

Mud Brick Conservation ProjectField Report

August 9, 1973

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Summary - Through arrangements by Dr. Rainey and the U.S. Park Service, field tests were established at Chaco Canyon and at Pecos National Monuments. Several acrylic emulsions were sprayed on 25-50 square feet segments of a freshly excavated pit house at Chaco Canyon. An ancient stone wall was also treated as a test for sand stone deterioration.

At Pecos several tests were established on ancient adobe walls. Acrylic emulsions were incorporated and used in adobe mortar and in adobe bricks.

These test panels are to be kept under observation to determine if, when and how they fail.

Details - Dr. Robert Lister, Chaco Center, National Park Service arranged for field trials on our acrylic resin conservation method at Chaco Canyon and at Pecos National Monument. Mr. Al Hayes, supervisor of all field operations at Chaco was the direct contact at Chaco. Mr. Gary Mattlock, archaeologist was the direct contact at Pecos.

A freshly excavated pit house was selected for most of the tests at Chaco Canyon. This structure consisted of about an 18 foot diameter pit with its benches, fire box, miscellaneous cists, an ante chamber and an adjacent 7-8 foot deep Kiva. The floor of the pit house was about 30 inches below present ground level.

Most test areas were selected to give an evaluation on a specific structure or exposure situation. About 25-50 square feet were treated in each test. A total of eight panels were established in this pit house. Their identity and location are indicated on the attached sketch.

Test A - Two Coats E-863

Two coats of E-863 (16% resin solids) were applied 24 hours apart with a simple 2½ gallon garden sprayer. The area was premoistened with water and sprayed with the emulsion to the point of "run off" for twenty minutes. Most of the absorption occurred during the first treatment. A floor section, the riser to the bench, the bench surface, the riser (bark of bench) to the present grade level and a one foot wide area at the lip of the excavation were sprayed. Most of the surface on the floor and bench was firm. The top rim of the excavation and the walls were not particularly well compacted and may well form a source of failure because of inadequate support for the resin film. Dr. Hayes did not like the gloss imparted to the treated surfaces. We killed the gloss fairly well in subsequent treatments by dusting the still wet final coat with fine soil dust from the excavation.

A total of 7.75 lbs. of E-863 (35% resin solids) was used on 64 square feet. Cost of E-863 per square foot was 3.3 cents.

Test B - Two Coats E-330

This again was a segment of the pit house floor, bench and excavation rim. The hearth was included in this test. Two coats of E-330 (9.4% resin solids) were applied. Again all surfaces were premoistened for the first application.

A total of 5 lbs. of E-330 (47% solids) was used on 40 square feet. Cost of E-330 per square foot was 3.0 cents.

Test C- Two Coats E-826

This was a floor and bench section but also included a segment of free standing excavation wall between the pit house and the antechamber. This wall was about 12 inches thick and 30 inches high. Also included were several thin slabs of rock.

A total of 8.5 lbs. of E-826 (35% resin solids) was used as the first coat on 69 square feet. Cost for 1st coat was 4.2 cents per square foot.

Test D - First Coat E-826 -- Second Coat Silicone

This area was primarily free standing excavation walls with several fairly thin (6 inch) sections and again about 30 inches high. The 5% silicone in mineral thinner was applied by the garden sprayer. This silicone solution, obtained from Sherwin Williams Paint store was applied over 20 minutes time at the rate of one gallon per 66 square feet or 9.1 cents per square foot. Therefore, total cost per square foot for E-826 and silicone was 13.3 ¢ (4.2 + 9.1). (Note -- This silicone is quite expensive from the paint store, another source may be cheaper).

Test E - First Coat E-330 -- Second Coat Silicone

This was primarily a free standing excavation wall between the ante chamber and the vent shaft trench. A part of the trench was also treated. One narrow portion of the wall should give a very vigorous test.

E-330 was applied at the 9.4% level, silicone was sprayed on as purchased from Sherwin Williams (5% resin). First Coat of E-330 consumed 3.8 lbs of E-330 on 39 square feet or 2.3¢ per square foot for the 1st coat of E-330. Silicone cost was 9.1¢ per square foot giving a total cost of 11.4¢ per square foot.

Test F - Two Coats E-330

This test area comprised a 46 square feet stripe down the east side of the Kiva excavation wall. The soil was fairly well composted but was not the original surface. Some original plastered surfaces in wall cavities were included.

Total consumption of E-330 was 4 lbs. at a cost of 2.1¢ per square foot.

Test G - Two Coats of E-863

The area comprised an uncovered stone and mud brick wall between the vent shaft and the Kiva wall. It is a narrow wall about 9-10 inches thick and should be a good test for a stone and mud wall.

Amount of emulsion used was 4.75 lbs. on 18 square feet or 7.1¢ per square foot for two coats.

Test H - Two Coats of E-330

This test area was the underside of a pear shaped storage cyst. The cavity was hollowed out like a large narrow mouthed jar. Only the under side and lip of the cavity was treated. Thus the top side on the canyon floor will be exposed to the weather. The thickness of this wall segment is 6-12 inches. It may cave in at its own weight. The excavated surface was soft and sandy.

Stone Wall - Two Coats E-863

This test was primarily to evaluate these resins in the protection of a deteriorating sand stone wall. Portions of the wall base were very soft and mushy. The failure seemed to be due to ground moisture since comparable stones in the upper part of the wall were firm.

A trench was dug on both sides of the 4.5 foot high stone wall. On one side a 48 inch long portion of the foundation was exposed, on the opposite side a 24 inch long portion was exposed. Holes were drilled diagonally downward under the base of the wall and about six inches apart. These 18-24 inch deep holes served as entry ports for soaking the base of the wall with about six gallons of 4.4% E-863 emulsion. The soil absorbed the emulsion very rapidly for the 1st hour. After drying overnight a second soak was attempted but practically no liquid was absorbed.

The sides of the wall and its foundation were coated twice with an 8.8% E-863 emulsion. Since the stone wall retained its structural strength when wet

a more dilute emulsion was selected to enhance the penetration.

After treatment the foundation trenches were backfilled to their normal levels leaving 54 inches of exposed wall on the westerly side and 36 inches exposed on the easterly side.

Total area of wall surface treated was 40.0 square feet using 6.5 lbs of E-863 at a cost of 4.4¢ per square foot. Six lbs. of E-863 were used to treat the base of the wall (\$1.60).

#### Tests at Pecos National Monument

A 16 x 16 feet former cell in the old spanish compound served as the primary test site. These walls had not been disturbed since they were built by the Indians about 300-350 years ago. Approximately 4-5 feet high walls remained. They were badly eroded on the tops and were soft. The sides of the walls showed the original outline of blocks, but even these were soft and easily rubbed away with modest finger pressure. We do not have a solid base for the resin coating.

All of the adobe walls at Pecos are quite dark in color and a number of the old bricks seem to have an oily appearance. These "oily" bricks did not take the emulsion solution at all well.

In general, the soil at this site did not absorb or "wet" with the emulsion like it did at Chaco Canyon. As a result the gloss was much more pronounced at Pecos. Mr. Matlock considered the glossy appearance unacceptable. An effort was made to kill the shine with light dustings of soil while the coating was still wet.

All areas were premoistened with water before emulsion treatment.

#### Test #1 - Two Coats of E-826

Both sides of a wall comprising about 65 square feet were premoistened and then sprayed with a 16% E-826 emulsion. More gloss than expected was obtained with this resin on this wall. Wetting was spotty. Six lbs. of E-826 was consumed on

65 square feet -- cost 3.1¢ per square foot for the 1st coat. One half of this was given a second coat of E-826.

Test #2 - 1st Coat E-826 - 2nd Coat Silicone

One half of the once treated wall in test #1 was given a spray with 5% silicone in mineral thinner. The wall showed spotty wetting with the silicone solution but was beginning to dry to a uniform color in about one day.

Test #3 - 1st Coat E-330 - 2nd Coat Silicone

A seven foot length of the same wall used in test #1 was premoistened with water and then sprayed with 9.4% E-330. A total of 2.8 lbs of E-330 was absorbed by 64 square feet of wall surface - cost for the 1st coat 1.1¢ per square foot.

One half of this once coated wall was sprayed with a 5% silicone solution.

Test #4 - Two Coats of E-330

One half of the once sprayed E-330 wall described in test #3 was given a second coat of E-330. This wall was quite glossy. An effort was made to kill the shine with dusting.

Test #5 - Wall and Foundation with Two Coats E-826

This test was conducted on a partially buried wall on one side with the other side exposed down to a badly eroding base just above grade. A trench was dug to the bottom of an ancient mud and stone foundation wall (about 36 inch deep wall). Holes were drilled between the stones in the wall and in the soil below the wall. These holes served as entrance ports for soaking with a 4.4% E-826 emulsion. About four gallons of solution were poured into the foundation. Several holes drilled into the wall led to unfillable cavities.

The upper section of the wall was coated twice with 16% E-826.

After standing overnight the foundation was back filled to the original level.

Test #6 - One Coat dilute E-826

One small (24x36 inch) section of an adobe wall was sprayed for 20 minutes with 4.4% E-826. This soaked in readily and showed no evidence of coating after treatment. It will not give protection against heavy rains. It is a test on a

bare minimum treatment such as might be given for temporary protection to an excavation in progress.

Test #7 - One spray with Silicone

This was a small test of 16x36 inches with the leftover silicone solution. A spray for 10 minutes was achieved.

Polymer Containing Mud Mortar

An existing unpointed stone wall was pointed with mud mortar containing 8.8% E-863 as the wetting solution. Mud was chunked into the deep cavities between stones. After drying overnight the mortar had cracked but the locked in mortar was firm. Segments of wall with the Park Service regular mud mortar containing soil seal and plain mud mortar containing no chemical additive were also prepared for comparison. These mortars cracked in the same fashion as E-863.

One section of the E-863 wall was sprayed after one day drying with a 4.4% E-826 emulsion to water seal the cracks in the mortar.

Polymer Containing Adobe Bricks

Four samples (two bricks each) of adobe bricks were prepared using E-330 and E-863. These were made by the Park Service laborer who normally makes their bricks. They were packed in wooden molds, the mold removed immediately and the bricks covered with wet burlap in accordance with their standard procedure. The drying cycle is to be the same as their own bricks.

