Scaling Resistance of Concrete Improved Through Silicones

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● IT IS today an accepted fact among concrete technicians that air entrainment has been effective in completely eliminating or greatly reducing surface scaling of concrete pavements resulting from freezing and thawing and de-icing salt attack. However, there continue to be some cases of scaling, of reduced magnitude, under certain conditions of placement or exposure which occur apparently despite air entrainment. The opinion is held by many engineers that the latter usually occurs in concrete pavements which are placed so late in the year that the concrete is saturated with water and at the same time too low in strength when the first freeze and salt application occurs.

That scaling resistance of concrete is affected by length of curing or aging is indicated by the work of Hansen (1) which showed complete scaling of test slabs field placed in late November and early December after 55 cycles of freezing and thawing with de-icing salt application. First signs of scaling were noted for these test slabs at 10 and 5 freeze-thaw cycles, respectively. A test slab placed in the field during mid-November required $2\frac{1}{2}$ to 5 times as many cycles to develop initial scaling, although its tested flexural strength was less and its compressive strength was only slightly more than for similar slabs placed later. The essential difference between the mid-November test slab and the later ones was its age and the fact that it had an opportunity to lose moisture before the first severe freeze occurred.

Further indications that age and probably moisture loss of concrete has a bearing on its scaling resistance is given by the very comprehensive series of tests reported by Timms (3), which involved, among others, two sets of outdoor tests, one in 1951 and the other in 1952. The 1951 specimens were subjected to 19 severe freezing and thawing cycles with salt application during the first winter whereas the 1952 series specimens were subjected to 17 mild cycles in the first year and 34 mild cycles in the second year, a total of 51. Scaling was less severe for the second series which fact Timm states is probably due to the mildness of the freeze-thaw cycles and the greater age of the specimens in the second series. A comprehensive study of curing as related to scaling resistance has been summarized by Klieger (15).

Microscopic investigations in recent years have revealed that size and spacing of air voids as well as quantity of entrained air are important factors in the frost and scaling resistance developed by air entrainment in concrete (2). It is now fairly well established that the type of air entraining agent used controls bubble size and spacing for a given percentage of air in concrete and that large air bubbles widely spaced do not give satisfactory frost and scaling resistance (3,4). Where insufficient entrained air is present in concrete or where the air void spacing factor is too great, supplementary methods of protecting concrete against scaling are necessary. A suitable silicone water repellent for concrete can help in this connection if properly applied, and to aid in evaluating such silicone treatment, a brief review of the theory and mechanism of scaling seems desirable.

MECHANISM OF SCALING

One of the earlier theories assumed that the de-icing salts themselves crystallized out of solution within the pores of the concrete. Forces resulting from crystal growth were believed in this theory to cause disintegration of the concrete. Since, in pavement concrete, the salt solution could enter only from the top surface of the concrete, and since evaporation of the water holding the salts in solution could occur only from the top, crystal deposition according to this theory tended to occur in the surface concrete only; hence disintegration started at the surface but could be progressive.

A later theory held that the applied de-icing salts reacted with the tri-calcium aluminate of the cement to form a compound whose volume was greater than the sum of the absolute volumes of the original materials forming the compound. The resulting compound was crystalline, and its greater volume per unit of weight, taken in conjunction with hydraulic pressures resulting from freezing of uncombined water in the concrete, was held to be responsible for the disintegration. Since both the chemical reaction and the lowest freezing temperatures occurred at the surface of the concrete, this theory readily accounted for the disintegration starting at the surface.

More recently it has been found that scaling can be produced by the application of suitable solutions of anti-freeze chemicals like ethylene glycol and alcohol along with the usual cycles of freezing and thawing. Uric acid also produces scaling (3,16). These do not react with the hydrates of portland cement nor do they cause salts to be deposited from solution; hence their action casts considerable doubt upon the theories previously held. Furthermore, if chemical reaction of the applied salts with tri-calcium aluminate hydrate were involved, there should be a relationship between the rate of scaling and the C_3A content of the portland cement, but none such has been found to exist. One case of this kind of chemical reaction has been reported from Canada, but the conditions were unusual and did not involve freezing and thawing.

The bulk of the evidence now available points to internal hydraulic or osmotic pressures as the cause of the scaling or over-all concrete disintegration associated with freezing and thawing and/or the use of de-icing salts (5,6). When water in the pores of concrete freezes, expansion of the combined water-ice system occurs causing hydraulic pressures which can be relieved only by movement of the water from the point of ice formation to some point where empty air voids exist to accommodate the expelled water. These hydraulic pressures may exceed the strength of the cement paste causing localized failure and eventually, concrete disintegration.

