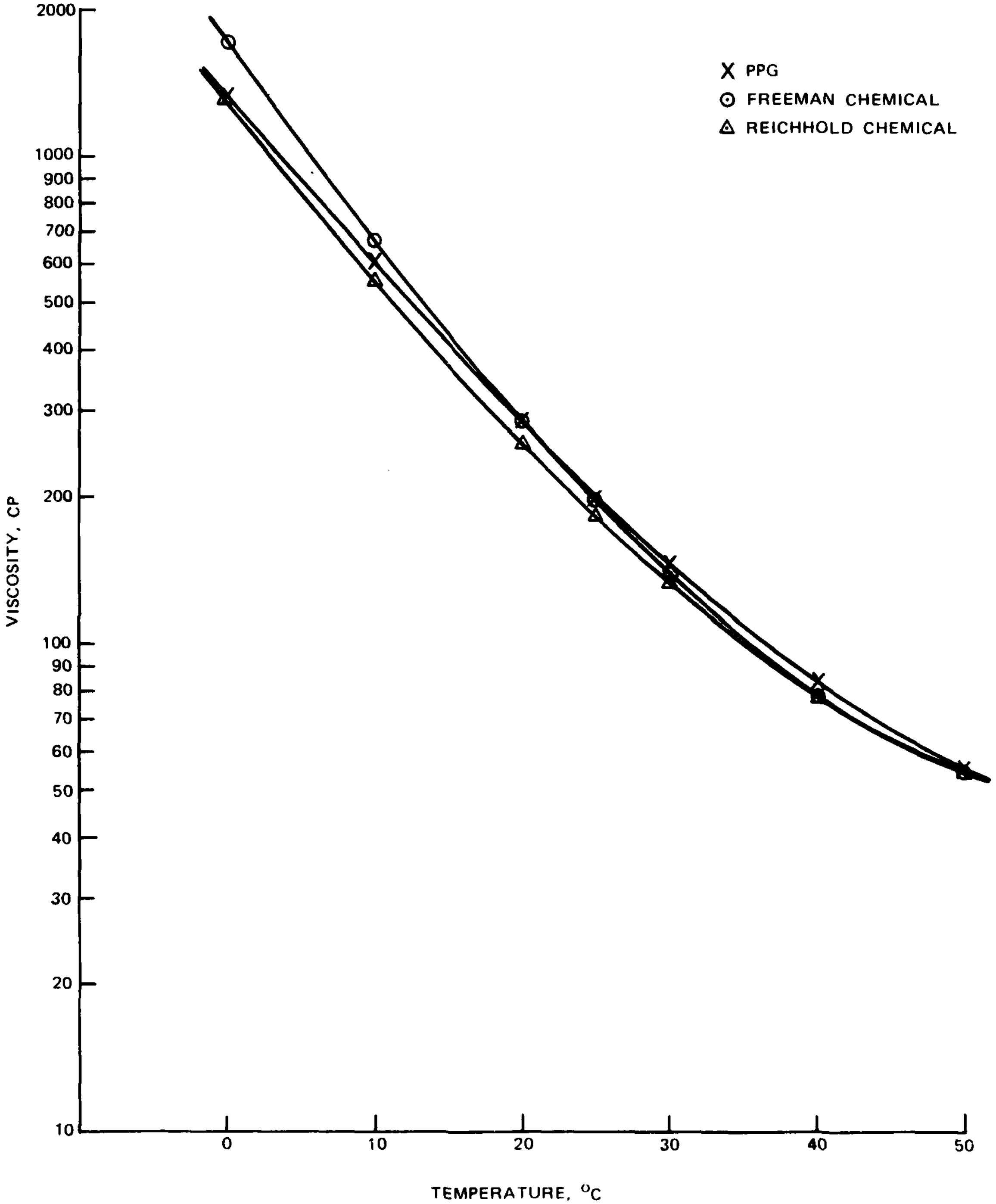

FIGURE 6. Viscosity vs. Temperature for Polyester Resins.

to correspond to 1,601 cp at 4.4°C. In comparison, the viscosity of an aged Freeman sample was 302 cp at 25°C and 1,755 cp at 4.4°C. Therefore, the PPG and Reichhold resins were considered acceptable until their 25°C viscosity reached 350 cp. However, the Freeman resin could only be acceptable up to 300 cp. These criteria were used in determining the shelf lives of the resins.

The accelerated aging data are shown in Figures 7-10 and in Appendix D. The aging of only the RS50338 was carried out at 60°C because the long time required did not permit it to be fitted into the program for the other two resins. The 60°C data is quite scattered. Therefore, a regression analysis was carried out with the data to give a shelf life of 693 hours. The data at the other temperature give fairly smooth curves.

The shelf lives, as determined from the curves, are presented in Table 3 and are plotted as a function of 1/T (reciprocal of absolute temperature) in Figure 11. A regression analysis of each set of points resulted in each calculated shelf life at 25°C shown in Table 3. An extrapolation of this magnitude is certainly not too accurate, but it at least gives a rough estimate and a good comparison among the resins.

TABLE 3. Shelf Lives of Polyester Resins.

Temp. °C	$1/T \times 10^3$ °K	Shelf life (hours)		
		PPG*	Reichhold*	Freeman**
60	3.001	693.0	...	...
80	2.831	107.0	182.0	123.0
100	2.680	16.4	31.7	21.0
120	2.543	4.1	6.2	4.0
25 (Calculated)	...	4.7 years	9.6 years	7.0 years

* Hours to reach 350 cp.
** Hours to reach 300 cp.

It is obvious that the shelf lives of the two candidate resins compare very favorably with that of the baseline resin which, in fact, did not have quite the desired shelf life. With a shelf life of 9.6 years, the Reichhold resin probably contains too much inhibitor which could be the reason for its somewhat longer gel times.

The density-temperature relationship for RS50338 is shown in Figure 12 and in Table 4. In addition, the densities at 30°C (86°F) for the Freeman and Reichhold resins are in Table 4. The change in density with temperature in the 0-50°C range should be practically identical to that of the PPG resin. The higher density of the Freeman resin is probably due to the lower styrene monomer content.

