Silicone Influence on Concrete Resistance to Freeze-Thaw and De-Icer Damage

PAUL KLIEGER, and WILLIAM PERENCHIO, respectively, Manager, Field Research Section, and Associate Research Engineer, Applied Research Section, Research and Development Laboratories, Portland Cement Association, Skokie, Ill.

This paper presents the results of a comprehensive laboratory study on the effect of various silicones, used as surface treatment or as integral admixture, on the resistance of concrete to freezing and thawing and de-icer scaling. Various types of non-air-entrained and air concretes were used.

Results indicate that the surface silicone treatments resulted in lower resistance to freezing and thawing and to de-icer scaling, particularly for the non-air-entrained concretes and the concretes with an inadequate amount of intentionally entrained air. Although applications of silicone surface treatments reduced the initial rate of absorption of water, on continued immersion for periods ranging from 7 to 14 days, the total absorptions for treated and untreated concretes were essentially identical.

These studies indicate that the use of silicones for treatment of horizontal concrete surfaces such as pavement slabs or bridge decks may be detrimental rather than beneficial with regard to resistance to freezing and thawing and de-icer scaling. The most effective means for insuring such durability was to provide an adequate amount and character of entrained air in a concrete of relatively low water-cement ratio.

Silicone as an integral admixture appeared of little benefit in the performance of the non-air-entrained concretes. Vertical surfaces of air-entrained concretes were treated with silicones and then subjected to freezing in air and thawing in air with intermittent water spraying. These showed a reduced tendency to wet; however, both treated and untreated vertical surfaces showed excellent resistance to this type of exposure.

• THE USE of chemical de-icers on pavements, bridge decks, and similar elements has resulted in a marked contrast between the performance of concretes containing intentionally entrained air adequate in amount and character and the performance of those without intentionally entrained air. In the absence of entrained air, the use of chemical de-icers will result in a progressive surface deterioration (scaling). Laboratory and field studies and field performance records have clearly demonstrated that surface scaling caused by chemical de-icers can be eliminated by using intentionally entrained air and adhering to other requirements for quality concrete.

In those cases where entrained air had not been provided, or the amount provided was inadequate, the use of silicone surface treatments has been suggested to avoid the development of surface scaling (1, 2).

This study was started in 1958 to evaluate the effectiveness of surface treatment by silicone solutions with respect to both de-icer scaling and resistance to freezing and thawing in the presence of water.

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TABLE 1

OXIDE AND COMPOUND COMPOSITION OF TYPE I BLEND,[a] LOT 19741

Component	% by Wt.
Major:	
SiO_2	20.97
Al_2O_3	5.78
Fe_2O_3	2.92
Total CaO	62.96
MgO	2.60
SO_3	2.37
Ignition loss	1.28
Minor:	
Mn_2O_3	0.26
Free CaO	0.97
Insoluble residue	0.20
Alkali:	
Na_2O	0.22
K_2O	0.63
Total as Na_2O	0.63
Calculated potential composition:	
C_3S	43.2
C_2S	27.6
C_3A	10.4
C_4AF	8.9
$CaSO_4$	4.0
Free CaO	0.97

[a] A blend of equal parts by weight of four Type I cements; chemical analyses made in accordance with ASTM C114-58T; correction for free CaO made for potential compound composition calculation.

TEST PROGRAM

Surface scaling tests and freezing and thawing tests were conducted in the laboratory on both non-air-entrained and air-entrained concretes. Two water-cement ratios were used— one typical of high-quality paving concrete, the other considerably higher. Companion specimens were given surface treatments of water silicone solutions and mineral solvent silicone solutions, each at two concentrations of silicone solids. Tests on untreated specimens and on specimens treated with boiled linseed oil were included.

Specimens were prepared and treated for exposure outdoors, adjacent to the PCA Laboratories at Skokie, Ill. These were subjected to applications of de-icer during the winter months to melt snow and ice accumulating on their surfaces.

The effectiveness of the silicone treatment on vertical, exposed concrete surfaces subjected to freezing and thawing both in the laboratory and outdoors was also studied. In addition, a water silicone solution was used in different concentrations as an integral admixture to evaluate the effect of such an addition on durability.

Materials

The cement used in these tests was a blend prepared from four different brands of Type I cement purchased in the Chicago area. Tables 1 and 2 give the chemical composition, calculated potential compound composition, and the results of various physical tests of the cement blend and of pastes and mortars made with this cement. A natural sand from Elgin, Ill., was used as the fine aggregate. A crushed gravel from Eau Claire, Wis., typical of sound, durable coarse aggregate commonly used in concrete pavement construction, was used as the coarse aggregate in these tests. Table 3 gives data on their grading, specific gravity, and absorption properties.

Aggregates were air dried and screened into various size fractions—six sizes for the fine aggregate and three sizes for the coarse aggregate. During batching, the sizes were recombined to yield the gradings given in Table 3. Aggregates were weighed in the air-dried condition (moisture content known) and, 18 to 20 hr before use, inundated with a known amount of water. Before mixing, excess water was drawn off and weighed to permit calculating the net water-cement ratios.

For those mixes containing intentionally entrained air, neutralized Vinsol resin solution was added at the mixer as the air-entraining admixture.

Three different silicone solutions were used:

1. Brand A.—A mineral spirit (petroleum thinner) solution of silicone used at two concentrations of silicone solids (2% and 5% by weight).
2. Brand B.—A mineral spirit solution of silicone used at two concentrations of silicone solids (3% and 5% by weight).
3. Brand C.—A water solution of silicones used at two concentrations of silicone solids (3% and 5% by weight).

TABLE 2

PHYSICAL TESTS[a] OF CEMENT BLEND AND MORTARS—LOT 19741

Test Type	Property	Value
Cement	Specific surface (cm^2/g):	
	Wagner	1,725
	Blaine	3,360
	Passing No. 325 mesh (%)	92.5
	Specific gravity	3.16
	Normal consistency (%)	26.0
	Time of setting, Gillmore (hr:min):	
	Initial	4:40
	Final	7:10
	Autoclave expansion (%)	0.11
	Air content, 1:4 mortar (%)	11.2
Mortar strength	Tensile (C190 briquets) (psi)	
	3 days	305
	7 days	420
	28 days	415
	Compress. (C109 cubes) (psi)	
	3 days	2,590
	7 days	3,450
	28 days	4,900

[a]Made in accordance with ASTM methods of tests current May 1959.

