ACID RESISTANT CONCRETE COATINGS

by

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Submitted to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree, Doctor of Philosophy, in the Department of Chemistry.

Indiana University

Bloomington, Indiana

May 1941

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To

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INTRODUCTION

The work reported in this paper was undertaken to find suitable coatings to be used on concrete stave silos that would resist the disintegrating action of the acids generated by the ensilage. Almost all the materials used in this problem were furnished by nationally known manufacturers; and, for the most part, are regularly offered for sale by these concerns (1).

1. The following companies kindly donated samples of the materials that were used in this investigation: American Cyanamid and Chemical Corp.; Bakelite Corp.; The Barrett Co.; Concvango Refining Co.; E. I. DuPont de Nemours and Co.; Durez Plastics and Chemicals, Inc.; Glyco Products Co., Inc.; The B. F. Goodrich Co.; Halowax Corp.; Hercules Powder Co.; Innes, Spoiden and Co.; Maurice A. Knight; Monsanto Chemical Co.; Naugatuck Chemical, Division of the U. S. Rubber Co.; The Procter and Gamble Co.; Quigley Co, Inc.; Reichhold Chemicals, Inc.; Reilly Tar and Chemical Corp.; Standard Oil Co. (Ohio); Stoner-Mudge, Inc.; Wishnick-Tumpeer, Inc.

This paper attempts to give a comparative picture of the value of each of these materials under the action of weak acid, abrasion, and water absorption.

EXPERIMENTAL

Each coating used was subjected to two different tests. First, an accelerated acid flow test (2) subjected the coating to

2. Miller, D. G., Rogers, C. F., and Manson, P. W., "A Flow Method for the Determination of the Effects of Soluble Chemicals on Concrete". This paper was presented before the Forty-second Annual Meeting of the American Society for Testing Materials, June 26-30, 1939.

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acid action and abrasion. In this test paraffin dykes ¼ inch wide were placed along the edge of concrete bars 15 inches long, 2 inches wide, and 2 inches deep. This left exposed an area 15 inches long and 1½ inches wide which was coated with the material to be tested. The coated concrete bar was then placed at an angle under a capillary through which two liters of 0.2 normal acetic acid (the acid mainly generated by the ensilage) flowed down the bar every twenty four hours (Fig. 1). Once every twenty four hours each channel was brushed with a flat steel brush about the size and shape of a one inch paint brush and simultaneously washed with a stream of distilled water. The material loosened by the brushing was caught in a filter paper, oven dried, and weighed. Ten days was the maximum period of this test.

The second test consisted of drying a 2 inch cube of concrete, entirely coated, in an electric oven (75-85 C.) for a period of twenty four hours. This temperature was used since the ensilage often approaches this temperature. The cubes were then weighed, placed in beakers, and allowed to remain under tap water at room temperature for another twenty four hours. The cubes were then removed, weighed again, and the percentage of absorption was calculated from the two weights.

All the concrete bars and cubes used in this investigation were made by the "dry tamped" method. The proportions of the ingredients were: gravel, 3.84; coarse sand, 2.42; fine sand, 1.00; cement, 1.52. Enough water was then added to give a water-cement ratio of 3.1/1. The concrete was steam cured for twenty four hours and then given a seven days curing in air at room temperature.

