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Tests and Investigations of Retarding Admixtures for Concrete

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Tests of Retarding Admixtures for Concrete

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This investigation was made to obtain data of the effects of commercial retarders on certain properties of portland cement concrete. The data obtained were used to prepare a specification for the acceptance and use of these retarders. In addition, the methods of testing retarders for chemical properties as well as their effects on the physical properties of plastic and hardened concrete were studied. The tests for chemical properties or identification are reported in a separate paper. The tests herein reported were made with 25 brands of retarders from 11 marketers and cover time of retardation, reduction of water, durability, and flexural and compressive strengths at various ages. A recommended specification for retarders is appended to this report.

●THE USE of chemicals for delaying the initial setting time of portland cement concrete is not new. The effects of sugar and other retarders on concrete have been known for many years. In 1945, Tuthill (1) reported that a retardant admixture had been used during 1942 to 1945 in lightweight concrete for the construction of concrete ships. The admixture was used in non-air-entrained concrete to reduce the amount of mixing water, or to increase slump and to prevent the early stiffening and formation of "cold joints."

Since that time there have been many "news" articles in current literature on the use of retardants in concrete for prestressed beams or piles and bridge structures. The report of Tuthill and Cordon (2) and the discussion and closure of this report (3) contain much valuable test data.

Several Federal agencies have used temporary or interim specifications for retarders. The Bureau of Reclamation suggested a specification in 1954 and the Bureau of Public Roads proposed a specification for certain local use in November 1956, which was revised in November 1958. These specifications were based mainly on field experiences with retarders from two manufacturers, and on a limited amount of laboratory test data. The need for a specification for all types of commercially available retarders has become greater since the possible benefits of retarders have been recognized more fully. The large increase in the number of commercial retarders and the claims of their marketers present problems of acceptance and performance tests to the engineer who is responsible for the selection and use of a satisfactory retarder.

CLASSIFICATION OF RETARDERS

Retarders are classified, according to their constituents, into three main groups, as follows:

1. Salts of lignosulfonic acids (lignosulfonates);
2. Organic acids of the hydroxylated carboxylic type or their salts; and
3. Carbohydrates.

A questionnaire was sent in 1957 to all marketers of retarders known to the Bureau of Public Roads with a request for samples and information. From the samples received,

25 samples from 11 companies were chosen for testing. The remainder of the samples were considered not to meet the Bureau's conditions for inclusion in the testing program because they were not essentially retarders and were not available commercially at the time of receipt.

The classification of the 25 retarders and their general properties are given in Table 1. The information supplied by the marketer and tests by the Bureau are the bases for the classification. Chemical methods of analysis and identification tests by ultra violet and infrared spectrometry are given in another report.

CONCRETE MATERIALS USED

A blend of equal parts by weight of four brands of type I cement was used for all concretes. About 32 bags (one lot) of each of the four cements were stored in sealed 55-gal steel drums. Three lots of each of the four cements were used during the investigation and average chemical and physical properties for each cement and the blend of the four cements are given in Table 2.

The air-entraining admixture used was an aqueous solution of neutralized Vinsol resin. The solution contained 15 percent of solids when calculated on a residue dried at 105 C, and the ratio of sodium hydroxide to Vinsol resin was 1 to 6.4 parts by weight.

A natural siliceous sand having a fineness modulus of 2.90, a specific gravity, bulk dry of 2.65 and an absorption of 0.4 percent, and a crushed limestone of 1-in. maximum size having a specific gravity, bulk dry of 2.75 and an absorption of 0.4 percent were used. When the aggregates for a batch of concrete were weighed, the sand

TABLE 1

PROPERTIES OF RETARDERS

Retarder No	Physical State	Amount Recommended by Manufacturer[a] (oz/bag)	Amount Used: Material as Received[a] (oz/bag)	Amount Used: Dry Solids[b] (oz/bag)	Amount Used: Volatile Organic Material[c] (oz/bag)	Major Chemical Constituent
(a) Group I - Salts of Lignosulfonic Acids (Lignosulfonates)						
7	Powder	-	3 5	3.3	3 3	Ammonium salts
10	Powder	3 8	3 2	3.0	3 0	Ammonium salts
17	Powder	-	3 2	3.0	2.9	Ammonium salts[d, e]
15	Powder	3.8 to 7.5	4.0	3.7	2.8	Sodium salts
19	Powder	4.0	4 0	3.8	2.8	Sodium salts
22[f]	Powder	0.8	4.0	3.7	2.0	Sodium salts
23	Powder	3 8	6 4	5 9	3 9	Sodium salts
2	Powder	8 0	14.4	14.3	0.40	Calcium salts[g]
3	Powder	3 8 to 7.5	4.0	3.7	3.1	Calcium salts
11	Powder	4 0	4 8	4.5	3 2	Calcium salts[h]
12	Powder	-	4 0	3 8	3 0	Calcium salts
13	Powder	4.5 to 7 5	4.8	4.4	2 3	Calcium salts
14	Powder	3 to 4	5 0	4.7	4.0	Calcium salts[e]
16	Powder	4.0	4 8	4.5	3.8	Calcium salts
18	Powder	4 to 5	4.0	3.7	3.4	Calcium salts
20	Liquid	9 0	9 0	3.3	2.6	Calcium salts
21	Liquid	9.0	9.0	3 2	2.5	Calcium salts
24	Powder	12 0	9 6	9.2	5.1	Calcium salts[h]
25	Powder	3 to 4	4 0	3.7	3 1	Calcium salts[d, i]
(b) Group II - Derivatives of Organic Hydroxylated-Carboxylic Acids						
4	Liquid	2 to 4	3 0	1.2	0.88	Metal salts[j]
8	Powder	8 to 16	12.0	11.9	1.2	Metal salts
9	Liquid	2 to 4	2.8	1.1	0 77	Metal salts
5	Liquid	2.7 to 7.1	4.0	2.1	2.1	Triethanolamine salt
6	Liquid	2 0	4 0	1 3	0.91	Zinc borate complex
(c) Group III - Carbohydrates						
1	Liquid	1 to 4	1 1	0 4	0.43	Sucrose[d]

[a]Amount of retarder necessary to retard set of concrete from 2½ to 3 hr as determined by Proctor test at 500 psi Liquid materials given in fluid ounces, powdered materials given in avoirdupois ounces. [b]Determined by drying at 110 C. [c]Determined by ignition [d]Contained 10 percent or more carbohydrate. [e]Contained more than 5 percent reducing sugars. [f]Derived from Kraft process. [g]Contains less than 5 percent calcium lignosulfonate. Remainder is zinc oxide and dolomitic limestone [h]Contained calcium chloride [i]Contained foaming agent. [j]Contains less than 10 percent of active organic constituent Remainder is iron oxide and siliceous material.

TABLE 2

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF PORTLAND CEMENT

Determination	Cement A	Cement B	Cement C	Cement D	Blend[a]
Chemical composition (%):					
Silicon dioxide	21.4	21.4	21.9	21.4	21.6
Aluminum oxide	5.9	5.1	5.6	5.4	5.4
Ferric oxide	2.8	2.2	2.3	2.4	2.4
Calcium oxide	63.4	62.5	66.1	65.2	64.3
Magnesium oxide	2.1	3.8	1.2	1.6	2.2
Sulfur trioxide	1.8	2.4	1.7	1.9	2.0
Loss on ignition	1.7	1.5	1.2	1.1	1.4
Sodium oxide	0.20	0.30	0.02	0.14	0.18
Potassium oxide	0.82	0.95	0.14	0.79	0.69
Equivalent alkalies as Na_2O	0.74	0.93	0.11	0.66	0.63
Chloroform-soluble organic substances	0.016	0.008	0.004	0.007	0.008
Free lime	0.97	0.93	0.97	0.66	0.94
Computed compound composition (%):					
Tricalcium silicate	47	48	57	58	52
Dicalcium silicate	26	26	20	18	23
Tricalcium aluminate	11	10	11	10	10
Tetracalcium aluminoferrite	8.5	6.7	7.0	7.3	7.4
Calcium sulfate	3.05	4.08	2.89	3.23	3.31
Merriman sugar test:					
Neutral point, ml	7.6	2.4	2.3	2.5	3.3
Clear point, ml	8.8	2.8	2.6	2.8	4.2
Physical properties:					
Apparent specific gravity	3.12	3.13	3.14	3.14	3.12
Specific surface (Blaine), cm^2/g	3,375	3,590	3,110	3,145	3,310
Autoclave expansion, %	0.07	0.19	0.04	0.06	0.07
Normal consistency, %	25.3	24.3	24.4	24.6	24.0
Time of setting (Gillmore):					
Initial, hr	2.9	2.8	3.4	4.0	2.3
Final, hr	6.2	5.1	6.8	6.0	7.5
Compressive strength:					
At 3 days, psi	2,500	2,500	2,030	2,610	2,490
At 7 days, psi	4,165	3,450	3,225	4,175	3,840
At 28 days, psi	5,690	4,565	5,585	5,510	5,285
Tensile strength:					
At 3 days, psi	340	320	300	320	315
At 7 days, psi	400	395	365	435	400
At 28 days, psi	470	465	475	465	480
Mortar air content, %	8.0	8.8	7.5	7.8	8.6

Note: All determinations except the Merriman sugar test made in accordance with current AASHO methods for portland cement.

[a]Tests made on blend of equal parts by weight of all four cements.

contained free water but the stone was weighed in a saturated surface-dry condition.

Three mixes of air-entrained concrete with air contents of 5 to 6 percent and a slump of 2 to 3 in. were used in the investigation. Mix No. 1, the reference mix without retarder, and Mix No. 2, a test mix with retarder, both had cement contents of 6 bags per cubic yard of concrete. Mix No. 3, a test mix with retarder, had cement

contents which varied from 5.25 to 5.75 bags and the water-cement ratio was equal to that of the reference mix (No. 1). The water content of Mix No. 2, was reduced below that of the reference mix (No. 1), but sufficient aggregates were added to compensate for the reduced volume. A summary of the mix proportions is given in Table 3.

A sufficient amount of retarder was used in the tests of Mix No. 2 at 73 F to cause a delay in setting time of 2½ to 3 hr beyond the setting time of the reference mix. The correct amount of each retarder for the desired retardation was predetermined by trial mixes. The same amount of retarder in ounces per bag of cement was used in Mix No. 3. Additional tests of some retarders were made using four times the amount of the retarder used in Mixes No. 2 and 3.

MIXING, FABRICATION, AND CURING OF SPECIMENS

Mixing was done in an open-pan-type Lancaster mixer with a rated capacity of 1¾ cu ft. Most batches were from 1½ to 2 cu ft in volume. The mixing cycle was as follows: The blend of four cements and the moist fine aggregate were mixed for ½ min; water was added and the mortar was mixed for 1 min. After the addition of the coarse aggregate the concrete was mixed for 2 min. Following a "rest" period of 2 min, the concrete was mixed for 1 more minute. This 2-min rest period and the additional minute of mixing is a standard procedure in the Bureau of Public Roads.

Retarder in powder form was added with the cement and sand, but a liquid retardant admixture was added with part of the mixing water. Vinsol resin solution was added in part of the mixing water and was not mixed with the liquid retarder before each was placed in the mixer.

Consideration was given to adding the soluble powdered admixtures in an aqueous solution. Although the soluble powders could have been prepared in a stock solution or suspension, it was believed that during the period of months required for the program, evaporation or chemical changes of the retarder due to exposure to light might result. An attempt was made to dissolve in water the weighed amount of lignosulfonate powder required for a single batch of concrete but difficulty was experienced with some powders in obtaining a uniform solution or suspension. Therefore the procedure of adding the powdered admixture with the cement and wet sand was used. It is believed that a uniform distribution of the powdered admixture in the concrete was obtained.

A control mix (No. 1) was made on each mixing day together with Mixes No. 2 and 3 which contained retarders. Because of limitations of time and molds a total of one control mix and two test mixes for each of 3 to 5 different retarders was made on one mixing day. Two rounds of specimens for retardation tests and five rounds for strength tests were made but each round did not necessarily include the same retarders as in the preceding round.

Concrete used for slump and unit weight tests was returned to the mixer and remixed for 15 sec before molding specimens for strength tests. Concrete used in the air meter

TABLE 3

CONCRETE MIXES

Properties of Concrete	Mix				
			No. 3[b]		
	No 1	No. 2[a]	Group A	Group B	Group C
Mix, lb	94-190-310	94-193-314	94-205-330	94-215-345	94-230-360
Cement, bags/cu yd	6 0	6 0	5 75	5 50	5 25
Water, gal/bag	5 8	5.1 to 5.7	5 8	5 8	5 8
Water-cement ratio by vol	0.77	0 68 to 0.76	0 77	0 77	0 77
Slump, in	2½	2½	2½	2½	2½
Air, %	5 5	5 5	5 5	5 5	5 5
Retarder, amount used	None	To give 2½ to 3 hr retardation	Same as Mix No 2	Same as Mix No 2	Same as Mix No 2

[a]Had same cement content as Mix No 1 [b]Had same water-cement ratio (± 0.2 gal/bag) as Mix No. 1 Group A—cement content reduced 0.25 bags per cubic yard for retarders that reduced water for Mix No 2 by 0 to 5 percent. Group B—cement content reduced 0.50 bags per cubic yard for retarders that reduced water for Mix No. 2 by 5 to 10 percent. Group C—cement content reduced 0 75 bags per cubic yard for retarders that reduced water for Mix No. 2 by 10 percent or more

was discarded. Specimens made at standard conditions were mixed and molded in air at 73 F and 50 percent relative humidity.

Specimens for strength or durability tests were 6- by 12-in. cylinders and 6- by 6- by 21-in. or 3- by 4- by 16-in. beams. These were molded (except for vibrated specimens) in accordance with standard AASHO methods. Specimens for strength tests were removed from the steel molds at 20 to 24 hr except when an overdose of a retarder was used. Small beams for volume change and freezing and thawing were removed from the steel molds at 44 to 48 hr.

For a study of delayed vibration, 6- by 12-in. cylinders and 6- by 6- by 21-in. beams were molded by the standard procedure and later vibrated for 30 sec using an internal spud vibrator of 1⅛-in. diameter with a frequency of 7,000 impulses per minute.

The original program required that the specimens be vibrated when the screened mortar showed a Proctor penetration (4) load of 500 psi, which was approximately 5 hr after mixing for unretarded concrete and 7½ to 8 hr for the retarded concretes. This could not be accomplished, as many of the mixes were then too stiff for vibration. Therefore, the time of 3 hr after mixing for the unretarded concrete and 5½ hr for the retarded concrete was used. A small amount of concrete was removed from each specimen just prior to vibration and it was replaced as the vibration was completed. No additional concrete was added to compensate for the decrease in volume.

All specimens for standard strength tests were cured under wet burlap while in the molds in the mixing room. After removal from the molds they were cured in moist air at 73 F and 100 percent relative humidity until they were tested. Small beams for volume change and freezing and thawing were cured in the molds for 44 to 48 hr under wet burlap in the moist room. One-third of the number of beams for volume change were cured continuously in the moist room, one-third were removed from the moist room at 2 days and stored in laboratory air at 73 F and 50 percent relative humidity, and one-third were cured 14 days in the moist room and then stored in laboratory air. Beams for freezing and thawing after removal from the molds at 44 to 48 hours were cured in the moist room for 12 more days, then cured in laboratory air at 73 F and 50 percent relative humidity for 7 days and then were completely immersed in water for 7 days prior to freezing.

When strength specimens were made under nonstandard conditions, the laboratory air had a temperature of 90 F and a relative humidity of 20 to 25 percent. All materials were at 90 F when used. After 20 to 24 hr curing under wet burlap at this temperature, the specimens were removed from the molds and stored in the moist room at 73 F and 100 percent relative humidity until tested.

TESTING PROCEDURES

Tests on the plastic concrete for slump, unit weight, and air content were made in accordance with AASHO standard methods. The determination of the air content was made with a water-type pressure meter that is similar to the meter described in AASHO Method T 152.

Determination of the retardation of the set of concrete was made by the Proctor penetration test, ASTM Method C 403-57 T, and by the bond pin (5) pullout test which is described in the ASTM Proceedings for 1957. The Proctor apparatus with a hydraulic indicating dial and the pullout device are shown in Figures 1 and 2. Both were built in the Bureau of Public Roads instrument shop.

The mortar for the Proctor test was obtained by sieving the plastic concrete on a No. 4 sieve. The sieve was vibrated and the concrete was moved over the sieve by hand or by use of a small trowel. Two 6- by 6-in. watertight steel cylinder molds were filled with mortar, and were immediately covered with glass plates. Water was pipetted from the mortar as it collected on the surface.

Concrete for the pin pullout test was vibrated around the pins in a 6- by 6- by 24-in. mold using a laboratory internal vibrator and screeded on the surface by a steel straight edge. The specimens were covered with wet burlap which was removed only while a pin was pulled from the concrete. No two consecutively pulled pins were adjacent to each other.

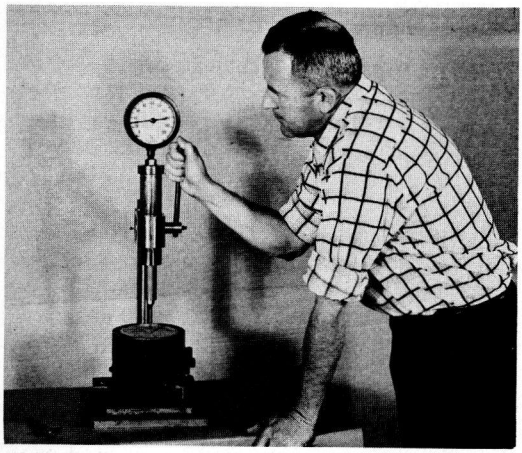

Figure 1. Proctor penetration device.

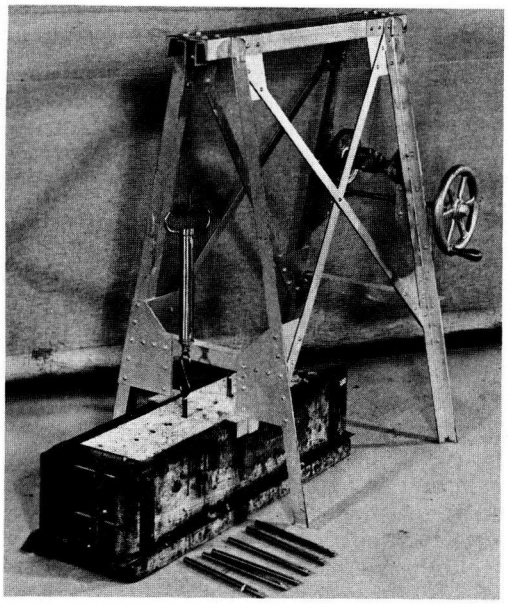

Figure 2. Pin pullout device.

Typical curves for retardation on a 6-bag concrete of Mixes No. 1 and 2 by the Proctor and pin pullout methods are shown in Figure 3.

Two series of tests were made to determine the temperature rise of mortar or concrete prepared with retarders. In the first series, 6- by 6-in. cardboard cylinder molds were filled with screened mortar from concrete that was mixed at 90 F. The specimens were then sealed by a glass plate and heavy grease and stored in a curing cabinet at 90 F. In the second series, 6- by 12-in. cardboard cylinder molds were filled with concrete made at 73 F, sealed with a glass plate and heavy grease, and placed in a metal can 11 in. in diameter and 15 in. in height. Expanded mica was placed around all surfaces of the cylinder mold and on the glass plate, and the cans were stored in laboratory air maintained at 73 F. Each cylinder was molded with a copper-constantan thermocouple at its symmetrical center and the temperatures were recorded on an eight-point potentiometer. The

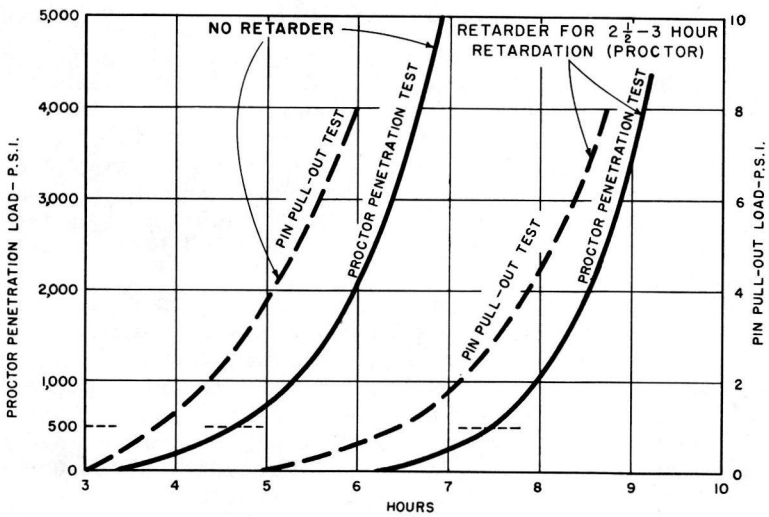

Figure 3. Typical curve for Proctor and pin pullout test for retardation time on concrete.

amount of each retarder used was that amount necessary for 2½ to 3 hr retardation at 73 or 90 F.

All cylinders for compressive strength tests were capped on both ends with high-alumina cement after removal from the molds, and at least 48 hr prior to testing. All caps were within 0.001 in. of planeness. The cylinders were loaded at a rate of 35 psi per sec.

Beams for flexural strength were tested in accordance with AASHO Method T 97. When bearings on beams did not meet the requirements for planeness, they were ground with a power-driven carborundum wheel.

Beams measuring 3 by 4 by 16 in., were tested for resistance to freezing and thawing in accordance with AASHO Standard Method T 161 for fast freezing and thawing in water.

Measurements for volume change of 3- by 4- by 16-in. beams were made on a horizontal comparator with a micrometer dial reading to 0.0001 in. at one end and a micrometer barrel reading to 0.0001 in. at the other end. Stainless steel gage studs were cast in the ends of the beams and the beams were stored with the 4-in. axis in a vertical position during the drying period.

Tests for static modulus of elasticity were made on 6- by 12-in. cylinders at 7 and 28 days by an autographic stress-strain recorder with a 6-in. gage length. These tests were paralleled by sonic modulus of elasticity tests on 6- by 6- by 21-in. beams which were made from the same batch of concrete as the cylinders.

Density and absorption tests were made on 2 disks, each 1 in. in thickness, which were cut from the top, middle and bottom of 6- by 12-in. concrete cylinders. The cylinders were molded from Mixes No. 1 and 2. The disks were cut by a diamond wheel at an age of 28 days from moist-cured cylinders and were weighed in air and under water. They were then dried to constant weight in a forced air oven at 190 to 200 F.

TABLE 4

RETARDATION TIME FOR CONCRETE (Mix No 2) AT 73 F

Retarder				Retardation[b]					
				Proctor Pen Test[c]				Pin Pullout Test[d]	
				At 500 Psi		At 4,000 Psi		At 8 Psi	
No	Amount Used (oz/bag)	Air[a] (%)	Slump (in)	Hr	Min	Hr	Min	Hr	Min
1	1.1	5 0	2 6	2	50	2	45	2	40
2	14 4	5 0	2 5	2	30	2	10	2	20
3	4 0	6 1	3 0	2	45	2	35	2	30
4	3 0	5 4	3 2	2	30	2	30	2	55
5	4 0	5 4	3 1	2	40	2	20	1	25
6	4 0	5 7	3 2	2	20	2	15	2	30
7	3 5	5 0	2 7	2	45	2	40	3	00
8	12 0	6 3	3 2	2	50	3	00	2	25
9	2 8	6 0	2 8	2	30	2	35	2	15
10	3 2	6 2	2 6	2	30	2	45	2	20
11	4 8	5 4	3 0	2	50	2	30	2	50
12	4 0	5 2	3 0	2	50	2	50	2	05
13	4 8	5 4	3 0	2	20	2	30	2	15
14	5 0	4 3	3 3	2	40	2	45	2	40
15	4 0	7 5	3 0	2	35	3	00	1	55
16	4 8	6 2	3 0	2	50	2	35	1	50
17	3 2	5 5	2 6	2	50	3	00	2	20
18	4 0	5.0	2 8	2	20	2	00	1	00
19	4 0	5 5	2 8	2	40	3	00	2	05
20	9 0	5 0	2 2	2	25	2	30	2	35
21	9 0	6 4	3 5	2	30	2	40	2	10
22	4 0	10	2 6	2	30	2	30	1	50
23	6 4	7 0	3 0	2	40	2	40	1	40
24	9 6	5 4	2 4	2	40	2	25	1	55
25	4 0	7 0	2 8	2	35	2	35	1	30

Note Each value is average of two tests made on different days

[a]Neutralized Vinsol resin solution used when needed

[b]Retardation is the delay in time of hardening of the concrete containing the retarders as compared with the concrete without retarder made on the same day Time for concrete without retarder to reach
Proctor penetration load of 500 psi—5 hr 10 min (± 20 min)
Proctor penetration load of 4,000 psi—7 hr 35 min (± 30 min)
Pin pullout load of 8 psi—6 hr 40 min (± 20 min)

[c]Proctor penetration test made in accordance with ASTM Method C 403-57T A Proctor penetration load of 500 psi is assumed to be the vibration limit of the concrete A Proctor penetration load of 4,000 psi is assumed to indicate hardened concrete

[d]Pin pullout test made as described in ASTM Proceedings, Vol 57, 1957, pp 1029-1042

One procedure in the mixing and testing of the plastic concrete and the testing of hardened concrete should be emphasized. As stated previously, a reference mix (No. 1), without retarder, was made on every mixing day and all tests on plastic or hardened concrete which were made on any one day included specimens from this reference mix.

