THE CONSERVATION OF LIMESTONE OBJECTS
AND STRUCTURES

The advanced and, indeed, precarious state of decay of a large number of artistically or historically significant stone objects that have been subjected to long periods of exposure to wind, sun, water, microorganisms, and atmospheric pollutants is strikingly evident to even the most casual observer. As a consequence of the general anxiety felt by the community of scholars, curators, and public officials for the future existence of this irreplaceable heritage, the Conservation Center of the Institute of Fine Arts of New York University resolved early in 1964 to make this problem one of its principal concerns.

A comprehensive survey was made of the technical literature bearing on the chemical and physical nature of the various kinds of sculptural and building stone, of the types of deterioration that have been observed and described, and of the techniques of preservation and restoration that have been tried or proposed. This literature survey is included as an appendix to this report. Critical evaluation of this information led to the conclusion that the most urgent problem is presented by the current status of limestone objects, and that the various expedients in use at the present time for the treatment of limestone are at best ineffective, and in many cases, actually deleterious.

Consequently, an experimental program as initiated that was aimed at disclosing the fundamental phenomena which occur in the deterioration of limestone, and at providing objective data on the details of the nature of the effects of various chemical agents on the constituents of natural limestones.

Financial assistance provided in mid-1965 in the form of a grant from the Alfred P. Sloan Foundation, plus an equal grant from the trustees of the Metropolitan Museum of Art made it possible to prosecute this research program vigorously and efficiently.

The results obtained to date have shown that previous approaches to the preservation of limestone are based upon inadequate appreciation of the dynamic instability of the crystallites present in the microstructure of the stone. A new principle has emerged from the present investigation that makes it possible for the first time to develop a rational and scientifically sound method of permanently indurating and strengthening a weak or deteriorated limestone. A formulation for the treatment of limestone based on

this principle has been devised, and initial test results on three typical limestones have proven highly successful.

Experimental Technique

Three different types of limestone, representative of the broad range of properties encountered in practice, were employed in these investigations. They were : (1) a dense, firm oolitic limestone, (2) a dense, but friable travertine having a chalky texture, and (3) a porous, but hard travertine, approaching marble in texture and luster.

Small cubes of the limestone, approximately 1 cm on a side, were cut from larger blocks. Each cube was mounted in a 3/8-inch thick, 1 1/4-inch diameter disc of bakelite, so that one face of the cube was exposed, while the other five faces were embedded in the resin.

These mounted specimens were then immersed in solutions containing various chemical agents for controlled periods of time. After the desired period of immersion, the specimen was removed from the solution, rinsed, allowed to dry, and cross-sectioned. The effect of the chemical substance in solution on the structure of the stone was studied by microscopic examination of (a) the exposed surface, (b) the cross-section, and (c) a thin-section petrographic slide made from the cross-section. Dissolution effects were evidenced by the etching pattern and by the degree of undercutting of the exposed surface relative to the plane of the bakelite disc. New species formation was detected by the modification of the optical properties of the crystal grains visible in the thin section. Alteration of the cohesion and induration of the stone was investigated by performing micro-hardness measurements with a Knoop diamond indenter mounted on a microscope objective. The micro-hardness was measured at numerous points throughout the cross-section of the specimen.

The compostions of the solutions in which the stone specimens were immersed were designed to yield information about the following types of effects :

1. The effect on limestone of prolonged contact with solutions of salts which have no ion in common with the $CaCO_3$ of the stone, and which do not form with either Ca^{++} or CO_3^{--} a salt of sparing solubility. Examples of this class include NaCl, $NaNO_3$, and CH_3COOK solutions.

2. The effect of contact with solutions containing an ion which is in common with one of the ions of the stone, viz., solutions of Na_2CO_3, $CaCl_2$ and $Ca(NO_3)_2$.

3. The effect of contact with solutions containing an ion or ions which can form a salt of sparing solubility with either the Ca^{++} or CO_3^{--} of the limestone ; e.g., NaF, Na_2SO_4, Na_3PO_4, NaOH, $NaAlO_2$, $SrCl_2$, $BaCl_2$, $Ba(OH)_2$, $AlCl_3$.

4. The effect of contact with acidic media, e.g., solutions containing HCl, H_2SO_4, H_3PO_4, HF.

5. The effect of contact with solutions which have been proposed as agents for the deposition of insoluble or adhesive material within the pores and interstices of the stone. These media include solutions of alum, of sodium silicate, of silicic esters, and of organo-metallic compounds. Also included in this category were experiments in which the stone specimen was treated successively with two different solutions, the combination of which might be expected to yield a deposit of insoluble material, e.g., immersion first in a $CaCl_2$ solution, followed by immersion in Na_3PO_4 solution.

The Structure of Limestone

In order to interpret and properly to evaluate the results of the exposure of the stone specimens to various substances in solution, it is first necessary to form a clear picture of the nature of the original stone. In general, limestone is an agglomerate composed of small, and often imperfectly crystalline, particles of calcite, which is the thermodynamically stable form of $CaCO_3$ at ordinary temperatures and pressures. The other form of $CaCO_3$, which is metastable under ordinary conditions, is aragonite ; this occurs in certain limestone deposits of recent or unusual origin, but was absent in the limestone samples employed in the present investigation.