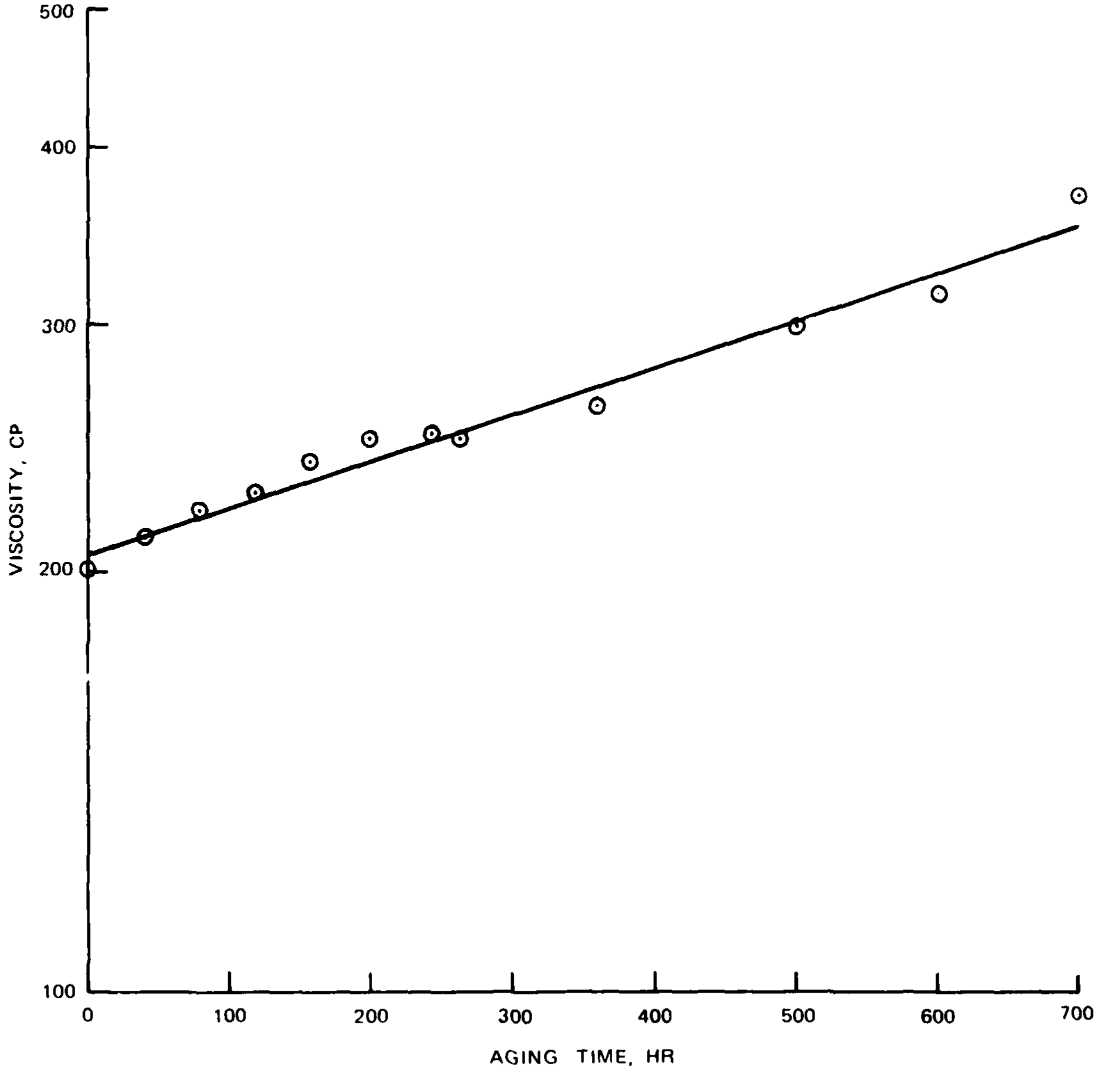

FIGURE 7. Viscosity at 25°C of PPG Resin Aged at 60°C.