TABLE 3

AGGREGATE DATA

Aggregate Type	Source	Fineness Modulus	Bulk Spec. Gravity[a]	24-Hr Absorp. (% by wt.)	Grading	
					Sieve Size	% Retained
Natural sand	Elgin, Ill.	2.90	2.65	2.25	No. 4	0
					No. 8	18
					No. 16	33
					No. 30	57
					No. 50	87
					No. 100	95
Crushed gravel	Eau Claire, Wis.	---	2.69	1.33	1½-in.	0
					1-in.	---
					¾-in.	25
					⅜-in.	70
					No. 4	100
Combined	---	---	2.69	1.33	1½-in.	0
					1-in.	---
					¾-in.	50
					⅜-in.	75
					No. 4	100

[a]Saturated, surface dry.

TABLE 4

CONCRETE CHARACTERISTICS[a]

Mix No.	Cement Content (bags/cu yd)	Net W/C (gal/bag)	Slump (in.)	Net Air Content (% pressure)	28-Day Comp. Str.[b] (psi)
3	6.02	4.67	2.3	1.60	6,360
4	6.00	4.49	2.6	5.15	5,370
5	4.07	7.20	2.3	2.40	3,350
6	4.10	6.46	2.6	5.25	3,510

[a]Cement Type I laboratory blend, Lot 19741; aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel (1-in. maximum size); air-entraining admixture of neutralized Vinsol resin added at mixer to entrain 5 ± ½% air. Cylinders cured moist at 73 ± 3 F and 100% relative humidity.

[b]6- by 12-in. cylinder.

The lower concentration of silicone solids was that recommended by the manufacturer for each of the brands.

Two coats of boiled linseed oil were applied—the first coat was 50 percent linseed oil plus 50 percent mineral spirits; the second, 100 percent boiled linseed oil.

In addition, companion specimens were treated with applications of 100 percent mineral spirits and 100 percent water, each applied in the same manner and at the same time as the silicone solutions.

The de-icer used in these tests was commercial flake calcium chloride.

Concrete Mixtures

Concretes had cement contents of 4 or 6 bags per cu yd and a slump of 2 to 3 in. Non-air-entrained and air-entrained concretes were prepared for each cement content. The air contents for the air-entrained concretes ranged from 5 to 6 percent. The maximum size of aggregate used was 1 in. for the specimens tested in the laboratory and 1½ in. for those in outdoor exposure. Data on the concretes are given in Table 4.

Fabrication of Specimens

Materials, equipment, and the mixing room were maintained at 73.4 ± 3 F. The relative humidity of the mixing room was maintained at 50 percent. Batches were mixed for 2½ min in a 1¾-cu ft open-tub mixer. For the major portion of the work, a slump test and an air content determination by the pressure method were made on three of six like batches. For each concrete mixture, six batches were prepared, two on each of three successive days. The two batches on each day comprising one round contained sufficient concrete to make ten 3- by 6- by 15-in. slabs, ten 3- by 3- by 11¼-in. prisms, and one 6- by 12-in. cylinder. Thus, for each concrete mixture 30 slabs, 30 prisms, and 3 cylinders were fabricated. All specimens were cast in watertight steel molds. Compaction was attained by hand rodding in accordance with ASTM practice. Slab surfaces were struck off and finished with a cork float. Approximately 3 hr after casting, a rich, air-entrained mortar dike was cast around the edges of the finished slab surface.

Curing Conditions and Surface Treatment

After 24 hr in the molds, during which time they were protected from drying by damp burlap covers, the slabs and prisms were cured in a moist room at 73.4 ± 3 F and 100 percent relative humidity for 13 days, followed by 14 days in air at the same temperature and 50 percent relative humidity. Slabs were then stored in air for an additional three days with a ¼-in. layer of water on the top surface. Prisms were

immersed in water during this 3-day period. Cylinders were cured continuously moist until the age of 28 days.

On the seventh day of the 14-day drying period, those slabs and prisms designated for surface treatment were given applications by flooding the surface and brushing (Table 5). All materials and specimens were at 73 F during treatment.

TABLE 5

SURFACE TREATMENTS

Surface Treatment			Specimen No. in Each Round
Type	% Solids	Sq Ft per Gal	
None	---	---	1
Silicone A	2	100	2
	5	100	3
Silicone B	3	100	4
	5	100	5
Silicone C	3	100	6
	5	100	7
Linseed oil	---	450[a]	8
		600[b]	8
Mineral spirits	---	100	9
Water	---	100	10

[a]First coat: $\frac{1}{2}$ linseed oil + $\frac{1}{2}$ mineral spirits.
[b]Second coat: 100% linseed oil.

Testing Procedure

The 6- by 12-in. cylinders were tested in compression at the age of 28 days.

The slab specimens were used to evaluate the resistance of the surface to de-icer scaling. The top surface (6 by 15 in.) was covered with a ¼-in. layer of water retained by the mortar dikes. This water and the slab were frozen in a room maintained at 0 F and thawed at approximately 70 F. At the start of the thawing portion of the cycle, flake calcium chloride was applied to the ice in an amount equivalent to 2.4 lb per sq yd of surface area, the amount used in all earlier standard laboratory tests of resistance to de-icer scaling. The slabs were subjected to one cycle of this procedure each day of the week. Visual examination at regular periods determined the amount of scaling, and numerical ratings were assigned as follows:

TABLE 6

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement (bags per cu yd)	Surface Treatment			Absorption (% by weight)									
				Non-Air-Entrained Cement					Air-Entrained Cement				
	Type	Solvent	% Solids	5 Min	6 Hr	1 Day	2 Days	3 Days	5 Min	6 Hr	1 Day	2 Days	3 Days
6	None	---	---	0.3	0.8	1.0	1.2	1.2	0.4	1.0	1.2	1.3	1.4
	Silicone A	Mineral	2	0	0.4	0.7	0.9	0.1	0	0.4	0.7	0.9	1.0
			5	0	0.2	0.4	0.6	0.7	0	0.2	0.5	0.6	0.7
	Silicone B	Mineral	3	0	0.2	0.6	0.8	0.9	0	0.3	0.7	0.9	1.0
			5	0	0.1	0.4	0.6	0.7	0	0.2	0.4	0.6	0.8
	Silicone	Water	3	0	0.3	0.7	0.9	1.1	0	0.4	0.7	1.0	1.2
			5	0	0.2	0.5	0.8	1.0	0	0.3	0.6	0.9	1.1
	Linseed oil[b]	---	---	0	0.2	0.4	0.4	0.5	0	0.2	0.4	0.5	0.6
	Mineral spirits[c]	---	---	0.3	0.8	1.0	1.2	1.2	0.3	0.9	1.1	1.2	1.3
	Water[c]	---	---	0.3	0.8	1.0	1.2	1.2	0.3	0.9	1.1	1.3	1.3
4	None	---	---	0.5	1.8	2.3	2.5	2.6	0.6	1.6	2.1	2.3	2.3
	Silicone A	Mineral	2	0.1	0.7	1.3	1.6	1.8	0.1	0.8	1.4	1.7	1.9
			5	0.1	0.3	0.6	0.9	1.0	0	0.4	0.7	1.0	1.2
	Silicone B	Mineral	3	0.1	0.4	0.9	1.2	1.5	0	0.5	1.0	1.3	1.6
			5	0.1	0.3	0.6	0.9	1.2	0	0.3	0.7	1.0	1.2
	Silicone C	Water	3	0.1	0.4	0.9	1.4	1.9	0	0.4	1.0	1.6	2.1
			5	0.1	0.4	0.9	1.4	1.9	0.1	0.4	1.0	1.6	2.0
	Linseed oil[b]	---	---	0.2	0.6	1.1	1.4	1.6	0.1	0.5	1.0	1.2	1.4
	Mineral spirits[c]	---	---	0.5	1.8	2.3	2.4	2.5	0.4	1.6	2.0	2.2	2.3
	Water[c]	---	---	0.6	1.8	2.2	2.4	2.5	0.5	1.7	2.0	2.2	2.3

[a]3-day immersion period.
[b]Two coats.
[c]100%; same coverage rates as for silicone solutions.

TABLE 7

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement		Surface Treatment			Absorption (% by weight)							
Bags per Cu Yd	Type	Silicone	Solvent	% Solids	5 Min	6 Hr	1 Day	3 Days	7 Days	14 Days	4 Weeks	42 Weeks
6	Non-air-entr.	None	---	---	0.4	1.0	1.2	1.3	1.4	1.5	1.6	1.8
		B	Mineral	3	0	0.3	0.7	1.1	1.3	1.5	1.6	1.9
				5	0	0.3	0.6	0.9	1.2	1.4	1.5	1.9
		C	Water	3	0	0.4	0.8	1.3	1.4	1.6	1.7	1.9
				5	0.1	0.3	0.7	1.2	1.4	1.5	1.7	1.9
	Air-entr.	None	---	---	0.4	1.0	1.2	1.4	1.5	1.6	1.7	2.0
		B	Mineral	3	0	0.4	0.8	1.1	1.4	1.5	1.7	2.2
				5	0	0.4	0.6	1.0	1.2	1.4	1.5	2.1
		C	Water	3	0	0.4	0.9	1.2	1.5	1.6	1.8	2.1
				5	0.1	0.4	0.8	1.2	1.4	1.6	1.8	2.2
4	Non-air-entr.	None	---	---	0.7	2.0	2.3	2.6	2.8	3.0	3.0	3.1
		B	Mineral	3	0.1	0.4	0.8	1.7	2.6	3.0	3.1	3.3
				5	0	0.3	0.7	1.4	2.4	3.0	3.1	3.4
			Water	3	0	0.5	1.3	2.6	3.1	3.2	3.2	3.4
				5	0	0.4	1.0	2.3	2.9	3.0	3.0	3.2
	Air-entr.	None	---	---	0.6	1.9	2.3	2.6	2.8	2.8	2.9	3.2
		B	Mineral	3	0	0.4	1.0	1.9	2.6	2.8	2.9	3.2
				5	0	0.3	0.7	1.5	2.4	2.6	2.8	3.1
			Water	3	0.1	0.6	1.6	2.6	2.9	3.0	3.1	3.3
				5	0.1	0.6	1.2	2.4	2.8	2.9	3.0	3.2

[a]42-week immersion period.

0 = no scale.
1 = slight scale.
2 = slight to moderate scale.
3 = moderate scale.
4 = moderate to heavy scale.
5 = heavy scale.

The concrete prisms were used to determine the rate of absorption during the 3-day immersion period before the start of the freezing and thawing tests. The rates were determined by weighing the specimens after the following immersion periods: 0, 5, 15, and 30 min, 1, 3, 6, 24, 48, and 72 hr. At the end of the 3-day immersion period, the prisms were frozen and thawed while immersed in water. Two complete cycles of freezing and thawing were obtained each day. The minimum specimen temperature attained was approximately -10 F and the maximum was approximately +55 F. Rate of cooling was about 20 F per hr. At regular periods during the test, determinations were made of changes in length, weight, and fundamental frequency of transverse vibration (sonic modulus, ASTM C 215). This freezing and thawing test procedure produces results comparable to those obtained by the procedure outlined in ASTM C 290, "Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water." Changes in fundamental transverse frequency are presented as durability factors, calculated as shown in C 290 for an endpoint of 300 cycles or the number of cycles for the ratio of the square of the frequency to reach 60 percent, whichever is reached first. The larger the numerical value of DF, the greater the potential durability. Durability factors below about 65 are indicative of poor resistance to freezing and thawing under these test conditions.