Microscopic views of thin-sections of the three types of limestone involved in this study are reproduced in Figure 2. Figure 2A shows the oolitic limestone. The finer the grain-size in the thin-section, the greater is the amount of light scattering that occurs at the particles boundaries and interfaces, and the darker does the photomicrograph appear (the same effect is evident in comparing the transparency of large chunks of glass with that of the same glass when ground to a fine powder). With this in mind, it will be seen that the ooliths in general consist of a center or nucleus of moderate sized grains, around which has been built up a sheath of very fine particles. The outermost layer or skin of this sheath is occasionally composed of particles which are slightly larger than those composing the bulk of the sheath. Between the individual ooliths, moderate to large sized crystal grains are present, serving to fill in the interstices of the structure.

The travertine thin-sections shown in Figures 2B and 2C show that this type of limestone is composed primarily of very small, but well-defined crystallites of calcite. In the case of the hard, marblelike travertine of Fig. 2C, the crystallites are fairly large, the average particle size being about 0.1 - 0.05 mm. The centers of most of these crystallites appear opaque in the thin-section (but are white in reflected light), showing that they consist

of very minute particles, which were the primary nuclei around which the crystallite grew. The soft travertine of Figure 2B consists of much smaller, less densely packed crystallites (average particle size about 0.01 mm), which, however, show no evidence of the opaque primary nuclei noted in the preceding. The soft travertine contains fewer and smaller visible pores than does the hard specimen, so that the bulk density is greater for the former, despite the less dense packing of the individual crystallites.

The presence of a substantial proportion of very minute crystallites in the structure of a limestone is a fact of major importance for understanding the properties of the stone under conditions of exposure. Figure 3 shows a microscopic view of the surface of a sample of the oolitic limestone over which a stream of water had been caused to flow for a period of one month. It is evident that the water has primarily leached away those portions of the ooliths which consisted of the smallest primary particles, leaving behind a skeleton network of the larger crystallites.

A second fact of fundamental importance is the existence in these limestones of an extensive network of discrete (though submicroscopic) channels between and along the particle-to-particle boundaries, extending even to the tiniest and apparently most densely packed crystallites. This is strikingly shown in Figure 4, which is a thin-section photomicrograph of a sample of oolitic limestone taken from the surface of a building where it had been exposed to the New York City atmosphere for several decades. It will be noted that tiny aggregations of soot particles are deposited deep within the ooliths a considerable distance beneath the exposed surface along the submicroscopic channels. In fact, the greatest concentration of soot deposits occurs in those regions of the ooliths where the primary particle size is the smallest.

Thus, it is evident that both air and water have ready and intimate access to all parts and to substantial depths within these limestones, and that the tiniest crystallites are most subject to alteration and dissolution under the influence of a contacting medium.

Induced Structural Changes

If crystals of $CaCO_3$ are allowed to remain in contact with a medium containing an ion (say, X^{--}) that forms a sparingly soluble substance with either Ca^{++} or CO_3^{--}, the principles governing chemical equilibrium predict that some of the new phase will form. Thus, if the solubility product expressions involved are :

$$(a_{Ca^{++}})(a_{CO_3^{--}}) = K_1$$

$$(a_{Ca^{++}})(a_{X^{--}}) = K_2$$

then for both equilibria to be satisfied simultaneously, the relative activities of CO_3^{--} and X^{--} must adjust themselves until

$$\frac{a_{X^{--}}}{a_{CO_3^{--}}} = \frac{K_2}{K_1}$$

If the solution originally contains the activity $\underline{b}$ of X^{--}, then the $CaCO_3$ will dissolve and CaX will precipitate until the activity of CO_3^{--} in the solution phase is, say $\underline{y}$, and that of X^{--} is $\underline{b} - \underline{y}$, where

$$\frac{b - y}{y} = \frac{K_2}{K_1}$$

Hence, it might be anticipated that if a sample of limestone is immersed in a solution containing, e.g., dissolved NaF, some of the $CaCO_3$ at and near the exposed surface of the specimen would be converted into CaF_2. This does in fact occur, as is illustrated by the thin-section shown in Figure 5.

In the experiments carried out so far, only the fluoride ion has been observed to penetrate into the surface of the stone, forming thereby a thin skin of fluorite (CaF_2). Other ions which are capable of forming sparingly soluble compounds with Ca^{++}, such as SO_4^{--}, PO_4^{---}, OH^-, and SiO_3^{--}, tend to cause the surface of the specimen to be more or less eroded, but without any evidence of conversion of the remaining calcite into any other species.

