# CONSOLIDATION OF STONE OBJECTS WITH EXPOXY RESINS

## INTRODUCTION

The process involved in the ageing of stone objects are well known and of course may be chemical, physical or biological in nature. A knowledge of the general process or processes bringing about deterioration is essential as it provides the basis for the overall remedial measures to be taken for the preservation of stone objects.

The remedial measures are usually undertaken with the object not only of stopping the deterioration but also of improving the physical state of the object as well. Most of the preservation and consolidation techniques used in the past have been based on the filling of the surface pores by brushing, spraying, or sometimes injecting the object with solutions that fill the pores by simple evaporation of the solvent or by the formation of new chemical compounds. For the surface impregnation of stone objects, solutions of fluorosilicases, hydrafluoric acid, soluble gass, calcium hydroxide, barium hydroxide, organo-silicon compounds, waxes, casein, and thermoplastics have been most commonly used. Even though many of these substances have low viscosity, the depth of penetration may be very small even when nearly complete saturation is achieved. With the soluble preservatives, the migration of solutes to the outer layers as evaporation of the solvent takes place serves to concentrate the pore filling substances near the surface. With substances that form new compounds by reacting with the stone, the compounds generally tend to concentrate in the surface pores as well and thus inhibit penetration of the solution. The surface layer formed as a result of either of the two processes acts in very much the same way as the surface layer formed during normal ageing with the result that disintegration, cracking and the formation of cavities may take place under the surface skin.

Epoxy resins solidify as a result of polymerization process produced by the action of hardening agents. The solidification process with epoxy resins does not depend on the evaporation of solvent nor on the formation of new compounds by reaction with the components of the stone. These resins, therefore, offer the possibility of solidifying stone objects without the formation of surface layers or " skins ". This study was undertaken with the object of evaluating and developing techniques for using epoxy resins for the stabilization of stone objects. In this study four Polish made resins were used and they had the following epoxy counts :

Epidian 1 : 0,16 - 0,2
2 : 0,12 - 0,3
3 : 0,32 - 0,43
4 : 0,42 - 0,45
5 : 0,48 - 0,52

Two siliceous sandstones, Nietsuliko and Zerkowice, and two soft limestones, Welcz and Pinczow, were the materials employed for testing the effect of resin impregnation and their properties are given in table I. Studies of the following factors were undertaken :

1. properties of the epoxy solutions;
2. techniques for impregnation of the stones;
3. effect of the resins on the properties of the impregnated stones.

TABLE PROPERTIES OF THE INVESTIGATED STONES

| Stone | Bulk density g/cm³ | Open porosity % | Imbibition in water % | Resistance to pressure of a 5 × 5 × 5 cm sample kg/cm² | Resistance to water (1) kg/cm² | Resistance to frost (2) kg/cm² |
|---|---|---|---|---|---|---|
| Sandstone " Nietulisko | 1.78 | 21.6 | 12.1 | 149 | 161 | 148 |
| Sandstone " Żerkowice " | 1.97 | 14.3 | 7.6 | 373 | 336 | 234 |
| Limestone " Welcz " | 1.62 | 27.9 | 17.4 | 98 | 56 | 62 |
| Limestone " Pińczów | 1.64 | 30.3 | 19.7 | 110 | 52 | |

(1) Resistance to pressure after 48 hours of saturating a stone with water.
(2) Resistance to pressure after freezing and defrosting a stone.

## PROPERTIES FOR RESIN SOLUTIONS

A number of studies were made of the properties of resin solutions to determine the effect of resin concentration, kind of solvent, and hardeners on the viscosity, hardening rate, and other characteristics of the solutions. It is not the purpose of this section to provide a detailed tabulation of these properties but rather to illustrate the principles involved in preparing and using resin solutions for the preservation of stones (Table 2-5).

In the first experiment, the viscosity of the resin solutions was measured by the rate of outflow from a viscometer. The viscosity of the 10 % solutions increased only slightly with time but the rate of increase of viscosity was greater for the 20 % solution than for the solutions containing 10 % resin. The marked increase in viscosity of the 20 % solutions was observed to be due to gelation resulting from the high resin concentration (Table 3).

The effect of solvent composition on the hardening time of resin preparations is illustrated by the data in Table 5 for Epidian 5 resin with 18 % TETA as hardener. In this and other experiments the degree of hardening was measured by determining the solvent content of wood resin mass formed after 3 days in closed containers where there was essentially no evaporation. With xylene, toluene, benzene, cyclohexane, methyl ethyl ketone, and ethylene glycol ether as solvents, there was no detectable hardening of the resin (Table 4).

TABLE 2. - LIMITING RATIOS OF TOLUENE TO METHANOL IN COMPOSITION USED AS SOLVENTS FOR THE EPOXY RESINS

| Resin | Resin : Toluene | Toluene : Methano |
|---|---|---|
| Epidian 1 | | Independently of toluene : resin 1 : 2,5 |
| Epidian 2 | | |
| Epidian 3 | 0,33 | |
| | 0,66 | 1 |
| | 1,33 | ∞ |
| Epidian 4 | 0,5 | |
| | 0,75 | 7 |
| | | ∞ |
| Epidian 5 | 0,25 | 12 |
| | 0,5 | ∞ |

TABLE INCREASE OF THE VISCOSITY OF SOLUTIONS AS A FUNCTION OF TIME OF HARDENING

Solvent: Toluene + Butanol (1 : 2)
Hardner: TETA

| Resin | Concentration of solution % | Time of hardening of a resin in hours | | | | | | Maximal increase of time of outflow of a solution from the viscosimeter in % |
|---|---|---|---|---|---|---|---|---|
| | | Time of outflow of a solution from the viscometer in sec. | | | | | | |
| Epidian | | | | | 55.1 | 56.9 | | |
| | | 61.0 | | | 71.2 | | | 43 |
| Epidian | | 48.2 | 50.2 | 51.8 | 52.3 | | 58.2 | |
| | | 52.8 | | | 64.8 | | 108.5 | 106 |

By adding an alcohol (propanol) to a hydrocarbon solvent like benzene, the hardening time was decreased and the degree of hardening in the 3 days period increased as the proportion of alcohol was increased. The ratios of alcohol to aromatic solvents are limited. The maximal ammounts of alcohol (methanol) which may be added to the toluen solution of resin are presented in Table 2.