RESULTS

Influence of Treatment on Absorption

Table 6 gives the absorptions of concrete prisms with and without the various surface treatments which were determined during the 3-day immersion period immediately before the start of the freezing and thawing tests. Although the surface treatments effectively reduce the absorption during the early hours of immersion, with continued

TABLE 8

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement		Surface Treatment			Absorption at End of Immersion Period (% by weight)								
Bags per Cu Yd	Type	Silicone	Solvent	% Solids	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	5th Cycle	6th Cycle	7th Cycle	8th Cycle	9th Cycle
6	Non-air-entr.	None	---	---	1.4	1.4	1.3	1.4	1.4	1.5	1.5	1.5	1.4
		B	Mineral	3	1.2	1.2	1.2	1.1	1.2	1.4	1.4	1.4	1.4
				5	1.2	1.1	1.1	1.0	1.0	1.4	1.4	1.4	1.4
		C	Water	3	1.4	1.4	1.4	1.3	1.3	1.5	1.4	1.4	1.4
				5	1.4	1.4	1.4	1.3	1.3	1.5	1.5	1.4	1.4
	Air-entr.	None	---	---	1.5	1.5	1.4	1.4	1.4	1.6	1.6	1.5	1.5
		B	Mineral	3	1.4	1.4	1.4	1.4	1.4	1.7	1.7	1.6	1.6
				5	1.2	1.2	1.1	1.1	1.1	1.5	1.5	1.4	1.5
		C	Water	3	1.5	1.5	1.6	1.5	1.5	1.7	1.6	1.6	1.6
				5	1.4	1.4	1.4	1.4	1.4	1.6	1.5	1.5	1.5
4	Non-air-entr.	None	---	---	2.8	2.8	2.8	2.8	2.8	3.0	3.0	3.0	3.0
		B	Mineral	3	2.5	2.6	2.4	2.5	2.6	3.0	3.1	3.1	3.2
				5	2.1	2.0	1.8	1.9	2.0	2.9	3.0	3.1	3.2
		C	Water	3	3.0	2.9	2.9	2.9	2.9	3.1	3.1	3.0	3.1
				5	3.0	2.9	3.0	3.0	3.0	3.1	3.1	3.1	3.1
	Air-entr.	None	---	---	2.6	2.6	2.6	2.6	2.6	2.9	2.9	2.9	2.9
		B	Mineral	3	2.5	2.5	2.4	2.4	2.4	2.9	2.9	2.9	3.0
				5	2.2	2.0	1.8	1.9	2.0	2.8	2.9	3.0	3.0
		C	Water	3	2.7	2.6	2.6	2.7	2.7	2.9	2.9	2.9	2.9
				5	2.8	2.8	2.8	2.8	2.8	3.0	3.0	3.0	3.0

[a]Alternate immersion and drying periods: first 5 cycles, 7 days in water followed by 7 days in air; last 4 cycles, 28 days in water followed by 28 days in air.

immersion, the absorptions approach those for the uncoated concretes. This is particularly true for the silicone solutions.

These results prompted a repetition of a portion of the tests to provide information on absorption beyond the 3-day period, because horizontal surfaces of pavements and bridge decks may be covered with water or de-icer solution for considerable periods of time during the winter. Prisms were fabricated using concretes essentially identical to the mixtures given in Table 4. Silicones B and C, each at the 3 and 5 percent silicone solids concentrations, were applied to the surfaces in the manner previously described. One set was used for determining absorption during continuous immersion for as long as 42 weeks; a duplicate set was used to determine the influence of alternate periods of immersion and drying on absorption.

Table 7 gives the absorption results for various periods up to 42 weeks of immersion. At 7 to 14 days, the absorptions are essentially equal, regardless of surface treatment and remain so until the end of the period shown.

Table 8 gives the absorptions at the end of the immersion period portion of a number of alternate cycles of wetting and drying. Absorptions at the end of each immersion period following a drying period are essentially equal, and the absorption during each of the immersion periods followed the pattern given in Table 7. During the drying periods, the rate of water loss was the same for the control and treated concretes at each cement content.

Since performing these absorption tests to evaluate the influence of immersion time, a reference (3) to similar work was found which indicated that, although there were differences in absorption initially, with continued immersion the absorption of silicone-coated and uncoated concretes was essentially identical.

Influence of Treatment on Resistance to Freezing and Thawing in Water

The durability factors for the concrete prisms frozen and thawed while immersed in water are given in Table 9. The durability factors for all the non-air-entrained concretes were low, and differences caused by either the various silicone treatments or the linseed oil application were of little practical significance. The durability factors for all the air-entrained concretes were high (none less than 95); again, there would

TABLE 9

FREEZING AND THAWING TESTS OF CONCRETES[a], DURABILITY FACTORS[b]

Surface Treatment			Durability Factor[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	20	103	17	104
Silicone A	Mineral	2	12	98	10	101
		5	12	98	13	99
Silicone B	Mineral	3	13	99	13	102
		5	13	97	12	100
Silicone C	Water	3	15	98	15	99
		5	15	100	17	100
Linseed oil[d]	---	---	14	95	14	97
Mineral spirits[e]	---	---	15	100	19	103
Water[e]	---	---	18	101	28	105

[a]Specimens 3- by 3- by 11¼-in. prisms.
[b]Results are average of tests of three specimens.
[c]Based on 300 cycles or 60% relative dynamic E, whichever was reached first.
[d]Two coats.
[e]100%, same coverage rate as for silicone solutions.

appear to be little influence of surface treatment. However, for both types of concrete, the durability factors for the surface-treated concretes were always slightly lower than for the untreated or control concretes. Those concretes treated with 100 percent mineral spirits or water can also be considered as control concretes. These treatments were added to see whether the silicone vehicle (that is, mineral spirits or water) would have any influence on the durabilities.

The expansion data in Figure 1 lead to conclusions similar to those based on durability factor. Table 10 gives the changes in weight of these concretes during the freezing and thawing tests. In general, specimens treated with silicone solutions showed greater weight loss than untreated specimens, particularly for the 4-bag mix. The linseed oil treatment, however, appeared somewhat beneficial with respect to weight loss.

It appears, therefore, that concretes frozen and thawed while immersed in water are not benefited by surface applications of silicone solutions; in fact, their use may be detrimental to the performance of non-air-entrained concretes. This applies also to the linseed oil treatment; however, this treatment did reduce weight loss during freezing and thawing.