Induced Recrystallization

However, the very remarkable fact was observed that in the case of all the ions cited above, as well as even with ions which do not form sparingly soluble compounds with either of the ions of the calcite lattice, a certain amount of recrystallization was found to have taken place. That is, immersion of the limestone in these media for extended periods of time resulted in the disappearance of some of the smallest particles, their places being taken by a smaller number of larger, better-formed, more massive crystals. This is illustrated by the thin-section photomicrographs reproduced in Figure 6, which shows the effect of immersion for one week in a saturated $CaCl_2$ solution.

The manner in which large numbers of the minute particles composing the sheath of an oolith are transformed under the influence of the immersion medium into massive calcite rhombs is strikingly shown in Figure 7.

Investigation of the rate and extent of this recrystallization phenomenon discloses that it is a general effect characteristic of prolonged interaction of the smallest crystallites in limestone with any aqueous solution, including simply distilled water itself. It would appear to be a consequence of the thermodynamic instability of these tiny particles, which, due either to strains, imperfections, or highly curved bounding surfaces, have a higher free energy than

that characteristic of larger crystals.

It is, however, highly significant that the rate of this recrystallization is sensitive to the nature of the solute present in the aqueous medium. The results of the experiments to date may be summed up in the following generalization : Recrystallization of calcite occurs at a greater rate, the stronger the adsorption of the solute on the calcite crystal lattice.

Thus, the most pronounced catalysts for the recrystallization phenomenon have been found to be, in the order named, solutions of : barium hydroxide, the alkali aluminates, any of the soluble barium salts, the strontium salts, and the calcium salts. Saturated solutions of strontium or calcium hydroxides are more effective than solutions of the same concentrations of other strontium or calcium salts ; however the limited solubility of these hydroxides prevents large rates of recrystallization from being achieved with these compounds.

Less effective, though distinctly catalytic in nature, are solutions containing fluoride, sulfate, phosphate, and/or hydroxyl ions. The heavy metal ions also show catalytic effects on the recrystallization rate.

Application to the Conservation of Limestone

The discovery of practical means of inducing and controlling the recrystallization of minute crystallites within the structure of a limestone opens up hitherto unrecognized avenues of approach to the problem of strengthening and preserving decayed or poorly indurated stone. If such a specimen is caused to undergo recrystallization, the following desirable effects may be anticipated:

1) The reduction in numbers of minute particles will decrease the internal surface area and decrease the adsorptive and absorptive capacity of the stone for discoloring and deteriorating pollutants.

2) The growth of large crystals in place of the smallest ones will tend to decrease the internal network of inter-particle channels and capillaries, thereby slowing up the rate of penetration of corrosive agents and of leaching out of solubilized material.

3) In the process of growth, bridges will tend to form between contiguous crystallites, and a three-dimensional network of partially and wholly fused crystals will form, thereby greatly increasing the strength, cohesion, and hardness of the stone.

4) If macroscopic holes, cracks, lacunae, etc. in the stone are filled with finely powdered $CaCO_3$, either mechanically, or by precipitation from solution, this new material can be caused to recrystallize and consequently fuse with and become an integral part of the surrounding stone. Thus, breaks can be repaired, and pores may be filled, with a material that is chemically and physically

identical with the remainder of the stone, and hence that cannot break down, separate, alter, or corrode it during the subsequent life of the object.

5) The recrystallization process occurs throughout the bulk of the stone, wherever the aqueous solution penetrates, and does not produce merely a surface alteration of properties.

6) The recrystallization process is capable of achieving the desirable effects detailed above without producing significant changes in the color, texture, volume, or external appearance of the stone.

Practical Test of the New Technique

The fact that the desirable effects enumerated above can indeed be fully realized in practice has been demonstrated as follows. Samples of each of the three types of limestone were kept immersed for a period of one month in a solution containing 8 % by weight of $Ba(OH)_2 \cdot 8H_2O$ and 4 % by weight of urea. The barium hydroxide is strongly adsorbed on all the internal surfaces and interfaces within the stone, and during the prolonged immersion, brings extensive recrystallization.

The urea slowly decomposes in the alkaline medium, according to the equation :

$$CO(NH_2)_2 + H_2O = CO_2 + 2 NH_3$$

The carbon dioxide released from the urea reacts with the barium hydroxide, converting it to insoluble barium carbonate. This barium carbonate is formed at a slow and continuous rate within all the pores and channels of the stone, and, in fact, undergoes crystal growth and recrystallization under the influence of the immersion medium in the same way as the calcite crystallites. Thus, the desirable effects of the recrystallization process are by this means supplemented and reinforced through the simultaneous deposition and incorporation of barium carbonate throughout the bulk of the stone.

It will be noted that when the immersion has persisted long enough, no soluble or reactive substance remains. The original barium hydroxide has been converted to barium carbonate, the urea has decomposed, and the ammonia produced in its decomposition, being volatile, escapes.