When the freezable liquid is a salt solution, the hydraulic pressure developed by a given amount of ice formation may be 8-10 times as great as obtained with plain water, possibly as a result of selective adsorption. These greater hydraulic pressures with salt solutions are obviously concentrated in the surface concrete of a pavement slab being de-iced with salt. This plus the greater likelihood of freezing in the surface concrete is believed to account for scaling and progressive surface deterioration. In addition, there may be superimposed in the hydraulic pressures osmotic pressures resulting from local increases in salt solution concentration caused by separation of pure ice from the salt solution.

All these theories have certain points in common, namely, that internal pressures resulting from freezing of water in the concrete pores are responsible for deterioration of concrete if sufficient number of liquid-free air voids are not readily available to relieve these pressures. If the internal pressures exceed the strength of the concrete, rupture occurs locally and, if repeated over widespread areas, is followed by disintegration of the concrete. Since present-day thinking attributes scaling of concrete from de-icing salt application to essentially the same immediate causes as concrete disintegration resulting from plain freezing and thawing, it would appear that the function of silicone treatment of concrete pavements is to keep out water or salt solutions, either permanently or until the concrete has cured and aged to a point where it can absorb the internal pressures built up during wintertime freezing and thawing with salt application. On the latter premise is predicated the desirability of applying silicones to new concrete in freezing areas when pouring of the new concrete is not completed until late fall, and de-icing salts are used during the first winter.

FIELD AND LABORATORY EXPERIENCE

It is not within the scope of this paper to discuss in detail the field application and performance of silicones. This is much more capably handled by Harold Britton of the New York State Department of Public Works who discusses in his paper the relatively extensive use of water soluble silicones on the New York State Thruway and elsewhere (7,9). New York's experience with the water soluble types and the experience of other states, such as New Hampshire and Vermont, with solvent solutions of silicone resin indicates quite clearly that silicone treatment of highway and airport pavements can be a useful tool in prolonging the serviceable life of such concrete under normal conditions of freezing and thawing and de-icing salt application. However, silicone treatment is not a cure-all and is not a substitute for air entrainment, good mix design, and job control or the other factors which constitute good concrete practice.

Paramount in the minds of all engineers who must justify the expenditure of construction or maintenance funds is the question of how much good silicone treatment does, how long does it prolong serviceable life? Insufficient actual field experience is available to give a quantitative answer to this question. Furthermore, accurate field comparisons are difficult, if not impossible, to establish for obvious reasons. There are known cases, such as the New Hampshire Toll Road Plaza at Hampton now going into its fifth winter with silicone treatment, where scaling started but appears to have been arrested or minimized by silicone application. Based on the scaling which occurred during the first year before silicone treatment, it is estimated by New Hampshire engineers that the silicone treatment has been 90 percent effective. As in all such cases, it is impossible to know definitely what would have happened to this concrete in the subsequent years if silicone had not been applied.

Some quantitative information may be obtained by laboratory tests, although translating such test results into equivalent field performance may not be possible. For example, Figure 1 shows the results of 11 freeze-thaw cycles on non-air-entrained concrete pans, one of which has been surface treated with a solvent silicone solution (left) and the other has not. Specimens were fog room cured for 14 days before being subjected to freezing (-150 F) and thawing (73 F approximately). The freezing liquid was a

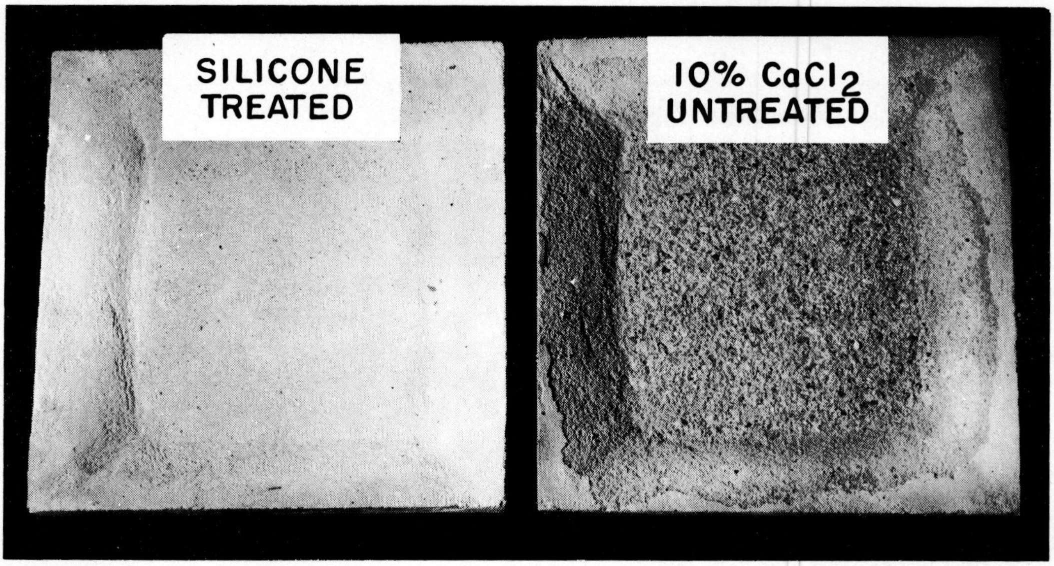

Figure 1. Silicone treated concrete (left) shows no scaling after 11 cycles of freezing and thawing in 10 percent $CaCl_2$ solution.