DISCUSSION OF TEST RESULTS

The test data are given in Tables 4 to 14, inclusive, and shown in Figures 4 to 12. The effect of retarders on the concrete are discussed in terms of the main objectives of the investigation. They were (a) the effect of the retarder on retardation of setting time, (b) the effect on water content and air-entrainment, (c) the effect on strength, (d) the effect on durability, and (e) the effect on volume change. Additional tests, such as the effect of overdosage of retarders, retardation and strength at elevated temperature, modulus of elasticity, delayed vibration, density and absorption, and temperature rise are also discussed.

EFFECT OF ADMIXTURES ON TIME OF RETARDATION

The amount of each retarder and the resulting retardation, as measured by the Proctor test at 500-psi or 4,000-psi penetration pressure or by the pin pullout test at 8 psi are given in Table 4. Each value is the average of two tests that were made on two days. Retardation is the difference in setting time between that for the reference mix (No. 1) and that for the concrete with the retarder (Mix No. 2). Recommendations for the amount of retarder to be used were furnished by the manufacturers of 22 of the retarders included in these tests. For each of 13 of the retarders, the amount recommended was found to give the desired retardation of 2½ to 3 hr. For two retarders, 80 percent of the recommended amount was found to be sufficient, and for three other retarders, 120 or 125 percent of the recommended amount was needed. For the remaining 4 of the 22 retarders, from 150 to 500 percent of the recommended amount was required to obtain an effective amount of retardation. These four were retarders No. 2, 6, 22, and 23. Except for No. 6, they were lignosulfonates.

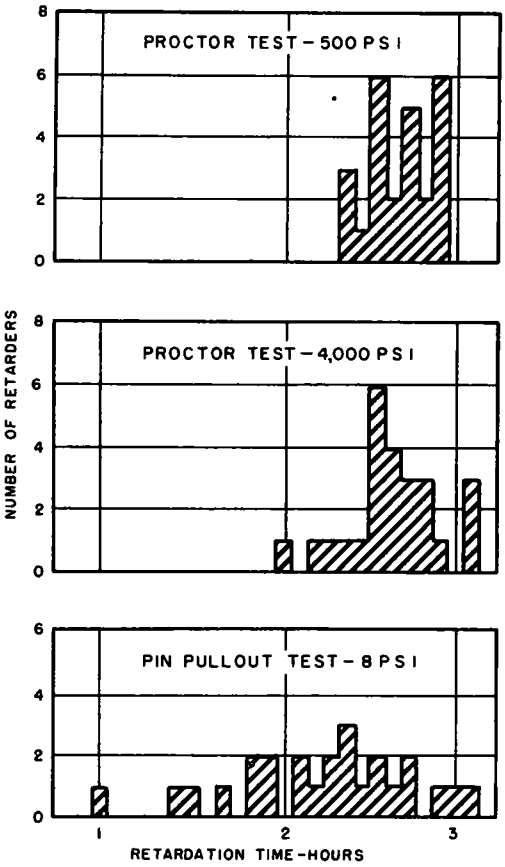

Figure 4. Distribution of determinations for retardation.

The 500-psi penetration pressure of the Proctor test is believed to indicate the initial setting of the mortar used. At this time, the mortar may still be remolded without injury to its strength. When determinations are made using a penetration pressure of 4,000 psi, a condition at or near the final setting of the mortar is indicated. Attempts to rework the mortar at this time would result in its disruption. In the pin pullout test, no attempt is made to define or determine the setting time of concrete. Conducted under defined conditions, the test is intended to permit comparisons of the rate of hardening of different concretes.

The comparison of typical retardation values for the Proctor and pin pullout tests in Figure 3 indicates that a 500-psi penetration corresponds to a pin pullout load of 2½ to 2¾ psi. However, the ranges of values shown in Figure 4 indicate that for the concretes used in these tests, the Proctor penetration test with either of the loads used, appears to be more suitable for measuring setting time and retardation than the pin pullout test. The wide range of values for the pin pullout test and lack of a definite central point indicate that the test result probably is affected by uncontrolled variables to a greater extent than the Proctor penetration test.

EFFECT OF RETARDERS ON AIR CONTENT, WATER CONTENT, AND AMOUNT OF AIR-ENTRAINING AGENT USED IN CONCRETE

Table 5 gives the amount of Vinsol resin solution (air-entraining agent) used in concretes for Mixes No. 2 and 3 for strength tests at 73 F and the resulting water and air contents of the concrete. (The retarders generally were given their identification numbers in ascending order of the reduction in water requirements for Mix No. 2. The exception is retarder No. 12 which is slightly out of place in the table.) The detail data for the reference mix (No. 1) are not tabulated because it would be different for each retarder, but average values are given in a footnote. The values given in Table 5 are averages of five rounds of tests.

The reduction in water content for Mix No. 2 is the difference between the amount of water used for Mix No. 1 and Mix No. 2 made on the same day. This is shown as a percentage of the amount of water used for Mix No. 1. A comparison between this reduction in water content and the amount of retarder used for Mix No. 2 is shown in Figure 5. It is noted here that some retarders are much more effective in permitting a reduction in the amount of water required to obtain concrete of a given slump. A comparison between the amount of reduction in water and the amount of retarder used per bag of cement shows that retarder No. 25 is the most effective and No. 2 is the

TABLE 5

MIX DATA FOR STRENGTH TESTS

		Mix No 2—Same Cement Content as Reference Mix (No. 1)						Mix No 3—Same Water Content (± 0 2 gal/bag) As Reference Mix (No. 1)				
Retarder No.[a]	Water for Mix No 1[b] (gal/bag)	AEA[c] Added (ml/bag)	Cement (bags/cu yd)	Slump (in)	Air (%)	Water (gal/bag)	Reduction in Water[d] (%)	AEA[c] Added (ml/bag)	Cement (bags/cu yd)	Slump (in.)	Air (%)	Water (gal/bag)
1	5 75	17.1	6.0	2 8	5.0	5 69	1 1	19 0	5 7	2 7	5 6	5.89
2	5 77	16 2	6 0	2.6	5 2	5 61	2 8	18 0	5 7	2 9	5.6	5.93
3	5.79	None	6.0	3.1	5 9	5.49	5.2	None	5 5	2.8	5.6	5.89
4	5 81	13 7	6 0	2 9	5.7	5 50	5 3	14 5	5.4	2 8	5 8	6.01
5	5 74	11 5	6 0	3 1	5.5	5 41	5.7	12.3	5 5	2.7	5.8	5 81
6	5 87	15 1	6.0	2 7	5.4	5 53	5.8	16.4	5 5	2.9	5.9	6 03
7	5 76	8 3	6 0	2 7	5 4	5.42	5.9	9.2	5 5	2 6	5 5	5 84
8	5 78	15.8	6.0	2.6	5.5	5 43	6.1	14 7	5 5	2.8	5 6	5 88
9	5.91	14 5	6.0	2 9	5.2	5.52	6 6	16.6	5 5	2.6	5.7	6.04
10	5 86	9.4	6.0	3.0	5 4	5.44	7.2	8 6	5 6	2.7	5 1	5.76
11	5 71	3.7	6.0	2 7	5.7	5.29	7 4	4 1	5.5	2 7	5 5	5.71
12	5.86	2.5	6 0	2.6	5 4	5.37	8 4	None	5 5	2.7	5 6	5 87
13	5 77	2.6	6.0	2 7	5.7	5.30	8 1	1.3	5.5	2 6	5 7	5 75
14	5.67	2.2	6 0	3.0	5 7	5.21	8 1	2.8	5.5	2 7	5 8	5.72
15	5.73	None	6 0	3.0	6 8	5.26	8.2	None	5 5	2.8	7 0	5 67
16	5.67	4 4	6.0	2.9	6.1	5 20	8 3	3.7	5.5	2.8	5 8	5.74
17	5.79	11 5	6.0	2.8	5.5	5 31	8 3	11.3	5 5	2.9	5.5	5 81
18	5.77	4.5	6 0	2 7	5 6	5.27	8.7	4.4	5 5	2 6	5 7	5 75
19	5.74	7.2	6.0	2.5	5.7	5 24	8 7	6.4	5 5	2 6	5.4	5 78
20	5.86	None	6.0	2.8	5 3	5 30	9 6	1 8	5 5	2 6	5.5	5.81
21	5 84	4 0	6.0	2.7	5 7	5 27	9.8	2.8	5 5	2.6	5.7	5.72
22	5 80	None	6.0	3 2	10.0	5.22	10.0	None	5 2	3.1	10.0	5 88
23	5.75	None	6.1	2.6	5.8	5.15	10.4	None	5 3	2 6	5.4	6 03
24	5 78	None	6.0	2 6	5.9	5 13	11.2	None	5.2	2 6	5 8	5 86
25	5 76	None	6.0	2.8	7.6	5.08	11 8	None	5 2	2.8	9.5	5.72

Note Each value is an average of five tests made on different days.

[a]Amount of retarder used same as given in Table 4.

[b]Water content for Mix No. 1 is water used in reference mix made on same day as retarded concrete mixes. Average values for Mix No. 1 are AEA added, 20 ml/bag, cement, 6.0 bags/cu yd, slump, 2.9 in., air, 5 4 percent.

[c]Air-entraining agent.

[d]Average reduction in water-cement ratio as compared with that required for the reference mix made on the same day.

least effective. These retarders reduced the water required for Mix No. 2 by 2.9 percent and 0.2 percent, respectively, per ounce of retarder used per bag of cement. Of the other retarders, the most effective included retarders No. 9, 10, 12, 15, 17, 18, 19, and 22. Of the nine most effective retarders with respect to reduction in water, one is an organic acid salt and the others are lignosulfonates.

The concretes of Mix No. 3 were prepared with cement contents reduced in accordance with the amount of reduction in water found possibe for Mix No. 2. For retarders which permitted a reduction in water of 5 percent or less in Mix No. 2, the cement content for Mix No. 3 was reduced 0.25 bag per cubic yard. For retarders which permitted a reduction of water of more than 5 but less than 10 percent, the cement content for Mix No. 3 was reduced 0.5 bag per cubic yard. For retarders permitting a reduction in water of 10 percent or more, the cement content was reduced 0.75 bag per cubic yard. It was found that due to uncontrollable variables, it was not possible to prepare all batches of concrete with these exact cement contents, and at the same time maintain a slump of 2.8 ± 0.3 in. and use the same amount of water in Mix No. 3 as was used in the reference mix (No. 1). To hold the cement content and slump as nearly as possible to the desired values, slight variations in the water content had to be permitted. For 18 of the 25 retarders, the water contents agreed within 0.1 gal per bag of cement, and in only one case (retarder No. 23) did the water contents differ by more than 0.2 gal per bag. In view of these small differences, it is considered that Mix No. 3 may be stated to have the same water content as the reference mix (No. 1).

The amount of Vinsol resin solution required to entrain 5 to 6 percent air in concrete (Mix No. 2) prepared with an organic acid type of retarder (Nos. 4, 5, 6, 8, or 9) was approximately two-thirds of that used in the reference mix. The water reduction caused by these 5 retarders varied from 5.3 to 6.6 percent. The amount of air-entraining solution used in concrete (Mix No. 3) with a decreased cement content of ¼ to ¾ of a bag per cubic yard was approximately the same as the quantity needed for Mix No. 2. As past experience has shown that the organic acid type of retarders causes no air-entrainment in concrete, these data indicate that they aid air-entrainment and permit a moderate reduction in water content when used at the rate of 2.8 to 12 oz per bag of cement.

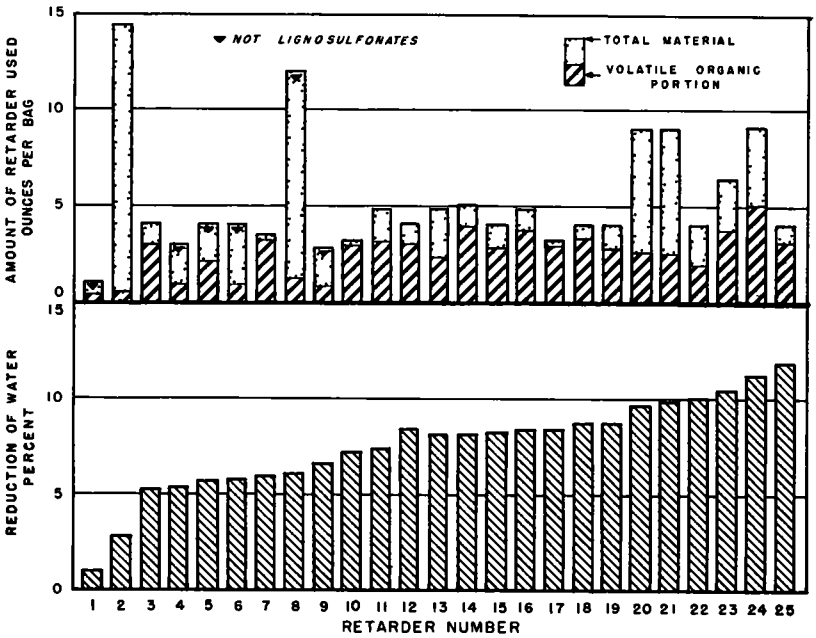

Figure 5. Amount of retarder used and effect on water content.

The concrete prepared with each of the lignosulfonate retarders showed a wide range of 2.8 to 11.8 percent in water reduction. The reduction of 2.8 percent was obtained by use of a powdered lignosulfonate which contained over 95 percent of an inorganic filler. Two lignosulfonates permitted reduction of 5.2 and 5.9 percent, 12 permitted reductions of 7 to 10 percent, and 4 permitted reductions of 10 to 12 percent. It should be noted that although the water reduction for concrete containing retarders No. 1 and 2 was lower than is usually required, satisfactory retardation was obtained.

It is not the purpose of this report to explain the reasons for the variations in the effects of any admixtures, when used at a rate which causes a 2½- to 3-hr retardation of setting time, on the water content or air content of concrete. The paper on chemical composition and identification tests of retarders (6) provides ample data for any reader who desires to explain or theorize about the reasons for the effects of chemical composition of retarders on the physical properties of retarded concrete.

Seven of the 19 lignosulfonate retarders, without the use of an air-entraining solution, entrained more than 5 percent of air in the concrete. Three of these retarders caused air contents about 6 percent and the maximum air content was obtained for concrete containing retarder No. 22. The air content for concrete containing this retarder was 10 percent calculated gravimetrically. The effect of each of the 25 retarders on air content of concrete and the amount of air-entraining admixture used in shown in Figure 6.

The amount of air-entraining solution needed with each of the other 12 lignosulfonate retarders to entrain 5 to 6 percent of air in concrete (Mix No. 2) varied from about ⅛ to ½ of the quantity used in the reference mix, except in the case of retarder No. 2. The powdered extender and the small amount of lignosulfonate in this retarder might account for the larger quantity of air-entraining solution required.

Retarder No. 1, sucrose of the carbohydrate group, caused a small reduction (1.1 percent) in water content and required almost as much air-entraining solution as the reference mix.

EFFECT OF ADMIXTURES ON STRENGTH OF CONCRETE

Compressive Strength Test Results

The results of the compressive strength tests on concrete containing the 25 retarders are given in Table 6. This table gives the average of five compressive strength tests for Mixes No. 2 and 3 on 6- by 12-in. cylinders made on different days and tested at 3, 7, 28, and 365 days. It also gives the ratios of these strengths to the strengths of concrete without retarder (Mix No. 1) made and tested on the same day as the concrete containing the retarder.

Average values for the compressive strength of all concretes prepared with and

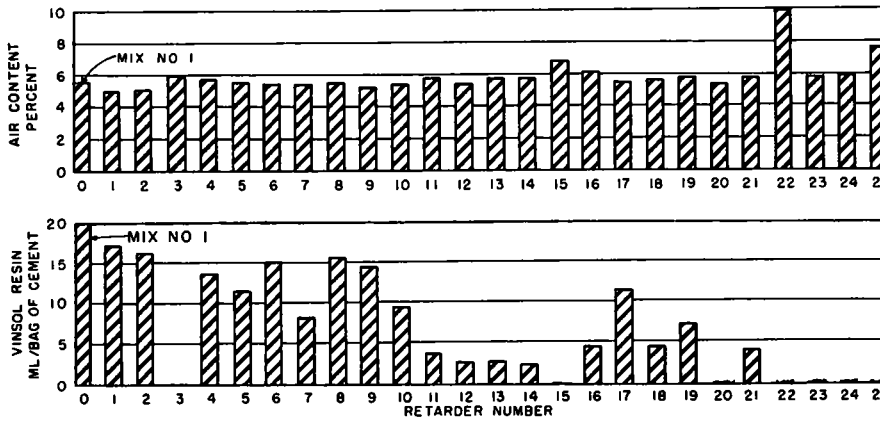

Figure 6. Effect of retarder on air content of Mix No. 2.

TABLE 6

COMPRESSIVE STRENGTH TESTS

Retarder No [a]	Compressive Strength (psi) for Mix No. 2				Compressive Strength (psi) for Mix No. 3			
	3 Days	7 Days	28 Days	1 Yr	3 Days	7 Days	28 Days	1 Yr
1	2,910 (126)	4,210 (118)	5,700 (115)	6,890 (114)	2,700 (117)	3,950 (111)	5,450 (110)	6,510 (107)
2	2,910 (123)	3,980 (110)	5,370 (108)	6,520 (109)	2,620 (111)	3,840 (106)	5,090 (102)	6,070 (102)
3	2,910 (125)	3,990 (116)	5,240 (110)	6,400 (113)	2,430 (105)	3,460 (100)	5,030 (106)	6,050 (107)
4	2,930 (126)	4,430 (125)	5,900 (120)	6,890 (117)	2,410 (103)	3,970 (112)	5,180 (105)	6,180 (105)
5	3,260 (132)	4,600 (124)	6,090 (120)	7,080 (115)	2,920 (119)	4,120 (111)	5,580 (110)	6,590 (108)
6	2,910 (126)	4,290 (124)	5,610 (118)	6,740 (118)	2,480 (107)	3,800 (110)	5,160 (109)	6,130 (107)
7	3,030 (122)	4,310 (118)	5,720 (114)	6,890 (115)	2,680 (108)	3,790 (104)	5,420 (108)	6,500 (109)
8	3,070 (127)	4,370 (123)	5,840 (114)	7,200 (119)	2,640 (109)	3,800 (107)	5,370 (105)	6,520 (107)
9	3,060 (130)	4,400 (124)	5,830 (116)	7,070 (117)	2,600 (110)	3,810 (107)	5,470 (109)	6,420 (106)
10	3,000 (124)	4,340 (121)	5,790 (116)	7,090 (116)	2,680 (111)	4,020 (112)	5,390 (108)	6,640 (108)
11	3,340 (140)	4,610 (127)	6,130 (120)	7,420 (125)	2,910 (122)	4,150 (114)	5,480 (108)	6,620 (111)
12	3,260 (132)	4,560 (128)	5,910 (122)	7,290 (123)	2,530 (103)	3,920 (110)	5,290 (109)	6,460 (109)
13	3,280 (133)	4,500 (124)	5,870 (115)	7,240 (119)	2,770 (112)	3,830 (105)	5,350 (104)	6,570 (108)
14	2,940 (123)	4,330 (119)	5,890 (117)	7,230 (120)	2,500 (105)	3,910 (107)	5,330 (106)	6,300 (104)
15	3,000 (120)	4,370 (118)	5,610 (110)	7,020 (113)	2,550 (102)	3,940 (107)	5,120 (101)	6,430 (104)
16	3,240 (136)	4,570 (125)	6,100 (121)	7,120 (118)	2,740 (115)	4,100 (112)	5,480 (109)	6,590 (109)
17	3,150 (128)	4,430 (125)	5,900 (115)	7,220 (119)	2,520 (102)	3,800 (107)	5,280 (103)	6,410 (106)
18	3,270 (131)	4,500 (120)	5,860 (112)	7,050 (113)	2,880 (116)	4,050 (108)	5,420 (104)	6,470 (104)
19	3,280 (133)	4,490 (124)	5,990 (117)	7,310 (121)	2,710 (110)	3,900 (107)	5,400 (107)	6,490 (107)
20	3,230 (138)	4,620 (131)	6,110 (122)	7,470 (123)	2,830 (121)	4,110 (117)	5,620 (113)	6,930 (115)
21	3,200 (132)	4,440 (125)	5,830 (116)	7,340 (121)	2,780 (115)	4,090 (115)	5,550 (110)	6,750 (111)
22	2,290 (99)	3,300 (93)	4,520 (91)	5,550 (94)	1,830 (79)	2,750 (77)	3,940 (79)	4,740 (80)
23	3,200 (139)	4,500 (129)	5,950 (122)	7,410 (123)	2,540 (108)	3,920 (109)	5,180 (105)	6,360 (105)
24	3,470 (163)	4,580 (130)	6,030 (121)	7,490 (125)	3,140 (136)	4,010 (114)	5,280 (106)	6,470 (108)
25	2,940 (129)	4,160 (118)	5,420 (110)	6,760 (115)	2,140 (94)	3,280 (93)	4,460 (90)	5,390 (92)

Notes· Each value is the average of five tests made on five different days. Specimens stored in moist air until tested. Figures in parentheses represent the ratios (in percent) of the strength of the concrete containing the retarders to the strength of the concrete without retarder (Mix No. 1) made on the same day

[a]Amount of retarder used is the same as given in Table 4.

without the retarders are shown in Figure 7. The curves show that both Mix No. 2 with a reduced water content, and Mix No. 3 with a reduced cement content, furnished higher average compressive strengths at all ages to one year than was obtained without the use of retarders. This increase in compressive strength might be considered a secondary benefit obtained by the use of retarders, but it is a real and definite improvement in the characteristics of concrete.

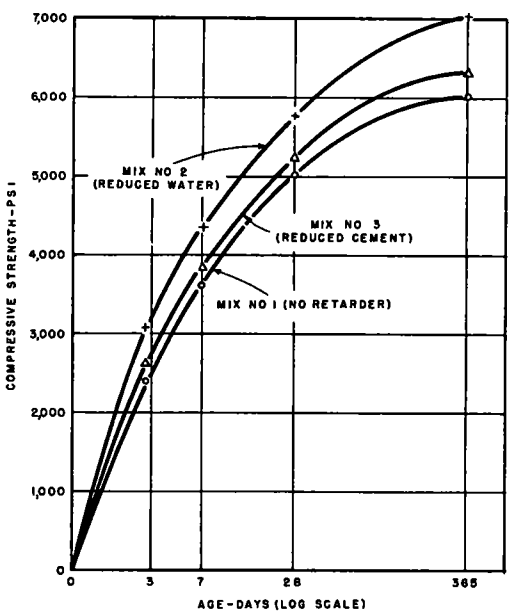

Figure 7. Influence of retarders on compressive strength of concrete average values for all retarders.

As given in Table 6, all retarders except Nos. 22 and 25 furnished concrete of equal or higher strength at all ages than was obtained in the nonretarded concrete. Retarder No. 22 caused the entrainment of an excessive amount of air, and the strength suffered accordingly. Retarder 25 gave good results when used in Mix No. 2 with a reduced water content. When it was used in Mix No. 3 where the cement content was reduced, the concrete containing this retarder had lower strengths at all ages than the reference concrete. This retarder caused the entrainment of an excessive amount of air in Mix No. 3.

Study of the strengths obtained at all ages failed to show that any type of retarder gave better results than any other type. In this study, the types considered were the ammonium, sodium, and calcium lignosulfonates, the organic acid derivatives, and the carbohydrate.

Flexural Strength Test Results

The results of the flexural strength tests for Mixes No. 2 and 3 are given in Table 7. This table gives the average of five tests on the 6- by 6- by 21-in. beams made on different days and tested at ages of 7 and 28 days. The ratios of these strengths to the strengths of concrete without retarder (Mix No. 1), made and tested on the same day as the concrete containing the retarders, are also given.