Small blocks of the limestone specimens employed in this study were prepared, and several 1/4-inch holes were drilled in each (Figure 8). These holes were then filled with finely-ground (to the state of an impalpable powder) chalk, mixed with some powdered charcoal to impart a distinctive color to the added material. After one month of immersion in the solution described above, the chalk powder was found to have recrystallized and fused to a solid

that was as hard and coherent as the remainder of the original stone, and the latter had become harder, stronger, and less porous than it was before the treatment. The added chalk dust was now directly bonded to the surrounding stone as well as to itself. The macroscopic appearance of typical test specimens is shown in Figure 8, and a thin-section photomicrograph showing the crystallites of the stone and added material is reproduced in Figure 9. Measured on the Mohs hardness scale, the soft, friable travertine was found to have been increased in induration enough to raise its hardness from the rank of 2 to 4.

These changes in the specimens were not associated with any appreciable modification in the gross appearance of the stone ; the color and texture remained substantially as they were before the treatment. There was no evidence of any tendency toward a volume increase, skin formation, crack or fissure production, or other alteration in the stone that might militate against the application of this technique to the treatment of valuable artifacts or structures.

Conclusion

It appears justified to conclude that the specific formulation described in the preceding section, which is only one of several that have been found to produce the desired improvement in the properties of limestone, is suitable for application, without further development, to the treatment of any object that can be immersed.

Further investigation of this new technique, particularly in application to a wide range of limestones of different types and in various states of deterioration is desirable, and is currently under way at the Conservation Center of New York University.

Acknowledgement

Valuable assistance was rendered in various phases of this investigation by Jeanne A. Danker, George Stassinopoulos, Norman Weiss, Shirley Alexander, and Janet Stone.

S.Z. LEWIN.

List of Figures

Figure 1. Typical stone specimen mounted in bakelite disc; manner of cross-sectioning and of mounting for grinding of thin section.

Figure 2. A. Thin-section of the oolitic limestone.
B. Thin-section of the soft travertine.
C. Thin-section of the hard travertine.

Figure 3. Surface appearance of a water-eroded specimen of oolitic limestone.

Figure 4. Thin-section of a soot-infiltrated sample of oolitic limestone.

Figure 5. Thin-sections showing the effect of immersion in NaF solution on the oolitic limestone.

Figure 6. Thin-sections showing the effects of saturated $CaCl_2$ solution on the structure of the oolitic limestone.

Figure 7. Thin-sections showing the effects of sodium aluminate solution on the structure of the oolitic limestone.

Figure 8. Photograph of the test blocks of limestone before and after treatment.

Figure 9. Thin-sections of the recrystallized plug of chalk powder in limestone.

Chronological Survey of the U.S. Patent Literature Relating to
Compositions for the Impregnation of Stone (Including
summaries and abstracts of preferred formulations).

1863   1   J.C.Coombe, U.S. Patent 38,287, April 28, 1863 -
"Improvement in Indurating and Preserving Stone, Ce-
ments, Wood, etc."

    If the stone contains potash, alkaline earths, or
bases capable of forming insoluble compounds with hy-
drofluosilicic acid, the latter is applied by washing the
surface of the stone with it, immersing the stone in it,
or other means. If the former are absent, the stone is
first impregnated with a solution of potash or its salts,
or with lime, baryta, magnesia, or other alkaline earths;
the stone is dried, then treated with the hydrofluosilicic
acid.

1870   2.   E.J. Salisbury, U.S. Patent 102,869, May 10, 1870 -
"Improvement in Preserving and Hardening Stone, Brick,
Etc."

    The stone is first treated with a solution of magne-
sia containing 2 pounds per gallon of water ; this opera-
tion is repeated until the stone has become saturated to
the depth required. Then, the surface is coated with a
solution of a soluble silicate, e.g. a mixture of sodium
silicate and potassium silicate of neutral pH and specific
gravity about thirteen hundred.

1879   3   J.A. Greer, U.S. Patent 222,694, Dec. 16,1879 - "Im-
provement in Compounds for Artifical Stone".

    An insoluble coating can be applied to stone or
brick as follows. Immerse for one hour in a solution
made by boiling 2.1 pounds of carbonate of soda in 25.5
pounds of water for 2-3 hours, then adding 5.1 pounds
additional water. Dry for 36 hours ; then place in a so-
lution containing 3 ounces of alum per gallon of water
for 20 minutes.

4   H.G. Hosmer, U.S. Patent 214,142, April 8, 1879 -
"Improvement in Processes of Making Artificial Marble".

    The stone (limestone or alabaster) is subjected to
moist heat or steam, then immersed in a 5 % alum so-
lution for 24 hours. A coloring agent may be added to
the latter if the stone is to be tinted.

1882   5. H.C. Jewell, U.S. Patent 259,863, June 20, 1882 -
"Manufacture of Artificial Stone and Marble".

    Sand, gravel and hydraulic cement are mixed and
dampened with a solution of 1 lb of deutosulfate of copper
in 75 gallons of water to give the artificial stone. This
is hardened and made impenetrable to moisture by sa-
turating it with the following solution : 1 lb alum ammonia
ferri, 2 lbs borate of soda, 3 lbs nitrate of potash, 1 pint
carbolic acid, 3 lbs muriate of ammonia, 0.5 lb nitrate
of ammonia, 2lbs oxalic acid, 2 quarts lime water, suff-
icient water to give a saturated solution.