Mix A - About 5% E-330 Solids

4 shovels soil  
1.5 shovels sand  
2.5 lbs. E-330 solids

Mix B - About 1.7% E-330 Solids

6 shovels soil  
2 shovels sand  
1.0 lbs E-330 solids

Mix C - About 2.2% E-863 Solids

6 shovels soil  
2 shovels sand  
1.3 lbs E-863 solids

Mix D - About 1.6% E-863 Solids

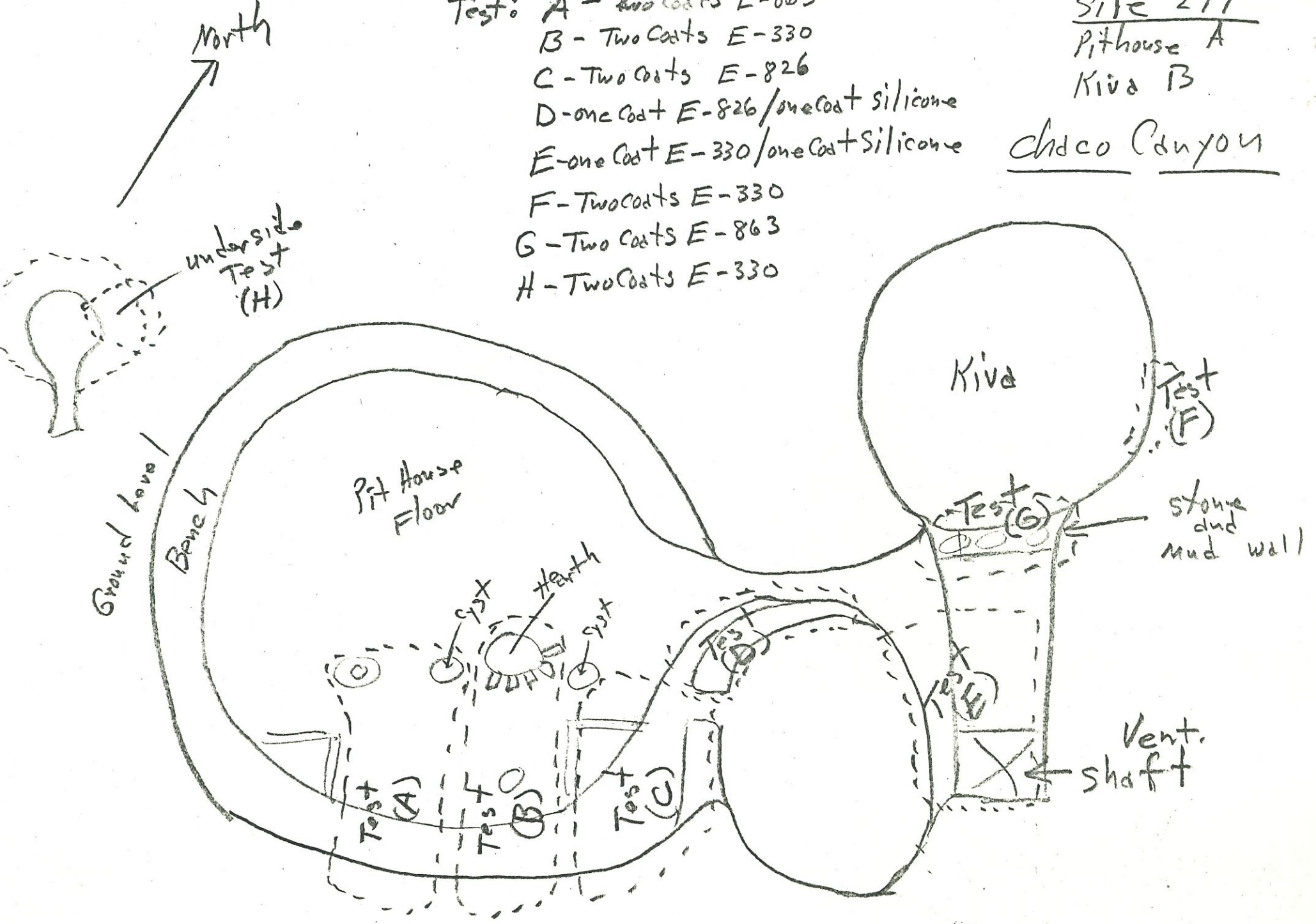
6 shovels soil  
2 shovels sand  
0.9 lbs. E-863 solids

*of Butterbaugh*

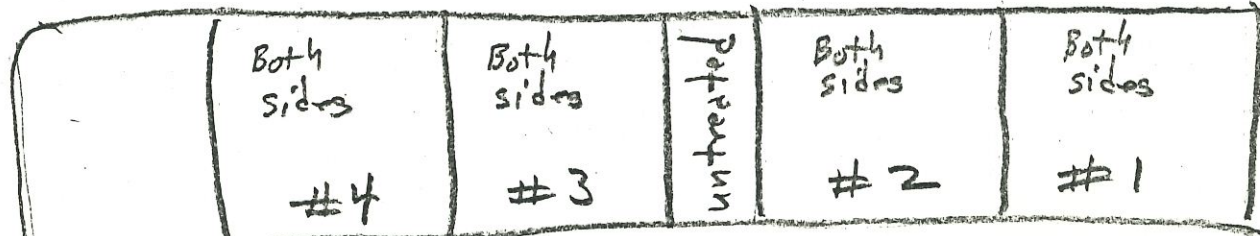
- Test: A - two coats E-330  
 B - Two Coats E-330  
 C - Two Coats E-826  
 D - one coat E-826 / one coat silicone  
 E - one coat E-330 / one coat silicone  
 F - Two coats E-330  
 G - Two coats E-863  
 H - Two coats E-330

Site 211  
 Pithouse A  
 Kiva B

Chaco Canyon



West ↑



untreated

untreated

- Test:
- #1 Two coats E-826
  - #2 one coat E-826 / one coat Silicone\*
  - #3 one coat E-330 / one coat Silicone
  - #4 Two Coats E-330
  - #5 Two Coats E-826
  - Foundation dilute E-826
  - #6 one dilute coat E-826
  - #7 one coat Silicone



one side only



Foundation Treatment

Both sides #5

Foundation Treatment

\* 5% Silicone in Mineral Thinner

## MUD BRICK CONSERVATION PROJECT

Interim Report No. 2

Period Covered: June 7, 1973 - November 8, 1973

Date: November 14, 1973

Author: D. J. Butterbaugh

### Summary

Silicone, Rhoplex E-330 and combinations of these are still giving complete protection to adobe clods after more than a year of outdoor exposure on the museum roof. Twenty-five additional adobe samples along with four wood samples have been placed on outdoor exposure. Four courtyard tests on stone and wood have been started.

Field trials on a freshly excavated pit house at Chaco Canyon and on old adobe walls at Pecos National Monument have been established.

Rhoplex E-826, a small particle size emulsion, and F-325, a polysiloxane, are new materials of promise. Soak treatments with 2% emulsion have given deep penetration and excellent consolidation and water repellency. Deglossing of the treated adobe and stone surfaces can be achieved by the simple technique of dusting the emulsion wet surface with dry soil or powdered stone. This dust is not removed by long term showering under the water faucet. Rhoplex treated adobe clods have excellent resistance to sand blasting. Incorporation of Rhoplex emulsion in powdered adobe soil makes a strong, tough water repellent mud for patching or new adobe block preparation.

Underfired old brick and soft sandstone (from Chaco Canyon) have been treated with the Rhoplex emulsions. Penetration is 1-2 inches with even a 16% emulsion. Such treatment gives water protection and binds the sand and brick grains.

A groundwater simulator has been set up to study the effect of groundwater movement and salt growth in adobe and sandstone. Preliminary results indicate that adobe and sandstone will have significant protection from salt growth deterioration if treated with Rhoplex emulsions. Soft

sandstone deteriorated badly in the simulator test, while treated stone was not affected.

Long term freeze/thaw and wet/dry cycling of treated stone and brick samples is under way.

### Details

#### Outdoor Exposure Results

Ten pieces were placed on museum roof exposure test in October 1972. These were placed in a location where they would have sun, rain, and drifting snow exposure. By early February 1973, the untreated control samples had almost washed away leaving only a muddy stain on the roof. None of the other samples showed evidence of failure.

By mid June 1973, the small particle size emulsion, Rhoplex E-863, at the 8% resin double coat level was failing. Rhoplex E-863 at 16% one coat appeared to be marginal. All Rhoplex E-863 samples seemed to be picking up a slight amount of soiling from the sooty atmosphere. Rhoplex E-330, a harder resin, showed no change in color or appearance. The silicone in mineral thinner treated sample looked the most natural; it was still fragile and abraded easily but had retained its original weight.

By mid July the silicone sample showed some soiling and spalling but otherwise looked good. No change occurred in the Rhoplex E-330 samples. The Rhoplex E-330 silicone samples kept their good appearance and did not pick up any weight as absorbed moisture even though it had been a rainy season. The Rhoplex E-863 plus penetrant samples began to show failure by cracks in the resin coat exposing the untreated clay.

The double coated Rhoplex E-863 at 16% sample showed no deterioration.

By mid August no change had occurred in the silicone, the Rhoplex E-330, and Rhoplex E-863 16% samples. Others were failing.

By mid October 1973, the silicone sample looked good. It had retained its weight but was easily abraded.

The Rhoplex E-330 9.4% double coated sample looks good. The resin skin is still tough; perhaps a little of the top shine is disappearing. The

Rhoplex E-330 9.4% silicone samples are good. The Rhoplex E-863 16% double coated has failed rapidly.

Thus, after one year of outdoor exposure, the silicone, the double coated Rhoplex E-330 at a 9.4% level and the Rhoplex E-330 9.4% single coat part treated with silicone are still holding up well.

#### New Materials and Combinations

Previous testing demonstrated that Rhoplex E-330 one coat at the 9.4% level protected a clod under a shower equivalent to 1200 inches of rainfall per hour for about 1.5 to 2.0 hours before the first break up occurred. A double coat of Rhoplex E-330 gave protection for about 4.0 hours. Rhoplex E-863, a small particle size emulsion made especially for deep penetration of leather, at the 16% level gave protection for about 5 hours.

Continuous testing has shown this resin to protect for more than 40 hours if the clod is double coated.

Rhoplex E-826, again a very small particle size emulsion at the 16% level and with one coat, gives 3-5 hours protection. In one instance as much as 12 hours protection was obtained with one coat of Rhoplex E-826. A double coat gave more than 40 hours protection.

Incorporation of a new G.E. water soluble silicone (G.E. S.C. 50) at about the 1% level improves the performance of Rhoplex E-826 by about 25% (protection with one coat was slightly over 5 hours).

Another silicone water repellent, a water insoluble polysiloxane, F-325, was obtained from Professor Sultan of the College of Engineering, University of Arizona. This material is an excellent water proofing agent for adobe. Its binding power is quite poor. Preliminary testing indicates it is not compatible with Rhoplex E-826 or E-863 but does complement the performance of Rhoplex E-330. It can be used as a second coat or post treatment on Rhoplex E-330 or in combination with Rhoplex E-330 as a single coat to achieve more than 27 hours protection. Even after 27 hours the clod was still firm. When broken open it was damp inside but crumbly, not sticky mud. Further work with these mixtures is to be done.

### Air versus Oven Drying

While it has been the practice to oven dry the treated clods before water testing, such a procedure would be impractical in the field. Accordingly comparisons were made and it was determined that ordinary drying for 16-20 hours was equal to or better than oven drying.

### Prewetting

Even though the experimental results are somewhat inconclusive, it appears that prewetting of the clay surface with a light spray of water helps the penetration of the clod. More consistent results and generally lengthened shower times are attained.

Multiple wettings before treatments are not advantageous and wetting before a coating with resin containing silicone is not a good practice.

### Wick or Soak Treatment

Two resins, Rhoplex E-826 and Rhoplex E-330, were used in dilute concentration to impregnate a clod from the bottom by a soak or wick action. This was an attempt to study in the laboratory the problem of treating the base or foundation of an adobe wall to stop the movement of groundwater into the wall.

The procedure consisted of grinding a flat surface on the bottom of a 3-4 inch high piece of adobe block. This was then placed on a paper towel pad in a flat dish. The paper towel was kept wet with emulsion and the penetration was measured in inches as the wet zone progressed up the clod. After drying thoroughly the zone of treatment was measured by non wetting to a drop of water placed on the surface. The zone of treatment was generally quite sharp.

With Rhoplex E-826 the wet zone during treatment with 4% emulsion advanced a total of  $1\frac{1}{4}$  inches in two hours. With 2% emulsion the wet zone was  $1\frac{3}{4}$  inches and with 1% emulsion the wet zone was 3 inches. After drying the non wetting zones were  $1\frac{1}{8}$ ,  $2\frac{1}{8}$ , and  $2\frac{3}{4}$  inches for 4, 2, and 1% emulsions respectively.

It should be noted that adobe treated with 2% E-826 in this soak

treatment fashion did not transmit water even in contact with a wet paper pad for 2-3 days. Thus it is believed that a wall treatment by periodic holes drilled into the base of a wall and soaking with dilute emulsion followed by drying will water proof the base of the wall against ground moisture.

Rhoplex E-330 was also tested by the above described wick action. The rate of travel was somewhat slower and the non wetting zone somewhat shorter but not markedly so (non wetting at 1/2, 2 1/4, 1 1/2 inches respectively for 4, 2, 1% emulsion concentration).

### Deglossing

Adobe surface sprayed with these emulsions take on a slight glaze or shine appearance. The shine is more pronounced with E-330.

A variety of commercial delustering agents were tried by incorporating them in the emulsion mix. This was not effective.

A practical method of killing the shine on treated adobe surfaces was to sift a little finely powdered dry soil on the freshly sprayed wet surface. Such treatment was most effective if applied to the second resin coat. This dusted soil was incompletely wet, hence no gloss, but was also tightly held so that subsequently heavy rain showering for several hours at the 1200 inches per hour rate would not remove the powdered soil coating.

Such a dusting technique should also be applicable for coated sandstone monuments and stone walls. The method was used with complete success at Chaco Canyon.