10 percent $CaCl_2$ solution which was continually in contact with the treated or untreated concrete surface. This plus the fact that a slow freeze-thaw cycle was involved, greatly increased the severity of the test. It will be noted that no scaling occurred on the silicone-treated surface whereas the untreated surface has scaled almost to the point of complete failure. Considerable substantiating laboratory data are available (8,10,11).

MECHANICS OF SILICONE PROTECTION

Where field performance is not of sufficient duration to show clearly the economic value of a process or treatment, it is sometimes helpful to consider the mechanism involved in order to gain a clearer insight into the potential value of the treatment. The following discussion of the theory and mechanism of water repellents and their application to concrete surfaces is given with this thought in mind.

Figure 2 shows the effect of silicone treatment on the water repellency of a 5 3/4 sack per yard concrete surface. The right third of the specimen is untreated and exhibits no water repellency, i.e. water wets the surface completely and shows a zero contact angle with the concrete. The center portion was treated with a rather dilute solvent silicone solution and shows only mild water repellency with a contact angle between the water and the concrete surface of less than 90 deg. The left portion was thoroughly saturated by means of a flooded-on brush application with a high solids silicone solution utilizing a penetrating type solvent as the vehicle. Here water repellency as demonstrated by beading effect is excellent, the contact angle in this case being greater than 90 deg.

Figure 3 shows more clearly how contact angle is measured (12). It is of interest to note that precise measurements of the contact angle between water and silicone-treated glass show much the same values as for water and paraffin wax, i.e. 100-110 deg. Paraffin wax, though lacking in

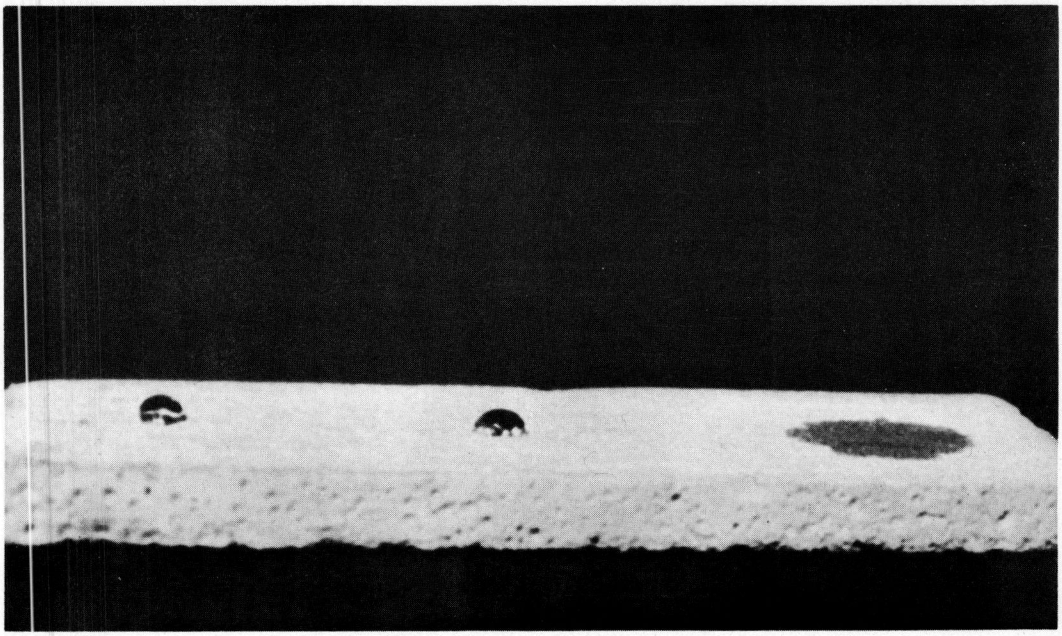

Figure 2. Beading effect and contact angle for various degrees of water repellency of concrete (right section has no repellency).