6. R. Josia, U.S. Patent 265,501, October 3, 1882 -"Com-
position for Treating Sulfates of Lime for the Manufacture
of Artificial Marble".

    Gypsum blocks are heated at 260-300°F for about
twelve hours, then immersed in a solution of 200 parts
water, 4-5 parts alum, 2-2.5 parts oxalic acid, by weight,
for 12 hours. Best results are obtained by repeated dipp-
ings in this solution alternating with equal drying periods,
starting with seconds, increasing to minutes, then hours.

R. Josia, U.S. Patent 265,502, October 3, 1882 -"Com-
position for Treating Sulfates of Lime for the Manufacture
of Artificial Marble".   ·

    Similar to preceding, but to yield a black stone,
the impregnating and indurating solution used consists
of : 200 parts water, 3 parts sulfate of iron, 0.5 parts
sulfate of copper, 3 parts Campeachy wood, 6 parts gall-
nuts, 0.5 parts logwood, by weight.

8. R. Josia, U.S. Patent 265,503, October 3, 1882 - "Com-
position for Treating Sulfates of Lime for the Manufacture
of Artificial Marble".

    Similar to preceding, but to yield a rose or pink
tint in the stone, use the following solution : 200 parts
water, 4-5 parts alum, 2-2.5 parts oxalic acid, 0.01-0.02
parts rose of aniline, by weight.

9   R. Josia, U.S. Patent 265,504, October 3,1882 - "Com-
position for Treating Sulfates of Lime for the Manufacture
of Artificial Marble".

    Similar to preceding, but to yield an ivory color,
use the following solution : 200 parts water, 4-5 parts
alum, 2-2.5 parts oxalic acid, 1 part Brazil wood (Per-
nambuco), 0.5 part sulfuric acid, 0.005-0.01 part rose
of aniline, by weight.

1882 10. R. Josia, U.S. Patent 265,505, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a red color, use the following solution : 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 6 parts Brazil wood, 1 part chloride of zinc, 0.2 part cream of tartar, by weight.

11. R. Josia, U.S. Patent 265,506, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having yellow spots on a red background, use the following solution : 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 6 parts Brazil wood, 1 part chloride of zinc, 0.2 part cream of tartar, 0.5 part sulfuric acid, by weight.

12. R. Josia, U.S. Patent 265,507, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a yellow color , use the following solution : 200 parts water, 6 parts sulfate of iron. The stone is then immersed in a solution of 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 2 parts bichromate of potash. The object may be alternately dipped in these two solutions a number of times, and finally left in the first until it has acquired the desired hardness and color.

13 R. Josia, U.S. Patent 265,508, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a yellow color, use the following solution : 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 4-6 parts logwood.

14. R. Josia, U.S. Patent 265,509, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a light green color, use the following solution : 200 parts water, 3-4 parts alum, 2-3 parts logwood, 1-2 parts sulfate of indigo.

5. R. Josia, U.S. Patent 265,510, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a dark green color, use the following solution : 200 parts water, 2 parts alum, 4 parts logwood, 2-3 parts sulfate of iron.

6. R. Josia, U.S. Patent 265,511, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a lilac color, use the following solution : 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 8 parts Campeachy wood, 5-10 parts carbonate of soda.

17. R. Josia, U.S. Patent 265,512, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a sky blue color, use the following solution : 200 parts water, 2-2.5 parts oxalic acid, 10-11 parts alum, 0.015-0.03 parts cyanide of potassium.

18. R. Josia, U.S. Patent 265,513, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a dark blue color, use the following solution : 200 parts water, 4-5 parts alum, 2-2.5 parts oxalic acid, 1 part aniline blue, 0.5 parts sulfuric acid.

19. R. Josia, U.S. Patent 265,514, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a light green color, use the following solution : 200 parts water, 16 parts sulfate of copper, 20 parts ammonia.

20. R. Josia, U.S. Patent 265,515, Oct. 3, 1882 - "Composition for Treating Sulfates of Lime for the Manufacture of Artificial Marble".

Similar to preceding, but to yield a stone having a white color, use the following solution : 100 parts water, 1 part sulfate of iron.

21. R. Josia, U.S. Patent 267,310, Nov. 7 1882 - Composition for Treating Sulfates of Lime".

Similar to preceding, but to yield a stone having an ivory color, use the following solution : First solution : 200 parts water, 6 parts sulfate of copper. Second solution : 200 parts water, 6 parts cyanide of potassium.

1883   22. J.A. Greer, U.S. Patent 269,849, Jan. 2, 1883 - "Compound for the Manufacture of Artificial Stone".

