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Bulletin 197

Improving the Water Repellency Of Hardened Concrete

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Improving the Water Repellency Of Hardened Concrete

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Scaling Resistance of Concrete Improved Through Silicones

F. J. MARDULIER, Dewey and Almy Chemical Company
Division of W. R. Grace and Company

● 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 2½ 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

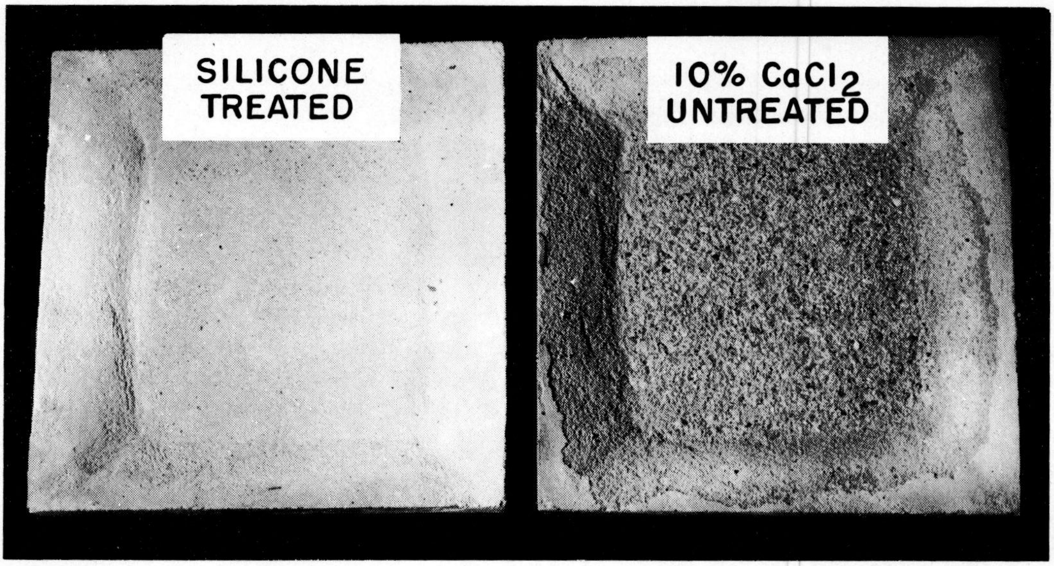

Figure 1. Silicone treated concrete (left) shows no scaling after 11 cycles of freezing and thawing in 10 percent $CaCl_2$ solution.

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

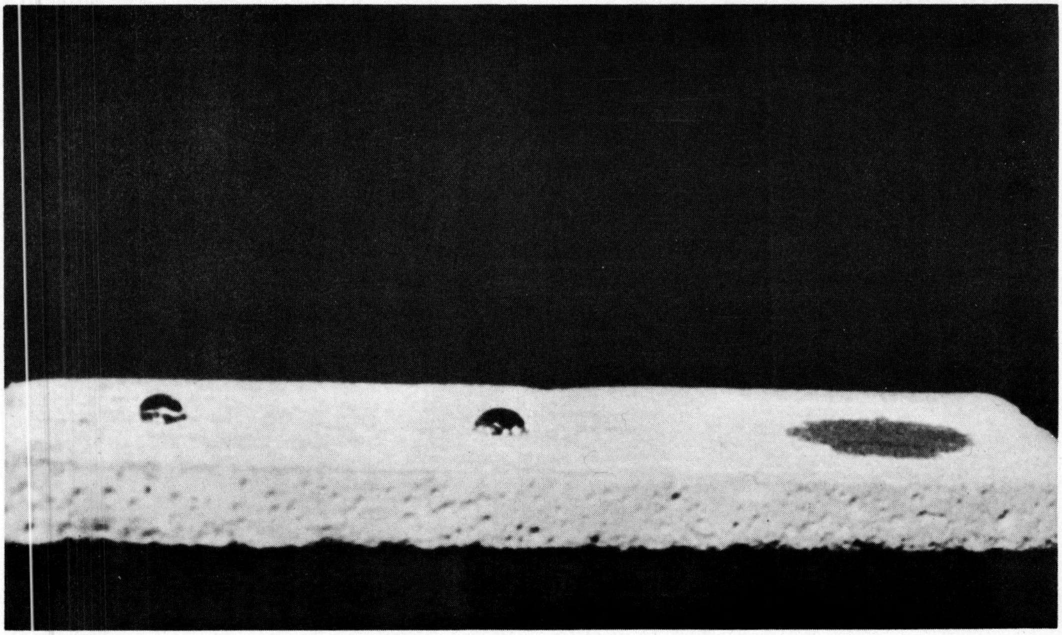

Figure 2. Beading effect and contact angle for various degrees of water repellency of concrete (right section has no repellency).

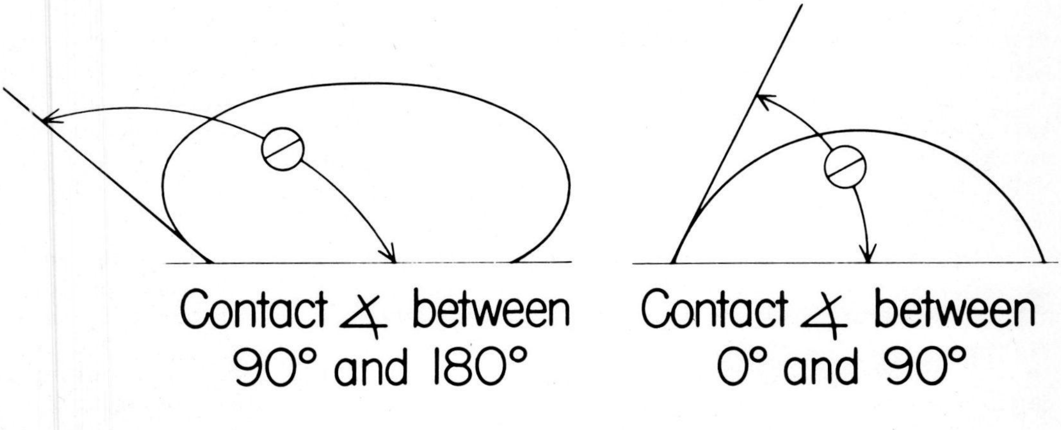

Figure 3. How contact angle is measured.