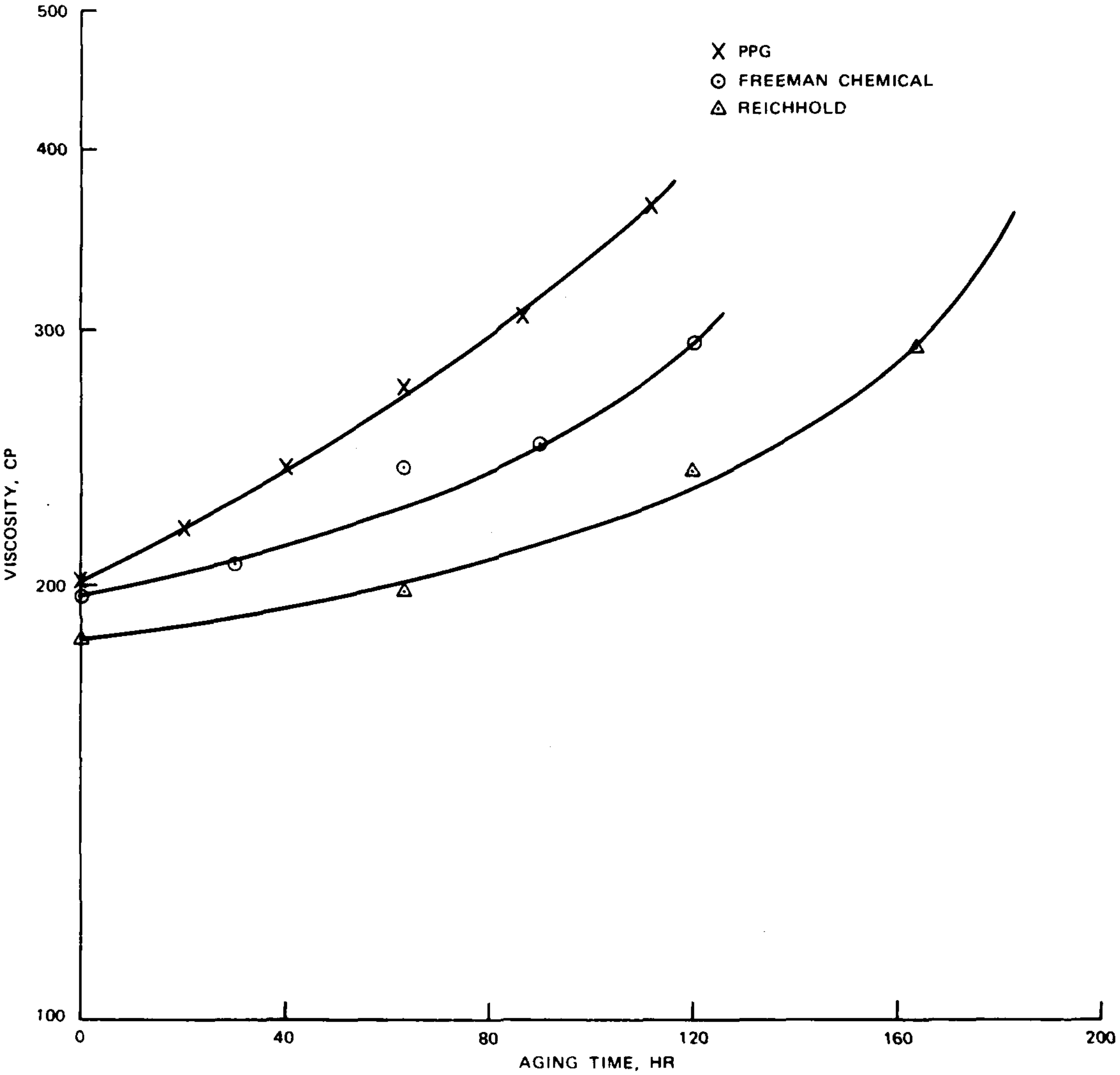

FIGURE 8. Viscosity at 25°C of Polyester Resins Aged at 80°C.

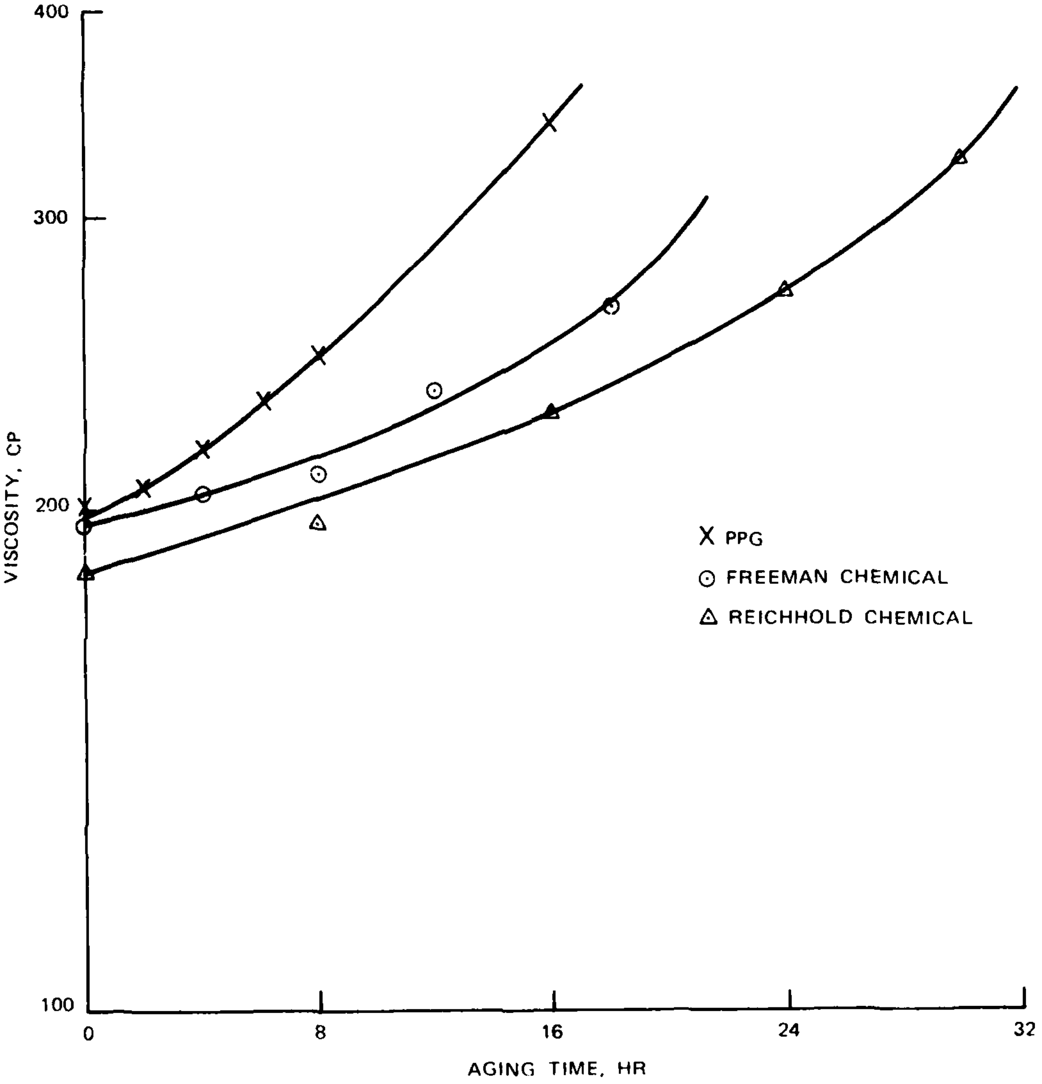

FIGURE 9. Viscosity at 25°C of Polyester Resins Aged at 100°C.