Influence of Treatment on Resistance to De-Icer Scaling

The results of the de-icer scaling tests are given in Table 11. The non-air-entrained concrete slabs treated with silicone solutions generally reached a rating of 5 (heavy scaling) sooner than the control concretes. For the 6-bag non-air-entrained concretes, the average number of cycles for the three controls (uncoated, mineral spirits, and water) to reach a rating of 5 was 117 cycles, whereas the average for all silicone-

TABLE 10

FREEZING AND THAWING TESTS OF CONCRETES[a], WEIGHT CHANGES[b]

Surface Treatment			Weight Change (%)[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	+0.2	+0.1	- 5.1	-3.4
Silicone A	Mineral	2	-0.3	-0.3	-10.9	-5.7
		5	0	-1.5	-10.7	-7.5
Silicone B	Mineral	3	-0.2	-0.2	-10.9	-4.4
		5	-0.4	-0.9	-12.2	-4.0
Silicone C	Water	3	-0.3	-0.6	- 9.2	-5.3
		5	-0.4	-0.9	- 7.5	-4.8
Linseed oil[d]	---	---	+0.9	-0.1	- 2.4	-4.8
Mineral spirits[e]	---	---	-0.3	+0.4	- 6.3	-1.5
Water[e]	---	---	-0.5	+0.3	- 4.8	-1.8

[a]Specimens 3- by 3- by 11¼-in. prisms.
[b]Results are averages of tests of three specimens.
[c]At 100 cycles for non-air-entrained concretes; at 300 cycles for air-entrained concretes.
[d]Two coats.
[e]100%, same coverage rate as for silicone solutions.

treated specimens was 84. Similarly, for the 4-bag non-air-entrained concretes, the average for the controls was 85 cycles and for the silicone-treated specimens 60 cycles. The linseed oil-coated specimens performed better than the silicone-treated ones, particularly for the 6-bag non-air-entrained concretes which failed by general deterioration rather than by de-icer scaling.

For the air-entrained concretes, the 6-bag concretes appeared relatively unaffected by the surface treatments; that is, the resistances were all at a sufficiently high level by virtue of such qualities as adequate air entrainment and low water-cement ratio. For the 4-bag air-entrained-concretes, however, the mineral spirit silicone solutions resulted in a lower resistance to de-icer scaling, with one exception at a 5 percent silicone solids concentration. The water solution of silicone, however, showed no detrimental influence. For both the 6-bag and the 4-bag air-entrained concretes the linseed oil application appeared beneficial.

The ineffectiveness of silicone treatments in providing protection for non-air-entrained concretes against damage from freezing and thawing and de-icer scaling in the field has been reported recently (4). The beneficial effect of linseed oil, a treatment in use for some time, was described recently by Finney (5).

Effect of Silicone Surface Treatment on Concrete Containing Less Than Recommended Air Content

In a series of preliminary tests, concretes having a cement content of 6 bags per cu yd were prepared using a blend of cements which entrained 2.8 percent air in the concrete (in contrast with the 1.6 percent in the non-air-entrained concrete given in Table 4). For comparison, neutralized Vinsol resin was added at the mixer to entrain