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

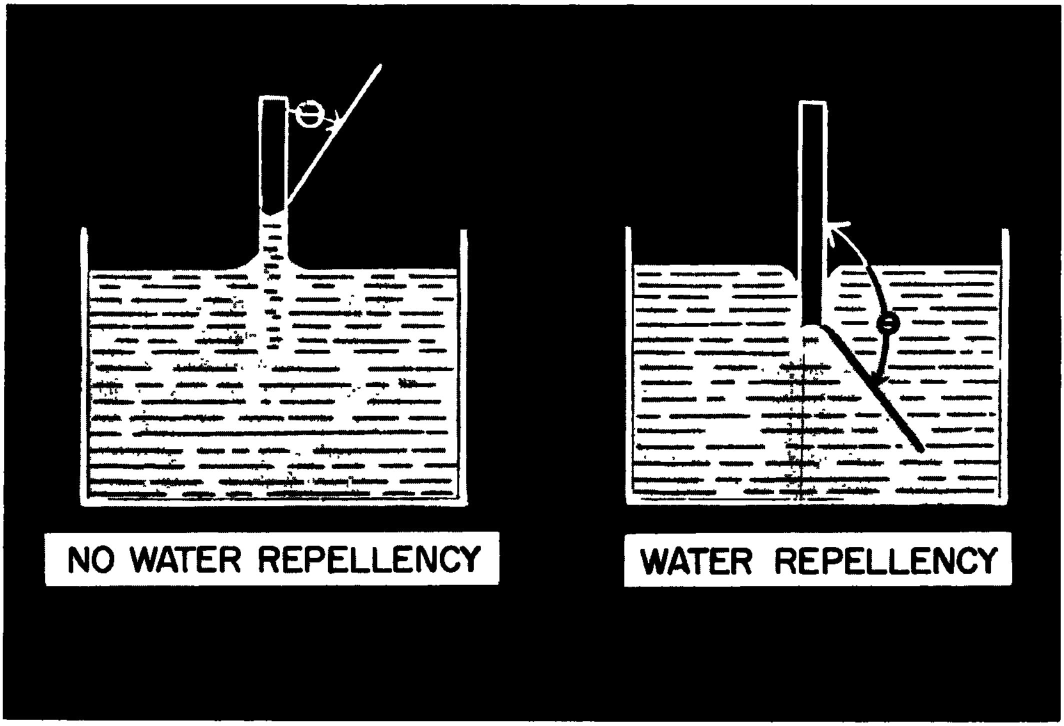

Figure 4. Effect of water repellency on capillary absorption of water.

(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.

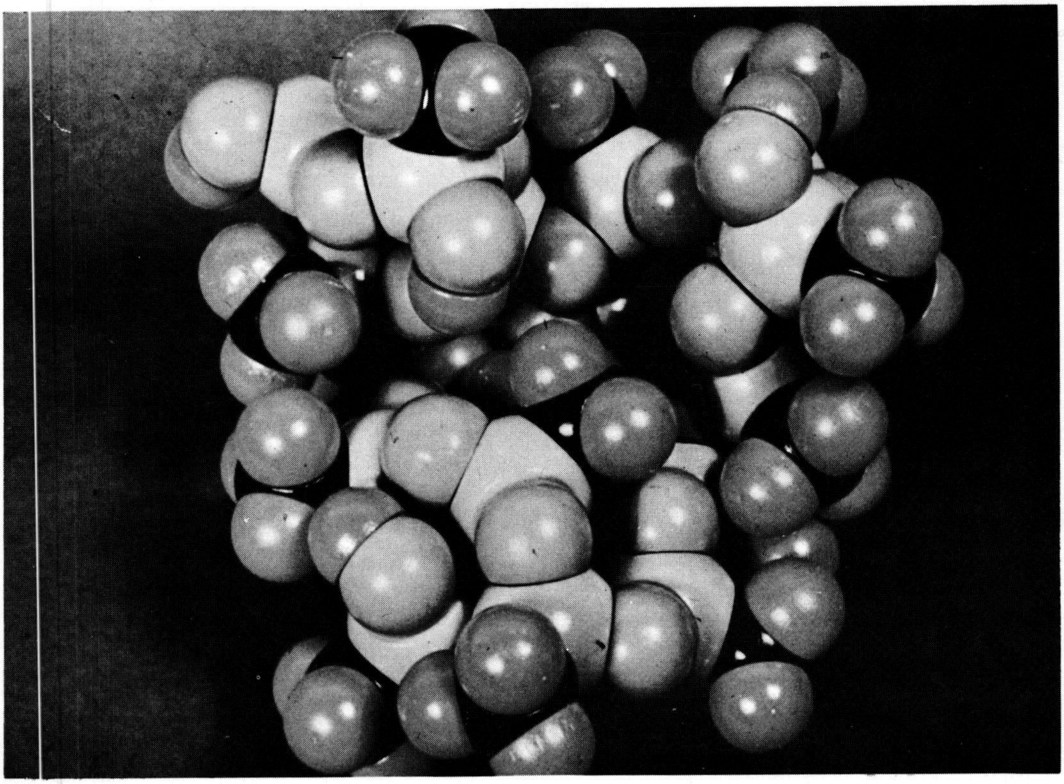

Figure 5. Silicone molecule - portion in contact with concrete.