As shown by the data in Table 5, the degree of hardening decreased with decreasing molecular weight of the resin. The effect of molecular weight was somewhat greater in toluene than in benzene. The rate of hardening increased rapidly as the concentration of the resin was increased (Table 6). Even though attempts were made to counteract the effect of resin concentration by changing the toluene-methanol ratio (Table 7), the hardening rate still increased with resin concentration. The same general factors which affected the rate of hardening also affected the rate of precipitation and gelation (Table 8). It can be seen that the time for initiation of precipitation increased as the proportion of methanol was increased. On the other hand, the rate of precipitation increased with resin concentration.

Temperature also affected the rate of hardening of resins and, as is the case with chemical reactions, an approximately two fold increase in rate of hardening was observed for each 10° C rise in temperature. The data in Table 9 are interesting as they show that the presence of water has little effect on the hardening of Epidian 1 resin. The similar results were in our studies

TABLE 4. - THE INFLUENCE OF SOLVENTS ON THE CONTENT OF SOLUBLE FRACTIONS OF EPOXY RESIN IN A SOLUTION

Concentration of solution: 10 %
Temperature of hardening: 17-18° C
Time of hardening: 3 days

| Resin | Quantity of TETA in % | Solvent | Content of soluble fractions in % |
|---|---|---|---|
| Epidian 5 | 18.0 | xylene + propanol / 20 : 1 / | ∞ |
| | | xylene + propanol / 1 : 8 / | 14.8 |
| | | xylene + propanol / 1 : 6 / | 16.9 |
| | | xylene + propanol / 1 : 4 / | 19.4 |
| | | xylene + propanol / 1 : 2 / | 29.9 |
| | | xyl. + prop. + benzine / 1 : 2 : 1 / | 18.0 |
| | | xyl. + prop. + benz. / 1 ; 5 : 1,5 : 1 / | 19.2 |
| | | xyl. + prop. + benzine / 2 : 1 : 1 / | 25.7 |
| | | xylene | ∞ |
| | | benzene | ∞ |
| | | toluene | ∞ |
| | | cyclohexanen | ∞ |
| | | dioxane | ∞ |
| | | ethylene-glycol-ether | ∞ |
| | | acetone | ∞ |
| | | methylethyl keton | ∞ |

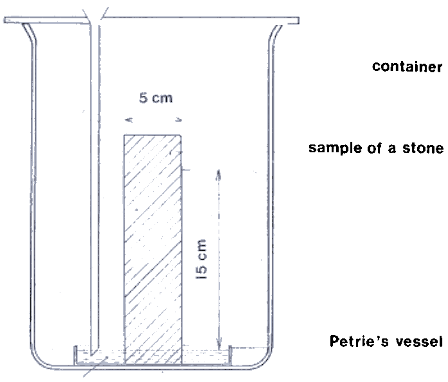


Fig. 1. — The capillary saturation of a stone via the whole cross-section of a sample (vertical displacement).

TABLE 5. - THE INFLUENCE OF A KIND OF EPOXY RESIN ON THE CONTENT OF SOLUBLE FRACTIONS IN SOLUTIONS AFTER 3 DAYS

| Resin | Quantity of TETA in % | Solvent | Content of soluble fractions in a solution in % | Increase of the content of soluble fractions in % |
|---|---|---|---|---|
| Epidian 1 | 7,2 | benzene | 26,0 | |
| Epidian 2 | 10,8 | benzene | 30,2 | 16,1 |
| Epidian 3 | 14,4 | benzene | 31,8 | 22,3 |
| Epidian 4 | 16,2 | benzene | 34,0 | 30,7 |
| Epidian 5 | 18,0 | benzene | 37,1 | 42,7 |
| Epidian 1 | 7,2 | toluene | 20,7 | |
| Epidian 2 | 10,8 | toluene | 26,9 | 30,0 |
| Epidian 3 | 14,4 | toluene | 30,4 | 46,8 |
| Epidian 4 | 16,2 | toluene | 31,3 | 51,2 |
| Epidian 5 | 18,0 | toluene | 34,4 | 66,1 |

**TABLE 6. - THE INFLUENCE OF THE CONCENTRATION OF EPOXY RESIN ON THE CONTENT OF SOLUBLE FRACTIONS IN A SOLUTION**

**Temperature of hardening: 30° C**
**Time of hardening: 2 days**
**TETA: Epidian 1 - 6 %**

| Concentration of solution % | Epidian 1 in xylene + propanol (1 : 1) | | |
|---|---|---|---|
| | Content of soluble in fractions in solution % | Decrease of the content of soluble fractions % | The amount of soluble fractions in solution % |
| 5 | 60.1 | | 3.00 |
| 10 | 45.7 | 23.7 | 4.57 |
| 20 | 35.2 | 38.7 | 7.04 |

**TABLE 7. - THE CONTENT OF SOLUBLE FRACTIONS IN SOLUTIONS AS A FUNCTION OF THE HARDENING TIME AND RESIN CONCENTRATION**

**Resin: Epidian 4**
**Concentration of TETA: 16 %**
**Temperature of hardening: 18-20° C**

| Concentration of solution % | Toluene : Methanol | Time of hardening in days | Content of soluble fraction in a solution % | The decrease of solubility % |
|---|---|---|---|---|
| 2,5 | 1 : 26 | 2 | 63.1 | |
| | | 3 | 51.0 | 19.2 |
| | | 5 | 40.9 | 35.2 |
| | | 9 | 26.3 | 58.3 |
| 5 | 1 : 12 | 2 | 37.0 | |
| | | 3 | 30.3 | 18.1 |
| | | 5 | 21.7 | 41.3 |
| | | 9 | 15.7 | 57.6 |
| 10 | 1 : 6 | 2 | 21.7 | |
| | | 3 | 18.1 | 16.6 |
| | | 5 | 14.0 | 32.5 |
| | | 9 | 7.6 | 65.0 |
| 20 | 1 : 3 | 2 | 12.1 | |
| | | 3 | 8.0 | 33.9 |
| | | 5 | 5.5 | 54.5 |
| | | 9 | 6.3 | 46.7 |

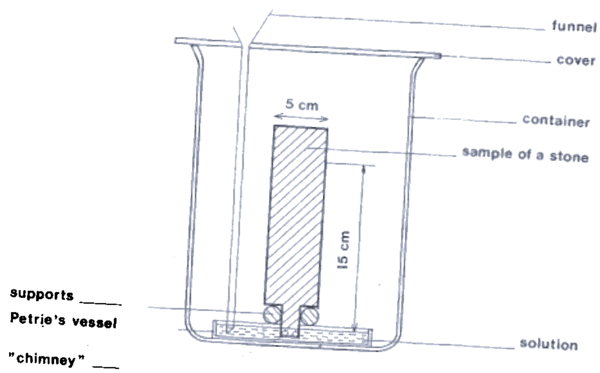


Fig. 2. — The capillary saturation of a stone via a "chimney" (vertical displacement).