TABLE 7

FLEXURAL STRENGTH TESTS

Retarder No.[a]	Modulus of Rupture (psi)				
	Mix No. 2			Mix No. 3	
	7 Days[b]	28 Days[b]	15 Mo[c]	7 Days[b]	28 Days[b]
1	665 (102)	790 (110)	785 (101)	645 (98)	770 (108)
2	675 (112)	750 (103)	780 (100)	630 (105)	695 (96)
3	665 (110)	750 (103)	875 (105)	630 (104)	745 (103)
4	725 (118)	785 (104)	840 (102)	620 (101)	770 (102)
5	680 (106)	765 (98)	870 (104)	665 (104)	710 (91)
6	670 (111)	755 (109)	830 (99)	590 (98)	710 (102)
7	675 (107)	760 (100)	845 (101)	645 (102)	730 (96)
8	690 (108)	830 (112)	885 (106)	630 (98)	755 (102)
9	690 (109)	805 (106)	855 (104)	655 (103)	745 (98)
10	670 (104)	805 (113)	740 (90)	690 (107)	750 (106)
11	665 (108)	725 (95)	835 (102)	650 (106)	710 (93)
12	720 (118)	760 (105)	760 (97)	620 (102)	685 (94)
13	685 (107)	785 (102)	805 (96)	655 (102)	725 (94)
14	675 (109)	800 (102)	850 (104)	625 (101)	750 (96)
15	715 (111)	770 (110)	845 (101)	645 (100)	685 (98)
16	630 (102)	730 (94)	890 (109)	610 (98)	705 (90)
17	690 (112)	750 (103)	815 (98)	655 (106)	745 (103)
18	660 (107)	755 (97)	810 (99)	600 (98)	685 (88)
19	720 (110)	790 (103)	755 (90)	675 (103)	755 (98)
20	695 (107)	800 (109)	815 (99)	630 (97)	730 (99)
21	660 (104)	800 (109)	825 (101)	640 (101)	740 (101)
22	595 (98)	695 (96)	675 (87)	535 (88)	640 (89)
23	670 (108)	810 (114)	715 (92)	625 (100)	750 (107)
24	635 (106)	745 (101)	810 (104)	600 (100)	650 (88)
25	655 (107)	750 (105)	775 (99)	590 (97)	660 (92)

Note: Figures in parentheses represent the ratios (in percent) of the strength of the concrete containing the retarders to the strength of the concrete without retarder (Mix No. 1) made on the same day. Specimens stored in moist air until tested.

[a]Amount of retarder used is the same as given in Table 4.

[b]Each value is the average of five tests made on five different days. Specimens were 6- by 6- by 21-in. beams tested in accordance with AASHO Method T 97 with third point loading on an 18-in. span. Side as molded in tension.

[c]Each value is the average of three tests. Specimens were 3- by 4- by 6-in. beams tested with third point loading on a 12-in. span with a 4-in. depth; bottom surface as molded in tension.

For some reason which is not apparent, the use of retarders failed to improve the flexural strength of concrete to the same extent as was found for the compressive strength. In the compression tests, the average strength of the Mix No. 1 reference concrete was 5,040 psi at an age of 28 days. The strength of Mix No. 2 retarded concrete was 115 percent of this, and that for Mix No. 3 was 104 percent. In the tests

for flexural strength, the reference concrete had a strength at 28 days of 740 psi, and Mixes No. 2 and 3 of retarded concretes had strengths of 104 and 97 percent, respectively, of this. It will be noted, however, that the ratio of the values for compressive strength, 115 against 104, is practically the same as the ratio of values for flexural strength, 104 against 97. Consequently it can be assumed that the results of the two sets of strength tests are valid and that the use of a retarder furnishes concrete of lower relative flexural than compressive strength.

Studies of the different groups of retarders show that concretes prepared with the calcium lignosulfonates had lower flexural strength than those prepared with the carbohydrate, the ammonium and sodium lignosulfonates, and the organic acids. No explanation can be given for this, nor can any reasonable explanation be given for the behavior of concrete prepared with retarder No. 22. In the compression tests, concrete containing this retarder had the lowest strength, most likely due to the large amount of air entrained. In the flexural tests, this concrete had strengths lower than those of the reference concrete but with respect to the other retarded concretes, the strengths were reduced but slightly. It appears probable that in the acceptance testing of retarders, consideration should be given to the behavior of individual retarders and not assume that all retarders of a given type will affect concrete in the same manner.

In Figure 8 average values of the effect of all retarders on the flexural strength of concrete are shown. These data are taken from two sets of specimens. The tests at ages of 7 and 28 days were made on 6- by 6- by 21-in. beams and the results obtained are given in Table 7. When these results were studied, it was observed that at an age of 28 days the average strength for the reference mix was greater than that for Mix No. 3 and was approaching the strength for Mix No. 2. A determination of the relative strengths of these concretes at greater ages was believed desirable.

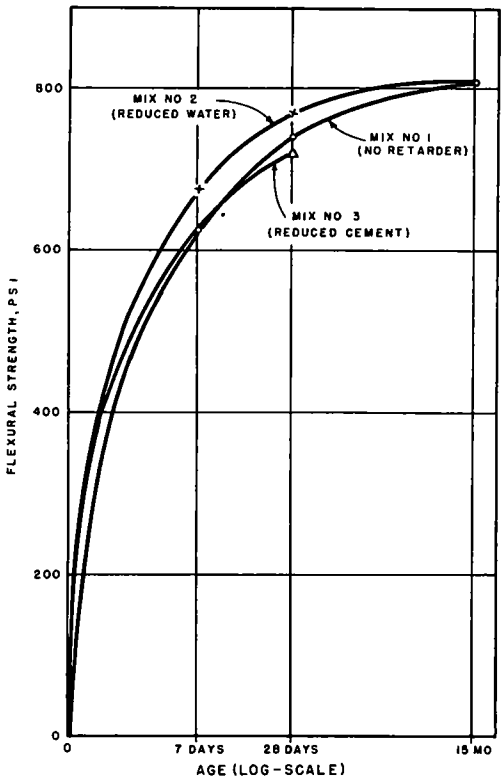

Figure 8. Influence of retarders on flexural strength of concrete average values for all retarders.

As no other beams of 6- by 6-in. cross-section were available, plans were made to test the 3- by 4- by 16-in. beams used for reference purposes in volume change tests for flexural strength. These beams, representing Mixes No. 1 and 2 only, had been kept continuously in moist storage. When the volume change tests were completed, these beams were stored in water for 2 weeks and tested for flexural strength at an age of 15 months. The results obtained are included in Table 7 and Figure 8.

These results show that at an age of 15 months, the flexural strength of nonretarded concrete was the same as that of retarded concrete of reduced water content. At greater ages, the equality in flexural strength of nonretarded concrete and retarded concrete of reduced water content might be maintained.

Modulus of Elasticity

The results of tests for modulus of elasticity for concretes prepared with each of the 25 retarders are not shown in this report, as significant differences were not, in general, obtained. Average values for all concretes of a type are given in text table on page 15. The sonic moduli for the retarded concretes were from 3 to 6

Mix No.	Age at Test, Days 7	28
	Sonic Modulus, Psi	
1 (nonretarded)	5,440,000	5,890,000
2 (reduced water)	5,780,000	6,210,000
3 (reduced cement)	5,690,000	6,080,000
	Static Modulus, Psi	
1	4,970,000	5,580,000
2	5,350,000	6,000,000
3	5,030,000	5,710,000

percent higher than those for the nonretarded concrete. The static moduli of the retarded concretes were from 1 to 8 percent higher than those for the nonretarded concretes, but the average static modulus for all retarded concretes was 7 percent less than the average of the sonic values.

In general, the use of retarders did not affect adversely the modulus of elasticity of concrete unless an excessive amount of air was entrained. Retarder No. 22 which caused entrainment of an excessive amount of air, produced concrete having sonic and static moduli from 7 to 13 percent lower than those for nonretarded concrete.

Effect of an Elevated Temperature

Tests were made to determine the effect of an elevated temperature on the properties of concrete containing each of the retarders. The materials used were stored at 90 F for several days prior to mixing, the concrete was mixed at 90 F, the test specimens were cured at 90 F under wet burlap for 24 hr, and then stored in moist air at 73 F until tested.

The amount of retarder necessary to give the desired retardation (2½ to 3 hr as measured by the 500-psi Proctor test) was determined and the results given in Table 8. It was found that at 90 F more retarder per bag of cement was required for the concretes containing 19 of the retarders than for similar concretes at 73 F, but with the other 6 retarders the same amount was required as at 73 F. These 6 retarders are Nos. 14, 15, 16, 17, 20, and 24, all lignosulfonates. The increase in amount used for the 19 retarders varied from 105 percent for retarder No. 3 to 175 percent for retarder No. 6. With respect to type of retarder, the change in temperature from 73 to 90 F required an increase of 27 percent in the amount of the carbohydrate, and an average increase of 14 percent for lignosulfonates and 48 percent for organic acid retarders.

Retarder No. 5 caused an unusual effect on the setting or stiffening of the screened mortar at 90 F. The mortar developed a firm crust or skin at an early age but remained soft under this crust for some time. When a Proctor penetration pressure of 500 psi was used, this crust caused the mortar to have an apparent retardation time of only 1 hr and 50 min. However, higher penetration pressures of more than 500 psi broke through the crust and revealed the softness of the interior portion of the test specimen. Tests were continued to an age of 9 hr and the penetration pressure was less than 4,000 psi. At an age of 24 hr, the mortar was found to be hard and there was no difficulty in removing the concrete specimens prepared with this retarder from the molds. For a penetration load of 4,000 psi this retarder retarded the mortar more than 4 hr. Tests of the concrete specimens at an age of 3 days had a satisfactory strength.

Compressive strength tests for Mix No. 2 were made at ages of 3 and 28 days. The results of these tests and the ratios of these strengths to the strength of concrete without retarder, made on the same day, are given in Table 9.

In general, the same trends were shown in tests on specimens made at 90 F as were shown on those made at 73 F. The strength ratios were approximately the same. However the average compressive strength at 3 days, of the concretes containing the

TABLE 8

RETARDATION TIME FOR CONCRETE (Mix No. 2) AT 90 F

Retarder		Slump (in.)	Air (%)	Retardation[a]			
				Proctor Penetration Test[b]			
No.	Amount Used (oz/bag)			At 500 Psi Hr	Min	At 4,000 Psi Hr	Min
1	1.4	3.2	4.9	3	05	2	50
2	16.3	3.2	5.8	2	45	2	10
3	4.2	3.1	5.6	2	35	2	35
4	4.2	4.4	5.5	2	20	2	15
5	6.0	4.4	5.8	1	55[c]	4	+
6	7.0	3.6	5.8	2	45	3	35
7	4.5	3.0	5.4	2	40	2	55
8	16.0	3.3	5.1	2	35	2	50
9	4.0	2.9	6.0	3	10	3	20
10	4.3	3.2	5.2	3	10	3	00
11	6.0	2.9	5.8	2	50	2	35
12	5.3	2.7	6.9	2	35	2	55
13	5.3	2.8	5.3	3	05	2	50
14	5.0	2.7	5.6	2	20	2	30
15	4.0	3.0	4.8	2	15	2	25
16	4.8	3.0	5.3	2	20	2	00
17	3.2	2.9	5.2	3	00	2	40
18	5.0	2.9	6.5	2	25	2	40
19	4.5	2.8	5.0	2	40	2	15
20	9.0	2.9	5.4	2	30	2	25
21	12.0	2.7	5.3	2	40	2	55
22	4.5	3.5	8.+	2	25	2	45
23	7.2	3.0	5.0	2	30	2	25
24	9.6	3.0	5.4	2	40	2	30
25	5.0	2.7	7.1	2	35	2	20

[a]Retardation is the delay in time of hardening of the concrete containing the retarder as compared with the concrete without retarder made on the same day. Time for concrete without retarder to reach:

Proctor penetration load of 500 psi— 3 hr 15 min (± 15 min).

Proctor penetration load of 4,000 psi—4 hr 45 min (± 15 min).

[b]Proctor penetration test made in accordance with ASTM Method C 403-57T.

[c]Top surface appeared to crust.

retarders (Mix No. 2) made at 90 F, was 3,020 psi and for similar concretes made at 73 F it was 3,080 psi. At 28 days, the average compressive strength of retarded concretes made at 90 F was 5,040 and for concrete made at 73 F it was 5,760 psi.

A comparison of the compressive strengths at ages of 3 and 28 days of concrete specimens made at 90 F and at 73 F is shown in Figure 9. At an age of 3 days, the points representing each concrete, retarded or nonretarded, are well grouped with respect to the 45-deg line. The concretes made with retarders Nos. 3 and 25 show the greatest reduction in strength due to fabrication at an elevated temperature. At an age of 28 days, almost all of the concretes show a lower strength due to the 90 F temperature. Those prepared with retarders Nos. 5, 7, 11, 13, 18, and 25 show this to the most marked extent. With respect to type of retarder, some differences are found but no outstanding influence of any one type is noted. Concretes prepared with retarders Nos. 3, 6, and 15, showed either none or only slight reduction in strength due to the elevated temperature.

Freezing and Thawing Tests of Retarded Concrete

Table 10 gives the results of freezing and thawing tests made with Mixes Nos. 2 and 3 of the retarded concrete. The computed durability factors for concrete prepared with each retarder after 300 cycles of freezing and thawing are given in this table. Because of the limited capacity of the freezing and thawing apparatus, the specimens for these tests were prepared on 10 mixing days.

To permit comparisons between the concretes containing the different retarders a reference concrete (Mix No. 1) was made on each mixing day. The specimens made with the reference mix were tested with the specimens containing the retarders, and the durability factors for each concrete of Mixes Nos. 2 and 3 expressed as a percentage of the durability factor for the reference concrete made on the same day are given in Table 10. These values are described as relative durability factors. The durability factors for the reference concrete were quite uniform, varying from 85 to 92 with an average of 90. Reference to the relative durability factor is made in the remainder of this discussion.

TABLE 9

COMPRESSIVE STRENGTH TESTS OF SPECIMENS MADE AT 90 F (Mix No. 2)

Retarder No.[a]	Compressive Strength (psi)	
	3 Days	28 Days
1	2,880 (121)	5,090 (115)
2	2,550 (107)	4,410 (99)
3	3,250 (132)	5,260 (125)
4	2,890 (117)	5,220 (119)
5	3,220 (135)	5,080 (114)
6	2,770 (116)	5,400 (122)
7	2,880 (117)	4,700 (112)
8	3,210 (130)	5,330 (121)
9	3,060 (124)	5,220 (119)
10	3,090 (129)	5,280 (119)
11	3,470 (140)	5,070 (115)
12	2,840 (119)	5,070 (114)
13	2,810 (114)	4,540 (108)
14	3,180 (129)	5,210 (119)
15	3,320 (134)	5,470 (125)
16	3,350 (136)	5,350 (122)
17	2,960 (120)	5,270 (120)
18	3,080 (124)	4,650 (111)
19	3,160 (128)	5,390 (128)
20	3,030 (123)	5,170 (123)
21	3,110 (130)	5,420 (122)
22	2,340 (95)	3,940 (94)
23	3,020 (126)	5,100 (115)
24	3,580 (146)	5,180 (123)
25	2,410 (101)	4,280 (96)

Notes Each value is an average of three tests. Specimens were made at 90 F and were stored in air at 90 F for 24 hr, then stored in moist air at 73 F until tested Figures in parentheses represent the ratio (in percent) of the strength of concrete containing the retarder (Mix No. 2) to the strength of the concrete without retarder (Mix No. 1) made on the same day

[a]Amount of retarder used is the same as given in Table 8.

Concretes of equal cement content (Mix No. 2) prepared with each of 3 retarders, Nos. 12, 15, and 24, had relative durabilities of 80 percent or less, whereas concretes

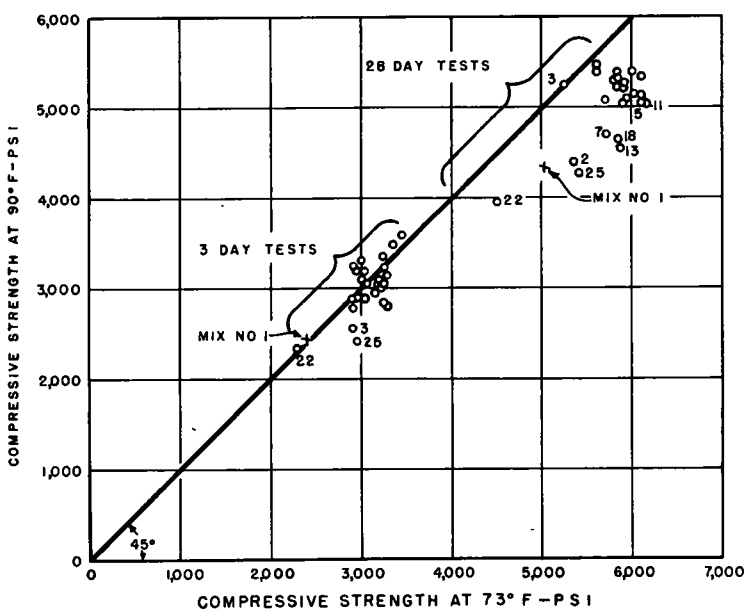

Figure 9. Effect of elevated temperature on compressive strength of concrete containing retarders.

TABLE 10

RESULTS OF FREEZING AND THAWING TESTS

Retarder No.[a]	Mix No. 2				Mix No. 3			
	Air Content (%)	AEA Added (ml/bag)	Durability Factor at 300 Cycles (%)	Relative Durability Factor[b] (%)	Air Content (%)	AEA Added (ml/bag)	Durability Factor at 300 Cycles (%)	Relative Durability Factor[b] (%)
1	4.9	16.3	92	101	5.4	21.5	91	99
2	5.2	16.3	91	100	5.6	21.5	91	99
3	6.5	None	87	96	5.6	None	68	75
4	5.2	14.3	91	101	5.1	18.0	89	99
5	5.1	10.2	87	96	4.9	13.5	82	91
6	5.3	14.3	91	100	5.4	20.2	85	94
7	6.1	10.2	90	99	5.5	13.5	87	96
8	5.0	15.1	91	99	5.3	19.3	91	106
9	4.9	14.3	94	102	5.3	18.0	87	97
10	6.0	18.4	91	99	5.7	13.5	88	97
11	5.4	4.1	88	95	5.3	9.0	84	93
12	5.7	4.1	74	80	5.9	6.7	72	85
13	5.3	4.1	88	96	6.0	6.7	79	93
14	6.0	4.1	87	94	5.3	11.2	84	99
15	6.3	None	72	79	5.0	None	64	75
16	6.2	6.1	92	101	5.5	6.7	83	98
17	5.2	10.2	92	102	5.2	13.5	86	101
18	6.2	6.1	90	99	5.0	6.7	82	93
19	5.9	8.2	91	101	5.0	11.2	87	98
20	5.1	None	85	94	5.9	13.5	91	103
21	5.0	4.1	82	91	5.2	11.2	92	103
22	10.0	None	92	101	7.9	None	91	102
23	6.1	4.1	88	97	5.0	4.7	76	86
24	5.0	None	56	61	5.9	2.4	68	76
25	7.6	None	87	96	6.6	None	87	97

Note: Each value is an average of tests on three 3- by 4- by 16-in. beams. Beams frozen and thawed in accordance with AASHO Method T 161 for fast freezing and thawing in water.

[a]Amount of retarder used is the same as given in Table 4.

[b]Relative durability factor is the ratio in percent of the durability factor of the concrete containing the retarder to the durability factor of concrete without retarder (Mix No. 1) made on the same day and given the same treatment.

with the remaining 22 retarders had relative durabilities of 90 percent or more. Concretes of reduced cement content (Mix No. 3) prepared with the same 3 retarders had relative durabilities of less than 90 percent. Concretes containing retarders Nos. 3 and 23 also had relative durabilities of less than 90 percent when the cement content was reduced.

If an assumption is made that a relative durability of 80 percent for concrete with an admixture is acceptable as is specified in AASHO Specification M 154 for Air-Entraining Admixtures for Concrete, and in the proposed specification for retarders of Subcommittee III-h of ASTM Committee C-9, then only two retarders, Nos. 15 and 24 for Mix No. 2, and three retarders, Nos. 3, 15 and 24 for Mix No. 3 would not be acceptable.

Retarders Nos. 3, 15, and 24 are all of the lignosulfonate type. The air contents of the concretes containing these retarders varied from 5.0 to 6.5 percent and with one

exception (retarder No. 24, Mix No. 3) no air-entraining agent was added. Concretes containing four other lignosulfonate retarders, Nos. 20, 22, 23 and 25, to which no air-entraining agent was added in six of the eight cases, had relative durability factors for Mixes Nos. 2 and 3 varying from 86 to 103 percent. Concrete containing the other lignosulfonate retarders to which air-entraining agent was added, with two exceptions (retarder No. 12, Mixes Nos. 2 and 3), had durability factors of more than 90 percent.

Retarders Nos. 4, 5, 6, 8 and 9 of the organic acid type, which required considerable Vinsol resin solution to entrain the required amount of air in concretes for Mixes Nos. 2 and 3, had relative durability factors in excess of 90 percent. Considerable amounts of air-entraining agent were also required for Mixes Nos. 2 and 3 with retarder No. 1, the carbohydrate-type retarder. The relative durability for this concrete was 101 percent for Mix No. 2 and 99 percent for Mix No. 3.

Concrete having an air content of 5 to 7 percent is usually considered to have an adequate resistance to the effects of freezing and thawing. The fact that the concretes prepared with retarders Nos. 3, 15, and 24 contained at least 5.0 percent of air and still showed relatively poor resistance to freezing, raises a question of the beneficial value of air entrained by some lignosulfonates. The only explanation which might be given of this is that the air was not in the finely divided and uniformly dispersed form most advantageous in furnishing durability to concrete. However, no study of air void size and spacing was made. The information obtained in these tests indicates that freezing and thawing tests may be of particular significance in acceptance or qualification tests of a retarder which requires no air-entraining admixture to obtain the specified air content in concrete.

Effects of Delayed Vibration

The results of tests to determine the effects of delayed vibration on the properties of concretes prepared with retarders are given in Table 11. During three rounds of making specimens for flexure and compression tests, an extra beam and cylinder were made for each batch. The three extra beams and three cylinders were vibrated at 3 or 5½ hr after molding. Mix No. 1, without retarders, was vibrated at 3 hr and Mixes Nos. 2 and 3, with retarders, were vibrated at 5½ hr. The unit weight of each concrete, vibrated and nonvibrated, was determined by weighing cylinders in air and under water prior to testing at an age of 28 days.

The average increase in unit weight of all vibrated retarded concretes was 3.1 and 3.4 pcf for Mixes Nos. 2 and 3, respectively, over the unit weights of corresponding concretes from the same batch which had not been vibrated. In general, a greater increase in weight was obtained by vibration of the concretes which had high air contents. For example, concretes of an air content of 8 or more percent (retarder No. 22) showed increases in unit weight of 6.5 and 7.4 lb on vibration.

The average unit weight of vibrated, nonretarded concrete (Mix No. 1) prepared on 18 mixing days was 151.3 pcf and 148.3 pcf for corresponding concretes that were not vibrated. The average gain in weight of 3 pcf of nonretarded concrete on vibration checks with the average increase in weight of 3.1 pcf for Mix No. 2, and 3.4 pcf for Mix No. 3 for retarded concretes on vibration.

The average compressive strength at an age of 28 days of vibrated, nonretarded concrete (Mix No. 1) was 5,680 psi. This value was 11 percent higher than that for the same concrete which was not vibrated. Vibration did not improve the retarded concretes to the same amount. The 28-day compressive strengths of vibrated retarded concrete were 4.1 and 7.3 percent higher, for Mixes Nos. 2 and 3, respectively, than the strengths of the same concrete which was not subjected to delayed vibration. All vibrated concrete for Mix No. 3 (reduced cement content) and 22 of the 25 concretes with reduced water content (Mix No. 2) showed a gain in strength over nonvibrated concrete.

The 28-day flexural strength of vibrated retarded concrete averaged 2.9 percent lower for Mix No. 2 than the strength of the same concrete without delayed vibration. For Mix No. 3 the vibrated and nonvibrated concretes had about the same flexural strength.