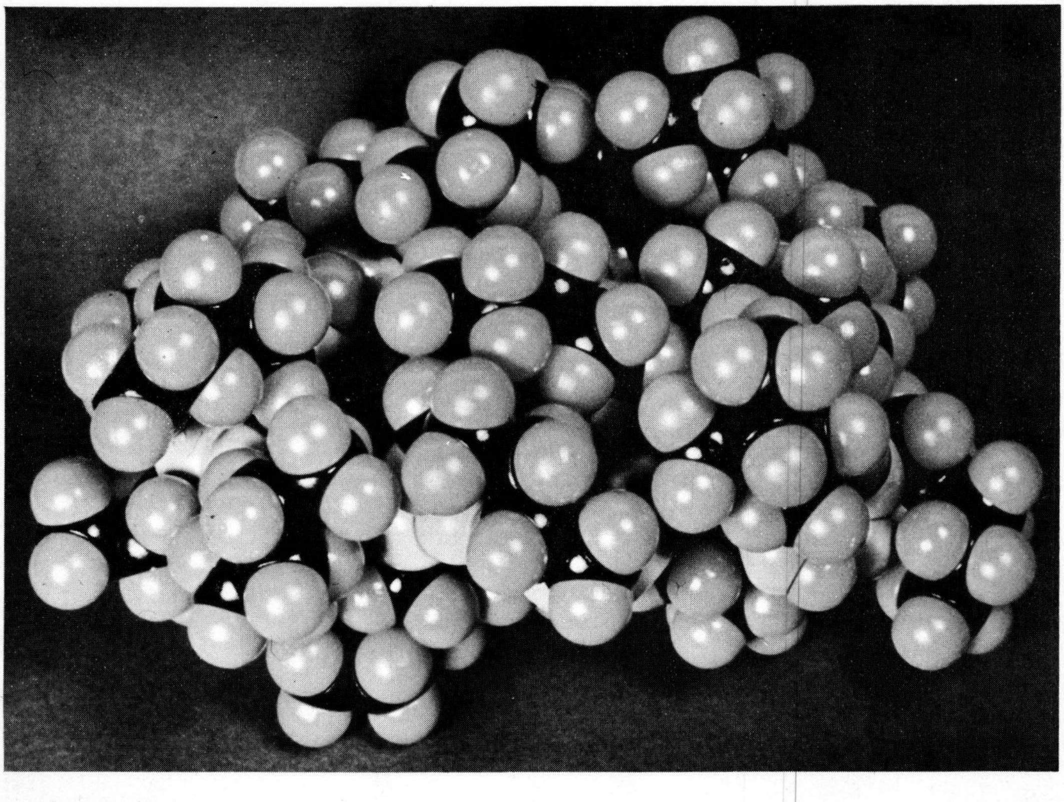

Figure 6. Silicone molecule - surface which repels water.

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.

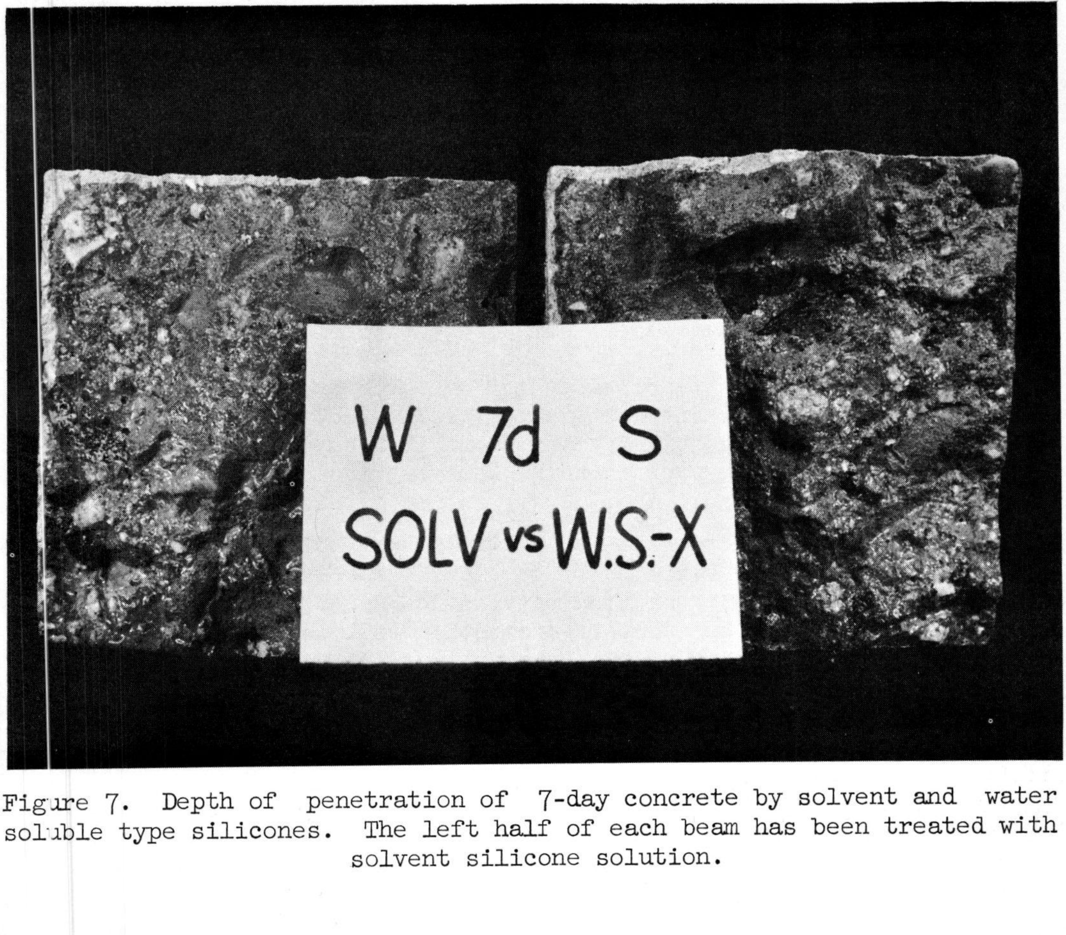

Figure 7. Depth of penetration of 7-day concrete by solvent and water soluble type silicones. The left half of each beam has been treated with solvent silicone solution.