TABLE 8. THE INFLUENCE OF RELATIVE TOLUENE TO METHANOL CONTENT ON THE RATE OF HARDENING OF AN EPOXY RESIN IN A SOLUTION

Resin: Epidian 4
Content of TETA: 16 %

Content of Versamid: 50 %
Temperature of hardening: 20-22° C

| Concentration of a solution % | Toluene / Methanol | *TETA* | | *VERSAMID* | |
|---|---|---|---|---|---|
| | | Time after which the precipitation of a resin starts hrs | The increase of the time of hardening % | Time after which the precipitation of a resin starts hrs | The increase of the time of hardening % |
| 5 | 12 | | | 5 | |
| | 1:8 | 6 1/2 | | 9 | 80 |
| | 1:4 | 15 | 131 | 19 | 280 |
| | 3 | 20 | 208 | 33 | 560 |
| | 2 | 39 | 500 | 77 | 1440 |
| | 6 | | | 7 1/2 | |
| | 5 | 6 1/2 | | 9 | 20 |
| | | 8 | 23 | 13 | 73 |
| | | 10 1/2 | 62 | 19 | 153 |
| | | 20 | 208 | 34 | 352 |
| | | 36 | 454 | | |
| 20 | | | | 10 | 80 |
| | | 9 1/2 | 58 | 18 | 80 |
| | | 14 1/2 | 142 | 33 | 230 |
| | | | 200 | 40 | 300 |
| 30 | | | | | |
| | | 12 | 33 | 16 | |
| | | | | 24 | 50 |
| | toluene | 15 | 67 | 26 | 63 |

obtained with the other epoxy resins. The data demonstrate that it is possible to impregnate damp stones. These experiments illustrate primarily how the viscosity and hardening rate of resin solutions may be controlled within limits by changing the resin concentration, the kind of solvent, and the temperature. Controlling these properties can be of considerable importance as a means of assuring adequate penetration of stone objects with epoxy resin solutions because of course, it is necessary to achieve as uniform saturation as possible.

Aside from controlling the hardening rate and viscosity it should be pointed out that it is also necessary to maintain the content of soluble fractions at as low a value as possible. If the soluble fractions are too high, solvent may migrate away from the surface and so bring about the sealing of the surface pores.

TABLE 9. - THE INFLUENCE OF THE QUANTITY OF WATER ON THE CONTENT OF SOLUBLE FRACTIONS OF EPOXY RESIN

Resin: Epidian 1
Solvent: Xylene + Propanol (1 : 2)
Concentration of solution: 10 %
Temperature of hardening: 30° C
Time of hardening: 3 days
TETA: 6 %

| Water : resin % | Content of soluble fractions in a solution % | Increase of the content of soluble fractions % |
|---|---|---|
| | 20.2 | |
| 25 | 22.6 | 11.9 |
| 50 | 24.6 | 21.8 |
| 100 | 27.1 | 34.2 |

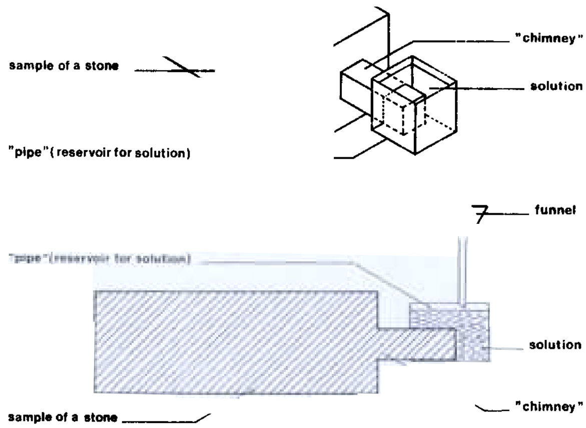


Fig. 3. — The capillary saturation of a stone by means of a " pipe " (horizontal displacement).

TABLE 10. THE INFLUENCE OF THE CONCENTRATION OF SOLUTIONS ON THE RATE CAPILLARY RISE IN STONES

Resin: Epidian 4 Solvent: Toluene + Methanol (1 : 2)

| | Concentration of solution % | Height of rise of a solution, cm: 2.5 | 5.0 | 7.5 | 10.0 | 12.5 | 15.0 | The increase of a time of rise % |
|---|---|---|---|---|---|---|---|---|
| | | Time of rise of a solution, min | | | | | | |
| Nietulisko | 2.5 | 0.5 | 1 | 4 | 8 | 14 | 23 | 9 |
| | 5.0 | 0.5 | 1.5 | 3.5 | 9 | 15 | 24 | 14 |
| | 7.5 | — | 3 | 6 | 10 | 17 | 27 | 28 |
| | 10.0 | 1 | 3 | 6.5 | 12 | 21 | 31 | 48 |
| | 15.0 | 1 | 2.5 | 6.5 | 12,5 | 22 | 34 | 62 |
| | 20.0 | 1 | 3 | 9 | 18 | 30 | 48 | 128 |
| | 30.0 | — | 5 | 14 | 27 | 47 | 75 | 257 |
| Żerkowice | 2.5 | 1 | 6 | 12 | 23 | 41 | 71 | 20 |
| | 5.0 | 2 | 6 | 13 | 26 | 44 | 68 | 15 |
| | 7.5 | 2 | 5 | 11 | 24 | 41 | 70 | 18 |
| | 10.0 | 2 | 7 | 15 | 30 | 54 | 89 | 51 |
| | 15.0 | 2 | 8 | 18 | 34 | — | 100 | 70 |
| | 20.0 | 3 | 11 | 26 | 50 | 84 | 135 | 129 |
| | 30.0 | 4 | 15 | 35 | 68 | 120 | 190 | 222 |
| | 2.5 | 12 | 45 | 84 | 162 | 254 | 358 | — |
| | 5.0 | 15 | 51 | 102 | 177 | 273 | 383 | 6 |
| | 10.0 | 13 | 46 | 98 | 182 | 288 | 420 | 16 |
| | 15.0 | 20 | 72 | 147 | 247 | 371 | 584 | 62 |
| | 20.0 | 21 | 88 | 186 | 313 | 485 | 742 | 106 |
| Pińczów | 5.0 | 15 | 50 | 97 | 165 | 259 | 365 | 22 |
| | 10.0 | 19 | 61 | 130 | 215 | 325 | — | 55 |
| | 20.0 | 33 | 116 | 235 | 397 | 565 | — | 170 |

## CAPILLARY RISE OF RESIN SOLUTIONS

It is clear from the studies of the last section that solvents composed of a mixture of a hydrocarbon and an alcohol served to delay hardening and to reduce the content of soluble constituents. After a number of preliminary experiments it was found that a mixture of approximately equal parts of toluene and methanol gave a solvent that exhibited as rapid capillary rise as did most of the organic solvents studied (Table 10). In addition to this, however, the volatility of methanol and toluene are approximately equal so that they evaporate at close to the same rate thereby ensuring a relatively constant solvent composition. A mixture of toluene and methanol was used as solvent in the remainder of the experiments.