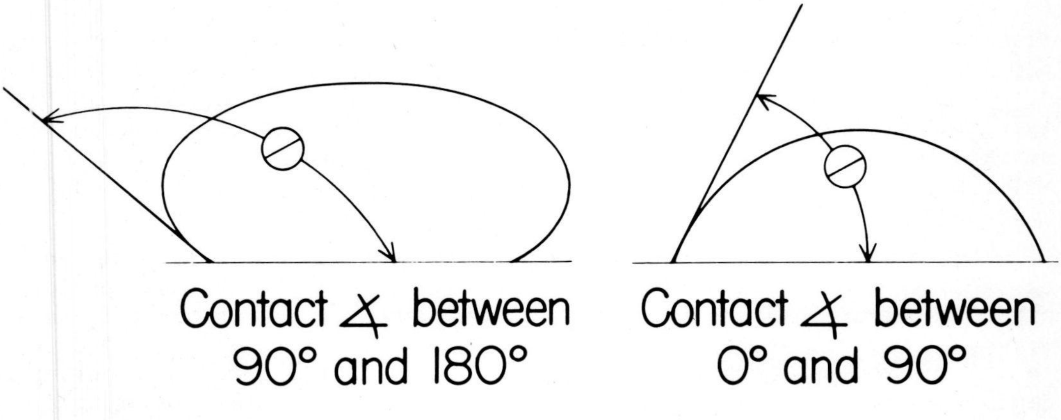

Figure 3. How contact angle is measured.

durability, has been accepted for years as an excellent water repellent. Contact angles for water on silicone treated concrete appear to be somewhat greater since an estimated angle of 135 deg was observed on a concrete beam used in tests described later in this paper to determine depth of penetration of the silicone treatment.

CAPILLARITY AND PENETRATION

What is the significance of contact angle with regard to penetrability of concrete by water (13)? Figure 4 shows a plain capillary glass tube

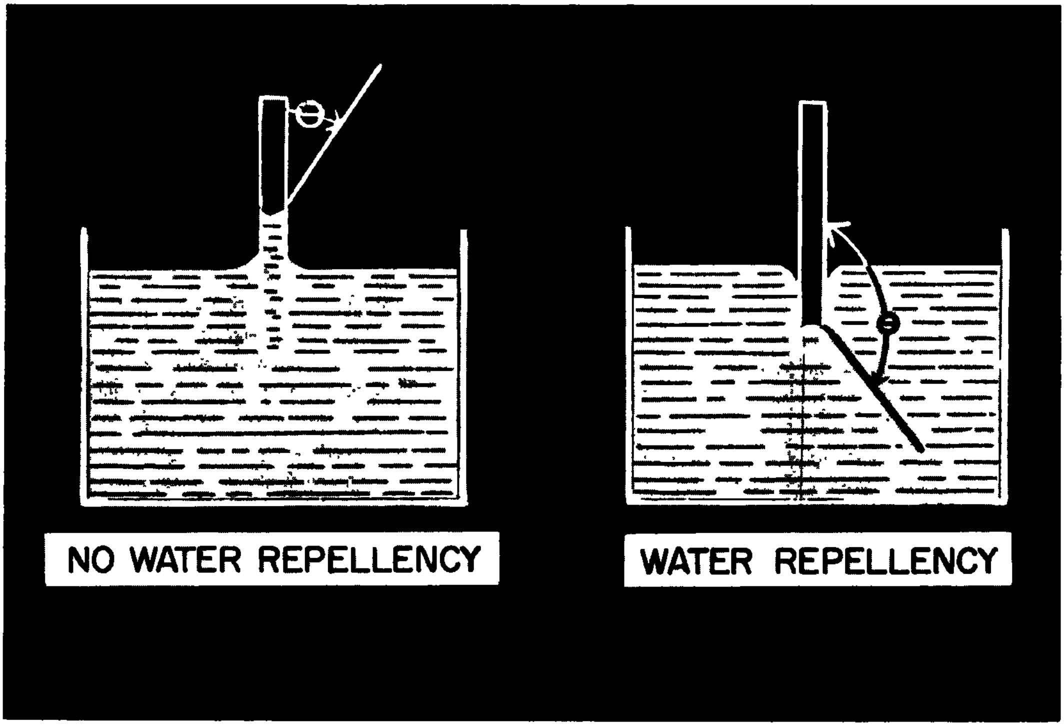

Figure 4. Effect of water repellency on capillary absorption of water.

(left), whose diameter is much greater than that of the normal capillary pores in concrete, partially immersed in plain water. Following the laws of physics, the liquid rises in the tube to a height which depends upon the capillary radius, the density of the liquid (in this case water), and surface tension of the water, and the angle of contact between glass and water at an air-water-glass interface. For pure water on a plane clean glass surface, the contact angle can be taken as zero.

If this glass tube is dried and then coated inside and out with a suitable silicone before insertion into the container of water, the level of the water in the tube is depressed below the surface of the main body of water, and the surface of the water in the tube will be concave down. In this case, the contact angle is between 90 and 180 deg, the exact angle depending on the effectiveness of the silicone coating as a water repellent for the solid surface involved. Also, the main water surface in contact with the outer surface of the tube is depressed.