TABLE 11

EFFECT OF DELAYED VIBRATION ON COMPRESSIVE AND FLEXURAL STRENGTH OF CONCRETE

Retarder No.[a]	Weight of Hardened Concrete[b] Vibrated (pcf)	Weight of Hardened Concrete[b] Non-Vibrated (pcf)	Compressive Strength, 28 Days Vibrated (psi)	Flexural Strength, 28 Days Vibrated (psi)
		(a) Mix No. 1 (No Retarder)		
None	151.3	148.3	5680 (111)	725 (99)
		(b) Mix No. 2		
1	151.8	149.8	6,070 (105)	765 (96)
2	151.7	148.5	5,680 (101)	740 (97)
3	151.8	147.8	5,790 (113)	665 (92)
4	151.9	148.8	5,990 (100)	775 (97)
5	153.5	150.3	6,500 (101)	755 (97)
6	151.2	147.6	5,550 (104)	715 (95)
7	152.9	150.8	5,950 (103)	750 (101)
8	152.5	150.1	6,050 (101)	790 (94)
9	151.2	149.7	6,240 (107)	725 (88)
10	152.4	150.2	6,120 (105)	765 (96)
11	152.2	147.0	6,240 (102)	735 (105)
12	150.8	145.3	5,690 (116)	740 (106)
13	152.6	150.7	6,140 (104)	760 (101)
14	153.8	150.9	6,270 (105)	775 (97)
15	152.3	149.1	5,880 (103)	725 (97)
16	152.4	150.0	6,170 (100)	765 (103)
17	152.3	150.1	5,900 (98)	740 (97)
18	152.8	151.4	5,740 (94)	760 (101)
19	153.8	151.1	6,170 (102)	750 (93)
20	152.5	150.6	6,260 (102)	790 (100)
21	152.1	149.9	6,210 (105)	745 (94)
22	150.8	144.3	5,420 (125)	705 (104)
23	152.3	149.8	6,290 (102)	790 (95)
24	154.0	151.1	6,020 (98)	725 (93)
25	153.3	148.1	6,120 (109)	745 (95)
Avg of 25 retarders	152.4	149.3	104.1	97.1
		(c) Mix No. 3		
1	151.6	147.6	5,810 (106)	695 (91)
2	152.0	148.4	5,360 (104)	730 (105)
3	152.2	148.6	5,610 (112)	710 (97)
4	152.0	148.7	5,560 (105)	725 (94)
5	153.5	149.8	6,270 (109)	705 (96)
6	151.1	148.9	5,320 (106)	675 (97)
7	152.2	149.8	5,830 (105)	735 (104)
8	152.4	149.7	5,690 (103)	725 (96)
9	152.4	149.3	5,910 (105)	755 (102)
10	153.2	150.7	6,000 (108)	720 (99)
11	153.6	149.7	5,710 (103)	685 (97)
12	151.7	147.8	5,360 (107)	745 (106)
13	153.8	149.6	5,890 (109)	720 (104)
14	153.0	149.3	5,610 (105)	740 (100)
15	153.5	148.8	5,950 (114)	670 (97)
16	153.2	150.0	5,690 (101)	735 (101)
17	152.1	149.4	5,790 (109)	750 (101)
18	152.6	150.5	5,600 (100)	760 (113)
19	152.8	150.1	5,790 (105)	735 (93)
20	154.0	151.0	6,380 (108)	680 (95)
21	152.5	150.5	5,800 (103)	720 (104)
22	152.4	145.0	5,190 (126)	670 (105)
23	153.0	149.9	5,580 (104)	765 (103)
24	153.6	150.7	5,600 (105)	670 (105)
25	152.6	147.6	5,880 (126)	670 (98)
Avg of 25 retarders	152.7	149.3	107.3	100.1

Note: Each value for Mix No. 1 is average of 19 tests and each value for Mixes No. 2 and No. 3 is average of three tests made on different days. Specimens stored in moist air until tested. Figures in parentheses represent the ratio (in percent) of the strength of vibrated concrete to the strength of the non vibrated concrete made on the same day.

[a]Amount of retarder used is the same as given in Table 4.

[b]Weight of hardened concrete determined on test cylinders at age of 28 days.

The average flexural strength of the vibrated, nonretarded concretes (Mix No. 1) was 725 psi. This was about 1 percent less than the average strength of the corresponding nonvibrated concrete.

The tests indicate that delayed vibration of retarded concrete at 5½ hr after placing is beneficial to the compressive strength. However, the 500-psi Proctor penetration pressure for delayed vibration was not applicable to concretes which were used in this investigation. This was probably due to the grading and the type of aggregate used.

The effect of delayed vibration on flexural strength of retarded concrete included in this investigation appears to be of no benefit, probably due to the method of vibration employed. It is difficult to vibrate a horizontal beam of 6- by 6-in. cross-section with a 1⅞-in. internal vibrator and obtain ideal compaction. In the case of a 6- by 12-in. cylinder, the vibrator spud is immersed for its full length in the concrete and effective vibration can be obtained.

Density and Absorption Tests on Retarded Concrete

Data on the density and absorption of concrete disks taken from cylinders prepared with and without retarders are given in Table 12. The concretes that contained each of the 25 retarders (Mix No. 2) were made on three different mixing days with a reference mix (No. 1) which was made for each day. Two disks 1-in. thick were sawed from the top, middle and bottom, as molded, of each of three similar 6- by 12-in. cylinders made on the same day. Each value for weight or absorption of the hardened concrete given in the table is an average for the 6 disks.

A temperature of 190 F to 200 F was used to dry the disks. This temperature was chosen because it was considered inadvisable to evaporate water above the boiling point and the uniformity of heating was better controlled at this temperature than in available ovens which operated at temperatures about 212 F.

The wet and dry densities (unit weight per cubic foot) of the disks from the bottoms

TABLE 12

DENSITY AND ABSORPTION TESTS (Mixes No. 1 and 2)

Retarder No.[a]	Weight Plastic Concrete (pcf)	Air In Plastic Concrete (%)	Weight of Hardened Concrete: Wet[b] Top (pcf)	Wet[b] Middle (pcf)	Wet[b] Bottom (pcf)	Dry[c] Top (pcf)	Dry[c] Middle (pcf)	Dry[c] Bottom (pcf)	Absorption[d] Top (pcf)	Absorption[d] Middle (pcf)	Absorption[d] Bottom (pcf)
None	145.7	4.5	150.8	151.6	152.0	142 6	143 6	144 1	5.8	5 6	5 5
4	145 9	4.9	151.0	150.8	152.6	143.1	142.8	145.2	5.5	5.6	5.1
9	145.3	5.1	149.5	150.2	152 5	141.2	141.9	144.8	5.9	5.8	5.3
10	144.3	5.5	149.8	150.1	152 6	141.5	142.1	145.3	5.9	5.6	5 0
11	145.9	4.7	151 9	152 6	154.2	144.1	144.6	147.0	5.4	5.5	4 9
14	145.9	4.9	152.1	152.1	153.3	144.4	144.3	146.0	5 3	5.4	5.0
16	144.3	6.5	151.0	151.0	152.7	143.6	143 3	145.8	5.2	5.4	4 7
18	145.7	5.0	151.2	151.4	154 1	143 1	143.3	146.9	5.7	5.7	4.9
20	144.3	6.0	149.5	150.1	152.4	141.2	142.2	145.0	5.9	5.6	5.1
21	144.7	5.6	150.9	151.2	152.8	143 1	143.2	145.5	5.5	5.6	5 0
None	144.3	5.0	149.6	149.8	151.7	141 7	141.7	144.5	5.6	5.7	5 5
3	143.1	6 5	151.6	150.3	151.8	144.3	142 6	144 7	5.1	5.4	4.9
5	145.5	5.1	152.6	151.6	153.3	145.5	144.1	146.5	4.9	5.2	4.6
6	144.7	5.2	150.1	149.7	152.0	142 3	141.8	144 8	5.5	5.6	5.0
7	144.9	5.3	151.2	150.5	152.5	143 7	142 9	145.7	5.2	5.3	4.7
8	144.1	5.5	150.3	150.1	152.0	142 5	142.3	144.9	5.5	5.5	4 9
13	143.1	6.4	149.2	149.3	151.2	141 5	141.7	144.3	5.4	5.4	4.8
15	141.9	6.7	148.8	149.0	150.9	141.1	141.4	144.2	5.5	5.4	4 6
17	144 5	5.9	151.0	150.2	152.4	143 5	142 5	145.6	5.2	5.4	4.7
19	145.5	5.0	150.9	150.6	152.5	142.9	142.6	145.3	5.6	5 6	5.0
None	143.5	5.0	148.3	149.1	150.6	139.5	140.5	142.7	6.3	6.1	5.5
1	144.3	5.2	149.0	149.5	151.8	140.5	141.3	144.6	6.0	5.8	5.0
2	143.9	5.2	148.2	148.4	151.1	139.7	139.9	143.4	6.1	6.1	5.4
12	144.3	5.1	151.9	151.7	152.8	144.4	144.2	145.7	5.2	5 2	4.9
22	138.6	8+	144.7	144.7	147.3	136.8	136.9	140.3	5 8	5.7	5.0
23	144.9	5.1	150.1	149.6	152.4	142.1	141.5	145.2	5.6	5.7	5.0
24	141.5	6.0	150 2	150.1	151.6	142.6	142.7	144.8	5.3	5.2	4.7
25	140.8	8+	147.8	147.9	150.0	139.8	140.0	141.9	5.7	5 6	5.7

Note: Two disks, 1-in. thick, were sawed from the top, middle and bottom of three 6- by 12-in. cylinders. Each value is average of tests on six disks. [a]Amount of retarder used is the same as given in Table 4. [b]Wet weight determined on disks after 28 days continuous moist storage. [c]Disks dried to constant weight at 190 to 200 F. [d]Based on wet weight after 28 days moist curing.

of the cylinders were higher than the densities of corresponding disks from the tops. However, the differences in densities of disks from the top and middle of cylinders were small and indicated no effects of any retarder. A comparison of densities of the retarded concretes with the densities of the reference concretes does not indicate any appreciable gain in weight above that normally obtained for the reduced water content and the term "densifier" as used for some retarders, is not justified by these data.

The absorptions in Table 12 are calculated from the wet weights at an age of 28 days and the weights after drying at 190 F to 200 F. The absorptions are higher for the disks from the tops of the cylinders than for the disks from the bottoms of the cylinder. There does not appear to be any appreciable effect of decreasing the absorption of the concrete in the top of a cylinder by the use of a retarder. Neither does the use of a retarder appear to decrease appreciably the range in absorption between the concrete in the top and bottom of a cylinder.

Volume Change Tests

The data in Table 13 indicate that 22 of the 25 retarders have no appreciable effect (more than 0.10 percentage points increase) on the drying shrinkage of concrete. No retarder caused any appreciable expansion (more than 0.10 percentage points increase) in continuously moist-cured concrete. This conclusion is based on a comparison of the volume change of the retarded concrete (Mix No. 2) with that of reference concrete (Mix No. 1) which was made on the same day. In general, the organic acid type of retarders (Nos. 4, 5, 6, 8 and 9) and the carbohydrate retarder (No. 1) caused little or no increase in shrinkage on drying. The shrinkage values appear to be larger for the retarder concretes that were moist cured initially for 2 days than those for similar concretes that were cured initially for 14 days. Some of the concretes with lignosulfonate retarders, particularly Nos. 11, 14, 16, 18 and 24 showed the greatest increase in shrinkage for 2-day moist-cured concrete. Retarders Nos. 17 and 24 caused the greatest increase in shrinkage for 14-day moist-cured concrete. Whether the calcium chloride content of retarders Nos. 11 and 24 affected shrinkage is subject to conjecture. The reducing sugar contents of retarders Nos. 14 and 17 are more than 5 percent and the shrinkage values for concrete with either of these retarders are among the highest. However, consideration is directed to the chemical composition of each retarder reported under chemical tests if an attempt to explain further the range in shrinkage values is desired.

The values for expansion under moist storage show no appreciable effect of retarders on concrete in 24 of the 25 cases. One value, 0.019 percent, for concrete with retarder No. 14 is the exception.

TABLE 13

TESTS FOR CHANGE IN VOLUME—MIXES NO 1 AND 2

Retarder No [a]	Contraction After Storage in Dry Air[b] for 200 Days After Initial Moist Curing for 2 Days (%)	14 Days (%)	Expansion After 200 Days Curing in Moist Air[c] (%)
None	0 044	0.048	0.009
4	0.046	0.041	0 011
9	0.046	0.044	0 011
10	0.047	0 047	0 013
11	0.059	0 048	0.012
14	0.052	0.048	0 019
16	0.055	0 049	0 012
18	0 057	0.049	0 008
20	0.049	0.046	0 011
21	0 047	0.048	0 011
None	0.049	0.046	0 009
3	0.049	0.045	0 011
5	0 052	0 044	0 010
6	0.044	0 046	0.011
7	0 051	0.047	0 011
8	0 044	0.040	0.010
13	0.053	0.045	0.010
15	0.047	0.046	0.012
17	0.053	0.056	0 011
19	0.052	0 046	0.010
None	0.048	0.044	0 008
1	0 046	0.047	0.011
2	0 048	0.048	0.008
12	0 047	0.039	0.009
22	0.049	0.044	0.014
23	0.052	0.044	0.009
24	0 056	0 051	0.011
25	0.053	0.042	0.011

Note. Each value is an average for three 3- by 4- by 16- in. beams. [a]Amount of retarder used is the same as given in Table 4 [b]Specimens stored in air at 73 F and 50 percent relative humidity. [c]Specimens stored in air at 73 F and 100 percent relative humidity.

Use of Excessive Amount of Retarder

A limited series of tests was made using four times the amount of retarder which had previously been determined as the amount necessary to obtain the desired retardation.

Only 10 of the 25 retarders were used in these tests. Tests were made to determine the effect on the retardation as well as on compressive strength at ages of 7 and 28 days. The mix data for these concretes as well as the result of the Proctor penetration tests and the compressive strength tests, and strength ratios, are given in Table 14.

The mix data show that when four times the normal amount of retarder was used, the air content of the concretes containing three of the ten retarders (Nos. 3, 7, and 11) was more than 8 percent. No air-entraining admixture was used in these mixes. The use of an overdosage of retarder had no effect on the air content of the concretes containing each of the other seven retarders. The water required for the concretes with an overdosage of each retarder was, with one exception, reduced from that required for corresponding concretes containing the normal amount of retarder.

The time required for the concretes prepared with each of these retarders to reach 500-psi penetration pressure by the Proctor test, varied from approximately 6 hr for concrete containing retarder No. 11 to more than 100 hr for retarders Nos. 3 and 7. For a penetration of 4,000 psi, the time varied from 23 hr to more than 150 hr. Retarders Nos. 11 and 12 which required approximately 6 to 10 hr, respectively, for a 500-psi penetration pressure, required 80 and more than 150 hr for 4,000-psi penetration pressure (Proctor). There appears to have been some crusting of the top surface of the concrete which caused this difference. The time shown for the Proctor penetration values is only approximate as readings could not be taken at regular intervals.

The strength tests show that at an age of 7 days, concrete prepared with only 3 retarders, Nos. 1, 2 and 9, gave compressive strengths greater than those of the concrete without retarder. Concrete containing these reached the Proctor penetration value of 4,000 psi in less than 50 hr.

At an age of 28 days the concretes containing each of six of the retarders had strengths greater than the strength of the nonretarded concretes. Of the four concretes which had strengths less than the unretarded concrete, three had air contents of more than 8 percent. The concretes containing retarders Nos. 7 and 12 had strength ratios of 90 or 91 percent of the unretarded concrete. As these concretes needed more than 100 hr to obtain a Proctor reading of 4,000 psi, it is possible that at a later age these concretes might equal the strength of the unretarded concrete.

Where the air content of the concrete is not high, it appears that if sufficient curing is given the concrete, the strength is not seriously lowered by using this overdosage of the retarders.

Figure 10 shows a partly factual and partly assumed representation of the effect of the overdosage of the 10 retarders on the compressive strength of concrete at ages of 7 and 28 days. The curves showing the effect of retarders Nos. 1, 2, and 9 have approximately the same shape as that for the reference concrete. The curves for the concretes prepared with retarders Nos. 3 and 11 have about the same slope as that

TABLE 14

TESTS USING FOUR TIMES NORMAL AMOUNT OF RETARDER[a] (Mixes No. 1 and 2)

Retarder							Proctor Test Time for				Compressive Strength[b] (psi)	
							500 Psi		4,000 Psi			
No.	Amount Used (oz/bag)	AEA Added (ml/bag)	Cement (bags/cu yd)	Water (gal/bag)	Slump (in)	Air (%)	Hr	Min	Hr	Min	7 Days	28 Days
None	None	27	6 0	5 9	2.7	5 4	3	50	5	25	3,650	4,900
1	4½	23	6.0	5 7	2 8	5 1	20	-	23	-	4,330 (119)	5,500 (112)
2	57	17	5.9	5 8	2 9	5.1	27	-	29	-	4,160 (114)	5,560 (113)
3	16	None	5 2	5.3	5 4	8+	100+	-	100+	-	1,480 (41)	2,640 (54)
4	12	25	6.0	5 4	3.0	5 1	80+	-	80+	-	2,380 (65)	5,900 (120)
5	16	12	6.0	5 3	4 3	4 8	15±	-	75	-	3,340 (92)	6,200 (127)
6	16	20	5 9	5 4	3 2	5.7	80+	-	150+	-	320 (9)	5,030 (103)
7	14	None	5.8	5.2	5 2	8+	100+	-	150+	-	-	4,420 (90)
9	11	25	5.9	5 4	3 8	5 6	40±	-	48	-	3,860 (106)	5,650 (115)
11	19	None	5.2	4 9	4.2	8+	6	-	80+	-	1,540 (42)	2,500 (51)
12	16	27	6 0	5 1	2 5	5.5	10±	-	150+	-	-	4,460 (91)

[a]Normal amount of retarder is amount required to retard the setting time of the concrete at 73 F for 2½ to 3 hr

[b]Figures in parentheses indicate the percentage of the strength of retarded concrete to the strength of the concrete without retarder

for the reference concrete. It is expected that these concretes would continue to develop strength at about the same rate as the reference concrete, and that little change in the ratio between the strengths of the retarded and the reference or nonretarded concrete would occur with increase in age.

The curves for the concretes prepared with retarders Nos. 4, 5, 6, 7, and 12 are similar but differ greatly from that for the reference concrete. These curves show a rapid increase in strength after a prolonged delay in hardening. The assumption drawn from these data is that for some retarders, a considerable delay in setting may cause a rapid gain in strength, and possibly the development of strength superior to that when normal rates of hardening occur. This does not apply to all retarders as concrete containing retarders Nos. 3 and 11 had a marked delay in setting but did not gain a normal amount of strength between ages of 7 and 28 days. For most of the retarders tested, use of an excessive amount did not cause an objectionable reduction in strength at an age of 28 days.

Effect of Retarders on Temperature Rise of Mortar or Concrete

Figure 11 shows the results of temperature measurements of retarded and unretarded concretes which were stored at 73 F for 48 hr. Retarded concretes required a longer period of time after mixing to reach the maximum temperature than unretarded concrete. The increase varied from approximately 1 to 7 hr. In only three cases were the maximum temperatures of retarded concretes higher than that of unretarded concrete. The greatest maximum temperature was with retarder No. 24. This developed almost 7 hr after the maximum temperature of the unretarded concrete had been reached. The lowest maximum temperature was 90 F, obtained with retarder No. 5.

Figure 12 shows the results of measurements for temperature rise of retarded and unretarded mortars which were screened from concrete made at 90 F. The mortar specimens were stored in air at 90 F for 24 hr. The increase in time for retarded mortars to reach a maximum temperature over the time required for unretarded mortars varied from about 2½ to 16 hr. The greatest maximum temperature was obtained with retarder No. 24. The lowest maximum temperature occurred with retarder No. 6. Retarder No. 5 caused the second lowest temperature rise but two maximums were obtained. One maximum temperature of 106 F occurred before the time that the maximum temperature of the unretarded mortar had been reached.

The data show, with one exception, that all retarders delay the time of maximum temperature rise beyond that of unretarded mortar or concrete. They also show that, in general, retarders do not increase appreciably the maximum temperature rise but may decrease it. The exception to the last statement was found with retarder No. 24 which caused both mortar and concrete to develop a significantly higher temperature than the unretarded concrete.

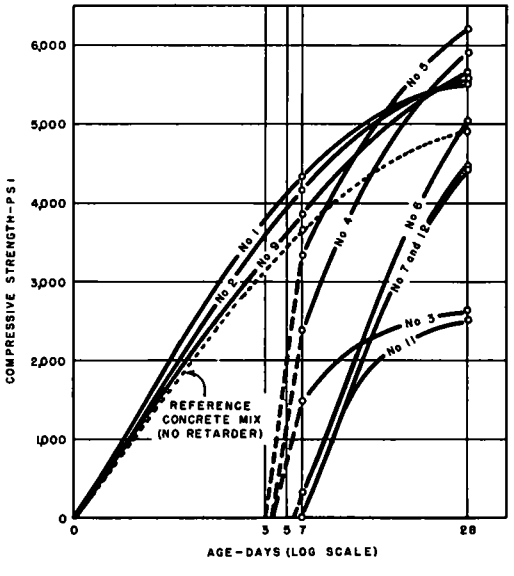

Figure 10. Effect of overdosage (4 times) of retarder on compressive strength.

SUMMARY

It is to be noted that the findings of this investigation of the effect of 25 retarders apply specifically to the concrete prepared with the following listed materials and properties:

Cement—blend of four type I cements having a calculated average equivalent alkali content of 0.63 percent.

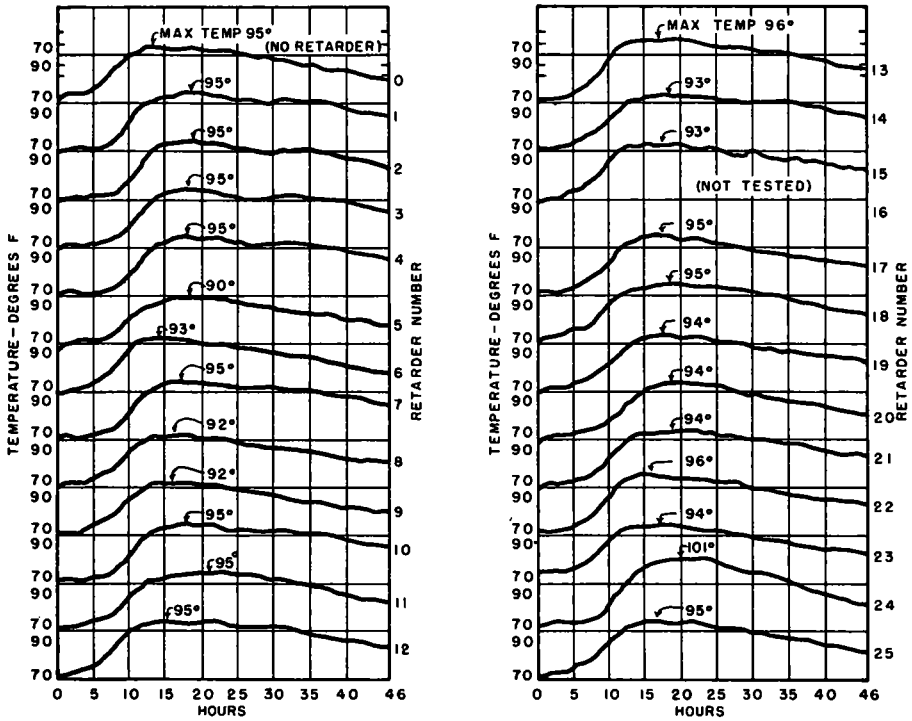

Figure 11. Effects of retarder on temperature rise of concrete specimens made and stored at 73 F.

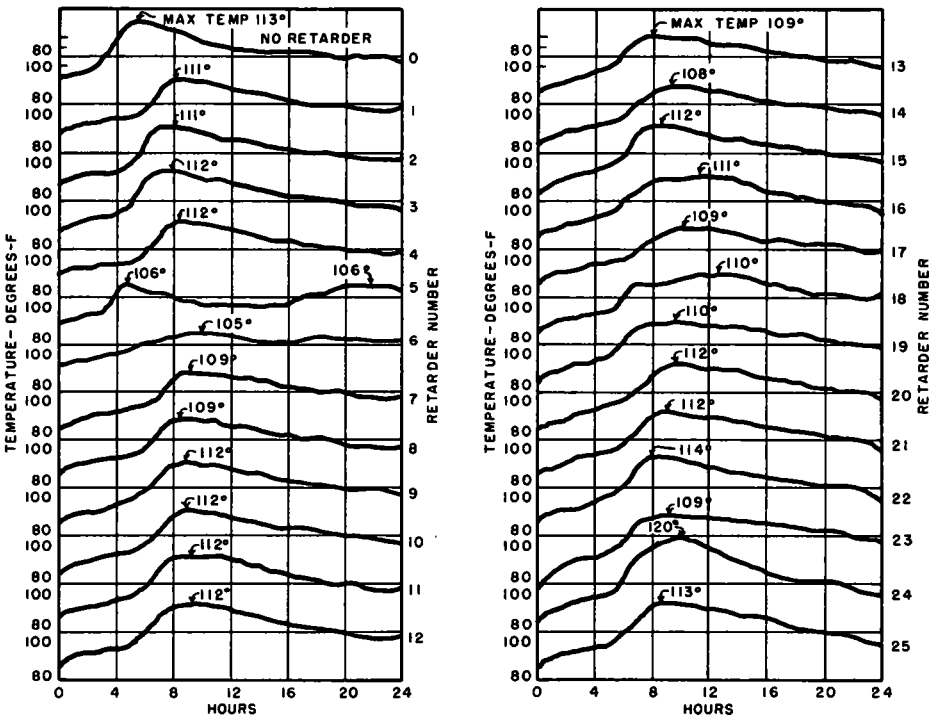

Figure 12. Effects of retarder on temperature rise of mortar specimens made and stored at 90 F.

Aggregates—natural quartz sand, and crushed limestone of 1-in. maximum size.
Slump—2 to 3 in.
Air content—5 to 6 percent.
Mixing—in laboratory pan-type mixer.