The rate of capillary rise was more rapid in the more porous sandstones than the limestone samples. The rate of capillary rise decreased as the resin concentration increased reflecting the increased of viscosity. Using the data in the table, it was possible to relate the time of capillary rise, to the height of rise, by the relation

$$x = y\,(h - 6),$$

where y is the time required to reach a height of 5 cm. It was also possible to derive a simple linear relation between the time of rise A and the resin concentration c (in percent)

$$A = y\,(h - 6)\,(0{,}13\,c - 0{,}3)$$

where y and h have the same meaning as above. By means of these formular, it should be possible to estimate the time required to impregnate stone objects. It should be noted that the rate of capillary, rise depended on the kind of resin used because a solution of a less viscous liquid resin like Epidian 5 mounted the stones faster than more viscous solid resins like Epidian 1 or 2. Observations indicated that the rate of capillary rise was not affected by the orientation of the strata. Increasing the temperature 10° C only increased the rate of rise by 7 - 10 % because both the viscosity and surface tension were decreased at the higher temperature.
To study the effect of absorptive area on the rate of capillary saturation of stone chimneys were constructed (Figure 1) to reduce the area of absorption. As the

TABLE 11. THE INFLUENCE OF THE ABSORBING SURFACE AREA ON THE RATE OF CAPILLARY SATURATION OF STONES

Resin: Epidian 4 — Solvent: Toluene + Methanol (1 : 2)

| N° | Stone | Concentration solution % | Cross-section area of ample (b) | Cross-section area of a "chimney" (a) cm | a : b cm | Height of capillary rise in cm / Time of mounting, min: 2,5 | 5 | 7,5 | 10 | 12,5 | 15 | The increase of time of mounting over the same time for samples with no "chimneys" % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Nietulisko | 5 | 25,92 | "without chimney' | | 0,5 | 1,5 | 3,5 | 9 | 15 | 24 | |
| 2 | | | 25,86 | 3,96 | 1 : 6,5 | 4 | 9 | 17 | 23 | 39 | 48 | 100 |
| 3 | | | 27,01 | 2,24 | 1 : 13,1 | 5 | 12 | 21 | 31 | 45 | 59 | 146 |
| 4 | | | 26,80 | 0,99 | 1 : 27,1 | 8 | 19 | 32 | 49 | 66 | 88 | 266 |
| 5 | | 10 | 28,03 | "without chimney' | | 1 | 3 | 6,5 | 12 | — | 31 | |
| 6 | | | 28,04 | 3,94 | 1 : 7,2 | 5 | 10 | 19 | 30 | 45 | 64 | 106 |
| 7 | | | 27,03 | 2,13 | 1 : 12,7 | 6 | 15 | 27 | 41 | 59 | 78 | 152 |
| 8 | | | 26,30 | 0,95 | 1 : 27,7 | 9 | 22 | 39 | 60 | 86 | 117 | 277 |
| 9 | | 20 | 26,70 | "without chimney' | | | 3 | 9 | 18 | 30 | 48 | |
| 10 | | | 25,98 | 3,82 | 1 : 6,8 | | 18 | 31 | 50 | 74 | 100 | 104 |
| 11 | | | 27,83 | 2,15 | 1 : 13 | 10 | 23 | 42 | 64 | 94 | 125 | 160 |
| 12 | | | 27,42 | 1,07 | 1 : 25,6 | 17 | 38 | 57 | — | 140 | 182 | 279 |
| 13 | Welcz | 5 | 25,81 | "without chimney' | | 15 | 51 | 102 | 177 | 273 | 383 | |
| 14 | | | 25,76 | 3,88 | 1 : 6,6 | 100 | 210 | 340 | 480 | 630 | 780 | 104 |
| 15 | | | 27,22 | 2,03 | 1 : 13,4 | 120 | 240 | 380 | 540 | 740 | 910 | 138 |
| 16 | | | 26,34 | 0,99 | 1 : 26,6 | 155 | 300 | 480 | 690 | 900 | 1440 | 276 |
| 17 | | 10 | 27,40 | "without chimney' | | 13 | 46 | 98 | 182 | 288 | 420 | — |
| 18 | | | 26,44 | 3,63 | 1 : 7,3 | 120 | 250 | 370 | 550 | 780 | 910 | 110 |

TABLE 12. — THE RATE OF MOUNTING OF SOLUTIONS OF EPOXY RESINS IN IMPREGNATED STONES

a) Stones impregnated once by means of 10 % solution of epidian 4 + 16 % TETA
solvent: Toluene + Methanol (1 : 2)

b) Second impregnation: resin epidian 4
solvent: Toluene + Methanol (1 : 2)

| Height of capillary rise of solution cm | Solution 5 % | Solution 10 % | | | | Solution 20 % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nietulisko | Nietulisko | Żerkowice | Welcz | Pińczów | Nietulisko | Żerkowice | Welcz | Pińczów |
| | Time of mounting of solutions, min | | | | | | | | |
| 2.5 | | | 3.5 | 32 | 26 | 2 | 4 | 46 | 33 |
| 5.0 | 3 | 4 | 11 | 66 | 82 | 5 | 14 | 138 | 113 |
| 7.5 | 7 | 8 | 22 | 187 | 156 | 13 | 35 | 269 | 225 |
| 10.0 | 12 | 15 | 45 | 306 | 270 | 23 | 57 | | |
| 12.5 | 20 | 26 | 70 | 457 | 394 | 43 | 99 | 637 | 555 |
| 15.0 | 32 | 43 | 110 | | 598 | 69 | 154 | | |
| Increase of time with respect to samples from table 11 | 33.3 % | 38.7 % | 23.6 % | 58.6 % | 21.2 % | 43.7 % | 14.0 % | 31.3 % | |

