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DEVELOPMENT OF IMPROVED POLYMERIC MATERIALS FOR REPAIRING PORTLAND CEMENT CONCRETE USING COMBINATIONS OF VINYL ESTERS AND METHACRYLATES

FINAL REPORT FHWA/CA/TL-94/14

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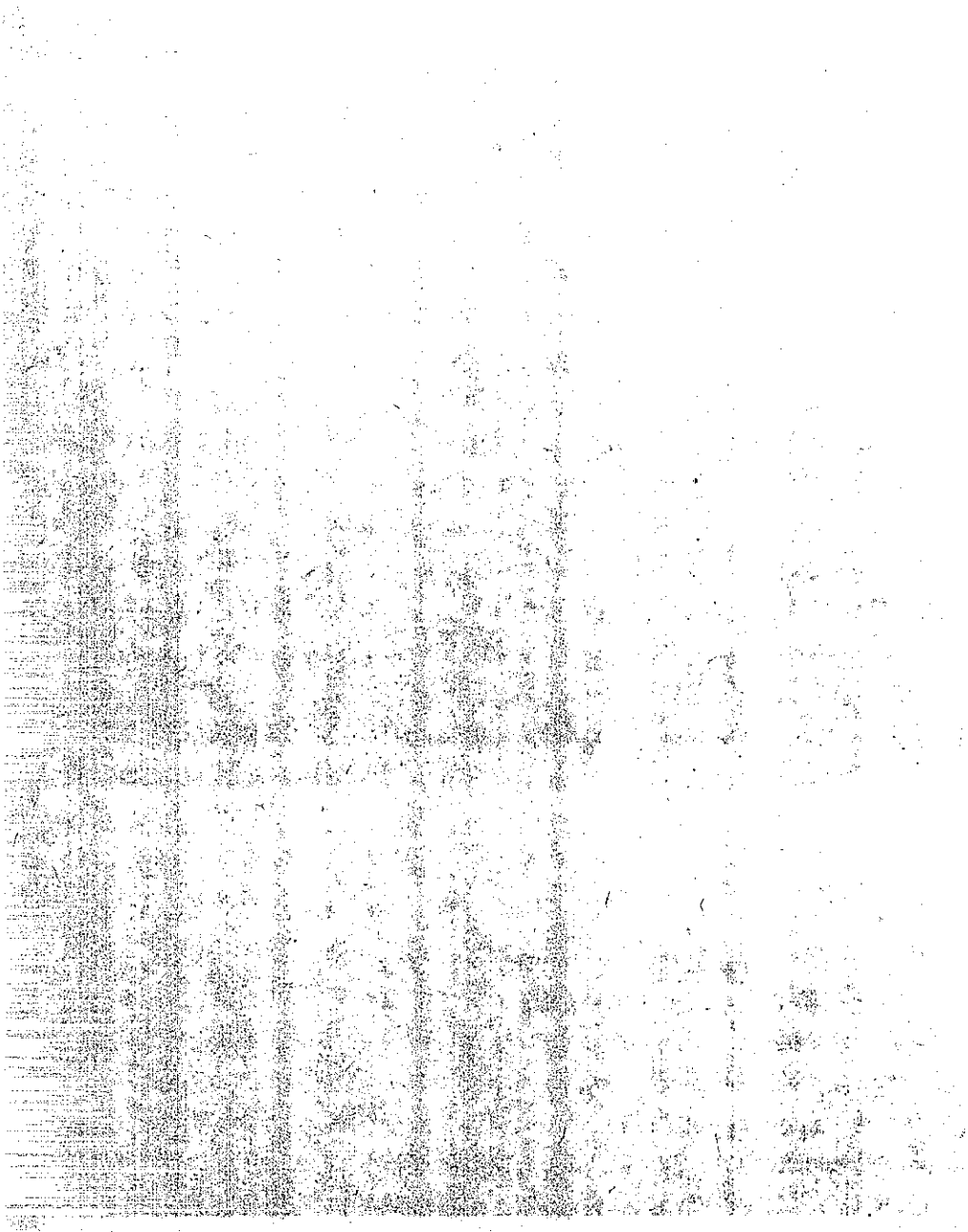

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A mechanistic approach was used to develop improved polymer concrete (PC) for repair of portland cement concrete (PCC). The VEPM binder system (vinyl esters containing acrylonitrile-butadiene copolymer, polar methacrylates, styrene and a silane coupling agent) produced PCs with tensile, flexural and compressive strengths superior to existing polyester PCs. VEPM PCs have excellent bonding characteristics to steel and PCC (both dry and moist), and the bonds are highly resistant to degradation by harsh freeze-thaw-soak cycles. They also have good properties in glass transition temperature, oil absorption, water absorption, chemical resistance and volume shrinkage. Because this contract had only a year's duration, additional research will be needed to lower the binder modulus without sacrificing good bond characteristics and strength, to improve control of pot-life and cure time, and to study the effect of types, sizes and size distributions of aggregates. Preliminary results in these areas suggest that it will indeed be possible to develop a superior polymer concrete based on the VEPM binder system.

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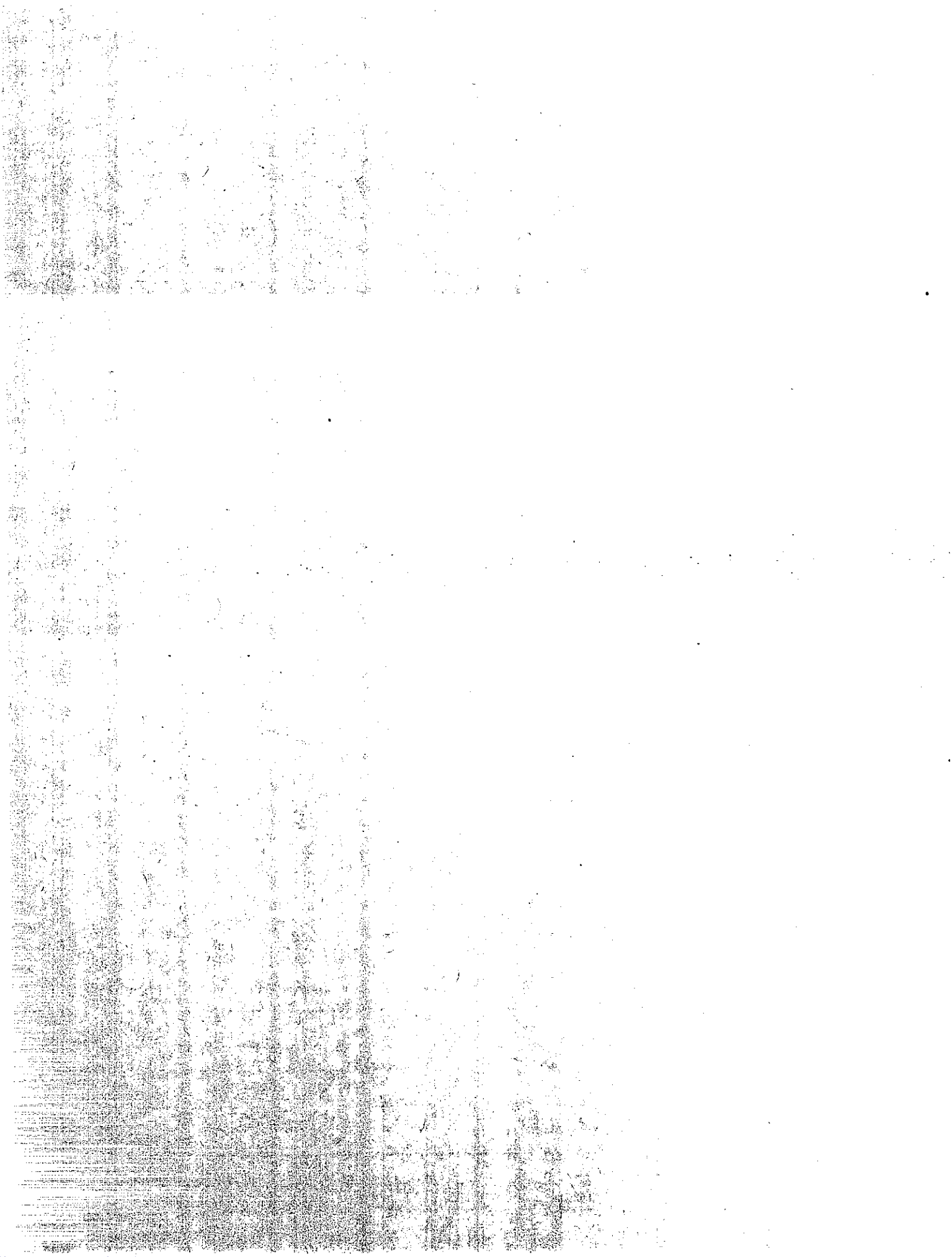

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DISCLAIMER

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the California Department of Transportation or the Federal Highway Administration. This report does not constitute a standard, specification or regulation.

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GLOSSARY

ACI: American Concrete Institute
ACS: American Chemical Society
A-174: γ-methacryloxypropyltris-(trimethylsiloxy)-silane
A-PE: unsaturated polyester resin C2062B from Aristech Chemical Corp.
BYK-5740: top coating material from Chemie, USA
CHP: cumene hydroperoxide
DEGDM: diethylene glycol dimethacrylate
DER411-35: vinyl ester from Dow Chemical
DMA: dynamic mechanical analysis
DMT: N,N-dimethyl-o-toluidine
DSC: differential scanning calorimetry
Der8084: rubberized vinyl ester from Dow Chemical
G-33: Goodrich Hycar 33 acrylonitrile butadiene rubber
GPC: gel permeation chromatography
HEMA: hydroxyethyl methacrylate
HMWM: high molecular weight methacrylate
HPMA: hydroxypropyl methacrylate
MEKP: mixture of methyl ethyl ketone peroxides
MMA: methyl methacrylate
PC: polymer concrete
PCC: portland cement concrete
PE: polyethylene
Poloplate PE: unsaturated polyester resin, Poloplate 100 Type II (Revolan)
RI: refractive index detector for GPC
RPM-2000: HMWM primer from Revolan Systems
T-70M: HMWM from Transpo Industries
Tg: glass transition temperature
TRIS: Transportation Research Information System database
uv: ultraviolet light (270 nm) detector for GPC
VE-16 (α-VE): rubberized vinyl ester from Alpha Resins
VE8520: vinyl ester from Interplastic Chemicals
VEPM: vinyl ester-polar methacrylate systems
VOC: volatile organic compound
WRDA: WRDA-19, superplasticizer from W. R. Grace

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I. INTRODUCTION

Overview of Report Contents:

The objective of this project was to develop improved polymer concrete for repair of portland cement concrete in bridges and highways. Combinations of vinyl ester and polar methacrylates were used as basic ingredients for the binders of polymer concrete. This project was originally proposed to have a three-year contract; however, it was reduced to a one-year contract with a limited budget. Because of limited time and budget, not all of the work needed to develop the final formulations was possible. However, it has been demonstrated that some of our polymer concrete (PC) samples show excellent bonding to steel and portland cement concrete (PCC) even when the substrates are moist, and also show excellent strength properties. Our approach of developing improved PC was a mechanistic one, and effects of 15 parameters on properties of PC were analyzed as much as the time and budget allowed.

The Introduction to this report contains a statement of the research problem and its background, a summary of the literature searches performed, and the objective and scope of the project.

The Results and Discussion section begins with a selection of the binder ingredients to be used and their properties, as well as the theoretical bases used in developing improved polymeric materials for repairing PCC. The remainder of this section describes analyses and evaluations of the 15 parameters listed in the Introduction (Objective and Scope), and finally the performance of the new PCs developed. All the pertinent tables and figures are compiled together at the end of this section.

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The Conclusions and Recommendations section summarizes key results and makes recommendations for future research. The Implementation section describes our accomplishments and recommends tasks to be performed in the near future.

Many test procedures and much of the equipment needed to evaluate the 15 parameters had to be devised and continually modified to obtain more meaningful data. Some of the test procedures were developed to obtain relative values for screening purposes only, with Aristech unsaturated polyester used as the reference. For example, samples used for testing tensile and flexural properties were only 2.54 x 2.54 cm (1" x 1") in cross section, so that our small-scale instrument could measure the properties. There is a disadvantage in using such small samples, because greater variability in test values occurs, especially in weak PCC samples. However, our test results appear to be consistent with those of a larger scale test, California Test 551.

All test procedures and the raw data from infrared spectroscopy and gel permeation chromatography, dynamic mechanical analysis scans (used to determine glass transtion temperature (Tg) values of the binder), and Caltrans test results are included in the Appendices.

The report ends with a listing of all literature references cited in the report, and a bibliography of pertinent papers which were found in the literature searches but were not cited.

Problem:

There are five basic materials which have been used and/or tested extensively for repair of bridges and highways. They are epoxies, polyurethanes, methyl methacrylate (MMA), high molecular weight

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methacrylates (HMWM) and unsaturated polyester resins[1-26]. Each of them has advantages and disadvantages. MMA has been used extensively. With its very low viscosity, MMA has a strong advantage of being able to penetrate into fine cracks; however, its high volatility and flammability are strong disadvantages. Recently HMWMs have been used in place of MMA in order to improve the volatility and safety characteristics. There are a variety of HMWMs available. Some of the HMWMs evaluated have marginal bonding characteristics, and are too brittle and/or expensive. Unsaturated polyesters have poor bonding characteristics to PCC and aggregates, although incorporation of silane coupling agents[1,27] improves the bonding to a degree. Epoxies have the advantages of being tough, with low volume shrinkage and superior bond adhesion. However, they tend to have poor cure characteristics (difficult to control pot-life and cure time over a wide application temperature range). Polyurethanes have many of the good characteristics of epoxies, but also have poor cure behavior similar to epoxies and marginal bonding characteristics.

Background:

Based on the above analysis, we proposed to develop PCs which have good bonding characteristics and toughness similar to epoxies and also have good processability and cure characteristics similar to methacrylates. This was to be accomplished through combining appropriate vinyl esters and methacrylates. Vinyl esters have structural features similar to epoxies but have the cure characteristics of methacrylates. Vinyl esters are sold as solutions in about 35-55% styrene, in a manner similar to unsaturated polyesters. However, they have chemical structures and functional groups for polymerization which

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are different from unsaturated polyesters. Furthermore, they are superior to unsaturated polyesters in physical and mechanical properties. Bisphenol-A based vinyl esters have excellent resistance to oil, salt, and alkalinity, and have superior strengths and bonding characteristics. This means their pot-life and cure time may be controlled in a manner similar to that used for HMWMs, but their physical and mechanical properties can be optimized to approach those of Bisphenol-A epoxies. In addition, there is the flexibility of further modifying the chemical structure and configuration of vinyl esters, through incorporation of appropriate methacrylates and monomers, additives and/or elastomers to create materials which would meet various specifications depending on the types of repair.

Literature Studies:

Extensive literature studies including TRIS, ACS and patent database searches were performed. The database search results were:

a. TRIS:

Combination of (1) Portland cement or concrete, (2) patching or patch, and (3) vinyl esters produced zero articles.

b. TRIS:

Combination of (1) concrete or cement, (2) patching or patch, and (3) vinyl esters produced zero articles.

c. TRIS:

Combination of (1) polymeric and (2) patch gave two articles.

d. TRIS:

Combination of (1) polymer concrete and (2) patch

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gave 37 articles.

e. ACS:

Combination of (1) Portland cement or concrete,

(2) patch or patching, and (3) vinyl ester gave zero articles.

f. U.S. Patent:

General search under

(1) Polymeric materials for concrete repairs;

(2) Polymer concrete for bridge overlays;

(3) Polymer concrete for overlays of concrete floor;

(4) Polymeric materials for repair of roads and bridges;

(5) Polymeric materials and/or polymer concrete for concrete floors including airport runways, roads, bridges, parking lots, and warehouse floors; and

Material search pertinent to repair of concrete under

(1) Methacrylates; e. g. high molecular weight methacrylates or any other methacrylates

(2) Unsaturated polyesters

(3) Vinyl esters

produced many patents.

The search indicated that vinyl esters have not been tested and/or used as a patching material for rehabilitation of bridges or highways. However, silica filled vinyl esters have been used as chemical resistant overlays for industrial floors (28). Papers and patents pertinent to patching materials including more recent publications have been reviewed in conjunction with this project, and are listed in the Bibliography (Section VI) if they are not cited in the text.

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Objective and Scope:

The objective of this project was to develop improved organic polymeric materials for rehabilitation of Portland cement concrete in bridges and highways. The specific objective of this one-year project was to develop improved patching materials which have the good mechanical properties of epoxies and also have the good processing and cure characteristics of methacrylates. Combinations of Bisphenol-A vinyl esters and methacrylates were selected as the basic binder ingredients for the polymer concrete. Special emphasis has been placed on effective bonding of PC to polar and/or moist substrates, while other parameters listed below were also considered.

a. Specific gravity;
b. Safety, volatility and toxicity;
c. Cost;
d. Viscosity;
e. Permeation into cracks and pores;
f. Resistance to degradation;
g. Shelf life;
h. Control of pot-life and cure time;
i. Glass transition temperature;
j. Volume shrinkage during cure;
k. Thermal expansion coefficient;
l. Aggregates: types, sizes and their distributions;
m. Modulus and ultimate stress-strain properties;
n. Freeze-thaw-soak cycles; and
o. Thermal cycling with intermittent oil immersion.

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A mechanistic approach was made, and for each parameter a working hypothesis for the relationship between the molecular structures and the properties was developed and evaluated, as much as the time allowed during this one year contract period.

II. RESULTS AND DISCUSSION:

Our primary objective in this project was to develop polymer concretes which give strong bonding to polar substrates even when they are moist. Polar substrates are inorganic solid aggregates such as sands, silica, cement, calcium carbonate, fly ash, and gravels; metals such as steel and aluminum; and Portland cement concrete. In order for an effective bonding to occur, we desire the binders not only to undergo strong adsorption on the polar solid surfaces, but also to undergo extensive permeation into the substrates when they are porous. This will allow not only effective physical and chemical bonding, but will also create good mechanical bonding. This means at least certain portions of the binder components should have solubility parameters which approach that of water.

It was hypothesized that certain portions of the binder components have to be adsorbed on polar substrates during mixing of slurries and casting. All the binder components, however, should be uniformly dispersed initially, i.e., should be in one phase. During mixing and casting, polar molecules in the binder tend to undergo preferential adsorption to create a gradient of solubility parameter near the interfaces. The gradient will depend on the relative affinity of the molecules toward polar solids vs. binder matrix. In other words, thermodynamic properties

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including surface energy, cohesive energy, and interfacial energy will affect the adsorptivity and the gradient. During the polymerization (cure process), the gradient of the polar components near the interface may become even more prominent because of changes in entropy parameters and surface energy. One would expect the molecules to become less soluble while becoming more surface active as they grow to larger molecules.

Our initial approach was to manipulate the solubility parameters of binders through adjustment of relative amounts of Bisphenol-A vinyl esters, styrene, acrylonitrile-butadiene elastomer, and water soluble methacrylates. Acrylonitrile-butadiene elastomer was used to create more resiliency in PCs. Initial design of the binder components was guided by (1) the Flory-Huggins theory of polymer solutions, (2) the concept of Hildebrand's solubility parameters, and (3) the Flory-Krigbaum theory (29). These theories were developed for bi-component systems and for nonpolar solutions. Our binder premixes are multi-component systems containing highly polar functional groups including alcohol groups which undergo hydrogen bonding. Nevertheless, the theories were useful in our initial design of the formulations.

Bisphenol-A based vinyl esters are available through Interplastic Corporation, Ashland Chemicals, Alpha Resins, Dow Chemicals, Reichold (Atlac and Dion series) and Quaker. They are usually dissolved in styrene monomer (35 - 55% styrene), as is the case with unsaturated polyesters. The cost per pound ranges from $1.80 to $2.30. Variation of the vinyl esters appears to be in the molecular weight, crosslink density, additives, and the amount of styrene monomer present. Bisphenol-A based vinyl

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esters have been shown to be tougher and more corrosion resistant, and to have better bonding capability to polar substrates than unsaturated polyesters or HMWM. There are about 40 different methacrylate monomers and crosslinkers available at $1.10 - $4.75 per pound. Major vendors are Rohm Tech, Inc. and Rohm & Haas.

Combinations of Bisphenol-A based vinyl ester resins and polar methacrylates were used as the basic ingredients, and other components such as monomers, crosslinkers, coupling agents and/or elastomers were incorporated in order to modify the properties, guided by the criteria discussed below:

a. Specific Gravity: Components were selected so that the binder would have a minimum specific gravity of 0.97 as specified by Caltrans. All the formulations in Table I have specific gravity greater than 1.0.

b. Safety, volatility and toxicity: Toxicity was guided by the material safety data sheets supplied by the manufacturers. Although there are many acrylates available which will toughen the binders, they are usually not acceptable because they tend to be toxic and cause the resins to be more prone to hydrolytic attack. This is why methacrylates were selected instead of acrylates. All the components in the binder have vapor pressure lower than 0.01 mm Hg at 25°C (77°F) and flash point higher than 98°C (208°F) except styrene. In 1987, the South Coast Air Quality Management District in Southern California adopted Rule 1162 related to "Unsaturated Polyester Resin Operations", which regulates Volatile Organic Compound (VOC) emissions. This would restrict the styrene content to be less than 35%. All our binder formulations have styrene content less than 35%. Furthermore, if styrene is ruled to be too volatile under future State

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environmental requirements, it can be substituted with vinyl toluene with little change in overall properties.

Another method of reducing evaporation of styrene is to use a wax/resin top coat or other top coat. For example, the top coating using BYK-5740, developed by Chemie, USA, reduces the VOC emission significantly(30). BYK-5740 is currently used by Caltrans for overlays of unsaturated polyester PC.

c. Cost : Although some more expensive ingredients such as silane coupling agents and methacrylates are used in the formulations, an effort was made to limit the binder cost to $2.50/lb or less.

d. Viscosity: It is desirable to have a low binder viscosity in order to improve permeation into fine cracks and pores and improve the processability and castability. Most of the binders can be formulated to give viscosity of around 250 cps or less through incorporating less viscous methacrylate monomers. A plot of viscosity of a vinyl ester resin against monomer content is shown in Figure 1.

e. Permeation into cracks and pores : Low viscosity is definitely an important factor for effective permeation. The cumulative degree of binder premix permeation with time is shown in Figure 2. The degree of permeation after 10 minutes vs. viscosity of various binders is plotted in Figure 3, without considering the chemical types of binder premixes. The degree of permeation should also be affected by relative affinity of binder components toward polar surfaces, and those in Figure 3 may be affected both by viscosity and relative affinity. The effects of these two variables could be clarified by varying the viscosity of binders with the same polarity, and by varying the polarity of binders with the same viscosity.

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f. Resistance to degradation: PC should be inert to oils, aqueous salts, acid and alkaline media. As discussed before, vinyl esters have greater hydrolytic stability than unsaturated polyesters, because the former have mainly ether groups along the polymeric chains, whereas the latter have mostly ester groups. Furthermore, the esters used in our formulations are hindered methacrylates rather than acrylates, and therefore are more resistant to hydrolysis. Our cured binders absorb about the same or lesser amounts of oil and water when compared with Aristech's unsaturated polyester. Intermittent oil immersion of our binders (Formulations #16, #17 and #23) shows a maximum of 0.05% oil absorption throughout 20 cycles (Figure 4). Water absorption through two cycles by Formulations #17 and #23 is less than that of Aristech's polyester (#15), and the maximum amount of absorption by #17 and #23 is less than 0.15% throughout 20 cycles (Figure 5). The percentage mass change of PC binders #16, #17 and #23 during the intermittent oil or water immersion cycles is minimal (less than 0.15%), which is comparable to or less than that of Aristech's polyester (#15) as shown in Figures 6 and 7. In fact, Aristech's polyester binder shows a trend of gradual mass loss during oil immersion cycles, whereas our VEPM binder #23 does not. Mass losses during the first three or four cycles must be due to extraction of small molecules by oil.

g. Shelf life: Caltrans' specification of one year minimum shelf life under controlled environment should not be a problem if binders are not prepromoted. Viscosity measurements of resins and monomers indicate that they can be stored for at least one year if appropriate amounts of stabilizers are incorporated. However, prepromoted resins are expected

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to have problems based on the viscosity change of Aristech's unsaturated polyester; the viscosity changed from 118 to 274 cps after storage for five months under ambient conditions at 16-29°C (60-85°F).

h. Control of pot-life and cure time: Specification by Caltrans is to have about 45 minutes of pot-life and four hours of cure time at 25°C (77°F). Detailed trial and error cure studies to meet the Caltrans specification are deferred until the final formulations are selected by Caltrans, since cure properties depend on so many different parameters. However, the pot-life of each test formulation was adjusted to be between 30 and 60 minutes (Table I), and cure time to be less than 24 hours at room temperature. In order to warrant proper cure of these test samples, they were taken out of the molds and placed in the 57°C (135°F) oven for an additional 24 hours. Meanwhile, kinetic and mechanism studies have been performed to create a good technical foundation for controlling the overall cure process.

As soon as an initiator system is incorporated into the binder, free-radical interpolymerization is initiated to create a highly cross-linked binder. The polymerization proceeds in three steps: the initiation step where active radicals are created; the propagation step where vinyl groups in monomers and resins are hooked up rapidly to create cross-linked polymers; and finally termination of active radicals.

Initiation: Peroxides & monomer $\xrightarrow{\text{promoters}}$ $R'O-CH_2-\dot{C}H$ (R)

Propagation: $R'O-CH_2-\dot{C}H + CH_2=CH \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow R'O-(CH_2-CH)_n-CH_2-\dot{C}H$ (R)

Termination: $2\ R'O-(CH_2-CH)_n-CH_2-\dot{C}H \rightarrow R'O-(CH_2-CH)_n-CH_2-CH-CH-CH_2-(CH-CH_2)_n-OR'$ (R)

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A general polymerization rate plot is depicted in Figure 8, which gives an S-shaped curve. The induction period (IP) is equivalent to the pot-life, and cure-time (CT) is equivalent to the time required for about 90 to 95% polymerization. The induction period is the time required to produce a substantial concentration of propagating radicals for polymerization. Under steady state conditions, radical concentrations are usually 10^{-7} - 10^{-9} moles/liter. The propagation step involves rapid hooking up of monomers. A chain typically grows for only 0.1 - 10 seconds prior to termination of its radical. Usually 5,000 to 100,0000 vinyl groups can be hooked up by each radical depending on the chemical structure of the vinyl groups and the reaction medium, but the degree of polymerization may be reduced by chain transfer agents, retarders and inhibitors. The most likely mechanism of the initiation step is as follows:

$$ROOH + CO^{+2}complex \rightarrow RO\cdot + OH^{\ominus} + CO^{+3}complex$$

$$R\text{-}OOR + (CH_3)_2N\text{-}C_6H_5 \rightarrow \left[C_6H_5\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}\text{-}OR \right]^{+} \rightarrow C_6H_5\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{+}_{\bullet}}} + RO\cdot$$

Hydroperoxides such as cumene hydroperoxide (CHP) are readily catalyzed by cobalt salts, and peroxides such as benzoyl peroxide are more readily catalyzed by tertiary aromatic amines. Commercially available methyl ethyl ketone peroxides (MEKP) are mixtures of hydroperoxides and peroxides, and each vendor offers MEKP with slightly different compositions. Since radical chain reactions involve such low concentrations of radicals, trace amounts of certain impurities can affect the overall cure process significantly. Inhibitors (stabilizers) present in

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the resins and monomers act as radical traps by combining with radicals to prevent the chain propagation process. They are incorporated by vendors in order to prevent the polymerization of monomers or resins during synthesis, shipping and storage. Since inhibitors are consumed whenever radicals are created, the concentration gradually decreases with storage time. This is why pot-life must always be determined immediately prior to mixing batches.

Based on the discussions above, pot-life is expected to be affected by many parameters such as type and concentration of stabilizers (inhibitors) used by vendors, impurities present, history of storage, etc. Furthermore, oxygen is known to be an inhibitor/retarder for polymerization of methacrylates and styrene. Hence, the degree of oxygen absorption during the mixing, casting and cure process will influence the pot-life as well as the cure time. There are wax/resin solutions available to top-coat the PC to minimize oxygen absorption (30). They are not only useful in maximizing a more complete cure through minimizing oxygen absorption, but are also useful in preventing emission of VOC.