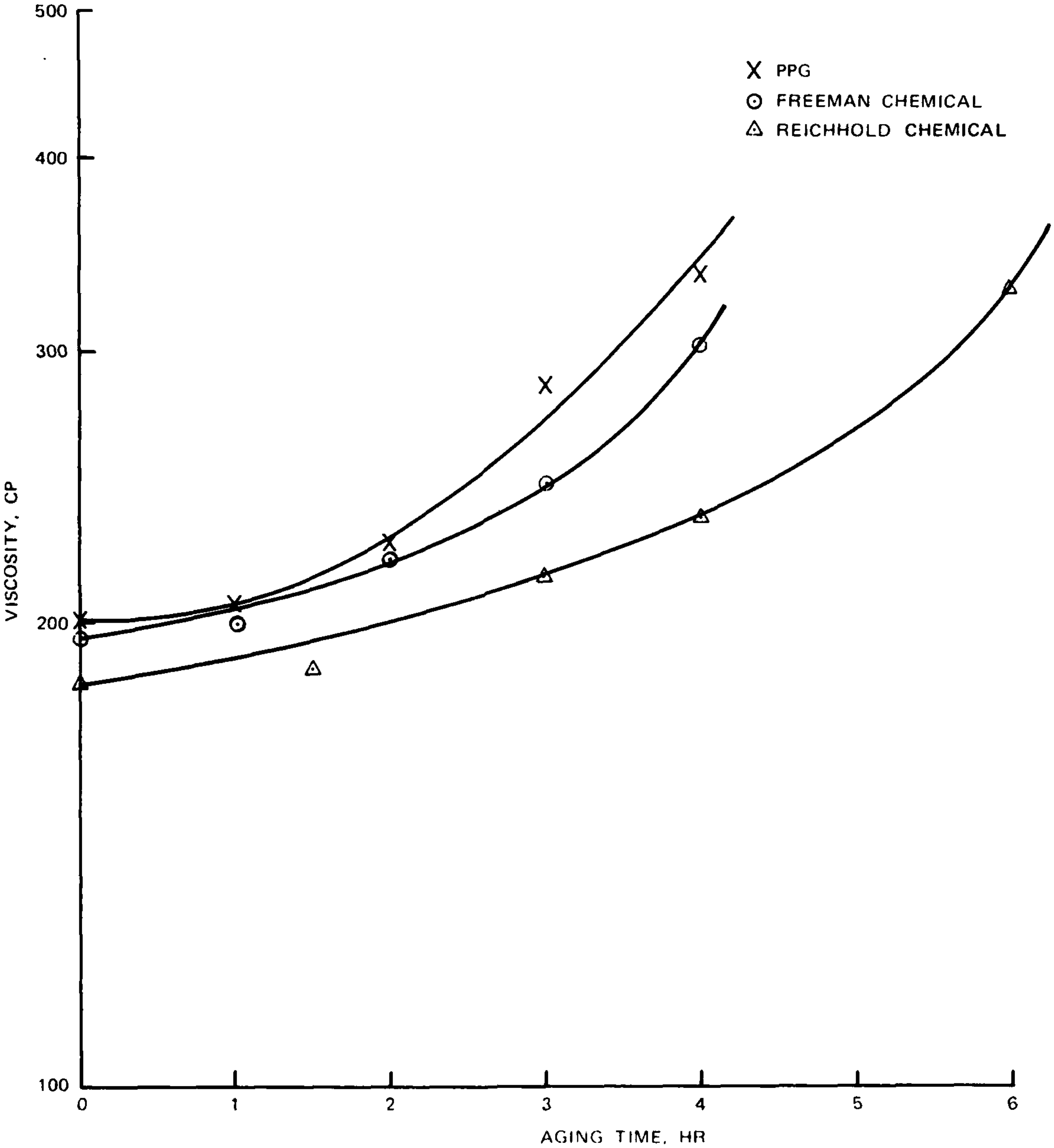

FIGURE 10. Viscosity at 25°C of Polyester Resins Aged at 120°C.