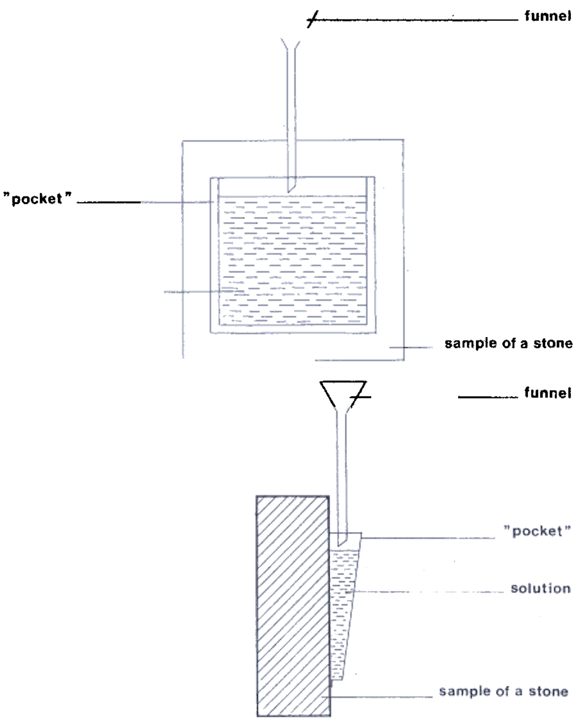


Fig. 4. — The capillary saturation of a stone by means of a "pocket" (horizontal displacement).

TABLE 13. - THE INFLUENCE OF THE ABSORBING SURFACE AREA ON THE RATE OF TOTAL SATURATION OF STONE SAMPLE (20 × 20 × 5 cm) with water

| Sucking surface | Sucking surface total frontal surface | Time of soaking through the whole sample min | Time of saturation of the whole sample min | Increase of the time of saturation % |
|---|---|---|---|---|
| 18 × 18 | 1 : 1.23 | | | |
| 16 × 16 | 1 : 1.56 | 2 | 4 | 33 |
| 10 × 10 | 1 : 4.00 | 2 | 7 | 133 |
| 4 × 4 | 1 : 25.00 | 4 | 28 | 833 |
| 2 × 2 | 1 : 100.00 | | 75 | 2400 |

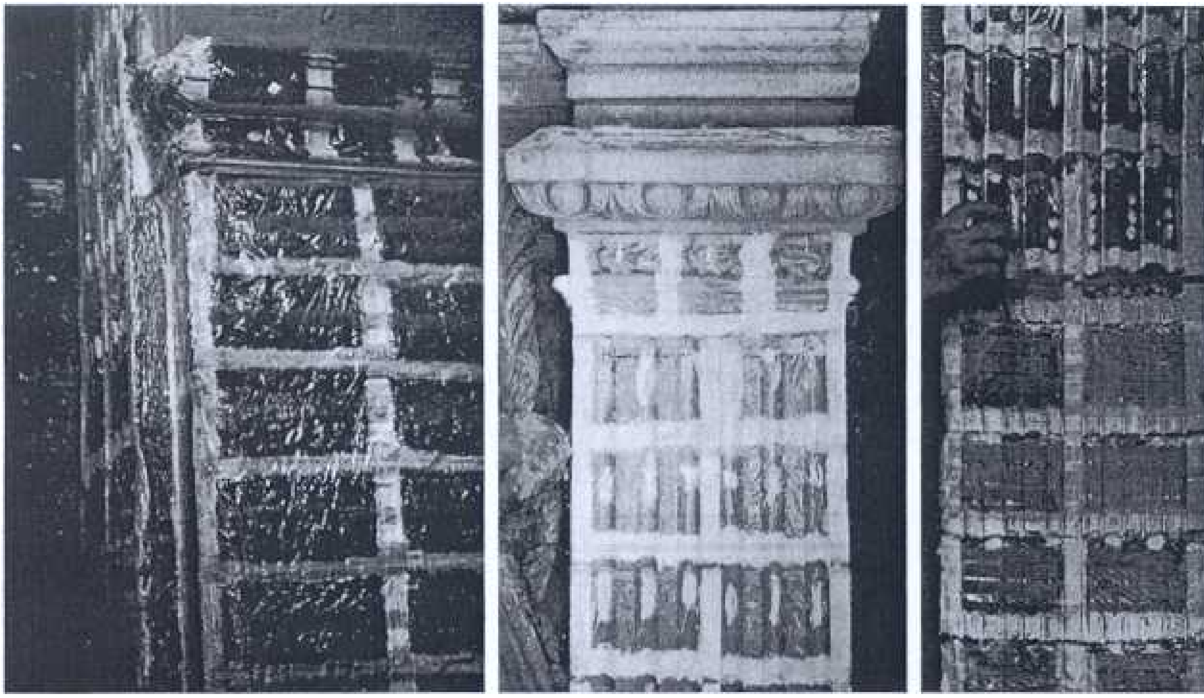

Fig. 5. — Application of the method on a

area of absorption (a) was reduced (Table 11), the rate of capillary rise, for heights of 15 cm or less, decreased. From the reported data it was possible to derive the relation between the relative increase, y, of the rate of capillary rise and the ratio of the sample cross sectionnal area to that of the chimney, x, as follows,

$$y = 8{,}5\ x - 46$$

From this equation it is possible to calculate the approximate time necessary to wet a stone to a given distance above any wetting surface. If the time of rise up to a height of 15 cm for a whole unrestricted surface is " d " then for a restricted imbibing surface the time of rise (e) to a height of 15 cm is given by the relation

$$e = \frac{d\ (8{,}5\ x - 146)}{100}$$

where x has been defined previously.

Other observations indicated that the factors affecting vertical capillary rise also control the horizontal movement of liquids. When the distance from the imbibing surface becomes appreciable, however, the rate of lateral capillary translocation is more rapid than the vertical because there is no gravitational force to reduce the rate of movement.

Up to about 8 hours, hardners were observed to have little effect on capillary flow. Once the hardening process started, however, the capillary flow became slower as the viscosity decreased. As a result, the time of utilization of resin solutions cannot be extended to any significant extent by reducing the content of hardener. Stone objects that have once been impregnated can be readily reimpregnated. The capillary rise of resin solutions in treated stones is, however, 20 to 40 % lower than in untreated materials (Table 12).