An artificial stone is made by mixing 100 lbs of hydraulic cement, 400 lbs. sharp sand, 20 lb. black oxide of manganese, and dampening this mixture with a solution of 32 gallons water, 3 lbs. precipitate of carbonate of iron, 1 lb. of carbonate of potassium, 2 lbs. of sulfate of aluminium, 2 lbs. of ferri oxide, and 16 ounces of muriatic acid. Finally, moisten the resulting stone 3 times a day for five days with a solution of 1/4 lb. of carbonate of potassium in two gallons of water. To waterproof this stone, coat with the following solution : 0.5 lb. tallow, 1/4 lb. carbonate of potassium, 2 gallons water - all boiled until the ingredients are dissolved and applied hot. To harden the stone, coat it with a solution of 0.5 lb. of sulfate of alumina in 1 gallon water.

1884   23. J.L. Kessler, U.S. Patent 308,263, Nov. 18, 1884 - "Process of Treating Natural and Artificial Stone".

The stone is hardened by impregnating it with the fluo-silicates of iron or the fluo-silicates of manganese, or the fluoride or the fluo-silicate of chromium, cobalt, nickel or other metals. The impregnation may be carried out in two stages by using first the fluo-silicates of lead or mercury, followed by treatment with an iodide or chromate. Clay or china clay made into a paste with fluo-silicate acid of 40° Baumé will become hard as stone. The earthy or metallic phosphates dissolved in hydrofluosilicic acid or fluor-hydric acid are also useful as impregnating agents.

The impregnation may also precede or follow the treatment of the articles with other agents. For instance, after having hardened the substance to an alkaline silicate, if it be caused to absorb fluosilicate or fluoride of aluminum, the soda or the potash is thereby rendered completely insoluble in the state of or similar to cryolite, and nothing soluble remains in the material.

If the acid employed is hydrofluosilicic acid or fluor-hydric acid combined with alumina, it forms an

Nous regrettons de ne pouvoir publier les illustrations concernant ce rapport, qui ont été présentées par l'auteur lors du colloque.

It is our regret not to be able to publish the documents illustrating this report, presented by the author at the conference.

insoluble alkaline silico-aluminate and a cryolite equally insoluble.

To impart a water-proof, polished, and enameled quality to the stone, it is then treated with wax, stearine, or paraffine, or similar encaustic, oily, or water-proofing composition.

1887 : 24. H. Bacon, U.S. Patent 368,269, Aug. 16, 1887 - "Manufacture of Artifical Stone and Cement"

To make artificial stone, take 10 parts of fine, sharp silicious sand or gravel and 1 part of Portland or other suitable cement, and after mixing, dampen with the following solution : 3 lbs. ferrocyanide of potassium, 1 lb. caoutchouc, 2 lbs. chloride of lime, 2 quarts spirits of ammonia, 100 gallons of water. After 3-4 days, immerse in a solution of 3-4 quarts of oil of vitriol and 3 lbs. of chloride of lime in 100 gallons of water for 3-4 days. "This finishes the stone, which then becomes perfectly crystallized and carbonized or petrified, whereby it is rendered impervious to water and extremely hard and durable, the particles adhering together with the greatest tenacity, and the mass becoming harder and more solidified the longer it stands..."

25. A. J. Cushman, U.S. Patent 367,372, Aug. 2, 1887 - "Composition Bath for Treating Slate or other Porous Stone".

The stone is soaked for 24 hours in the following solution : 40 gallons water, 1 bushel common salt, 1/2 bushel finely pulverized charcoal, 2 pounds sal-soda, 2 pounds saltpeter. If desired, 4 pounds of water-slaked lime may also be added, though it is not essential.

1895 : 26. G.W. Parker, U.S. Patent 549,151, Nov. 1895 - "Process of Treating Gypsum Rock to Imitate Chalcedony".

Gypsum rock is heated to drive off its water of hydration, then treated with the following solution to develop coloring imitative of onyx, agate, or other varieties of chalcedony : (a) copper nitrate and aqua ammonium solution, or (b) sulfate of iron, nitric acid, and potassium sulfo-cyanide solution. To harden, the rock is next immersed in a solution of aluminium sulfate for 15 hours or until the pores of the rock are completely filled.

1899 : 27. F.W. Prentice, U.S. Patent 620, 178, Feb. 28, 1899 - "Process of and Composition for Cleaning Stone".

The surface is cleaned by using a metal wire brush and the following detergent solution : 6 parts ether, 8 parts chloroform, 16 parts aqua ammonia (26 % conc.), plus 2 parts cologne spirits (not essential ; for ameliorating odor).After cleaning,the stone surface is finished by rubbing in a mixture of 2 ounces of precipitated chalk in one pint of alcohol.

1919 : 28. M.J.Reusz, U.S. Patent 1,319,178, Oct. 21, 1919 - "Antifreezing Solution".

Brick and cement is impregnated with the following solution : calcium magnesium chloride, $CaCl_2 \cdot MgCl_2 \cdot 12H_2O$, dissolved to give a 17° to 50° Baumé solution, plus 6 % by weight of a solution made from 5 % sulfate of copper, 10 % hydrate of lime and 85 % water.

1921 : 29. A.R. Green & H.L. Roscoe, U.S. Patent 1,371,555, Mar. 15, 1921 - "Composition for Treating Concrete Surfaces".