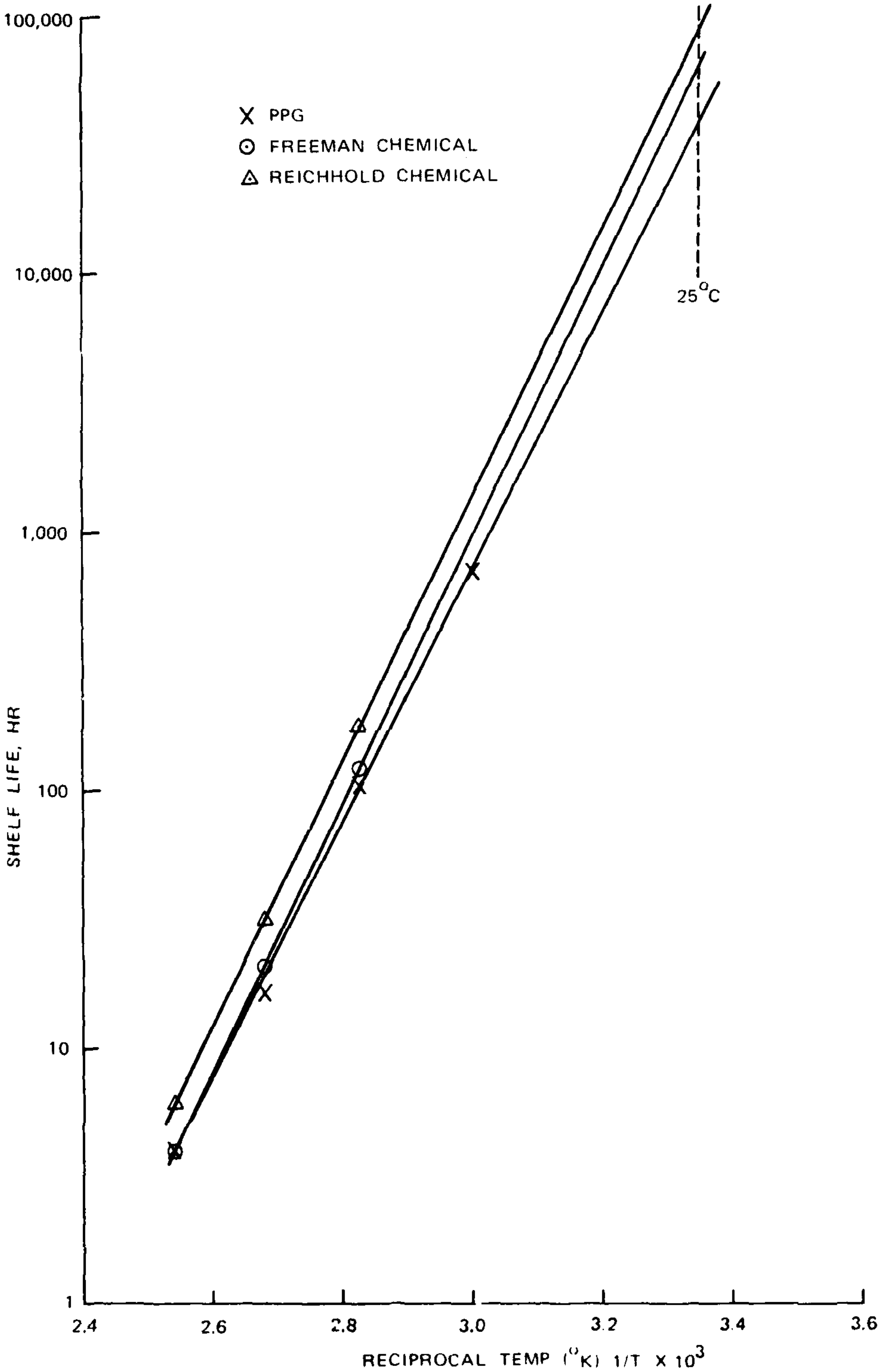

FIGURE 11. Shelf Life vs. Reciprocal of Absolute Temperature for Polyester Resins.

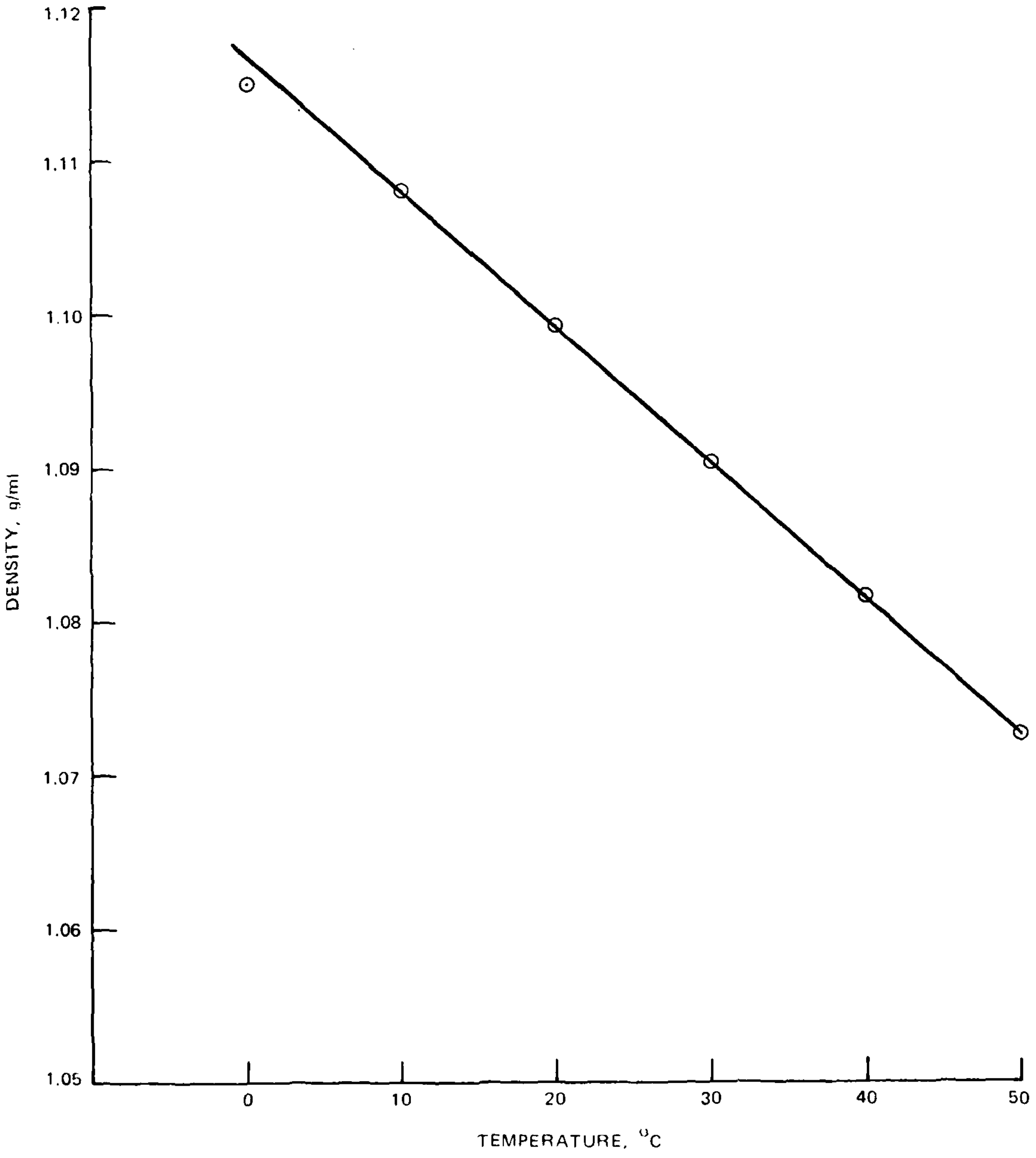

FIGURE 12. Density vs. Temperature for PPG Resin.

TABLE 4. Densities of Polyester Resins.

Temp. °C	Density (g/ml) PPG	Freeman	Reichhold
0	1.1148	...	...
10	1.1082	...	...
20	1.0994	...	...
30	1.0906	1.1179	1.0939
40	1.0819	...	...
50	1.0730	...	...

Table 5 lists the average flexural strengths of the fiberglass laminates made with the various resins under either dry or wet conditions. Each strength value is the average of 6-9 specimens (all of which are presented in Appendix E). All of the laminates except the two made under wet conditions with the Freeman and PPG resins met or exceeded the desired 28,000 psi. The wet Freeman laminate was close with a strength of 24,200 psi, but the wet PPG laminate possessed a strength of only 18,200 psi. Previous laminates made from other batches of PPG resin and water saturated mats have had flexural strengths very close to or exceeding 28,000 psi.[4]

TABLE 5. Flexural Strengths of Polyester-Glass Mat Laminates.