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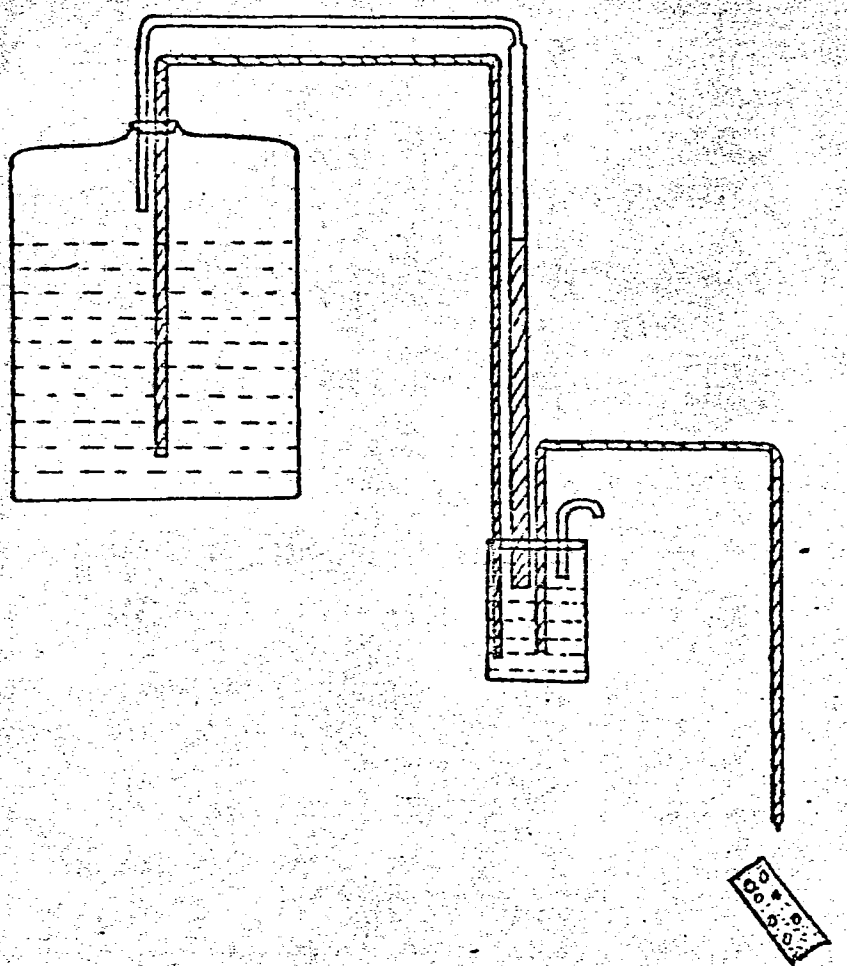

FIG. 1 - SIDE VIEW OF A SINGLE UNIT OF THE ACCELERATED ACID FLOW TEST.

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DESCRIPTION OF COATINGS

The coatings tested can be divided generally into six classifications: waxes, asphalt coatings, rubber base paints, drying oils, resin varnishes, and miscellaneous.

The waxes were applied to the concrete by the method of Brassert (3). The wax was first melted and then brushed on the

3. Brassert, H. C., U. S. Patents, 1,892,864 (Jan. 3, 1933), 1,920,627 (Aug. 1, 1933), 2,016,886 (Oct. 8, 1935), 2,213,687 (Sept. 3, 1940), and 2,232,837 (Feb. 25, 1941).

concrete with an ordinary paint brush. The concrete was then gone over with a burner to drive the wax into the bar or cube; only a thin film was left on the surface. This method requires that the melting point of the wax is low enough that the brush is not burned, and that the wax does not cool so rapidly that it hinders easy application.

The application of the asphalt coatings, rubber base paints, and drying oils is fully described in the table.

Resin Varnish Group:

At the present time the protective coating used by many silo manufacturers is a cumarone resin varnish. The Concrete Silo Company uses a coating containing the proportions of 50 grams of resin, 15 cc. of fish oil, and 40 grams of xylol. Because of its present use and low cost the cumarone resin varnish was studied first and most extensively in this investigation. The results obtained from the study of the cumarone varnish can be applied to similar resin formulas. Keeping the above formula as a standard with respect to proportions variations of the constituents were introduced and tested as coatings. In each case the ingredients

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were mixed together and stirred mechanically to affect homogeneity. One coat only was applied.

The next step consisted in adding finely divided materials to the standard cumarone resin, fish oil, xylol formula in an attempt to increase the chemical inertness and the body of the coating. Five grams of the material were added in each case, and one coat was applied.

Another variation consisted of putting on primer coats of drying oils before coating with the standard cumarone resin-fish oil-xylol varnish. The primer coats were allowed to stand for twenty four hours before the top coats were put on.