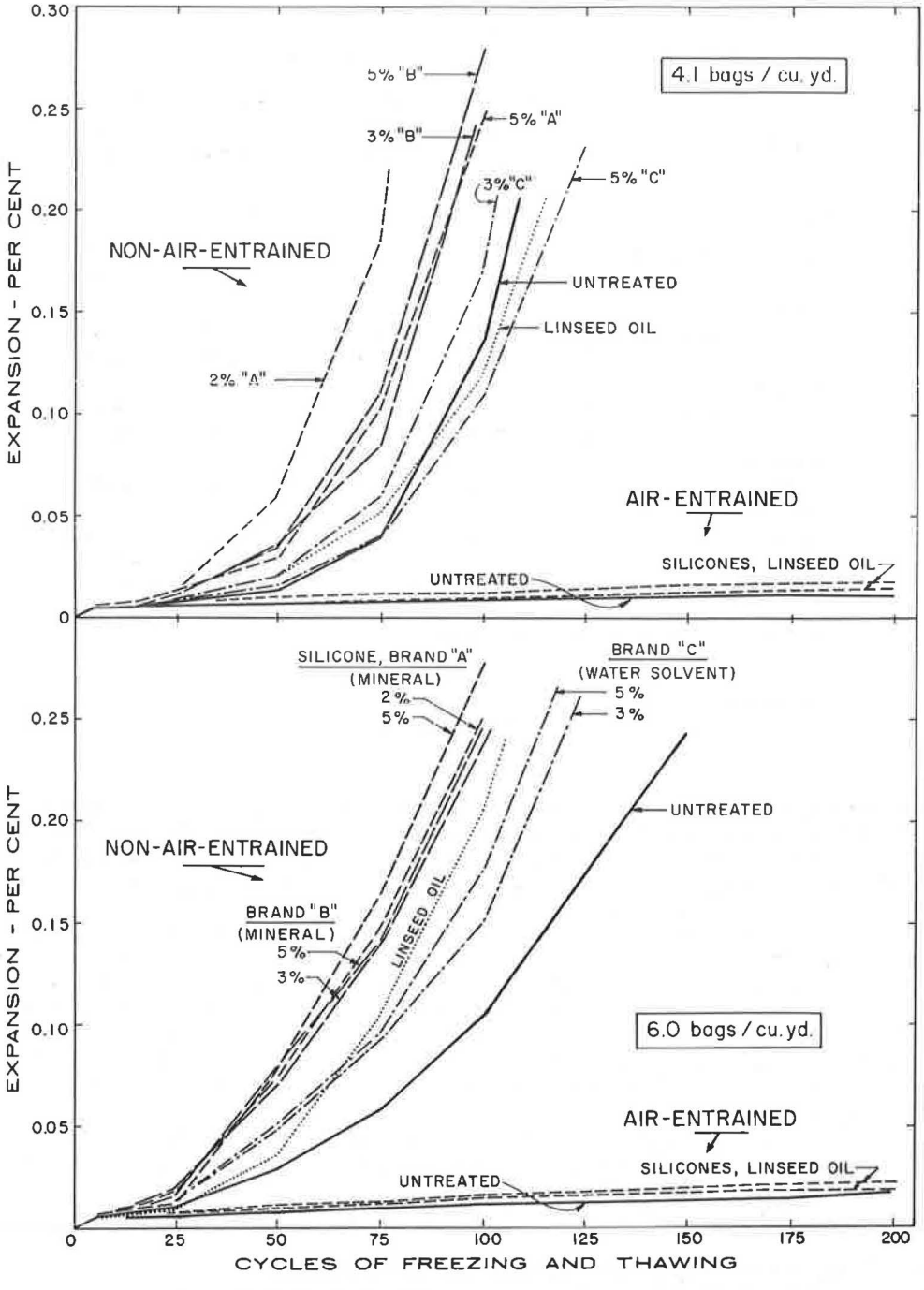

Figure 1. Expansion of 3- by 3- by $11\frac{1}{4}$-in. concrete prisms frozen and thawed immersed in water.

TABLE 11

DE-ICER SCALING TESTS[a] OF CONCRETES[b]

Surface Treatment			Scale Rating at 300 Cycles[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	(115)	1	(100)	3
Silicone A	Mineral	2	(71)	1-	(55)	4-
		5	(80)	1	(73)	(238)
Silicone B	Mineral	3	(80)	1	(55)	4-
		5	(109)	1-	(66)	2+
Silicone C	Water	3	(83)	1	(58)	3
		5	(80)	1-	(55)	3
Linseed oil[d]	---	---	(122)[e]	0+	(79)	2+
Mineral spirits[f]	---	---	(130)	1-	(80)	3
Water[f]	---	---	(107)	1	(75)	3

[a]Results are averages of tests of three specimens.
[b]Specimens 3- by 6- by 15-in. prisms.
[c]Numbers in parentheses are cycles at which surface attained a rating of 5 and test was discontinued.
[d]Two coats.
[e]Surface rating was 1, but interior of slab badly cracked and disintegrating.
[f]100%, same coverage rate as for silicones.

5.0 percent air, an adequate amount of air for this concrete. The same aggregates, fabrication procedures, curing, application of silicone treatments, and testing technique were used. The silicone solutions were the same three brands but were obtained at an earlier date.

The results of freezing and thawing and de-icer scaling tests are given in Table 12. These preliminary test results were similar in character to the more extensive data developed in the major portion of this study (Tables 9, 10, and 11, and Fig. 1). It is apparent that the surface silicone treatments were not beneficial to concrete containing some, but not an adequate, amount of intentionally entrained air. In fact, the treatments appeared to have reduced the durability, particularly the resistance to de-icer scaling. For the adequately air-entrained concrete, the effect of the treatment was slight and probably of little practical significance. Also, the 6-bag concretes in all cases showed greater resistance to de-icer scaling than the 4-bag concretes.

Effect of Silicone as an Admixture

The water silicone solution (brand C) was used as an admixture in the 6-bag per cu yd concrete at three different silicone solids concentration: 0.1, 0.2, and 0.4 percent by weight of the laboratory blend of Type I portland cements used in this study. In addition, a control non-air-entrained concrete and an air-entrained concrete were included. Data on these concretes are given in Table 13. The silicones increased the water requirements slightly and their use did not result in any intentionally entrained air, except that at 0.4 percent silicone solids a slight increase in air content and number of voids is evident.

TABLE 12

DURABILITY OF CONCRETES[a] WITH LESS THAN RECOMMENDED AMOUNTS OF INTENTIONALLY ENTRAINED AIR

Air Content (%)	C. F. (bags/ cu yd)	Net w/c (gal/bag)	Surface Treatment			Durability Factor	Expansion at 300 Cycles	Weight Change at 300 Cycles	Scale Rating
			Type	Solvent	% Solids				
2.8	6.0	4.4	None	---	---	92	0.033	-0.5	2-
			Silicone A	Mineral	2	76	0.062	-3.9	4-
					5	81	0.056	-4.4	4+
			Silicone B	Mineral	3	80	0.059	-3.4	3-
					5	81	0.051	-3.0	2+
			Silicone C	Water	3	90	0.042	-2.6	2-
					5	87	0.041	-2.0	1+
5.0	6.1	4.3	None	---	---	103	0.018	+0.2	1-
			Silicone A	Mineral	2	98	0.022	-1.5	2+
					5	98	0.025	-2.5	1-
			Silicone B	Mineral	3	100	0.021	-1.2	0+
					5	99	0.023	-1.5	1-
			Silicone C	Water	3	101	0.021	-0.1	1+
					5	101	0.020	-0.5	1-

[a]Freezing and thawing specimens 3- by 3- by 11¼-in. prisms; de-icer scaling specimens 3- by 6- by 15-in. slabs. Curing 14 days moist at 73 F and 100% relative humidity, 14 days in air at 73 F and 50% relative humidity; prisms in water and water on slab surface for 3 days thereafter. Results are averages of tests of three specimens. Concrete slump 2.4 in. for both concretes.

TABLE 13

DATA ON CONCRETES[a] CONTAINING SILICONES AS AN ADMIXTURE

Admixture	Cement Content (bag/ cu yd)	Net w/c (gal/ bag)	Slump (in.)	Net Air Content (% pressure)	Air in Hardened Concrete		
					%	Voids	
						Per In.	Per Cu In.
None	6.2	4.6	1.5	1.70	1.52	0.7	23,000
Vinsol resin	6.0	4.7	1.6	4.90	3.77	8.4	1,532,000
Silicone C[b]:							
0.1%	6.2	4.7	1.7	1.65	1.21	0.8	74,000
0.2%	6.2	4.7	1.6	1.65	0.96	0.7	23,000
0.4%	6.1	4.9	1.3	2.05	1.54	1.3	96,000

[a]Cement Type I laboratory blend, Lot 19741; aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel (1-in. maximum size); air-entraining admixture of neutralized Vinsol resin added at mixer; silicone brand C, water solution.
[b]Silicone solids as percentage of weight of cement.