Resin	% Resin content	% Initial water content in glass mat	Average flexural strength* GPa	Psi
PPG	58.1	0	0.262 ±.021	38,000 ±3,400
PPG	57.8	0	0.289 ±.029	41,900 ±4,200
PPG	54.9	76.5	0.125 ±.021	18,200 ±3,000
Freeman	57.8	0	0.315 ±.023	45,600 ±3,300
Freeman	57.2	69.6	0.167 ±.021	24,200 ±3,000
Reichhold	57.1	0	0.287 ±.017	41,600 ±2,500
Reichhold	55.8	74.0	0.195 ±.027	28,200 ±4,000

* Average of 6-9 specimens.

Appendix F is a list of the requirements considered most important for the use of a polyester resin as a soil surfacing material. However, revisions in these requirements or new ones may arise as more experience is gained in working with these materials.

Care must be taken in the handling and storing of polyester resins because of the volatility and polymerizability of the styrene monomer. Some precautions are noted in Appendix G.

SUMMARY AND CONCLUSIONS

1. Baseline properties were measured for the PPG resin, RS50338, Batch 45419.

2. Similar measurements made with the Freeman Chemical resin, Stypol XP40-A273-89/Batch A307-55, and a Reichhold Chemical resin, AZ-7809-Polylite, F3, T-42, RED, indicated that these two resins should behave reasonably similarly to the PPG resin for the Marine Corps soil surfacing application. Differences in gel times can be taken into account by adjusting the valve settings on the spray equipment. A rough check on the gel time should be carried out in the field routinely before a large scale laminate is to be made.

3. A slight reduction in the inhibitor content of the Reichhold resin might result in a resin almost identical to the PPG resin.

4. The styrene concentration can be easily determined by NMR. Styrene content is not too critical as long as the gel time and viscosity are within limits.

5. A shelf life of 5 years can be readily obtained for the polyester resins.

6. There are chemical differences between the Freeman resin and the other two resins, but mixing of the resins does not have any deleterious effect.

7. Fiberglass laminates made from any of the resins should behave similarly when manufactured under comparable conditions.

8. The following resins have been determined to be acceptable for Marine Corps applications:

PPG Industries, Inc.: RS50338
Freeman Chemical Corp.: STYPOL XP40-A273-89
Reichhold Chemicals, Inc.: AZ-7809-Polylite, F3, T-42, RED
(with reduced amount of inhibitors)

9. Preparation of a test pad by the Marine Corps using the alternate resins would be the next step in the evaluation procedure.

Appendix A

POLYESTER RESIN SUPPLIERS

The following companies were solicited for polyester resin samples:

Owens Corning Fiberglass Corp.
5933 Telegraph Road
Commerce, CA 90040

Reichhold Chemicals, Inc.
107 South Motor Avenue
Azusa, CA 91702

Interplastic Corp.
2015 Broadway Street., Northeast
Minneapolis, MN 55413

Alpha Chemical Corp.
P.O. Drawer A
Collierville, TN 38017

Cargill, Inc.
2801 Lynwood Road
Lynwood, CA 90262

Freeman Chemical Corp.
222 East Main Street
Port Washington, WI 53074

Ashland Chemical Company
6608 East 26th Street
Los Angeles, CA 90040

U.S.S. Chemicals
1605 Elizabeth Avenue, West
Linden, NJ 07036

Koppers Company, Inc.
P.O. Box 22066
Los Angeles, CA 90022

Appendix B

STYRENE CONTENT IN UNPOLYMERIZED POLYESTER RESIN, NMR ANALYTICAL PROCEDURE

PROTON NMR METHOD

Any high-resolution NMR spectrometer operating either in continuous-wave sweep mode or Fourier transform mode can be used to determine the styrene content. The usual precautions to avoid radio frequency saturation in swept spectra or incomplete relaxation in pulsed spectra apply here, as in any procedure which attempts to use NMR for quantitative analysis. The spectrum of Figure 1 was obtained at 100 MHz in FT mode using a Varian XL-100-15 interfaced with a Nicolet TT-100 instrument computer.

ANALYTICAL PROCEDURE

1. Approximately 0.3-0.5 g of resin is weighed into a 5-mm thin-walled NMR tube and dissolved in 0.4 ml deuterochloroform.

2. The proton NMR spectrum is obtained under conditions which provide a baseline noise level less than 0.5% of maximum peak height. The 18 Hz vinyl doublet at 5.70 δ and the methyl multiplet at 1.24 δ are carefully integrated. The ratio of the vinyl signal integral to that of the methyl pattern is determined. In the absence of a clearly defined methyl signal, the use of approximately 1% of tetramethylsilane will provide an adequate reference for integration.

3. A weighed amount of styrene monomer approximately equal to that in the original sample is added and thoroughly mixed in the NMR tube. The spectrum is run again and the vinyl signal integral again measured with respect to the methyl integral.

4. The weight of styrene in each case is proportional to the integral of the vinyl doublet normalized to the methyl integral:

$$\frac{W_1}{W_1 + W_2} = \frac{A_1}{A_2}$$

where W_1 and W_2 refer to styrene weight before addition and the weight of the added monomer, and A_1 and A_2 refer to the corresponding integral values. Thus, the weight in the original sample is

$$W_1 = \frac{W_2 A_1}{(A_2 - A_1)}$$

and the styrene content is

$$\% \text{ styrene} = \frac{W_1}{\text{Sample Weight}} \times 100$$

CARBON-13 METHOD

Carbon-13 spectra must be obtained using the pulsed Fourier transform method because of the low natural abundance of the isotope and its lower gyromagnetic ratio. Consequently, there are several more impediments to quantitative applications: (a) unequal relaxation times of carbon nuclei in different molecular environments, (b) unequal nuclear Overhauser enhancement factors when proton-decoupling is used, and (c) nonuniform distribution of pulse power across the spectral bandwidth. Nevertheless, the carbon-13 method offers much greater resolution, and in polymer systems with overlapping proton peaks may be the only way to make quantitative measurements of composition.