### Anti-Abrasion

Only preliminary testing has been done on this problem but it does appear that Rhoplex emulsion treated surfaces will be quite resistant to sand blasting or wind driven dust such as might occur in the desert.

An untreated adobe surface was subjected to the miniature abrasive cleaning jet in the Museum Conservation Laboratory. Dolomite at 50 psi gas pressure was used. The surface was very rapidly eroded, a hole 1/4 to 1/2 inch deep being eroded in 10 seconds. The same jet was directed against an adobe surface that had been coated twice with Rhoplex E-863. This surface did not erode in 3 minutes of exposure and repelled water in a normal fashion after

treatment. Only a minor darkening of the surface occurred under the dolomite jet. The fail point was not determined.

#### Mud Plaster and Mud Cakes

Rhoplex emulsions used in the liquid mix to make a mud plaster or an adobe mud cake provide marked binding action and meet rub resistance. This makes possible a more or less permanent patching plaster or adobe block for restoration purposes. Emulsions of different resin contents were used as the wetting liquid with powder and several dry adobe soils to make a thick, non pourable mud.

This mud was cast into cakes or used to coat or plaster clods of adobe. Rhoplex E-330 at the 7.8% resin level based on dry soil gives a hard, normal appearing cake when dry. This cake shows darkening when wet with water. Hard rubbing on the wetted surface shows only a trace of "rub off." Rhoplex E-330 at the 3.2% level gives a cake comparable in hardness and wetting characteristics. Rub off with a wetted surface is slightly easier with heavy finger pressure but such a cake would be stable to heavy rain pressure. At the 1.25% resin level the cake can be abraded wet with modest finger pressure. It probably would eventually erode away with heavy rain pressure.

With Rhoplex E-826 at the 3.7% resin to soil level a hard, tough, slightly darkened cake was produced. Water does not wet readily. Rubbing hard in a small puddle of water on the surface does not produce any "rub off." When finally wet the surface does take on a darkened appearance.

Rhoplex E-826 at the 1.65% level gives a hard cake that appears normal color when dry. Water puddles on its surface. Hard rubbing in this puddle produced some "rub off."

At the 0.79% level Rhoplex E-826 produces a hard, normal colored cake that will rub off when wet. This is probably too little resin to withstand heavy showering.

Rhoplex E-863 does not perform well as a mud additive. At the 6.0% and at the 2.2% levels soft, wet looking cakes were produced. These cakes absorbed water and rubbed off when wet. This was an unexpected performance for this resin.

### Brick Treatment

The Park Service has a problem with underfired bricks in the Society Hill section of Philadelphia. It was agreed with Dr. Cotter that we would do some preliminary work to determine the performance of the Rhoplex emulsions on the bricks.

The bricks are quite soft; they can be sawed easily with a wood saw or hack saw. The brick absorbed water very rapidly, much like a piece of dry blotter. The brick also absorbed the Rhoplex emulsions rapidly. Rhoplex E-330 at the 9.4% level tended to form an undesirable glossy surface. Rhoplex E-826 at the 16% level did not produce gloss. Dried, the appearance was only an enhanced red brick coloration.

While the treated surface was non wetting to droplets of water, penetration occurred under heavy showering or immersion. This situation prevailed even after three coats of Rhoplex E-826. For example, the untreated sample absorbed 13% of its weight (as wet emulsion) when sprayed for 30 minutes. After one coat of resin, the pick up was 12%, after two coats 10% was absorbed, and after three coats 6% was still absorbed.

It should be noted that the resin treatment consolidates and binds the clay particles in the surface and even under the surface of the brick. Penetration is in excess of one inch. The effect on freeze/thaw and wet/dry cycling is under investigation and will be discussed later in this report.

### Stone Treatment

At the base of a number of Chaco Canyon pueblo walls a soft sandstone has been used which is rotting away to loose sand. This failure is occurring at just the ground level and appears to be associated with ground moisture augmented with the effects of freezing and thawing or with wetting and drying. Samples of this soft sandstone have been studied in the laboratory.

First of all, this stone absorbs all of the Rhoplexes readily without forming a glossy surface. The small particles size emulsion, Rhoplex E-826 at the 16% level, penetrates at least  $1\frac{1}{4}$  inches into the stone (determined by sawing through a treated sample). Even at the inside depth of 1 inch the grains of sand in the soil are bound tightly and can be brushed

vigorously with a stiff brush without dislodgement, whereas the unpenetrated section abraded away easily with comparable brushing.

Treated samples of stone repelled droplets of water but like the underfired brick absorbed water when immersed or under heavy showering.

An 80 g. chunk of stone in multiple treatments with Rhoplex E-826 16% absorbed 8 g. of wet emulsion the first time, 4.0 g. the second time, and 2.0 g. the third time. When dried thoroughly this corresponded to a total resin deposit of about 2.0 g.

### Salt Growth

It has been reported that adobe walls and stone monuments fail because ground moisture moves through the adobe block to the surface and then evaporates leaving the dissolved salts from the interior deposited as crystalline material on the surface. These salt deposits break up the surface of the adobe or stone and cause a spalling off or washing away of the loose material.

A laboratory test of this problem was attempted by dipping a paper towel wick into a source of distilled water. This wick was laid across a flat glass surface. On the wet wick were placed several samples of adobe and stone. An electric fan blew against the samples to accelerate evaporation. The samples placed on the test were as follows:

1. Two clods of untreated adobe;
2. One Rhoplex E-826 clod with the end filed off to expose a flat of untreated adobe;
3. One adobe clod that had been treated on the bottom end by wick treatment with a 20% Rhoplex E-826 emulsion;
4. A treated piece of sandstone in which one flat (bottom) side was untreated and exposed to the water wet wick;
5. A piece of thrice treated E-826 stone, all sides treated;
6. A piece of untreated sandstone.

The test consisted of running the wick wet for 4-5 days per week, then removing the source of water to the wick for 2 days followed by a resumption of the water. This alternate wet and dry treatment was repeated for 8 cycles and a total wet time of 31 days.

During this test yellowish and white salt crystals formed in quantity on the untreated adobe and stone samples. Moderate salt crust formed on the top of the coated adobe. A small amount of white salt crystals formed on the top of the sawed off stone sample. No salt formed on the thrice treated stone sample. The wick treated 2% Rhoplex E-826 sample normally did not show wetness; a small amount of hard yellow glossy salt formed on the side away from the fan. This area remained non wetting to water droplets.

It was observed that the adobe surface under the salt growth on an untreated clod was very fragile in the dried state. In fact even the breeze of the fan was enough to dislodge flakes of soil and salt. This softness extended into the clod for several millimeters.

While salt forms on some of the resin treated adobe surface this skin remained intact after drying. This seems to indicate that a coating on an adobe wall at the foundation line might give significant protection from groundwater damage.

Resin treatment of the Chaco Canyon stone had a marked effect. As stated previously both the untreated and the treated piece with an untreated core but exposed to the wick grew salt. Careful dissolving away of these salt deposits, followed by thorough air drying, revealed that the surface on the treated piece was firm and water repelling, even under the area of salt growth.

Contrary to this, the surface of the untreated piece was soft and powdery, much more so than a sample of the original stone. Approximately the lower 1/3 of the untreated stone piece was so soft that it could be almost completely crushed with mere finger pressure. On this 1/3 portion the stone had completely lost its natural cement and was little more than tightly packed sand. It was also interesting to note that the original sandstone showed little or no carbonate fizz from drops of hydrochloric acid. The soft base of the untreated piece that had been subjected to 31 days of "groundwater" also showed no carbonate fizz but the top half of the stone showed heavy carbonate fizz.

It would appear that movement of the water up through the stone has removed most of the salts and these seem to be contributing mainly to

the binding power holding the individual sand grains in place in the natural stone. On the resin treated portion of the stone either the water movement was much less (as would be expected) or the rubbery resin still holds the sand grains together and the strength of the stone is retained. In any case there is considerable encouragement here for a treatment of these soft rocks with a small particle size acrylic emulsion.

#### Freeze/Thaw and Wet/Dry Cycling

In an attempt to assess damage caused by repeated freezing and thawing or wetting and drying, a series of stone and brick specimens have been prepared with Rhoplex E-330 at 6%, Rhoplex E-863 at 4% and 16%, and Rhoplex E-826 at 16%. In addition, untreated brick and stone control samples have been included in the series. Each sample was carefully dried and then one selected face was brushed for 1000 strokes of a stiff nylon bristle brush. The grains of stone or brick were collected in 250 stroke intervals and weighed to the nearest milligram.

The one set of samples was then immersed in water for 30 minutes, dried for at least 30 minutes, and then placed in a freezer for at least 16 hours (one night). After the freeze period the samples were allowed to thaw. They were then ready for a second, third and so on cycle. At the end of 10 such cycles the samples were oven dried and again subjected to the same 1000 stroke brushing and weighing test.

The other set of samples was subjected to a 30 minute immersion in water, drying overnight at room temperature, oven drying at 80 deg. C. for 3-4 hours, and again ready for subsequent cycling through wetting and drying. After 10 such cycles these samples were also brushed and weighed.

After 10 freeze/thaw cycles the untreated Chaco stone control lost 220 milligrams of dust with 1000 brush strokes. This compared with 146 mg. brushed off the same surface before the test. The stone sample with the two coats of Rhoplex E-863 at a 4% level lost 77 mg. compared to 1.5 mg. initially. One edge of the film has loosened during the first 10 cycles. All other stone samples are firm and tight.

After 10 freeze/thaw cycles the brick control lost 38 mg. vs. 62 mg. per 1000 strokes initially. The Rhoplex E-330 9.4% single coated sample

lost 10.7 mg. (6.9 mg. as a single chip compared to 1.0 mg. initially. All other brick samples were firm and tight with dusting less than 0.5 mg.).

On the wet/dry cycling test after 10 cycles the control Chaco stone sample dusted off 238.5 mg. compared to 326.2 mg. initially. Rhoplex E-330 6% with two coats lost 2.2 mg. compared to 0.1 mg. initially. All other stone samples were less than 1.0 mg. dust off.

Of the brick samples the untreated control dusted off 17.4 mg. compared to 17.1 mg. initially. Rhoplex E-330 9.4% one coat with one side dusted off 2.2 mg. compared to 0.1 mg. initially. The Rhoplex E-330 9.4% all sides are coat treated sample lost 5.9 mg. (3.0 mg. in 5 chips) with 1000 brush strokes compared to -.5 mg. initially. All other brick samples were tight with less than 0.5 mg. losses.

These cycling tests seem to show that they will sort out the weaker treatments and spot the failures. Brush cycling tests are to be continued this winter.

#### Roof Tests

In addition to continuing the five clods placed on the Museum roof in October 1972, 16 large clod samples, 9 mud pancake samples and one simulated totem pole of western red cedar with four different resin treatments were placed on the roof in November 1973. The details of these roof samples are listed in the attached table.

Four courtyard outdoor tests have also been established. The west stone lion in the lower courtyard has been sprayed twice with a 10% Rhoplex E-826. The west marble urn in the upper courtyard has been sprayed twice with a 10% Rhoplex E-863. The south marble cap on the stairway into the old anthropology wing has been sprayed once with a 16% Rhoplex E-863. And finally a portion of the totem pole on the northwest corner of the museum has been sprayed once with a 16% Rhoplex E-863.

#### Field Trials

Field tests were established at Chaco Canyon and at Pecos National Monuments in July 1973. Three acrylic emulsions - Rhoplex E-330, E-826, E-863 - were sprayed on eight 25-50 square feet segments of a freshly exca-

vated pit house at Chaco Canyon. An ancient stone wall was also treated as a test for sandstone deterioration. A stone wall has also been built close to one of the residences. One half of this wall is to be treated with Rhoplex E-863; the other half is to be untreated. The entire wall is to be sprayed daily with water to provide an accelerated weathering test panel.

At Pecos seven 25-50 square feet segments of ancient stone walls were spray treated. Acrylic emulsions were also incorporated and used in adobe mortar and in adobe bricks.

All of these test panels are to be kept under observation to determine if and how they fail.

A more detailed report of these field tests has been made in the Author's Field Report of August 9, 1973.