The relationship between height of capillary rise and the other factors involved is given by a conventional formula to be found in any textbook on physical chemistry as follows (14):

$$h = \frac{\gamma \cdot 2 \cos \theta}{r\ g\ d}$$

where h = capillary rise
γ = surface tension
θ = contact angle
r = capillary diameter

g = gravitational constant
d = liquid density

It will be noted that when the contact angle is less than 90 deg, cosine θ is positive and capillary rise is positive, but when the contact angle is between 90 and 180 deg, cosine θ is negative, and capillary depression occurs instead of capillary rise. Since coating the surfaces of the capillary pores in concrete with a suitable silicone increases the contact angle between water and concrete to more than 90 deg, this analysis clearly depicts the mechanism by which silicone treatment prevents water or salt solution from entering the concrete pores.

SILICONE LINES CONCRETE PORES

Figures 5 and 6 show how the silicone molecule probably attaches itself to the surface of concrete pores. Figure 5 is believed to show the portion of the silicone molecule which is bonded to the surfaces of the concrete pores. Oxygen atoms are represented by blue, silicon by green, carbon by black, and hydrogen by orange. (In black and white reproduction, these colors appear as shades of gray; that is, black is black, orange is dark gray, blue is medium gray, and green is light gray.) Oxygen is believed to provide the chemical link or bond to the hydrated silicates of the cement paste; hence the silicone molecule probably orients itself as shown so as to form as many oxygen links as possible with the cement silicates.

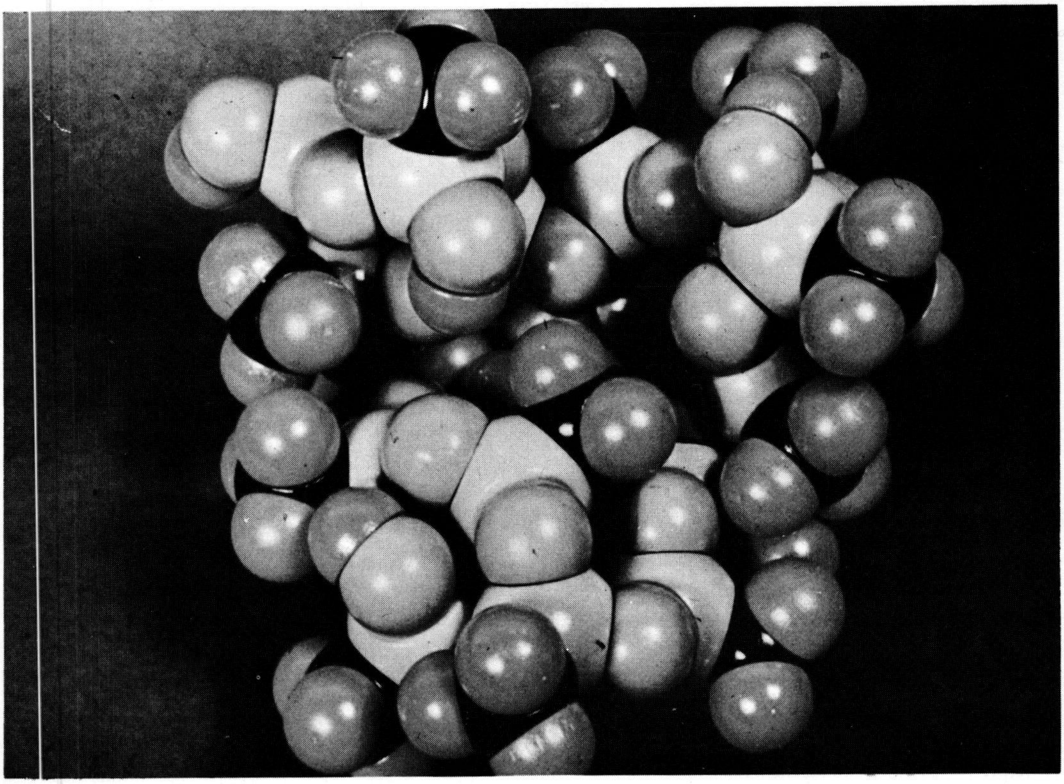

Figure 5. Silicone molecule - portion in contact with concrete.