The next group of coatings tested were previously prepared formulas recommended and sold for their acid resisting properties by nationally known companies. Their application is described in the table of results.

A subgroup of the above series of coatings was made by mixing in equal proportions a saturated solution of 10 centipoise chlorinated rubber in toluene with the prepared coatings mentioned above. In the table of data these coatings are submarked "A" under the numbers given the prepared resin varnishes. Two coats were applied in all cases.

Another subgroup was made by mixing in equal proportions the standard cumarone resin formula with the prepared resin coatings. One coat only was applied. These coatings are submarked "B" under the numbers of the respective resin varnishes.

The final group of resin varnish coatings was made from ten synthetic and natural resins. These resins were made into coating compounds using the standard formula of 50 grams of resin, 15 cc.

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of drying oil, and 40 grams of xylol or toluene. The mixtures were mechanically stirred until solution was effected and one coat was then applied.

RESULTS

The accelerated acid flow test gives a comparative picture of the acid resisting qualities of each coating. The evidence of disintegration used as a criterion in this test was the appearance of sand, gravel, and cement from the bar in the filter paper upon brushing. Although the loosened material obtained by the brushing was dried and weighed the table merely gives the number of days the coating withstood the test before disintegration appeared. The author feels that the weights of the disintegrated portions of the concrete bars are not of enough extra value to be included in the table.

The accelerated acid flow test also brings out several other important properties of a coating. It must have good coverage or else the brushing will seek out thin parts of the coating and permit disintegration to start. The coating must also form a good bond with the concrete to prevent peeling or pitting both of which permit disintegration to begin.

The water absorption test while contributing less to the estimation of the value of a coating than the acid flow test is however a good measure of porosity. Very porous coatings soon collect water and acid at the bond between coating and concrete which soon leads to peeling or pitting.

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION (4) Weight gained by 2 inch coated cube in tap water for 24 hours (%).
	Uncoated concrete	1	6.2
	Waxes:		
1.	Beeswax	7	0.91
2.	Stearic acid	3	7.3
3.	Paraffin (m.p. 49°C.) Cost: 2-3 cents per pound.	6	4.5
4.	A micro-crystalline petroleum hydrocarbon wax (m.p. 140-145° F.) Cost: 5 5/ cents per pound.	5	0.33
5.	Cetyl acetamide. Cost: $0.35 per pound.	2	-
6.	Carnauba Wax. Cost: $0.50 per pound.	4	0.2
7.	Candelilla Wax. Cost: $0.20 per pound.	7	0.2
8.	Yellow Ceresine Wax (m.p. 162°F.). Cost: $0.21 per pound.	2	-
9.	White Ceresine Wax. Cost: $0.14 per pound.	2	-
10.	White Ozokerite Wax (m.p. 170°F.).	1	-
11.	Yellow Italian Ozokerite (m.p. 158°-176°F.). Cost: $0.26 per pound.	3	4.1
12.	Hard Green Ozokerite (m.p. 74°-76° C.). Cost: $0.46 per pound.	4	1.3
13.	Ozokerite Composition Molding Wax. Cost: $0.38 per pound.	6	0.27
14.	Paraffin plus Butyl Methacrylate Polymer (equal parts by weight). The burner was not used, and only one coat was applied.	Greater than 10	3.1

4. A dash indicates that no test has been made.

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
15.	Paraffin plus the petroleum hydrocarbon wax (Number 4.. equal parts by weight.	8	-
16A.	Paraffin plus stearin pitch (equal parts).	Greater than 10	0.24
16B.	Paraffin plus stearin pitch (three parts of paraffin to one part of pitch).	5	0.37
16C.	Paraffin plus stearin pitch (one part of paraffin to three parts of pitch).	Greater than 10	2.7
17.	Paraffin plus chlorinated diphenyl resin (Number 74) in equal parts.	3	0.0
Asphalt Coatings (Two coats applied in all cases with twenty four hours between coats).			
18.	Liquid asphalt coating. Cost: [illegible] per gallon.	Greater than 10	1.2
19.	Special coating compound. Cost: [illegible] per gallon.	7	7.6
20.	Heavy duty black coating. Cost: $2.10 per gallon.	Greater than 10	5.7
21.	Hydraulic black coating.	5	0.1
22.	Black asphalt protective coating.	6	2.7
Rubber Base Paints:			
23.	An acid resisting paint with a rubber derivative as a base and containing graphite. Two coats were applied with four hours between coats. Cost: $3.80 per gallon.	Greater than 10	8.3
24.	Latex water emulsion. This coating was applied in the same way as Number 23.	Greater than 10	3.7