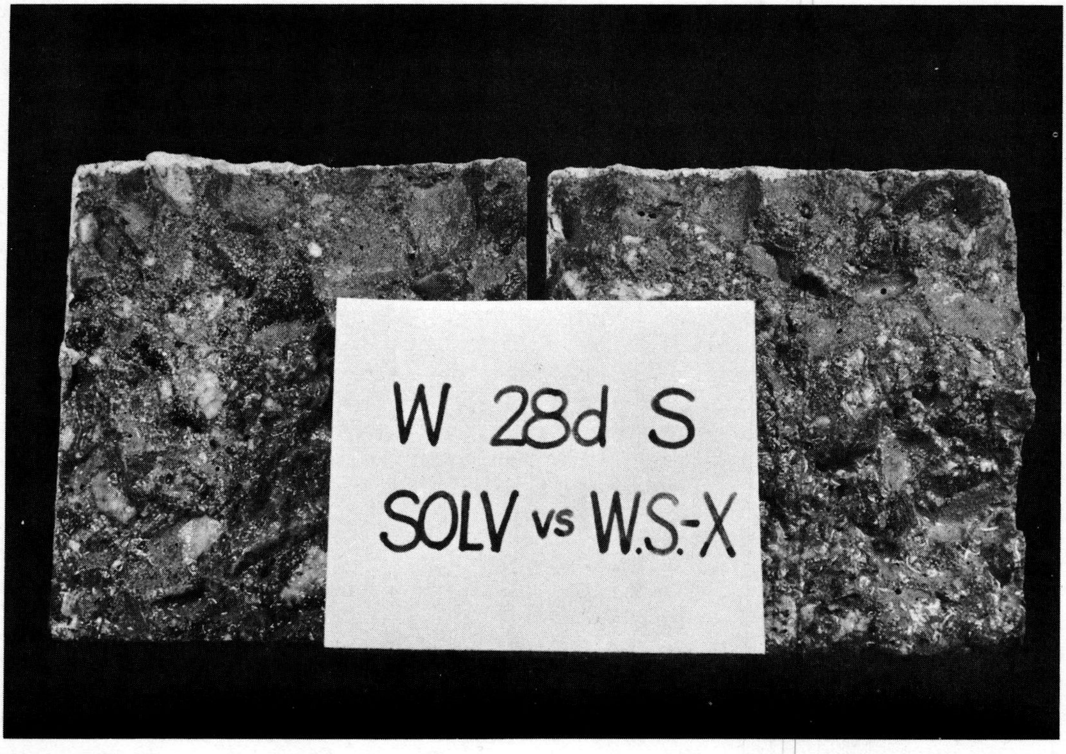

Figure 8. Same as Figure 7 except concrete cured 28 days. Left beam in both figures was wood floated; right beam steel trowelled.

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.

ACKNOWLEDGMENTS

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Grateful acknowledgment is also made to H. B. Britton of the New York State Department of Public Works and W. J. LeFleur with whom the writer was privileged to discuss field performance of silicone water repellents in New York.

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New York State's Experience in Use of Silicones

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The study of silicone treatment of concrete has been carried on by the New York State Department of Public Works since 1953. After determining that there might be merits in its use, a decision had to be made as to the type of silicone to use. For various reasons, the water soluble silicone was selected.

Then followed months of testing with various types of concrete mixes. This was necessary as the use of silicones prior to this time had been limited primarily to building materials. Testing methods were developed that would approximate field conditions applicable to bridge construction. Particular attention was given to rate of absorption of water, freezing and thawing, resistance to action of sodium chloride and light reflectance.

In 1954, field test experiments were made on 13 panels of the New York State Thruway. Silicone treatment of varying concentrations from one-half of 1 percent to 5 percent were placed on five panels. Six panels had no treatment and were used for control, and two panels were treated with a petroleum distillate.

A retreatment of the panels with a 2 percent silicone was made in November of 1956. The rate of application varied with the percentage of concentration in the original treatment, indicating a defense in depth after two years use.

The fascia and pier facings in the approaching lane of one structure over the New York State Thruway were treated for study of light reflectance on silicone treated concrete.

In June 1955 an interim specification was drawn for the use of water soluble silicone on all exposed concrete in new structures. This specification is now incorporated in the latest edition of the Public Works Specifications adopted January 2, 1957.

There are ten structures that have been completed utilizing water soluble silicone which have been opened to traffic for at least one winter season. Inspection of these structures in October of 1957 shows no deterioration or spalling of the concrete.

● THE SURFACE treatment of concrete by highway departments in an attempt to give it a protecting covering against the elements and thereby increase its durability is not new. Upon introduction to silicones in 1953, the New York State Department of Public Works became interested in the unusual possibility exhibited by this comparatively new product.

New York State's geographical location is such that there are widespread areas of the highway system that can expect to be subjected to as many as 75 freeze-thaw cycles, 80 wet-dry cycles together with 35 salt applications per year. This in the light of their effects upon concrete together with an expanded highway and bridge construction program pointed up the fact that building must be in a manner that would minimize future maintenance. These were the basic reasons why E. W. Wendell, then Deputy Chief Engineer (Bridges, Grade Separations and Structures) since retired, caused a study of silicone treatment for concrete to be inaugurated.

The first phase in this study was to evaluate the two types of silicones that were available, namely the water soluble and the solvent type. Consideration was given to the penetration, hazard and economy of each type.

Conditions involved in that initial study and the conclusions were as follows:

Penetration. Application of the silicone solution under construction conditions and schedules would most likely have to be made on moist concrete or at best surface dry concrete. It was felt that under these conditions the water soluble silicone solution would penetrate to a greater depth than the solvent type silicone solution. This is greatly due to the difference in the method of curing of the silicone materials. The water soluble silicone solution could penetrate a moist surface without resulting in a chemical reaction, whereas the solvent type silicone solution would tend to cure upon contact with the moist surface without penetrating.

Hazard. Recognizing the lack of controls on large highway and bridge construction projects the hazards involved in the use of the water soluble silicone which is very caustic and the solvent type silicone which is toxic, due to the large volume of solvent mist, had to be carefully studied. Water soluble silicone solution with a pH factor of 13 was considered to be less hazardous than the solvent type silicone solution containing Toluol with a flash point of 40 F or Xylol with a flash point of 75 F.

Economy. Recommendation of the manufacturers indicated that a two percent water soluble silicone solution would offer the same repellency as a five percent solvent type silicone solution and result in a considerable saving in the cost of the silicone solids. Furthermore, water being a prerequisite of a construction project, its availability and low or negligible cost in contrast to the cost of material, packaging and shipping charges of solvents indicated that the water soluble silicone would be the most economical.

Based on the advantages that accrue to the water base material after giving due consideration to all these factors; namely, penetration, hazard and economy, the water soluble silicone was selected for testing.

Since prior to this time the use of silicones in construction had been limited primarily to building materials, testing procedures would have to be developed that would approximate field conditions applicable to bridge construction.

The Silicone Products Department of the General Electric Company located at Waterford, N. Y., which is only 10 miles north of Albany, cooperated by making their laboratory and personnel available to the Department for any testing desired.