When a retarder was used in sufficient amount to delay the setting time for 2½ to 3 hr as indicated by a 500-psi Proctor penetration load, the results obtained may be summarized as follows:

1. For concrete of equal cement content and equal slump all retarders permitted reductions of the water content of a 6-bag concrete mix from 1 to 12 percent (0.1 to 0.7 gal per bag of cement) below the water content of similar concrete that was not retarded.
2. The chemical composition of the retarders generally affected the reduction of water. The carbohydrate (sucrose) permitted the least reduction of water (1 percent), the organic acid type of retarder permitted 5 to 7 percent reduction, and the lignosulfonate type (without insoluble extender) permitted a reduction of 5 to 12 percent in water content.
3. Final hardening of retarded concretes at 4,000-psi Proctor penetration pressure was less than 11 hr.
4. Final hardening of retarded concretes at a pin pullout load of 8 psi was less than 10 hr.
5. Concretes of a 6-bag mix which contained each of 24 of the 25 retarders had higher compressive strengths at 3, 7, 28, and 365 days than similar unretarded concrete. Increases in strength at 365 days were from 9 to 25 percent. Concrete prepared with one retarder, with an air content in excess of 8 percent, had compressive strengths which were less at 3, 7, 28 and 365 days than the strengths of corresponding unretarded concrete.
6. Concretes which were prepared with each of 23 retarders and had cement contents of 5.75, 5.5, or 5.25 bags, had equal or higher compressive strengths at 3, 7, 28 and 365 days than unretarded concrete with a cement content of 6 bags. Concretes containing 5.25 bags of cement which were prepared with each of two retarders had air contents of more than 8 percent. These two concretes had lower compressive strengths than 6-bag unretarded concrete. Increases in compressive strengths of the other 23 retarded concretes were 2 to 15 percent at an age of 365 days.
7. Flexural strengths of 6-bag retarded concretes, of less than 8 percent air content were 2 to 18 percent higher at an age of 7 days than the strengths of corresponding unretarded concrete. Flexural strengths at 28 days were higher with the use of 20 of 25 retarders than the strengths of unretarded concrete. The flexural strengths of the specimens which had been moist cured for 15 months were from 0 to 9 percent higher for concretes prepared with each of 14 retarders and from 1 to 10 percent lower for 10 retarders than the strengths of unretarded concrete. The flexural strengths at all ages for the retarded concretes containing more than 8 percent entrained air were lower than unretarded concrete.
8. Flexural strengths of concretes of reduced cement contents (5.25 to 5.75 bags per cu yd) prepared with each of 17 retarders were equal to or greater at 7 days than that of the 6-bag unretarded concrete. At 28 days, concretes prepared with each of 9 retarders showed increased strengths. Concretes containing 7 retarders showed reductions of 2 to 3 percent at 7 days and concretes made with 16 retarders showed reductions of 1 to 12 percent in flexural strength at 28 days when compared with the strength of 6-bag concrete.
9. The sonic moduli of elasticity for concretes of 6-bag retarded concrete (excluding the one with the high air content) were higher at 7 and 28 days in all cases, except one, than the moduli of corresponding unretarded concrete.

The sonic moduli of elasticity for concretes of reduced cement content (5.25 to 5.75 bags) with each of 24 retarders in all cases, except three were equal to or greater than the modulus of unretarded concrete of 6-bag cement content.

Values for static modulus of elasticity in general were lower than those that were determined sonically.

Retarded concretes, both 6-bag and reduced cement content, which had air contents of more than 8 percent, had lower moduli of elasticity at 7 and 28 days than the moduli of 6-bag unretarded concrete.

10. Delayed vibration increased the compressive strengths at 28 days of 6-bag retarded concrete over that of the nonvibrated concrete in 22 of 25 cases. The 28-day compressive strength of retarded concrete of less than 6 bags was equal to or greater than the corresponding nonvibrated concrete. The effect of delayed vibration on 28-day flexural strength of retarded concrete was not as beneficial as on compressive strength, possibly due to the method of vibration employed. Vibration increased the density of retarded concrete and a reduction of entrained air probably occurred.

11. Shrinkage due to loss of moisture of retarded concrete was slightly greater with some retarders than for unretarded concrete. After 200 days of storage in dry air, reductions in length of 0.044 to 0.049 percent for 6-bag unretarded concrete and 0.039 to 0.059 percent for retarded concrete were obtained.

The increase in length of retarded concretes during 200 days of continuous moist storage was generally only slightly greater than that for concrete prepared without a retarder.

12. Relative durability factors for 6-bag retarded concretes, when frozen and thawed in water were 61, 79, and 80 with the use of each of three lignosulfonate retarders and were 91 or greater for the other 22 retarders. Relative durability factors for retarded concrete having a cement content of 5.25 to 5.75 bags varied from 75 to 86 for 5 lignosulfonate retarders and were 90 or greater for the other 20 retarders.

13. The average absorptions at 28 days of the unretarded concretes were 5.9, 5.8 and 5.5 percent for the top, middle, and bottom sections, respectively, of a 6- by 12-in. cylinder. For retarded concretes in 6- by 12-in. cylinders, average absorptions at 28 days were 5.7, 5.5, and 5.0 for the top, middle and bottom sections, respectively, when an organic acid type of retarder was used. Average absorptions at 28 days for concretes with lignosulfonate retarders were 5.5, 5.5, and 5.0 percent for the top, middle, and bottom sections of cylinders, respectively. In general the weight per cubic foot of the retarded concretes was only slightly higher than the weight of the corresponding unretarded concrete.

14. For 6 of the 19 lignosulfonate retarders, the same amount of retarder caused a retardation of about 2½ hr (at 500-psi Proctor) whether the concrete was prepared at a temperature of 73 F or 90 F. For all other retarders more material was required to retard the set of concrete prepared at a temperature of 90 F than at a temperature of 73 F. This increase in the amount of retarder needed varied from 33 to 75 percent for the organic acid retarders and from 5 to 37 percent for the lignosulfonate retarders other than the 6 previously mentioned, and was 27 percent for the carbohydrate retarder. Concrete prepared with all except one retarder developed a final hardening (4,000-psi Proctor) at a temperature of 90 F in approximately 7 to 8 hr. Concrete prepared with the other retarder became hard at some time between 9 and 24 hr.

15. Retarded concrete prepared at 90 F with each of 24 retarders (omitting retarder No. 22) had a 3-day compressive strength that was from 1 to 46 percent greater than the strength of corresponding unretarded concretes. With the use of 2 retarders, 28-day compressive strengths of 96 and 99 percent of the strength of the unretarded concrete were obtained, but the other 22 retarders caused strength increases of 8 to 28 percent.

Concretes with the one retarder which entrained more than 8 percent of air had compressive strengths that were less (5 to 8 percent) than the corresponding strengths of similar unretarded concretes.

16. An overdosage of four times the normal amount of each retarder required to obtain a retardation of 2½ to 3 hr, caused setting times of from 23 to more than 150 hr at a Proctor penetration pressure of 4,000 psi. Of 5 lignosulfonate retarders used, 3 caused air contents of more than 8 percent and the other 2 required the addition of Vinsol resin for entrainment of 5 percent of air. Setting time of concrete for the overdose of the carbohydrate (sucrose) retarder was 23 hr at 4,000-psi Proctor. Setting time of concretes (4,000-psi Proctor) with the four organic acid-type retarders used varied from 48 to more than 150 hr.

Compressive strengths at 7 and 28 days for concretes with an overdosage of each of three lignosulfonate retarders (Nos. 3, 7, and 11), which entrained more than 8 percent, were less than the strengths of corresponding unretarded concretes. The reductions in strength at an age of 28 days were from 10 to 49 percent and concrete prepared with one of the retarders had not hardened at an age of 7 days.

Concretes with an overdosage of each of 3 organic acid types of retarders (Nos. 4, 5, and 6) had compressive strengths at 7 days that were less than the strengths of unretarded concrete but were 3 to 27 percent higher at 28 days. A fourth organic acid retarder (No. 9) caused increases in compressive strength of 6 percent at 7 days and 15 percent at 28 days.

The overdose of the carbohydrate (sucrose) retarder caused increases in the 7- and 28-day compressive strengths of concrete of 19 and 12 percent, respectively, over the strengths of similar unretarded concrete.

Overdoses of the two lignosulfonate retarders (Nos. 2 and 12) which caused little air entrainment, did not affect the strength of concrete in the same manner. One retarder furnished concrete which had strengths 14 and 13 percent higher at 7 and 28 days, respectively, than corresponding unretarded concrete. Concrete prepared with the other retarder had no measurable strength at 7 days due to excessive retardation of set, and at 28 days had only 91 percent of the strength of unretarded concrete.

18. Only one retarder, No. 24, caused concrete to have a maximum rise in temperature significantly higher than that of unretarded concrete made and stored at 73 F. Development of the maximum temperature of concrete prepared with the 24 retarders tested, occurred approximately 1 to 8 hr later than in the concrete without a retarder.

In tests of mortar specimens made and stored at a temperature of 90 F, only one retarder, No. 24, caused the maximum rise in temperature to exceed that of mortar prepared without a retarder more than 1 deg. One of the retarded mortars had a maximum rise in temperature of 8 F lower than that for unretarded mortar. Mortar prepared with another retarder (No. 5) developed its maximum temperature of 106 F at two times, one about 1 hr before the unretarded concrete reached its maximum temperature and the other about 17 hr later.

CONCLUSIONS

The following conclusions apply to concrete prepared with the materials mentioned in this report, with the stated proportions and conditions of mixing, molding, curing, and testing:

1. To retard the setting time of concrete 2½ to 3 hr, more retarder was required in some cases than that recommended by the manufacturer. This may have been due to the cement used in these tests, and it indicates that acceptance tests of retarders should be made with the cement which will be used in the proposed construction.

2. All retarders permitted a reduction in the amount of water required to prepare concrete with a specific consistency. For 23 of the 25 retarders tested, this reduction was more than 5 percent. The maximum reduction was approximately 12 percent.

3. The use of retarders increased the compressive strength of concrete when the air content was less than 8 percent. This applied to concrete having the same cement content or the same water content as was used in concrete prepared without a retarder.

4. The flexural strength of concrete in general was not reduced by the use of retarders if the air content was less than 8 percent. When the cement content of the concrete containing the retarder was the same as that for concrete without a retarder, use of the retarder generally furnished higher flexural strength at both 7 and 28 days. When the two concretes had the same water content, those containing the retarder generally had higher flexural strength at 7 days and about the same strength at 28 days.

5. As determined by freezing and thawing tests in the laboratory, the durability of concrete containing the retarder was in most cases less than that for concrete prepared without the retarder. The decrease in relative durability was generally less than 20 percent.

6. The contraction of concrete with 22 of the 25 retarders during continuous dry storage in laboratory air or the expansion for 24 retarders during continuous moist

storage was about the same for concretes prepared with or without a retarder.

7. An overdose of four times the normal amount of retarder caused in most cases a long delay in the hardening of the concrete. However, if the air content of this concrete was not more than 8 percent, the compressive strength at an age of 28 days was usually greater than that of the concrete prepared without a retarder.

8. More retarder was usually required to retard the setting of concrete at a temperature of 90 F than at 73 F. With few exceptions, the compressive strength of concrete prepared with a retarder at 90 F was greater than that prepared at the same temperature without a retarder.

9. The Proctor penetration test was found to be satisfactory for determining the retardation of the setting of concrete.

10. Sixteen of the 25 retarders used in this investigation met all of the requirements of the suggested specification included in this report.

SUGGESTED SPECIFICATION FOR WATER-REDUCING RETARDERS FOR PORTLAND CEMENT CONCRETE

I. General

When required by specifications, or special provisions, or permitted by the engineer on written request from the contractor, an approved, set-retarding admixture that meets the requirements herein specified shall be added to the concrete.

II. Admixtures

The admixture may be in liquid or powder form, and of one of the following types:[1]

A. A calcium, sodium, potassium or ammonium salt of lignosulfonic acid.
B. A hydroxylated carboxylic acid or its salt.
C. A carbohydrate.

III. Acceptance Requirements for Approval of Admixtures

A. Source of test data for approval of admixture - Data from a recognized laboratory that show the water-reducing retarding admixture conforms to the following requirements in this section shall be submitted. A "recognized" laboratory is any State highway, Bureau of Public Roads, or cement and concrete laboratory, inspected regularly by the Cement Reference Laboratory of the American Society for Testing Materials.

B. Type of test data - The test data shall be obtained by the use of concreting materials and by methods that meet the requirements of current standards of the American Association of State Highway Officials or the American Society of Testing Materials as listed in Section 5 of this specification.

C 1. The properties of retarded concrete prepared with the admixture under test, shall be compared with those of a reference concrete, which contains the same cement and aggregates, without retarder, and has the following composition:

Cement content - 6.0 ± 0.1 bags per cubic yard
Air content - 5.5 ± 0.5 percent
Slump - 2½ ± ½ inches
Fine aggregate, by solid volume of total aggregate - 36 - 41 percent.

C 2. The mixes of concrete containing the retarder shall have an air content of 5 to 7 percent, inclusive. An approved air-entraining admixture shall be used if the retarder does not entrain sufficient air.

C 3. A sufficient amount of retarding admixture shall be used to cause an increase of 50 to 60 percent in setting time over the setting time of the reference mix. The

[1]Other types of retarders may become available.

setting time for both mixes shall be determined using a Proctor penetration pressure of 500 pounds per square inch at a temperature of 73.4 ± 3 F for the concretes and ambient air.

D 1. Required properties of retarder - When added to concrete in powder or liquid form, in the manner prescribed by its manufacturer or marketer and in sufficient amount to retard the setting time 50 to 60 percent, the retarding admixture shall cause the concrete to have the following properties in comparison with those of the reference concrete:

D 2. When the test and reference concrete have equal cement content and equal slump:

a. The water content shall be decreased at least 5 percent.
b. The air content of the retarded concrete, with or without an air-entraining admixture, shall not exceed 7 percent.
c.1. The compressive strength at ages of 3, 7, and 28 days shall be increased at least 10 percent.
c.2. For concrete for use in pavement, the flexural strength shall not be reduced at an age of 7 days; at an age of 28 days, the strength shall not be reduced more than 5 percent.
d. The relative durability factor for the freezing and thawing test shall not be less than 80.
e. The drying shrinkage at 200 days, after 2 days initial moist curing, shall not increase more than 0.01 percentage points over the shrinkage of the unretarded concrete.

D 3. When the test concrete has a reduced cement content of ½ bag per cubic yard but the same slump as the reference concrete:

a. The compressive strength at ages of 3, 7, and 28 days shall not be reduced.
b. The air content of the retarded concrete, with or without an air-entraining admixture, shall not exceed 7 percent.
c. The flexural strength shall not be reduced more than 5 percent at an age of 7 days nor more than 10 percent at an age of 28 days.
d. The relative durability factor for the freezing and thawing test shall not be less than 80.

IV. Performance Requirements

When a contractor proposes to use an approved water reducing retarding admixture he shall submit a certificate stating that the admixture is identical in composition with the sample that was used for the acceptance tests. If the admixture varies in concentration from the acceptance sample, a certificate will be required stating that the product is essentially the same for chemical constituents as the approved admixture, and that no other admixture or chemical has been added. Either prior to or at any time during construction, the Engineer may require the selected admixture to be tested further to determine its effect on the strength of the concrete. When so tested, 3 and 7 day compressive strengths or 7 day flexural strengths of the concrete, made with the admixture and specified cement and aggregates, in the proportions to be used or being used on the job, shall meet the requirements of Section III (D) for either equal cement content or reduced cement content. A reference mix of equal or higher cement content, without the retarder shall be made and tested with the concrete containing the retarder as a basis for comparison.

The strength relations shall be calculated on the results of at least 5 standard 6- by 12-in. cylinders or 5 standard 6- by 6- by 21-in. beams, made, cured, and tested in accordance with the current AASHO Methods T 22, T 97 and T 126, for each class of concrete at each age of test.

V. Applicable Specifications

A. AASHO Specification M 85 for Portland Cement, Type I or II.
B. AASHO Specification M 6 for Fine Aggregate for Portland Cement Concrete.

C. AASHO Specification M 80 for Coarse Aggregate for Portland Cement Concrete.
D. AASHO Specification M 154 for Air-Entraining Admixtures for Concrete.
E. AASHO Method T 126 for Making and Curing Concrete Compression and Flexure Test Specimens in the Laboratory.
F. AASHO Method T 119 for Slump Test for Consistency of Portland Cement Concrete.
G. AASHO Method T 152 for Air Content of Freshly Mixed Concrete by the Pressure Method.
H. ASTM Method C 403 for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles.
I. AASHO Method T 121 for Weight per Cubic Foot, Yield, and Air Content (Gravimetric) of Concrete.
J. AASHO Method T 22 for Compressive Strength of Molded Concrete Cylinders.
K. AASHO Method T 97 for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading).
L. AASHO Method T 160 for Volume Change of Cement Mortar or Concrete.
M. AASHO Method T 161 for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water.
N. ASTM Method C 215 for Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens.

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Appendix

WATER-REDUCING RETARDERS USED IN TESTS

Trade Name	Manufactured by
Conaid I	Techkote Co., El Segundo, Calif.
Conaid II	
Conaid III	
Daratard C	Dewey and Almy Chemical Co., Cambridge, Mass.
Daratard D	
Maracon A	Marathon Corp., Rothschild, Wis.
Maracon C	
Marasperse N	
Moore	E.L. Moore Co., Pasadena, Calif.
Orzan A	Crown Zellerbach Corp., Camas, Wash.
Orzan AH3	
Orzan S	
Plastiment A	Sika Chemical Corp., Passaic, N.J.
Plastiment B	
Plastiment C	
Polyfon T	West Virginia Pulp and Paper Co., Charleston, S.C.

Pozzolith 3R	Master Builders Co., Cleveland, Ohio
Pozzolith HP-18	
Pozzolith HP-75	
Product 135	Crown Zellerbach Corp., Camas, Wash.
Protex R1A	Autolene Lubricants Co., Denver, Colo.
Protex R2A	
Retardwel R	Johns-Manville Co., New York, N.Y.
Sonotard (liquid)	L. Sonneborn Sons, New York, N.Y.
Sonotard (powder)	

Water-Reducing Retarders for Concrete—Chemical and Spectral Analyses

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The purchaser of a concrete retarder is primarily interested in the performance of the material and his initial evaluation is based on tests to show the effect of the material on concrete. He must, however, assure himself that the composition of each lot purchased has not been materially altered subsequent to his initial acceptance of the product. To explore the best means of doing this, chemical as well as ultraviolet and infrared spectral analyses were made on 25 commercial retarders. The results are reported in this article. These materials were found to be of three general types: lignosulfonates, salts of hydroxy-carboxylic acids, and carbohydrates. It was found that infrared spectral analysis offers the most promising and rapid means of clearly identifying such products. Ultraviolet techniques were also found to be of value in identifying lignosulfonate retarders and in establishing the concentration of the major active ingredient. Conventional chemical procedures, although useful, were tedious and time-consuming, and often yielded empirical or doubtful results for certain major organic constituents.

●IN the past several years, admixtures to reduce water content and retard set in portland cement concrete have come into prominent use in construction. These materials are usually complex organic products which are sold under various trade names. As yet there are no standard specifications or methods for testing retarders, but the American Society for Testing Materials (ASTM) is now considering these specifications and methods for testing such admixtures. These include among other items, requirements for the effects of water-reducing retarders on the compressive strength of the concrete, resistance to freezing and thawing, and change in volume. These tests may require a period of 1 yr or more for completion and consequently are intended for the primary evaluation of such admixtures.

After an admixture has been found acceptable under these specifications subsequent purchases of the same material for use on specific projects may not be subjected to extensive testing because of the time and cost involved. Consequently, the presently proposed specifications for retarding and water-reducing admixtures suggest that the purchaser obtain assurance that the admixture supplied for use on each field job or project be equivalent in composition to the original or reference admixture subjected to the exhaustive tests required by the specifications. To explore the best means of doing this, chemical analyses, as well as ultraviolet and infrared spectral analyses, were made on 25 commercial or trade-name retarders. All materials were analyzed for specific properties and chemical composition.

Another objective of the analyses was to establish the chemical composition of typical commercial products to show possible relationships between chemical composition and the performance of concrete prepared with the retarders.

TYPES OF RETARDERS STUDIED

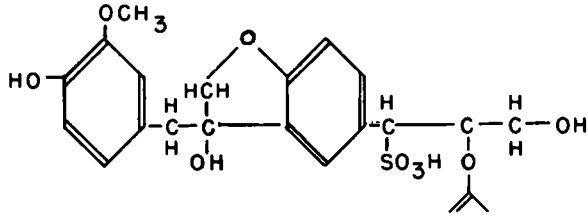
The retarders investigated were found to be of three general chemical types: lignosulfonates, salts of organic hydroxy-carboxylic acids, and carbohydrates. A general discussion of the origin and characteristics of these major types of retarders studied is given in the following paragraphs.

Lignosulfonates

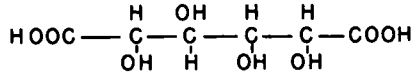
With one exception, the lignosulfonate materials studied were derived from spent sulfite liquor obtained in the acid process of wood pulping. The single exception was derived from the Kraft (alkaline) process. Materials were supplied as the calcium, sodium, or ammonium salts, and either as a powder or in a water solution.

Lignosulfonates are considered to be polymers of high molecular weight. A single sample may contain molecules ranging in molecular weight from several hundred to 100,000 with an average molecular weight of approximately 10,000 (1, 2). Structurally, these materials are polymers of a substituted phenyl propane grouping. The repeating monomer unit has been represented as shown in Figure 1A (2). The functional units of interest are hydroxyl (OH), methoxyl (OCH_3), phenyl ring, and the sulfonic group (SO_3H). In the lignosulfonate salts, a metal or ammonium cation replaces the hydrogen in the sulfonic grouping.

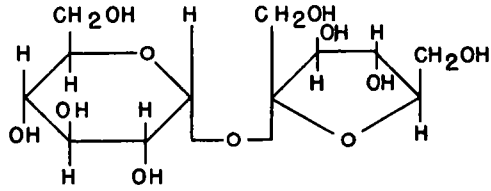
Many commercial lignosulfonates also contain varying amounts of reducing sugars. A typical analysis showed the following percentages of wood sugars based on total



A STRUCTURAL UNIT OF LIGNOSULFONIC ACID



B HYDROXY-CARBOXYLIC ACID



C. CARBOHYDRATE (SUCROSE)

Figure. 1. Typical chemical structures of retarders studied.

sugar content (3): mannose—48 percent; glucose—15 percent; xylose—15 percent; galactose—10 percent; arabinose—6 percent; fructose—under 2 percent; and sugars unaccounted for—4 percent. Much of these sugars can be removed by suitable processing techniques.

Organic Hydroxy-Carboxylic Acids

Salts and complexes of organic hydroxy-carboxylic acids, sometimes referred to as sugar acids, are derived from the fermentation or oxidation of carbohydrates, such as dextrose, glucose, or starch. They are characterized by several hydroxyl groups and either one or two terminal carboxylic acid (COOH) groups attached to a relatively short carbon chain as illustrated in Figure 1B. As retarders, they are generally supplied as metal salts in which the hydrogen in the carboxylic acid group is replaced by sodium, potassium, etc.

Carbohydrates

Carbohydrates, such as reducing sugars (for example, glucose), have been used as retarders (4). However, non-reducing sugars, sucrose or cane sugar, are more illustrative of the type of carbohydrate evaluated in this study. The structure of sucrose is shown in Figure 1C. Here again, hydroxyl groups are characteristic of the material.

PHYSICAL PROPERTIES

The physical properties of each retarder evaluated in this study are shown in Table 1. Most of the materials were powders, the rest were aqueous solutions. The color code was obtained by a visual comparison with the closest color standard available in Federal Standard No. 595. Although this Federal Standard is intended primarily for paints, it is useful for describing colors of other materials by standardized code number.