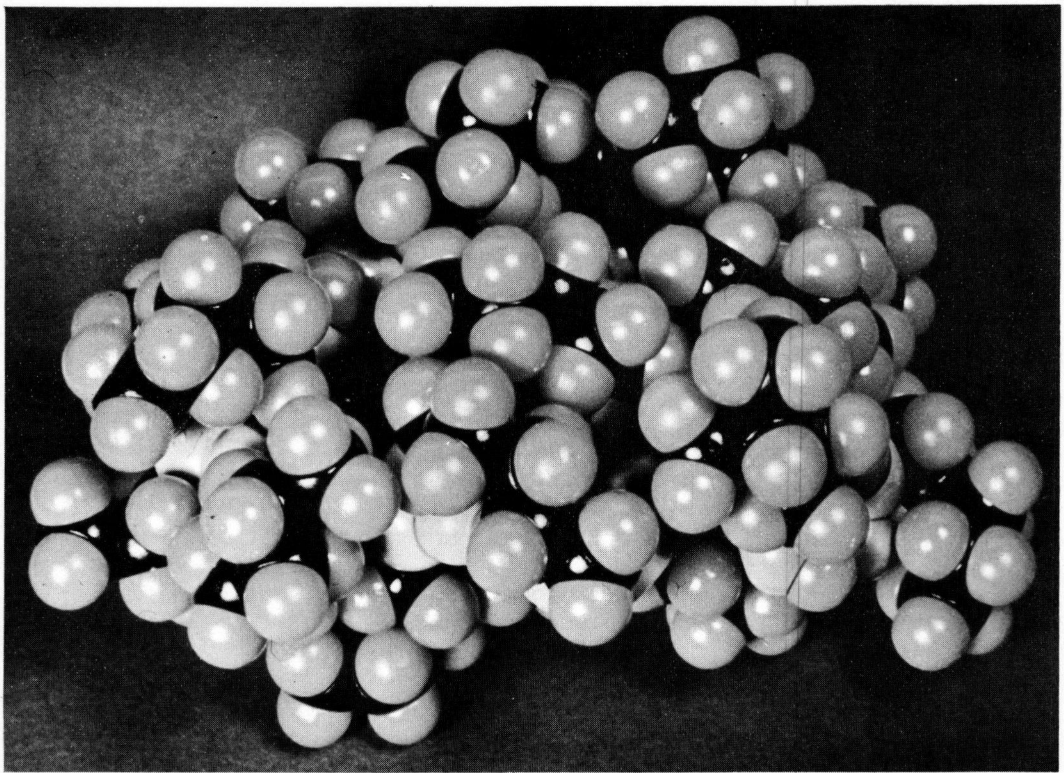

Figure 6. Silicone molecule - surface which repels water.

Figure 6 is believed to depict the silicone molecule when viewed from the center of the pore looking toward the pore surface. Note the concentration of hydrogen atoms at the surface of the molecule and the fact that groups of these atoms are associated with single carbon atoms. The hydrogen/carbon groups are the water repellency units. Their grouping is sometimes referred to as the "umbrella effect." These two excellent photographs were made available through the courtesy of the Union Carbide and Carbon Corporation, Silicones Division.

However, the lined pores are still open. Since the pores are not plugged or sealed, only the relatively small water repellency forces prevent water from entering. For this reason, silicone-coated concrete pores will not keep out water applied under large pressures. Consequently, some of the water or salt solution lying on the surface of a concrete pavement is, according to laboratory attempts to simulate this action, more than likely pushed into the pores of the concrete by the pressure of passing automobile or truck tires. However, the depth of penetrations of the salt solution will depend to some extent upon the depth of the silicone water repellency barrier, i.e. the depth to which the applied silicone has lined the concrete capillary pores. Field performance on the New Hampshire Toll Road indicates that such infiltration of the silicone treated concrete by salt solution under pressure was not enough to cause significant deterioration in the tire lanes; in fact, much of the slight deterioration observed there was confined to the gutters where salt concentration and continuity of immersion was greatest but tire traffic was least.

DEPTH OF PENETRATION

To check depth of penetrations for the two types of silicone solutions, $3\frac{1}{2}$- by 4- by 12-in. cured concrete beams were coated with a minimum 5 percent silicone solvent solution on one-half of their area and a 2 percent water soluble silicone solution on the other one-half. Masking tape was used to assure a reasonably sharp line of demarcation between the two types of silicone solution. Two brands of water soluble silicone water repellent were tested and two beams were made and treated for each condition of test. These beams were then broken in center loading and depth of silicone penetration checked by immersing a broken end in water and observing the depth of the unwetted area. Figure 7 shows typical depth of penetration of concrete cured for 24 hr under wet burlap and then 6 days under paper with a 3-hr drying period prior to silicone application. The top surface of the specimen on the left was wood floated (denoted by W) and the one on the right was steel trowelled (denoted by S). The concrete used was 5 3/4 sack mix with 3/4-in. maximum size aggregate.