TABLE 14

DURABILITY OF CONCRETES[a] WITH SILICONE ADMIXTURES

Admixture	Net Air Content (% pressure)	Water Loss (% during 14-day drying)	Absorption (% during 3 days in water)	Durability Factor[b]		Scale Rating at 300 Cycles	Expansion at 100 Cycles (%)		Weight Change at 100 Cycles (%)	
				Moist Cured	Air Dried		Moist Cured	Air Dried	Moist Cured	Air Dried
None	1.70	1.7	1.3	6	24	(156)[c]	(0.4 at 75 cy.)	0.098	(-0.4 at 75 cy.)	0
Vinsol resin	4.90	1.6	1.4	93	101	2	0.007	0.008	+0.2	+0.4
Silicone C[d]:										
0.1%	1.65	1.5	1.2	23	22	2+[e]	0.105	0.092	+0.1	+0.5
0.2%	1.65	1.5	1.2	15	12	2+[f]	0.220	0.209	-0.2	+0.2
0.4%	2.05	1.6	1.3	20	19	2+	0.076	0.108	-0.1	-0.7

[a]Freezing and thawing specimens 3- by 3- by 11¼-in. prisms; de-icer scaling specimens 3- by 6- by 15-in. slabs. Results are average of tests of three specimens. Curing: (a) 28 days moist at 73 F and 100% relative humidity plus 3 days in water (for prisms only) and (b) 14 days moist at 73 F, 14 days at 73 F and 50% relative humidity, plus 3 days in water (for both prisms and slabs; slab surface covered with water last 3 days).
[b]Based on 60% relative dynamic E or 300 cycles, whichever was reached first.
[c]Slab disintegrated before surface reached rating of 5.
[d]Silicone solids as percentage of weight of cement.
[e]One of three slabs discontinued at 258 cycles, general cracking.
[f]One of three slabs discontinued at 151 cycles, general cracking.

Table 14 gives the results of the freezing and thawing tests of the prisms and the de-icer scaling tests of the slabs. The concretes containing intentionally entrained air show high durability factors and low expansions, whereas the control concrete and those containing silicones as an admixture show low durability factors and excessively high expansions. There is little choice between the control concrete and those containing silicones. Also, there is little difference between these concretes with respect to moisture loss on drying and absorption of water during immersion.

The de-icer scaling test results indicate that the silicone admixtures improved the resistance to surface scaling. However, general cracking and deterioration developed internally in contrast to the air-entrained concretes which showed no internal cracking or other evidence of distress.

Outdoor Exposure Specimens

Specimens prepared for outdoor storage were 18- by 24-in. slabs, 6 in. thick. Both non-air-entrained and air-entrained concretes were used. Surface treatments included the same three silicones and linseed oil. In addition, the water solution silicone was used as an admixture. Storage was outdoors at Skokie, Ill.

Table 15 gives the data on these concretes including details of curing, surface treatment, admixtures, and observations as to surface condition after two winters (1960-62) of exposure which included the use of calcium chloride as a de-icer. During these two winters, one of which was relatively mild, 15 applications of calcium chloride were made. Examination of the surfaces has disclosed few significant differences in appearance. The results of continued exposure will be of interest.

Influence of Silicones on Durability of Vertical Concrete Surfaces

Concrete blocks 8 by 12 by 12 in. in size were cast using a 6-bag per cu yd concrete containing 5.3 percent entrained air and having a slump of 2 in. These blocks were cured for 14 days moist at 73 F and 100 percent relative humidity followed by 14 days in air at 73 F and 50 percent relative humidity. After 7 days in air (21 days old), one of the 12- by 12-in. faces which was cast against a vertical mold surface (plastic-coated plywood) was treated with a silicone solution. Silicone B (mineral spirits) and silicone C (water solution) were both used at concentrations of 3 and 5 percent silicone solids. Control specimens were left uncoated. All but this one surface of each block were covered with a 1-in. layer of styrofoam. During test, the uncovered surface was kept vertical, thus simulating an exposed concrete architectural wall surface.

TABLE 15

OUTDOOR EXPOSURE SPECIMENS[a]

Concrete Type	Surface Treatment			Cement Content (bag/cu yd)	Net w/c (gal/bag)	Slump (in.)	Air Content (% pressure)	Admixture	Comp. Str.[b] (psi)	Comments After Two Winters' Exposure
	Type	Solvent	% Solids							
Non-air-entr.	None	---	---	5.9	4.8	2.4	1.5	None	---	OK
	Silicone A	Mineral	2	5.9	4.8	2.2	1.5	None	5,790	Mod. paper scale
			5	5.9	4.8	1.9	1.5	None	---	Mod. paper scale
	Silicone B	Mineral	3	5.9	4.8	2.8	1.5	None	5,440	Mod. paper scale
			5	5.9	4.8	2.8	1.5	None	5,760	Slight paper scale
	Silicone C	Water	3	5.9	4.8	2.1	1.4	None	6,070	Slight paper scale
			5	5.9	4.8	2.3	1.5	None	5,480	Slight pitting
	Linseed oil[c]	---	---	5.9	4.8	2.2	1.5	None	---	Slight flaking
	None	---	---	5.9	4.6	1.9	1.5	0.1% Silicone C	6,640	OK
		---	---	5.8	4.8	1.8	2.6	0.4% Silicone C	5,960	OK
Air-entr.	None	---	---	5.9	4.5	2.3	5.7	NVX	---	OK
	Silicone A	Mineral	2	5.9	4.5	2.5	5.6	NVX	4,680	OK
			5	5.9	4.5	2.4	5.3	NVX	---	Mod. paper scale
	Silicone B	Mineral	3	5.9	4.5	3.4	6.0	NVX	4,220	Mod. paper scale
			5	5.9	4.5	2.8	6.0	NVX	4,340	Slight paper scale
	Silicone C	Water	3	5.9	4.5	2.3	5.7	NVX	4,980	OK
			5	5.9	4.5	2.7	5.9	NVX	4,540	Slight pitting
	Linseed oil[c]	---	---	5.9	4.5	2.6	5.6	NVX	---	Slight pitting
	None	---	---	5.9	4.4	2.2	5.8	NVX + 0.1% Silicone C	5,240	OK
					4.7	2.5	6.2	NVX + 0.4% Silicone C	5,220	OK

[a]Cement Type I laboratory blend, Lot 19741; specimen 18 by 24 by 6 in., placed on sandy loam with crushed rock around slab up to one-half depth, with redwood dikes around surface edges. Aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel ($1\frac{1}{2}$-in. maximum size). Curing of slabs, 7 days moist at 73 F and 100% relative humidity plus 7 days in air at 73 F and 50% relative humidity, stored outdoors at 14 days; curing of cylinders, 28 days moist. Silicone and linseed oil treatments applied at end of 7-day drying period. Neutralized Vinsol resin as air-entraining admixture (NVX) Silicone C (water solution). Exposed outdoors at Skokie, Ill.; during winters, flake $CaCl_2$ applied, as required to de-ice, to produce a 2 to 3 percent solution on thawing.
[b]Of 6- by 12-in. cylinders.
[c]Two coats.