In general the overall cure process is controlled by types and concentrations of catalysts and initiators. Cobalt salts are known to be the most effective metal salts, and dimethyltoluidine (DMT) is a favored tertiary aromatic amine. Dimethylaniline was used in the past; however, it appears to be more toxic than DMT. Furthermore, a mixture of CHP and MEKP is more effective in modifying the pot-life and cure time than MEKP alone. However, it becomes difficult to adjust the pot-life by varying only the catalysts and initiators when the application temperature varies from 10°C (50°F) in the morning to 35°C (95°F) in the afternoon. There has to

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be a simpler and more effective method. Furthermore, there is a danger of incomplete cure if the amount of initiator is reduced to less than the 0.1% level. Our planned approach is to adjust the pot-life to around 45 minutes at 21°C (70°F) using proper catalysts and initiators, but retention of a good pot-life at the higher temperature will be through incorporation of a chelating agent to tie down the catalytic activity of cobalt catalyst for a while. Evaluation of this approach has not been performed because of limited time.

i. Glass transition temperature (Tg): Our binder formulations have equivalent or higher Tg values than those of currently available unsaturated polyesters (Table I). We determine the Tg through dynamic mechanical analysis (DMA), which actually measures relative strain capability of the binder with changing temperature, under a constant load which is applied on the sample intermittently. This method is more sensitive and informative than the ASTM D-3418 procedure using differential scanning calorimetry (DSC). Each thin sample (ca. 1.5 mm (0.06 in)) is tested in the range of 10 to 100°C (50 to 212°F) at a scan rate of 10°C/min (18°F/min). The 150 mN (0.034 lb) force is oscillated in a square wave (on and off) pattern at a frequency of 0.1 Hz. Two runs are made with each sample to see the effect of the exposure of the sample to 100°C (212°F) during the first run. Usually the second run shows a slight change from the first scan, and this may be due to additional polymerization or crosslinking during heating of the sample. The DMA scan not only gives information on Tg but also gives information on potential mechanical behaviors of PC with changing temperature. (See original scans in Appendix, Section V-4.) For example, Sample #15,

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Aristech polyester binder, shows a gradual modulus change from 20°C (68°F) and finally becomes very soft at 75°C (167°F). Although Tg of 57°C (135°F) is approximated to be the midpoint of the overall modulus change (Table I), one would expect gradual changes of certain properties in the PC beginning as low as 20°C (68°F) and large changes occurring at around 55°C (131°F). In other words, one would expect decrease in tensile and compressive strengths of PC and increase in the binder volume as the temperature rises, and the extent of the changes will be similar to the pattern shown in the DMA scan. Furthermore, one expects a significant increase in values of the thermal expansion coefficient with increasing temperature near 55°C (131°F). Recently, a rather steep decrease in the compressive strength of polyester PC with increasing temperature was reported (31). The strength decreased drastically from 21°C (68°F), reaching only 10% of the original strength at 82°C (180°F). We believe this was due to softening of the binder associated with a low Tg value.

j. Volume shrinkage during cure: The volume shrinkage of PC during cure will cause stress at the interface, which may eventually contribute to interfacial failure. Our formulations show volume shrinkages comparable to that of an unsaturated polyester (Table I). The degree of shrinkage is affected by the amount of vinyl groups present and also by the structure of monomers and resins. Monomers with bulky side-chains should give a lower degree of shrinkage during cure, because the bulky groups would not allow close packing of the polymeric chains. It has been claimed that methacrylates substituted with cycloaliphatic groups (which are bulky) have a lower degree of volume shrinkage during cure (32). Our study also

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tends to be consistent with the above theory. When the entire hydroxyethyl methacrylate (HEMA) portion of Formulation #16 is replaced by hydroxypropyl methacrylate (HPMA), the volume shrinkage is reduced from 9.92 to 9.74% (Formulation #16 vs. #23 in Table I), even though only 10% of the binder is involved, .

One would expect that stress would build up only after the resin is reasonably rigid, and therefore, shrinkage after the "gel" point would be more critical in the case of patching spalls or overlay applications. Usually the "gel" point is when about 50% of monomer is consumed. Hence, volume shrinkage after the "gel" point is more meaningful for stress analysis than the entire volume change from the binder premix to the cured binder. Future plans should involve this type of study. Furthermore, increasing the solids content in PC would minimize the shrinkage. "Shrinkage reducing agents" (32-35) are also available if needed.

k. Thermal expansion coefficient: The difference between the thermal expansion coefficient of PC and that of substrate (PCC) would create interfacial stress during thermal cycling. Usually PC has much higher thermal expansion coefficient than PCC, and an attempt should be made to minimize the difference. One of the methods would be to increase the solids content in PC as high as possible. Although we are aware that this is one of the most important parameters to evaluate, we did not have time to study this area during our one-year contract period.

l. Aggregates: types, sizes and their distributions: Aggregates content and/or their distributions influence the viscosity and the volume shrinkage, the strength properties, and the thermal expansion coefficient of PC. It is advantageous to maximize the solids content in terms of

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volume shrinkage, thermal expansion coefficient, and cost. Maximum solids content is limited by processability and cohesiveness of the polymer concrete.

Selection of optimum aggregate composition was guided by Farris's relationship for minimum viscosity(36). His theory was developed based on the concept that big particles see small particles as a part of the liquid. Therefore, a higher polydispersity should give a lower slurry viscosity at the same volumetric loading.

Compositions of solids giving minimum viscosity at 90 weight per cent solids were estimated using Farris's theory for tri- and tetramodal systems:

Trimodal system:	18.5% fine; 30.5% medium; 51.0% coarse
Tetramodal system:	13.0% finest; 19.0% fine; 27.5% medium; 40.5% coarse

It is to be emphasized that these ratios are valid only when the particles are spherical and the size differences are greater than a factor of ten. Since commercial aggregates are not monomodal and also deviate from the above conditions in sizes and shapes, additional trial and error experiments have to be performed to achieve the best processability.

Aggregates--#60, #1/20, #3 and coarse aquarium (CA)--from Lonestar along with calcium carbonates and Portland cement were used for our study. Grading of sand is supplied by Lonestar (Table II). Trimodal systems using these aggregates did not seem to show appreciable

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improvement in processability over aggregates currently used by Caltrans (54 parts B-11 to 26 parts B-39 pea gravel, weight ratio). Partial replacement of B-11 with Portland cement creates a more thixotropic mix at the same solids level, but improves the tensile and flexural strengths of PC appreciably (Ia vs. Ib in Table III). Very fine particles, Portland cement and fumed silica, tend to give a thixotropic mix. A tetramodal system gives a marked improvement in processability over Caltrans' aggregates (IIa vs. IIb in Table III). The tetramodal distribution of aggregates allows increase in the solids content from 88.7% to 89.7% with little sacrifice in strength. Replacement of CA in IIa with B-39 pea gravels or other pea gravels had no effect on processability or tensile or flexural properties.

Incorporation of additional solids which are finer than Sand #60 could create a pentamodal system. When an additional 5 g (0.2 oz) of Portland cement or 5 g of calcium carbonate (74 μ - 420 μ) is incorporated into 70 g (2.5 oz) solids of IIa to increase the solids content from 89.7% to 90.4 %, a good processability is still retained (Table III). However, it is interesting to observe that PC with calcium carbonate (item III-b in Table III) has tensile and flexural properties similar to PC without calcium carbonate (III-a), in spite of the increased solids content. PC with an additional amount of Portland Cement (III-c) shows an increase in tensile and flexural strengths as expected. The difference between III-b and III-c may be due to preferential debonding of calcium carbonate particles from the binder matrix. Further study is needed in this area.

Our preliminary results indicate that (1) Farris's theory is a good approach to increasing the solids content, and (2) certain very fine

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particles tend to create a thixotropic mix. Future study should include optimization of aggregate compositions to maximize the solids content, and evaluation of effect of type, size and amount of very fine particles on the processability and mechanical properties.

m. Modulus and ultimate stress-strain properties: Our initial evaluation of HMWMs (Transpo T-70M and Revolan RPM 2000) for polymer concrete indicated that they are extremely brittle, although RPM 2000 appears to be slightly less brittle than T-70M. Although their PCs show good tensile and flexural strengths, they shattered with one drop of our impact test from the height of 1.30 m (4'3"), whereas PC with Revelan Poloplate unsaturated polyester required five drops from 1.30 m (4'3") and two drops from 1.75 m (5'9"). (Compare items 1, 2 and 3 in Table IV). This may be why the repair job with T-70M PC at the Sacramento Metro Airport in 1990 failed within a month. The failures occurred at the PC/PCC interfaces.

Our objective was not only to develop PCs with good bonding capabilities to moist PCC and metals such as steel and aluminum, but also to develop PCs with some resiliency to retain good bonding even after thermal and freeze thaw cycles. Our approach was to incorporate elastomeric components into the binders to create resiliency. Incorporation of 20% acrylonitrile-butadiene rubber (Goodrich Hycar 33 which has methacrylate end groups) into the vinyl ester-methyl methacrylate premix binder resulted in a significant increase in the impact strength with little changes in tensile and flexural strengths. (Compare items 4 and 5 in Table IV.) Butadiene rubber containing acrylonitrile was selected because the nitrile group has one of the highest

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group molar attraction constants[37]. The presence of nitrile groups in the rubber should allow better compatibility with vinyl esters and polar methacrylates, and also allow more favorable bonding to the polar surfaces. Based on these results, commercially available rubberized vinyl esters were searched. Two rubberized vinyl esters have been located: Derakane 8084 by Dow Chemical Company and an experimental VE-16 by Alpha Resins Corporation. Although detailed compositions are company proprietary information, our analysis indicates that VE-16 has about 16% elastomer and Derakane 8084 has about 10%. Infrared and GPC scans for both samples are attached in the Appendices (Sections V.2 and V.3).

Properties of selected PCs using both rubberized vinyl esters are tabulated in Tables V and VI along with bond properties. (Tables V-(a) and VI-(a) are in metric units, and Tables V-(b) and VI-(b) are in standard engineering units.) All the data in Table V were acquired in this laboratory through using small samples with 2.54 x 2.54 cm (1" x 1") cross sections, and those in Table VI were obtained by Henry Jerzak of Caltrans using California Test 551. Raw data from Caltrans are attached in the Appendices (Section V-5). PC binder #15 is Aristech, binders #16, #23 and #24 are combinations of Derakane 8084 and polar methacrylates, #14 is VE-16, and #17 is a combination of VE-16 with polar methacrylates. It is clearly demonstrated that vinyl ester systems have tensile, flexural, compressive and impact strengths which are superior to those of Aristech polyester PC. Furthermore, vinyl ester-polar methacrylate (VEPM) systems have greater strain energies (estimated from compressive strength and modulus) than Aristech polyester PC (Table VI). Although ultimate strain values of samples #16 and #17 are 80% of that of

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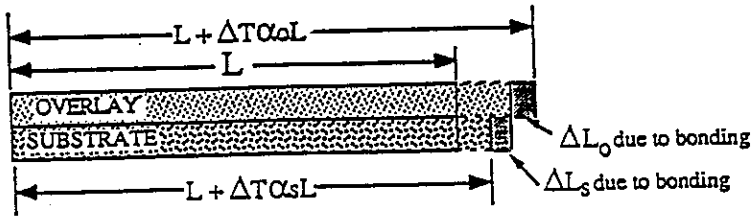
Aristech polyester PC, their strain energies are 30 to 40% greater than that of Aristech PC. Strain energy is calculated as the area under the stress-strain curve assuming that the curve is a straight line. Vinyl ester PCs #14 and #17 have the highest impact values (Table V) although their strain energies and strains are not the highest (Table VI). This impact resistance may be due to the presence of greater amounts of the elastomer. This result is consistent with that of item #5 in Table IV.

Based on the experience of Caltrans' overlay work during the past ten years with unsaturated polyester systems, it is suggested that the compressive modulus of elasticity of PC should be from 1,000,000 to 2,000,000 psi. Force, F, at the interface of the overlay work (38) during thermal changes is governed by the equation below:

$$F=\Delta T(\alpha_o-\alpha_s)\left(\frac{1}{E_oA_o}+\frac{1}{E_sA_s}\right)^{-1}$$

Where: F is force developed
ΔT is change in temperature
α_o and α_s are thermal coefficients for overlay and substrate
E_o and E_s are Young's Modulus for overlay and substrate
A_o and A_s are cross sectional areas
L is length before temperature change



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The modulus can be lowered by using one or more of the following approaches:

(1) Incorporate methacrylates having long alkyl chains or polyalkylene oxide chains. These methacrylates have low Tg and should create free volumes in the binder, thus acting as internal plasticizers.

(2) Incorporate additional elastomers to create more resiliency.

(3) There are many flexible epoxies available, and these can be reacted with methacrylic acid to create flexible vinyl esters.

(4) Modification of aggregate types, sizes and size distributions may also lower the modulus.

A detailed discussion of each approach above, including the advantages and disadvantages, will be incorporated into our next proposal.

n. Freeze-thaw-soak cycles: As previously discussed, our main objective is to develop PCs with greater bonding capabilities than unsaturated PCs and HMWM PCs. It has been fairly well established that one of the disadvantages of polyester PCs is poor bonding characteristics under wet or damp conditions.

As demonstrated in Tables V and VI, our vinyl ester PCs give bonding characteristics far superior to those of Aristech PC. Selected test samples #16, #23, #24, #14 and #17 show excellent bonding, even to moist PCC surfaces and metals. However, the bonds should not fail during thermal and freeze-thaw weather cycles. Hence, thermal and freeze-thaw cycling tests are also performed, as discussed below.

Because of the limited time for this project, we chose a very harsh cycling method for this study. The samples are first heated at 57°C (135°F) for 24 hours, followed by soaking in water for 24 hours at room

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temperature and then freezing the soaked samples at -20°C (-4°F) for 24 hours. The frozen samples are then immediately heated again to 57°C (135°F) for the second cycle. In other words, the samples are exposed to drastic changes in conditions, such as a sudden large change in temperature and freezing of water soaked composites. One would expect severe stresses caused by these cycles not only near the bond interfaces, but also at the aggregate interfaces within composites. Stresses caused by thermal cycles are affected by the difference in the thermal expansion coefficients and moduli of two composites. In addition, volume shrinkage of PC during cure and large water absorption by PCC before its freezing would create additional stresses near the interfaces. Since VEPM binders absorb less than 0.16% of water during 20 water immersion cycles (Figure 5), one would not expect much water absorption by the PC composites. VEPM PCs #17 and #23 have less than 0.11% water absorption (Figure 5), and the binders and their PCs show little change in water absorption and mass loss during cycling (Figures 5, 7, 9 and 10). A slight loss of mass by the binders during the first few cycles may be attributed to loss of water soluble components such as catalysts, initiators and monomers. However, Aristech polyester PC shows the tendency to increase in water absorption and mass loss with increasing freeze-thaw cycles (Figures 9 and 10). This may indicate a gradual damage in the binder through hydrolysis and/or at the interfaces between the binder matrix and aggregates.

The effect of 20 freeze-thaw cycles on strength properties of PCC and PCs are shown in Tables VII, VIII and IX. (Tables VII-(a) and VIII-(a) are in metric units, and Tables VII-(b) and VIII-(b) are in standard engineering units.) PCC shows deterioration in tensile and flexural

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strengths, with wide variations in the values. Because of the weak nature of PCC composites, slight variations in flaws in these small specimens (one inch cross sections) cause large variations in properties. Smaller variations are generally observed with PCs, although the effect of cycling on the tensile strength of PC was not evaluated because of our shortage of molds. There is definitely a greater weakening of Aristech polyester PC than of vinyl ester PCs after the 20 cycles (Table VIII). Impact strengths of VEPMs #24 and #17 did not change appreciably after the 20 cycles, while others showed some deterioration (Table IX).

The effects of these harsh freeze-thaw cycles are significant on PC/PCC bond properties. Aristech polyester PC (#15) showed almost complete damage near the interface, especially for those samples bonded to wet PCC, while vinyl ester PCs showed varying amounts of damage (Tables VII & VIII). In general tensile properties appear to be more sensitive to freeze-thaw cycles than flexural and impact properties. VEPM PC samples #16 and #23 show no interfacial failures in flexural and impact bond tests although they show some interfacial failure in tensile tests. However, their tensile bond strengths still show high values of about 3.0 MPa (440 psi) after cycling. Overall, VEPM #17 shows excellent bond properties.

It is important to point out that in most cases vinyl ester PCs bonded to wet PCC survived the freeze-thaw-soak cycles far better than PC/PCC(dry) samples, in spite of the fact that they may not bond as well to the wet PCC initially. In other words, the PC/PCC(wet) samples tend to show greater bond strengths and lower degrees of interfacial failure than the corresponding PC/PCC(dry) samples after 20 freeze-thaw-soak cycles

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(#16, #23, #24 and #14 in Tables VII & VIII). This may be due to the difference in degree of stress near the interfaces. Dry PCC was subjected to baking at 110°C (230°F) for 24 to 48 hours, which caused partial dehydration. Consequently, dry PCC absorbs a greater amount of water (5.5%) than wet PCC (3.5%) during the first soaking cycle. When the soaked PC/PCC samples are frozen at -20°C (-4°F), there is a significant degree of swelling of PCC through freezing of the 5.5% absorbed water, in addition to shrinkage of PC due to lowering the temperature by about 45°C (80°F). The difference in water absorption (2.0%) between the wet and dry PC/PCC samples must cause additional damage. PCC stored under ambient conditions absorbs only 3.5% water, the same amount as the wet PCC, because the % water absorption is the difference between the mass of soaked PCC and that of heated PCC at 57°C (135°F). In other words, baking PCC at 110°C (230°F) is causing dehydration, and this leads to additional aggravation near the PC/PCC interfaces for samples frozen after soaking in water. Greater initial water absorption and greater mass gain of PC/PCC(dry) samples during the first freeze-thaw cycle are demonstrated in Figures 11 and 12.

o. Thermal cycling with intermittent oil immersion: Each cycle involves heating samples for 24 hours at 57°C (135°F) followed by soaking in engine oil (SAE 10W-30 motor oil by Shell) for 24 hours at room temperature. This was repeated 20 times with the binders and 32 times with PC and PC/PCC samples. This study allowed us to look at the thermal cycling effect as well as the effect of engine oil. As previously discussed, VEPM binders absorb less than 0.03% oil (Table I and Figure 4).

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However, soaking the samples and heating at 57°C (135°F) causes loss of mass in some of the binders (Figure 6). Some of the binders, including Aristech polyester, tend to show gradually increasing loss in mass (#15 and #16), although it is a minor degree (less than 0.2%). This may be caused by slow leaching out of oil soluble components and/or deterioration of binder.

PC composites of VEPM show less than 0.1% oil absorption and mass gain, while those of Aristech polyester show about 0.2% mass gain during the 32 cycles (Figures 13 and 14). After the 32 cycles, PCs and PCC/PCC samples #15 and #17 show no deterioration in response to the impact test, while #16 and #14 show some deterioration (Table X). Impact strengths of dry and wet PCC/PC samples are affected in a similar manner by the 32 cycles.

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Table I
Binder Formulations and Properties

Expt. #	Type Binder *1	Pot-life (min)	Vicosity (cps)	Permeation (cm/10min)	DMA(Tg) midpoint	Specific Gravity at 23°C (73°F)	Cure Shrinkage (Vol.%) *2	Oil Absorption (wt.%) Cycle 1	Water Absorption (wt.%) Cycle 1
15	A-PE / - / A-174 (99) / (0) / (1)	42	118	4.0 (1.6")	57°C (135°F)	1.08	9.22±0.08	<0.03	<0.15
16	Der 8084 / HEMA / A-174 (85) / (15) / (1)	30	174	2.5 (1.0")	75°C (167°F)	1.04	9.92±0.03	<0.03	<0.16
23	Der 8084 / HPMA / A-174 (85) / (15) / (1)	30	184	2.4 (0.9")	- -	1.03	9.74±0.03	<0.02	<0.10
24	Der 8084 / HEMA / DEGDM / A-174 (85) / (10) / (5) / (.5)	35	209	2.5 (1.0")	- -	1.03	-	-	-
14	α-VE / - / A-174 (100) / (0) / (0.5)	43	430	1.8 (0.7")	- -	1.03	-	<0.01	<0.11
17	α-VE / HEMA / DEGDM / A-174 (100) / (10) / (5) / (0.5)	35	210	2.5 (1.0")	85°C (185°F)	1.03	9.05±0.12	<0.01	<0.12

*1 Values in ( ) are weight ratios.
*2 Average of 4 Tests.

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Table II

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LAPIS LUSTRE SAND GRADING AVERAGES

TYPICAL GRADING PARAMETERS

Cumulative Percent Passing U.S. Sieves

March 1992

Product		SPECIAL BLEND	COARSE AQUARIUM	MEDIUM AQUARIUM	6 Mesh	8 Mesh	#3	2/12
Nom. Sieve Sz.	mm	3/8 X 6	4 X 12	6 X 16	6 X 12	8 X 16	8 X 20	12 X 20
#3/8	9.52	100 - 100						
#3	6.7	87 - 99						
#1/4	6.35	81 - 98						
#4	4.750	18 - 62	94 - 100	99 - 100	98 - 100			
#6	3.350	0 - 5	46 - 75	78 - 86	62 - 89	100 - 100	100 - 100	
#8	2.360	0 - 1	7 - 17	43 - 55	20 - 39	92 - 97	97 - 99	100 - 100
#12	1.700		1 - 4	12 - 21	5 - 14	28 - 43	61 - 75	97 - 99
#16	1.180		0 - 2	1 - 3	0 - 4	1 - 5	13 - 20	29 - 49
#20	0.850				0 - 2	0 - 2	1 - 2	3 - 11
#30	0.600					0 - 1	0 - 1	0 - 2
N		26	35	27	20	42	75	81

Product		#2-/16	#1C	#1/20	#0/30	#60	#30/70	Product	LAPIS ALL PURPOSE
Nom. Sieve Sz.	mm	16 X 30	16 X 40	20 X 40	30 X 50	40 X 70	30 X 70	Nom. Sieve Sz.	
#12	1.700	100 - 100	100 - 100						
#16	1.180	91 - 95	95 - 97	100 - 100				#4 4.750	100 - 100
#20	0.850	20 - 33	56 - 64	87 - 97	100 - 100		100 - 100	#8 2.360	99 - 100
#30	0.600	1 - 6	10 - 15	14 - 29	91 - 94	100 - 100	91 - 97	#16 1.180	70 - 91
#40	0.425		1 - 3	1 - 5	30 - 52	91 - 97	50 - 73	#30 0.600	34 - 58
#50	0.300				3 - 17	35 - 57	16 - 30	#50 0.300	11 - 22
#70	0.212				0 - 1	5 - 12	3 - 7	#100 0.150	0 - 1
#100	0.150					1 - 2	0 - 1	#200 0.075	0 - 0
N		67	43	82	151	43	15	FM	
								N	8

NOTE: THESE ARE AVERAGE GRADINGS. DESTROY PREVIOUS EDITIONS. FOR SPECIFIC DATA OR CUSTOMER CERTIFICATION, CONTACT QUALITY CONTROL - 510/866-2780.

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Table III

Effect of Aggregate Composition on Processability and Strength Properties

Binder	Aggregates (wt. Ratio)	% Solids	Processability	Tensile Strength		Flexural Strength	
				MPa	(psi)	MPa	(psi)
I. Polyester poloplate 10	a. B-11 / Pea Gravel (54) / (26)	88.7	good	6.8	(990)	3.9	(560)
	b. B-11 / Pea Gravel / Portland Cement (44) / (26) / (10)	88.7	thixotropic	9.9	(1430)	5.4	(780)
II. Vinyl Ester/Methacrylates	a. #60 Sand / #1Sand / #3 Sand / CA* (12) / (13) / (15) / (30)	89.7	good	13.1	(1900)	6.6	(960)
	b. B-11 / Pea Gravel / Portland Cement (44) / (26) / (10)	88.7	thixotropic	13.8	(2000)	6.8	(980)
III. Aristech Polyester	a. #60 Sand / #1Sand / #3 Sand / CA* (12) / (13) / (15) / (30)	89.7	good	6.5	(940)	4.5	(650)
	b. #60 Sand / #1Sand / #3 Sand / CA* / CaCO3 (12) / (13) / (15) / (30) / (5)	90.4	good	6.3	(920)	4.3	(630)
	c. #60 Sand / #1Sand / #3 Sand / CA* / Port. Cement (12) / (13) / (15) / (30) / (5)	90.4	good	10.5	(1530)	5.2	(760)

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Table IV

Properties of Different Polymer Concretes

(89.2% Solids)

Item	Notebook Reference	Binder	Tensile Strengh		Flexural Strengh		Impact Prop. *1	
			MPa	(psi)	MPa	(psi)	130cm *2	175cm *2
1	T-B-1	RPM-2000	6.2	(900)	3.3	(480)	1	-
2	T-B-3	T-70M	5.2	(750)	3.9	(560)	1	-
3	L-7	Poloplate PE	9.9	(1430)	5.4	(780)	5	2
4	R-C-2	Der411-35 / MMA / G-33 (6.0) / (4.0) / (0.0)	10.5	(1520)	5.7	(830)	2	-
5	R-C-8	Der411-35/MMA/G-33 (5.0) / (3.0) / (2.0)	11.4	(1650)	5.6	(810)	6	-

*1 Number of drops to break; sample size: 60ml in 100ml PE cup

*2 Drop height (4'3") and (5'9"); 1240 g (2.72 lb) weight.

*3 After 5 freeze - thaw-soak cycles; each cycle consists of:

(a) 2 days immersion in water

(b) 2 days at -20°C

(c) 2 days at 50°C

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Table V-(a)

Effect of Binder on Mechanical and Bonding Properties of PC

2.54cm X 2.54cm Cross Section Specimens

(89.7% Solids)

Experiment	Type Binder	*Type Bond*	Tensile Properties*1		Flexural Properties*1		Impact Properties*2
			MPa (Range)*3	FM %CF*4	MPa (Range)*3	FM %CF	Drops(Range)*3
Ref.	PCC (Dry) *5		4.1	-	1.9 (1.7-2.2)	-	1.0 (1-1)
	(Wet)		4.1 (3.6-4.7)	-	2.2 (2.0-2.3)	-	1.0 (1-1)
15	A-PE/ - /A-174	PC Only	6.5 (6.2-6.6)	-	4.5 (4.1-5.0)	-	2.7 (2-3)
	(99) / (0) / (1)	PC/PCC (Dry)	5.0 (4.4-5.5)	80%(PCC)	2.0 (1.8-2.2)	80%(PCC)	1.7 (1-2)
		PC/PCC(Wet)	1.4 (1.4-1.4)	5%(PCC)	1.1	5%(PCC)	1.7 (1-2)
		PC/Al	7.2	65%(PC)	3.3 (3.3-3.3)	50%(PC)	-
		PC/Steel	7.3	25%(PC)	2.6 (2.3-2.7)	45%(PC)	-
		PC/Brass	5.2	25%(PC)	0.3 (0.3-0.3)	5%(PC)	-
16	Der 8084/HEMA/A-174	PC Only	11.0 (10.4-11.4)	-	6.8 (6.3-7.4)	-	3.0 (2-4)
	(85) /(15)/ (1)	PC/PCC (Dry)	4.6 (4.6-4.7)	100%(PCC)	1.9 (1.9-1.9)	100%(PCC)	2.0 (2-2)
		PC/PCC(Wet)	3.7 (3.3-4.1)	85%(PCC)	1.9 (1.6-1.9)	100%(PCC)	1.3 (1-2)
		PC/Al	13.7	100%(PC)	6.5 (6.0-6.9)	90%(PC)	-
		PC/Steel	11.9	100%(PC)	6.5 (6.8-7.2)	100%(PC)	-
		PC/Brass	12.1	100%(PC)	6.9 (6.9-6.9)	100%(PC)	-
23	Der 8084/HPMA/A-174	PC Only	10.8		6.8 (6.6-6.9)		3.0 (3-3)
	(85) /(15)/ (1)	PC/PCC (Dry)	3.3 (2.5-4.1)	100%(PCC)	1.9 (1.9-1.9)	100%(PCC)	1.7 (1-2)
		PC/PCC(Wet)	3.2 (3.2-3.2)	75%(PCC)	2.1 (1.9-2.2)	100%(PCC)	1.3 (1-2)
		PC/Al	9.8 (9.4-10.2)	100%(PC)	6.7 (6.3-7.0)	100%(PC)	
		PC/Steel	11.0 (10.5-11.6)	100%(PC)	6.5 (5.7-7.3)	100%(PC)	
24	Der 8084/HEMA/DEGDM/A-174	PC Only	14.1		6.9 (6.5-7.6)		2.0 (2-2)
	(85) / (10) / (5) / (.5)	PC/PCC (Dry)	3.0 (3.0-3.0)	100%(PCC)	1.6 (1.4-1.9)	100%(PCC)	1.6 (1-2)
		PC/PCC(Wet)	2.5 (2.5-2.5)	100%(PCC)	1.4	40%(PCC)	1.3 (1-2)
		PC/Al	15.6 (14.6-17.1)	100%(PC)	6.8 (6.6-7.0)	100%(PC)	
		PC/Steel	16.3 (15.3-17.2)	100%(PC)	6.4 (5.8-7.0)	100%(PC)	
14	α-VE/ - /A-174	PC Only		-	7.0 (6.9-7.3)	-	4.3 (2-6)
	(100) / (0) / (0.5)	PC/PCC (Dry)	4.0 (3.9-4.1)	100%(PCC)	2.0 (1.8-2.2)	95%(PCC)	1.7 (1-3)
		PC/PCC(Wet)	3.0 (2.9-3.2)	85%(PCC)	1.9 (1.8-1.9)	100%(PCC)	3.3 (3-4)
		PC/Al	5.4	60%(PC)	6.3 (5.5-7.0)	90%(PC)	-
		PC/Steel	11.6	100%(PC)	6.2 (5.5-6.9)	90%(PC)	-
		PC/Brass	9.9	95%(PC)	7.2 (7.4-7.4)	100%(PC)	-
17	α-VE /HEMA/DEGDM/A-174	PC Only	12.9 (12.4-13.3)	-	6.6 (5.8-7.4)	-	4.3 (4-5)
	(100) / (10) / (5) / (0.5)	PC/PCC (Dry)	4.7 (5.2-4.1)	100%(PCC)	1.8 (1.7-1.9)	100%(PCC)	2.0 (2-2)
		PC/PCC(Wet)	3.4 (2.6-4.1)	100%(PCC)	1.7 (1.6-1.8)	100%(PCC)	2.3 (2-3)
		PC/Al	13.2	85%(PC)	5.5 (5.0-6.1)	90%(PC)	-
		PC/Steel	12.1	85%(PC)	6.8 (6.6-6.9)	100%(PC)	-
		PC/Brass	5.0	70%(PC)	6.3 (5.8-6.9)	70%(PC)	-

*1 Tensile and flexural specimens were cast 30 minutes after priming.