#### Future Work

Tests so far indicate that we can achieve good surface protection of adobe and probably good protection of soft sandstone. Penetration is still a badly needed quality. Consolidation deep inside the adobe wall is required. It is planned to attack this problem by means of different application techniques with existing resins but also to use monomeric materials that should have much greater penetration followed by polysimization within the adobe block. A smaller particle size version of Rhoplex E-330 needs to be tested to get the advantage of E-330 weatherability along with deeper penetration typical of the E-800 series resins. Combinations of Professor Sultan's F-325 water proofing polysiloxane and the Rhoplex emulsions need to be exploited.

Considerably more work needs to be done with the groundwater simulator to evaluate the degree of protection achieved with both the adobe material as well as the soft stone material.

A better field trial needs to be established on adobe walls. Those at Pecos were too soft to provide a reasonable anchor for the film. A firm base will give much improved results, as will also be desirable to establish a more extensive field evaluation of the foundation or base of the wall treatment against groundwater.

It would be desirable to establish some limited field testing of sandstone monuments or stelae.

TABLE I

Roof Tests

<u>Sample No.</u>	<u>Treatment</u>		
11	Coat #1 E-330 9.4% Coat #2 E-330 9.4% and dust		
12	Coat #1 E-330 9.4% Coat #2 E-330 9.4% Coat #3 F #325 1/30		
13	Coat #1 E-826 16% Coat #2 E-826 16% and dust		
14	Coat #1 E-826 16% Coat #2 Silicone in mineral thinner		
15	Coat #1 E-863 16% Coat #2 E-330 9.4%		
16	Coat #1 E-863 16% Coat #2 E-863 16%		
17	Coat #1 E-863 16% Coat #2 Silicone in mineral thinner		
18	Coat #1 E-863 16% Coat #2 E-863 16% and dust Coat #3 Silicone in mineral thinner		
19	Coat #1 E-826 16% Coat #2 E-330 9.4% and dust		
20	Coat #1 E-826 2% soak Coat #2 E-330 9.4% and dust		
21	Coat #1 E-863 2% soak Coat #2 E-863 16% Coat #3 E-863 16% and dust		
22	Coat #1 E-826 16% Coat #2 E-826 16% and dust Coat #3 Silicone in mineral thinner		
23	Coat #1 <table border="1"><tr><td>E-330 9.4%</td></tr><tr><td>F #325 1/30</td></tr></table>	E-330 9.4%	F #325 1/30
E-330 9.4%			
F #325 1/30			

24 Coat #1 [E-330 9.4%]  
F #325 1/30  
Coat #2 ditto

25 Coat #1 [E-826 10%]  
Coat #2 [E-330 9.4%]  
F #325 1/30

26 Coat #1 F #325 1/30

Pancakes

27 E-330 7.8% resin on dry soil

30 E-330 3.15% resin on dry soil

31 E-330 1.26% resin on dry soil

32 E-863 6.0% resin on dry soil

33 E-863 2.18% resin on dry soil

34 E-863 0.93% resin on dry soil

35 E-826 3.7% resin on dry soil

36 E-826 1.65% resin on dry soil

37 E-826 0.79% resin on dry soil

Wood Tests

No. 1 Two Coats E-863 16%

No. 2 Two Coats E-826 16%

No. 3 Control - No treatment

No. 4 Two Coats E-330 9.4%

No. 5 One Coat E-863 16%

TABLE II

Adobe Block Treatment

<u>Treatment</u>	Shower	<u>Water Pick Up</u>		<u>Remarks</u>
	Head Time <u>Minutes</u>	<u>grams</u>	<u>%</u>	
N-36-5 (Polish) 7.5% solids	1			No Protection
E-330 9.4% one coat	90	16.5	2.15	
E-330 9.4% one coat (water pre-wet)	200	14.5	19.0	
E-330 9.4% one coat 2nd coat F #325 1/30	735	42.0	20.5	Mushy-no silt
E-330 9.4% + F #325 (1/30) one coat	>1635	25.0	12.0	Incomplete
E-826 16% one coat	160	20.0	23.4	
E-826 16% one coat-dry clod-air dry	>360	10.0	—	Incomplete
E-826 16% one coat-dry clod	735	14.5	13.5	
E-826 16% one coat-pre-wet	590	15.5	18.6	
E-826 16% one coat once pre-wet	330	26.0	22.5	
E-826 16% one coat-twice pre-wet	135	9.0	9.0	
E-826 16% one coat-thrice pre-wet	390	21.5	14.0	
E-826 16% + 1% G.E. Silicone- dry clod	270	26.0	18.5	
E-826 16% + 1% G.E. Silicone-dry clod	310	15.0	13.3	
E-826 16% + 1% G.E. Silicone-pre-wet	195	—	—	
E-826 16% one coat-new block	330	9.0	14.5	
E-826 16% two coats-dry clod	>2335	13.0	15.0	Incomplete
E-826 16% one coat-post treat silicone mineral thinner	>2205	13.5	11.5	Incomplete
E-826 16% + F #325 (1/30) one coat	125	12.0	13.2	
E-826 1% wick treat-2nd coat E-826 16%	180	17.5	11.4	No silt
E-826 16% one coat- F #325 (1/30) 2nd coat	>520	14.5	11.0	Incomplete
E-863 16% one coat-dry clod	>2125	22.0	14.0	Incomplete

## A PROGRAM IN EXPERIMENTAL MUD BRICK PRESERVATION

A program of research and development on the conservation of mud and stone structures is being conducted at the University of Pennsylvania. The work was started about four years ago and has as its objectives the conservation of mud brick or mud structures, soft and friable stone, underfired and soft clay bricks and deteriorating stone statuary. A secondary study is the development of a weather resistant mud plaster, mud grout and mud brick.

Laboratory test methods involve treatment of baseball size chunks of adobe brick, pieces of friable stone and soft brick with a variety of polymer solutions, polymer emulsions and monomeric materials which are subsequently polymerized in situ. Treated samples are evaluated by simulated rain at 1200 inches per hour, placed 18 inches from the sample, by wet freeze-thaw cycling and by simulated ground-water using a wide paper wick and air fans. Treatments that show promise in laboratory testing have been placed in outdoor exposure in larger test specimens in Philadelphia, Florida, in New Mexico, in Iran and in Guatamala.

### Emulsion Spray Treatment

Early work has shown that adobe sprayed with a variety of acrylic and methacrylic emulsions will possess a resistance time of about 25-30 hours to a 1200 inch per hour simulated rain. Untreated adobe disintegrates completely in 2-3 minutes under these conditions. Rohm and Haas Co. Rhoplex E-330 treated adobe samples have survived more than four years of outdoor exposure in the Philadelphia climate. Ultra small particle size emulsions give deeper penetration and little or no gloss. Rhoplex treatment followed by a silicone treatment also provides weather protection for more than four years. However, all of these emulsion spray treatments suffer from low penetration into the adobe; most of the polymer forms a rubbery coating on the surface. This surface eventually cracks or breaks exposing the interior untreated portions of the adobe block to weathering and disintegration.

### Chemically Modified Mud

While the Rhoplex emulsions do not appear to be suitable as a spray-on treatment they do appear to be admirably suited as an additive to

clay/mud mixtures. These chemically modified muds have been used as plaster, grout or mortar, cast mud bricks and other comparable applications. Rhoplex E-330 which is a polymer specifically designed as a concrete additive has been the polymer of choice. Mud compounded with this emulsion "works" easily, dries faster than ordinary water-mud and gives crack-free mud bricks in 4-5 inch thicknesses. When dried this chemically modified mud has a natural appearance almost identical to the untreated plaster or brick. Adhesion to stone surfaces is excellent. Adhesion to dry adobe surfaces is less firm but equal to ordinary water-mud in this application.

The polymer solids content must be 5-7% on the dry soil weight to produce a dried soil plaster or brick that is completely resistant to 1200 inch per hour simulated rainfall. A mixture of one volume of Rhoplex E-330 (47% polymersolids) diluted with 3 volumes of water produces a diluted emulsion that is suitable as the sole wetting agent for dry soil to form a workable mud. Most dry clay soils absorb 40-45% of their weight of diluted emulsion.

Since such dried mud is completely resistant to 1200 inch per hour rainfall, a more severe wet-freeze-thaw test was applied. Samples were immersed in water for 1-2 minutes, drained and then placed in a freezer overnight. The next day they were removed from the freezer, thawed at room temperature (generally 3-4 hours) and then again immersed in water and returned to the freezer. A 1-3 dilution failed after 19 cycles, a 1-2 dilution lasted for 42 cycles and a 1-4 dilution failed after 7 cycles.

Cakes and bricks of chemically modified mud have been on outside exposure for more than three years in the Philadelphia climate and for almost 24 months in the subtropical south Florida climate without showing any deterioration. This mud grout and mortar has been in place in restored or repaired ancient stone walls in the southwestern U.S. for more than two years with no evident deterioration. Extensive tests with this material have been established at Hasanlu Tepe in northwestern Iran.

#### Monomer Treatment

Since the polymer emulsion particles were largely filtered out of suspension by the clay, no deep penetration could be achieved with a spray-on emulsion treatment. An alternate system has been investigated in which properly catalyzed methyl methacrylate monomer was soaked into the adobe surface.

Polymerization subsequently took place in situ giving thereby stabilization 1-2 inches deep. It was necessary to catalyze heavily the monomer to achieve rapid polymerization in the presence of soil. Shelf life of about 15-20 minutes was about the maximum before rapid polymerization occurred.

Monomer mixture of butyl and methyl methacrylate gave tougher and less brittle polymer than straight methyl methacrylate.

Adobe absorbed about 10% of its weight of monomer but only about 4% remained as polymer after polymerization. Properly treated specimens were rock hard, showed slight darkening in color and no gloss. They wet with water very slowly and could be soaked in water for days without softening. The surface was quite resistant to wet and dry rub resistance.

One small field trial was attempted at Chaco Canyon but it was concluded that such a catalyzed system was not practical in a hot desert application.

Another aspect of monomer treatment has involved the use of water soluble monomeric materials which in aqueous solution can be soaked into stone or adobe and then subsequently polymerized by soaking in a catalyst solution. Such materials as zinc, calcium, barium or magnesium acrylates have been tested.

The method in general involves making a 30% monomeric zinc acrylate solution by reacting the appropriate amounts of glacial acrylic acid, water and zinc oxides.

Adobe and stone chunks were bathed with this 30% solution. Adobe becomes soft from the wetting thus necessitating careful handling and control of the rate of applications. Soft stone readily soaks up the aqueous zinc acrylate. After absorption is essentially complete the piece is allowed to dry for one to several days. The sample is next treated with an aqueous solution containing 4-5% ammonium persulfate and 4-5% sodium bisulfate. This converts the zinc acrylate to zinc polyacrylate, the reaction taking place both within the material and on the surface. The zinc polyacrylate is a water repelling, water soluble binder that covers and cements the individual grains of soil and rock, producing thereby a surface that is mostly resistant to rainfall, freezing, thawing, wind erosion and ground water damage.

Chunks of adobe so treated can be subjected to 1200 inch per hour simulated rainfall for more than twenty hours with no erosion or break up.

Water absorption is fairly rapid in the early stages of rainfall treatment but then the adobe chunk remains saturated but hard and firm to further wetting.

Zinc acrylate appears to be unique in this performance on adobe and stone. Although polymers are formed with calcium, magnesium and barium acrylates, these materials do not give any appreciable protection to the adobe chunks under a 1200 inch simulated rainfall.

#### Solution Polymer Treatment

Previous attempts have been made to stabilize mud walls by treating with polymer solutions. One of the U.S. Park Service preferred treatments is a soaking with 5% mineral thinner solution of a silicone resin. This waterproofs the wall, but the grains of clay and soil are not bound together by the resin. Attempts to treat with a binding-type polymer have generally been done with relatively concentrated (10-20%) solution. Under these circumstances the polymer solution is viscous and the polymer does not get carried under the surface to any significant extent. As a result, the polymer sits on the surface as a hard, crusty mass of unattractive appearance.