As the time of saturation of stone objects depended markedly on the absorbing surface especially if the depth of penetration is 5-15 cm (Table 13), the time for impregnation could be reduced by the use of « pockets » as illustrated in fig. 5. Pockets such as these were particularly useful for assuring adequate penetration of vertical surfaces. The rate of saturation with pockets increased, of course, with the number of pockets.

The studies on capillary rise of resin solutions in stones show that this is a propertie that can also be controlled by simple adjustment of solvent composition and resin concentration.

TABLE 14. - THE INFLUENCE OF IMPREGNATION WITH 20 % SOLUTION OF A RESIN ON THE CHANGE IN PROPERTIES OF STONES

Resin : Epidian 4
Solvent : Toluene + Methanol (1 : 2)
Impregnation time : 1 to 3.5 months

| Stone | % Increase of | | | Decrease of imbibition in water % |
|---|---|---|---|---|
| | Resistance to pressure | Resistance to water | Resistance to frost | |
| Welcz " 45 | 192 | 300 | 335 | 88 |
| " Nietulisko " 55 | 228 | 103 | 166 | 79 |
| Żerkowice " 55 | 72 | 68 | 90 | 82 |

TABLE 15. THE INFLUENCE OF THE CONCENTRATION OF EPOXY RESIN SOLUTION ON THE PROPERTIES OF IMPREGNATED STONES

Resin : Epidian 4 Solvent : Toluene Methanol (1 : 2)

| Stone | Concentration of solution % | $R_1$ kg/cm² | Increase of $R_1$ due to impregnation % | $R_2$ kg/cm² | Increase of $R_2$ due to impregnation % | Decrease of resistance relative to dry samples % | $R_3$ kg/cm² | Increase of $R_3$ due to impregnation % |
|---|---|---|---|---|---|---|---|---|
| Welcz " | no treat | 98 | — | 56 | — | 42.8 | 62 | |
| | 5 | 169 | 72 | 99 | 77 | 31.4 | 119 | 92 |
| | 10 | 189 | 93 | 127 | 127 | 32.8 | 147 | 137 |
| | 20 | 286 | 192 | 224 | 300 | 21.7 | 219 | 253 |
| | 30 | 349 | 256 | 262 | 332 | 24.9 | 317 | 411 |
| " Nietu-lisko " | no treat | 149 | — | 161 | — | | 148 | — |
| | 5 | 273 | 83 | 268 | 66 | 1.9 | 228 | 54 |
| | 10 | 313 | 110 | 340 | 116 | | 332 | 124 |
| | 20 | 417 | 180 | 325 | 102 | 22.1 | 333 | 125 |
| | 30 | 484 | 225 | 356 | 121 | 26.4 | 423 | 186 |
| ' Żerko-wice " | no treat | 373 | — | 336 | — | 9.9 | 234 | |
| | 5 | 469 | 26 | 420 | 25 | 10.5 | 317 | 35 |
| | 10 | 498 | 34 | 425 | 27 | 14.7 | 336 | 44 |
| | 20 | 651 | 75 | 511 | 52 | 21.5 | 491 | 120 |
| | 30 | 684 | 83 | 586 | 74 | 14.3 | 471 | 101 |
| " Pińc-zów " | no treat | 110 | | 52 | — | 52.7 | 81 | |
| | 5 | 192 | 75 | 134 | 158 | 30.2 | — | |
| | 10 | 205 | 86 | 170 | 226 | 17.1 | — | |
| | 20 | 348 | 216 | 233 | 348 | 33.0 | — | |

$R_1$ : Resistance to pressure
$R_2$ : Resistance to water
$R_3$ : Resistance to frost

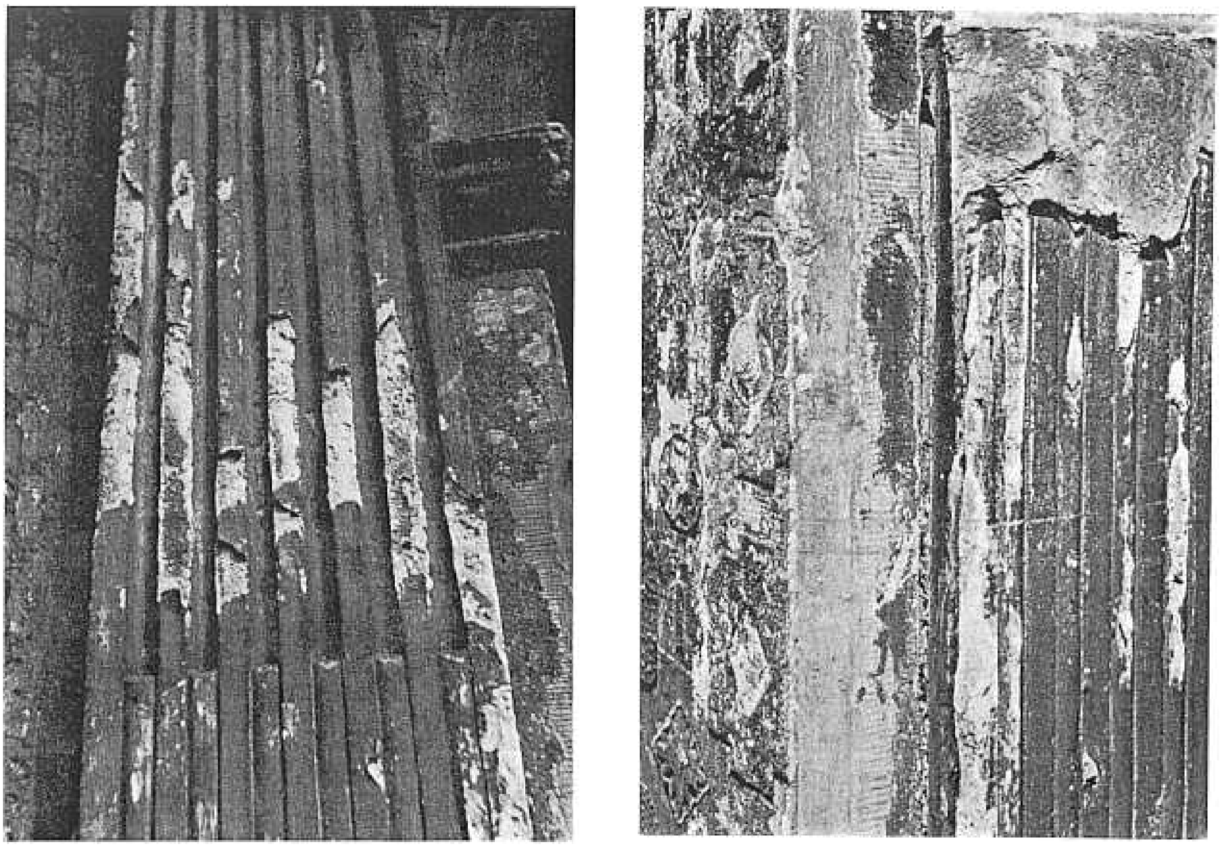

Fig. 6 Examples of stones before treatment.