*2 Impact samples were cast 70 minutes after priming, except 30 minutes after priming for #23 and #24. Number of drops to failure. No delamination was observed

*3 Min. and max. values of multiple samples. Range is not available for single samples.

*4 FM = Failure Mode, %CF = % Cohesive failure in ( ); The rest is interfacial failure.

*5 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table V-(b)

Effect of Binder on Mechanical and Bonding Properties of PC

1"X1" Cross Section Specimens

(89.7% Solids)

Experiment	Type Binder	*Type Bond*	Tensile Properties*1		Flexural Properties*1		Impact Properties*2
			psi (Range)*3	FM %CF*4	psi (Range)*3	FM %CF	Drops(Range)*3
Ref.	PCC (Dry) *5		600	-	280 (250-320)	-	1.0 (1-1)
	(Wet)		600 (520-680)	-	320 (290-340)	-	1.0 (1-1)
15	A-PE/ - /A-174	PC Only	940 (900-960)	-	650 (600-720)	-	2.7 (2-3)
	(99) / (0) / (1)	PC/PCC (Dry)	720 (640-800)	80%(PCC)	290 (260-320)	80%(PCC)	1.7 (1-2)
		PC/PCC(Wet)	200 (200-200)	5%(PCC)	160	5%(PCC)	1.7 (1-2)
		PC/Al	1040	65%(PC)	480 (480-480)	50%(PC)	-
		PC/Steel	1060	25%(PC)	370 (340-400)	45%(PC)	-
		PC/Brass	760	25%(PC)	40 (40-40)	5%(PC)	-
16	Der 8084/HEMA/A-174	PC Only	1590 (1510-1650)	-	990 (920-1080)	-	3.0 (2-4)
	(85) /(15)/ (1)	PC/PCC (Dry)	670 (660-680)	100%(PCC)	280 (280-280)	100%(PCC)	2.0 (2-2)
		PC/PCC(Wet)	540 (480-600)	85%(PCC)	270 (260-280)	100%(PCC)	1.3 (1-2)
		PC/Al	1980	100%(PC)	940 (880-1000)	90%(PC)	-
		PC/Steel	1720	100%(PC)	940 (840-1040)	100%(PC)	-
		PC/Brass	1760	100%(PC)	1.000 (1000-1000)	100%(PC)	-
23	Der 8084/HPMA/A-174	PC Only	1560		980 (960-1000)		3.0 (3-3)
	(85) /(15)/ (1)	PC/PCC (Dry)	480 (360-600)	100%(PCC)	280 (280-280)	100%(PCC)	1.7 (1-2)
		PC/PCC(Wet)	460 (460-460)	75%(PCC)	300 (280-320)	100%(PCC)	1.3 (1-2)
		PC/Al	1420 (1360-1480)	100%(PC)	970 (920-1020)	100%(PC)	
		PC/Steel	1600 (1520-1680)	100%(PC)	940 (820-1060)	100%(PC)	
24	Der 8084/HEMA/DEGDM/A-174	PC Only	2040		1.000 (920-1100)		2.0 (2-2)
	(85) / (10) / (5) / (.5)	PC/PCC (Dry)	440 (440-440)	100%(PCC)	230 (200-280)	100%(PCC)	1.6 (1-2)
		PC/PCC(Wet)	360 (360-360)	100%(PCC)	200	40%(PCC)	1.3 (1-2)
		PC/Al	2260 (2120-2480)	100%(PC)	990 (960-1020)	100%(PC)	
		PC/Steel	2360 (2220-2500)	100%(PC)	930 (840-1020)	100%(PC)	
14	α-VE/ - /A-174	PC Only	-	-	1.020 (1000-1060)	-	4.3 (2-6)
	(100) / (0) / (0.5)	PC/PCC (Dry)	580 (560-600)	100%(PCC)	290 (260-320)	95%(PCC)	1.7 (1-3)
		PC/PCC(Wet)	440 (420-460)	85%(PCC)	270 (260-280)	100%(PCC)	3.3 (3-4)
		PC/Al	780	60%(PC)	910 (800-1020)	90%(PC)	-
		PC/Steel	1680	100%(PC)	900 (800-1000)	90%(PC)	-
		PC/Brass	1440	95%(PC)	1.040 (1080-1000)	100%(PC)	-
17	α-VE /HEMA/DEGDM/A-174	PC Only	1870 (1800-1930)	-	960 (840-1080)	-	4.3 (4-5)
	(100) / (10) / (5) / (0.5)	PC/PCC (Dry)	680 (760-600)	100%(PCC)	260 (240-280)	100%(PCC)	2.0 (2-2)
		PC/PCC(Wet)	490 (380-600)	100%(PCC)	250 (240-260)	100%(PCC)	2.3 (2-3)
		PC/Al	1920	85%(PC)	800 (720-880)	90%(PC)	-
		PC/Steel	1760	85%(PC)	980 (960-1000)	100%(PC)	-
		PC/Brass	720	70%(PC)	920 (840-1000)	70%(PC)	-

*1 Tensile and flexural specimens were cast 30 minutes after priming.

*2 Impact samples were cast 70 minutes after priming, except 30 minutes after priming for #23 and #24. Number of drops to failure. No delamination was observed

*3 Min. and max. values of multiple samples. Range is not available for single samples.

*4 FM = Failure Mode, %CF = % Cohesive failure in ( ); The rest is interfacial failure.

*5 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table VI-(a)

Effect of Binder on Mechanical and Bond Properties of PC*1

(California Test 551 with 7.6cm X 7.6cm X 22.8cm Specimens)

Experiment	Type Binder	Type Bond	Flexural Test		Compressive Test			
			Strength MPa	Failure Mode	Modulus MPa	Strength MPa	Strain*2	Relative*3 Strain Energy
Ref.	PCC	PCC (No WRDA) PCC (W/WRDA)	6.6 5.9	- -	39,000 37,000	53.8 67.6	0.0014 0.0018	1.0
15	A-PE/ - /A-174 (99) / (0) / (1)	PC Only PC/PCC(dry) PC/PCC(SSD)	12.6 7.1 4.4	- 85%CF (PCC) 10%CF (PCC)	10,000	49.0	0.0047	1.9
16	Der 8084/HEMA/A-174 (85) /(15)/ (1)	PC Only PC/PCC(dry) PC/PCC(SSD)	18.4 6.3 7.4	- 100%CF (PCC) 100%CF (PCC)	23,000	89.6	0.0038	2.7
17	α-VE /HEMA/DEGDM/A-174 (100) / (10) / (5) / (0.5)	PC Only PC/PCC(dry) PC/PCC(SSD)	18.5 6.1 6.5	- 100% (PCC) 100% (PCC)	20,000	77.2	0.0039	2.5

1* Solids are different between PCCs and PCs.

PCC Formulation: Type II cement 17.5%; TPerkins PCC 30%; Lonestar pea gravel (B39) 45%; Water 7.5%; 1% WRDA based on cement was incorperated in certain cases.

PC Formulation: Binder 8.0g; L/S #60 Sand 12.0g; L/S #1 Sand 13.0g; L/S #3 Sand 15.0g; B-39 30.0g (89.7% Solids)

2* Estimated from modulus and strength data.

3* Area under the stress-strain curve to failure.

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Table VI-(b)

Effect of Binder on Mechanical and Bond Properties of PC*1

(California Test 551 with 3"X3"X9" Specimens)

Experiment	Type Binder	Type Bond	Flexural Test		Compressive Test			
			Strength (psi)	Failure Mode	Modulus (psi)	Strength (psi)	Strain*2	Relative*3 Strain Energy
Ref.	PCC	PCC (No WRDA) PCC (W/WRDA)	950 850	- -	5,600,000 5,300,000	7,800 9,800	0.0014 0.0018	1.0
15	A-PE/ - /A-174 (99) / (0) / (1)	PC Only PC/PCC(dry) PC/PCC(SSD)	1,830 1,030 640	- 85%CF (PCC) 10%CF (PCC)	1,500,000 - -	7,100 - -	0.0047	1.9
16	Der 8084/HEMA/A-174 (85) /(15)/ (1)	PC Only PC/PCC(dry) PC/PCC(SSD)	2,670 920 1,070	- 100%CF (PCC) 100%CF (PCC)	3,400,000 - -	13,000 - -	0.0038	2.7
17	α-VE /HEMA/DEGDM/A-174 (100) / (10) / (5) / (0.5)	PC Only PC/PCC(dry) PC/PCC(SSD)	2,680 890 940	- 100% (PCC) 100% (PCC)	2,900,000 - -	11,200 - -	0.0039	2.5

1* Solids are different between PCCs and PCs.

PCC Formulation: Type II cement 17.5%; TPerkins PCC 30%; Lonestar pea gravel (B39) 45%; Water 7.5%; 1% WRDA based on cement was incorperated in certain cases.

PC Formulation: Binder 8.0g; L/S #60 Sand 12.0g; L/S #1 Sand 13.0g; L/S #3 Sand 15.0g; B-39 30.0g (89.7% Solids)

2* Estimated from modulus and strength data.

3* Area under the stress-strain curve to failure.

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Table VII - (a)

Effect of Freeze-Thaw-Soak Cycles on Tensile Test

Experiment #	Tensile Properties*1 After 0 Cycles		Tensile Properties After 20 Cycles	
Sample type	MPa (Range)	FM %CF*2	MPa (Range)	FM %CF
PCC Only				
(Dry)*3	3.9 (2.3-5.1)	-	3.2 (1.1-5.8)	-
(Wet)	3.4 (2.1-5.2)	-	3.0 (1.2-4.6)	-
#15				
PC Only	6.5 (6.2-6.6)	-	- -	-
PC/PCC(Dry)	5.0 (4.4-5.5)	80%(PCC)	1.4 -	10%(PCC)
PC/PCC(Wet)	1.4 (1.4-1.4)	5%(PCC)	1.0 -	5%(PCC)
#16				
PC Only	11.0 (10.4-11.4)	-	- -	-
PC/PCC(Dry)	4.6 (4.6-4.7)	100%(PCC)	2.2 -	10%(PCC)
PC/PCC(Wet)	3.7 (3.3-4.1)	85%(PCC)	2.5 -	25%(PCC)
#23				
PC Only	10.7	-	9.5 -	-
PC/PCC(Dry)	3.3 (2.5-4.1)	100%(PCC)	1.9 (1.5-2.3)	0%(PCC)
PC/PCC(Wet)	3.1 (3.0-3.2)	75%(PCC)	3.8 (3.0-4.6)	50%(PCC)
#24				
PC Only	14.9 (14.1-15.7)		- -	-
PC/PCC(Dry)	3.2 (3.0-3.6)	100%(PCC)	1.9 (1.9-1.9)	0%(PCC)
PC/PCC(Wet)	2.9 (2.2-4.3)	100%(PCC)	3.3 (3.0-3.6)	15%(PCC)
#14				
PC Only	-	-	- -	-
PC/PCC(Dry)	4.0 (3.9-4.1)	100%(PCC)	3.7 -	10%(PCC)
PC/PCC(Wet)	3.0 (2.9-3.2)	85%(PCC)	3.6 -	10%(PCC)
#17				
PC Only	12.9 (12.4-13.3)	-	- -	-
PC/PCC(Dry)	4.7 (4.1-5.2)	100%(PCC)	2.8 -	10%(PCC)
PC/PCC(Wet)	3.4 (2.6-4.1)	100%(PCC)	2.8 -	5%(PCC)

*1 Tensil specimens were cast 30 min. after priming.

*2 FM=failure mode; %CF= % cohesive failure in ( ); The rest is interfacial failure.

*3 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table VII - (b)

Effect of Freeze-Thaw-Soak Cycles on Tensile Test

Experiment #	Tensile Properties*1 After 0 Cycles		Tensile Properties After 20 Cycles	
Sample type	psi (Range)	FM %CF*2	psi (Range)	FM %CF
PCC Only				
(Dry)*3	560 (340-740)	-	470 (160-840)	-
(Wet)	500 (300-750)	-	440 (180-660)	-
#15				
PC Only	940 (900-960)	-	- -	-
PC/PCC(Dry)	720 (640-800)	80%(PCC)	200 -	10%(PCC)
PC/PCC(Wet)	200 (200-200)	5%(PCC)	140 -	5%(PCC)
#16				
PC Only	1590 (1510-1650)	-	- -	-
PC/PCC(Dry)	670 (660-680)	100%(PCC)	320 -	10%(PCC)
PC/PCC(Wet)	540 (480-600)	85%(PCC)	360 -	25%(PCC)
#23				
PC Only	1560	-	1,380 -	-
PC/PCC(Dry)	480 (360-600)	100%(PCC)	280 (220-340)	0%(PCC)
PC/PCC(Wet)	450 (440-460)	75%(PCC)	550 (440-660)	50%(PCC)
#24				
PC Only	2160 (2040-2280)		- -	-
PC/PCC(Dry)	470 (440-520)	100%(PCC)	280 (280-280)	0%(PCC)
PC/PCC(Wet)	420 (320-620)	100%(PCC)	480 (440-520)	15%(PCC)
#14				
PC Only	-	-	- -	-
PC/PCC(Dry)	580 (560-600)	100%(PCC)	540 -	10%(PCC)
PC/PCC(Wet)	440 (420-460)	85%(PCC)	520 -	10%(PCC)
#17				
PC Only	1870 (1800-1930)	-	- -	-
PC/PCC(Dry)	680 (600-760)	100%(PCC)	400 -	10%(PCC)
PC/PCC(Wet)	490 (380-600)	100%(PCC)	400 -	5%(PCC)

*1 Tensil specimens were cast 30 min. after priming.

*2 FM=failure mode; %CF= % cohesive failure in ( ); The rest is interfacial failure.

*3 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table VIII - (a)

Effect of Freeze-Thaw-Soak Cycles on Flexural Test

Experiment #	Flexural Properties*1 After 0 Cycles		Flexural Properties After 20 Cycles	
Sample type	MPa (Range)	FM %CF*2	MPa (Range)	FM %CF
PCC Only				
(Dry)*3	2.1 (1.4-2.5)	-	1.4 (0.6-2.5)	-
(Wet)	1.9 (1.5-2.3)	-	2.0 (1.1-2.5)	-
#15				
PC Only	4.5 (4.1-5.0)	-	2.8 (2.6-2.9)	-
PC/PCC(Dry)	2.0 (1.8-2.2)	80%(PCC)	0.8 (0.7-1.0)	10%(PCC)
PC/PCC(Wet)	1.1	5%(PCC)	0.2 (0.0-0.4)	0%(PCC)
#16				
PC Only	6.8 (6.3-7.4)	-	5.9 (5.6-6.2)	-
PC/PCC(Dry)	1.9 (1.9-1.9)	100%(PCC)	1.0 (0.8-1.2)	5%(PCC)
PC/PCC(Wet)	1.9 (1.8-1.9)	100%(PCC)	2.2	70%(PCC)
#23				
PC Only	6.8 (6.6-6.9)	-	6.1 (5.8-6.3)	-
PC/PCC(Dry)	1.9 (1.9-1.9)	100%(PCC)	1.7 (1.6-1.8)	30%(PCC)
PC/PCC(Wet)	2.1 (1.9-2.2)	100%(PCC)	1.9 (1.6-2.2)	95%(PCC)
#24				
PC Only	6.6 (5.9-7.6)	-	4.8 (4.7-5.0)	-
PC/PCC(Dry)	1.6 (1.4-1.9)	100%(PCC)	1.0 (0.8-1.2)	10%(PCC)
PC/PCC(Wet)	1.7 (1.4-2.1)	90%(PCC)	2.2 (1.9-2.5)	10%(PCC)
#14				
PC Only	7.0 (6.9-7.3)	-	5.9 (5.5-6.2)	-
PC/PCC(Dry)	2.0 (1.8-2.2)	95%(PCC)	1.2 (1.1-1.2)	10%(PCC)
PC/PCC(Wet)	1.9 (1.8-1.9)	10%(PCC)	1.9 (1.9-1.9)	70%(PCC)
#17				
PC Only	6.6 (5.8-7.4)	-	5.5 (5.1-5.9)	-
PC/PCC(Dry)	1.8 (1.6-1.9)	100%(PCC)	0.8 (0.7-1.0)	100%(PCC)
PC/PCC(Wet)	1.7 (1.6-1.8)	100%(PCC)	1.2	100%(PCC)

*1 Tensil specimens were cast 30 min. after priming.

*2 FM=failure mode; %CF= % cohesive failure in ( ); The rest is interfacial failure.

*3 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table VIII - (b)

Effect of Freeze-Thaw-Soak Cycles on Flexural Test

Experiment #	Flexural Properties After 0 Cycles		Flexural Properties After 20 Cycles	
Sample type	psi (Range)	FM %CF	psi (Range)	FM %CF
PCC Only				
(Dry)*3	300 (200-360)	-	210 (80-360)	-
(Wet)	280 (220-340)	-	290 (160-360)	-
#15				
PC Only	650 (600-720)	-	400 (380-420)	-
PC/PCC(Dry)	290 (260-320)	80%(PCC)	120 (100-140)	10%(PCC)
PC/PCC(Wet)	160	5%(PCC)	30 (0-60)	0%(PCC)
#16				
PC Only	990 (920-1080)	-	860 (820-900)	-
PC/PCC(Dry)	280 (280-280)	100%(PCC)	150 (120-180)	5%(PCC)
PC/PCC(Wet)	270 (260-280)	100%(PCC)	320	70%(PCC)
#23				
PC Only	990 (960-1000)	-	890 (840-920)	-
PC/PCC(Dry)	280 (280-280)	100%(PCC)	250 (240-260)	30%(PCC)
PC/PCC(Wet)	300 (280-320)	100%(PCC)	270 (240-320)	95%(PCC)
#24				
PC Only	960 (850-1100)	-	700 (680-720)	-
PC/PCC(Dry)	230 (200-280)	100%(PCC)	150 (120-180)	10%(PCC)
PC/PCC(Wet)	240 (200-300)	90%(PCC)	320 (280-360)	10%(PCC)
#14				
PC Only	1,020 (1000-1060)	-	850 (800-900)	-
PC/PCC(Dry)	290 (260-320)	95%(PCC)	170 (160-180)	10%(PCC)
PC/PCC(Wet)	270 (260-280)	10%(PCC)	280 (280-280)	70%(PCC)
#17				
PC Only	960 (840-1080)	-	800 (740-860)	-
PC/PCC(Dry)	260 (240-280)	100%(PCC)	120 (100-140)	100%(PCC)
PC/PCC(Wet)	250 (240-260)	100%(PCC)	180	100%(PCC)

*1 Tensil specimens were cast 30 min. after priming.

*2 FM=failure mode; %CF= % cohesive failure in ( ); The rest is interfacial failure.

*3 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table IX

Effect of Freeze-Thaw-Soak Cycles on Impact Test

Experiment #	Impact Properties After 0 Cycles		Impact Properties After 20 Cycles	
	Drops (Range)	Delamination	Drops (Range)	Delamination
PCC Only				
(Dry)*1	1.0 (1-1)	-	- -	-
(Wet)	1.0 (1-1)	-	- -	-
#15				
PC Only	2.7 (2-3)	-	2.0 (2-2)	-
PC/PCC(Dry)	1.7 (1-2)	0%	1.0 (1-1)	0%
PC/PCC(Wet)	1.7 (1-2)	0%	1.0 (1-1)	0%
#16				
PC Only	3.0 (2-4)	-	2.0 (1-3)	-
PC/PCC(Dry)	2.0 (2-2)	0%	1.3 (1-2)	0%
PC/PCC(Wet)	1.3 (1-2)	0%	1.0 (1-1)	0%
#23				
PC Only	3.0 (3-3)	-	1.7 (1-2)	-
PC/PCC(Dry)	1.7 (1-2)	0%	1.0 (1-1)	0%
PC/PCC(Wet)	1.3 (1-2)	0%	1.3 (1-2)	0%
#24				
PC Only	2.2 (2-3)	-	2.3 (2-3)	-
PC/PCC(Dry)	1.3 (1-2)	0%	1.7 (1-2)	0%
PC/PCC(Wet)	1.3 (1-2)	0%	1.7 (1-2)	0%
#14				
PC Only	4.3 (2-6)	-	2.3 (2-3)	-
PC/PCC(Dry)	1.7 (1-3)	0%	2.0 (1-3)	0%
PC/PCC(Wet)	3.3 (3-4)	0%	1.3 (1-2)	0%
#17				
PC Only	4.3 (4-5)	-	5.0 (4-7)	-
PC/PCC(Dry)	2.0 (2-2)	0%	1.7 (1-2)	0%
PC/PCC(Wet)	2.3 (2-3)	0%	1.3 (1-2)	0%

*1 Dry and Wet(SSD) PCC : See test procedure, page 70.

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Table X

Effect of Intermittent Oil Immersion and Thermal Cycling on Impact Test

Sample #	Impact Properties After 0 Oil Imersion Cycles		Impact Properties After 32 Oil Immersion Cycles	
	Drops (Range)	Delamination	Drops (Range)	Delamination
#15				
PC Only	2.7 (2-3)	-	3.0 (3-3)	-
PC/PCC(Dry)	1.7 (1-2)	0%	2.0 (2-2)	0%
PC/PCC(Wet)	1.7 (1-2)	0%	1.5 (1-2)	0%
#16				
PC Only	3.0 (2-4)	-	1.5 (1-2)	-
PC/PCC(Dry)	2.0 (2-2)	0%	2.0 (2-2)	0%
PC/PCC(Wet)	1.3 (1-2)	0%	1.5 (1-2)	0%
#14				
PC Only	4.3 (2-6)	-	2.3 (2-3)	-
PC/PCC(Dry)	1.7 (1-3)	0%	2.0 (1-3)	0%
PC/PCC(Wet)	3.3 (3-4)	0%	1.3 (1-2)	0%
#17				
PC Only	4.3 (4-5)	-	5.0 (4-6)	-
PC/PCC(Dry)	2.0 (2-2)	0%	2.5 (2-3)	0%
PC/PCC(Wet)	2.3 (2-3)	0%	2.5 (2-3)	0%

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Figure 1

Viscosity of Vinylester (VE8520) vs. % Monomer (HPMA)

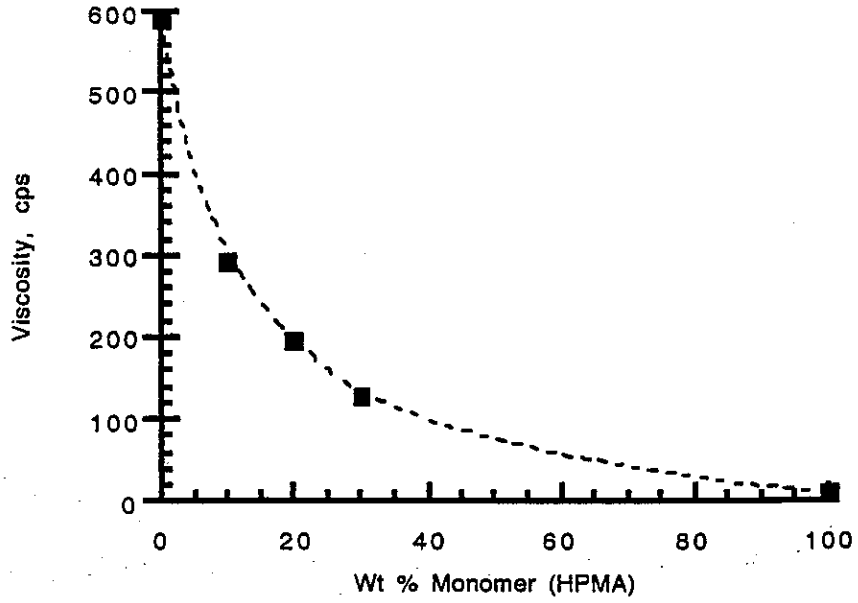

Figure 2

Degree of Permeation vs. Time

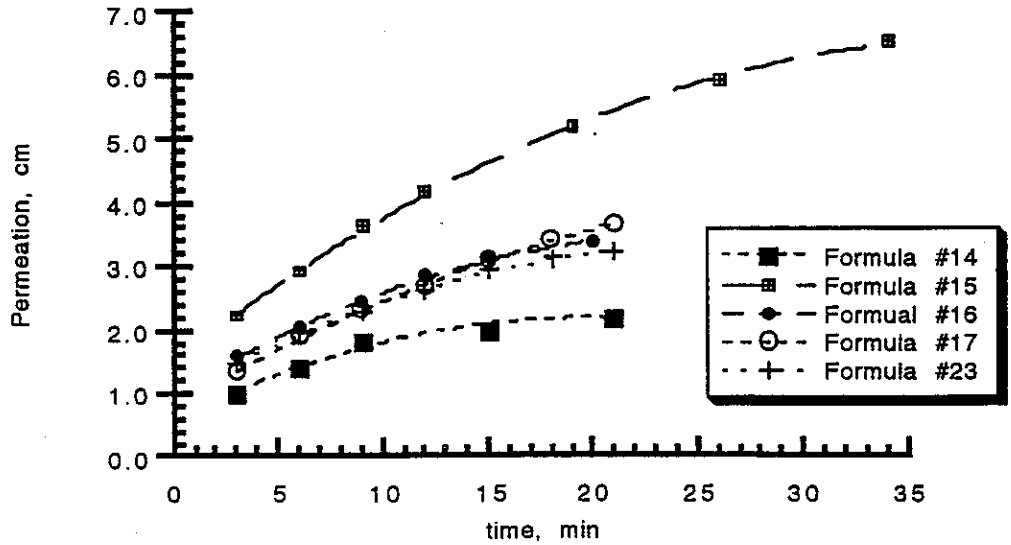

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Figure 3

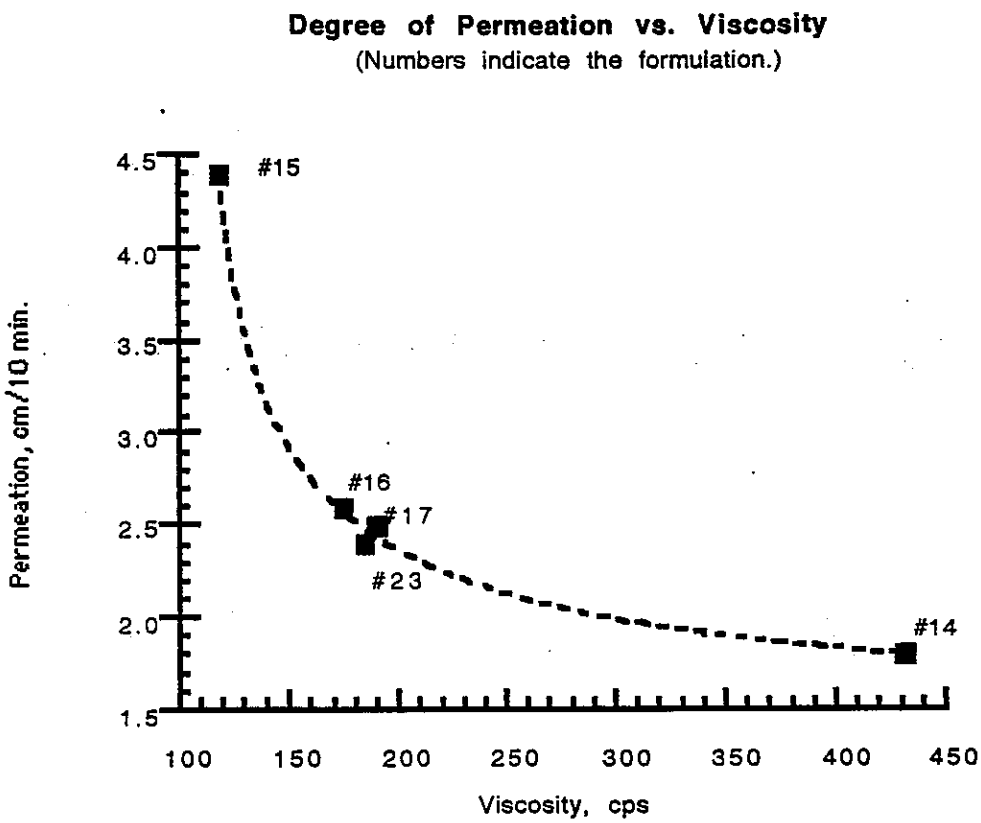

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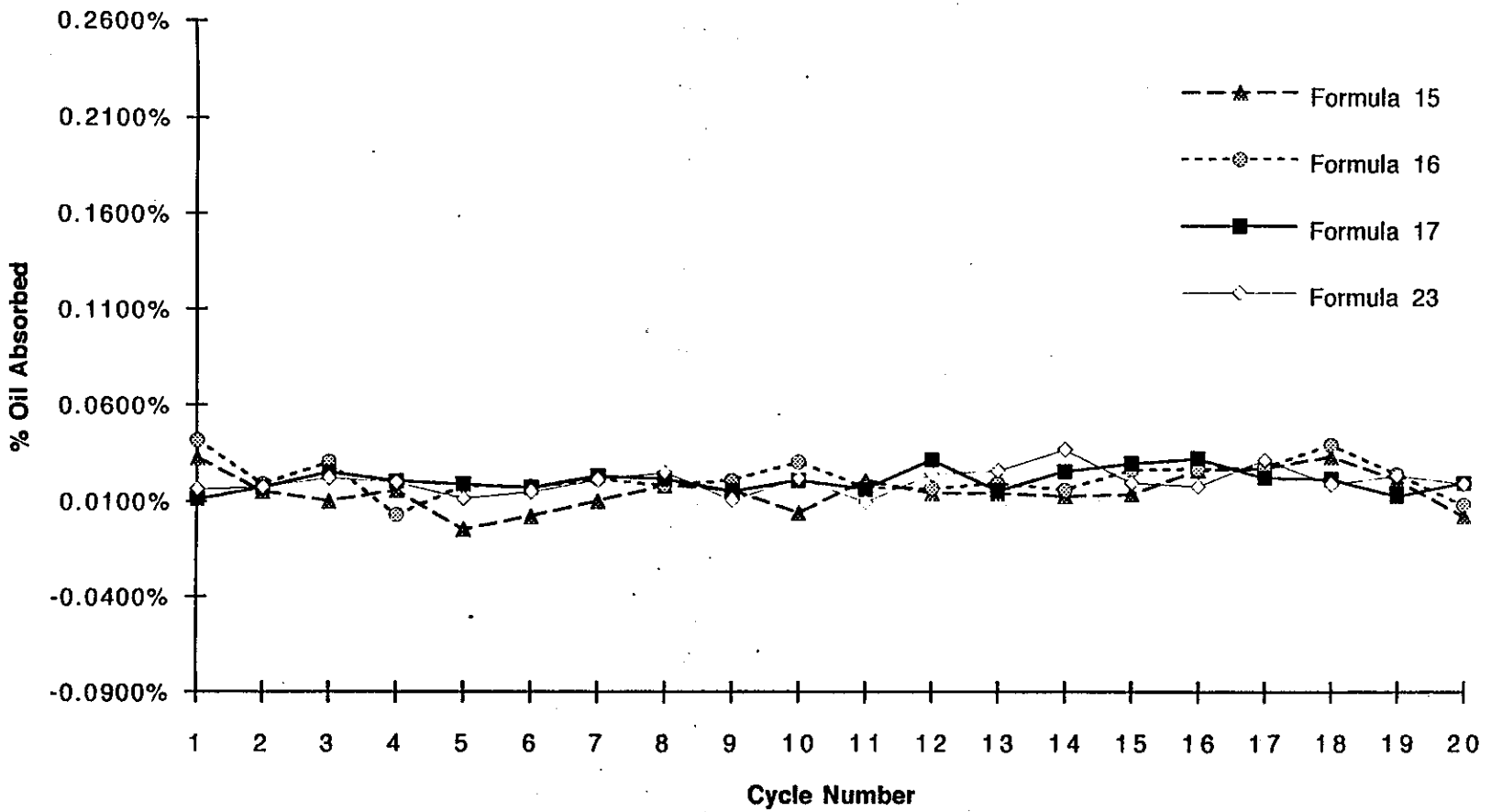
Figure 4