One group of specimens (one specimen per variable) was subjected to freezing and thawing tests in the laboratory. Each uncovered vertical surface was sprayed with approximately 1 pt of water and the specimen stored for 18 hr in an air freezer maintained at 0 F. At the end of this period, the specimens were moved to the thawing room maintained at approximately 70 F, and the exposed surface was sprayed immediately with the same amount of water. After 6 hr of thawing, the cycle was repeated: spray, freeze, etc. A companion group was stored outdoors at Skokie, Ill., for natural weathering.

In the laboratory after 5 cycles of test, the untreated concrete specimen showed slight "paper" scaling and a surface that wet readily, whereas the silicone-treated surfaces showed no paper scaling and did not wet. From 5 to 350 cycles, however, no further changes occurred except for a slight infiltration of water around the edges of the silicone-treated concrete surfaces. After two winters of exposure, the outdoor specimens show essentially the same performance as the laboratory specimens.

SUMMARY AND CONCLUSIONS

This study included tests of non-air-entrained and air-entrained concretes at two different water-cement ratios. Surface treatments evaluated for their influence on resistance to freezing and thawing and de-icer scaling included silicones in mineral spirits and water and a linseed oil treatment. A water solution of silicone was used in some of the tests as an admixture. The major portion of the work was performed in the laboratory. Outdoor exposure tests were included, but the time elapsed has been insufficient to develop conclusive results.

Based on these tests, the following comments and conclusions appear warranted:

1. Although applications of silicone solutions to concrete surfaces reduced the initial rate of water absorption, on continued immersion for periods of 7 to 14 days the total absorption of treated and untreated concretes were essentially identical.
2. Surface applications of linseed oil reduced the initial rate of absorption of water, and the 3-day absorption was significantly lower than for the silicone-treated concretes.
3. Non-air-entrained concretes frozen and thawed while immersed in water showed

poor durabilities. Durabilities were consistently lower with concretes surface-treated with silicones than with untreated ones. This was true for all three criteria of durability used; that is, durability factor, expansion, and weight loss. Although the linseed oil treatment was no more effective for this exposure, weight loss was no greater for concretes so treated than for the control concretes, in contrast with those treated with silicones.

Air-entrained concretes showed high durabilities, and there was no significant influence of any of the surface treatments on these durabilities.

4. Non-air-entrained concretes frozen and thawed and subjected to the use of calcium chloride as a de-icer showed low resistance to surface scaling. The use of surface silicone treatments further reduced this resistance. In the richer mix, the linseed oil treatment was effective in reducing scaling but did not prevent general deterioration typical of non-air-entrained concrete.

Air-entrained concretes having a cement content of 6 bags per cu yd showed excellent resistance to de-icer scaling, and there was no significant influence of the surface treatments on this resistance. The 4-bag per cu yd air-entrained concretes, however, showed significantly less resistance than the 6-bag concretes, and the silicone surface treatments generally further reduced this resistance.

5. The effects of the silicones were essentially the same for both the mineral spirits solutions and the water solutions.

6. Surface applications of mineral spirits or water (both used in preparing the different silicone solutions) had no influence on the resistance to freezing and thawing or de-icer scaling.

7. Concretes containing some intentionally entrained air, but less than an adequate amount, were not benefited by surface treatment with silicones. In fact, for non-air-entrained concretes the treatments were detrimental.

8. A water solution of silicone used as an admixture did not improve the resistance of non-air-entrained concretes to freezing and thawing while immersed in water. Significant improvement in resistance to de-icer scaling was apparent for these non-air-entrained concretes; however, general cracking and deterioration caused early failure.

9. Vertical exposed surfaces of air-entrained architectural concrete showed a reduced tendency to wet if treated with surface application of silicones. The silicone treatment appeared beneficial in laboratory tests, which showed untreated surfaces to develop a light paper scale or roughening, whereas the treated surfaces showed no change.

10. It would appear that the use of silicones for treatment of horizontal concrete surfaces such as pavement slabs or bridge decks has neither beneficial nor detrimental effects when used with a typical 6-bag concrete mix containing an adequate amount of intentionally entrained air. Detrimental effects of surface treatment with silicones were noted in the 4-bag mixes with and without intentionally entrained air and in the 6-bag mix with less than the recommended amount of intentionally entrained air.

11. The most effective means of insuring resistance is to provide an adequate amount and character of entrained air in a concrete of relatively low water-cement ratio.

REFERENCES

1. Mardulier, F. J., "Scaling Resistance of Concrete Improved Through Silicones." HRB Bull. 197, 1-12 (1958).
2. Britton, H. B., "New York State's Experience in Use of Silicones." HRB Bull. 197, 13-23 (1958).
3. Heiskell, R. H., and Crew, R. J., "Protective Coatings for Concrete." U. S. Naval Radiological Defense Laboratory, Technical Report (R & D) No. TR-148 (July 3, 1961).
4. LaFleur, W. J., "New Waterproofing Methods for Thruway Bridges." Roads and Streets (Feb. 1961).
5. Finney, E. A., "Preventive Measures for Obtaining Scale-Free Concrete Bridge Structures." HRB Bull. 323, 26-42 (1962).
6. "Tests on Waterproofing Coatings for Concrete Surfaces—Final Report." Purdue University Eng. Expt. Sta. Reprint 85 (March 1953).