The stock solution consists of 16 ounces aluminum sulfate, 1 ounce sulfuric acid, 111 ounces water. One gallon of this solution is mixed with 2 gallons of water and applied as the first coating to the concrete surface. The surface is maintained wet with this solution for 1 1/2 hours, then wiped and allowed to air-dry for one hour. A second coat is applied in similar fashion of the stock solution diluted 1 gallon to 1 1/2 gallons water. Finally, a third coat is applied of the stock solution diluted 1 to 1.

The aluminum sulfate in the solution is precipitated by the caustic lime in the cement, forming crystals of calcium aluminum sulfate, which in turn reacts with water to form hydrated alumina. "The sulfuric acid is added to produce the energy for the penetration that takes place and to supply an excess of sulfate for the production of the calcium aluminate crystals".

1924 : 30. J. Downes, U.S. Patent 1,495,138, May 20, 1924 - "Hardening and Bonding Composition Adapted for the Treatment of Concrete and Cement".

The solution is made up as follows : 300 pounds of a saline concentrate (derived from the saline lakes of the West and evaporated and burned in a cement kiln ; contains Na_2CO_3, Na_2SO_4, NaCl, KCl, and $Na_2B_4O_7$) are dissolved in enough water to give 30° Baumé and filtered ; 30 pounds of calcium chloride in hot water to a 10° Baumé solution ; 20 pounds of magnesium chloride in cold water to a 10° Baumé solution ; 10 pounds of

alum in 3 gallons of boiling water ; five pounds of zinc sulfate in 3 gallons hot water ; 5 pounds barium sulfate ; 5 lbs. iron oxide. The ingredients are thoroughly mixed and the final solution is filtered to give a clear solution. It may be used to harden and bond concrete and cement.

1926 : 31. A.P. Laurie, U.S. Patent 1,607,762, Nov.23, 1926 - "Preservation of Stone".

Alcohol (at least 90 %) is added slowly to $SiCl_4$ in equal volumes, and the HCl formed is driven off. The silicic ester is mixed with a volatile solvent (e.g., alcohol or benzene), and the stone is soaked in the solution. When exposed to the atmosphere, the solvent evaporates, leaving behind the silicic ester which slowly decomposes forming a film of hydrated silica which cements and waterproofs the stone.

If the silicic ester is slightly acid before it begins to hydrolyze, the hydrated silica which is deposited forms a hard glassy layer. If the silicic ester is slightly alkaline, however, the hydrated silica is deposited as a soft gelatinous precipitate which is useless as a cement or preservative. Limestones and calcareous sandstones are generally sufficiently alkaline in character to render the silicic ester alkaline and so to make the precipitate soft and useless. This is circumvented by adding strong sulfuric acid drop by drop to the solution of silicic ester with frequent shaking until there is 0.5 to 1.0 part of acid to 1000 parts of silicon ester.

1932 : 32. J.C. Kratoville, U.S. Patent 1,858,830, May 17, 1932- "Waterproofing Composition and Method of Preparing".

To keep a high concentration of aluminum stearate in solution from gelling or becoming too viscous to apply, a peptizing agent is added. The solution recommended is : 2-10 parts aluminum stearate in 100 parts of naptha, plus 0.3 - 1.5 % by weight of the solution of anhydrous acetic acid.

1936 : 33. E.B. Peck, U.S. Patent 2,058,821, Oct. 27, 1936 - "Waterproofing Composition".
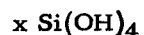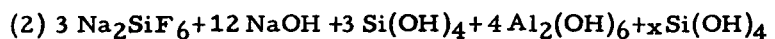
The sulfonic acids and ammonium sulfonates of high molecular weight petroleum oil fractions are recommended, since these form water insoluble calcium compounds with constituents of the exposed surfaces of concrete, cement, etc. Alkali sulfonates, such as sodium or potassium sulfonates are not suitable, for when applied,

plied to the surface, a metathetical reaction occurs in which calcium sulfonates and free alkali are formed. The latter greatly weakens the cement or concrete structure.

The compound is applied by brushing in an aqueous solution containing 20 - 50 % of the sulfonic compound.

1938   34. J.P. Ward, U.S. Patent 2,114,692, Apr. 19, 1938 - "Coating Process".

A coating for stone is achieved by mixing, just before using, in stoichiometric proportions, the following : (a) a solution of 70 parts barium fluosilicate in 100 parts water, by weight ; and (b) a powder composed of 300 parts sodium silicate, 60 parts chromium oxide, and 40 parts aluminum hydrate. The reactions occurring in the course of the formation of the coating are :

$$(1)\ 3\,Na_4Si\,(OH)_8 \xrightarrow{\ fluosilicate\ } 12\,NaOH + 3\,Si(OH)_4$$

$$(2)\ 3\,Na_2SiF_6 + 12\,NaOH + 3\,Si(OH)_4 + 4\,Al_2(OH)_6 + x\,Si(OH)_4$$

$$\longrightarrow 6\,NaF + 2\,Na_3AlF_6 + 6\,NaAlSiO_4 + 24\,H_2O + x\,Si(OH)_4$$

The products of the reaction include substances having the composition of the minerals cryolite and feldspar.