Average % Oil Absorption by Cured Binder During Thermal and Intermittent Oil Immersion Cycles*



* % Oil Absorbed = $\frac{\text{Oil Soaked Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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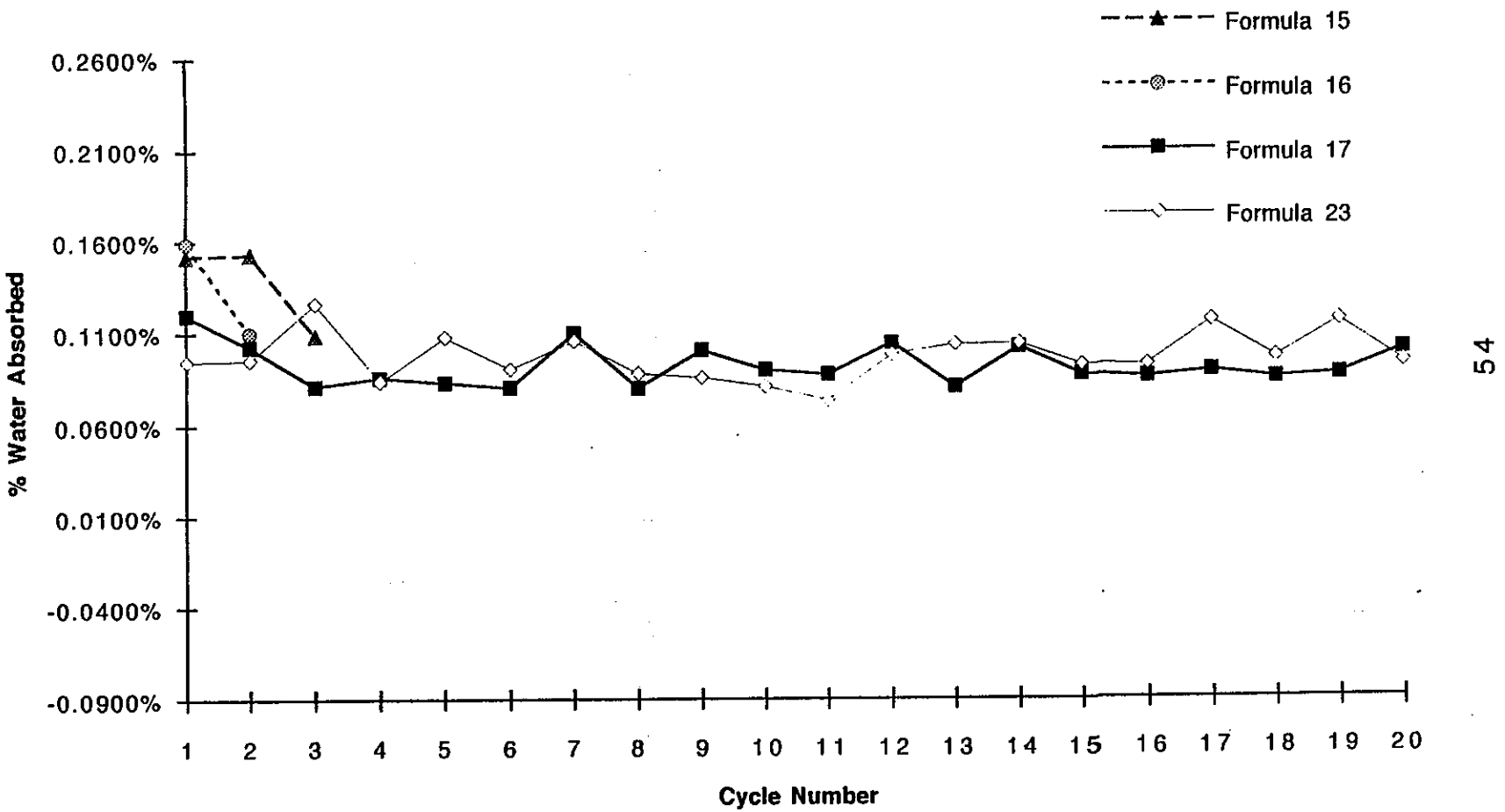
Figure 5

Average % Water Absorbed by Cured Binder During Thermal and Intermittent Water Immersion Cycles*



54

* % Water Absorbed = $\frac{\text{Wet Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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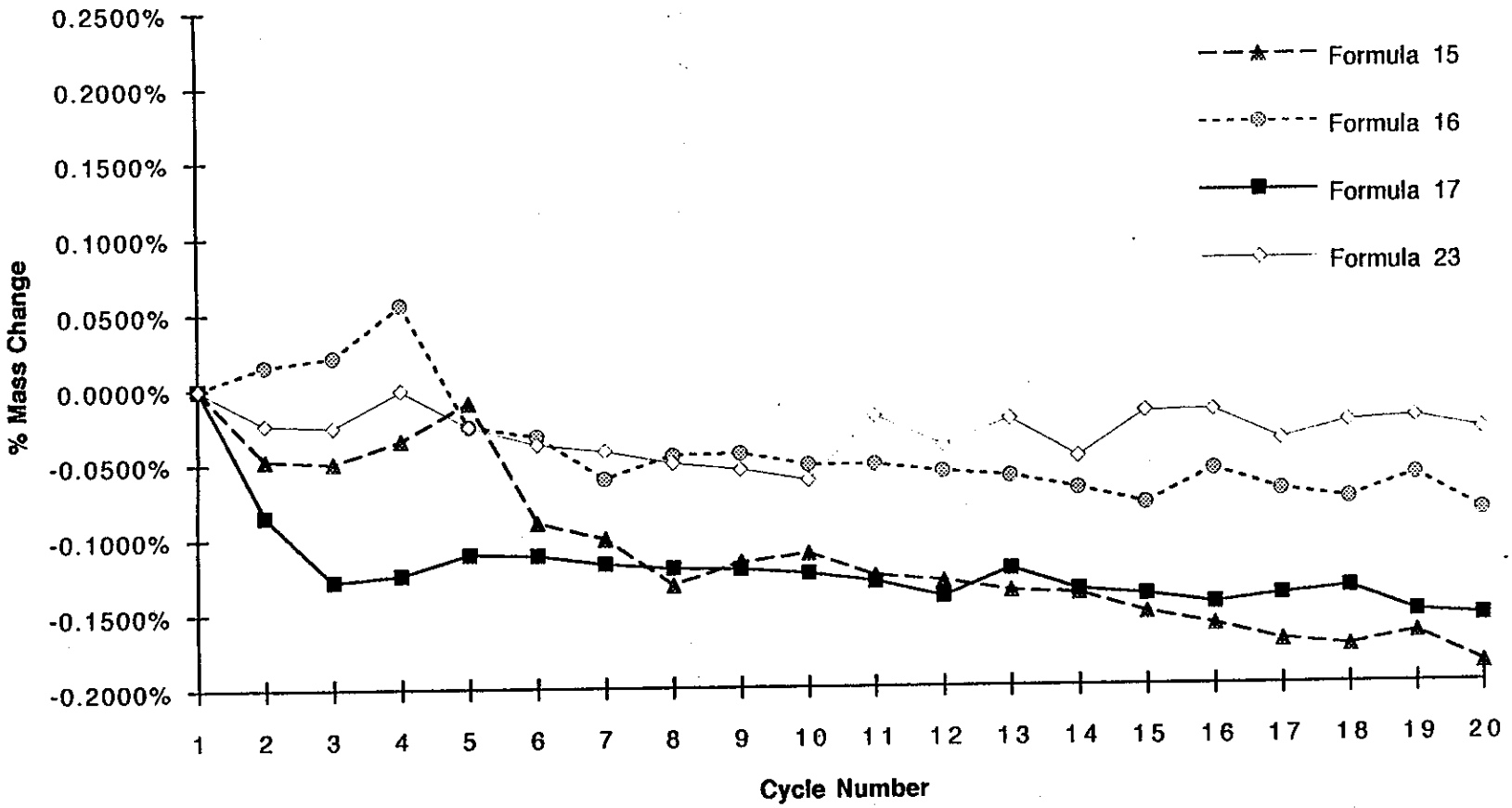
Figure 6

Average % Mass Change from Initial Mass of Cured Binder During Thermal and Intermittent Oil Immersion Cycles*



* % Oil Absorbed = $\frac{\text{Oil Soaked Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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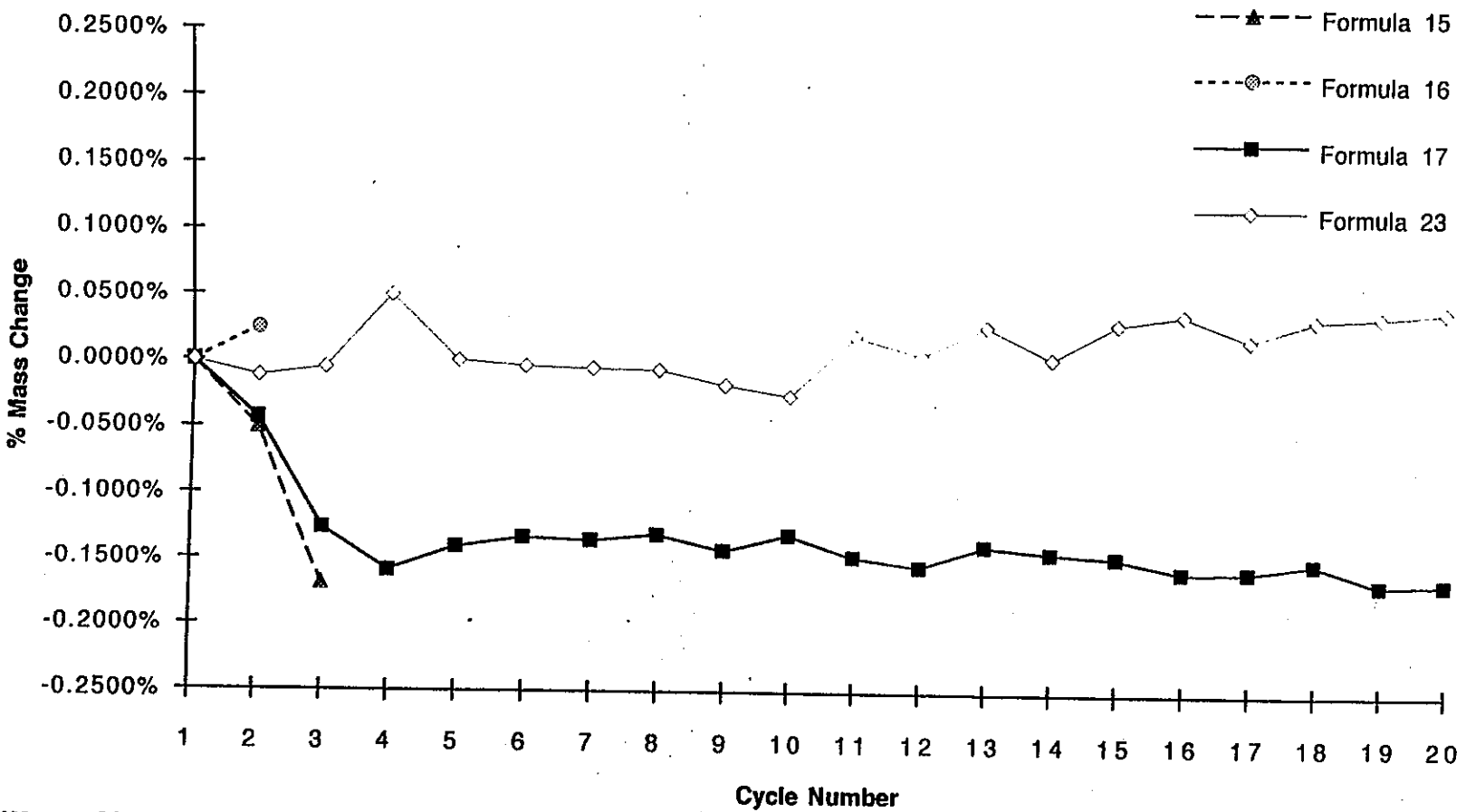
Figure 7

Average % Mass Change from Initial Mass of Cured Binder During Thermal and Intermittent Water Immersion Cycles*



* % Water Absorbed = $\frac{\text{Wet Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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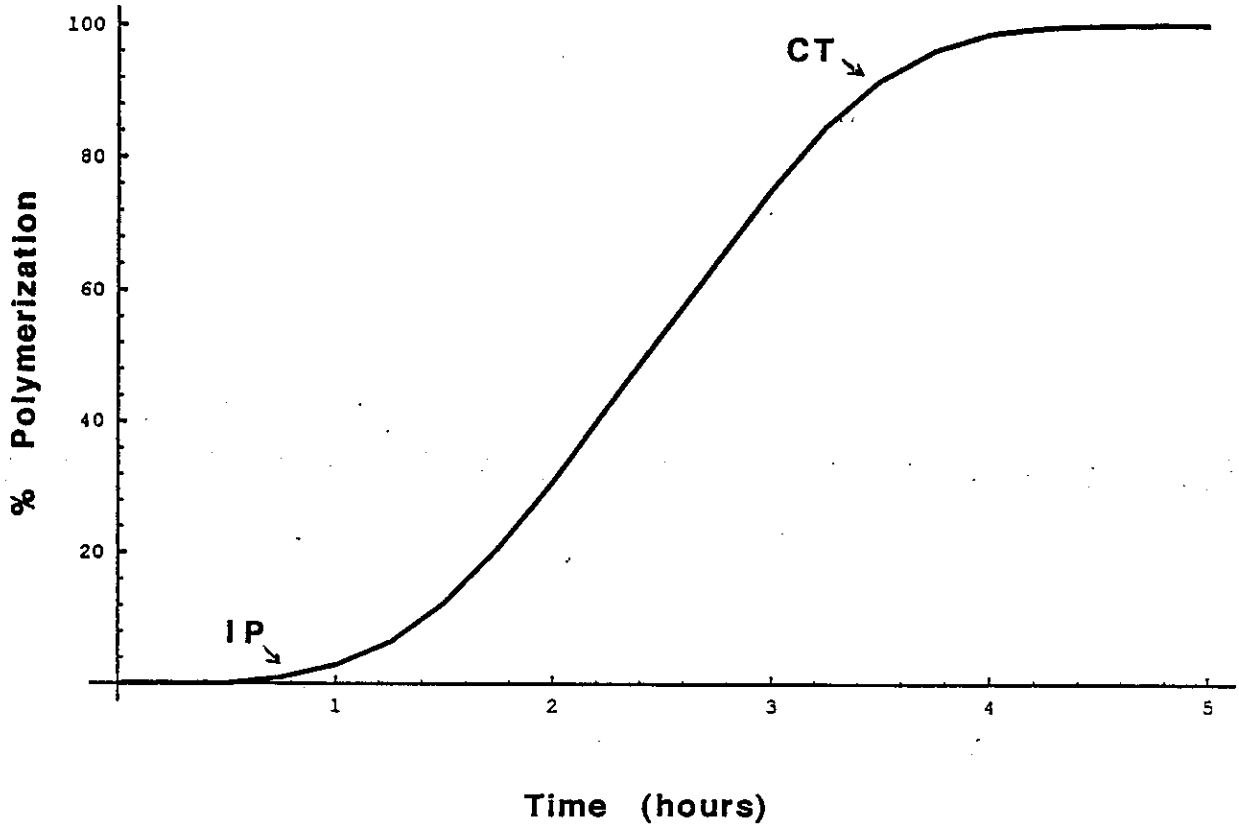
Figure 8

Typical Polymerization-Time Plot



(1) IP = Induction period (equivalent to pot-life)
(2) CT = Cure time

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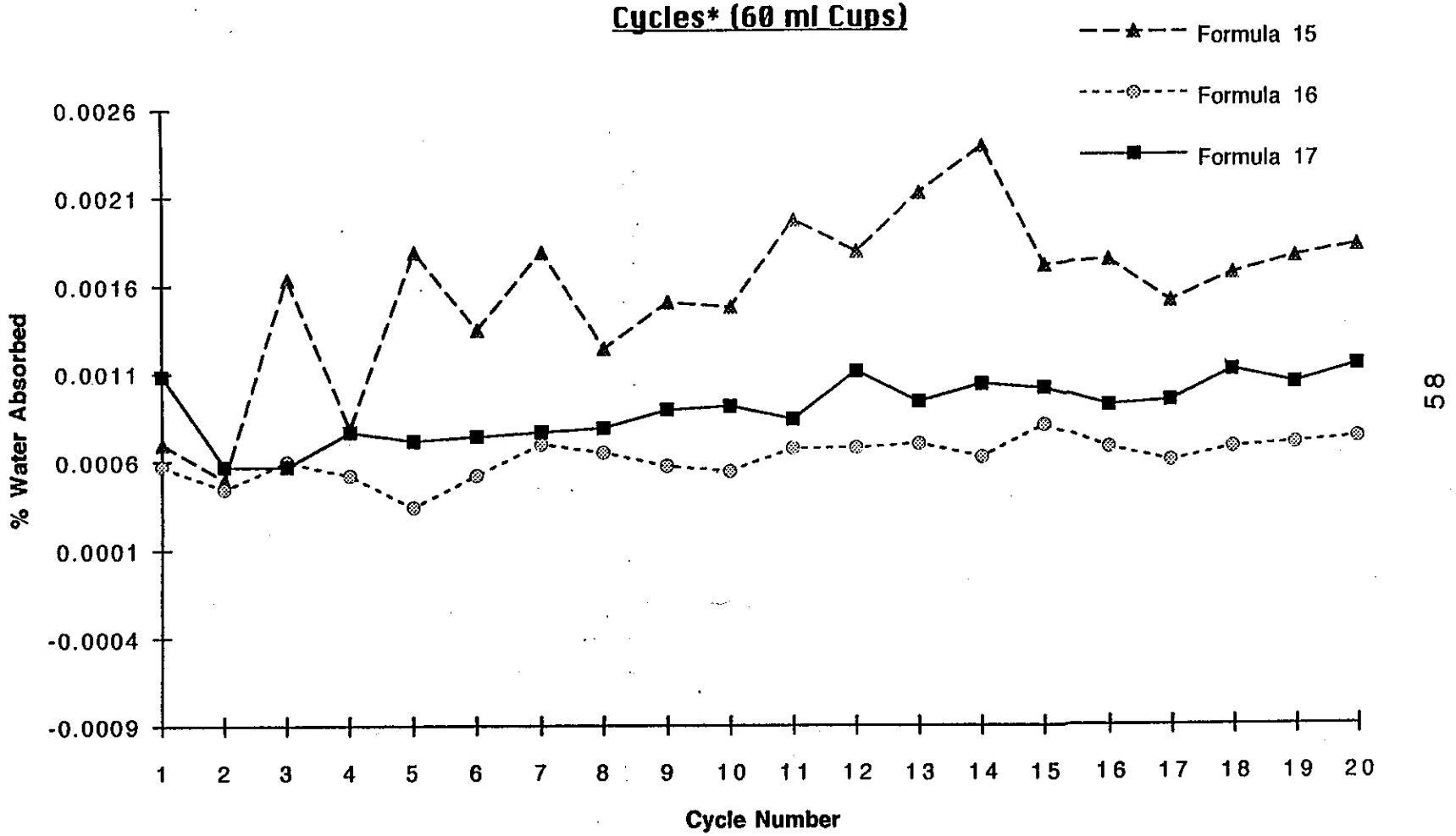
Figure 9

Average % Water Absorbed by PC Composites During Freeze-Thaw-Soak Cycles* (60 ml Cups)



* % Water Absorbed = $\frac{\text{Wet Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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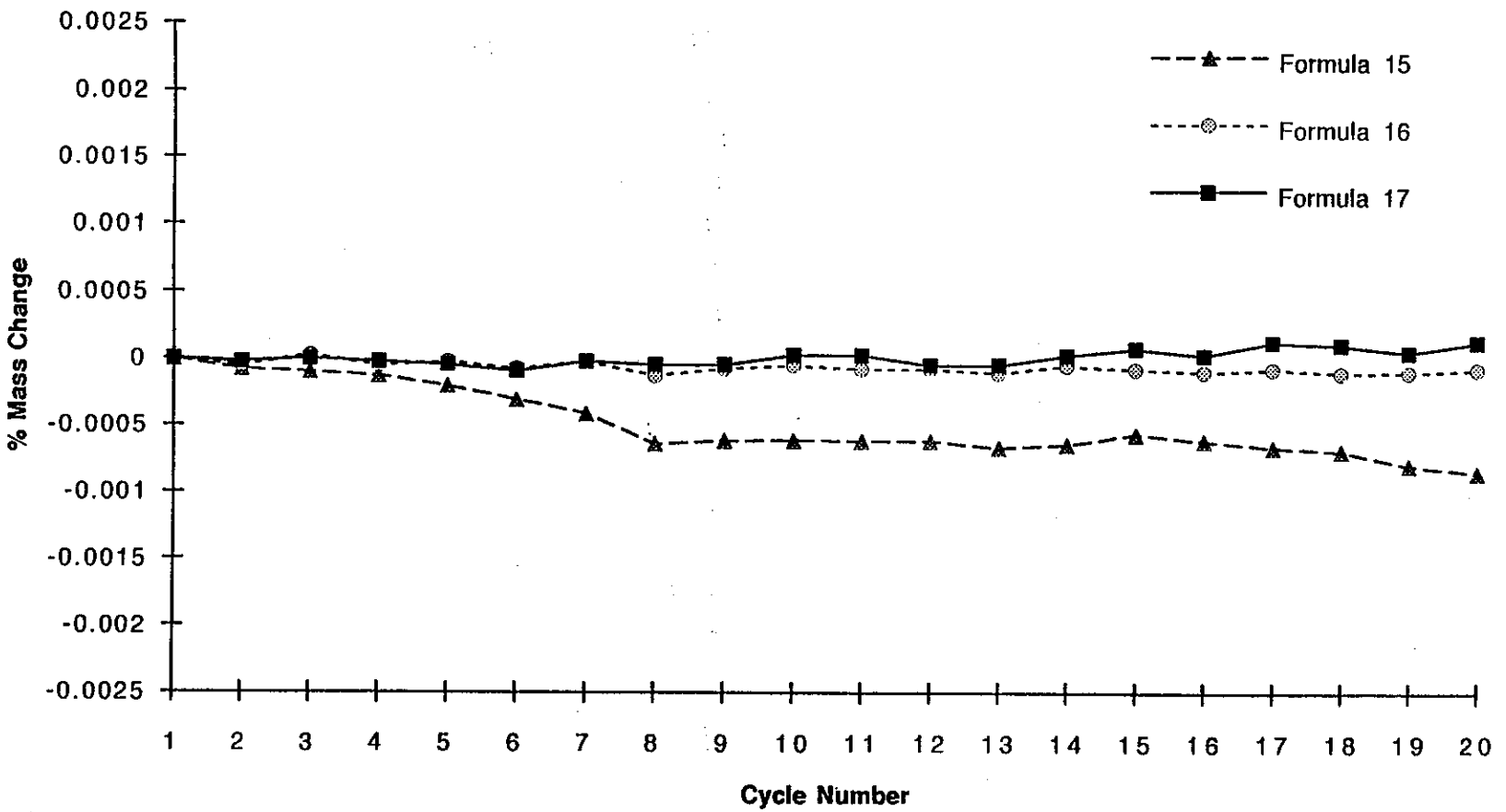
Figure 10

Average % Mass Change from Initial Mass by PC Composites During Freeze-Thaw-Soak Cycles* (60 ml Cups)



* % Mass Change = $\frac{\text{Heat Dried Mass - Initial Heat Dried Mass}}{\text{Heat Dried Mass}} \times 100$

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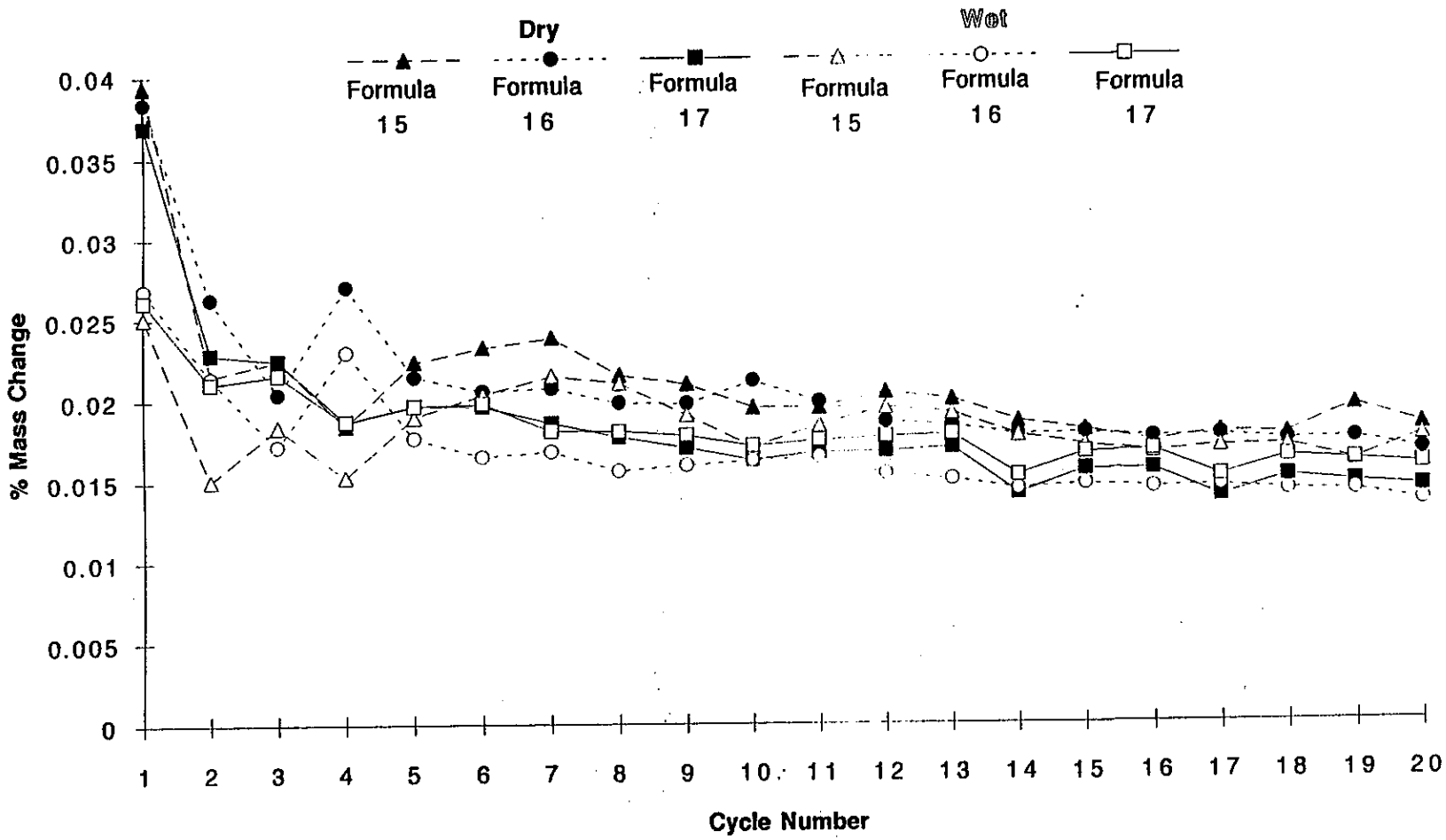
Figure 11