The carbon-13 spectrum in Figure 2 is of the same polyester formulation as that of Figure 1. It was obtained at 25.1 MHz and required coaddition of 5,000 transient signals in 2 hours. The β-styryl carbon is a single line and additional signals can be assigned to carbonyl, aromatic, oxymethylene, and methyl carbons. The procedure for quantitative determination of styrene is similar to the proton analysis.

1. A 1.0-g sample dissolved in 2.5 ml $CDCl_3$ is used in a 12-mm sample tube.

2. The β-styryl carbon integral is obtained and normalized to the integral of the methyl group or to added tetramethylsilane as in the proton NMR method.

3. A weighed amount of styrene monomer approximately equal to the amount present in the sample (0.3-0.4 g) is added and thoroughly mixed in the NMR tube.

4. The spectrum is rerun using identical instrumental conditions and the new vinyl carbon integral value obtained with respect to the methyl signal.

5. As in the proton case, the weight of styrene originally in the resin sample is

$$W_1 = \frac{W_2 A_1}{(A_2 - A_1)}$$

and the styrene content is

$$\% \text{ styrene} = \frac{W_1 \text{ X } 100}{\text{Sample Weight}}$$

Appendix C

TABLE C-1. Gel Time and Hardness Data for Polyester Resins.

No.	CHP added (phr)[a]	Temp. (°C)	Gel time (min)[b]	Time to max. temp. (min)[b]	Barcol hardness
PPG Resin - RS50338					
FC-1	1.1	25	23.2	36.5	46
FC-3	1.1	25	13.1	20.9	49
FC-4	1.1	25	13.4	21.75	50
FC-5	1.1	25	14.5	23.5	47
RE-1	1.1	25	13.7	22.0	46
1	1.1	25	19.7	32.25	49
4	1.1	25	19.7	31.0	45
5	1.1	25	17.2	27.5	46
6	2.0	25	4.8	8.0	45
7	1.8	25	5.9	10.0	43
8	1.6	25	9.1	14.75	46
9	1.4	25	9.1	14.5	48
10	1.2	25	12.6	20.0	45
11	1.1	25	15.1	23.75	45
12	1.0	25	15.6	25.0	45
13	0.8	25	37.7	64.25	48
14	0.7	25	42.5	72.0	48
15	0.9	25	30.1	49.0	48
16	1.1	25	16.7	26.5	45
22	2.0	0	46.1	...	50
24	2.8	0	23.0	33.5	46
25	3.2	0	17.3	24.0	43
26	4.0	0	10.4	15.75	44
27	2.8	10	9.3	15.5	46
28	2.4	10	17.8	28.75	42
29	2.0	10	16.7	26.25	46
30	1.6	10	37.0	58.5	46
31	2.4	10	17.1	26.5	45
32	2.8	10	9.7	15.25	47
33	2.0	10	27.6	42.5	47
34	0.8	50	5.0	11.5	47
35	0.6	50	8.6	16.5	46

TABLE C-1. (Contd.)

No.	CHP added (phr)[a]	Temp. (°C)	Gel time (min)[b]	Time to max. temp. (min)[b]	Barcol hardness
36	0.4	50	27.3	52.0	49
37	0.4	50	26.9	49.0	47
38	0.8	38	13.3	23.0	47
39	1.2	38	5.2	8.5	47
40	0.6	38	24.3	43.0	44
41	1.1	25	18.0	29.0	48
Freeman Chemical Resin					
6	1.1	25	13.8	23.0	38
7	1.1	25	13.3	22.0	40
8	0.8	25	20.0	32.75	44
9	1.4	25	6.6	11.75	36
10	0.6	25	34.1	55.0	35
11	2.8	0	20.6	30.75	40
12	3.2	0	17.3	25.75	39
13	4.0	0	9.3	16.0	30
14	0.4	50	13.2	23.0	...
15	0.6	50	8.2	14.75	33
16	0.2	50	45.9	83.5	too soft
Reichhold Chemical Resin					
3	1.1	25	19.1	33.5	48
4	1.1	25	19.8	34.75	48
5	1.1	25	23.8	41.75	45
6	0.6	50	20.6	37.25	47
7	0.8	50	7.4	14.0	49
8	0.4	50	36.2	71.25	...
9	1.4	25	19.2	32.75	46
10	1.8	25	7.0	12.0	49
11	0.9	25	34.0	58.75	45
12	1.4	25	17.9	30.25	47
13	1.1	25	21.0	35.5	47
14	1.6	25	11.5	19.75	49
15	4.4	0	7.1	12.25	36
16	4.0	0	8.2	13.5	36
17	3.2	0	16.3	24.0	40
18	2.8	0	26.2	41.5	46

[a] phr = parts per hundred parts resin.
[b] Does not include 1 minute mixing time.

Appendix D

TABLE D-1. Accelerated Aging of Polyester Resins.

Resin	Aging Temp. (°C)	Test No.	Aging Time (Hours)	Viscosity at 25°C (cp)
PPG	60	16	40	212.2
		17	80	220.8
		15	120	226.5
		20	161	238.9
		18	200	247.6
		19	244	249.0
		21	264	247.8
		22	360	263.5
		23	500	298.1
		24	600	313.9
		25	700.5	368.1
PPG	80	13	20	218.2
		14	40	242.0
		10	64	273.0
		11	88	305.7
		12	112	367.0
PPG	100	1	2	205.7
		3	4	219.1
		2	6	232.7
		4	8	247.8
		5	16	345.2
PPG	120	6	1	205.7
		7	2	225.2
		8	3	284.7
		9	4	335.5
Freeman	80	9	30	205.8
		12	64	241.1
		11	90	250.4
		10	120	293.4
Freeman	100	6	4	204.5
		5	8	210.3
		7	12	235.8
		8	18	264.2

TABLE D-1. (Contd.)