If the substrate contains free lime, it will damage the coating. In such cases, the surface is first treated with ammonium phosphate to react with the lime ;heating to 230° F is helpful.

An alternative recipe consists of the two dry powders :
a) 280 parts dry sodium silicate ($Na_2O . 3\ 1/4\ SiO_2$) ;
110 parts chromium oxide ; 80 parts aluminum hydrate.
b) 100 parts sodium fluosilicate ; 10 parts chromium oxide. 470 parts of (a) are dissolved in 380 parts of water. 110 parts of (b) are dissolved in 100 parts of water. The two solutions are finally mixed at the time of use.

1939   35. W.B. Houston, U.S. Patent 2,167,300, July 25, 1939 - "Waterproofing Solution for Cement and Stucco".

5 % sodium stearate soap, 2 1/2 % varnish, 7 1/2% solvent mixture (naphta, carbon tetrachloride and denatured alcohol), 15 % denatured alcohol, and 70 % water.

1940   36. L. Liberthson, U.S. Patent 2,203,302, June 4, 1940 - "Concrete Hardening Composition of the Metal Salt Type."

A surface tension depressant, viz. sodium salt of green petroleum sulfonic acid (from open-chain C_{10} - C_{18} hydrocarbon) is added to a conventional metal salt formulation (e.g., water soluble metal fluosilicates, alkali silicates, alkali aluminates, zinc, cupric, ferric, alumina, and nickel sulfates and alums). This facilitates the penetration of the solution while also retarding its reactivity. 0.05 to 0.5 % of the depressant lowers the surface tension to 40-45 dynes/cm. The salt solution may be as concentrated as 10-25 % solids.

1942 : 37 C. Luckhaupt, U.S. Patent 2,288,633, July 7, 1942 - "Method of Treating Porous Materials".

Object is immersed in terpin hydrate at 115° C.

1951   38. I. Silverman & A. Moscowitz, U.S. Patent 2,575,599, Nov. 20, 1951 - "Concrete Hardening Compositions of the Metal Salt Type".

The tendency of water-soluble metal fluosilicates to hydrolyze requires the use of an acidic solution to minimize this effect. A dry mixture containing urea sulfate as the source of acid in the eventual solution solves the problem of storing the formulation in a stable state. A wetting agent is included in the dry mix (e.g. oleyl alcohol condensed with 20 mls of ethylene oxide known commercially as "Emulphor O" , polyethylene glycols, polyethylene glycol esters, polyethylene glycol ethers). The urea sulfate should be present in amount sufficient to lower the pH of the solution formed to 1.7.

1953   39. C.E. Goulding, Jr., U.S. Patent 2,650,173, Aug. 25, 1953 - "Method for Decreasing the Porosity of Calcareous and Siliceous Materials".

The potassium salts of the cocoanut oil fatty acids in 20 % aqueous solution is applied to the concrete, plaster, or stone. After 24 hours, a 20 % solution of aluminum sulfate is applied. The first solution reacts with Ca^{++} ions to form a gel ; the second solution aids in the swelling, setting, and hardening of the gel.

40. K. Dietz, U.S. Patent 2,662,022, Dec. 8, 1953 - "Self-Hardening Water-Glass Compositions".

90 parts of fine quartz powder, 4 parts of clay, 2.5 parts of an active silicic acid and 3.5 parts of glycolide are mixed. 100 g of this cement powder are

mixed with 30 cc. of a potassium silicate solution in which the ratio of SiO_2 to K_2O is about 1.64 and that of SiO_2 to H_2O is about 0.46. This sets to a hard, acid-resistant mass in 3 days.

Other hardening agents that may be used are : dimethyl oxalate, glycol diformate, glycerol triformate, formamide, oxamide, triacetamide, malonamide, succinic anhydride, maleic anhydride.

1959   41. D.V. Brown, U.S. Patent 2,905,562, Sept.22, 1959 - "Process for Rendering Masonry Water-Repellent".

The solution consists of 2 parts of the sodium salt of methyl silanetrial (prepared by hydrolyzing methyltrichlorosilane with excess of water, and dissolving the resultant methylpolysiloxane gel in 50 % NaOH to give a 20 % methylpolysiloxane solids solution), 20 parts of sodium silicate solution (50 % solids aqueous solution ; $Na_2O.3\ SiO_2$), 70 parts water.

1962   42. L. Ehrenburg, U.S. Patent 3,047,407, July 31, 1962 - "Waterproofing Agents for Cement and Concrete".

The mixture is prepared as follows : 3 parts of a fatty soap, 2 parts of a saponifiable resin soap, 7 parts of NaOH, and 0.5 parts of glycerine are dissolved in water. To this is added, with stirring, a solution containing 36 parts of aluminum chloride and 42 parts of KOH. To this is then added, with stirring, a solution of 24 parts KOH, 30 parts caustic lime and 9 parts calcium chloride.