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
25.	A rubber base paint. Two coats were applied with twenty four hours between coats. The first coat was thinned with 15 percent xylol to aid in the penetration of the concrete. Cost: $2.50 per gallon.	Greater than 10	3.9
26.	A weakly chlorinated rubber solution.	1	-
	Drying Oils (One coat only).		
27.	Soya bean oil	1	-
28.	Linseed oil	1	-
28A.	Linseed oil containing lead and cobalt naphthenate type driers. The driers were added to give 0.5% lead and 0.05% cobalt by weight.	1	4.5
29.	Cottonseed oil	1	-
29A.	Cottonseed oil with driers in the same proportions as above.	1	5.2
30.	Tung oil	2	-
30A.	Tung oil containing driers in the same proportions as above.	3	3.9
31.	Alkali-refined perilla oil.	1	-
31A.	Alkali-refined perilla oil containing driers in the same proportions as above.	2	4.6
	Resin Varnishes:		
32.	Cumarone resin, fish oil, xylol. Resin cost: 4-5 cents a pound.	3	3.1
33.	Cumarone resin, cottonseed oil, xylol.	5	4.4
34.	Cumarone resin, linseed oil, xylol.	4	4.7

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
35.	Cumarone resin, tung oil, xylol.	2	1.8
36.	Cumarone resin, perilla oil, xylol.	2	2.3
37.	Cumarone resin, soya bean oil, xylol.	2	3.3
38.	Cumarone resin, fish oil, xylol. Lead and cobalt type driers were added to give 0.5 percent of lead and 0.05 percent of cobalt by weight of resin present.	2	3.4
39.	Cumarone resin, fish oil, xylol. Ten grams of 125 centipoise chlorinated rubber were dissolved in the xylol before it was added to the mixture.	Greater than 10	4.6
40.	Cumarone resin, fish oil, a weakly chlorinated rubber solution (Number 26).	8	2.8
	Materials Added to Standard Cumarone Varnish:		
41.	Flue dust	3	-
42.	Bentonite	3	-
43.	Infusorial earth	3	-
44.	Animal charcoal	2	-
45.	Sulfur	2	-
46.	Wood charcoal	2	-
47.	Basic calcium lignin sulfonate	4	3.04
	Primer Coats Plus Standard Cumarone Varnish:		
48.	Fish oil	3	-
49.	Cottonseed oil	5	2.2
50.	Linseed oil	3	-

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
51.	Tung oil	9	0.4
52.	Perilla oil	4	0.92
53.	Soya bean oil	4	0.33
54.	Waterglass	3	-
55.	A paraffin undercoat applied in the same manner as the ordinary paraffin coating.	5	0.1
	Acid Resisting Resin Formulas:		
56.	A phenol modified oxidizing type alkyd supplied as a 50 percent solution in mineral spirits to which was added naphthenate driers to yield 0.5 percent of lead and 0.05 percent of cobalt by weight of resin present.	8	1.8
56A.		2	4.5
56B.		Greater than 10	4.7
57.	A polystyrene resin varnish. Two coats applied with two hours between coats. The first coat was thinned with xylol to aid penetration. Cost: $0.41 per gallon.	4	3.2
57A.		3	5.2
57B.		3	5.7
58.	A phenolic resin varnish. Two coats were applied with four hours between coats.	4	1.1
58A.		2	3.5
58B.		7	4.3
59.	A polystyrene resin varnish. Two coats were applied with six hours between coats.	3	1.4
59A.		3	3.4
59B.		7	5.3