Average % Water Absorbed by PC/PCC Samples During Freeze-Thaw-Soak Cycles
(100ml Cups - 70ml PCC/30ml PC)



60

* % Mass Change = $\frac{\text{Heat Dried Mass - Initial Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100

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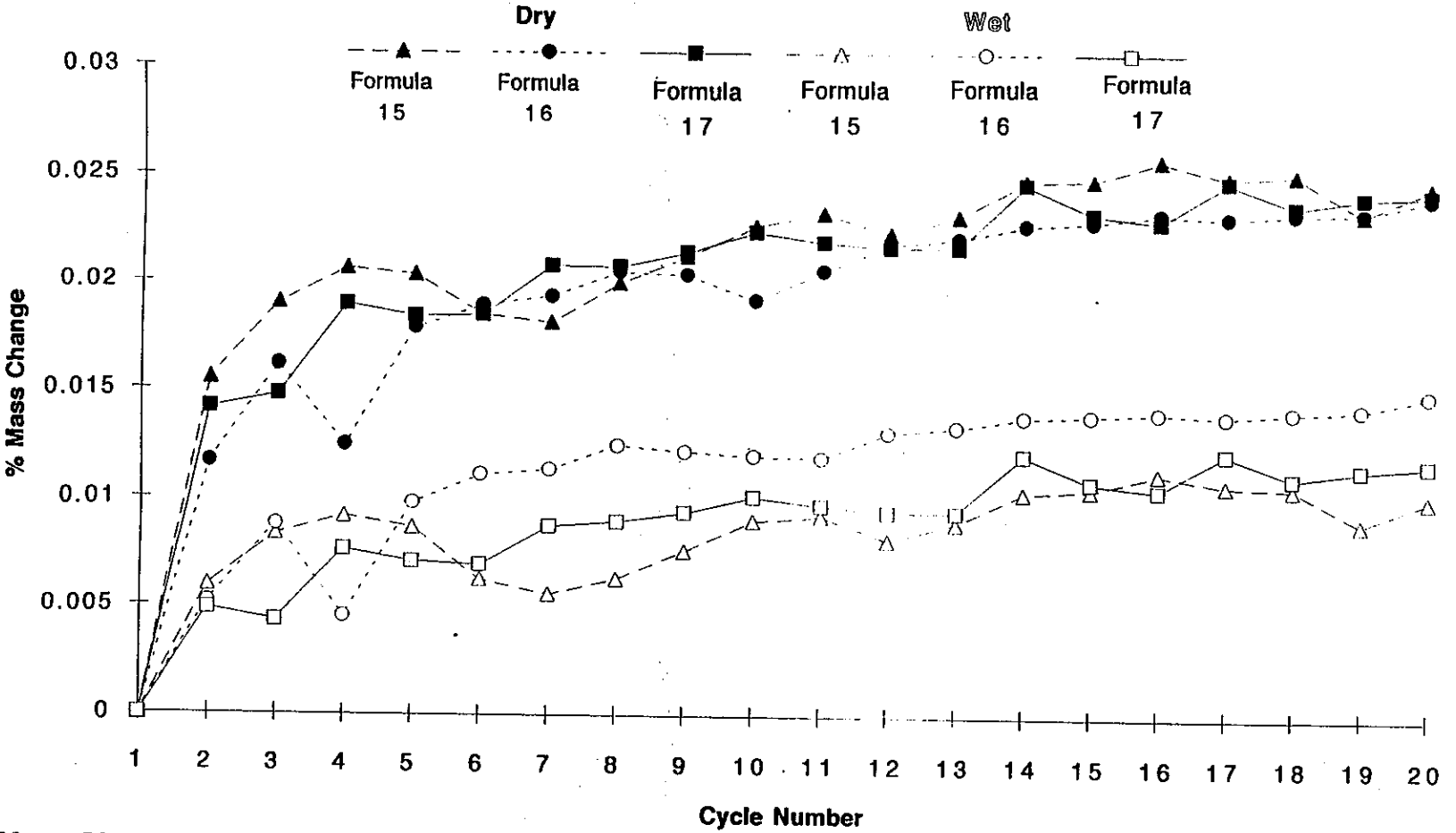
Figure 12

Average % Mass Change From Initial Mass by PC/PCC Samples During Freeze-Thaw-Soak Cycles (100ml Cups - 10ml PCC/30ml PC)



* % Mass Change = $\frac{\text{Heat Dried Mass - Initial Heat Dried Mass}}{\text{Heat Dried Mass}} \times 100$

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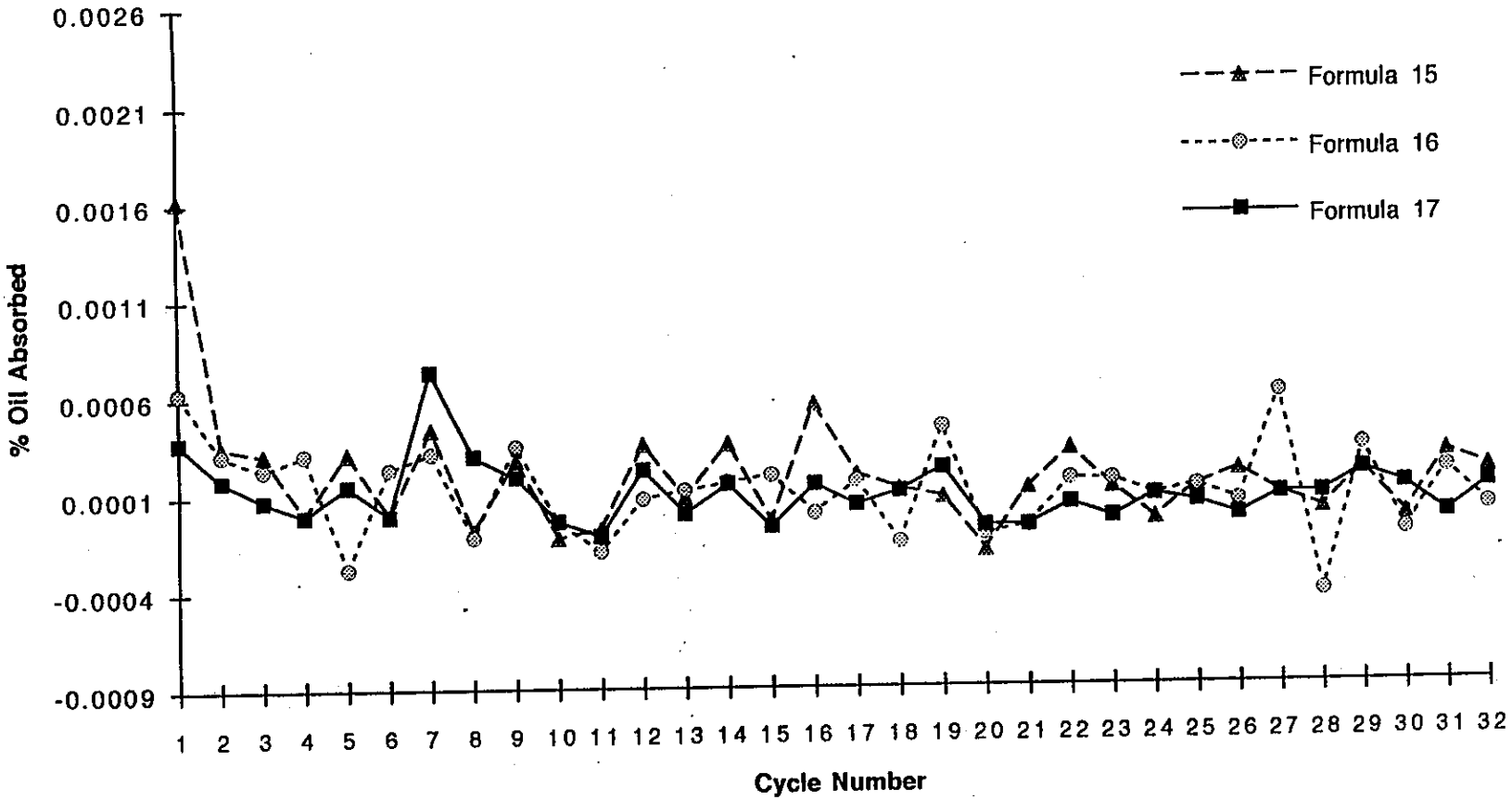
Figure 13

Average % Oil Absorbed by PC Composites During Thermal and Intermittent Oil Immersion Cycles* (60 ml Cups)



* % Oil Absorbed = $\frac{\text{Oil Soaked Mass - Heat Dried Mass}}{\text{Heat Dried Mass}}$ X 100 (Within Cycle)

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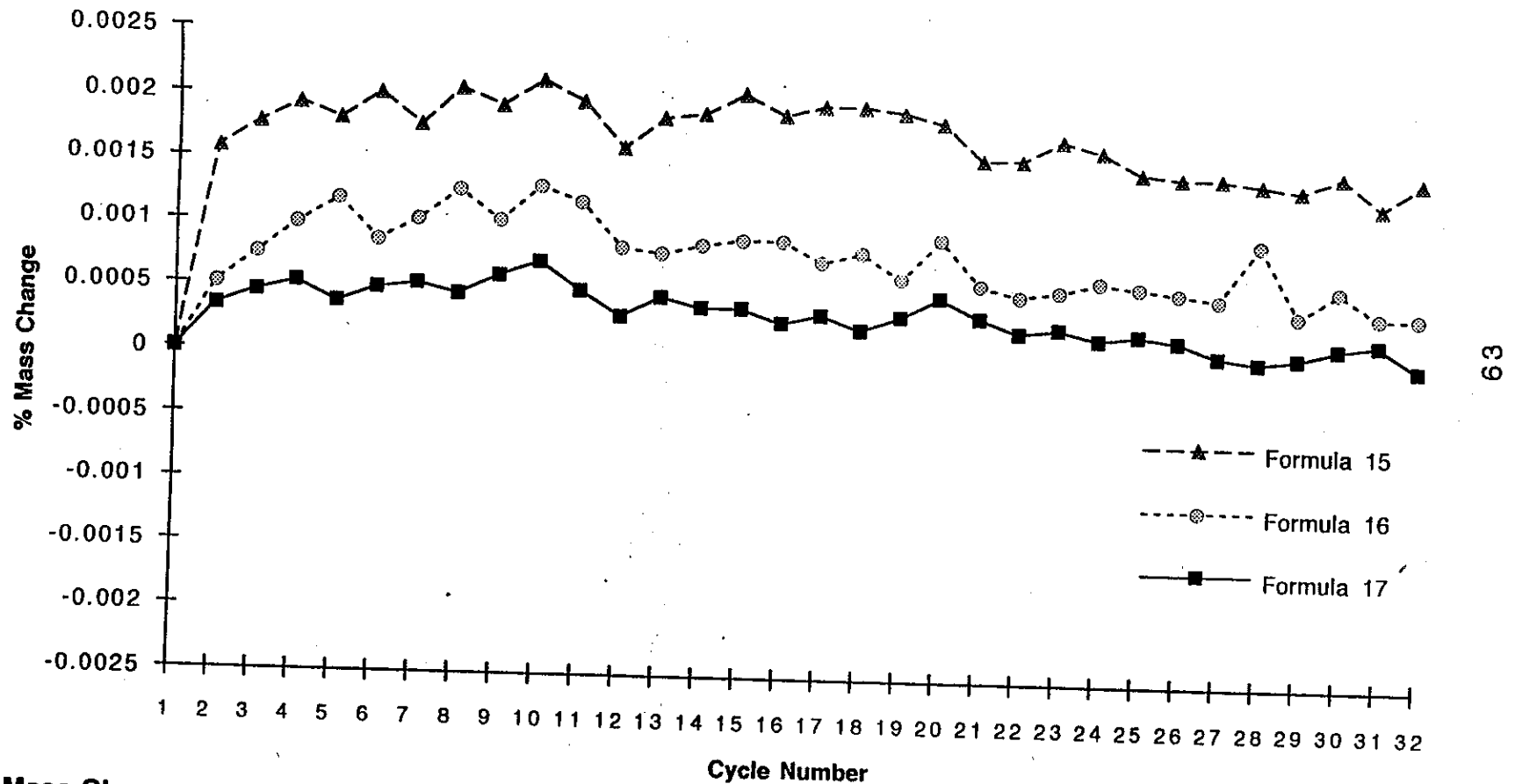
Figure 14

Average % Mass Change from Initial Mass by PC Composites During Thermal and Intermittent Oil Immersion Cycles* (60 ml Cups)



* % Mass Change = $\frac{\text{Heat Dried Mass - Initial Heat Dried Mass}}{\text{Heat Dried Mass}} \times 100$

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III. CONCLUSIONS AND RECOMMENDATIONS:

(1) We have conclusively demonstrated that our mechanistic approach in developing improved polymer concretes for repair of Portland cement concrete is successful. Within a limited time of one year, we have demonstrated that our new binder system, which has cure characteristics similar to those of unsaturated polyester systems, has excellent strength and bonding properties. The binder ingredients are combinations of vinyl ester resins containing acrylonitrile-butadiene copolymer, mono and/or difunctional polar methacrylates, styrene and a silane coupling agent. (They are called VEPM binders.) They show excellent bonding characteristics to steel and PCC including moist (SSD) PCCs. Even after 20 harsh freeze-thaw-soak cycles, some of the VEPM PC/PCC(SSD) bonds showed only minor damage. Conversely, Aristech's unsaturated polyester PC/PCC(SSD), our reference, showed interfacial failure in bond tests even prior to freeze-thaw-soak cycles, and after the 20 cycles, some samples were so damaged that they fell apart at the interface during handling. (Each freeze-thaw-soak cycle consists of heating at 57°C (135°F) for 24 hours, followed by soaking in water for 24 hours at room temperature, and then freezing the soaked samples at -20°C (-4°F) for 24 hours.) Our VEPM PCs have superior tensile, flexural and compressive strengths compared with Aristech's PC. Furthermore, VEPM binders and PCs have properties superior or equivalent to those of Aristech in Tg, oil absorption, water absorption, chemical resistance and in volume shrinkage. Viscosities of VEPM binders are around 200 cps vs. 120 cps for Aristech's unsaturated polyester. The modulus of elasticity of VEPM PCs ranges from 20,000 MPa (2,900,000 psi) to 23,400 MPa (3,400,000 psi), whereas that of

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Aristech's PC is 10,300 MPa (1,500,000 psi). Based on their experience, Caltrans recommends the modulus to be in the range of 7,000 MPa (1,00,000psi) to 14,000 MPa (2,000,000 psi). Additional modification of VEPM formulations is needed to lower the modulus while retaining good strengths and bonding characteristics.

(2) Although detailed trial and error cure studies were not performed on any of our VEPM formulations, our mechanistic studies lead us to believe that the cure process can be controlled to give about 45 minutes of pot-life and four hours of cure-time. Furthermore, there is a strong indication that a simple chelating agent may be used to control the pot-life when the application temperature is higher than 25°C (77°F).

(3) Studies have shown that types, sizes and size distributions of aggregates are important. It has been demonstrated that proper multimodal distribution of aggregate sizes would allow a substantial increase in solids content. The presence of very fine particles will influence mechanical properties in a way which depends on the type of chemical features.

It is strongly recommended that additional research work be performed on VEPM concretes, especially in the areas of modulus modifications, cure studies, and aggregate modifications.

IV. IMPLEMENTATION

(1) Although this study demonstrates the feasibility of developing potentially superior polymer concrete for repair of Portland cement concrete, the final formulations of PCs are yet to be optimized. Optimization of properties through simultaneous consideration of fifteen or more important parameters is required. However, some of our new

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formulations (#17 #23 and #24 in Tables I and V-X) can readily replace unsaturated polyester PCs to give much superior properties, especially in bonding and strength properties, if the modulus of elasticity can be lowered to 14,000 MPa (2,000,000 psi).

(2) There is a strong potential of developing a versatile and simple chelating agent to retain a good pot-life even at a higher application temperature. If a simple manipulation, such as an addition of small amounts of a certain chelating agent, prolongs the pot-life at a higher temperature without significantly affecting other parameters, it will be extremely useful.

(3) Study of types, sizes and size distributions of aggregates is warranted. We have already demonstrated that Caltrans' solids currently used can be replaced with our pentamodal aggregates to increase solids content from 88.7% to 90.4% (Compare item I-a with item III-c in Table III). Furthermore, the presence of different types of fine aggregates has been shown to give different mechanical properties (III-b vs. III-c in Table III).

(4) Test methods to evaluate the fifteen parameters discussed in this report should be continuously modified. For example, California Test 551 specifies that "dry PCC" samples for bonding studies be dried at 110°C (230°F) for 48 hours. Our study indicates that PCC subjected to this high temperature undergoes dehydration (chemical reaction) to lose about 2.0% of its water. It appears to be more realistic to heat the samples to say 57°C (135°F) to obtain dry samples.

Detailed discussions, including various approaches to studies of items (1), (2) and (3), above, will be included in our next proposal.

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V. APPENDICES

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Appendix 1: Testing Procedures for PC and PCC Samples

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1. Sample Preparation and Definition of Terms.

All **portland cement concrete ("PCC")** specimens are prepared as follows: The PCC is formulated with 45% Lone Star pea gravel B-39, 30% Teichert-Perkins PCC sand, 17.5% type II cement and 7.5% water. In addition, 500 g (1.1 lb) of WRDA-19 (manufactured by W. R. Grace Co.) water reducing agent is added for every 45 kg (100 lb) of cement. Four and twenty liter (one and five gallon) batches are thoroughly mixed with a **Mixal M-61-A unit ("the mixer")**, cast into appropriate molds using a Syntron jogger, and allowed to cure under damp paper towels and PE sheets for 24 hours. After removing from the molds, samples are cured by soaking in a water bath at room temperature (about 23 °C (73 °F)) for 21 days. Cured samples are allowed to air dry and are then cut with a water-cooled diamond blade saw. PCC blocks to be used as **dry PCC blanks ("dry samples")** are placed in an oven at 110 °C (230 °F) for 24 hours and cooled to room temperature before using. PCC blocks to be used as **Saturated Surface Dry PCC ("wet samples")** are immersed in water for 24 hours and blot dried with paper towels prior to use.

All **polymer concrete ("PC")** batches are prepared as follows:

(a) Prepromoted resin is mixed with an appropriate peroxide initiator. (This mixture is called the **"binder"**.)

(b) Binder and aggregates are combined and thoroughly mixed in the mixer to form a **PC slurry**.

(c) The PC slurry is cast immediately after mixing.

(d) PC samples are cured for 24 hours at room temperature followed by 24 hours at 57 °C (135 °F) before testing.

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If a PC formulation is being tested for bonding to another substrate, then the substrate surface is prepared as follows:

(a) PCC surfaces are saw cut (see above), and metal surfaces are ground with #150 sandpaper using an electric sander.

(b) Both types of surfaces are primed (with the same binder as the one in the slurry) 30 or 70 minutes before casting.

In all bonding tests between PC and other substrates, a visual examination of the broken surfaces is made to determine the failure mode. If the entire surface of the stronger material is covered with a layer of the weaker material in which the thickness is greater than about 0.2 mm (0.008"), then the failure mode is defined as 100% **cohesive failure** of the weaker material. If failure clearly occurs at the interface, or if the layer of weaker material is less than about 0.2 mm (0.008") thick at all points on the surface, then the failure mode is defined as 100% **interfacial failure.** In cases where a layer thicker than about 0.2 mm (0.008") covers only a portion of the surface, visual examination is used to estimate the percentages of cohesive and interfacial failure.

2. Tensile Strength (ASTM 192-81).

Samples are cast into 7.6 cm (3") long dogbone molds with a 2.5 cm x 2.5 cm (1" x 1") cross section at the midpoint. Samples consisting of 100% PCC or PC are prepared to evaluate tensile strengths of each material (bulk failure). To test for bond strength, half of the mold is filled with a previously primed PCC substrate, and PC slurry is cast into the empty half and cured.

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Each PC formulation is tested with both wet and dry PCC samples, as well as with several metals (aluminum, steel and/or brass).

Cured dogbones are clamped into a Comten Model 924MT testing machine set up in stretching mode. In this mode the machine measures both the applied force (0 to 56 MPa (4000 psi)) and the elongation of the sample. Samples are stretched at 1.0 cm (0.4") per minute, and the force and elongation at the failure point are noted. A semi-quantitative determination of cohesive vs. interfacial failure mode is made by visual examination of the broken surfaces.

3. Flexural Strength.

Rectangular samples measuring 2.5 x 2.5 x 30.5 cm (1" x 1" x 12") are prepared as follows: A 7.5 cm (3") length of primed substrate (PCC, aluminum, brass or steel) is placed at each end of the mold. PC slurry is then cast into the central 15 cm (6") segment and cured.

Cured samples are mounted in a Comten Model 924 MT testing machine run in compression mode. In this mode the sample sits on top of a two curved 1.9 cm (3/4") wide steel bars, the centers of which are 7.5 cm (3") apart. The machine drives a wedge down on the midpoint of the sample and records applied force (0 to 56 MPa (4000 psi)). Samples are compressed at 1.0 cm (0.4") per minute, and the force at the failure point is noted. Each sample yields two test results: (a) The bar is first broken in the middle to measure the flexural strength of PC. (b) The bar is then broken at

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each interface, to test for bond strength. A semi-quantitative determination of bulk vs. interfacial failure mode is made by visual examination of the broken surfaces. The flexural strength of PCC is determined using separate 2.5 x 2.5 x 14 cm (1" x 1" x 6") PCC samples.

4. Impact Strength.

A. PCC samples to be tested for impact strength are cast to the 100 mL mark of a 100-mL polyethylene beaker and cured in water for 21 days. The resulting tapered samples are 5.3 cm (2.1") in diameter at the top, 4.1 cm (1.6") in diameter at the bottom, and 5.1 cm (2.0") high.

B. PC samples to be tested for impact strength are cast to the 60 mL mark of the beaker (3.3 cm (1.3") high). Note: The PC samples are smaller than the PCC samples so that they will fail within a reasonable number of impacts.

C. Samples for testing bond strength upon impact are removed from the mold. No mold release agent is necessary, since the beaker molds are sufficiently flexible to allow easy removal by hand. The samples are then prepared as follows:

   (a) Cured PCC samples are cut with a water-cooled diamond blade saw at the 70 mL line (PCC height of 3.8 cm (1.5")), and primed with the same binder to be used in the PC slurry.

   (b) The primer is allowed to cure for 30 to 70 minutes, and the primed samples are placed back into a beaker mold.

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PC slurry is cast up to the 100 mL mark and cured (PC height of 1.3 cm (0.5")).

For the impact strength test the sample is placed with the smaller diameter (PCC) end resting on a rigid steel plate which is glued to a concrete floor (ground level). A 1242 g (2.736 lb) steel weight is dropped repeatedly onto the sample through a 1.75 m (5' 9") long aluminum tube with 6.35 cm (2.50") inner diameter until the sample fails. The weight is cylindrical with a 5.72 cm (2.25") diameter, and the end which strikes the sample is hemispherical with a radius of 2.86 cm (1.13").

5. Resin viscosity.

Resin viscosity is determined with a Brookfield Model DV-II digital viscometer. The Brookfield LV spindle set supplied with the instrument permits testing viscosity in the following centipoise (cps) ranges: 10-20K, 50-100K, 200-400K and 1K-2000K. Each spindle has been individually calibrated over a range of angular velocity with appropriate Brookfield viscosity standards.

The resin to be tested is placed in a polyethylene cylinder (10.8 cm (4.25") height, 5.1 cm (2") inner diameter), and cps readings are acquired using the appropriate combination of spindle and angular velocity. In each case the resin temperature is also noted.

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6. Permeation by Binder.

The penetrating ability of binders is tested using #60 sand packed with a vibrator into 19.7 x 0.48 cm (7.75 x 0.19") translucent polyethylene straws. A 2.5 cm (1") layer of binder is placed on top of a 16.5 cm (6.5") column of sand, and the depth of permeation is recorded at three minute intervals until movement of the binder stops. Samples are maintained in a vertical orientation without any mechanical disturbance during the entire test procedure.

7. Cure Shrinkage of Binder.

The degree of shrinkage of the binder upon cure is tested in two steps:

A. Specific gravity determination of prepromoted resin (duplicate runs).

(a) An empty 250 mL volumetric flask is immersed in a thermostatted water bath, then dried and weighed (Wa).

(b) The same flask is filled to a point above the mark with prepromoted resin and placed in the thermostat bath (temperature stability ±0.1 °C (±0.2 °F)). After 30 minutes the volume is adjusted to the mark on the flask by removing resin with a disposable pipet, and the flask is then dried and weighed (Wb).

The procedure above is performed at two different temperatures, and the specific gravity of the resin is calculated at each temperature as follows: sp. gravity = (Wb - Wa)/250.

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B. Volume determination of binder before and after cure (triplicate runs).

(a) Initiator is added to resin, and the temperature of the resulting binder is obtained.

(b) A tared polyethylene centrifuge tube is filled to the 15 mL mark with the binder and weighed.

(c) The volume of the binder (V1) is computed from its mass and the resin density determined above (applying a correction for temperature variation).

(d) The tube is covered with aluminum foil and cured at room temperature for 24 hours followed by 24 hours at 57 °C (135 °F).

(e) The cured binder is removed from the tube and weighed again (W1) to check for possible weight change during cure.

(f) A 500 mL glass-stoppered Erlenmeyer flask is completely filled with water at a known temperature and weighed (W2).

(g) The cured binder is added to the same flask, which is once again completely filled with water at a known temperature and weighed (W3).

The volume of displaced water (and hence, of the cured binder) is determined from V2 = (W2 - W3 + W1)/d(H_2O). Finally, the % shrinkage on cure is computed from 100 x (V1 - V2)/V1.

8. Dynamic Mechanical Analysis.

The ASTM D-3418 procedure for determining glass transition temperatures is by using a differential scanning calorimeter (DSC)

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and observing the baseline shift which accompanies the transition. In a report titled "DSC and DMA Analysis", by Paul N. Noble, submitted to Caltrans by the Polymer Research Institute on January 22, 1991, it was demonstrated that Dynamic Mechanical Analysis (DMA) gives glass transition temperatures which are consistent with those from DSC measurements. DMA is more sensitive than DSC and has the additional advantage of giving information about certain mechanical properties and possible variations in completeness of cure.

Binders (without aggregates) for DMA testing are first cast into thin (about 1.5 mm (0.059")) sheets and cured. Samples measuring about 3x3 mm (0.1" x 0.1") are cut out of the sheets, and the exact sample thickness determined using a micrometer gauge. Each sample is tested with a hemispherically tipped DMA probe in the range of 0 to 100 °C (32 to 212 °F) at a scan rate of 10 °C/min (18 °F/min). The 150 millinewton (0.00025 lb) loading force is oscillated in a square wave (on/off) pattern at a frequency of 0.1 Hz. In order to check for completeness of cure, the sample is immediately cooled back to room temperature, repositioned under the probe, and scanned a second time.

9. Per Cent Water Absorption of Binder.

Samples are cycled three to twenty times through the following steps:

(a) The sample is stored at 57 °C (135 °F) for 24 hours and weighed.

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(b) The sample is soaked in water at room temperature (about 23 °C (73 °F)) for 24 hours, blot dried and weighed.

10. Per Cent Oil Absorption of Binder and Composites.

Samples are cycled 20-32 times through the following steps:

(a) The sample is stored at 57 °C (135 °F) for 24 hours and weighed.

(b) The sample is soaked in oil at room temperature (about 23 °C (73 °F)) for 24 hours, blot dried and weighed.

11. Freeze-thaw Cycling of Composites.

Samples are run through 20 freeze-thaw cycles, each cycle consisting of the following steps:

(a) The sample is stored at 57 °C (135 °F) for 24 hours and weighed.

(b) The sample is soaked in water at room temperature (about 23 °C (73 °F)) for 24 hours, blot dried and weighed.

(c) The sample is stored in a freezer at -12 °C (10 °F) for 24 hours.

12. Infrared Spectroscopic Analysis of Resins

One drop of resin is pressed between sodium chloride plates and scanned from 4000 to 600 cm^{-1} using a Perkin Elmer Model 1800 Fourier transform infrared (FTIR) spectrophotometer (qualitative mode, 2 cm^{-1} resolution). Three spectra are generated from each scan:

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(a) Full-range scan (4000 to 600 cm^{-1}) with no expansion.