Resin	Aging Temp. (°C)	Test No.	Aging Time (Hours)	Viscosity at 25°C (cp)
Freeman	120	1	1	200.4
		2	2	220.2
		3	3	244.6
		4	4	302.0
Reichhold	90	17R	64	197.8
		18R	120	240.5
		16R	165	291.9
Reichhold	100	24R	8	196.8
		27R	16	229.8
		26R	24	269.5
		25R	30	324.9
Reichhold	120	20R	1.5	187.1
		21R	3	213.8
		22R	4	234.3
		23R	6	328.5

Appendix E

TABLE E-1. Flexural Strength of Laminates.

Resin	% Resin content	% Initial water content in glass mats	Specimen	Flexural strength	
				GPa	Psi
PPG	58.1	0	1	0.271	39,200
			2	0.280	40,600
			3	0.230	33,400
			4	0.267	38,700
			5	0.233	33,800
			6	0.281	40,700
			7	0.271	39,400
		Average		0.262 ±0.021	38,000 ±3,400
PPG	57.8	0	1	0.288	41,700
			2	0.325	47,100
			3	0.285	41,400
			4	0.291	42,100
			5	0.307	44,500
			6	0.239	34,600
		Average		0.289 ±0.029	41,900 ±4,200
PPG	54.9	76.5	1	0.147	21,300
			2	0.118	17,100
			3	0.125	18,100
			4	0.093	13,400
			5	0.108	15,700
			6	0.148	21,400
			7	0.139	20,200
		Average		0.125 ±0.021	18,200 ±3,000
Freeman	57.8	0	1	0.331	48,000
			2	0.287	41,700
			3	0.300	43,500
			4	0.342	49,600
			5	0.321	46,600
			6	0.304	44,100
			7	0.287	41,700
			8	0.344	49,800
		Average		0.315 ±0.023	45,600 ±3,300

TABLE E-1. (Contd.)

Resin	% Resin content	% Initial water content in glass mats	Specimen	Flexural strength GPa		Flexural strength Psi	
Freeman	57.2	69.6	1	0.171		24,900	
			2	0.184		26,700	
			3	0.199		28,800	
			4	0.156		22,600	
			5	0.145		21,000	
			6	0.149		21,700	
			7	0.187		27,100	
			8	0.146		21,100	
		Average		0.167	±0.021	24,200	±3,000
Reichhold	57.1	0	1	0.297		43,100	
			2	0.297		43,100	
			3	0.251		36,400	
			4	0.281		40,700	
			5	0.282		40,900	
			6	0.284		41,200	
			7	0.308		44,600	
			8	0.296		43,000	
		Average		0.287	±0.017	41,600	±2,500
Reichhold	55.8	74.0	1	0.169		24,400	
			2	0.193		28,000	
			3	0.213		30,900	
			4	0.219		31,800	
			5	0.227		33,000	
			6	0.189		27,400	
			7	0.160		23,200	
			8	0.158		22,900	
			9	0.223		32,300	
		Average		0.195	±0.027	28,200	±4,000

Appendix F

POLYESTER RESIN REQUIREMENTS

To be acceptable for use by the Marine Corps in soil surfacing applications, a polyester resin must meet certain requirements. The most critical of these are

1. A gel time of 10-20 minutes in the polymerization system used. The gel time-catalyst-temperature relationship must be reasonably close to that obtained with the PPG resin seen in Figure 3.

2. A viscosity of 180-200 cp at 25°C (77°F).

3. A minimum shelf life of 5 years at 25°C (77°F) as measured in accelerated aging tests. The shelf life is defined as the time required to attain a viscosity of 1600 cp measured at 4.4°C (40°F). The criteria used in the accelerated shelf life tests (50-55 ml resin in a 2-oz bottle) were a minimum of

110 hours at 80°C (176°F)
20 hours at 100°C (212°F)
4.3 hours at 120°C (248°F)

4. Must cure properly under wet conditions including in a composite prepared using fiberglass fabric that is completely saturated with water.

5. When made into a laminate using two layers of Fabmat C-4020 (wet or dry) with 0-60% resin content, the laminate should have a minimum flexural strength of 28,000 psi (3-point bend according to ASTM D790-71).

6. When cured, should have a minimum Barcol hardness of 40-45.

7. Acceptable resins thus far evaluated have had styrene monomer contents of 30-43% by weight as determined by NMR proton analysis.

8. The following resins have been determined to be acceptable for Marine Corps applications:

PPG Industries, Inc.: RS50338
Freeman Chemical Corp.: STYPOL XP40-A273-89
Reichhold Chemicals, Inc.: AZ-7809-Polylite, F3, T-42, RED
(with reduced amount of inhibitors)

Appendix G

PRECAUTIONS FOR HANDLING AND STORING OF POLYESTER RESINS

The problems and hazards associated with the handling and storing of these polyester resins are essentially the same as those for styrene monomers.

FLAMMABILITY

The flash point is 32°C (90°F) using a closed cup. Polyester resins are dangerous when exposed to heat or flame, closed container may explode if exposed to extreme heat. Use NFPA Class B extinguishing media (foam, carbon dioxide, or dry chemical). Water spray may be ineffective but may be used to cool closed containers to prevent pressure buildup and possible explosion when exposed to extreme heat.

HANDLING AND STORING

Treat polyester resin as a NFPA Class 1-C flammable liquid. It should be stored below 38°C (100°F) in a closed container and in a well-ventilated dry area. Keep the container away from all sources of ignition such as flames, hot surfaces, and electrical, static or frictional sparks. All containers should be electrically grounded. Avoid free fall of liquid in excess of a few inches when pouring.

HEALTH HAZARD

The threshold limit value (TLV) is 100 ppm. On inhalation, the polyester resin can act as an anesthetic and is irritating to all parts of the respiratory tract. It may cause headache, dizziness, unconsciousness, or coma. Both the liquid and the vapor can be extremely irritating to the eyes. If liquid comes in contact with the skin, moderate irritation may develop.

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  - MAT-03 (1)
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1 Radford Army Ammunition Plant
1 Air Force Flight Test Center, Edwards Air Force Base
1 Air Force Rocket Propulsion Laboratory, Edwards Air Force Base
1 Deputy Under Secretary of Defense, Research and Advanced Technology (Assistant Director, Engineering Technology)
12 Defense Technical Information Center
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