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
60.	A low viscosity polystyrene resin (supplied as a 75 per-cent solution in xylol) plus a solution of 5 g. of 125 centipoise chlorinated rubber in 40 cc. of xylol (1:1). Two coats applied.	6	6.2
60B.		2	2.5
61.	A toluol solution of a resin used ordinarily as a primer coating since it does not form a hard film. Two coats were applied with 24 hours between coats. Cost: $0.40 per gallon.	4	2.2
61A.		1	1.1
61B.		4	5.2
62.	One coat of Number 61 followed by a top coat of Number 59.	Greater than 10	4.5
63.	One coat of Number 61 followed by a top coat of Number 58.	9	4.3
64.	One coat of Number 61 followed by a top coat of Number 57.	2	5.4
65.	One coat of Number 60 followed by two coats of Number 57.	3	2.1
66.	One coat of Number 60 followed by two coats of Number 59.	3	1.03
67.	One coat of Number 60 followed by two coats of Number 58.	4	4.8
68.	An oily liquid polymerized terpene. Cost: $0.26 per pound.	1	-

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
69.	An acid resisting lacquer. The first coat thinned considerably with a special thinner; second coat applied without thinning. Cost: Lacquer-$8.50 per gallon; Thinner-$3.25 per gallon.	Greater than 10	0.82
70.	An inert base paint containing chlorinated rubber. Two coats were applied with the first coat thinned considerably with a special thinner. Cost: lacquer-$3.25 per gallon; Thinner-$0.60 per gallon.	Greater than 10	2.7
70B.		3	5.2
71.	A "Vinylite" lacquer. The first coat was thinned with 15 percent of a special thinner. The second, unthinned coat was applied after twenty four hours. Cost: Lacquer-$3.10 per gallon; Thinner-$0.45 per gallon.	Greater than 10	0.31
71A.		5	4.6
71B.		4	5.08
72.	A "Vinylite" lacquer. Two coats were applied with four hours between coats. No thinner.	2	5.4
72B.		2	5.8
73.	A cement made from a thermoplastic material having a depolymerized colloid resin base. Two coats were applied twenty four hours apart with the first thinned considerably with white gasoline.	3	5.7
	Natural and Synthetic Resin Varnishes (Standard Proportions):		
74.	Chlorinated diphenyl, fish oil, xylol. Cost: $0.27 per pound.	1	1.7

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
74A.	Chlorinated diphenyl, linseed oil, xylol.	1	0.85
74B.	Chlorinated diphenyl, tung oil, xylol.	3	0.5
74C.	Chlorinated diphenyl, perilla oil, xylol.	1	0.4
74D.	Chlorinated diphenyl, linseed oil, 10 grams of 10 centipoise chlorinated rubber dissolved in 40 grams of toluene.	8	1.6
74E.	Chlorinated diphenyl, linseed oil, 10 grams of 125 centipoise chlorinated rubber dissolved in 40 grams of toluene.	Greater than 10	0.7
75.	A terpene phenolic (m.p. 239°/248°F.), fish oil, xylol. Cost of resin: $0.14 per pound.	2	4.7
75A.	Linseed oil substituted for the fish oil in Number 75.	2	2.2
75B.	Tung oil substituted for the fish oil in Number 75.	1	4.9
75C.	Perilla oil substituted for the fish oil in Number 75.	9	1.8
75D.	Terpene phenolic, linseed oil, 10 grams of 10 centipoise chlorinated rubber dissolved in 40 grams of toluene.	2	1.7
76.	A terpene phenolic (m.p. 275°/285°F.), fish oil, xylol. Cost of resin: $0.14½ per pound.	3	2.8
76A.	Linseed oil substituted for the fish oil in Number 76.	7	2.2
76B.	Tung oil substituted for the fish oil in Number 76.	Greater than 10	3.4
76C.	Perilla oil substituted for the fish oil in Number 76.	1	1.6