(b) The range from 4000 to 2600 cm^{-1}.

(c) The range from 1800 to 1350 cm^{-1}.

In scans (b) and (c) the ordinate is expanded full scale, and the wavenumbers and absorbances of key peaks are labelled.

13. Gel Permeation Chromatography (GPC) Analysis of Resins.

Samples for analysis are prepared by dissolving 50 mg of resin in 10 mL of unstabilized chromatographic grade tetrahydrfuran (THF). A 250 μL sample is injected into a Waters GPC system equipped with four Styragel columns in series (1000, 500, 10,000 and 100 Å pore size). The system is thermostatted at 25°C (77°F), with a flow rate of 1 mL/min and a pressure of 8.3 MPa (1200 psi). Chromatograms are recorded using both refractive index and ultraviolet light (270 nm) detectors. A calibration of molecular weight vs. retention time is made using commercial polystyrene standards of low polydispersity. Retention times range from 22.5 min for 10^5 g/mol polystyrene to 41.9 min for styrene monomer. All samples are spiked with a trace of toluene (42.2 min retention time) as a check against system drift.

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Appendix 2: Infrared Scans of Three Resins

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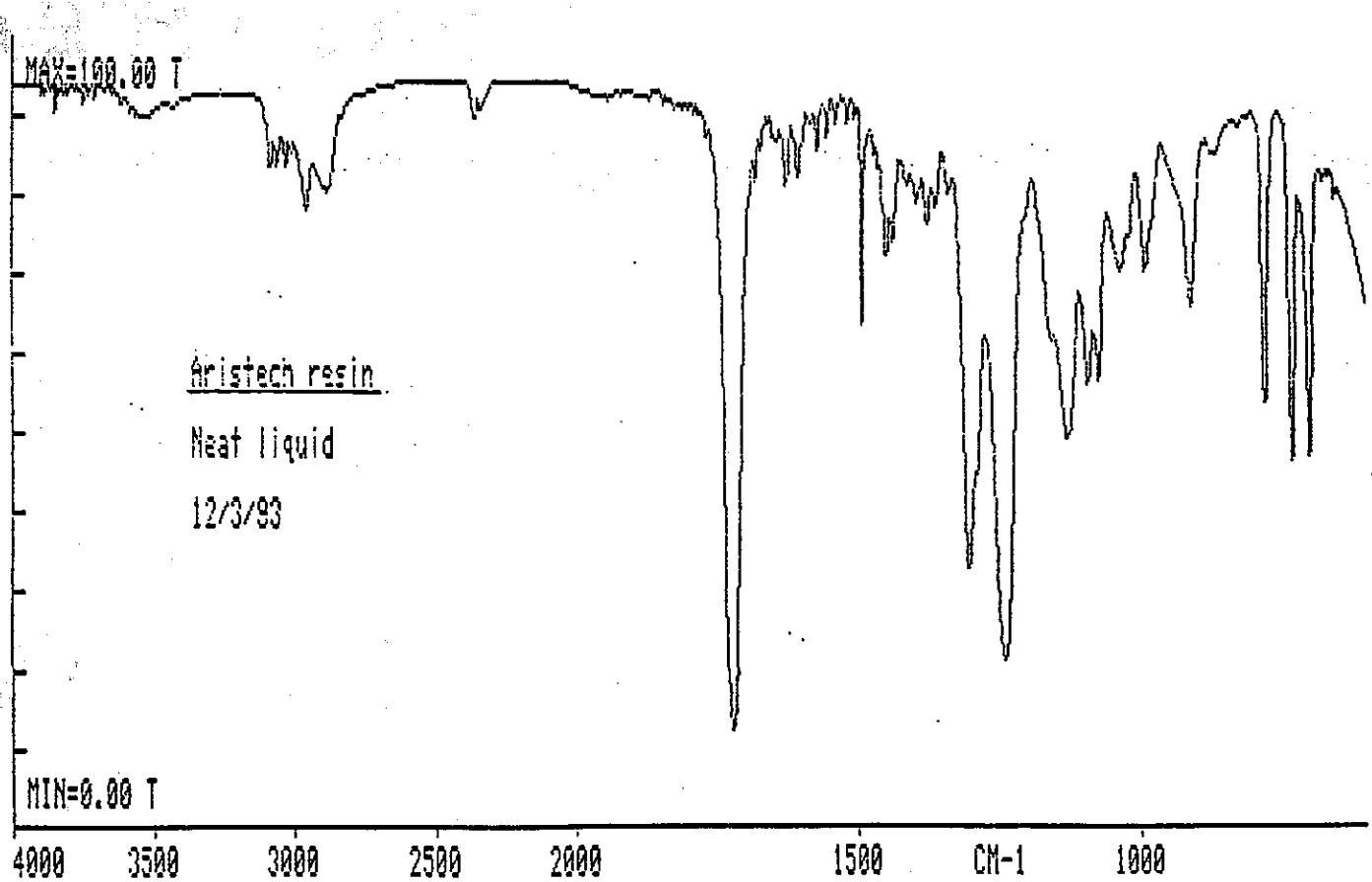

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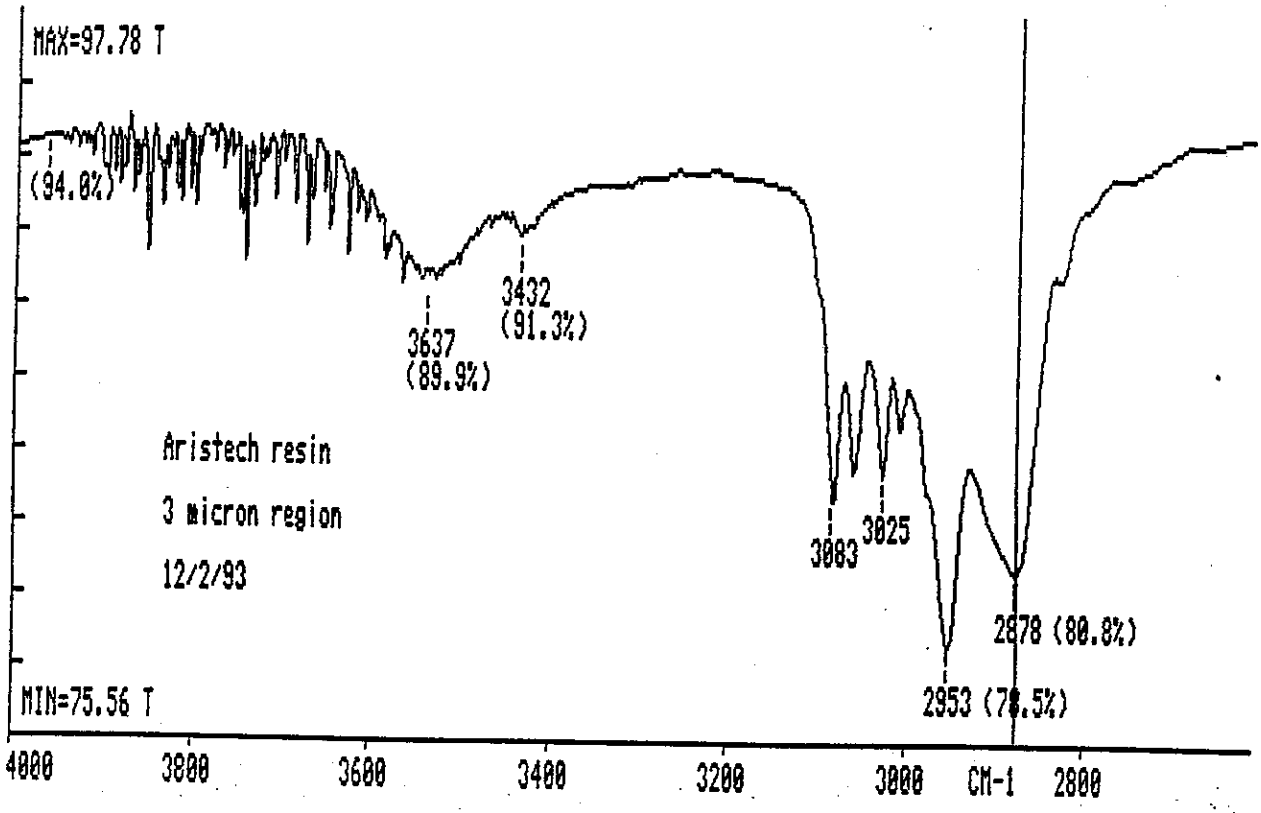

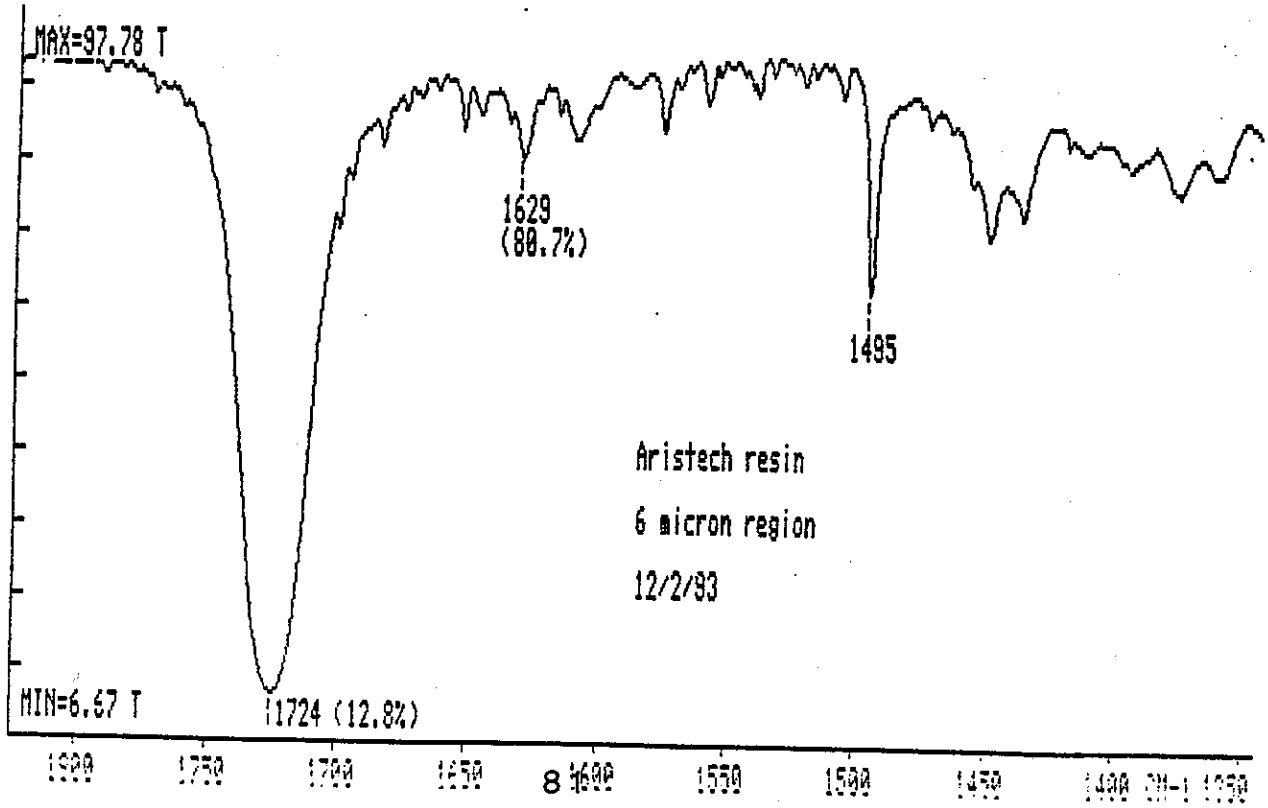

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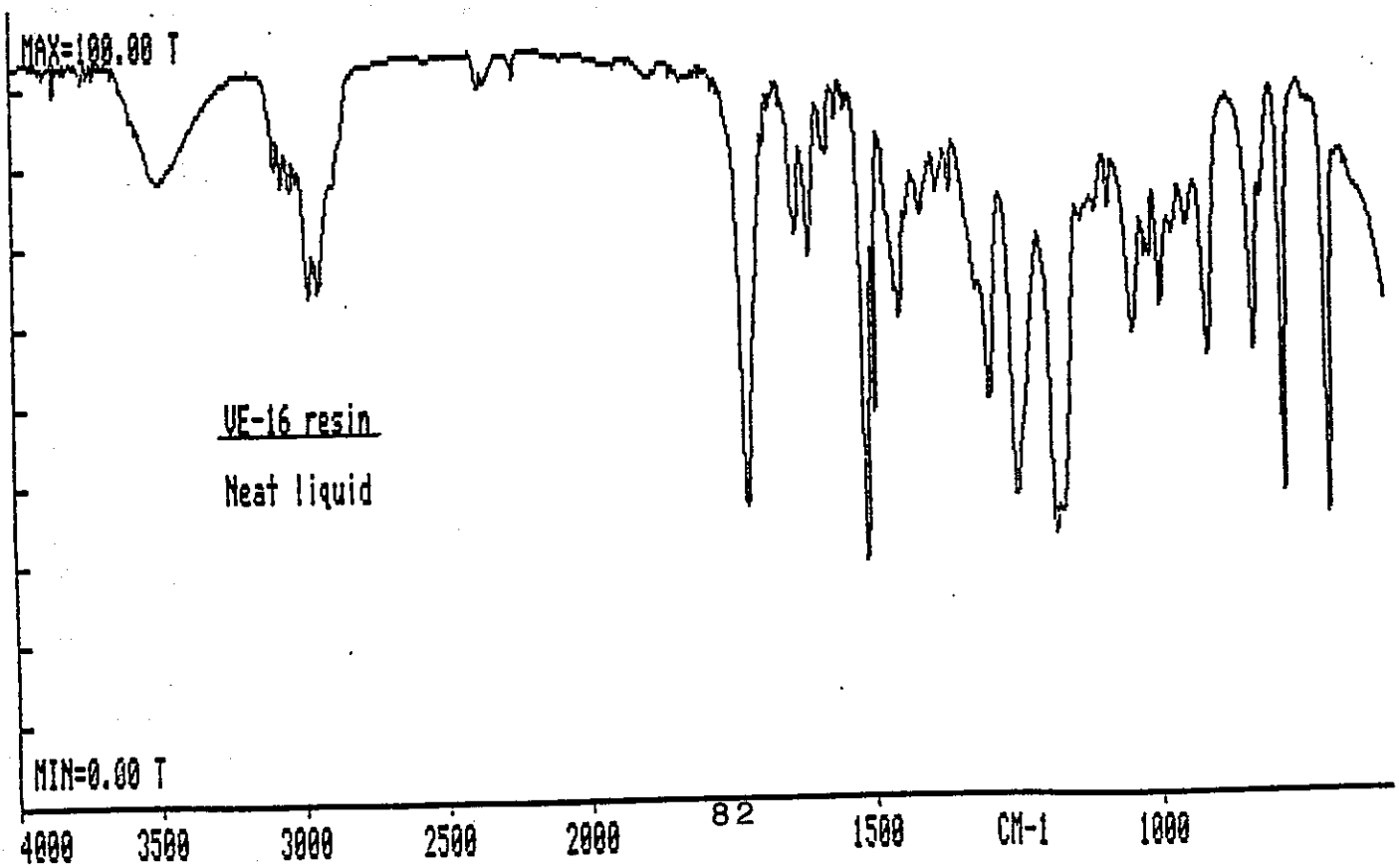

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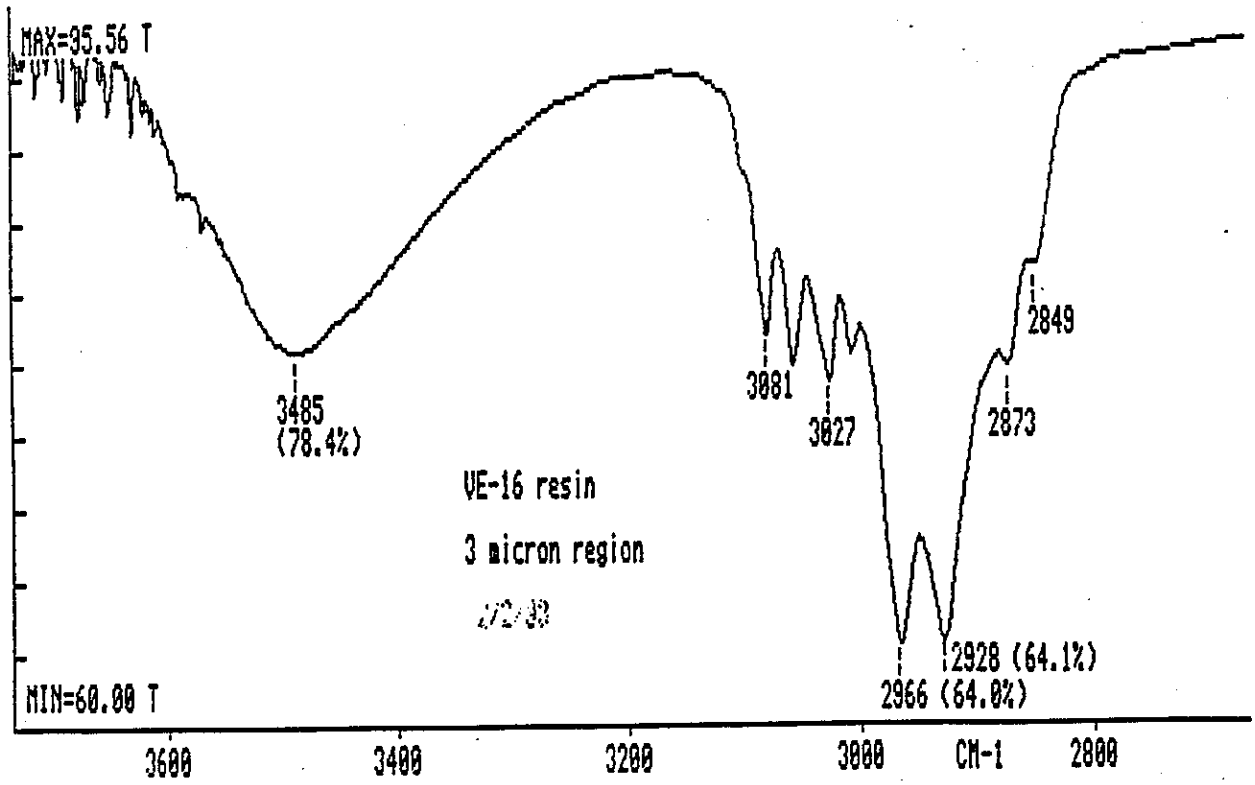

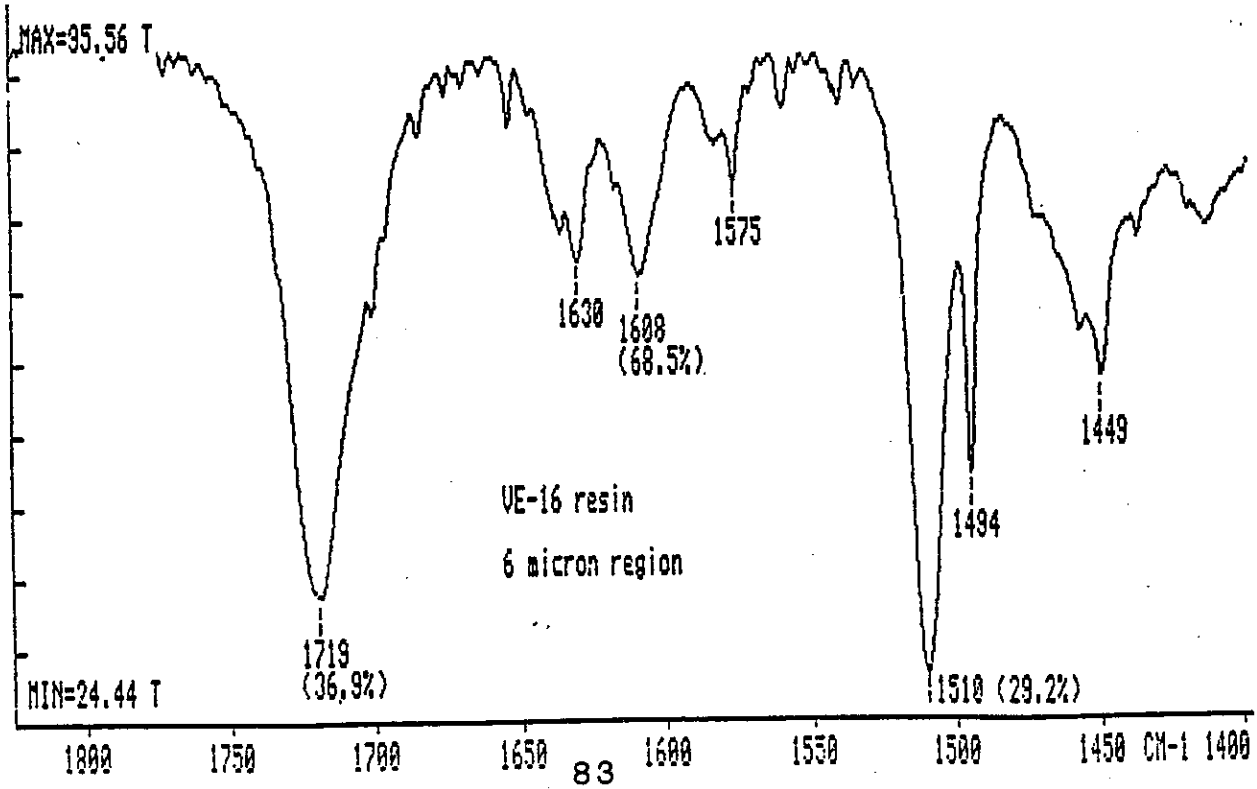

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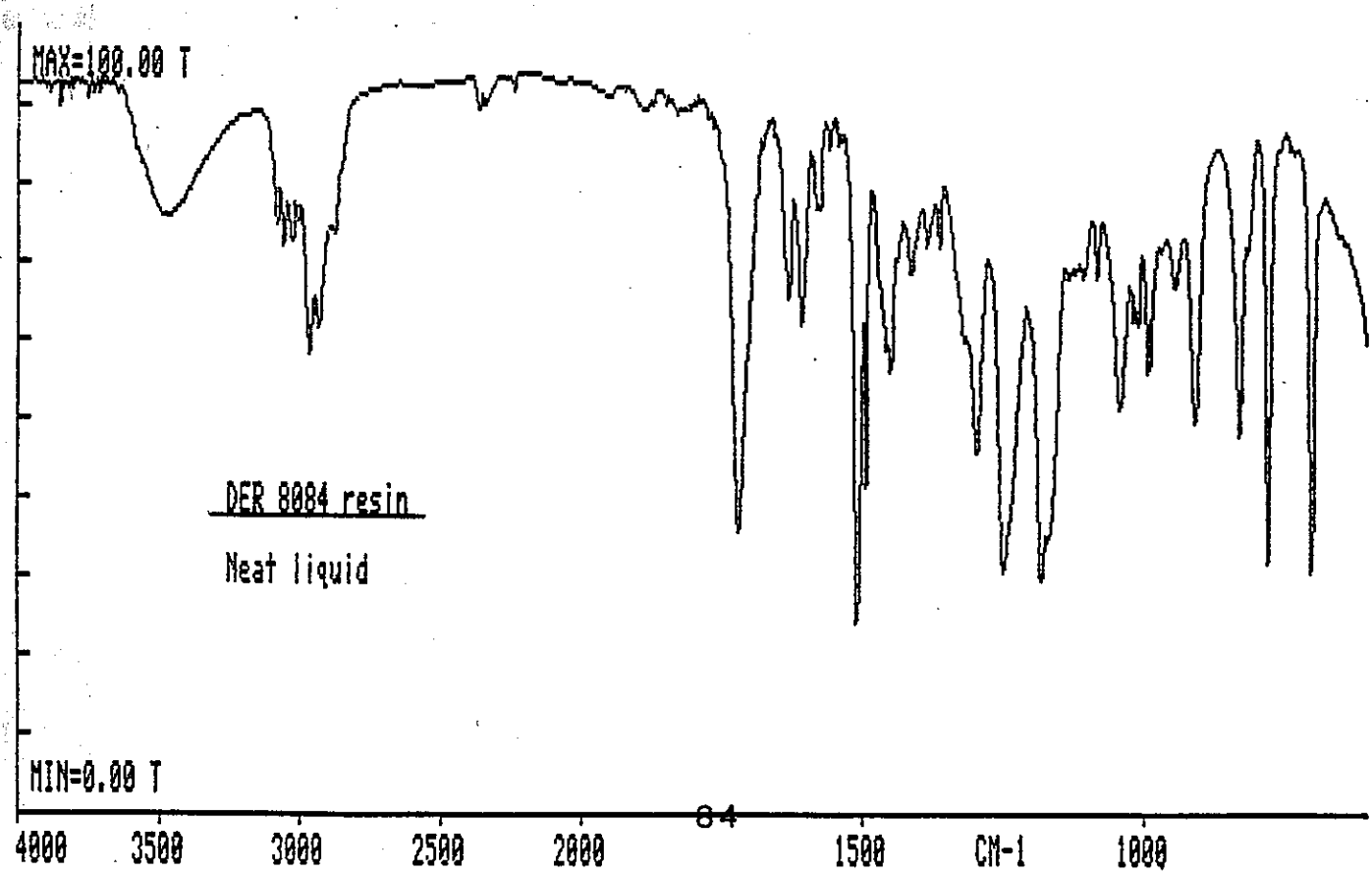

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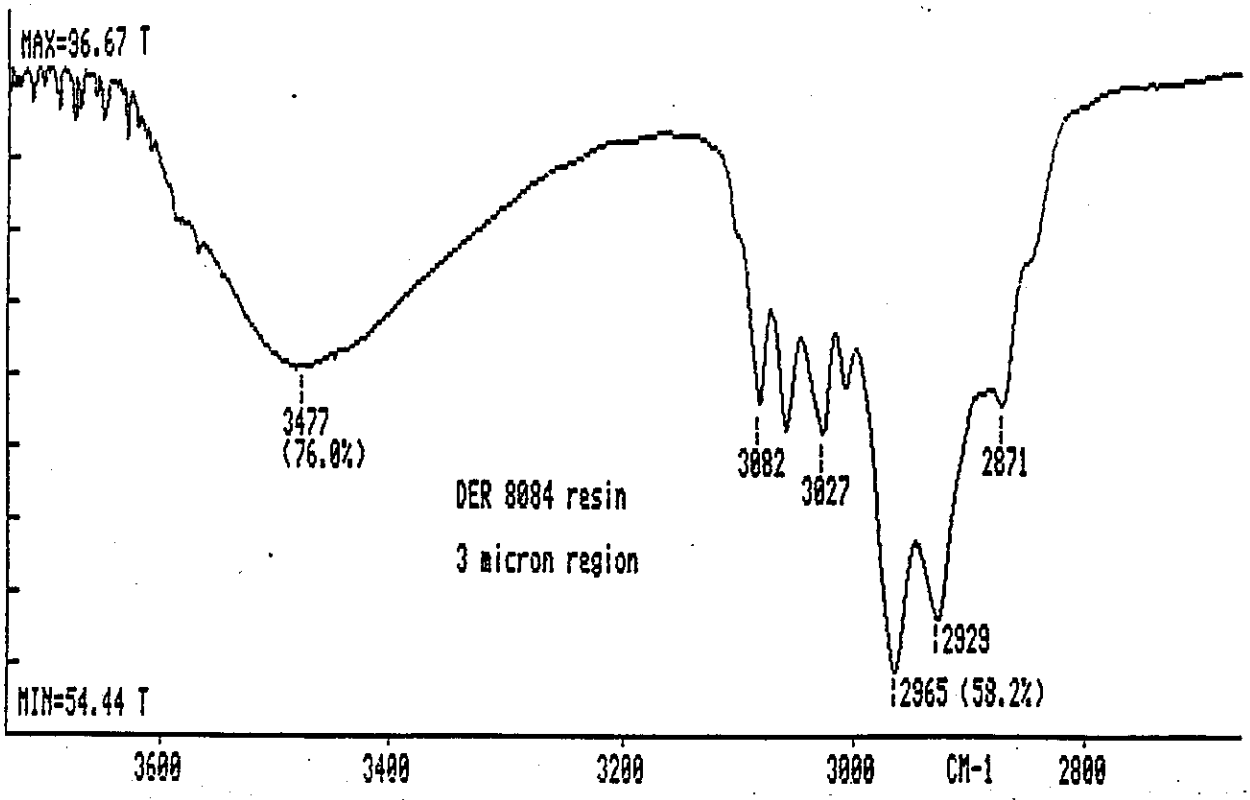