The specific gravities of the liquid samples were determined with a hydrometer. Values for pH were obtained electrometrically on liquid samples as received, and on aqueous solutions containing 1 percent of the solid materials. Rather low pH values, indicating significant acidity, were obtained on a complexed hydroxy-carboxylic acid

TABLE 1

PHYSICAL PROPERTIES OF RETARDERS

Retarder No	Form	Color: Observed	Color: Code[a]	Odor	Specific Gravity, 77 F/77 F[b]	pH[c]	Solubility in[d]: Water	Solubility in[d]: Alcohol Benzene Chloroform	Solubility in[d]: Dimethyl Sulfoxide	Foaming Properties, Milliliters of Foam After[e]: 1 Min	2 Min	5 Min	15 Min	Unusual Characteristics of 1 Percent Aqueous Solution
1	Liquid	None	-	Phenolic	1 143	7 4	-	-	-	0	0	0	0	-
2	Solid	White	37778	Woody	-	7 8	I	I	I	0	0	0	0	-
3	Solid	Olive	30118	Woody	-	7 2	S	I	I	10	5	3 5	1	-
4	Liquid	Amber[f]	23655[f]	Rancid	1 182	6 8	-	-	-	0	0	0	0	U V fluorescence
5	Liquid	Wine	20109	Pungent	1 148	7 1	-	-	-	0	0	0	0	-
6	Liquid	Amber	33538	None	1 178	2 8	-	-	-	0	0	0	0	-
7	Solid	Brown	10091	Woody	-	3 3	PS	I	I	10	7	4	1 5	Mold growth
8	Solid	Pink	30313	None	-	7 6	I	I	I	0	0	0	0	-
9	Liquid	Dark brown	10032	Rancid	1 196	8 2	-	-	-	0	0	0	0	-
10	Solid	Medium brown	10091	Woody	-	3 2	S	I	I	2	2	1 5	1	Mold growth
11	Solid	Light brown	20400	Woody	-	6 8	S	I	I	4	2	0	0	Mold growth
12	Solid	Mustard	30266	Woody	-	6 7	S	I	PS	0	0	0	0	-
13	Solid	Medium brown	30117	Woody	-	9 4	PS	I	I	1	0 5	0	0	-
14	Solid	Tan	31643	Woody	-	4 6	S	I	I	5	4	3	1 5	-
15	Solid	Olive	30009	Woody	-	7 4	S	I	I	11	8	4 5	2	-
16	Solid	Tan	31643	Woody	-	7 3	PS	I	PS	9	6	2 5	1	-
17	Solid	Light brown	20400	Woody	-	3 8	S	I	S	1 5	1	0 5	0	Mold growth
18	Solid	Tan	31643	Woody	-	7 4	S	I	I	3 5	2	1	0 5	-
19	Solid	Light brown	20400	Woody	-	6 6	S	I	I	0 5	0	0	0	-
20	Liquid	Dark brown	10032	Woody	1 155	4 8	-	-	-	12	8	4	1	-
21	Liquid	Dark brown	10032	Woody	1 147	4 7	-	-	-	10	7	3	0 5	-
22	Solid	Dark brown	30045	Woody	-	8 8	S	I	I	5	2 5	1	0 5	-
23	Solid	Medium brown	10091	Woody	-	9 5	S	I	I	0	0	0	0	-
24	Solid	Tan	31643	Woody	-	7 8	PS	I	I	1	1	0 5	0	-
25	Solid	Tan	31643	Woody	-	4 6	PS	I	I	7	7	7	7	-

[a]Federal Standard No 595 (by visual matchings) [b]Hydrometer method on liquid samples as received [c]Electrometric method on liquid samples as received, and on solid samples in 1 percent water solution [d]At room temperature I = insoluble (less than 0 01 g in 10 ml), PS = partially soluble (between 0 01 and 1 g in 10 ml), S = soluble (more than 1 g in 10 ml) [e]Twenty milliliters of 1 percent aqueous solution in 50-ml stoppered graduate Inverted 30 times Readings then noted at indicated time intervals (Modified from McCutcheon, J W , "Synthetic Detergents," 1950, p 79) [f]By transmitted light By reflected light, color had a greenish fluorescence (equivalent to Code 14187)

retarder (No. 6) and all the ammonium lignosulfonates (Nos. 7, 10 and 17). Several calcium lignosulfonates (Nos. 14, 20, 21, and 25) had moderately low pH values, possibly as a result of incomplete neutralization of the sulfonic acid groups during processing.

The apparent insolubility of samples Nos. 2 and 8 in water was caused by the large amount of inert filler in each material. Ultraviolet fluorescence was observed on a 1 percent aqueous solution of sample No. 4, most likely because of a fluorescent dye used by the producer to characterize his product. As noted in Table 1, a mold growth developed in several of the 1 percent aqueous solutions after standing for about one week. Only retarder No. 25 produced a lasting foam in the foaming test. This was apparently a result of some synthetic detergent which has been incorporated into the admixture.

QUALITATIVE CHEMICAL TEST RESULTS

Table 2 gives the results of qualitative chemical tests used to identify and classify each material for further evaluation.

Sulfonated organic material was identified with basic fuchsin. This reagent reacts with sulfonates in acid solution to form a magneta-colored complex which can be extracted with chloroform. The results are given in Col. 2. The method has been

TABLE 2

QUALITATIVE TES

Retarder No. (1)	Sulfonated Organics (Basic fuchsin test)[b] Original Material (2)	Alcohol-insoluble Fraction (3)	Alcohol-soluble Fraction (4)	Lignosulfonate (Proctor-Hirst test)[c] (5)	Chloride ($AgNO_3$ test) (6)	Sulfate ($BaCl_2$ test) (7)	Carbonate (acid effervescence) (8)	Calcium (oxalate test) (9)
1[gh]	N	-	-	N	N	N	N	N
2	P	P	N	T	N	N	P	N
3	P	P	N	P	N	Q	N	P
4	N	-	-	N	N	N	N	N
5[i]	N	-	-	N	P	N	N	N
6[j]	N	-	-	N	N	N	N	N
7	P	P	N	P	N	Q	N	N
8	N	-	-	N	N	N	N	P
9	N	-	-	N	P	N	N	N
10	P	P	N	P	N	Q	N	N
11	P	P	N	P	P	P	N	P
12	P	P	N	P	N	N	N	P
13	P	P	N	P	N	N	P	T
14	P	P	N	P	N	P	N	P
15	P	P	N	P	N	P	N	N
16	P	P	N	P	N	P	N	P
17	P	P	N	P	N	Q	N	N
18[k]	P	P	N	P	N	N	N	P
19	P	P	N	P	N	Q	N	N
20	P	P	N	P	N	N	N	P
21	P	P	N	P	N	N	N	P
22	P	P	N	P	N	Q	N	N
23	P	P	N	P	N	Q	N	N
24	P	P	N	P	P	T	N	P
25	P	P	P	P	N	P	N	P

[a]Code: P = positive indication; N = negative indication; T = trace indicated, Q = questionable indication. [b]Mod pp. 616-7. [c]Jour. ALCA, Vol. 51, No. 7, 1956, pp. 353-76. [d]Public Roads, Vol. 27, No. 12, 1954, p. 268. 3d ed., 1946. [f]Test procedure given in text. [g]A positive indication of phenols was obtained by the Millon test 3d ed., 1946, p. 330). [h]A positive indication of sucrose was obtained by the alpha-naphthol test (Griffin, R.C. p. 567). [i]A positive indication of triethanolamine was obtained by the Kraut test "Official Methods of Analysis, indications of zinc (sulfide test), and boron (flame and turmeric tests) were obtained. [k]A negative test for trie Kraut test (see footnote i).

described as a quantitative spectrophotometric determination of sulfonated and sulfated organic materials (5). When a positive result was obtained on the original material, additional tests were made on the alcohol-insoluble and alcohol-soluble fractions of the retarder. A positive result on the alcohol-insoluble fraction suggests the presence of lignosulfonates, because lignosulfonates are insoluble in alcohol. A positive test result on the alcohol-soluble fraction, as for retarder No. 25, suggests the presence of a sulfonated or sulfated synthetic detergent. Consequently, the result on sample No. 25 reinforces the findings of the foaming test, that this material contained a synthetic detergent.

A more specific indication of lignosulfonate is given by the Proctor-Hirst test. In this test, an acidified clear extract is treated with aniline. A resultant cloudiness is indicative of lignosulfonate. The test is considered to be reliable (6). In every case, these results are in agreement with the findings from the basic fuchsin test.

Cols. 6 through 11, Table 2, give the results of tests for chloride, sulfate, carbonate, calcium, sodium, and potassium using standard procedures. Positive test results for chloride and sulfate are not entirely reliable in the presence of some organics, such as were found in some retarders, because of the possible precipitation of organic salts in the presence of silver and barium reagents.

Test results for both ammoniacal and albuminoid nitrogen are given in Cols. 12 and 13. In the test for ammoniacal nitrogen, an alkaline solution of the sample was boiled

TS ON RETARDERS[a]

Sodium (flame phot.) (10)	Potassium (flame phot.) (11)	Nitrogen: Ammoniacal[d] (12)	Nitrogen: Albuminoid[d] (13)	Hydroxy Acids (dinaphthol test) (14)	Complexing Agents ($CuSO_4$+NaOH test)[f] (15)	Melting Point of Phenylhydrazine Derivative, °C[f] (16)
T	N	-	-	-	P (light blue)	-
T	N	N	N	-	-	No derivative
P	T	N	N	-	-	-
P	T	-	-	P (green)	P (light blue)	188 to 189
T	T	N	P	P (blue-green)	P (medium blue)	189 to 191
T	N	-	-	-	P (light blue)	No derivative
T	T	P	P	-	-	-
P	T	-	-	P (light green)	P (light blue)	No derivative
P	P	-	-	P (green)	P (blue-green)	180 to 182
T	T	P	P	-	-	-
P	P	N	N	-	-	-
P	T	N	N	-	-	-
P	T	N	N	-	-	-
P	T	N	N	-	-	-
P	T	N	N	-	-	-
P	T	N	N	-	-	-
T	T	P	P	-	-	-
P	T	N	N	-	P (light green)	No derivative
P	P	N	N	-	-	-
T	T	N	N	-	N	-
T	T	N	N	-	N	-
P	N	N	N	-	-	-
P	T	P	P	-	-	-
P	P	P	P	-	-	-
P	T	N	N	-	-	-

ified from Wallin, Anal. Chem., Vol. 22, 1950,
[e]F. Feigl. Qualitative Analysis by Spot Tests,
(Feigl, Qualitative Analysis by Spot Tests,
, Technical Methods of Analysis, 2d ed., 1927,
" A.O.A.C., 7th ed, 1950, p. 609. [j]Positive
thanolamine was obtained by means of the

and the vapor tested with red litmus paper for volatile ammonia. A blue color indicated the presence of an ammonium salt. Following the removal of volatile ammonia, permanganate was added and the test repeated to detect albuminoid nitrogen. Positive results suggest the presence of amines and similar nitrogenous compounds.

Zinc was detected in sample No. 6 by precipitation as a white sulfide, and boron by flame tests and turmeric paper. In sample No. 1, a phenolic odor was detected which was attributed to a phenol-type material. This phenolic material was confirmed by the Millon test. This material probably serves as a fungicide. The same retarder also gave a positive test result for sucrose. However, substances similar to sucrose may give positive results with alpha-naphthol reagent, so that these results were not conclusive.

The results of the dinaphthol test which has been used to identify many hydroxy-carboxylic acids are given in Col. 14. Acids such as tartaric, malic, tartronic, glucoronic, and gluconic reportedly give a green fluorescence (7). Where a positive test result was obtained, the nature of the color which developed is shown in parentheses.

Test results for complexing agents are given in Col. 15. Although not specific, the test may be used to detect such complexing agents as triethanolamine, sugars, hydroxy-carboxylic acids, etc. (Details of the test procedure are as follows: To 10 ml of a 1 percent solution of the admixture, add 1 ml of 10 percent NaOH, mix, and add 1 ml of 3 percent $CuSO_4$. Mix and note whether a soluble colored copper complex is formed.) Where positive results are shown, the color of the copper complex formed is also given.

A specific check for triethanolamine was made by means of the Kraut test. Sample No. 5 gave a positive indication of the presence of this compound, whereas sample No. 18 gave a negative test for triethanolamine.

Col. 16 gives the melting points of phenylhydrazine derivatives of several retarders. Ordinarily, such derivatives are obtained with carboxylic acids, and the melting points of these derivatives have been used for qualitative analyses. (Details of the test procedure are as follows: To a test tube (35 ml, 20 x 150 mm) add 1 ml of a 50 percent aqueous solution of active ingredient, add 4 ml H_2O, 0.7 ml of glacial acetic acid and 1.0 ml phenyl hydrazine. Fit with reflux tube approximately 8 in. long, heat in boiling water and reflux 3 hr. Filter while hot, collect filtrate, cool and let crystallize from 2 hr to overnight. Collect crystals by filtration, wash with 5 ml cold water, then 5 ml alcohol. Dry at room temperature and determine melting point.) This test was suggested by one producer of retarders; however, in this study it was found that duplicate determinations failed to give reasonably reproducible results.

On the basis of these qualitative tests, the following summarization was possible. Retarder No. 1 contained a sugar and a phenolic additive. Five samples were found to be the following derivatives of hydroxy-carboxylic acids: Nos. 4, 8, and 9 appeared to be metal salts; No. 6 a zinc borate complex; and No. 5 a triethanolamine salt. The other materials were lignosulfonate salts of various types.

QUANTITATIVE CHEMICAL ANALYSES

Inorganic Constituents

Table 3 gives the results of the analyses for inorganic constituents in each retarder sample. Moisture or water was determined by oven loss at 105 C except for sample No. 5. This material had a tendency to decompose or volatilize at that temperature, and therefore its moisture content was determined by heating at 50 C under vacuum.

Total ash content was determined by ignition at 600 C and HCl insoluble by treating the ash with hydrochloric acid (1:5). The acid-soluble ash constituents were then determined by conventional methods of analysis and reported as the oxides. The alkalies, Na_2O and K_2O, were determined by flame photometry, and zinc by ferrocyanide titration with an external indicator. Carbon dioxide was determined by wet evolution with hydrochloric acid and chlorides by the Mohr titration. Boron was analyzed by distillation with methyl alcohol followed by titration using an ASTM standard procedure. Total sulfur was obtained by wet oxidation followed by precipitation as barium sulfate.

Summary of Inorganic Results

Retarders Nos. 1, 5, 7, 10 and 17 appeared to be composed almost exclusively of organic material that was completely volatilized at 600 C. Retarder No. 2 contained limestone or dolomitic limestone along with zinc, perhaps as zinc oxide. Samples Nos. 4 and 9 were composed of sodium and potassium salts, respectively, of carboxylic acids. Sample No. 6 contained zinc and boron, most likely in the oxide form. Retarder No. 8 contained a large amount of insoluble siliceous material and iron oxide. Retarders Nos. 11 and 24 contained calcium chloride and No. 13 contained a substantial amount of sodium carbonate.

TABLE 3

INORGANIC CONSTITUENTS IN RETARDERS, BY PERCENT OF CONSTITUENT

Retarder No	Moisture or Water at 105 C	Analyses on Dry Solids Basis[b]											CO_2, Wet Evolution Method	Chloride as $CaCl_2$	B_2O_3[e]	Total Sulfur as SO_3[f]
		Total Ash at 600 C	HCl (1 5) Insoluble	SiO_2	R_2O_3[c]	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	ZnO[d]				
1	66 7	0 2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	0 4	97 2	5 6	Neg	0 8	-	34 3	5 1	Neg	Neg	0 9	6 7	37 8	-	-	0 6
3	6 8	17 7	0 1	0 2	0 4	-	3 2	1 0	5 2	0 1	6 3	-	-	0 0	-	9 8
4	68 2	24 8	Neg	Neg	Neg	-	Neg	Neg	12 6	0 2	Neg	-	-	-	-	-
5	57 1[g]	0 4	-	-	-	-	-	-	-	-	-	-	-	-	-	0 0
6	72 5	32 5	Neg	Neg	-	-	-	-	Neg	Neg	Neg	15 6	-	-	11 9	-
7	4 5	1 3	0 1	Neg	Neg	-	0 3	0 2	0 4	0 2	Neg	-	-	-	-	14 3
8	0 7	90 0	67 5[h]	2 2	14 0	6 7	5 2	2 0	0 9	0 1	Neg	-	-	-	-	-
9	66 5	32 4	Neg	0 8	4 0	-	Neg	Neg	0 5	16 5	Neg	-	-	-	-	-
10	5 1	0 7	Neg	0 2	0 1	-	Neg	Neg	Neg	Neg	Neg	-	-	-	-	14 0
11	6 2	28 2	0 6	Neg	Neg	-	11 4	0 2	2 1	0 3	6 7	-	-	9 8	-	13 2
12	4 4	21 2	0 2	Neg	0 2	-	10 8	0 7	0 2	0 2	6 0	-	-	0 0	-	11 4
13	8 8	47 0	0 2	0 1	0 6	-	3 1	0 6	16 3	0 1	10 1	-	12 6	-	-	9 6
14	6 5	15 2	0 1	Neg	0 1	-	4 6	0 4	0 1	0 3	3 3	-	-	-	-	9 2
15	7 4	23 7	0 3	0 2	Neg	-	0 6	1 1	9 2	0 1	9 0	-	-	-	-	12 0
16	5 3	16 4	0 2	Neg	Neg	-	6 7	0 5	0 7	0 4	7 1	-	-	0 0	-	13 5
17	7 6	0 8	Neg	Neg	Neg	-	Neg	Neg	0 1	0 3	0 2	-	-	-	-	13 5
18	7 2	9 4	0 1	Neg	0 6	-	5 2	Neg	Neg	Neg	3 2	-	-	-	-	11 8
19	5 4	25 4	0 1	0 3	0 1	-	Neg	Neg	9 6	0 1	13 6	-	-	-	-	16 9
20	69 0	22 5	Neg	0 2	Neg	-	9 5	Neg	Neg	Neg	10 8	-	-	-	-	13 1
21	70 3	22 3	Neg	0 2	Neg	-	9 1	Neg	Neg	Neg	11 9	-	-	-	-	15 6
22	8 5	45 2	0 3	Neg	0 3	-	Neg	Neg	20 0	0 1	22 2	-	-	-	-	27 2
23	7 2	34 7	0 2	Neg	Neg	-	0 6	0 1	12 8	0 3	10 2	-	-	-	-	7 6
24	4 0	44 8	0 6	0 1	Neg	-	17 7	0 3	3 2	0 4	9 5	-	-	25 0	-	16 0
25	6 5	17 2	0 1	Neg	0 1	-	6 9	0 7	0 7	0 1	6 7	-	-	-	-	15 6

[a]Loss at 105 C, calculated on basis of material as received [b]Neg = Negligible [c]Fe_2O_3 plus Al_2O_3 [d]Volumetric determination with ferrocyanide [e]Distillation method, modified from method C 169-53, sec 18, ASTM Standards Part 3, 1955, p 907 [f]TAPPI, T 629-m53 [g]Loss at 50 C, vacuum [h]Mainly siliceous matter

TABLE 4

ORGANIC CONSTITUENTS, IN PERCENTAGES BY WEIGHT OF DRY SOLIDS

Retarder No	Volatile Matter at 600 C	Methoxyl[a]	Ligno-sulfonate (cincho-nine method)[b]	Lignin, Calculated from Methoxyl[c]	Total Carbo-hydrates, as Glucose[d]	Reducing Sugars, as Glucose[e]	Sucrose (AOAC method)[f]	Anionic Sulfonated Synthetic Detergent[g]	Phenol[h]	Nitrogen			
										Total (as N)[a]	Ammo-niacal (as NH_3)[a]	Albu-minoid (as N)[i]	Fixed (as N)[j]
1	99 8	-	-	-	-	0 0	96 3	-	1 4	-	-	-	-
2	2 8	0 2	1 3	1 7	0 7	0 6	-	-	-	-	-	-	-
3	82 3	11 8	69 2	92 2	4 0	0 8	-	0 0	-	-	-	-	-
4	75 2	-	-	-	0 4	0 2	-	-	-	-	-	-	-
5	99 6	-	-	-	0 9	0 5	-	-	-	3 9	0 1	2 0	3 8
6	67 5	-	-	-	0 6	0 01	-	-	-	-	-	-	-
7	98 7	8 2	109 6	64 2	5 9	2 9	-	-	-	3 2	2 0	-	1 7
8	10 0	-	-	-	1 0	0 05	-	-	-	-	-	-	-
9	67 6	-	-	-	0 4	0 1	-	-	-	-	-	-	-
10	99 3	8 4	43 7	65 2	5 4	3 5	-	-	-	3 4	1 4	-	2 2
11	71 8	6 4	100 6	49 8	5 2	1 5	-	-	-	-	-	-	-
12	78 8	7 2	103 8	56 2	4 7	2 7	-	-	-	-	-	-	-
13	53 0	7 1	123 4	55 5	0 8	0 3	-	-	-	-	-	-	-
14	84 8	6 6	110 2	51 9	9 1	5 1	-	-	-	-	-	-	-
15	76 3	11 4	104 4	88 6	2 5	0 3	-	-	-	-	-	-	-
16	83 6	7 5	96 9	58 8	7 6	3 8	-	-	-	-	-	-	-
17	99 2	8 2	98 1	63 9	12 2	8 1	-	-	-	3 2	2 7	-	1 1
18	90 6	6 9	114 6	53 7	8 6	3 0	-	-	-	1 8	0 0	0 5	1 8
19	74 6	7 1	92 8	54 7	8 9	4 8	-	-	-	-	-	-	-
20	77 5	6 2	93 0	48 7	5 4	1 3	-	-	-	-	-	-	-
21	77 7	7 3	117 6	56 9	6 8	2 4	-	-	-	-	-	-	-
22	54 8	5 4	57 5	42 3	0 6	0 02	-	-	-	-	-	-	-
23	65 3	6 9	65 5	53 7	2 3	0 3	-	-	-	0 9	0 0	-	0 9
24	55 2	2 8	93 5	21 9	1 4	0 3	-	-	-	1 0	0 2	0 6	0 8
25	82 8	8 6	103 5	67 2	10 0	4 7	-	1 1	-	-	-	-	-

[a]Public Roads, Vol 27, No 12, p 268, 1954 [b]Jour ALCA, Vol 51, No 7, p 353, 1956 [c]TAPPI, T629-m53, methoxyl divided by 0 128 [d]Anthrone method, Morris, Science, Vol 107, 1948, p 254-5 [e]Somogyi iodometric volumetric method, Jour Biol Chem , Vol 160, No 1, 1945, p 61 [f]AOAC method 29 29 [g]Colorimetric method (basic fuchsin), Wallin, Anal Chem , Vol 22, 1950, p 616 [h]By spectrophotometric absorption at 270 millimicrons [i]AOAC method 2 37 [j]Calculated from total nitrogen—ammoniacal nitrogen

Organic Constituents

The organic constituents determined in each retarder are given in Table 4. The volatile matter at 600 C is an approximate measure of total organic material present. Methoxyl was determined by the Zeisel method.

Lignosulfonates were determined by a recommended cinchonine procedure. It appears from the results shown, as well as the results of duplicate determinations, that the cinchonine procedure yielded erratic results. Lignin content was also calculated from the methoxyl values as given by the Technical Association of the Pulp and Paper Industry (TAPPI method T 629, m-53). Although this procedure was empirical, the results appeared to be more realistic than those obtained by the cinchonine method.

A colorimetric procedure was used to determine total carbohydrates by the anthrone method (8), and reducing sugars were determined by the Somogyi-Iodometric method, after precipitation of non-carbohydrates with basic lead acetate. In both cases the constituent was calculated as glucose.

Sucrose was determined by the AOAC (Association of Official Agricultural Chemists) official chemical procedure by direct weighing of cuprous oxide. The anionic sulfonated detergent was determined colorimetrically with basic fuchsin after first extracting the detergent with alcohol. The method used was similar to that prescribed by Wallin (5) except that visual estimation was made in Nessler tubes because of the staining effect by the reagent on spectrophotometric cells.

Phenol was determined from the spectrophotometric absorption at 270 millimicrons, using a calibration curve of known concentrations of phenol plotted against absorbance.

Total nitrogen was obtained by the Kjeldahl distillation procedure, and ammoniacal nitrogen was determined by distillation from an alkaline solution. After removing ammoniacal nitrogen, permanganate was added and albuminoid nitrogen obtained by distillation. Fixed nitrogen was calculated by difference.