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
76D.	Terpene phenolic, linseed oil, 10 grams of 10 centipoise chlorinated rubber dissolved in 40 grams of toluene.	1	2.6
76E.	Terpene phenolic, linseed oil, 10 grams of 125 centipoise chlorinated rubber dissolved in 40 grams of toluene.	8	2.3
77.	A hard synthetic resin (m.p. 73°C.), linseed oil, xylol. Cost of resin: $0.20 per pound.	4	3.3
77A.	Resin Number 77, linseed oil, 10 grams of 10 centipoise chlorinated rubber dissolved in 40 grams of toluene.	7	4.6
78.	Butyl methacrylate polymer, linseed oil, xylol. Cost of resin: $0.75 per pound.	Greater than 10	
79.	Phenol-formaldehyde resin, linseed oil, xylol. Cost of resin: 19-48 cents per pound.	9	3.0
79A.	Resin Number 79, tung oil, xylol.	8	3.9
79B.	Resin Number 79, linseed oil, 10 grams of 10 centipoise chlorinated rubber dissolved in 40 grams of toluene.	4	3.5
80.	Paranol, linseed oil, xylol.	2	4.9
81.	Extra hard paranol, linseed oil, xylol.	2	5.0
82.	Amberol, linseed oil, xylol.	8	4.9
83.	Ester gum, linseed oil, xylol.	4	4.9

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (5).
	Miscellaneous Coatings:		
84.	Butyl methacrylate-cumarone resin formula. 25 grams of each resin, 15 cc. of linseed oil, and 40 grams of xylol were mixed together mechanically until homogeneous. One coat was applied.	5	4.4
85.	Oxidizing type alkyd-chlorinated rubber formula. Forty grams of the resin were dissolved in 40 grams of toluene and 0.5 grams of 4 percent cobalt naphthenate drier was added. Ten grams of 10 centipoise chlorinated rubber were dissolved in another 40 gram portion of toluene and the two solutions were mixed. Two coats were applied. Cost of resin: $0.12½ per pound.	Greater than 10	0.2
86.	Oxidizing type alkyd (Number 85) was melted and added to an equal weight of the standard cumarone resin formula. Cobalt and lead driers were added. One coat.	Greater than 10	4.7
87.	A coal tar derivative coating. One (cold) coat was applied. Cost: $0.75 per gallon.	Greater than 10	3.7
88.	Waterglass	1	-
89.	Stearin pitch (5). This coating was applied in the same manner as the waxes. Cost: $0.04 per pound.	Greater than 10	7.7

5. The stearin pitch was successfully dissolved in a number of coal tar solvents and drying oils, but these solutions failed as coatings because they possessed a brittleness that made them flake and come off easily when the concrete was brushed.

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COATING NUMBER	DESCRIPTION AND COST OF COATING	ACID FLOW TEST Age in days of first evidence of disintegration.	WATER ABSORPTION Weight gained by 2 inch coated cube in tap water for 24 hours (%).
90.	Equal parts of stearin pitch and stearic acid fused together and applied by brushing. The coating was then driven into the concrete with a burner.	Greater than 10	3.5
91.	One part of stearin pitch was dissolved in three parts of the liquid asphalt coating (Number 18) and one coat applied.	7	4.3

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CONCLUSIONS

1. The most important consideration with waxes is their ease of application. The failures among the waxes are mostly due to high melting points and difficulty in applying before the wax solidifies. Rapid solidification leads to brittleness and peeling permitting disintegration to start. Good results were obtained with paraffin or a mixture of paraffin and a softer, less brittle wax such as a micro-crystalline petroleum wax or stearin pitch, or a mixture of paraffin with a resin such as butyl methacrylate.

2. Asphalt coatings in general are very resistant to weak acids, but they have a tendency to pit and come off under abrasive action.

3. Rubber base paints usually have high acid resistance. Their difficulty in actual practice is the maintenance of a good bond between coating and concrete.

4. Drying oils in themselves are of little value as protective coatings, but they can be useful when used as a primer coat.

5. A chemically resistant resin varnish containing chlorinated rubber usually gave good results. The resin formula will penetrate the concrete and form a good bond while at the same time the chlorinated rubber gives toughness and extra resistance to the coating.

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