The first investigation was to attempt to determine the amount of penetration that could be expected with the water soluble silicone solution. Sample blocks 6- by $3\frac{1}{2}$- by $1\frac{1}{2}$-in. deep were made of both mortar and concrete. These blocks were immersed in a two percent water soluble silicone solution for six seconds, removed and let cure. The blocks were then broken and immersed in water, removed and the depth of the edges exhibiting evidence of no wetting were measured. The apparent penetration of the water soluble silicone solution into the mortar block averaged approximately $\frac{1}{4}$ in., while in the concrete block the measured penetration averaged approximately 1/8 in. The apparent difference in the depth of penetration is attributed to the fact that the coarse aggregate in the concrete blocks was topped by only 1/8 in. of cement matrix (Fig. 1).

A testing program using air-entrained concrete and non-air-entrained concrete was then set up. Sample blocks 6- by $3\frac{1}{2}$- by $1\frac{1}{2}$-in. deep would be molded so that a $\frac{1}{4}$-in. depression would be obtained in the top of the block, to permit the freezing of a layer of water. Untreated and treated blocks would be given identical tests. The two types of concrete sample blocks would be set up in three series; namely, untreated, oil treated in conformance with New York State Department of Public Works specifications and two percent water soluble silicone treated. The treated blocks were sprayed to simulate a field application.

Figure 1. Depth of penetration of silicone in mortar block on right and concrete block on left.

The General Electric Company constructed a rapid cycle freeze-thaw apparatus (6 cycles of freeze-thaw per day) and the conditions of the test were controlled as specified in ASTM Method C-291 with some exceptions. (One cycle out of six, the center of the block temperature did not reach 0 F and there was a 55-min delay before the frozen sample entered the 50 F water-thaw tank.) Both the treated and untreated blocks were mounted side by side on the endless belt of the apparatus and subjected to identical test conditions.

Typical data obtained from this test showed that non-air-entrained concrete blocks with no surface treatment or when treated with oil failed completely in from 35 to 40 cycles, whereas when treated with two percent silicone solution the blocks showed no failure and only slight surface scaling in 75 to 90 cycles (Fig. 2).

Air-entrained concrete blocks with no surface treatment or when treated with oil showed no failure and only moderate surface scaling after 90 cycles, whereas the silicone treated blocks showed no failure and practically no surface scaling after 90 cycles.

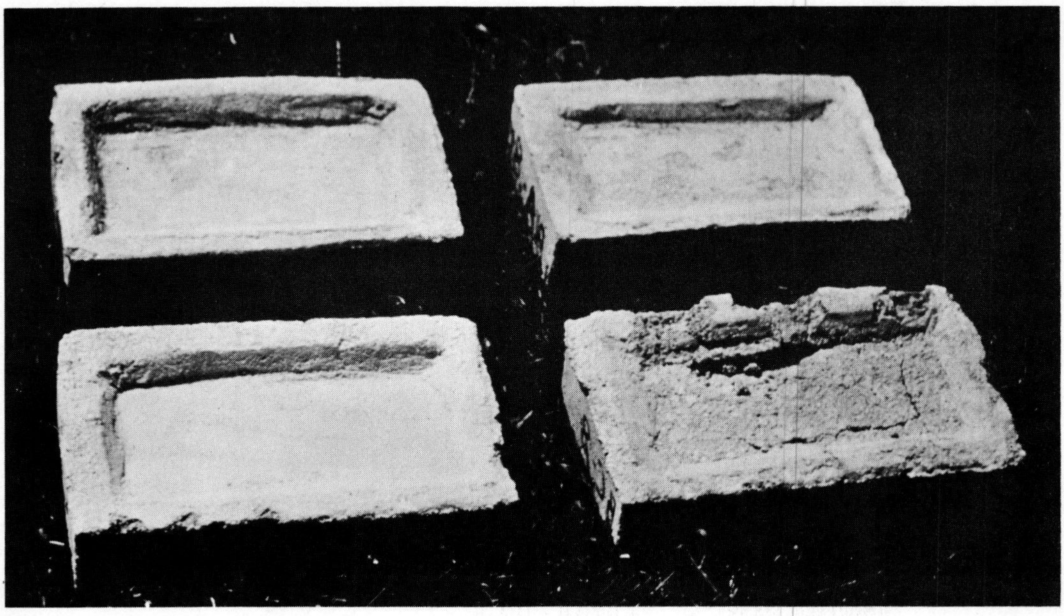


Figure 2. Effect of 35 cycles of freeze-thaw: upper blocks of air-entrained concrete, lower blocks of non-air-entrained concrete, blocks on left—silicone treated, blocks on right—untreated.

To simulate field conditions, rock salt was applied to frozen blocks of air-entrained concrete. Considerable surface scaling was noted on the untreated and oil treated blocks after 10 cycles, whereas there was no indication of any surface scaling of the silicone treated blocks after 20 cycles.

The results of these laboratory tests clearly indicated that portland cement concrete treated with silicone could be expected to exhibit superior durability.

Tests were then run on rate of water absorption of treated and untreated blocks. Blocks were selected which had been exposed to 25 freeze-thaw cycles, dried thoroughly, weighed, then placed in a tray having $\frac{1}{4}$ in. of water where they remained for 24 hr. The blocks were then wiped off and weighed again. The average absorption of untreated blocks was in excess of eight percent, whereas the average absorption of silicone treated blocks was less than $1\frac{1}{2}$ percent.

This indication that silicone treated concrete tended to repel the invasion of water prompted a request to the General Electric Company engineers to run tests on light reflectance of treated and untreated concrete. This was in recognition of the responsibility for providing the traveling public with the safest highway possible.

This resulted in laboratory measurements of light reflectance as well as some field measurements to determine what values of light reflectance existed.