Classification and Probable Composition

Based on the results of chemical analysis, the classification and probable composition

TABLE 5

CLASSIFICATION AND PROBABLE COMPOSITION OF RETARDERS, PERCENT OF CONSTITUENT ON DRY SOLIDS BASIS[a]

Retarder Type	Retarder No	Water[b]	Lignosulfonate Salt[c]	Carbohydrates[d] Non-reducing Types[e]	Carbohydrates[d] Reducing Sugars[f]	Calcium Chloride	Zinc Oxide	Iron Oxide and Alumina	Organic Carboxylic Material[g]	Miscellaneous Constituents (%)
Lignosulfonates										
Ammonium salts	7	4 5	76	3 0	2 9	-	-	-	-	-
	10	5 1	77	1 9	3 5	-	-	-	-	-
	17	7 6	76	4 1	8 1	-	-	-	-	-
Sodium salts	15	7 4	94[i]	2 2	0 3	-	-	-	-	-
	19	5 4	66	4 1	4 8	-	-	-	-	-
	22[h]	8 5	51	0 6	0 02	-	-	-	-	-
	23	7 2	64	2 0	0 3	-	-	-	-	-
Calcium salts	2	0 4	2	0 1	0 6	-	6 7	-	-	80-90 dolomitic limestone
	3	6 8	93[i]	3 2	0 8	0 0	-	-	-	0 0 synthetic detergent
	11	6 2	59	3 7	1 5	9 8	-	-	-	-
	12	4 4	67	2 0	2 7	0 0	-	-	-	-
	13	8 8	66	0 5	0 3	-	-	-	-	29 sodium carbonate
	14	6 5	62	4 0	5 1	-	-	-	-	-
	16	5 3	70	3 8	3 8	0 0	-	-	-	-
	18	7 2	64	5 6	3 0	-	-	-	-	-
	20	69 0	58	4 1	1 3	-	-	-	-	-
	21	70 3	68	4 4	2 4	-	-	-	-	-
	24	4 0	26	1 1	0 3	25 0	-	-	-	-
	25	6 5	80	5 3	4 7	-	-	-	-	1 1 synthetic detergent[k]
Organic acids										
Metal salts										
Sodium (9 3 % Na)	4	68 2	-	0 2	0 2	-	-	-	90	-
Calcium (3 7 % Ca)	8	0 7	-	0 9	0 1	-	-	14	10	71 inert siliceous matter
Potassium (13 7 % K)	9	66 5	-	0 3	0 1	-	-	-	86	-
Triethanolamine salt	5	57 1	-	0 5	0 5	-	-	-	57	42 triethanolamine[l]
Zinc borate complex	6	72 5	-	0 6	0 01	-	15 6	-	72	11 9 boric oxide (B_2O_3)
Carbohydrates										
Sucrose	1	66 7	-	96 3[j]	0 0	-	-	-	-	1 4 phenol

[a]Based on results given in Tables 1-4 [b]Based on weight of sample as received [c]Approximate value obtained by the following empirical calculations Methoxyl/0 128 = lignin (TAPPI, T 629 m-53), lignin x 1 154 = lignosulfonic acid (TAPPI, T 629 m-53), lignosulfonic acid + cation equivalent of SO_3 in lignosulfonic acid = lignosulfonate salt [d]Calculated as glucose [e]Total carbohydrates—reducing sugars [f]May include such wood sugars as mannose, glucose, xylose, galactose, arabinose and fructose [g]Estimated by difference [h]Derived from Kraft process [i]Maximum possible The empirical calculation gave unreasonably large values because of high methoxyl contents [j]Established as sucrose by infrared spectral analysis [k]Probably alkyl aryl sulfonate salt [l]Calculated from total nitrogen content

of each retarder are given in Table 5. The majority of the retarders analyzed were found to be ammonium, sodium, or calcium salts of lignosulfonic acid. The approximate amount of lignosulfonate salt shown was obtained by empirical calculations based on methoxyl values. In two samples, Nos. 3 and 15, the empirical calculation gave unreasonably high results because of high methoxyl contents. Consequently, the values shown for these samples were obtained by difference and therefore represented the maximum amounts of lignosulfonate possible. Carbohydrates, both nonreducing and reducing-sugar types, were calculated as glucose.

Only one lignosulfonate retarder, No. 25, was found to contain a sulfonated synthetic detergent, which was possibly a sodium alkyl aryl sulfonate. Two of the lignosulfonates, Nos. 11 and 24, contained substantial amounts of calcium chloride (9.8 and 25 percent, respectively). Retarder No. 2 contained 80-90 percent of dolomitic limestone and about 7 percent zinc oxide. Retarder No. 13 contained approximately 29 percent sodium carbonate.

The derivatives of hydroxy-carboxylic acids were found to be metallic salts—sodium, calcium, and potassium; triethanolamine salt; and zinc borate complex. These materials contained little or no carbohydrates. Retarder No. 8, a solid material, contained iron oxide and siliceous filler. The organic carboxylic material in each retarder was estimated by difference.

Only one retarder, No. 1, was found to be a carbohydrate. This was essentially a non-reducing sugar (sucrose). It contained some phenol to prevent fermentation or mold growth.

It is quite possible that these retarders may contain minor amounts of other organic

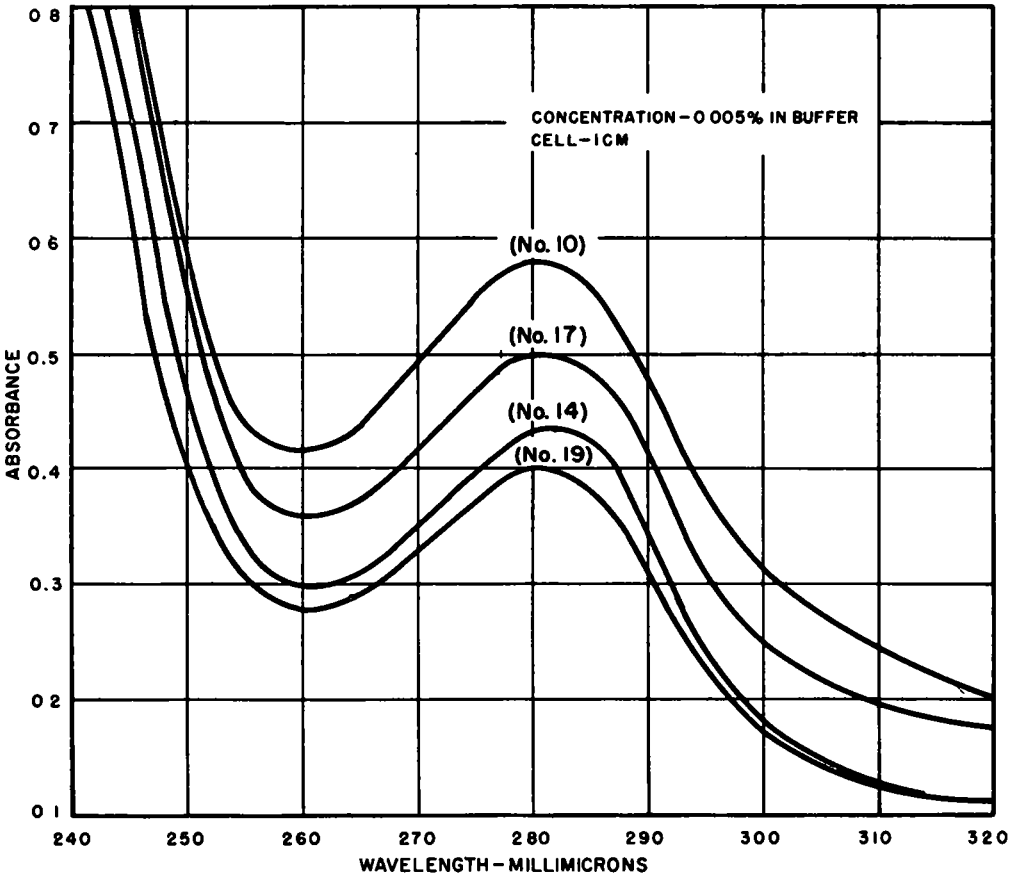


Figure 2. Typical ultraviolet spectra of lignosulfonates.

substances not discussed here, but no effort was made in this study to identify all such minor constituents.

ULTRAVIOLET SPECTRAL ANALYSIS

Each material was analyzed by ultraviolet spectroscopy to determine if it could be identified or characterized by its ultraviolet absorption spectrum. The apparatus used for ultraviolet work included a double beam quartz spectrophotometer, an ultraviolet power supply unit, and a hydrogen discharge lamp as a light source. Measurements were made in 1-cm matched silica rectangular cells.

Procedure for Lignosulfonates

Special Buffer.—495 ml of 0.2 N KH_2PO_4 and 113 ml of 0.1 N NaOH were mixed and diluted to 2 liters.

Sample Preparation.—0.5 g of solid sample or exactly 1 ml of liquid sample was dissolved and diluted with water to 100 ml. Insoluble material was removed by centrifuging. A 10-ml clear aliquot was diluted to 100 ml, and finally a 1-ml aliquot of the latter was diluted to exactly 10 ml with the buffer solution. Final concentration was 0.005 percent by weight or 0.01 percent by volume in the case of the liquid samples.

Measurements.—Absorbance for each material was measured at intervals between 220 and 350 millimicrons in 1-cm cells. Readings were made at wavelength intervals of 5 to 10 millimicrons, except where peaks appeared near 260 and 280 millimicrons. In these areas, readings were obtained at 0.5 to 1.0 millimicron intervals. The sensitivity of the instrument was adjusted so as to maintain the smallest slit openings. The lamp housing was cooled with circulating tap water.

Plotting.—The absorbance readings were plotted against wavelength and the resultant spectral curve was then drawn manually. Absorbance is defined as $\log_{10} I_0/I$, where I_0 equals incident radiant power, and I equals transmitted radiant power.

Results of Tests on Lignosulfonates

Figure 2 shows examples of typical ultraviolet spectra obtained on several lignosulfonate retarders. The shape of each curve was typical of all the other lignosulfonate retarders except one, retarder No. 22, which had been derived from the Kraft process. The spectrum of sample No. 22, shown separately in Figure 3, indicated a shoulder rather than a peak occurred at 280 millimicrons. It thus appeared that lignosulfonates as a class could be identified from their characteristic ultraviolet spectra. In addition, the height of the peak (absorbance) at 280 millimicrons could be utilized for quantitative information. Figure 4 shows that lignosulfonate concentration and absorbance values have a linear relationship in accord with Beer's law. These tests confirm previous reports that lignosulfonates may be analyzed quantitatively as well as qualitatively by ultraviolet spectrophotometry (9).

Table 6 gives the ultraviolet spectral data for all the lignosulfonate retarders tested. It can be seen from this table that the peaks for each material occurred within a narrow wavelength range.

Results on the Other Chemical Types

None of the other types of retarders studied had a significant ultraviolet spectrum that was characteristic of the active constituent. Retarder No. 1 did have a characteristic spectrum which was produced by a minor constituent, phenol. Generally, however, ultraviolet spectral analysis was not found suitable for identifying organic hydroxy-carboxylic acids or carbohydrates.

INVESTIGATION OF VISIBLE SPECTRA

The double-beam quartz spectrophotometer with a tungsten lamp as a light source was used to investigate the visible spectra of the materials other than lignosulfonates. The spectral patterns obtained are shown in Figure 5. Each spectrum is not sufficiently

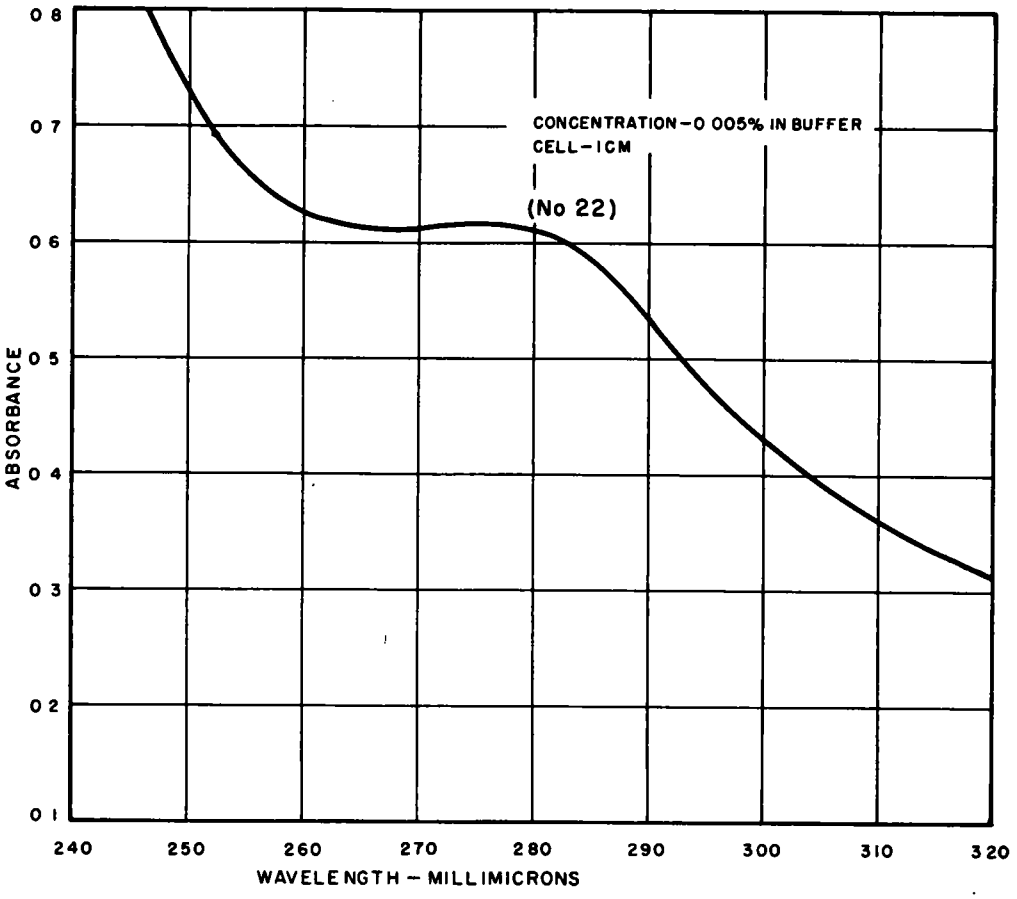


Figure 3. Ultraviolet spectrum of lignosulfonate from Kraft process.

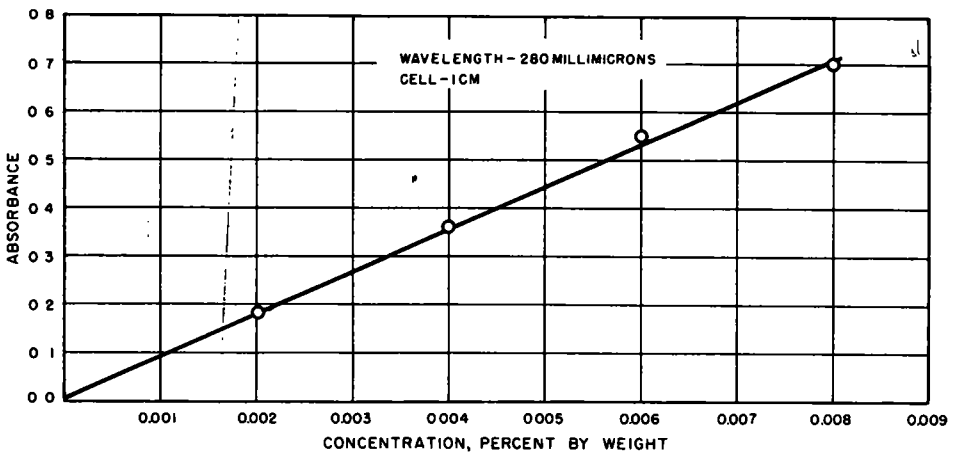


Figure 4. Relation between concentration and absorbance for lignosulfonate retarder.

TABLE 6

ULTRAVIOLET SPECTRAL DATA FOR LIGNOSULFONATE RETARDERS

Retarder No.	Final Concentration[a] (%)	Spectral Peaks[b] Maximum Wavelength (millimicrons)	Maximum Absorbance	Minimum Wavelength (millimicrons)	Minimum Absorbance	Relative Concentration of Lignosulfonate, Percent by Weight[c] Based on Original Material	Based on Dry Solids
2	0 05	281 0	0 151	260 5	0.121	2.0	2 0
3	0.005	278 0	0 457	262.5	0 396	60.9	65 3
7	0 005	280.5	0.589	259.5	0.431	78.5	82.2
10	0.005	280 0	0 582	260 0	0.419	77 6	81 8
11	0.005	283 0	0 362	260.0	0.225	48 3	51 5
12	0.005	280.0	0 474	261.0	0 395	63.2	66 1
13	0.005	279 0	0 328	262.0	0.292	43.7	47.9
14	0.005	282.0	0.438	261 0	0 298	58.4	62.4
15	0.005	278 0	0 442	262.0	0.390	58.9	63.6
16	0 005	281 5	0.408	260.5	0 281	54 4	57 4
17	0 005	280.5	0 502	260 0	0.359	66.9	72 4
18	0 005	281 0	0.393	260 5	0 272	52 4	56.5
19	0 005	280.0	0.400	260.0	0.278	53 3	56 3
20	0 01[d]	279 0	0 333	262 5	0 284	19 1	61.6
21	0.01[d]	280 0	0 290	260 5	0 248	16 8	56.6
22[e]	0.005	276.0[f]	0.618	267.5[f]	0 611	82 4	90 1
23	0.005	280 0	0.460	260 5	0.384	61 3	66.1
24	0 005	284 0	0 381	262.5	0.297	50 8	52 9
25	0.005	281.5	0.441	261 0	0 308	58.8	62 9
Median[g]	-	280 0	-	260.5	-	-	-

[a]In 0 2N KH_2PO_4-0 1N NaOH buffer solution [b]1 cm cell [c]Calculated from absorbance at maximum peak. Relative to retarder No 2 which was assumed to be 2 percent. [d]Percentage by volume (original material was liquid). [e]Derived from Kraft process [f]No sharp maximum and minimum, but rather a shoulder [g]Retarder No. 22 not included.

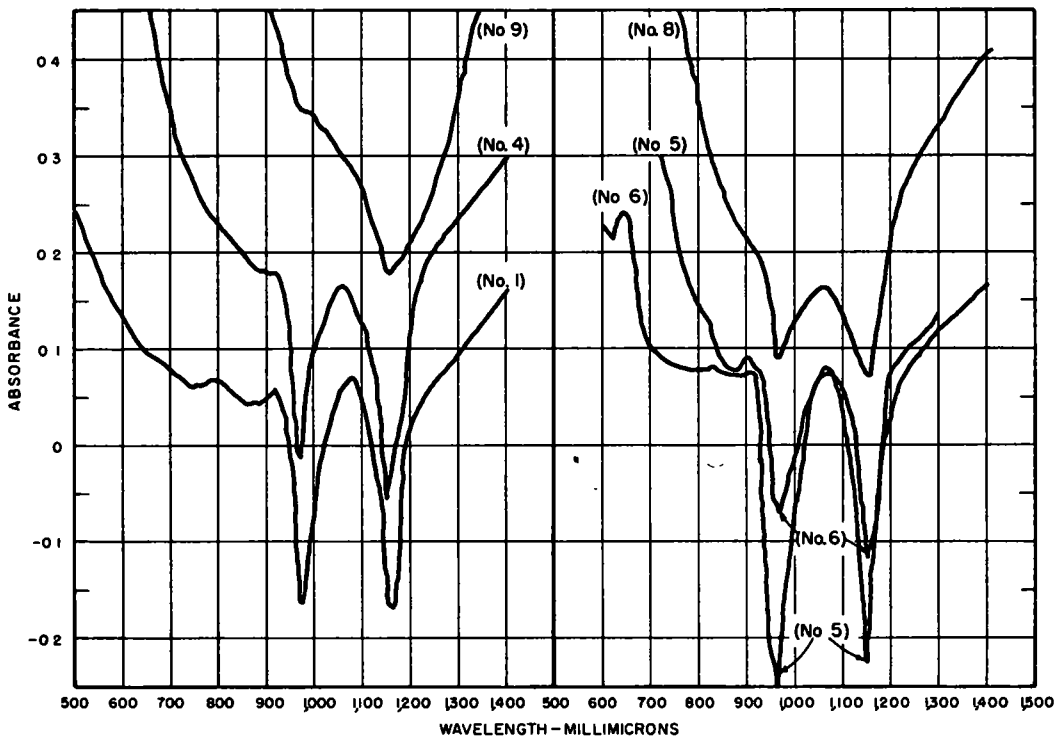


Figure 5. Visible spectra of retarders containing organic acids or carbohydrate.

unique to differentiate between different retarder types or specific retarders. It was found that phenol, sucrose, and even treithanolamine gave spectra similar to those shown in Figure 5 and, consequently, this approach was also not suitable for identifying retarders.

INFRARED SPECTRA

Infrared spectral curves were obtained for each material by means of a double-beam spectrophotometer. The equipment used included a Perkin-Elmer double-beam Infrared Spectrophotometer, Model 137 (Infracord), with automatic recording and a sodium chloride prism for operation between 2.5 and 15 microns. Scanning time was approximately 12 min. An evacuable die was used to prepare samples by the potassium bromide disk technique.

Procedure

The pressed disk technique was considered most suitable for the retarders studied because of the relative insolubility of these materials in appropriate organic solvents used in solution techniques. The mull method was discarded because of the effects of the mulling agent and the limited quantitative application of this method.

In the pressed disk method, solid samples were ground to a fine powder with mortar and pestle and then vacuum dried at 50 C for at least 24 hr. Liquid samples were evaporated to dryness at a low temperature, ground, and dried under the same conditions. Approximately 1 mg of sample and 0.35 g of potassium bromide (anhydrous spectroscopic grade, 200/325 mesh) were weighed into a special stainless steel capsule. Two stainless steel balls were added and the contents mixed for 30 sec by an electric amalgamator.

The powder was transferred to the evacuable die (shown disassembled in Figure 6), and the assembly was evacuated to an absolute pressure of less than 1 cm of mercury. Vacuum was maintained for 5 min prior to pressing as well as during pressing. A 1,000-lb load was applied for 1-2 min followed by a 20,000-lb load for 3-5 min. The potassium bromide disk was then removed and analyzed in the infrared spectrophotometer. The disk measured 13 millimeters in diameter and was approximately one millimeter thick and is shown in Figure 7.

A few of the dried retarder samples were tacky or viscous. These were slurried with alcohol, mixed with potassium bromide, vacuum dried, and then reground and pressed into disks.

Results of Infrared Analyses

Figures 8 through 12 illustrate typical infrared spectra of the different retarders. Each retarder gave a characteristic spectrum which could be used both to identify the

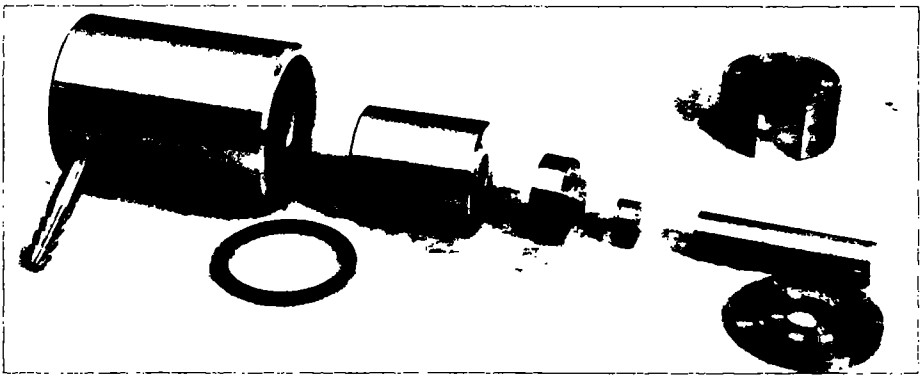


Figure 6. Evacuable die disassembled.

Figure 7. Potassium bromide disk and disk holder.

material and establish the concentration of major active constituents. In general, lignosulfonate retarders had the same characteristic spectra regardless of the type of salt (that is, sodium, calcium, or ammonium). Nevertheless, certain lignosulfonates containing carbonates or other major modifiers, as well as a lignosulfonate derived from the Kraft process, could be easily distinguished by their unique spectra.

Figure 8 shows the type of spectra obtained for the lignosulfonate-type retarders. The top spectrum (A), retarder No. 12, illustrates the typical spectrum of lignosulfonates derived from the sulfite liquor or acid process. The characteristic peaks at different wavelengths in the lignosulfonate spectrum are produced by the following chemical groupings present:

1. Intense peaks at 2.9 and 9.6 microns: hydroxyl (OH) groups.
2. Moderate peak at 3.4 microns: usual carbon-hydrogen stretching bonds.
3. Strong peaks at 6.25 and 6.62 microns: carbon-carbon bonds (phenyl ring).
4. Weak peaks at 6.9 and 7.3 microns: probably sulfur-oxygen bond (sulfone group).
5. Broad band at approximately 8.3 microns: sulfonate group.

Spectrum B (Fig. 8) is the curve for lignosulfonate retarder No. 13. The presence of substantial amounts of sodium carbonate produced strong bands which masked part of the characteristic lignosulfonate spectra. The broad peaks at 7.0 and 11.3 are characteristic of the sodium carbonate present (see Fig. 9A which illustrates the infrared pattern of sodium carbonate). If desired, the sodium carbonate interference may be removed by neutralization with hydrochloric acid, followed by an alcohol extraction of the sodium chloride thus formed. The lignosulfonate is insoluble in alcohol and should then give a good characteristic spectrum.

Curve C in Figure 8 represents a lignosulfonate (No. 22) obtained from the Kraft process for making paper. Although the curve shows the major peaks of a typical lignosulfonate, several additional characteristics help identify this material. For instance, at 8.3 microns (sulfonate group) absorption was at a greater intensity, and at 8.8 and 10.2 microns peaks were produced, probably by inorganic sulfate. Another characterization of this material was the weak absorption peak at 12.7 microns.

The last two spectra, D and E, in Figure 8 are of the same sample (No. 2), which contained a lignosulfonate. Curve D was obtained on the original sample, and it is apparent that it does not clearly show the characteristic lignosulfonate pattern. This was caused by the presence of a large quantity of dolomitic limestone which produced an intense spectrum of its own. When this constituent was removed by centrifuging an aqueous suspension, the characteristic spectrum of lignosulfonate was evident as shown in curve E. Spectrum D is useful in that it supplied ample evidence of the presence of dolomitic limestone in the original material. The peak at 14 microns was unique for calcium carbonate (limestone), while the smaller peak at 13.7 microns was unique for dolomite. From the relative intensities of these two peaks it was estimated that the ratio of dolomite to limestone was approximately 1:4.

Figure 9 shows the spectra obtained on several carbonate materials; namely, sodium carbonate, calcium carbonate, and dolomite. Spectra B and C illustrate the characteristic peaks for limestone and dolomite discussed above.