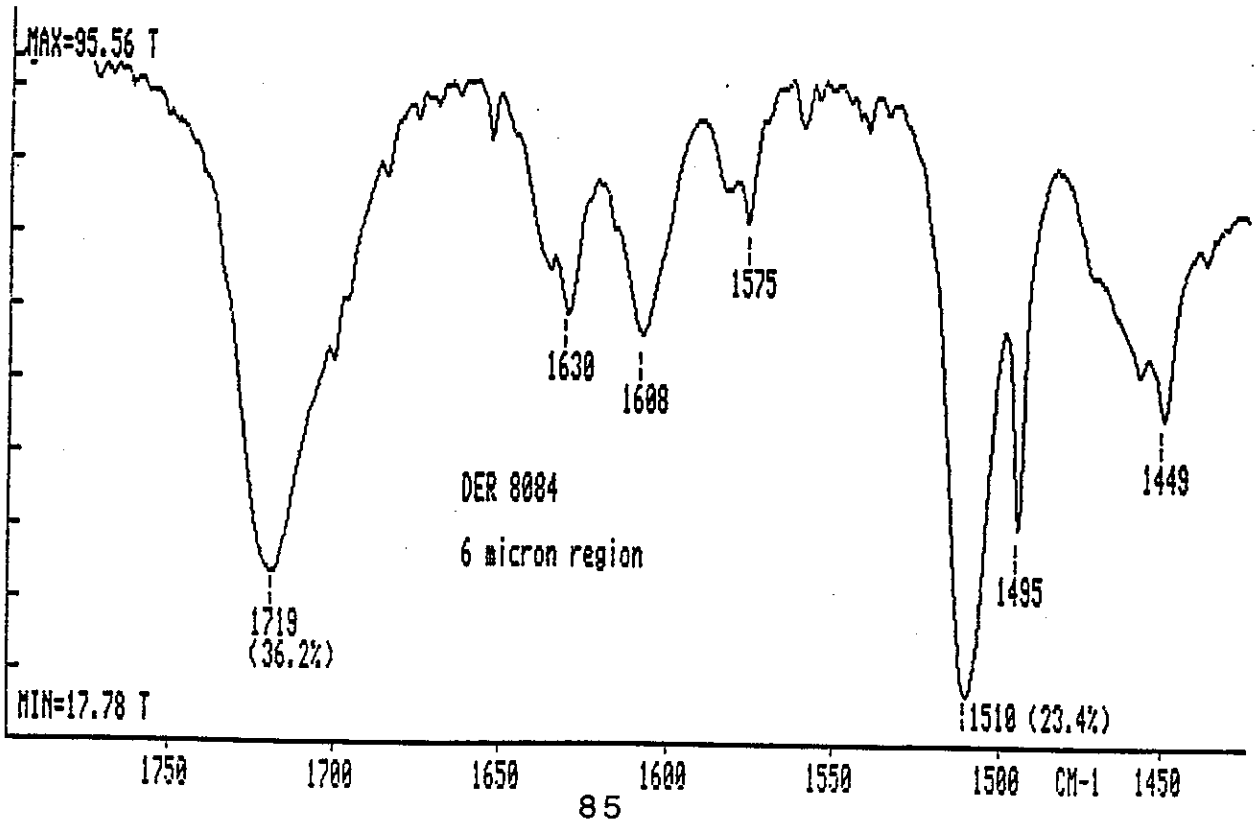

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Appendix 3: GPC Scans of Three Resins

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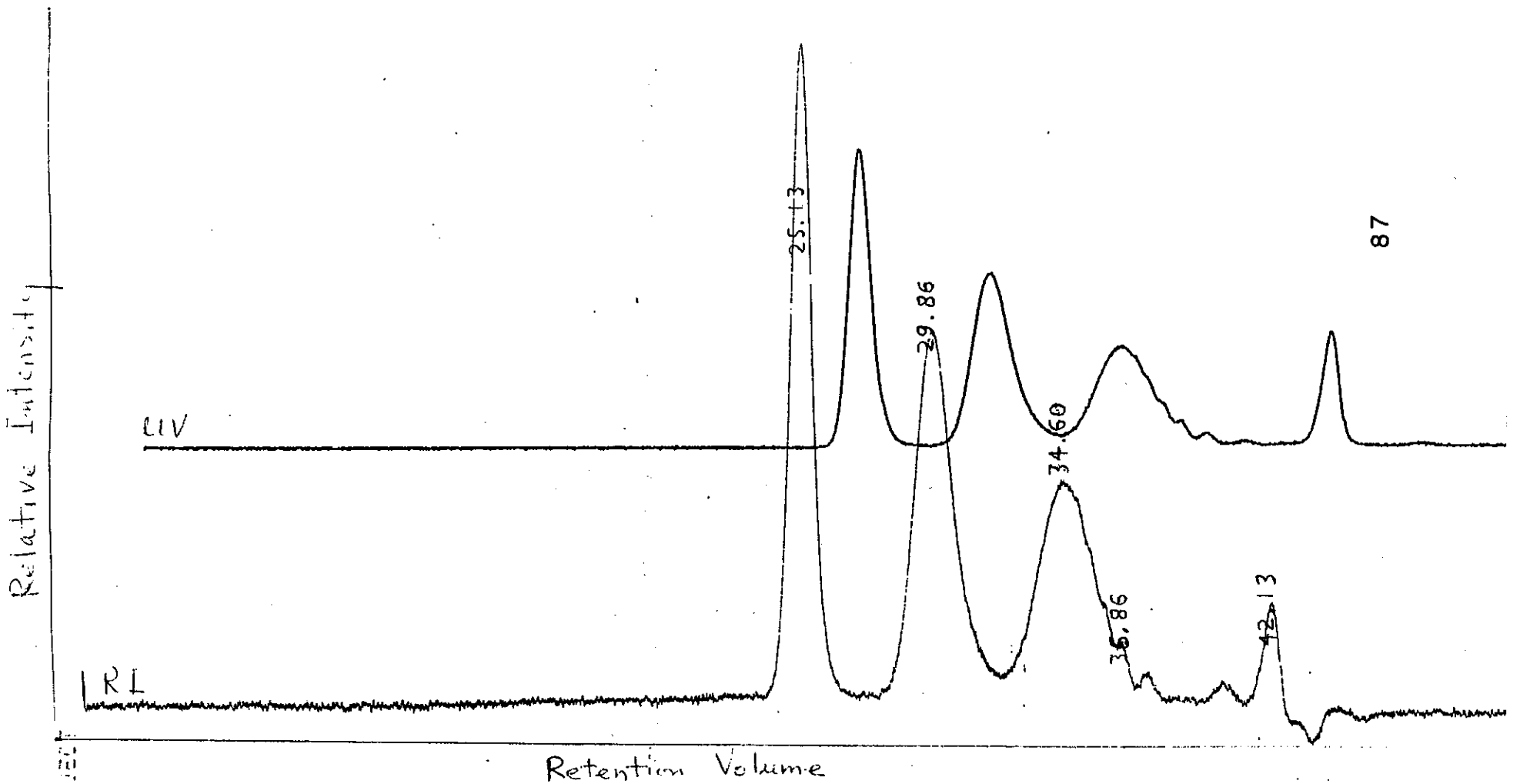
23K, 4K, 0.8K Standards (polystyrene)
(25mg/10mL) 150µL
2x atten, 0→1 AU
THF



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12/17/93

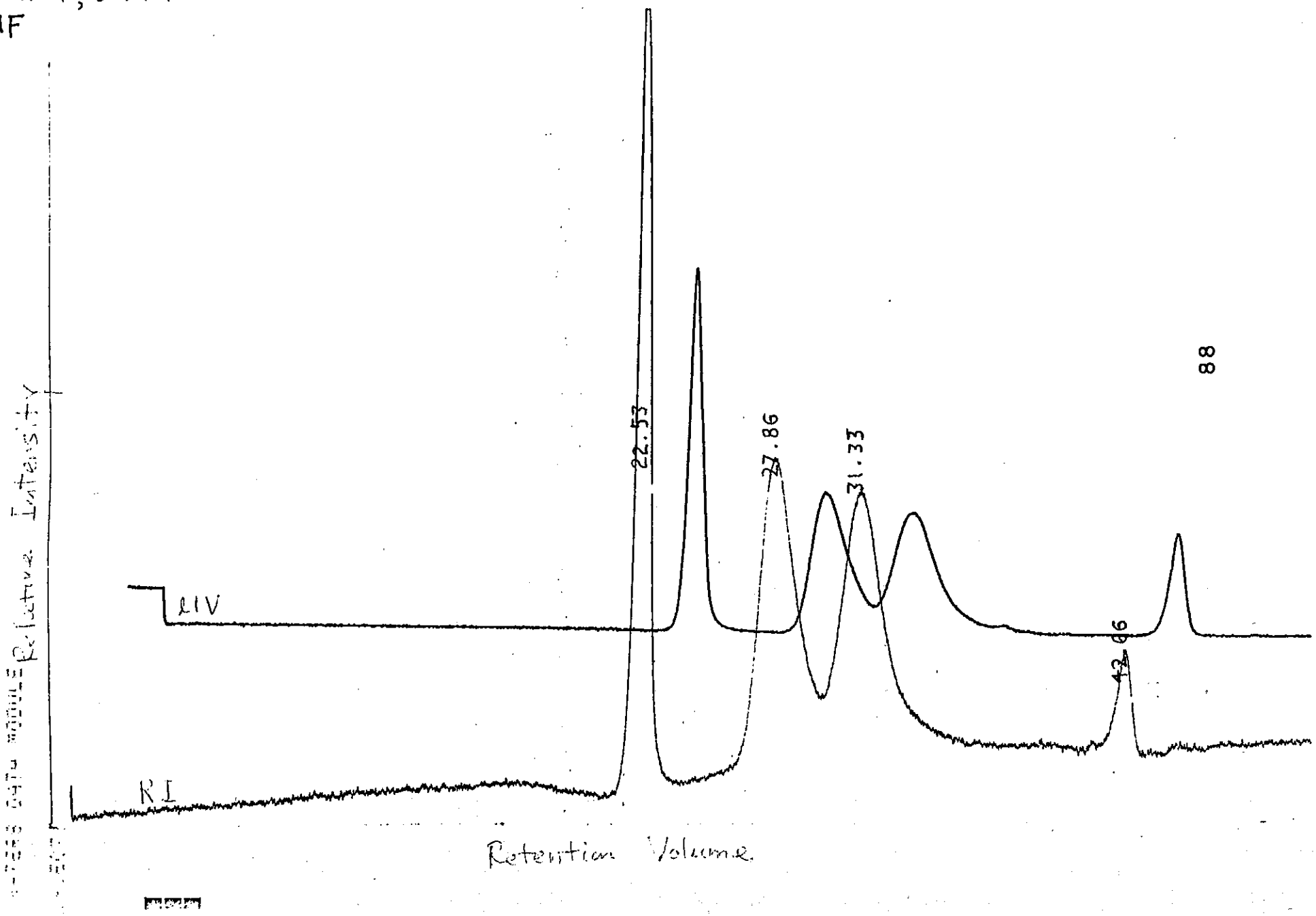
[redacted]

100K, 9K, 2K standards (polystyrene)

(25mg/10mL) 150uL

2x atten, 0 → 1 AU

THF



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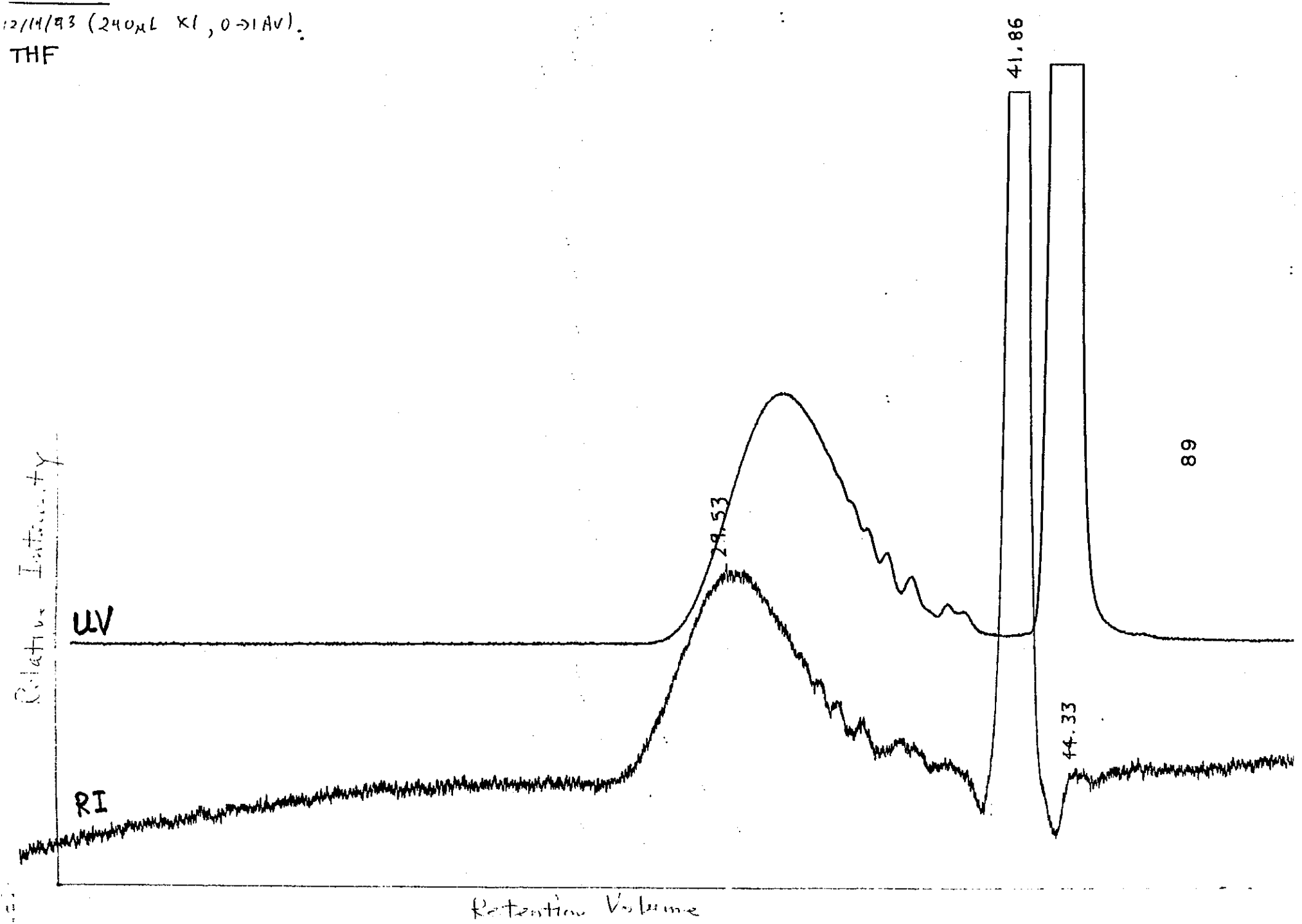
Aristech (59mg/10mL)
12/14/93 (240μL RI, 0→1 AV).
THF



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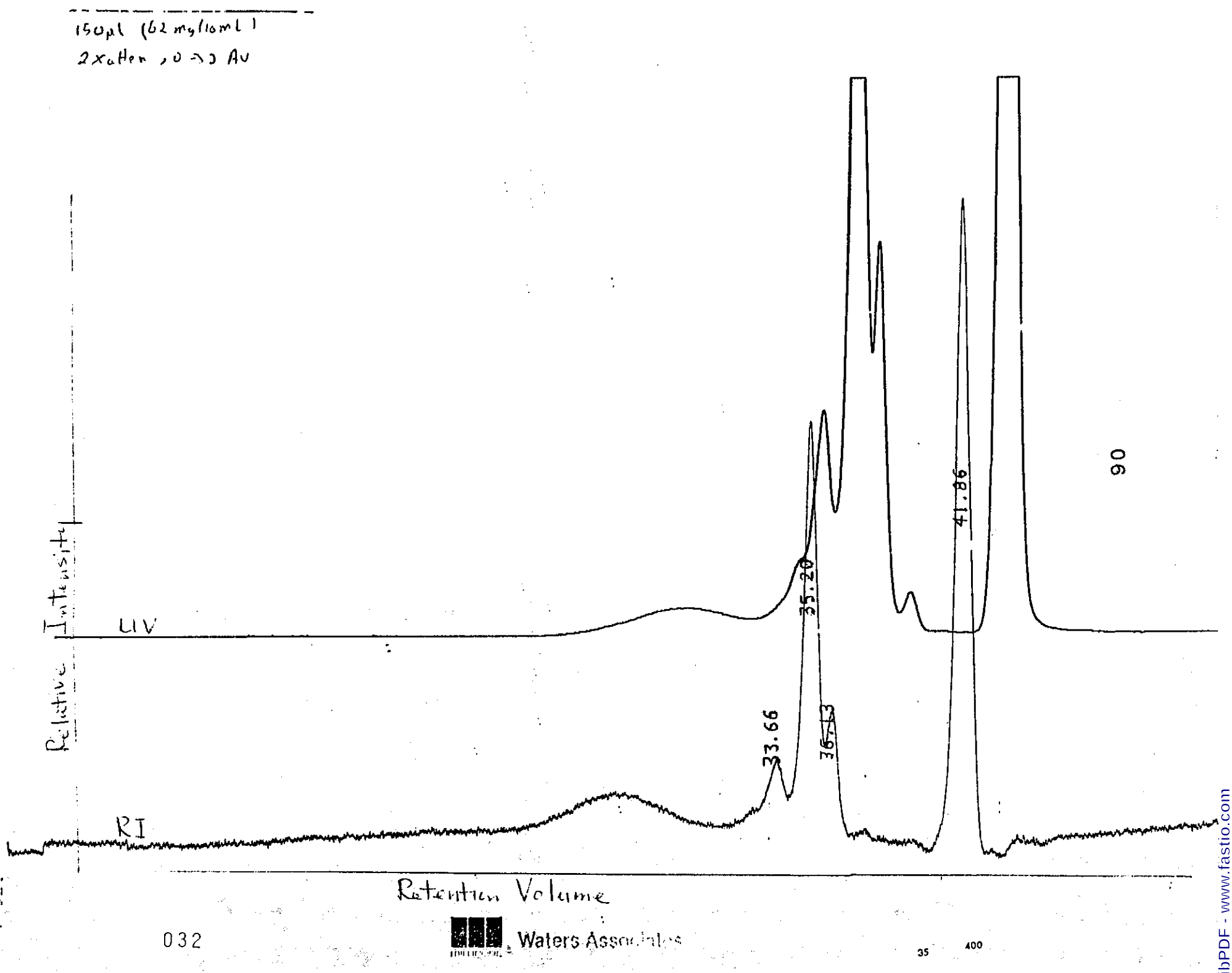

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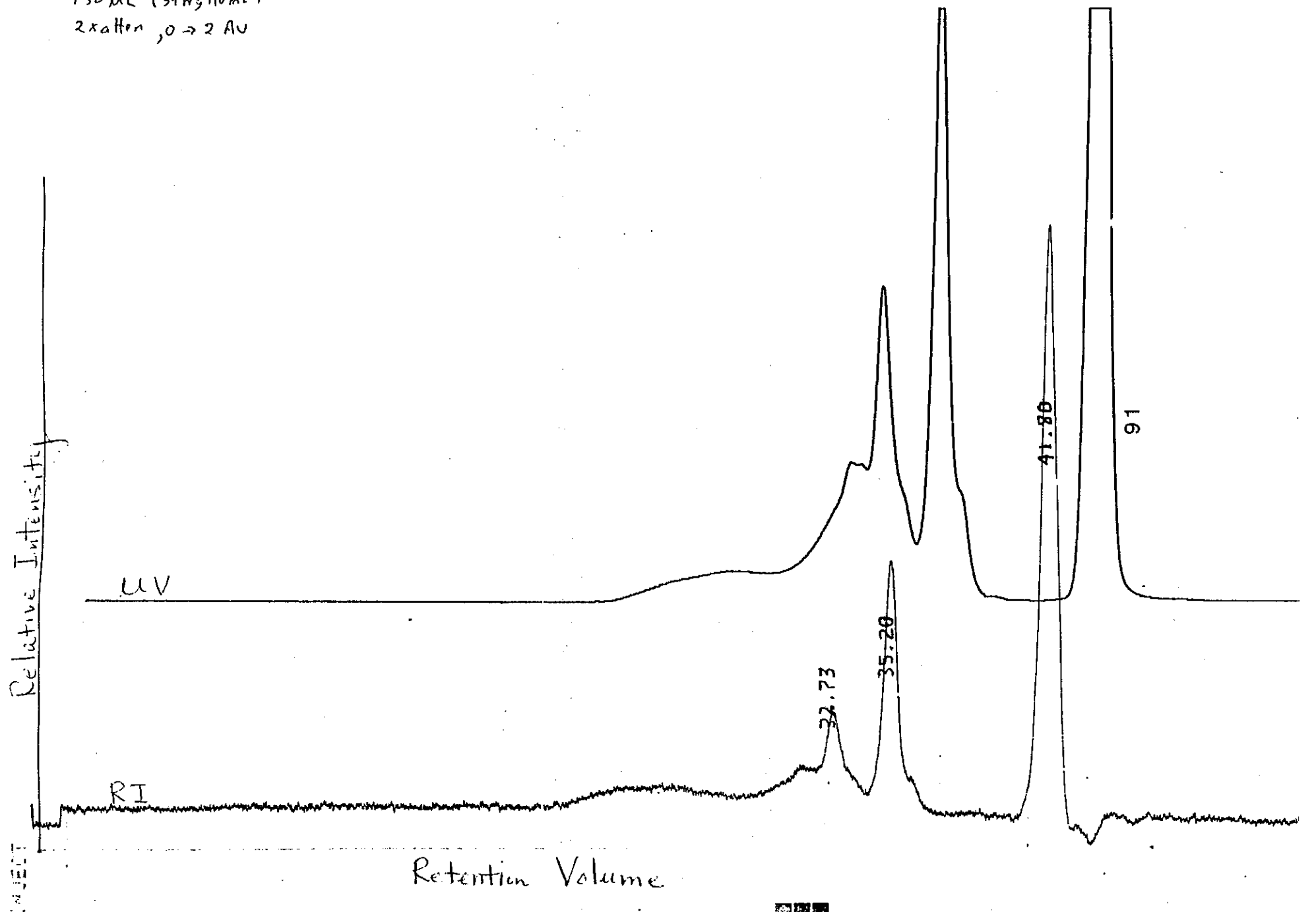
DER 8084 (Dow)
150 mL (54 mg/10 mL)
2x atten, 0 → 2 AU



Waters Associates

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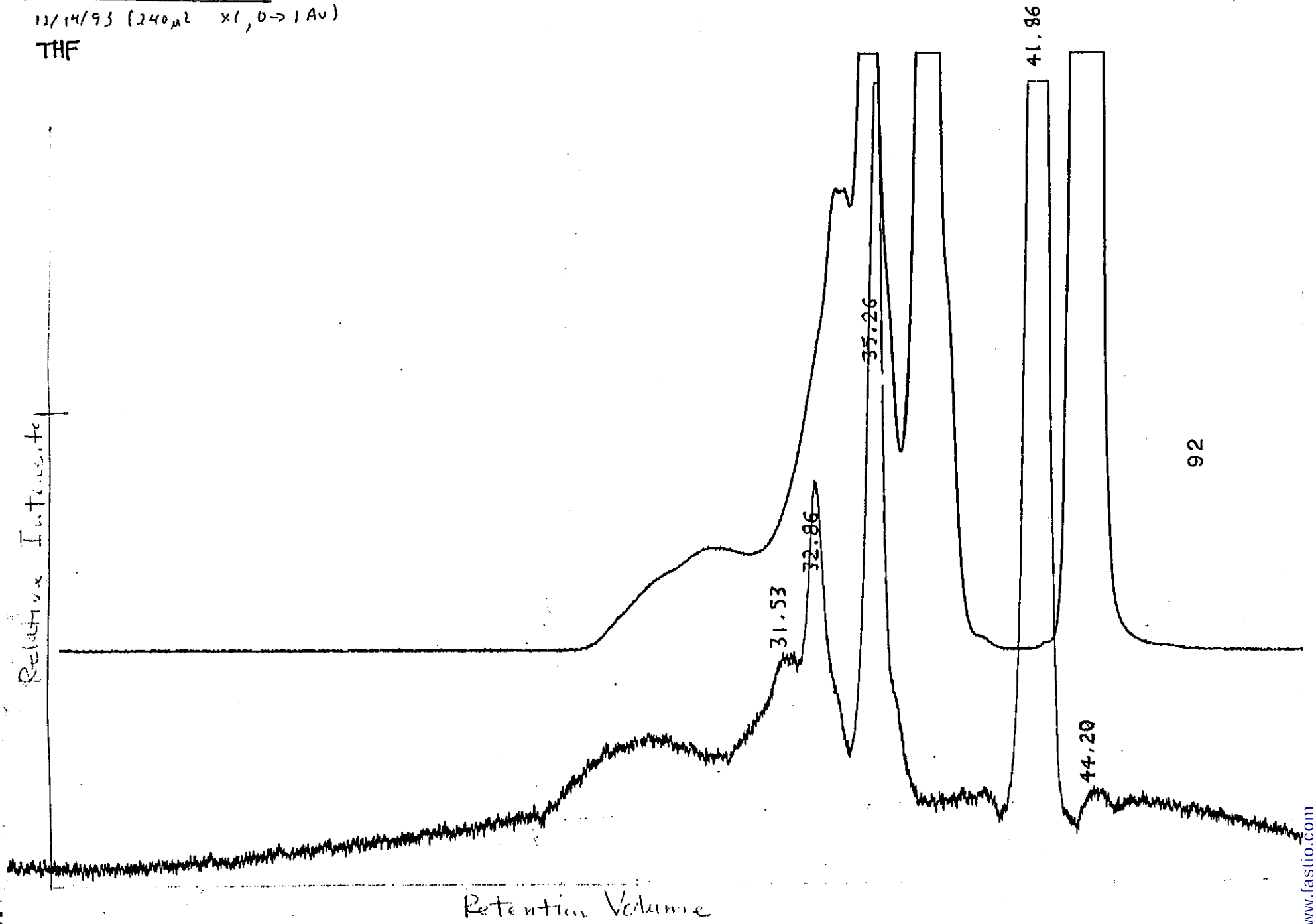
DER-8081 (54mg/10mL)

12/14/93 (240µL x1, 0->1 AU)

THF



400

025

Waters Associates

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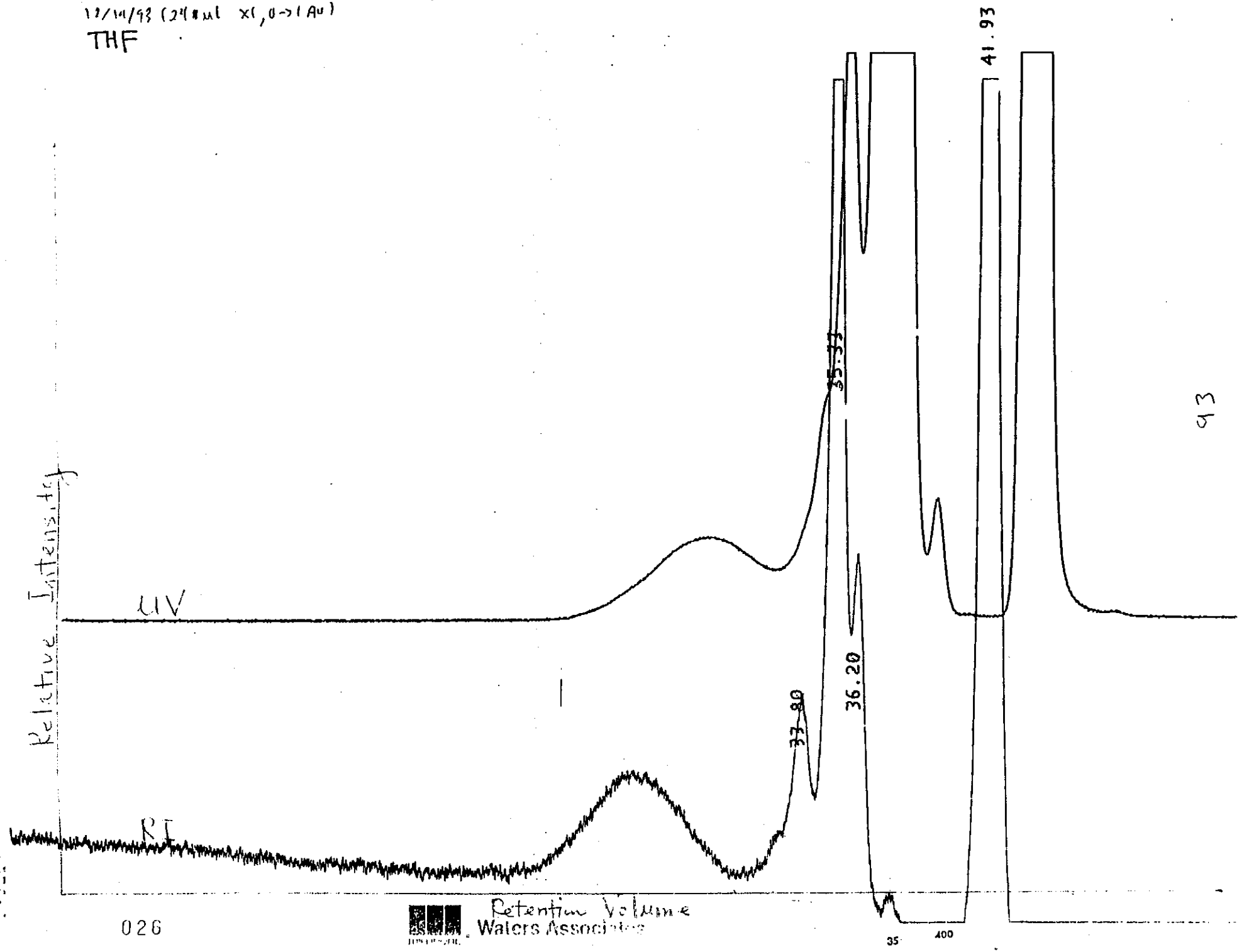
VE-16 (62 mg/10 mL)

12/14/93 (24 µl X1, 0->1 Au)

THF



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Waters Associates

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Appendix 4: DMA Scans of Three Binders

Note:

The fundamental difference between dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) is that the applied force in DMA oscillates on and off in a square wave pattern, whereas the applied force in TMA is continuous. The oscillating force causes DMA to be more sensitive to the onset of transitions than TMA. Our instrument uses the same chart paper for both types of analysis. Thus, despite the fact that the chart paper in the following scans is labelled "TMA", the oscillating trace indicates that all of them are in fact DMA scans.