Using dilute solutions (1-3%) of acrylic and methacrylic polymers as exemplified by the Rohm and Haas Co. Acryloids, a very low viscosity solution is obtained that penetrates adobe and dried mud structures of soft, friable stone materials readily. Being colorless, the polymers do not discolor or in any way change the appearance of the treated object. Also the organic solvents commonly used do not weaken the adobe surface such as water does, thus there is no tendency of the clay or soil to run or slump as the surface is saturated with solution.

Method of application is varied and simple. For horizontal surfaces, a coarse spray from a low air pressure sprayer, a paint brush or swab etc. can wet the surface. It is desirable to use a coarse spray to thoroughly wet or flood the surface so that the solution soaks in rather than evaporates on the surface.

While depth of penetration as determined by water repellency of the dried surface, is somewhat dependent on the material being treated, it was

generally possible to achieve water repellency at 2-3 cm. under the surface. Since no skin or film of polymer is formed on the surface, it is easy to retreat a structure merely by again wetting the surface with more polymer solution.

As previously stated, a dried, treated surface beads and sheds water under the simulated rainfall test. Treated adobe chunks or clay cookies can be immersed in water for days without softening. Treatment efficiency was determined generally by simulated rainfall and by wet-freeze-thaw cycling.

Most of the Acryloid polymers are dissolved in paint thinners, toluene, xylene or mixed solvents of this type. Since these are relatively expensive solvents and many times not available in remote parts of the world, an effort was made to find diluting solvents that could replace all or a significant part of the toluene. Kerosene, gasoline, fuel oil and xylene as well as acetone could be used in place of toluene for Acryloid A-21 and for the more soluble Acryloid B-67. Kerosene, gasoline or fuel oil was not a solvent for the A-21 polymer and was not a suitable solvent for B-67. Clay impregnated with kerosene solutions of B-67 were not bound at all well for water protection. It is interesting to note that even though Acryloid A-21 was readily soluble in acetone, such a solution was markedly ineffective in binding the clay or soil particles. In general rainfall times in excess of 50 hours could be achieved with toluene solutions of A-21 treated clay cookies. In contrast acetone solutions of A-21 produced rainfall times of only 15 minutes. Comparably toluene solutions of B-67 produced clay cookies that could resist more than 40 hours of simulated rainfall, while the same concentrations of B-67 in kerosene or gasoline gave rainfall times of 30-60 minutes. Thus it does not seem likely that we can substitute cheaper and more readily available solvents for toluene in these treatments.

A variety of polymers have been tested in toluene solutions. Some have been essentially hard methyl methacrylate polymers, others softer substituted methacrylate polymers, others copolymers and finally silicone water proofing resins. Acryloid A-21 in toluene seems to be the best overall polymer. It is effective in adobe at 1% concentration, but in the more severe freeze and thaw tests a 3% concentration seems to be best. At

this concentration there is high penetration but still good dry and wet bonding and no tendency to gloss or otherwise change the visual appearance of the specimen. A second best and very good polymer is Acryloid B-67. This is a softer polymer and more soluble in toluene, an advantage when working in the field.

Simulated rainfall times of more than 50 hours could be achieved with chunks of Acryloid A-21 treated adobe blocks and with Florida clay cookies. In contrast, a silicone resin at the 1% level gave only 0.5 hours of showering and gave practically no dry binding of the soil grains.

The following table gives the details of the various laboratory rainfall evaluations:

Simulated Rainfall Testing of Solvent Polymer Samples

Polymer	Clay	Dilution Solvent	Polymer Concentration (%)	Shower Time (hrs.)	Water Absorption (wt. %)
Acryloid A-21	Fla.	Toluene	0.30%	1:50	5.4%
Acryloid A-21	Fla.	Toluene	0.60%	23:45	6.9%
Acryloid A-21	Pa.	Toluene	0.60%	21:30 +	5.1%
Acryloid A-21	Tucson	Toluene	1.0 %	33:00 +	7.0%
Acryloid A-21	Tucson	Toluene	1.0 %	53:00 +	6.9%
Acryloid A-21	Tucson	Toluene	3.0 %	20:10 +	3.2%
Acryloid A-21	Tucson	Toluene	3.0 %	20:20 +	3.7%
Acryloid A-21	Fla.	15% Acetone 85% Xylene	1.0 %	10:30 +	8.1%
Acryloid A-21	Fla.	Acetone	1.0 %	0:15	----
Acryloid B-67	Fla.	Toluene	0.45%	1:00	6.8%
Acryloid B-67	Fla.	Toluene	0.90%	9:30	8.0%
Acryloid B-67	Fla.	Toluene	1.80%	43:15 +	6.7%
Acryloid B-67	Fla.	Gasoline	0.9 %	0:13	----
Acryloid B-67	Fla.	Gasoline	1.8 %	0:35	8.1%
Acryloid B-67	Fla.	Kerosene	0.9 %	1:00	5.4%
Acryloid B-67	Fla.	Kerosene	1.8 %	1:25	4.5%
Design Control*	Fla.	Toluene	1/200	0:03	----
Design Control	Fla.	Toluene	1/100	0:35	5.1%
Design Control	Fla.	Toluene	1/50	2:00	5.9%
Design Control	Fla.	Toluene	1/25	11:30 +	5.1%
Silicone	Fla.	Toluene	1.0 %	0:30	5.5%
Silicone	Fla.	Mineral Thinner	5.0 %	16:30 +	3.8%
Acryloid B 48 N	Fla.	Toluene	0.45%	0:45	6.0%
Acryloid B-82	Fla.	Toluene	0.40%	0:15	5.5%
Acryloid CU-10LU	Fla.	Toluene	0.40%	0:01	----
PVA (AYAF)	Fla.	Toluene	1.0 %	0:35	----
PVA (AYAF)	Fla.	Toluene	3.0 %	3:00	----
Polyvinylchloride**	Fla.	Acetone	1.0 %	13:30 +	----
Polyvinylchloride	Fla.	Acetone	3.0 %	20:15 +	6.1%

+ Discontinue without failure

\* Obtained from Design Control Inc. Westbury, N.Y.

S Simulated rainfall gives a good evaluation of treatment for adobe, but wet-freeze-thaw cycling of treated samples gives a much more severe test. Failure is determined subjectively when the adobe chunk cracks, gets soft to finger nail scratching, or other such tests.

Two pieces of adobe were treated with 1 and 3% Acryloid A-21 in toluene respectively and then subjected to wet-freeze-thaw cycling. After 12 cycles each piece of adobe was firm and showed no evidence of failure, but the 1% Acryloid A-21 sample had absorbed 8.9% of its weight as moisture while the 3% Acryloid A-21 sample had absorbed only 1.2% of its weight. On the 18-19th cycles the 1% Acryloid A-21 failed by cracking and softening of the interior of the sample. On the 60th cycle the 3% Acryloid A-21 sample began to break up. It should be remembered that an untreated sample of adobe could not survive a single immersion and freeze cycle.

A very useful application of the solution polymer treatment has evolved with adobe and modern plaster. As stated previously, adobe blocks if spray-treated with a 3% Acryloid A-21 solution, will be resistant to heavy rain and weathering by freezing and thawing. If this block is now plastered with Rhoplex E-330 modified mud or even water mud, the adhesion of the Acryloid A-21 stabilized adobe block or wall is much improved. If ordinary water mud is used as the plaster, a subsequent spray treatment of the dried plaster with an Acryloid A-21 spray provides a doubly protected surface. Such a construction was prepared at Hasanlu.

Even a simpler technique has evolved whereby the adobe surface (if firm) can be plastered with a  $\frac{1}{4}$  to  $\frac{1}{2}$  inch coat of water mud, allowed to dry thoroughly and then spray-treated with a 3% toluene solution of Acryloid A-21. This construction has proved to be very resistant to weathering in Philadelphia this past winter, in Florida and in Guatamala. Under the simulated rainfall tests such a construction shows no deterioration over a 49-hour period. Water absorption was 5.5%.

Acryloid A-21 treated adobe specimens have been on outdoor exposure to the Philadelphia climate for more than 14 months including the winter months and are showing no signs of deterioration. An Acryloid A-21 treated water-mud plastered specimen is also looking good after more than 12 months of exposure in Philadelphia.

### Groundwater simulation

An attempt has been made to devise a method of studying in the laboratory the adobe ground water and salt growth problem. A simple test method composed of a paper towel wick dipping into a distilled water source then spread across a flat glass plate with an electric fan blowing across the flat plate assembly seems to work quite well. The samples are placed on the wet wick resting on the glass plate, with the fan blowing, the moisture picked up by the samples is evaporated rapidly. Salt incrustation forms in 5-10 days on untreated adobe chunks. If the wick is allowed to go dry the adobe chunk dries out and brittle flakes of salt and soil spall off in the breeze of the fan, much as does a dry salt incrustated adobe wall in the desert.

Adobe chunks treated with Acryloid A-21 toluene solutions (1% and 3%) were cut in half to expose an inner core of 1 x 1.5 inch non treated adobe and an outer treated crust of about 0.75 inch thickness. The inner core was water wetting while the outer crust was non wetting. These chunks were placed cut side down on the paper wick so that the non treated inner cores would pick up water while the outer treated crust would repel liquid water but would still pass water vapor. The 1% Acryloid A-21 sample began to crack after about 10-15 days exposure. No salt growth was observed. The 3% Acryloid A-21 sample has shown no salt growth over eight months of exposure. One small crack developed through the 0.75 inch thick crust. Cutting the chunk vertically through the treated and untreated areas has shown no visible evidence of salt accumulation at the boundary of wetting and non wetting areas. Thus it would appear that salt growth is not occurring at the inside boundary of the treated crust.

A variation of this test was also performed with plastered chunks of adobe. Rhoplex E-330 plaster made from adobe soil was used to coat untreated adobe. These pieces were then cut in half to expose the untreated brick with a  $\frac{1}{4}$  inch thick coat of E-330 plaster. These pieces were placed cut side down on the simulator. In three to four days the outer plaster crust cracked in long cracks and profuse salt crystal growth formed along the cracks. Even though the E-330 plaster will wet it did not grow salt crystals through the plaster itself. This was verified by placing chunks of dried E-330 plaster on the wet brick. No salt growth has occurred over a 3 month exposure period.

### Field Trials

Four field trials have been conducted. Two, a large one in Iran and a small one in Guatamala on adobe are still intact. A small one on adobe in Chaco Canyon has been backfilled. A small one on stone is still on exposure at Quirigua in Guatamala.

In Guatamala the two sections of mud and straw wall (about 1 inch thick) hung on a chicken wire fence are doing very well with no deterioration or visible change in six months of exposure to heavy summer rains. One of these sections was Rhoplex E-330 mud plaster, the other was water-mud plaster, dried and then sprayed with Acryloid A-21 toluene solution. A section of wall composed of salvaged mud bricks laid in ordinary water-mud mortar, then dried and subsequently sprayed with 3% Acryloid A-21 in toluene is also showing no deterioration during the six months of summer rains.

The field trial at Hasanlu Tepe in northwest Iran represents a major effort.

Darrel J. Butterbaugh

February 26, 1977

MUD BRICK CONSERVATION PROJECT

Interim Report No. 3  
Period Covered: June 1973-July 1976  
Date: September 1, 1976  
Author: Darrel J. Butterbaugh

Summary

Rhoplex emulsion spray treatment on adobe has produced specimens that have withstood outdoor exposure in Philadelphia for more than 46 months. Field trials at Chaco Canyon with spray on emulsion has shown significant protection for two years. However, these are primarily surface treatments and failure will occur within five years. Repeat treatment of adobe with an emulsion spray is not practical.

Rhoplex emulsion incorporated in mud mortar, mud plaster or mud bricks produces weather resistant specimens that have withstood more than 32 months exposure in Philadelphia and more than 14 months out door exposure in south Florida. This type of chemically modified clay has withstood more than 140 wet-freeze-thaw cycles. Field trials have been set up in Iran and in Guatemala on Rhoplex emulsion plaster and mud brick systems.

Fine particle size emulsions have been used to spray treat two marble statues in the Museum courtyard. They show good bonding action after 22 months exposure but are also exhibiting city soil pick-up. A harder polymer will probably solve this problem.