## THE PROPERTIES OF IMPREGNATED STONES

Impregnation of stones with resins increased their resistance to pressure, the action of water and to frost but decreased the imbibition of water (Table 14). The magnitude of the effect produced by the resin depended on the nature of the stone as would be expected. For example, impregnation with resin markedly improved the resistance of the relatively soft Welcz limestone to water and frost whereas the resin had much less effect on the hard Zerkowice sandstone.

Increasing the resin concentration in solution used for impregnation served to produce greater consolidation of stones as shown by increased resistance to pressure, water and frost (Table 15). Again, the greater effect was observed with the less resistant stones than with the harder ones. Impregnation of the stones decreased the free pore space and the capacity of the stones to imbibe water and benzine (Table 16). The free pore space and the capacity of the stones to imbibe liquids also decreased with increasing resin concentration. The decreased porosity of the stones clearly resulted from filling of pores with the resins.

The results in Table 17 show that the saturation of a stone once with a high concentration of resin was as effective in reducing its porosity and capacity to imbibe liquids as were two saturations with one half that concentration. Thus, it appears that the degree to which pores were filled was determined by the total amount of resin absorbed and not by the number of treatments.

Preliminary work undertaken in this laboratory showed that the process of hardening should be allowed to go on for approximately 10 days with no appreciable loss of solvent. In the laboratory this could be readily achieved by keeping the object in a sealed container saturated with the solvent vapour. In the field, obviously, a technique such as this is not feasible. It was found, however, that good results could be obtained

TABLE 16. THE INFLUENCE OF THE CONCENTRATION OF EPOXY RESIN SOLUTION ON THE IMBIBITION AND FREE PORE SPACE OF IMPREGNATED STONES

Resin : Epidian 4 — Solvent : Toluene + methanol (1 : 2)

| Stone | Concentration of solution % | Nw[1] | Decrease of Nw due to impregnation % | Nb[2] | Decrease of Nb due to impregnation % | Po[3] | Decrease of Po due to impregnation % |
|---|---|---|---|---|---|---|---|
| Welcz | no impregnation | 17.4 | | 13.0 | | 27.9 | |
| | 5 | 9.2 | 47.1 | 11.9 | 8.5 | 25.3 | 9.3 |
| | 10 | 1.2 | 93.1 | 10.6 | 18.5 | 22.9 | 17.9 |
| | 20 | 1.4 | 92.0 | 8.4 | 34.5 | 18.4 | 34.0 |
| | 30 | 5.8 | 66.4 | 5.0 | 61.5 | 11.2 | 59.9 |
| "Nietulisko" | no impregnation | 12.1 | | 9.2 | | 21.6 | |
| | 5 | 2.4 | 80.2 | 8.3 | 9.8 | 19.5 | 9.7 |
| | 10 | 2.3 | 81.0 | 8.6 | 6.5 | 21.9 | |
| | 20 | 2.3 | 81.0 | 5.3 | 42.4 | 12.8 | 40.8 |
| | 30 | 7.3 | 39.7 | 5.2 | 43.5 | 12.6 | 41.7 |
| 'Żierkowice' | no impregnation | 7.6 | | 5.6 | | 14.3 | |
| | 5 | 1.3 | 82.9 | 5.2 | 7.1 | 13.2 | 7.7 |
| | 10 | 1.8 | 76.3 | 5.7 | | 14.0 | 2.1 |
| | 20 | 1.9 | 75.0 | 3.8 | 32.2 | 9.6 | 32.9 |
| | 30 | 3.7 | 51.3 | 1.8 | 67.9 | 4.7 | 67.1 |
| Pińczów" | no impregnation | 19.7 | — | 15.7 | | 30.3 | |
| | 5 | 4.0 | 79.7 | 12.3 | 21.7 | 26.0 | 14.2 |
| | 10 | 2.2 | 88.8 | 12.0 | 23.5 | 25.4 | 16.2 |
| | 20 | 0.9 | 95.4 | 8.9 | 43.3 | 19.3 | 36.2 |

Nw : Imbibition in water
Nb : Imbibition in bezine
Po : Free pore space

TABLE 17. THE INFLUENCE OF THE TWOFOLD SATURATION BY MEANS OF THE EPOXY RESIN SOLUTION ON THE INHIBITION AND OPEN FREE PORE SPACE OF STONES

Resin : Epidian 4 — Solvent : Toluene + Methanol (1 : 2)

| Stone | Number of saturating treatments % | Nw[1] % | Decrease of Nw due to saturation % | Nb[2] % | Decrease of Nb due to saturation % | Po[3] % | Decrease of Po due to saturation % |
|---|---|---|---|---|---|---|---|
| " Welcz " | no impregnation | 17.4 | | 13.0 | | 27.9 | |
| | 1 × 10 % soln | 1.2 | 93.1 | 10.6 | 18.5 | 22.9 | 17.9 |
| | 2 × 5 % soln | 4.9 | 71.9 | 10.3 | 20.8 | 22.0 | 21.2 |
| "Nietulisko' | no impregnation | 12.1 | | 9.2 | | 21.1 | |
| | 1 × 20 % soln | 2.3 | 81.0 | 5.3 | 42.4 | 12.8 | 40.7 |
| | 2 × 10 % soln | 1.3 | 89.3 | 5.5 | 40.2 | 13.1 | 37.9 |
| 'Żerkowice" | no impregnation | 7.6 | | 5.6 | | 14.3 | |
| | 1 × 20 % soln | 1.9 | 75.0 | 3.8 | 30.6 | 9.6 | 32.9 |
| | 2 × 10 % soln | 0.6 | 92.1 | 3.8 | 30.6 | 9.7 | 32.2 |

1 - Imbibition in water
2 - Imbibition in benzine
3 - Free pore space

Fig. 7. — The portal of the Esken house in Toruñ before restoration.