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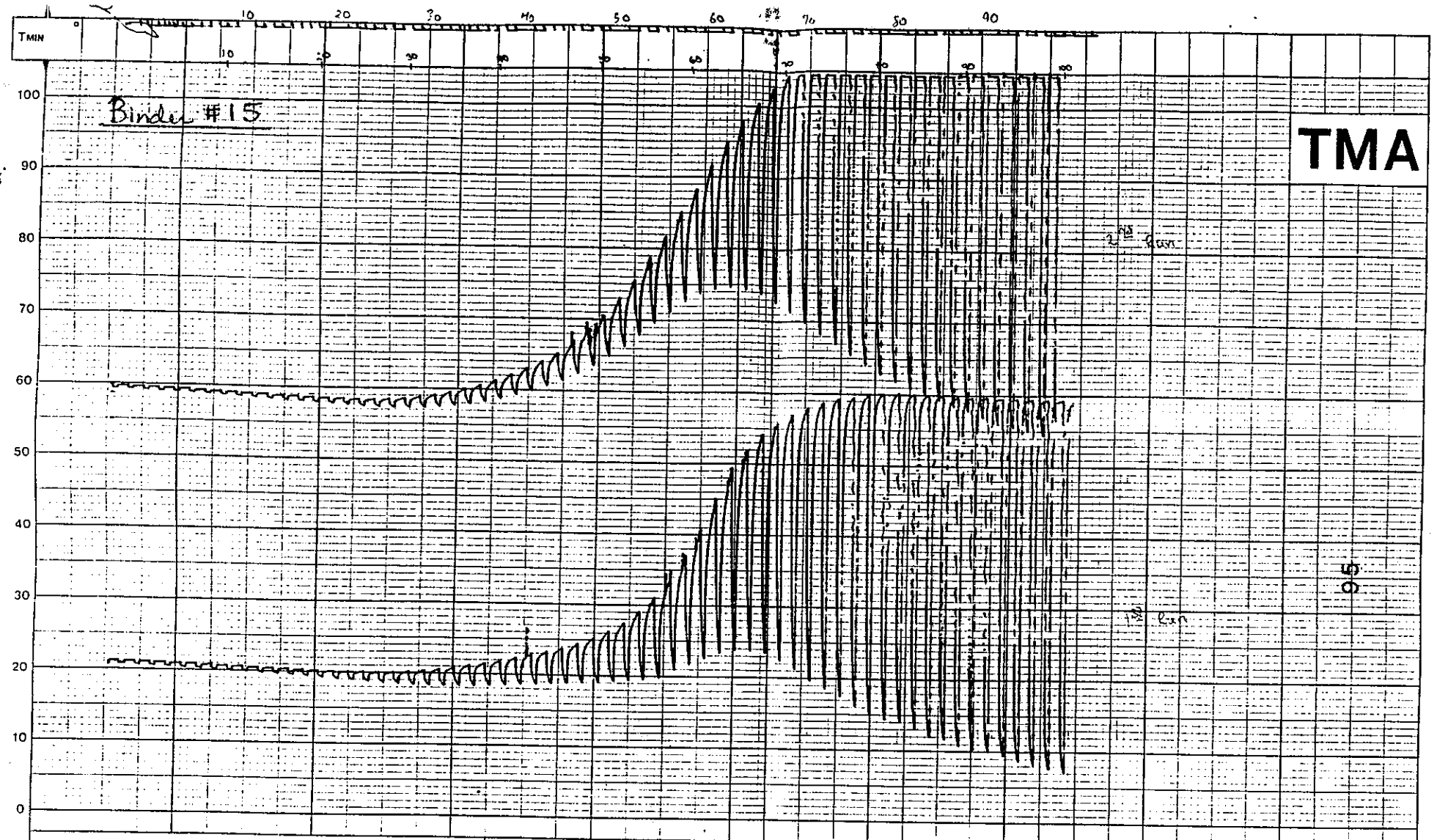
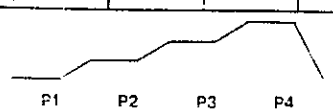


MULTI-STEP PROGRAMS



TMA SCALE

FULL SCALE RANGE _____ MILS X 50 / MILLIMETERS

PROBE: EXPANSION / EXTENSION / PENETRATION / DILATOMETER / FLEX / COMPRESS

TEMP SCALE

TMIN _____ °C

TSPAN _____ °C

ATMOSPHERE

TEMP PROGRAM

LOWER TEMP (TMIN) 0 °C

UPPER TEMP (TMAX) 100 °C

HEATING RATE 10 °C/min

100 °C/min

SAMPLE ID

MATERIAL [illegible]

Thickness ~~LENGTH~~ 1359 mm

DATE [illegible]

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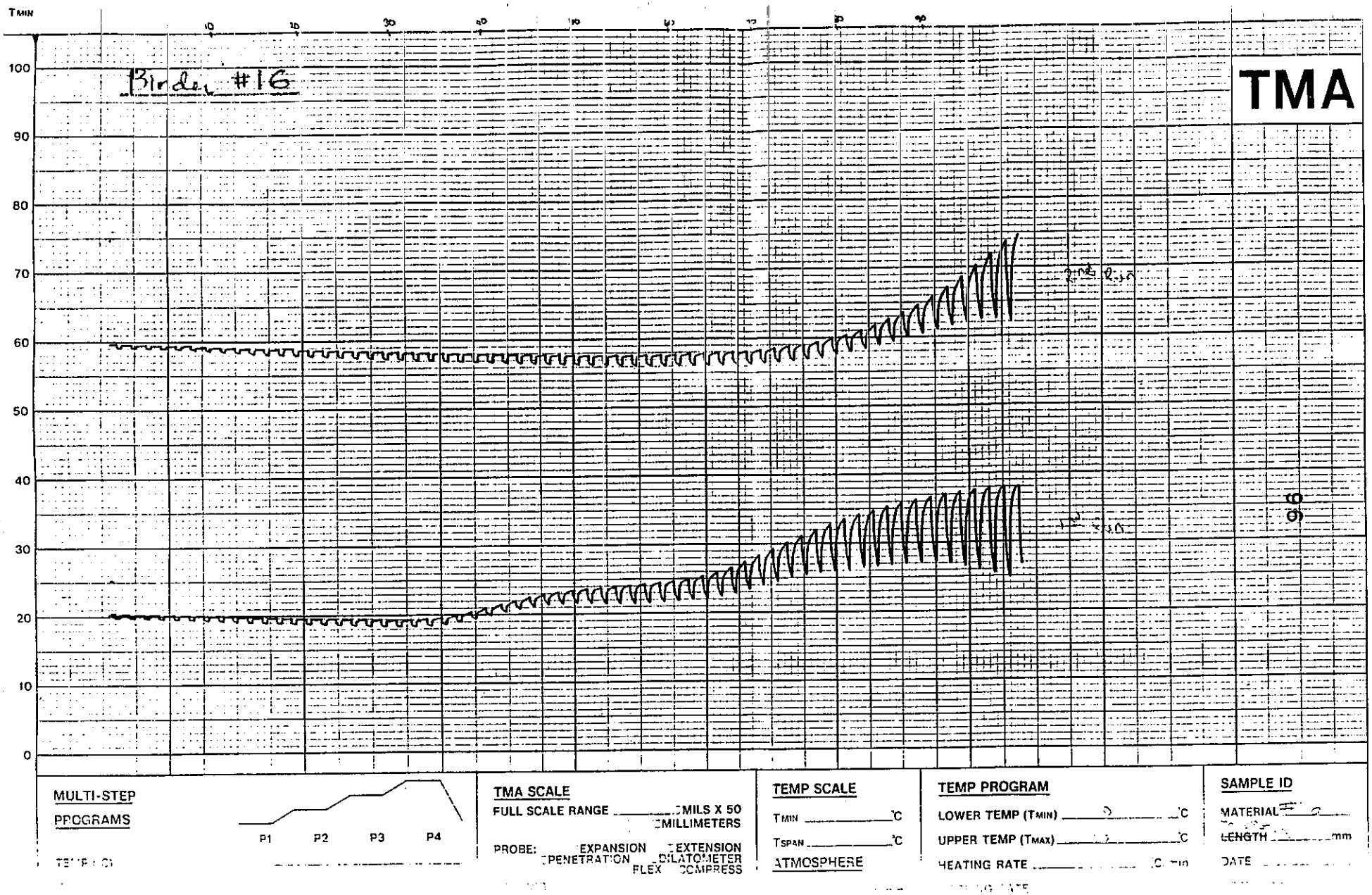

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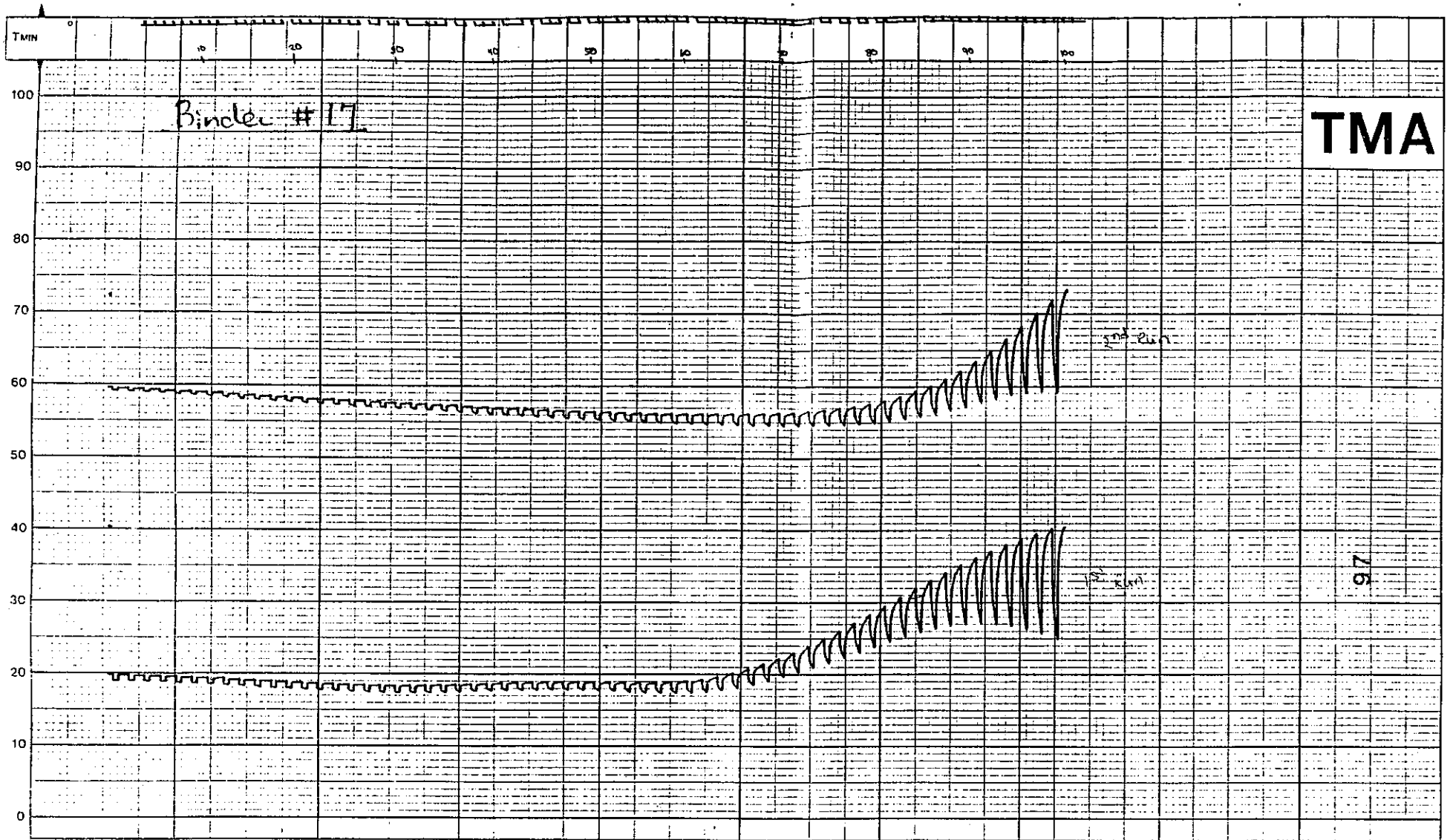

MULTI-STEP PROGRAMS

P1 P2 P3 P4

TEMP PROGRAM

TMA SCALE

FULL SCALE RANGE _____ MILS X 50
MILLIMETERS

PROBE: EXPANSION EXTENSION
PENETRATION DILATOMETER
FILM COMPRESS

TEMP SCALE

TMIN _____ C

TSPAN _____ C

ATMOSPHERE

TEMP PROGRAM

LOWER TEMP (TMIN) _____ C

UPPER TEMP (TMAX) _____ C

HEATING RATE _____ C/min

SAMPLE ID

MATERIAL _____

LENGTH _____ mm

DATE _____

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Appendix 5: Raw Data from Caltrans

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State of California
Department of Transportation
Division of Facilities Construction,
Transportation Laboratory
Rigid Pavement Branch

Report of Tests on

Contract No.	Resident Engineer	Phone		Material Received Laboratory No.

Test Date	By	Sample Number	Age	Area	TEST	Total Load	PSI	Mix---
5-27-93	HD	PCC NO WCOA		1-3	FLEXURE	2850	950	
		PCC W/WRDA		✓	✓	2550	850	
		POLY #15			✓	5510	1830	
		POLY #16			✓	8000	2670	
		POLY #17			✓	8050	2680	
		POLY #15		1/2	BOND TO DRY PCC	2010	1005	85% PCC
		POLY #15		✓	✓ ✓ ✓	2130	1065	85% PCC
		✓		✓	BOND TO SSD PCC	1300	650	15% COHESIVE
		✓		✓	✓ ✓ ✓	1250	625	5% COHESIVE
		POLY #16		✓	BOND TO DRY PCC	1725	863	100% PCC
		✓		✓	✓ ✓ ✓	1945	973	100% PCC
		✓		✓	BOND TO SSD PCC	2200	1100	100% PCC
		✓		✓	✓ ✓ ✓	2110	1050	100% PCC
		POLY #17		✓	BOND TO DRY PCC	1870	935	100% PCC
		✓		✓	✓ ✓ ✓	1700	850	100% PCC
		✓		✓	BOND TO SSD PCC	1875	940	100% PCC
		✓		✓	✓ ✓ ✓	1850	930	
		POLY #15		9"	COMPRESSION	63000	7000	
		✓		✓	✓	65000	7200	
		POLY #16		✓	✓	119000	13200	
		✓		✓	✓	115300	12,810	
		POLY #17		✓	✓	103400	11,490	
				✓	✓	97200	10,800	

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State of California
Department of Transportation
Division of Facilities Construction
Transportation Laboratory
Rigid Pavement Branch

Report of Tests on

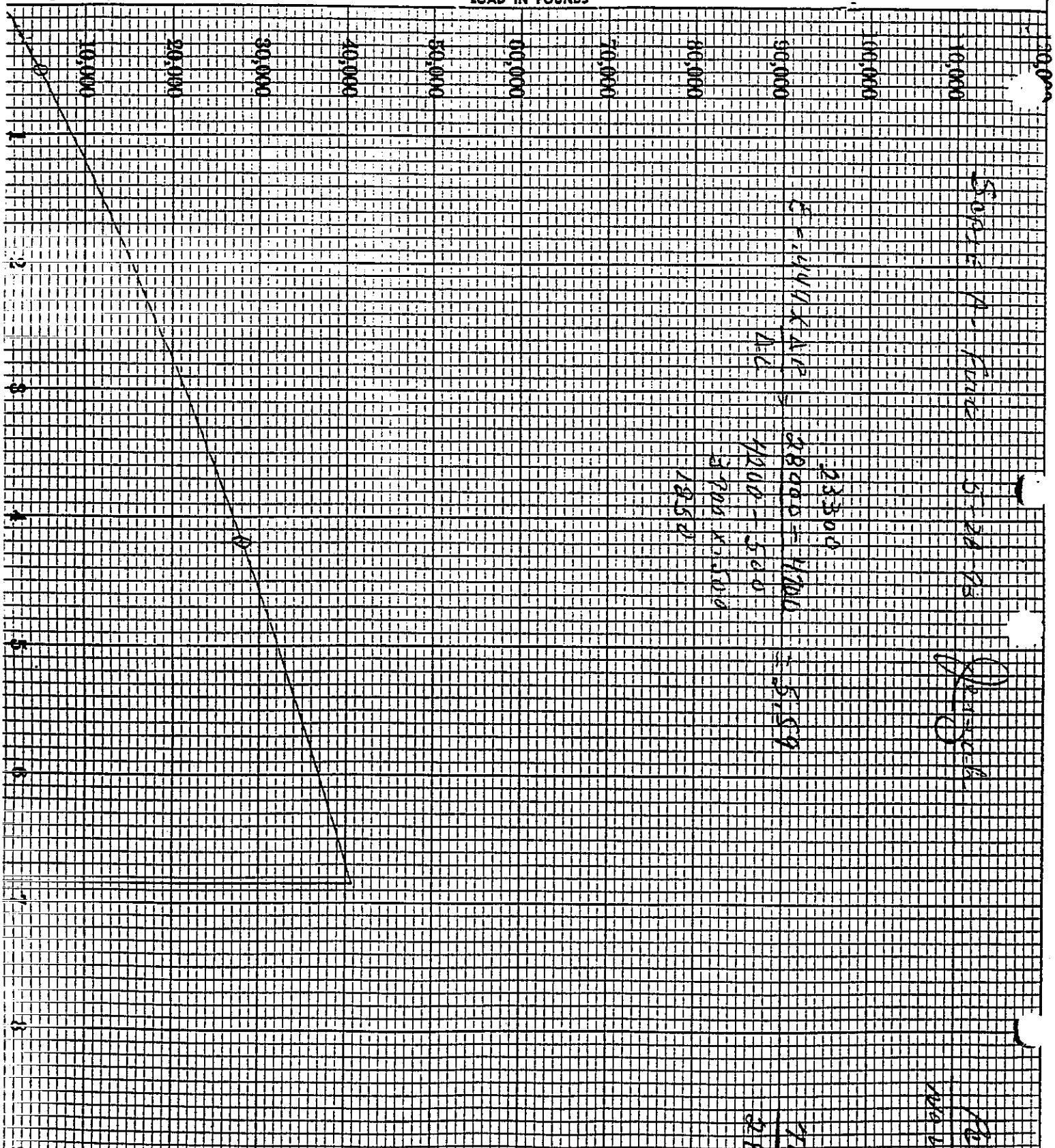
Contract No.	Resident Engineer	Phone		Material Received Laboratory No.
	SUE Kim			

Test Date	By	Sample Number	Age	Area	TEST	Total Load	PSI	Mix---
5-27-93	[illegible]	PCC w/WRDA		94"	Compression	93200	10355	15 - 64000
✓	✓	PCC ✓		✓	✓	84000	9335	16 11700
✓	✓	PCC No/WRDA		✓	✓	70300	7810	17. 10-0 000
5-28-93	[illegible]	PCC w/WRDA			"E"		5.32 x 10^6	
		PCC No/WRDA			✓		5.59 x 10^6	
		Poly #15			✓		1.50 x 10^6	
		Poly #16			✓		3.41 x 10^6	
		Poly #17			✓		2.93 x 10^6	

Test No.....Size.....Area.....Yield Point Lbs. Sq. In.....Ultimate Str. Lbs. Sq. In.....

Elongation } In.....Inches.....Per Cent. Elongation.....Per Cent. Reduced Area.....Date.....
Compression }

LOAD IN POUNDS



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VI. REFERENCES

1. Cited in Report.

1. P. D. Krauss, L. Ferroni and B. F. Neal, "New Materials and Techniques for the Rehabilitation of Portland Cement Concrete". State of California, Department of Transportation, Report No. FHWA/CA/TL-85/16, October, 1985

2. Technical Brochure, "Concrete Repair Applications for High Molecular Weight Methacrylate Monomers" by Rohm & Haas.

3. D. W. Fowler, A. H. Meyer and D. R. Paul, "Polymer Concrete for Pavement Repair and Rehabilitation" Center for Transportation Research, The University of Texas at Austin, Report No. 246-3, June, 1983

4. D. W. Fowler, A. H. Meyer and D. R. Paul, "Implementation Manual for Polymer Concrete", Center for Transportation Research, The University of Texas at Austin, Report No. 246-4F, December, 1983

5. W. D. Mangum, A. J. Bermudez-Goldman, D. P. Whitney, D. W. Fowler, and A. H. Meyer, "Repairing Cracks in Portland Cement Concrete Using Polymers", Center for Transportation Research, The University of Texas at Austin, Report No. 385-2F, November, 1986.

6. R. G. Kushner, D. W. Fowler, and D. L. Wheat, "Mechanical and Durability Properties of a High Molecular Weight Polymer Concrete" SP-99, p.113, ACI publication (1987).

7. R. E. Ottman, "High Molecular Weight Methacrylates for Portland Cement Concrete Crack Repair and Sealing", ICPIC Papers, San Francisco, CA, September 24-27, 1991.

8. D. J. Rodler and D. W. Fowler, "Repair of Cracked Concrete with High Molecular Weight Methacrylate" SP-116-7, in Polymers in Concrete: Advances and Applications , Peter Mendis and Charles McClaskey, Editors, ACI Publication (1989).

9. D. J. Rodler, "An Evaluation of High Molecular Weight Methacrylate as a Repair Material for Cracked Concrete", M.S. Thesis, The University of

ClibPDF - www.fastio.com

Texas at Austin, (1987).

10. P. D. Krauss, "Bridge Deck Repair Using Polymers", ICPIC Working Papers, San Francisco, CA, September 24-27, 1991.

11. T. J. Aminabhavi, P. E. Cassidy and L. E. Kukacka, "Use of Polymers in Concrete Technology", Rev. Macromol. Chem. Phys. C22(1), 1 - 55 (1982 - 83).

12. T. L. Ramirez, "Polymer Concrete Overlays - FLEXOGRID", Research Project 83-29E, Department of Transportation, Commonwealth of Pennsylvania, August, 1989.

13. N. E. Knight, "Polymer Concrete Overlays - FLEXOLITH", RESEARCH PROJECT 83-29, Department of Transportation, Commonwealth of Pennsylvania, June and September 1986.

14. J. L. Arellano, "Polymer Concrete Overlays for Bridge Decks", Research Project 83-29C, Pennsylvania Depaprtment of Transportation, June 1988.

15. F. Parker Jr., et al., "Evaluation of Rapid Setting Materials and Construction Techniques for Concrete Pavement Patches", Project 930-107, State of Alabama Highway Department, October, 1983.

16. T. Y. Chang and H. L. Stephens, "Development of Polymer Concrete as a Highway Patching Material", Report No. OHIO-DOT-01-75, Ohio Department of Transportation,December, 1975.

17. L. E. Kukacka, et. al., "Polymer Concrete Patching Materials", Implementation Package 77-11 Vol. II, Final Report, U.S. Department of Transportation, April 1977.

18. L. B. Steere and H. N. Swanson, "Evaluation of Bridge Deck Repair and Protective Systems", Report No. CDOH-DTP-R-80-15, Colorado Department of Highways, October 1980

19. G. E. Ramey, et. al., "Laboratory Evaluation of Four Rapid-Setting Concrete Patching Materials", Transportation Research Record 1041, 47 - 52, 1985.

ClibPDF - www.fastio.com

20. B. F. Neal and P. D. Krauss, "Experimental Overlays Utilizing Magnesium Phosphate, Methyl Methacrylate and Polyester-Styrene Concretes", Final Report, FHWA/CA/TL-85-19, California Department of Transportation, (1985).

21. U. R. Vaidya and V. M. Nadkarni, "Unsaturated Polyester Resins from Poly(ethylene terephthalate) Waste", Ind. Eng. Chem. Res. 26, 194-198 (1987).

22. K. S. Rebeiz, et. al., "Making Polymer Concrete with Recycled PET", Plastics Engineering, 33-34 (1991).

23. S. Kudlapur, et. al., "Evaluation of Cold-Weather Concrete Patching Materials", ACI Materials Journal, Vol. 86, No. 1, 36-44 (1989).

24. F. Parker, Jr., et. al., "A Study of Bond Strength of Portland Cement Concrete Patching Materials", Transportation Research Record 1041, 38-47 (1985)

25. ACI Committee, "Guide for Polymer Concrete Overlays", ACI Materials Journal, Vol. 90, No. 5, 499-522 (1993).

26. D. J. Roodler, "An Evaluation of High Molecular Weight Methacrylate as a Repair Material for Cracked Concrete", M. S. Thesis, University of Texas at Austin, 1987.

27. P. Mani, A. K. Bupta, S. Krishnamoorthy, "Efficiency of Some Silane Coupling Agents and of the Method of Their Application in Polyester Resin Concrete", Journal of Material Science , 18, 3599-3605 (1983).

28. R. A. Schoenberner, Jr., et. al., ICPIC Working Papers, San Francisco, CA (Sept., 1991).

29. R. J. Young, "Introduction to Polymers", pp. 95-105, Chapman and Hall, 1981.

30. "Elimination of Air Inhibition of Exposed Vinyl Ester Surfaces", Technical Information, Resin Products, The Dow Chemical Co., Midland, MI 48674.

ClibPDF - www.fastio.com

31. D. N. O'Conner and M. S. Saiidi, "Polyester Concrete for Bridge Deck Overlays", Concrete International, 36-39 (Dec., 1993).

32. U. Hense, L. Lech and R. Hinterwaldner, "Cartridge Having Hardenable Cycloaliphatic Derivatives for Bore Hole-Filling Masses", U. S. Patent 5,256,723, Oct. 1993.

33. P. Mani, S. Krishnamoorty and A. K. Gupta, "Role of styrene-based shrinkage reducing agent in polyester resin concrete", Int. J. Adhesion and Adhesives, Vol. 3, No. 2, (April 1983).

34. A. M. Rosenberg and D. A. Chapman, "Improved Unsaturated Polyester Resin Concrete with Shrinkage Control", ICPIC Working Papers, San Francisco, CA, (September 24-27, 1991).

35. J. M. Daly, et. al., "Designing a Better Polymer Concrete Based on Unsaturated Polymer", Polymer Concrete, SP-137-7, pp. 109-125, ACI publication (1993).

36. R. J. Farris, Trans. Soc. Rheol ., 12, p. 281 (1968).

37. J. Brandrup and E. H. Immergut, "Polymer Handbook", Second Edition, Wiley Interscience, New York, 1975, IV-337.

38. D. L. Glauz and R. Maggenti, "Bonded Polyester Concrete Overlays Used in California", Proceedings of papers presented at the Structures Congress '93, Structural Engineering in Natural Hazards Mitigation Vol. 2, 1002-1007 (April 19-21, 1993), American Society of Civil Engineers, 345 E. 47th St., New York, NY 10017-2398.

2. Additional References.

1. D. W. Fowler, "Future Trends in Polymer Concrete", SP-116-8, in Polymers in Concrete: Advances and Applications, Peter Mendis and Charles Mcclaskey, Editors, ACI Publication (1989).

2. C. R. Mclaskey, "New Materials for the 90s", ICPIC Working Papers, San Francisco, CA, (September 24-27, 1991).

ClibPDF - www.fastio.com

3. J. L. Brewbaker, R. M. Nowak, K. S. Dennis, "Stabilized Low Profile Resins", U. S. Patent 3,836,600, Sept., 1974.

4. J. J. Fontana, W. Reams, "High Temperature Polymer Concrete Compositions", U. S. Patent 4,500,674, Feb., 1985.

5. J. M. Daly, et. al., "Shrinkage Controlled Low-Temperature-Curable Polyester Resin Compositions", U. S. Patent 5,082,878, Jan., 1992.

6. G. W. Ceska, "Macromonomer-Based Polymer Concrete Compositions", U. S. Patent 4,722,976, Feb., 1988.

7. H. Valley, et. al., "Methods of Coating and Impregnating Concrete Substrates, and Products Obtained Thereby", U. S. Patent 4,460,625, July, 1984.

8. R. Hoene, A. Hesse, K. Demmler and H. Lawonn, "Low-Shrink Unsaturated Polyester Molding Compositions", U. S. Patent 4,172,102, Oct., 1979.

9. G. Ceska, "Method of Protecting or Reconditioning a Surface with a Polymer Concrete", U. S. Patent 4,874,675, Oct., 1989.

10. U. Hense, L. Lech and R. Hinterwaldner, "Use of Hardenable Cycloaliphatic Derivatives for Borehole-Filling Masses", U. S. Patent 5,157,072, Oct., 1992.

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