Measurements were made on laboratory prepared concrete samples with laboratory test equipment and the results obtained indicated that the light reflectance of untreated concrete surfaces dropped from 35 percent

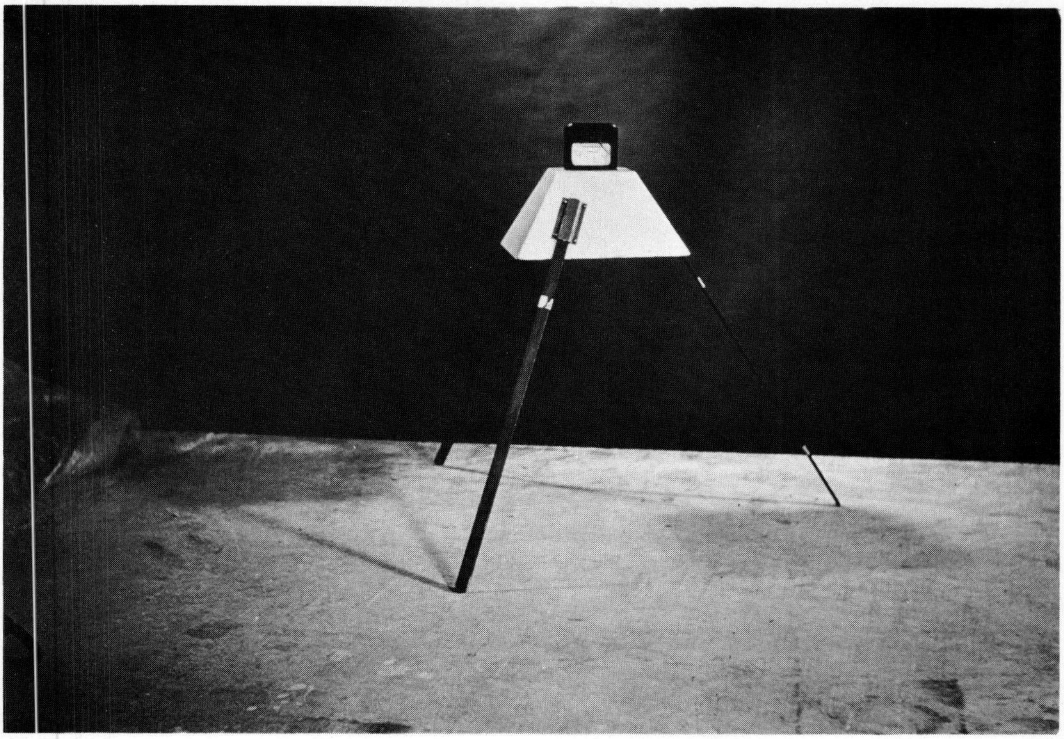


Figure 3. Apparatus for measuring light reflectance.

to 50 percent when they became wet, whereas the light reflectance of silicone treated concrete surfaces did not change appreciably when they became wet.

Readings were then made on untreated and treated outdoor concrete test panels, using a special reflectance standard and a foot candle meter as specified by the ASA Practice for Street and Highway Lighting.

Measurements were made using the method described on page 27 of Appendix C of the ASA Practice for Street and Highway Lighting, 1953. The 0- to 100-ft candlemeter, with a reduced aperture, was mounted on a tripod box (Fig. 3) and readings were taken over the various test areas. The reference standard (Reflectance Factor of 75 percent) was placed over the test areas and readings were recorded with the standard in place and with the concrete dry and wet (Figs. 4 and 5).

The 75 percent standard was used to calculate the reflectance levels of the various test areas and the average of the test results showed that the light reflectance value of the untreated panels was reduced 50 percent when wet, whereas the light reflectance value of the silicone treated panels was reduced only 13 percent when wet (Fig. 6).

In June 1955 the Deputy Chief Engineer (Bridges, Grade Separations and Structures), ordered an interim specification drawn for the use of water soluble silicone on all exposed concrete in new structures based upon the results obtained from the test program. This specification called for the dilute solution to contain two percent silicone and to be mixed by

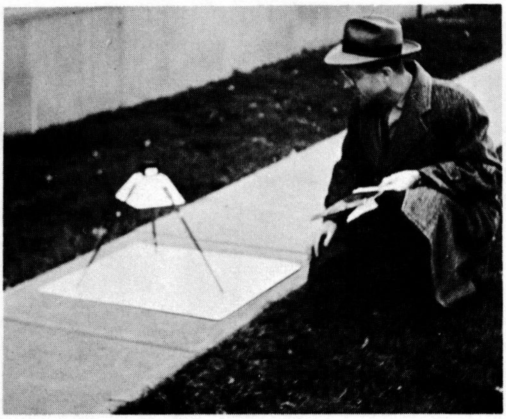


Figure 4. Measuring light reflectance—reference standard in place.

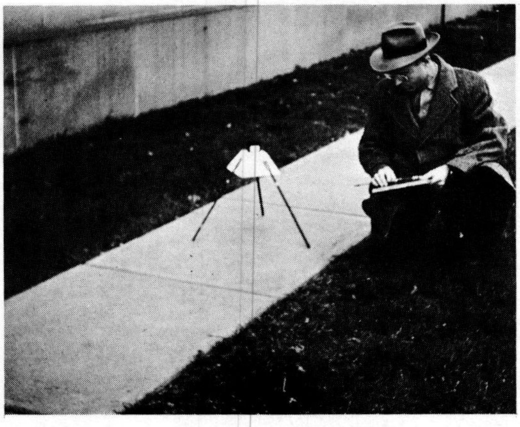


Figure 5. Measuring light reflectance—wet and dry treated and untreated concrete panels.

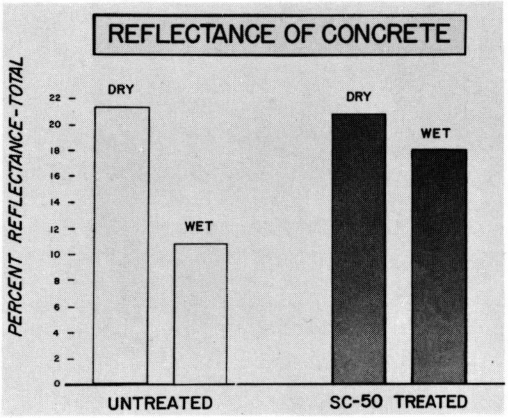


Figure 6.

weight 10 parts of silicone concentrate and 90 parts of water. In the revised specification the proportions are equated to gallons for ease of mixing in the field. To better insure field application and tp provide inspectors an opportunity to be sure that the silicone treatment had been accomplished, a fugitive dye (Phenolphthalein) was added to the silicone concentrate. The rate of application of the dilute solution is indicated as 12 square yards per gallon.