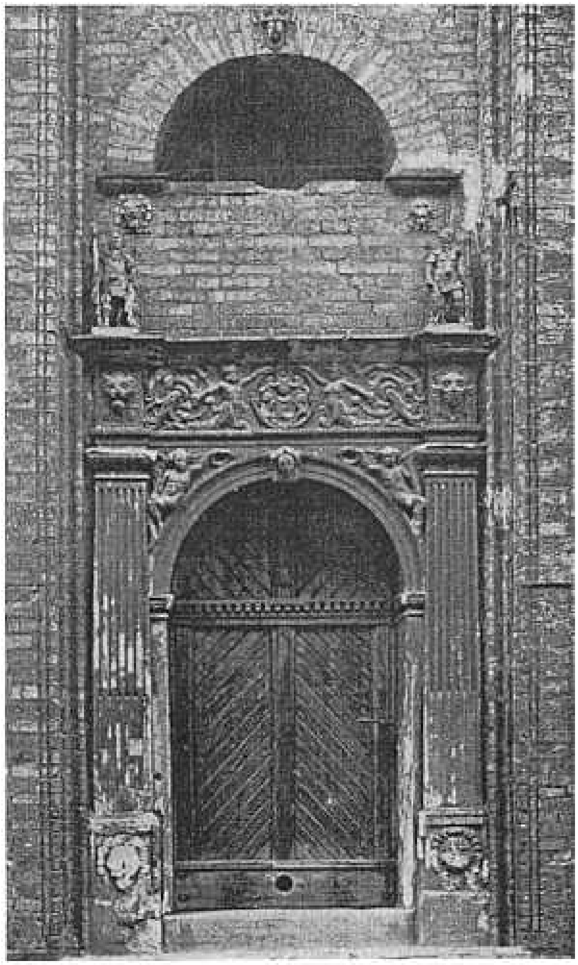

Fig. 8. — The same portal after restoration.

in the field by covering the object with solvent saturated cotton wool compresses and then wrapping it in polyethylene sheets. This procedure served to reduce the migration of solvent to the surface and to ensure minimum alteration of the color of the object.

Impregnation of stone objects can, as these experiments show, bring about a marked improvement in the mechanical properties of the object. Indeed, it is entirely conceivable that after treatment, weathered objects may exhibit greater mechanical strength and resistance to the action of water and frost, that the original unweathered material.

## CONCLUSION

These laboratory studies have demonstrated that the consolidation of stone objects to depths of several tens of centimeters below their surface may be achieved by the use of epoxy resin solutions. The effectiveness of the resin solutions was due partly to the fact that the solutions could be prepared with low viscosity to ensure maximum penetration. In addition, the hardening process in resin solutions is a chemical one so that the migration of resin to the surface as a result of solvent evaporation could be minimized by proper selection of hardening conditions. With epoxy resins, therefore, a better distribution of the consolidating agent was obtained than with the chemical agents previously used for stabilizing stone objects.

It was also evident that impregnated stone objects exhibited greater resistance to the effects of pressure, water, temperature changes and freezing than untreated stone. The improved resistance of stones to the effects of water and freezing resulted largely from the hydrophobic properties of the epoxy resins which prevented the penetration of water. It would be expected also that, owing to the inert nature of the resins, the chemical stability of stone objects would be increased as well. The stabilization of stone objects with resins, therefore, should increase their resistance to microorganisms, soluble satts, atmospheric gases and other chemical ageing agents. The impregnation of stone objects with epoxy resins appears to be an effective practical means of stabilizing stone objects.

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## *RESUME*

*Ce travail concerne la conservation des objets en pierre par l'imprégnation structurale affermissante. Il y est parlé des symptômes et des causes de la détérioration des pierres; puis, des méthodes de leur conservation, et, s'appuyant sur l'analyse des facteurs précités, des conditions auxquelles devrait répondre une conservation régulière des pierres. Pour sa mise en pratique, on a entrepris des recherches sur l'emploi des solutions de résines époxydes qui semblent les mieux adaptées à ce but.*

*L'étude précise donc successivement : a) les recherches sur les propriétés des solutions de résines époxydes; b) les recherches sur l'imprégnation structurale des pierres; c) les recherches sur les propriétés des pierres imprégnées.*

*Les résultats obtenus ont permis d'établir des paramètres qui fixent le degré du changement des résines époxydes dissoutes et polymères à « filets », la capacité de l'élèvement capillaire et le changement horizontal de place des solutions, ainsi que les propriétés mécaniques et la résistance à l'action des facteurs atmosphériques des pierres imprégnées.*

*On a constaté au cours de travaux que :*

*a) les solutions de résines époxydes s'infiltrent facilement dans les pierres, ce qui permet leur imprégnation et leur consolidation à une profondeur de quelques dizaines de centimètres;*

*b) lors de l'emploi des facteurs qui provoquent la solubilité, les résines ne subissent pas de migration à la surface de la pierre, mais elles se déposent dans les pores en l'affermissant du même coup dans les parties imprégnées. Elles ne rendent pas les pores de la pierre étanches et ne colorent pas sa surface;*

*c) l'imprégnation augmente à très grand degré la résistance mécanique des pierres ainsi que leur résistance à l'action des agents atmosphériques en leur donnant des facultés hydrophobes;*

*d) la méthode d'imprégnation exerce une influence décisive sur la vitesse de l'infiltration capillaire des solutions. La seule méthode effective consiste à imbiber toute la surface de l'élément qu'il faut conserver. Afin de réaliser ce principe, on a élaboré une méthode dite d'imprégnation « de poche ».*

*Ces résultats ont autorisé la conservation du portail en pierre de Toruń. La surface de ce dernier (environ 7,5 $m^2$) a nécessité l'emploi de 91 litres de solution de résines. Ce volume a permis de consolider la pierre sur une profondeur moyenne de 9 à 10 cm.*


*Fig. 1. — Saturation capillaire d'une pierre à travers la coupe d'un échantillon (déplacement vertical).*

*Fig. 2. — Saturation capillaire d'une pierre à travers une « cheminée » (déplacement vertical).*

*Fig. 3. — Saturation capillaire d'une pierre au moyen d'une « pipe » (déplacement horizontal).*

*Fig. 4. — Saturation capillaire d'une pierre au moyen d'une « poche » (déplacement horizontal).*

*Fig. 5 Application de la méthode. Détails.*

*Fig. 6. Cas de pierres avant le traitement.*

*Fig. 7. — Le portail de la maison Esken à Toruñ avant la restauration.*

*Fig. 8. — Le même portail après la restauration.*