Anhydrous acrylic and methacrylic monomer systems have given polymerization in situ. Good specimens can be obtained in the laboratory. The system did not work well at Chaco Canyon. More success has been achieved with water soluble monomeric systems such as zinc acrylate which

is soaked into adobe or stone and subsequently polymerized in situ by an aqueous catalyst system. Marked protection to sandstone has been achieved.

Methacrylic solution polymers have proved to be quite effective in stabilizing adobe and friable sandstone. A dilute solution is essential. Two-four centimeters of penetration can be obtained. Resistance to water erosion, freezing and thawing and dry binding is achieved. Field trials in Iran and Guatemala have been established and outdoor exposures have been started in Philadelphia and south Florida.

Preliminary evidence from simulated ground water tests indicate that treatment with those solution polymers will prevent the salt encrustation problems of adobe and sandstone.

## DETAILS

Emulsion Spray Treatment

Earlier work had shown that a spray with Rhoplex emulsion E-330 would, after two coats, impart a resistance time of about 25 hours to a 1200 inch per hour simulated rain. Rhoplex 826, an ultra fine particle size emulsion, showed 30-35 hours of shower time. Adobe clods treated with the E-330 emulsion possessed an undesirable gloss while the small particle size emulsion was markedly reduced in gloss. On the other hand the E-826 resin was a softer variety that picked up significant city soil when white marble sculpture pieces were exposed to the Philadelphia winter climate.

Accordingly a special small particle size Rhoplex E-330 was prepared. Two designations, RR 2460 and RR 2464 were tested and compared with E-826 and E-330. In general the RR 2460 resin was superior to RR 2464. Two coats of RR 2460 on adobe clods gave shower times of 10-20 hours. Addition of 1% Triton X-100 to the emulsion to enhance the wettability was detrimental as adjudged by the shortened shower times.

A marble urn in the Museum courtyard was given two spray coats of a 9.9% concentration of emulsion RR 2460 containing 0.5% Triton X-100 as a wetting agent. This application was made in October of 1974. No significant gloss was imparted to the treated object and no coloration was observable. Two years later the marble grains are still bound tightly compared to a very sandy "rub off" condition in an adjacent untreated piece. The polymer is attracting some soil and since the polymer does not wear away the film is not self cleaning. Soap and water scrubbing of the surface removes about half of the built up soil without any apparent damage to the film.

A stone lion in the lower courtyard was given two spray coats of 10% Rhoplex E-826 in November, 1973. No significant gloss shows on the freshly sprayed piece. During the first winter significant city soil accumulated on the piece. Not much additional soiling has occurred since. Now, after almost three years of exposure, the grains are bound tightly with no rub off under vigorous brushing. A companion piece, untreated, shows extensive rub off. Soiling can be scrubbed off to a considerable extent with a simple soap and water brushing.

#### Methyl Methacrylate Monomer Treatment

Since the polymer emulsion particles were largely filtered out of suspension by the clay and stone surface grains, no deep penetration could be achieved with a spray on emulsion treatment. An alternate system was tried in which properly catalyzed methyl methacrylate monomer was soaked into the adobe or stone surface. Polymerization subsequently took place in situ giving thereby stabilization 1-2 inches deep.

The methacrylate (MMA) monomer penetrated adobe and soft sandstone very readily but did not soften the adobe as does water. No tendency to slump or run was encountered. It was necessary to heavily catalyze the monomer mixture to achieve rapid polymerization in the presence of soil. A catalyst formulation consisting of the following was used:

X970 (1, 3 Butylene Dimethacrylate)	5.25% of MMA used
N,N Dimethyl p-Toluidine	1.05% of MMA used
Benzoyl Peroxide (Lucidal 98)	2.1 % of MMA used

This mixture gave water-thin solutions that had a shelf life of about 15-20 minutes after which time polymerization set in, the solution heated rapidly and gel formation occurred. It was necessary to complete the treatment before

gel formation began otherwise an unsightly, glossy appearance was imparted to the treated specimen. Polymerization occurred within the specimen at room temperature but the use of slightly elevated temperatures was helpful. This was achieved by warming (50-60°C) the adobe or stone prior to treatment or bagging the specimen in plastic or foil after treatment and immersing it in a warm water bath for 1-2 hours. Of course in the field such as a desert location the daytime sun-warmed soil surfaces would be warm enough for rapid polymerization.

A monomer mixture of 20% butyl methacrylate and 80% methyl methacrylate gave a tougher and less brittle polymer than straight methyl methacrylate. This became the monomer mixture of choice.

Adobe absorbed about 10% of its weight of monomer mixture but only about 4% remained as polymer after polymerization. Chaco sandstone absorbed a comparable amount of monomer and retained about the same amount of polymer.

Properly treated specimens showed a slight darkening in color and no gloss. They wet with water very slowly. They could be soaked in water for days without softening. The surface was quite resistant to wet and dry rub resistance. The depth of stabilization was about 0.5-0.75 inches.

While this method worked reasonably well in the laboratory on small specimens it did not adapt well to field conditions. The peroxide was hazardous to handle in the hot desert. The monomers needed to be kept cool and the catalyzed solutions had only minutes of shelf life. The one test tried at Chaco Canyon was not successful because of damp soil from a previous unexpected heavy rain. Although several days of sunshine preceded the test the soil was still damp about 1/2 to 3/4 inch under the surface. This impeded the soaking in of the monomer solution. Another test area was set up in Chaco Canyon but unfortunately this had to be covered in a back-filling operation to preserve the rest of the site.

### Water Soluble Monomers

Another aspect of monomer treatment has involved the use of water soluble monomeric materials which in aqueous solution can be soaked into stone or adobe and then subsequently polymerized by soaking in a catalyst solution. Such materials as zinc, calcium, barium or magnesium acrylates have been tested.

The method in general involves making a 30% monomeric zinc acrylate solution by reacting the appropriate amounts of glacial acrylic acid, water and zinc oxides. After about one hour the clear 30% zinc acrylate solution can be decanted from a small amount of white powder (presumably zinc oxide). The solution is essentially neutral to litmus paper.

Adobe or stone chunks are next bathed with this 30% solution. Adobe becomes soft from the wetting thus necessitating careful handling and control of the rate of applications. Soft stone readily soaks up the aqueous zinc acrylate. After absorption is essentially complete the piece is allowed to dry for one to several days. The sample is next treated with an aqueous solution containing 4-5% ammonium persulfate and 4-5% sodium bisulfate. This converts the zinc acrylate to zinc polyacrylate, the reaction taking place both within the material and on the surface. The zinc polyacrylate is a water repelling, water insoluble binder that covers and cements the individual grains of soil and rock, producing thereby a surface that is mostly resistant to rainfall, freezing, thawing, wind erosion and ground water damage.

Chunks of adobe so treated can be subjected to 1200 inch per hour simulated rainfall for more than twenty hours with no erosion or break up. Water absorption is fairly rapid in the early stages of rainfall treatment but then the adobe chunk remains saturated but hard and firm to further wetting.

Hens egg chunks of Chaco Canyon sandstone treated with zinc polyacrylate show no effect of treatment but have withstood 290 wet freeze and

thaw cycles with no softening or deterioration. Untreated pieces of Chaco sandstone completely disintegrate after 15-20 freeze and thaw cycles.

One large loaf (bread size) of Chaco Canyon sandstone was given the zinc polyacrylate treatment and then subjected to a wet freeze and thaw cycling. Nothing happened for the first 125 cycles, then one small corner chipped off the block. An additional 12 cycles produced two serious 4-5 inch cracks spreading from the broken corner. These cracks revealed that a hard 1 cm. thick weather-resistant crust had formed on the block of stone. However, if a break should occur in the crust, water will penetrate and normal weathering will take place. This aspect of zinc polyacrylate treatment seems to preclude its use on soft, water sensitive materials.

Soft, underfired bricks treated with zinc polyacrylate are hard and non-flaking after more than 250 freeze and thaw cyclings. The outside surface remains very tight compared to a loose and readily chipping surface on an untreated sample.

Marble urns, exhibiting serious surface rub off, in the museum courtyard were treated with zinc polyacrylate. After one winter and spring of natural weathering, some rub off again occurs. Presumably the marble is too hard and dense a material to adapt to this type treatment.

Under some circumstances of catalyst concentration and type of surface being treated, a whitening of the surface may occur with polymerization. (The bulk zinc polyacrylate is a white substance). This whitening can be eliminated by wetting the treated surface with concentrated ammonium hydroxide. This temporarily produces a soluble or gel-like form of zinc polyacrylate which subsequently reverts to a glass-like translucent surface when the ammonia evaporates. Such treatment does not adversely affect the weathering property of treated stone or adobe.

Sandstone treated with zinc polyacrylate permits the passage of water through the rock (simulated ground water test) but the formation of salt growth and the loss of natural cementation is greatly retarded or eliminated completely.

Zinc acrylate appears to be unique in this performance on adobe and stone. Although polymers are formed with calcium, magnesium and barium acrylates, these materials do not give any appreciable protection to the adobe chunks under a 1200 inch simulated rainfall. Only zinc acrylate gives protection to soft sandstone under freeze and thaw situations.

#### Chemically Modified Mud

The use of polymer emulsions to incorporate into fresh mud to form plaster, grout or cast mud bricks has been investigated. Rhoplex E-330, which is a polymer specifically designed as a concrete additive has been the polymer of choice.

A north Florida sandy clay, used for ball diamonds and tennis courts, was sun dried and sieved through a screen (16 squares per inch). This sieved dry clay was mixed with various dilutions of Rhoplex E-330 to form a thick plaster-like mud (non-pourable) that could be paddled into molds or free piled cakes at least 2-3 inches thick. This mixture could be used to grout stone walls, plaster adobe or concrete brick walls as well as form large cast mud blocks. The ruins stabilization people at Chaco Canyon have used this kind of mud successfully on some ancient stone walls at Chaco. Ancient mud walls at Hasanlu Tepe in northwest Iran have been plastered, new mud brick walls have been erected at Hasanlu. And finally Rhoplex E-330 mud walls have been placed on test in the highland area of Guatemala. Rhoplex E-330 is compatible with all clays so far encountered. The more natural binding power of a given clay

the stronger will be the chemically modified clay.

With a 1 volume of Rhoplex E-330 (47% polymer solids) diluted with 3 volumes of water an E-330 mixture of 11.8% polymer is formed which is suitable for most applications. The dry Florida clay absorbed 40-45% of its weight of diluted E-330 emulsion to form a workable mud. This corresponds to a 5.1% polymer solids based on the dry weight of soil.

Emulsion dilutions of 2, 3, 4, 5 and 6 volumes of water to one of E-330 were used to prepare 3 x 3 x 0.5 inch cakes for rainfall tests and 2 x 2 x 0.5 inch cookies for freeze/thaw testing. A number of bricks, 8 x 8 x 4 inches were cast with a wooden mold. Drying in the shade for two days, followed by full Florida sunshine produced hard, well-formed bricks with no cracks. Mud bricks, 21 x 21 x 8 cm., were made by the hundreds in Iran with no cracking or other problems and dried faster than ordinary water mud bricks.

Simulated rainfall testing of E-330 modified mud is not a severe enough evaluation test. A 6.7% emulsion (1-6 dilution) produced a mud cake that broke up after 45 minutes under the shower. A 7.8% (1-5 dilution) cake lasted 90 minutes. A 9.4% (1-4 dilution) cake showed no deterioration after 4.0 hours even though the cake was wet and could be broken by strong finger pressure and bending.

Another method of testing consisted of immersing cakes in water for four days. The following observations were obtained:

15.7% emulsion (1-2 dilution)	-----	Firm and stiff -- no wet rub off
11.8% emulsion (1-3 dilution)	-----	Firm and stiff -- with wet rub off
9.4% emulsion (1-4 dilution)	-----	Soft -- easily wet rub off
7.8% emulsion (1-5 dilution)	-----	Too soft to handle
6.7% emulsion (1-6 dilution)	-----	Too soft to handle

A third method of testing involved wet-freeze-thaw evaluations. All samples were immersed in water for 1-2 minutes, drained and then placed in a freezer overnight. The next day they were removed from the freezer, thawed at room temperature (generally 3-4 hours standing at room temperature) and then again immersed and returned to the freezer. Evaluations and comparisons were made on air-dried samples after a given number of cycles (generally 10). The following results were obtained:

1-6 dilution ----- Fail on 3 cycles  
 1-5 dilution ----- Fail on 5 cycles  
 1-4 dilution ----- Fail on 7 cycles  
 1-3 dilution ----- Fail on 19 cycles  
 1-2 dilution ----- Fail on 42 cycles.