It will be noted that depth of penetration was considerably greater for the solvent solution (left) than for the water soluble silicone resin (right) for both types of finishing. The difference in penetration is particularly marked on the sides of the beams where the thin residual film of form oil apparently seriously interfered with penetration of the water soluble type silicone. There seems to be no significant effect of method of finishing on penetration of the top surface by either silicone.

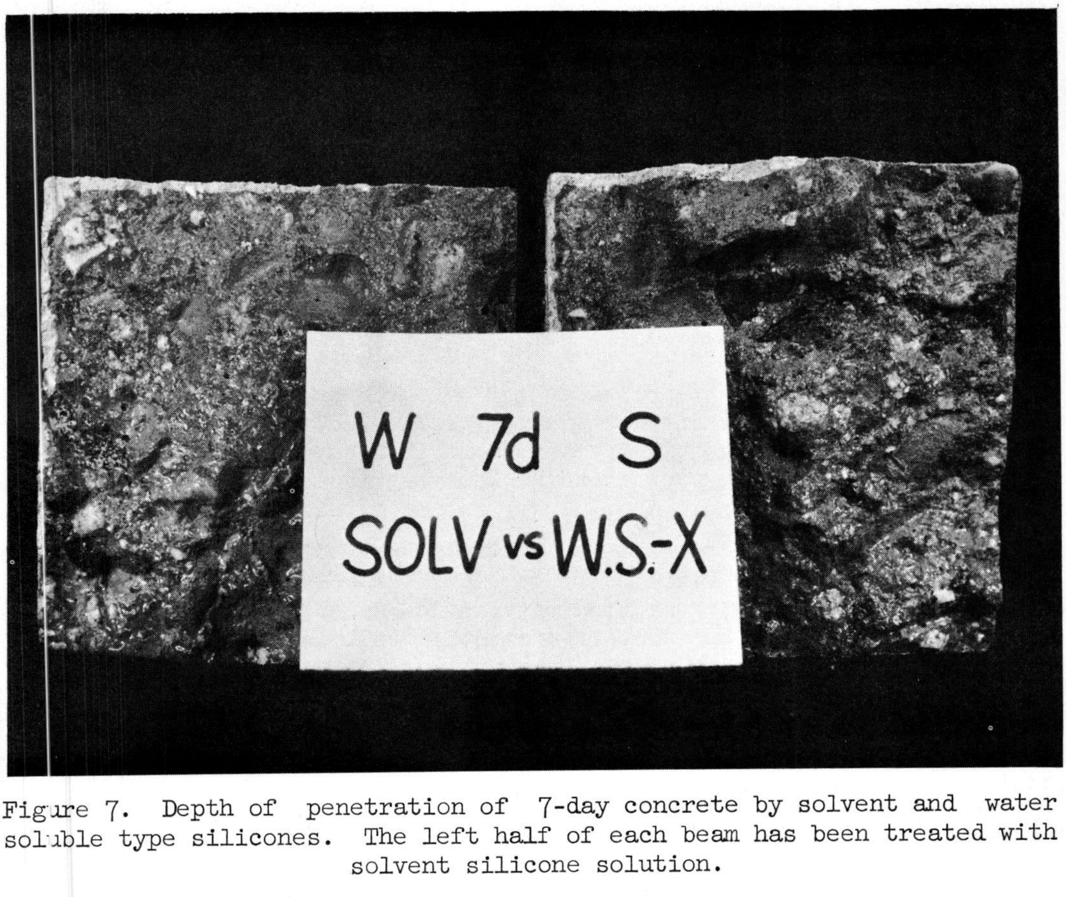

Figure 7. Depth of penetration of 7-day concrete by solvent and water soluble type silicones. The left half of each beam has been treated with solvent silicone solution.