Since the interim specification for water soluble silicone was introduced in June 1955, there have been ten structures, completed and open to traffic for at least one winter season which had the silicone application. These structures are in various parts of the state and are therefore subject to varying weather conditions. Inspection of these structures in October 1957 showed the concrete to be in excellent condition with no deterioration or spalling evident except in one instance which makes for an interesting observation. It was noted on one structure that all the concrete with the exception of a section of the curb facing some 20 feet long was in perfect condition. The curb facing in this 20-ft section showed deterioration approximately 2 in. above the wearing course. Upon investigation it was learned that the bridge engineer responsible for the construction of this structure had been visited by a salesman who gave him a 5-gal sample of a product purported to be superior to the material called for in the specifications. The engineer allowed the application of this material in the area involved with the attendant result.

A field test program was instituted on a section of the New York State Thruway in the vicinity of Albany consisting of thirteen 100-ft slabs of the driving lane. The silicone concentration from one-half percent to five percent were applied to five slabs. One slab was treated with one-half-percent silicone solution, one slab a five-percent silicone solution and the other three slabs a two-percent silicone solution. The silicone was applied at the rate of 100 sq ft per gal. Six slabs received no treatment, two slabs were treated with colorless petroleum distillate oil compound.

This test was inaugurated on May 11, 1954 and it is believed to be the first such demonstration on new highway construction in the United States.

This section of the Thruway was opened to traffic in October of 1954. On November 16, 1956 a reapplication of a two-percent water-soluble silicone solution on the panels originally treated with silicone was made (Fig. 7). The rate of application on retreatment of the slabs having the original treatment of five-percent and two-percent silicone solution was 153 sq ft per gal or approximatelt one and one-half times the original rate of application.

This would appear to indicate that the original silicone treatment had established a defense in depth. There is also an indication that the five percent silicone solution had provided no more protection than the two percent silicone solution. The rate of application on retreatment of the slabs having original treatment of $\frac{1}{2}$ percent silicone solution was 100 sq ft per gal which was identical to the initial rate of application indicating that this concentration of silicone is not suitable for long service. The color of the silicone treated slabs in this test area when wet is much lighter than the untreated or oil treated slabs.

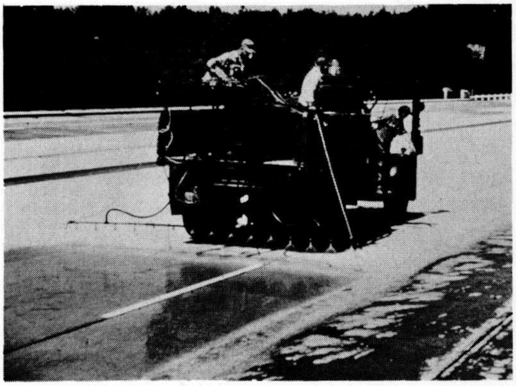


Figure 7. Equipment for spraying silicone solution on traveled way.

On November 16, 1956 the fascia and pier facing in the approaching lane of the Schenectady Interchange bridge over the Thruway were treated with a two-percent water-soluble silicone solution for a study in contrast of treated and untreated concrete during periods of wetting (Figs. 8 and 9). Figures 10 and 11 are pictures taken of this structure on November 28, 1957 after two days of rain. They clearly indicate that this kind of silicone application on structures of this type contribute greatly to the safety of the highway. Figure 12 illustrates the difficulty encountered in applying water-soluble silicone to the bridge pylon which has received a carborundum rubbed finish.

Products are discovered, developed, modified and improved as rapidly as research, time and money make it possible. Therefore, it is advisable that product users be kept informed of any developments by industry so that as materials or conditions change, the process of evaluation may be kept continuous.

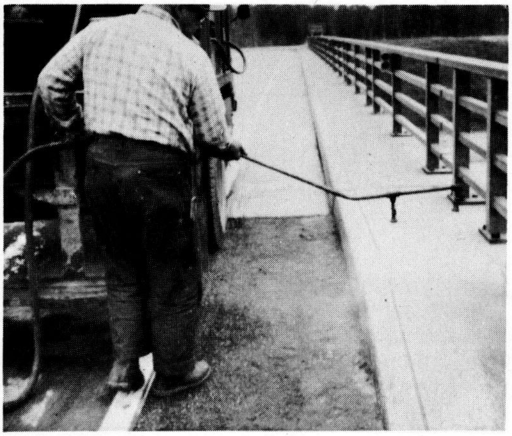


Figure 8. Equipment for spraying silicone solution on small areas and vertical surfaces.

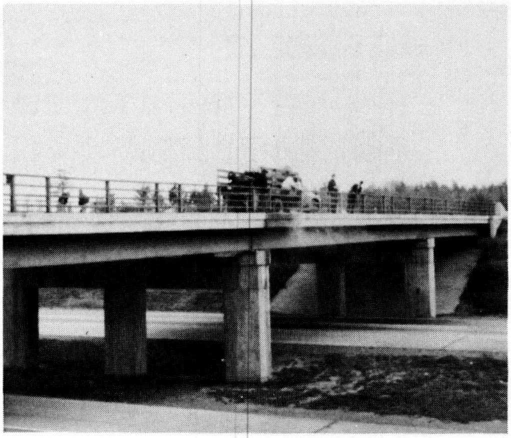


Figure 9. Treating fascia and pier facings of Schenectady Interchange bridge, November 16, 1956.