A 1 cm. thick mud plaster patch (1.5 x 3.0 inch) on a piece of concrete block subjected to the same freeze-thaw cycling showed failure after 22 cycles for a 1-3 dilution and no failure after 143 cycles for a 1-2 dilution. Adhesion of this chemically modified mud is excellent to brick or cement surfaces. It even sticks quite well to wood surfaces.

#### Emulsion "Mushed" Surface Treatment

An attempt to form a resin protective coat of soil and polymer on the surface of adobe blocks was largely unsuccessful. Use of 1-3 dilution emulsion and a brush on the surface of an adobe block or a Florida clay Cake, gave a surface "mush" of clay and emulsion that served essentially as a plaster made in place on the surface of the block. While this made-in-place plaster dried to a hard, slow-wetting crust about 1/4 to 1/2 inch thick, it did not give lasting protection to the simulated rainfall or to outdoor exposure at Florida Atlantic University.

### Solution Polymer Treatment

Previous attempts have been made to stabilize mud walls by treating with polymer solutions. One of the Park Service preferred treatments is a soaking with 5% mineral thinner solution of a silicone resin. This waterproofs the wall, but the grains of clay and soil are not bound together by the resin. Attempts to treat with a binding-type polymer have generally been done with relatively concentrated (10-20%) solution. Under these circumstances the polymer solution is viscous and the polymer does not get carried under the surface to any significant extent. As a result, the polymer sits on the surface as a hard, crusty mass of unattractive appearance.

Using dilute solutions (1-3%) of acrylic and methacrylic polymers as exemplified by the Rohm and Haas Co. Acryloids, a very low viscosity solution is obtained that penetrates adobe and dried mud structures of soft, friable stone materials readily. Being colorless, the polymers do not discolor or in any way change the appearance of the treated object. Also the organic solvents commonly used do not weaken the adobe surface such as water does, thus there is no tendency of the clay or soil to run or slump as the surface is saturated with solution.

Method of application is varied and simple. For horizontal surfaces, a coarse spray from a low air pressure sprayer, a paint brush or swab etc. can wet the surface. It is desirable to use a coarse spray to thoroughly wet or flood the surface so that the solution soaks in rather than evaporates on the surface.

While depth of penetration as determined by water repellency of the dried surface, is somewhat dependent on the material being treated, it was generally possible to achieve water repellency at 2-3 cm. under the surface. Solvent migration exceeded this depth but the clay seemed to filter out or

concentrate the polymer as the solution penetrated. Since no skin or film of polymer is formed on the surface, it is easy to retreat a structure merely by again wetting the surface with more polymer solution.

As previously stated, a dried, treated surface beads water and sheds water under the simulated rainfall test. Treated adobe chunks or clay cookies can be immersed in water for days without softening. Furthermore a binding of the dry surface grains of clay or soil is achieved. A semi quantitative method of testing involved a dry brushing with a small but stiff bristled nylon brush (twice the size of a tooth brush). Using the Florida clay cookies, which had very little natural binding, 100 strokes of the brush would remove 8.9 to 9.0 grams of clay. If these same cookies were treated with 0.4% Acryloid polymer solutions in toluene the brush off with 100 strokes was reduced to 0.05 to 0.25 grams.

Treatment efficiency was determined generally by simulated rainfall and by wet-freeze-thaw cycling. The latter method is about the only method severe enough to show failure on stone. No acid atmosphere testing has yet been done.

Most of the Acryloid polymers are dissolved in paint thinners, toluene, xylene or mixed solvents of this type. Since these are relatively expensive solvents and many times not available in remote parts of the world, an effort was made to find diluting solvents that could replace all or a significant part of the toluene. Kerosene, gasoline, fuel oil and xylene as well as acetone and some of the alcohols were tested. A mixture of 85% xylene and 15% acetone could be used in place of toluene for Acryloid A-21 and for the more soluble Acryloid B-67. Kerosene, gasoline or fuel oil was not a solvent for the A-21 polymer and was not a suitable solvent for B-67. Clay impregnated with kerosene solutions of B-67 were not bound at all well for water protection.

It is also interesting to note that even though Acryloid A-21 was readily soluble in acetone, such a solution was markedly ineffective in binding the clay or soil particles. In general rainfall times in excess of 50 hours could be achieved with toluene solutions of A-21 treated clay cookies. In contrast acetone solutions of A-21 produced rainfall times of only 15 minutes. Comparably toluene solutions of B-67 produced clay cookies that could resist more than 40 hours of simulated rainfall, while the same concentrations of B-67 in kerosene or gasoline gave rainfall times of 30-60 minutes. Thus it does not seem likely that we can substitute cheaper and more readily available solvents for toluene in these treatments.

A variety of polymers have been tested in toluene solutions. Some have been essentially hard methyl methacrylate polymers, others softer substituted methacrylate polymers, others copolymers and finally silicone water proofing resins. Acryloid A-21 in toluene seems to be the best overall polymer. It is effective in adobe at 1% concentration, but in the more severe freeze and thaw tests a 3% concentration seems to be best. At this concentration there is high penetration but still good dry and wet bonding and no tendency to gloss or otherwise change the visual appearance of the specimen. A second best and very good polymer is Acryloid B-67. This is a softer polymer and more soluble in toluene, an advantage when working in the field.

Simulated rainfall times of more than 50 hours could be achieved with chunks of adobe blocks and with Florida clay cookies. In contrast, a silicone resin at the 1% level gave only 0.5 hours of showering and gave practically no dry binding of the soil grains.

The following table gives the details of the various rainfall evaluations:

Simulated Rainfall Testing of Solvent Polymer Samples

Polymer	Clay	Dilution Solvent	Polymer Concentration (%)	Shower Time (hrs.)	Water Absorption (wt. %)
Acryloid A-21	Fla.	Toluene	0.30%	1:50	5.4%
Acryloid A-21	Fla.	Toluene	0.60%	23:45	6.9%
Acryloid A-21	Pa.	Toluene	0.60%	21:30 +	5.1%
Acryloid A-21	Tucson	Toluene	1.0 %	33:00 +	7.0%
Acryloid A-21	Tucson	Toluene	1.0 %	53:00 +	6.9%
Acryloid A-21	Tucson	Toluene	3.0 %	20:10 +	3.2%
Acryloid A-21	Tucson	Toluene	3.0 %	20:20 +	3.7%
Acryloid A-21	Fla.	15% Acetone 85% Xylene	1.0 %	10:30 +	8.1%
Acryloid A-21	Fla.	Acetone	1.0 %	0:15	----
Acryloid B-67	Fla.	Toluene	0.45%	1:00	6.8%
Acryloid B-67	Fla.	Toluene	0.90%	9:30	8.0%
Acryloid B-67	Fla.	Toluene	1.80%	43:15 +	6.7%
Acryloid B-67	Fla.	Gasoline	0.9 %	0:13	----
Acryloid B-67	Fla.	Gasoline	1.8 %	0:35	8.1%
Acryloid B-67	Fla.	Kerosene	0.9 %	1:00	5.4%
Acryloid B-67	Fla.	Kerosene	1.8 %	1:25	4.5%
Design Control*	Fla.	Toluene	1/200	0:03	----
Design Control	Fla.	Toluene	1/100	0:35	5.1%
Design Control	Fla.	Toluene	1/50	2:00	5.9%
Design Control	Fla.	Toluene	1/25	11:30 +	5.1%
Silicone	Fla.	Toluene	1.0 %	0:30	5.5%
Silicone	Fla.	Mineral Thinner	5.0 %	16:30 +	3.8%
Acryloid B 48 N	Fla.	Toluene	0.45%	0:45	6.0%
Acryloid B-82	Fla.	Toluene	0.40%	0:15	5.5%
Acryloid CU-10LU	Fla.	Toluene	0.40%	0:01	----
PVA (AYAF)	Fla.	Toluene	1.0 %	0:35	----
PVA (AYAF)	Fla.	Toluene	3.0 %	3:00	----
Polyvinylchloride**	Fla.	Acetone	1.0 %	13:30 +	----
Polyvinylchloride	Fla.	Acetone	3.0 %	20:15 +	6.1%

+ Discontinue without failure

\* Obtained from Design Control Inc. Westbury, N.Y.

\*\* Obtained from Dr. Dennis, U.S. National Park Service

While simulated rainfall gives a pretty good evaluation of treatment for adobe, it is of no value on treated sandstone or other friable rock-like materials. The wet-freeze-thaw cycling of treated samples gives a more severe test. Failure is determined subjectively when the rock or adobe chunk cracks, gets soft to finger nail scratching, or other such tests.

Two pieces of adobe were treated with 1 and 3% A-21 in toluene respectively and then subjected to wet-freeze-thaw cycling. After 12 cycles each piece of adobe was firm and showed no evidence of failure, but the 1% A-21 sample had absorbed 8.9% of its weight as moisture while the 3% A-21 sample had absorbed only 1.2% of its weight. On the 18 - 19th cycles the 1% A-21 failed by cracking and softening of the interior of the sample. On the 60th cycle the 3% A-21 sample began to break up. It should be remembered that an untreated sample of adobe could not survive a single immersion and freeze cycle.

A very useful application of the solution polymer treatment has evolved with adobe and modern plaster. As stated previously, adobe blocks if spray-treated with a 3% A-21 solution, will be resistant to heavy rain and weathering by freezing and thawing. If this block is now plastered with E-330 modified mud or even water mud, the adhesion to the A-21 stabilized adobe block or wall is much improved. If ordinary water mud is used as the plaster, a subsequent spray treatment of the dried plaster with an A-21 spray provides a doubly protected surface. Such a construction was prepared at Hasanlu.

Even a simpler technique has evolved whereby the adobe surface (if firm) can be plastered with a 1/4 to 1/2 inch coat of water mud, allowed to dry thoroughly and then spray-treated with a 3% toluene solution of Acryloid A-21. This construction has proved to be very resistant to weathering in Philadelphia this past winter, in Florida and in Guatemala. Under the simulated rainfall

tests such a construction shows no deterioration over a 49-hour period. Water absorption was 5.5%.

Acryloid A-21 has proved effective in preserving soft Chaco Canyon sandstone. A 1% solution will give significant protection, but for good wet-freeze-thaw performance a 3% solution is preferred. No change in color or appearance results from treatment of Chaco sandstone. Absorption of solution is about 7-8% of stone weight. Penetration as observed by a non-wetting border around a cut cross section of treated stone is at least 0.5 inches. Wet-freeze-thaw gives failure of the 2% A-21 sample after 178 cycles. The 3% A-21 sample shows no deterioration at this stage of cycling.

Samples of marble from the acropolis in Athens have been treated with 3% A-21 solution in toluene. While the exposed surface of these pieces of marble were pitted, the stone was still quite dense and tight. Sawed edges were hard with only a few minor flaws. Immersion of sawed pieces in A-21 solution showed only a few tiny streams of fine bubbles, indicating some slight absorption. This stone did not soak up a wet spot of A-21 placed on the surface. It would appear that absorption will be very slight and surface binding is not particularly required. Resistance to dilute acid such as  $\text{SO}_2$  in water is still to be tested. The surface reacted readily when a drop of dilute hydrochloric acid was placed upon it. Still further work is planned in protecting marble surfaces from atmospheric deterioration.

Finally, Acryloid A-21 solutions have been used to give weatherability to plaster of paris cast objects. Several pieces of plaster of paris cast objects have been soaked with 2% A-21 solution. Absorption was about 20-22% by weight. When dried, no appearance change had occurred. Outside weathering is showing a distinct advantage for the treated samples. This may make it possible to display plaster of paris art objects in outdoors locations.