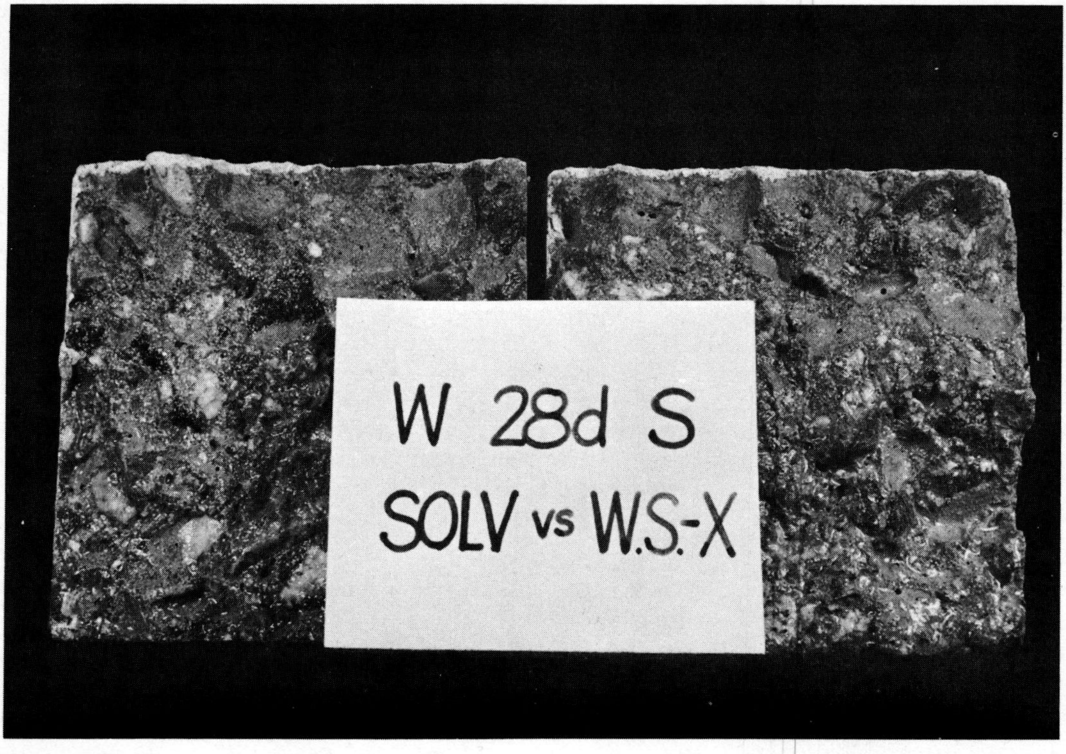

Figure 8. Same as Figure 7 except concrete cured 28 days. Left beam in both figures was wood floated; right beam steel trowelled.

Other beams were similarly treated but were cured for a total of 28 days before the 3-hr drying period. As shown by Figure 8, neither type silicone penetrated quite as deeply as in the case of 7-day curing, but penetration of the solvent type was again greater than that of the water soluble type and by approximately the same amount. At this curing age, the steel trowelled surfaces did not allow as much penetration as the wood-floated ones, possibly due to the greater density of the former. It is possible that the lesser depth of penetration for the 28-day cure was due to either carbonation or the greater surface area of the gel structure at that age. Selective adsorption of the silicone (not the vehicle) by either would have to be sufficiently great to more than compensate for the reduced diameter of the capillary pores of the concrete if lesser rather than greater penetration is to result from longer curing of concrete.

The differences in penetration shown for the solvent vs. the water solutions of silicone are believed to be significant from the point of view of depth of water or salt solution penetration under the pressure of tires. It also seems obvious that deeper penetration will mean longer lasting water repellency with wear of the pavement surface under the abrasive action of tires, chains, etc. It should be borne in mind that the penetration differences which are reported here were obtained under the stated finishing and curing conditions and do not necessarily apply to other conditions.

DISCUSSION AND CONCLUSIONS

The rather striking difference in depth of penetration reported here between the solvent and water soluble silicone solutions and the obvious importance of depth of penetration to effectiveness and life of the silicone treatment, emphasize the need for more work along these lines. Is there a difference between a broom finish and wood floated finish as regards depth of penetration? What effect will mechanical finishing have? How about wet burlap curing and ponding vs. paper curing? What effect does the degree of moisture saturation of the wearing surfaces concrete have on penetration?

Obviously a completely saturated concrete will not permit penetration of either the solvent or water soluble types since there can be no capillary flow or spread wetting into pores already filled with water. However, the lesser depth of penetration of the water soluble silicone shown in Figure 7 is not attributable to moisture content of the surface concrete since the 3-hr drying period following 6 days or paper curing was ample to permit effective application of the solvent solution. Hence it is surmised that selective adsorption of the silicone by one or more ingredients of the concrete or cement paste is limiting depth of penetration of the silicone resin, not only for the water soluble solution but also for the solvent solutions for which penetration of the solvent is believed to be greater than the water repellency barrier created by penetration of the solvent. If this surmise is correct, differences in silicone penetration may be attributable to variations in the selective adsorptivity of the silicone resins per se - the water soluble resin being a sodium resinate with a different molecular structure than the solvent type which is an unneutralized resin, either completely or partially condensed.

Despite the many questions which must yet be answered, the fact remains that silicone water repellents have established themselves as useful tools for the highway engineer in protecting new and old highway concrete. The extent to which they can and should be utilized depends to a large extent on their use cost, i.e. their material and application cost per year of serviceable life of the treated concrete. It is expected that average serviceable life, which is a function of the extension of the serviceable life of treated concrete over the untreated, will vary with the two basic types of silicone solutions and possibly even with the degree of polymerization of the basic resin used in solvent solutions. Further laboratory and field determinations of comparative depth of penetrations will aid in estimating the use costs for various silicones. However, field performance over a period of years is necessary to establish actual costs.

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