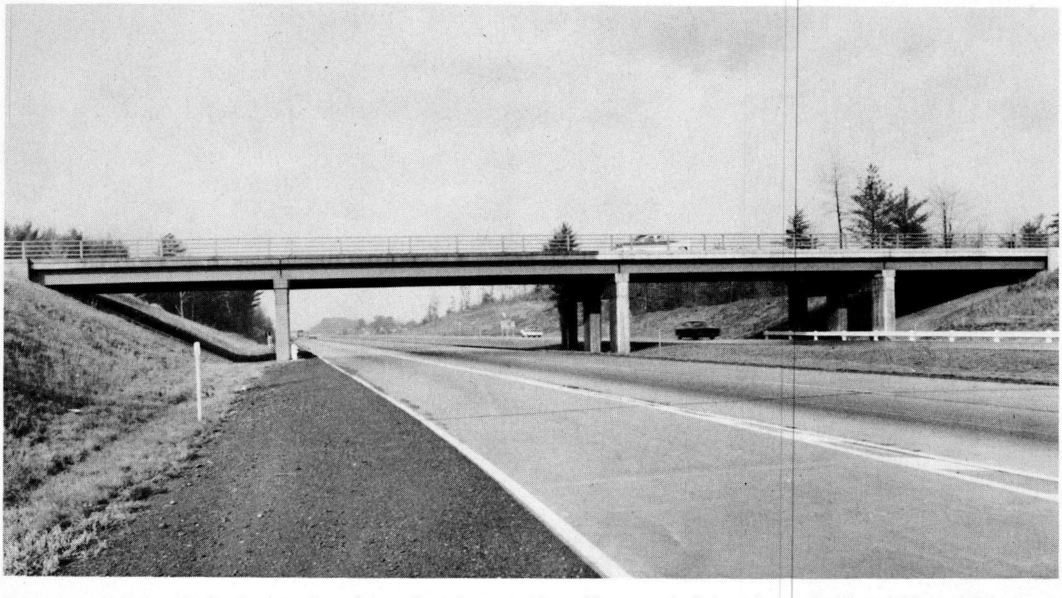


Figure 10. Fascia and pier facings to the right treated with silicone appears much lighter than the rest of the structural concrete (November 28, 1957).

There have been developments in the field of silicone chemistry since the first evaluation in 1953 and 1954. The solvent type silicone in particular shows the result of research in that higher polymer silicones are available today. There is an indication that a two percent solvent type silicone would offer the same repellency as the original five percent solvent type silicone. It would then appear that the cost of the silicone solids for either the water soluble or solvent type would be the same. Also the use of mineral spirits, with a flash point of from 110 F as sol-

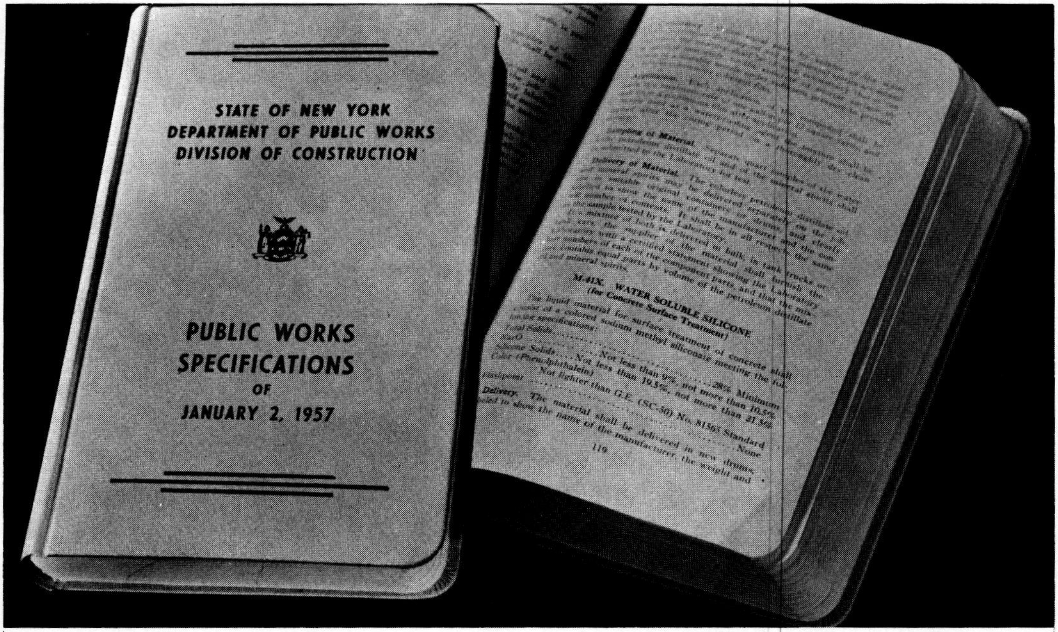
Figure 11. Close-up of pier facing and fascia (November 28, 1957).

Figure 12. Carborundum rubbed pylon exhibits very little benefit from treatment.

vents has removed the objectionable hazard that applied to the original solvent type silicone studied.

In July 1957, a test program was entered into with the Silicone Division of the Union Carbide Corporation in Tonawanda, New York, in order to evaluate solvent type silicones. The concrete used in this program conforms with the New York State Department of Public Works Specifications for structural concrete. Tests are being conducted on four types of concrete; namely, non-air-entrained, non-air entrained plus Plastiment, air-entrained and air-entrained plus Plastiment. This program has not been completed to date but the results that have been obtained are very encouraging.

In October 1957, a problem was confronted where all the prestressed units of several structures had been cured, contrary to specifications, with a wax-resin type curing compound. This, of course, made the application of the specified water soluble silicone impossible. It was necessary then to write an amending specification in which it was required that the surface treated with the curing compound be abraded with power driven wire brushes, blown clean and a two percent solvent type silicone be applied.



STATE OF NEW YORK
DEPARTMENT OF PUBLIC WORKS
DIVISION OF CONSTRUCTION

PUBLIC WORKS
SPECIFICATIONS
OF
JANUARY 2, 1957

M-41X. WATER SOLUBLE SILICONE
(for Concrete Surface Treatment)

The liquid material for surface treatment of concrete shall consist of a colored sodium methyl siliconate meeting the following specifications:

Total Solids	28% Minimum
Na_2O	Not less than 9%, not more than 10.5%
Silicone Solids	Not less than 19.5%, not more than 21.5%
Color (Phenolphthalein)	Not lighter than G.E. (SC-50) No. 81565 Standard
Flashpoint	None

Delivery. The material shall be delivered in new drums, led to show the name of the manufacturer, the weight and

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Figure 13. Material specification as included in the construction specifications of the New York State Department of Public Works.

On November 11, 1957 the first such treatment was applied. The rate of application was approximately 100 sq ft per gal. The temperature at the time of application was 18 F.

It is the opinion that the durability of concrete can be greatly increased if given a surface treatment of silicone. Tests and experience clearly prove that any concrete treated with silicone will give better performance in that it will absorb less moisture, demonstrate greater light reflectance, repel intrusion of deleterious salt solutions and demonstrate a greater resistance to freeze-thaw action.

For the reasons enumerated the Water Soluble Silicone specification has been incorporated in the Construction Specifications that were approved January 2, 1957 (Fig. 13).

ACKNOWLEDGMENTS

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