### Groundwater simulation

An attempt has been made to devise a method of studying in the laboratory the adobe ground water and salt growth problem. A simple test method composed of a paper towel wick dipping into a distilled water source then spread across a flat glass plate with an electric fan blowing across the flat plate assembly seems to work quite well. The samples are placed on the wet wick resting on the glass plate, with the fan blowing, the moisture picked up by the samples is evaporated rapidly. Salt incrustation forms in 5-10 days on untreated adobe chunks and Chaco sandstone. If the wick is allowed to go dry the adobe chunk dries out and brittle flakes of salt and soil spall off in the breeze of the fan, much as does a dry salt incrustated adobe wall in the desert.

Chaco Canyon soft sandstone in addition to growing a salt crust loses much of its natural cementation during a 1-2 month exposure to the ground water simulator.

Adobe chunks treated with acryloid A-21 toluene solutions (1% and 3%) were cut in half to expose an inner core of 1 x 1.5 inch non treated adobe and an outer treated crust of about 0.75 inch thickness. The inner core was water wetting while the outer crust was non wetting. These chunks were placed cut side down on the paper wick so that the non treated inner cores would pick up water while the outer treated crust would repel liquid water but would still pass water vapor. The 1% A-21 sample began to crack after about 10-15 days exposure. No salt growth was observed. The 3% A-21 sample has shown no salt growth over eight months of exposure. One small crack developed through the 0.75 inch thick crust. Cutting the chunk vertically through the treated and untreated areas has shown no visible evidence of salt accumulation at the boundary of wetting and non wetting areas. Thus it would

appear that salt growth is not occurring at the inside boundary of the treated crust.

A variation of this test was also performed with plastered chunks of adobe. Rhoplex E-330 plaster was used to coat untreated adobe. These pieces were then cut in half to expose the untreated brick with a 1/4 inch thick coat of E-330 plaster. These pieces were placed cut side down on the simulator. In three to four days the outer plaster crust cracked in long cracks and profuse salt crystal growth formed along the cracks. Even though the E-330 plaster will wet it did not grow salt crystals through the plaster itself. This was verified by placing chunks of dried E-330 plaster on the wet brick. No salt growth has occurred over a 3 month exposure period.

Zinc polyacrylate treated Chaco sandstone has been put on exposure. Even though such a sample wets (less readily than untreated stone) no salt crusts have formed over an eight month period. No softening of the sandstone has occurred.

#### Philadelphia Museum Roof Exposures

As has been the earlier practice, those methods and procedures that have shown significant performance in the rainfall tests and in the freeze/thaw tests have been used to prepare larger specimens for Museum rooftop exposure. Periodic evaluation of these specimens is made. When 5-10% of the sample has eroded the specimen is classified a failure.

Two samples, Rhoplex E-330/silicone treated, are still performing after more than 46 months of exposure. However the E-330 film is now showing cracks and failure can be expected in the next few months.

Two samples of double coated Rhoplex E-330 survived for 41-46 months. Rhoplex E-330 in combination with F#325 (from Dr. Sultan of the

University of Arizona) has been on exposure for 32 months and is still performing.

Next to Rhoplex E-330, Rhoplex E-826 appears to be the best of the emulsion treatments. Some of these have lasted 18-20 months. Acryloid A-21 in toluene specimens have been on exposure for more than 10 months and are showing no signs of deterioration. An A-21 soaked water-mud plaster specimen is also looking good after more than 8 months of exposure.

Mud cakes made with Rhoplex E-330 and with Rhoplex E-826 have been on exposure for more than 32 months and are showing no signs of deterioration.

Details of these Museum roof exposure tests are given in the following table.

<u>ADOBE ROOF EXPOSURES</u>					
Number	Specimen Treatment	Start	Fail*	Months**	Remarks
1	Untreated adobe	10/72	2/73	4	muddy stain
2	5% silicone in Mineral thinner	10/72	9/75	35	total disintegration by 2/76
3-1	E-330-9.4%/E-330-9.4%	10/72	2/76	41	Erosion inside shell
3-2	E-330-9.4%/E-330-9.4%	10/72	7/76	46	Top crack; 10% erosion
4	E-330-9.4%/5%Silicone in Mineral thinner	10/72		46+	2-3%gone 7/76
5	E-330-9.4%/5% Silicone in Mineral thinner	10/72		46+	1-2% gone 7/76
6	E-863-16.0% one coat plus penetrant	10/72	7/73	9	
7	E-863-16%/E-863-16% plus penetrant	10/72	8/73	10	deep crack
8	E-863-16%/5%Silicone in Mineral thinner	10/72	8/73	10	deep crack
9	E-863-16%/E-863-8% plus penetrant	10/72	7/73	9	
10	E-863-16%/E-863-16% no penetrant	10/72	10/73	12	
11	E-330-9.4%/E-330-9.4%	11/73	9/75	22	
12	E-330-9.4%/E-330-9.4%/F#325	11/73	7/75	20	

\* 5-10% gone  
\*\* as of 7/76

13	E-826-16%/E-826-16%	11/73	7/75	20	
14	E-826-16%/5% Silicone in Mineral thinner	11/73	2/76	28	
15	E-863-16%/E-330-9.4%	11/73	12/74	13	
16	E-863-16%/E-863-16%	11/73	5/75	18	
17	E-863-16%/5% Silicone in Mineral thinner	11/73	3/75	16	
18	E-863-16%/E-863-16%/ 5% Silicone in Mineral thinner	11/73	3/75	16	
19	E-826-16%/E-330-9.4%	11/73	5/75	18	
20	E-826-2% soak/E-330-9.4%	11/73	10/74	11	
21	E-863-2% soak/E-863-16%/ E-863-16%	11/73	5/75	18	
22	E-826-16%/E-826-16%/ 5% Silicone in Mineral thinner	11/73	7/75	20	
23	E-330-9.4% + F#325 1/30 one coat	11/73	9/75	22	
24-1	E-330-9.4% + F#325 1/30/ E-330 -9.4% + F#325	11/73	7/76	32	5% gone
24-2	E-330 -9.4% + F#325 1/30/ E-330 -9.4% + F#325 1/30	11/73		32+	2% gone
25	E-826-10%/E-330-9.4% + F#325 1/30	11/73	3/75	16	
26	F#325 1/30 one coat	11/73	12/74	13	
27	Cake-E-330 7.8% on dry soil	11/73		32+	no change
30	Cake-E-330 3.15% on dry soil	11/73	6/74	7	gone
31	Cake-E-330 1.2% on dry soil	11/73	6/74	7	gone
32	Cake-E-863 6.0% on dry soil	11/73	6/74	7	gone
33	Cake-E-863 2.2% on dry soil	11/73	6/74	7	gone
34	Cake-E-863 1.0% on dry soil	11/73	6/74	7	gone
35	Cake-E-826 3.7% on dry soil	11/73		32+	no change
36	Cake-E-826 1.7% on dry soil	11/73		32+	no change
37	Cake-E-826 0.8% on dry soil	11/73	6/74	7	gone
40	RR 2460-13.3% + 0.5% T-X100 (one coat)	10/74	9/75	12	gone
41	RR 2460-13.% + 0.5% T-X100/ Ditto	10/74	7/75	10	
42	E-330-9.4% + 1.0% T-X100 (one coat)	10/74	5/75	8	10% gone
43	RR 2464-9.9% + 1.0% T-X100/ Ditto	10/74	5/75	8	80% gone
44	Sara Bond 9.4%/Sara Bond 9.4%	10/74	5/75	8	80% gone
45	MMA 80/BMA 20-(50-55°)temp- one treatment	10/74	7/75	10	10% gone
46	MMA/E-826-4.4% 2nd treat- ment	10/74		21+	
47	MMA 80/BMA 20-(50-55°)temp- one treatment	10/74	5/75	8	40% gone
48	Zn Polyacrylate/Zn Poly- acrylate	10/74	3/75	6	
49	Zn Polyacrylate/Zn Poly- acrylate	10/74	5/75	8	

50	Zn Polyacrylate/E-330-9.4%/ E-330-9.4%	10/74	5/75	8	
51	Zn-NH <sub>3</sub> -Acrylate	10/74	5/75	6	
52	Pecos Block-E-330 + o.5% T-X100/Ditto	10/74	7/6	21	30% gone
53	Pecos Block-Zn Polyacrylate	10/74	7/6	21	30% gone
54	Pecos Block-No treatment	10/74	5/75	8	
60-1	2% A-21 in toluene-Tucson Adobe	9/75		10+	no change
60-2	2% A-21 in Toluene-Tucson Adobe	9/75		10+	no change
61-1	1% A-21 in Toluene-Tucson Adobe	9/75	7/76	10	25% gone
61-2	1% A-21 in Toluene-Tucson Adobe	9/75	7/76	10	30% gone
65	E-330-6%/1-3 E-330 Plaster/ 1-3 E-330 Plaster	11/75	2/76	3	
66	Tucson Adobe/1-3 E-330 Plaster/ 1-3 E-330 Plaster		11/75	2/76	3
67	Pa. Adobe/1-3 E-330 Plaster/ 1-3 E-330 Plaster	11/75	2/76	3	
68	Pa. Adobe/H <sub>2</sub> O-Mud Plaster/ H <sub>2</sub> O-Mud Plaster/A-21	11/75		8+	no change
69	Tucson Adobe/3% A-21 in Toluene	11/75		8+	no change
70	Florida bricks (1-3 E-330)	11/75		8+	no change

#### Florida Atlantic University Exposures

A small exposure station has been established beside the Anthropology research building on the Florida Atlantic University campus at Boca Raton.

Rhoplex E-330 mud plaster (1 to 3 dilution) on concrete block surfaces has shown no deterioration in 14 months of exposure. Also large blocks (4"x8"x8") of E-330 modified mud have shown no deterioration in 14 months. There appears to be some mildew growth on the chemically modified clay products. There also is some mildew growth on the concrete pad upon which these samples rest.

Exposure of once plastered New Mexixo adobe blocks with an E-330 modified mud did not last for more than two months. A double coating with E-330 plaster extended the life by only one additional month. Precoating

the New Mexico adobe block with 6% Rhoplex E-330 emulsion prior to plastering with E-330 mud plaster gave a product that survived for 3-4 months but failed rapidly thereafter.

Soaking a New Mexico block with a 3% toluene solution of Acryloid A-21 has given a specimen that has been on exposure since February 1976. So far no significant changes have occurred. Such has also been the case with a water-mud plastered New Mexico adobe block that had been dried and then subsequently soaked with 3% Acryloid A-21 in toluene.

### Field Trials

Four field trials have been conducted during the report period. Two, a large one in Iran and a small one in Guatemala on adobe are still intact. A small one on adobe in Chaco Canyon has been back filled and a small one on stone is still on exposure at Quirigua in Guatemala.

The trial at Hasanlu in Iran involved some 1500 square feet of test surfaces. Both E-330 plastered and Acryloid-toluene soaked areas were treated. Rhoplex E-330 mud bricks were also laid in two large adobe wall sections. As of August 1976 most of the areas have survived a winter, spring and summer. The Acryloid A-21 seems to be somewhat better than the softer Acryloid B-67, as was predicted by laboratory tests. The Rhoplex E-330 plastered samples have held up better than expected. The seriously softened walls have not responded well to stabilization which indicates that protective measures should be taken as the walls are uncovered, not after they have weathered 6-10 years.

In Guatemala the two sections of mud and straw wall (about 1 inch thick) hung on a chicken wire fence are doing very well with no deterioration even under heavy summer rains. One of these sections was

E-330 mud plaster, the other was water-mud plaster, dried and then soaked with Acryloid A-21 toluene solution. A section of wall composed of salvaged mud bricks laid in ordinary water-mud mortar, then dried and subsequently sprayed with 3% A-21 in toluene is also standing up well in the heavy summer rains.

Several areas of stone at Quirigua were sprayed with Acryloid A-21 solution. No reports have been received on this test since it was established in late April.

#### Future Work

The search will continue for more efficient binders for adobe. A simpler solvent system, one more readily available in out of the way places in the world is needed. Also needed is a more extensive U.S. exposure test, one which will give a good field trial on ground water control.

On stone the work will be concentrated on methods of protecting marble and limestone structures and statuary. Particular attention is to be given to the effect of acid gas ( $\text{SO}_2$  and water vapor) atmospheres on treated stone samples. More effective binders for soft friable sandstone is needed and we need a faster and better test method than wet-freeze-thaw on treated stone.