Figure 10 illustrates the unique infrared patterns which may be used to identify different hydroxy-carboxylic acid salts. It is quite apparent that these curves are distinctly different

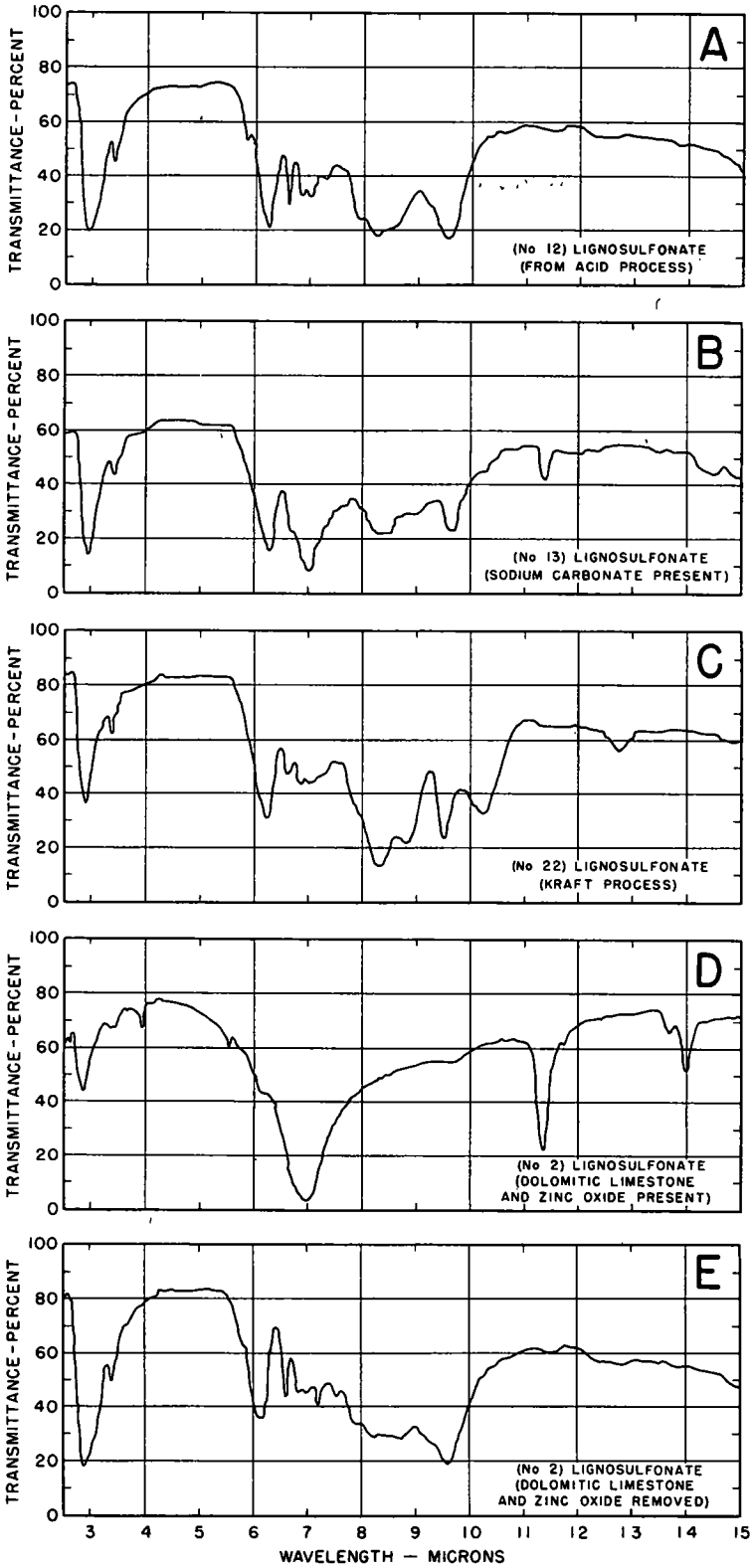


Figure 8. Typical infrared spectra of lignosulfonate retarders.

from the lignosulfonate pattern as well as from each other. Spectrum A (retarder No. 8) shows the masking effect of a large amount of siliceous matter and iron oxide present in the material. To eliminate this interference, an aqueous suspension of the retarder was centrifuged to remove insoluble siliceous material and iron oxide. The remaining material then gave a distinctive infrared pattern of organic material as seen in spectrum B. The following chemical groups accounted for the more significant peaks in spectrum

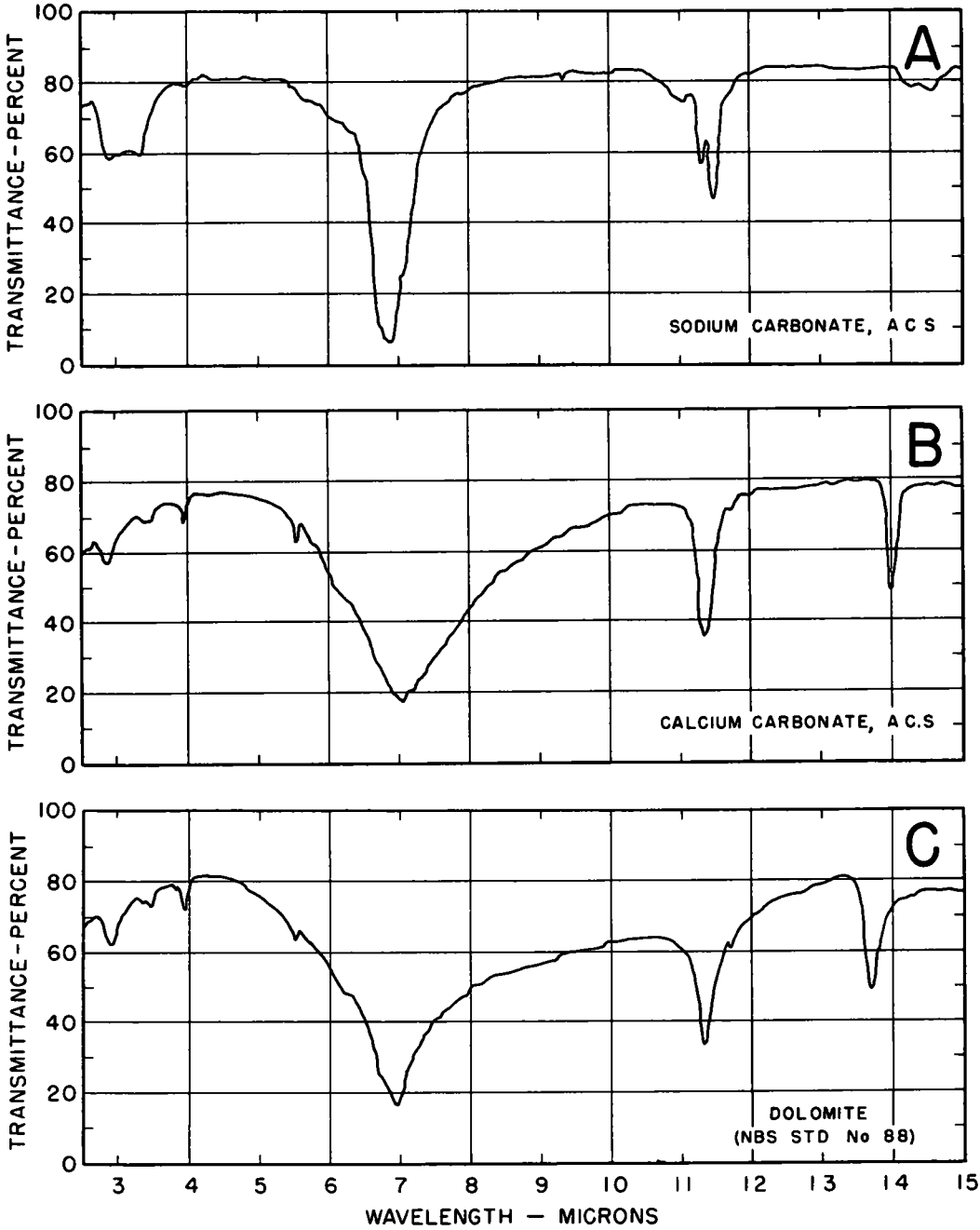


Figure 9. Infrared spectra of related inorganic carbonates.

B: (a) Hydroxyl—intense peak at 3.1 microns; (b) carbon-hydrogen stretching—minor peak at 3.4 microns; (c) carboxyl and carboxyl salt—intense peaks at 6.3, 9.1, and 9.6 microns; and (d) overtones of the carbon-hydrogen linkages accounted for the other peaks from 7.3 to 8.3 microns.

The spectrum of a triethanolamine salt of a hydroxy-carboxylic acid is shown in spectrum C, Figure 10. Although the major peaks of hydroxyl, carbon-hydrogen, and

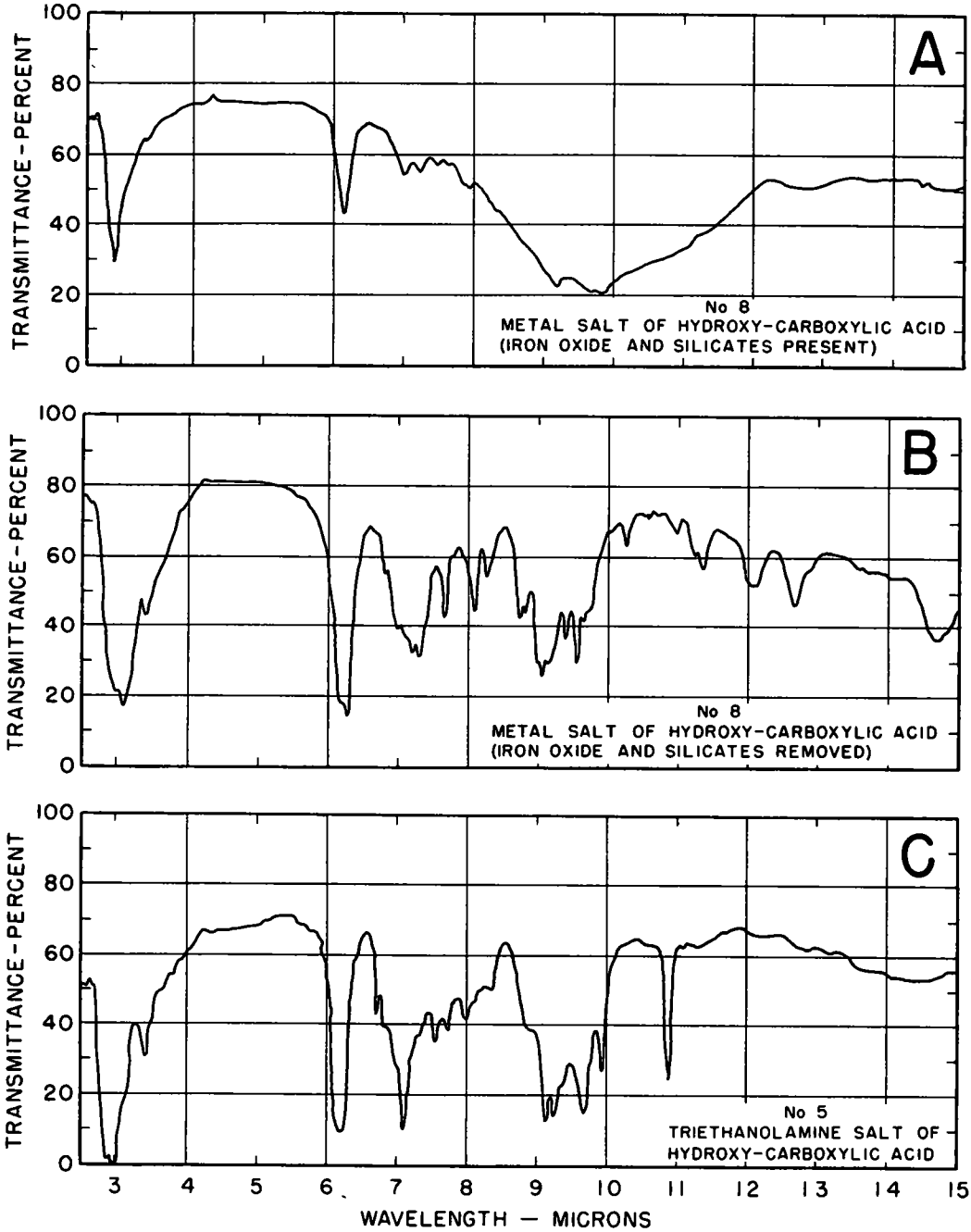


Figure 10. Infrared spectra of organic acid retarders.

carboxylic groups were evident, this spectrum had sufficiently unique features to clearly identify the retarder. For instance, there was a prominent peak at 10.9 microns, probably caused by a carbon-nitrogen bond, and the usual hydroxyl peak at 3.0 microns was accentuated by the presence of nitrogen-hydrogen groups in this material.

Figure 11 shows the spectra of still another organic acid retarder (No. 6). Curve A shows the spectrum of the original material, whereas Curve B was obtained after zinc

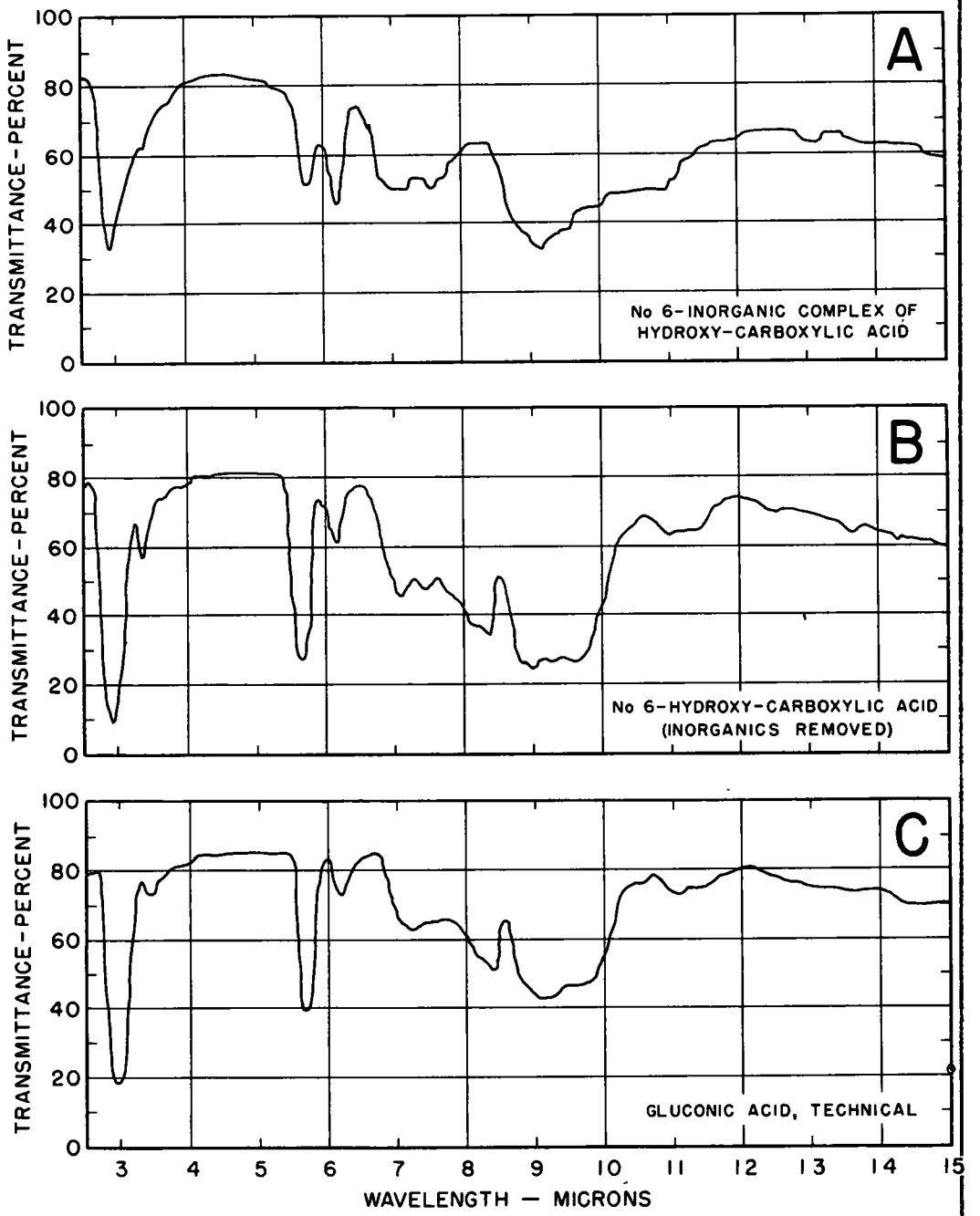


Figure 11. Infrared spectra of complexed organic acid retarder and gluconic acid.

and borates were removed. Zinc was removed by two batchwise treatments with a cation exchange resin, 200-400 mesh hydrogen-form (Amberlite IR-120 or Downex-50) followed by vacuum distillation with methyl alcohol to remove the boron as volatile methyl borate (10). Spectrum B shows many of the usual peaks of a hydroxy-carboxylic acid, and is sufficiently distinctive to be used to identify this material. The prominent peak at 5.6 microns was undoubtedly caused by a lactone formation. Spectrum C in the same figure is that of a technical grade of gluconic acid which showed a striking resemblance to sample No. 6 (spectrum B).

The infrared spectrum of the carbohydrate retarder is illustrated in Figure 12. Spectrum A (retarder No. 1) presents a pattern that was quite unique and therefore useful for identification. A comparison of this spectrum with the spectrum of sucrose or cane sugar (curve B) clearly demonstrates that retarder No. 1 is essentially sucrose.

Although no effort was made in this report to use the infrared spectra for quantitative analysis of the materials, such techniques could be easily applied. For solid samples, such as potassium bromide pellets, the baseline technique is most appropriate and has been well described. Generally, this technique involves the measurement of the depth of a single significant peak, compared to a reference baseline.

Uniformity of Trade Products

The ability of infrared analysis to "fingerprint" or measure the uniformity of different batches of specific proprietory products is illustrated by Figures 13 and 14. Figure 13 shows the spectra of four different lots of a solid lignosulfonate retarder sold under one

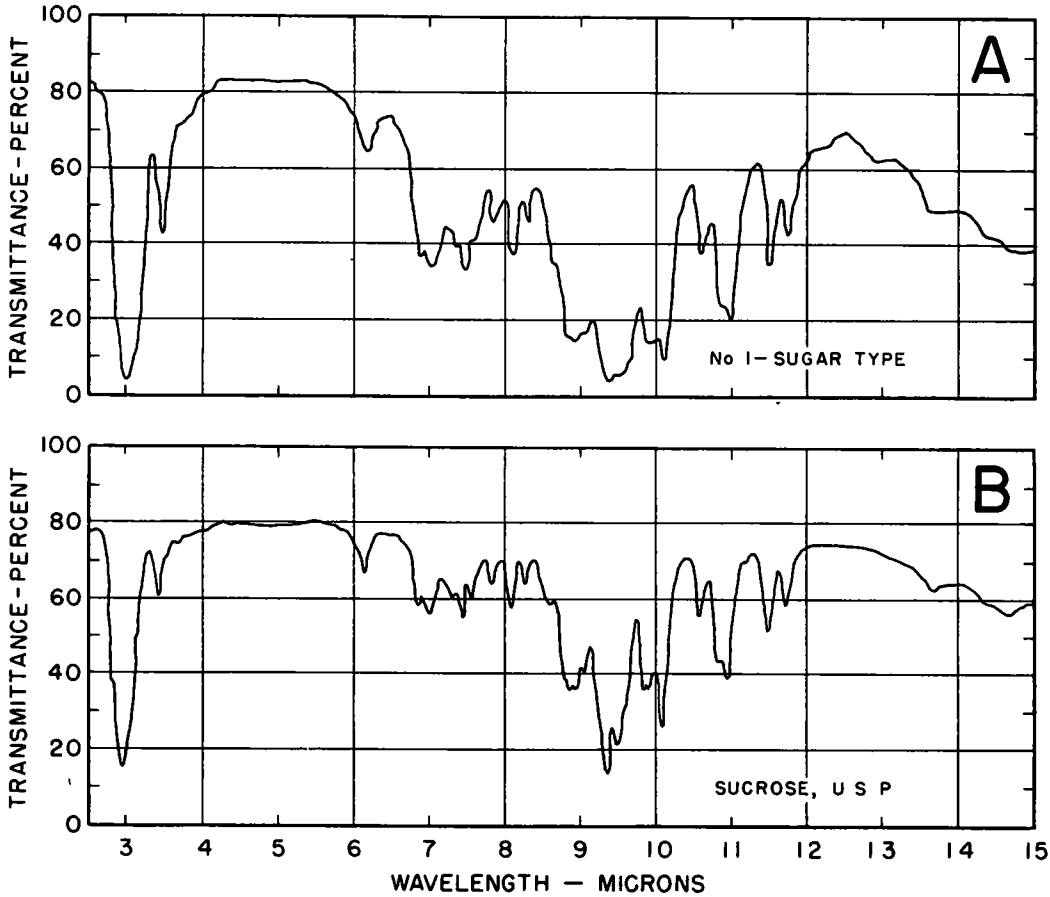


Figure 12. Infrared spectra of carbohydrate retarder and sucrose.

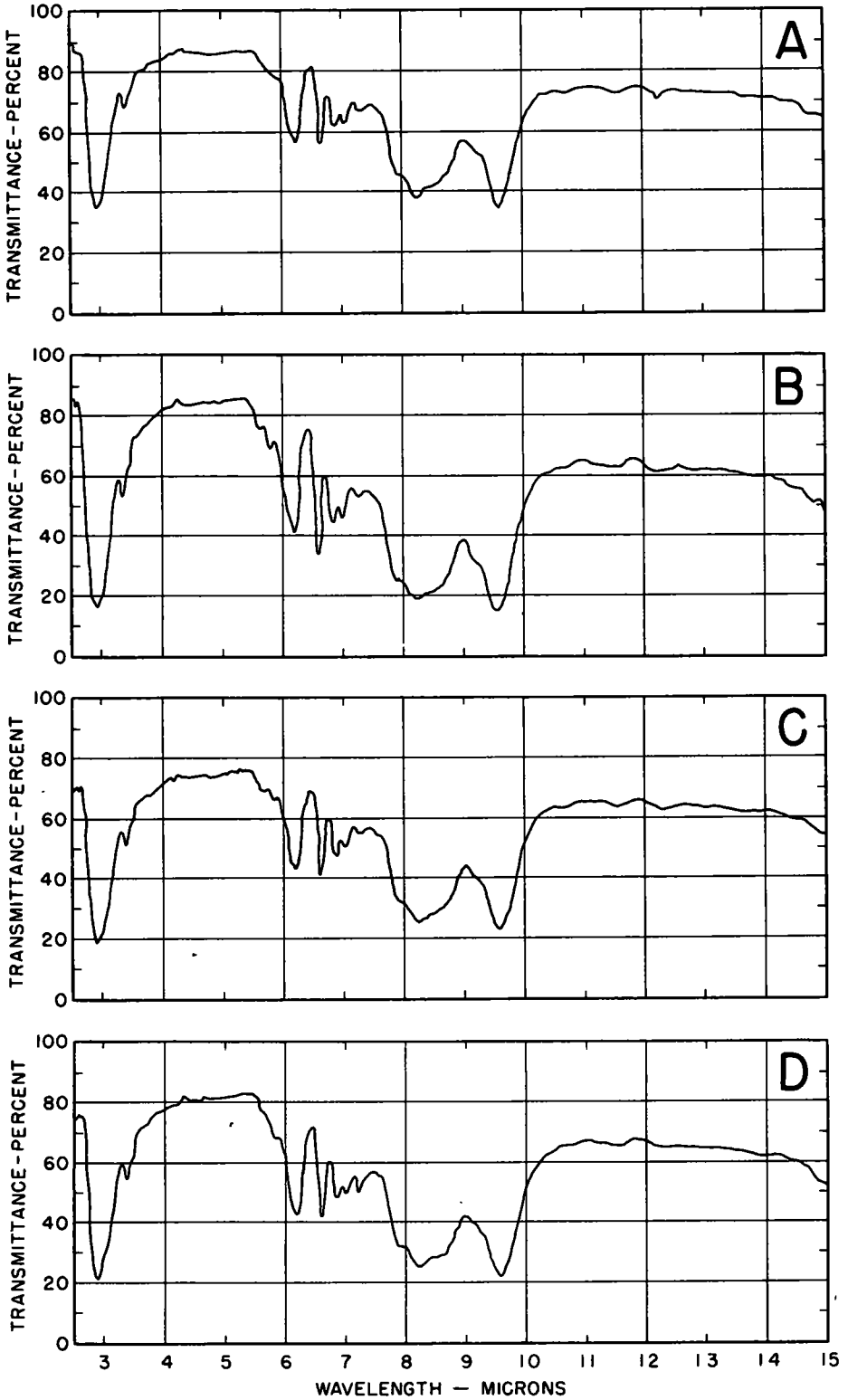


Figure 13. Infrared spectra of four different lots of the same trade name retarder (lignosulfonate type).

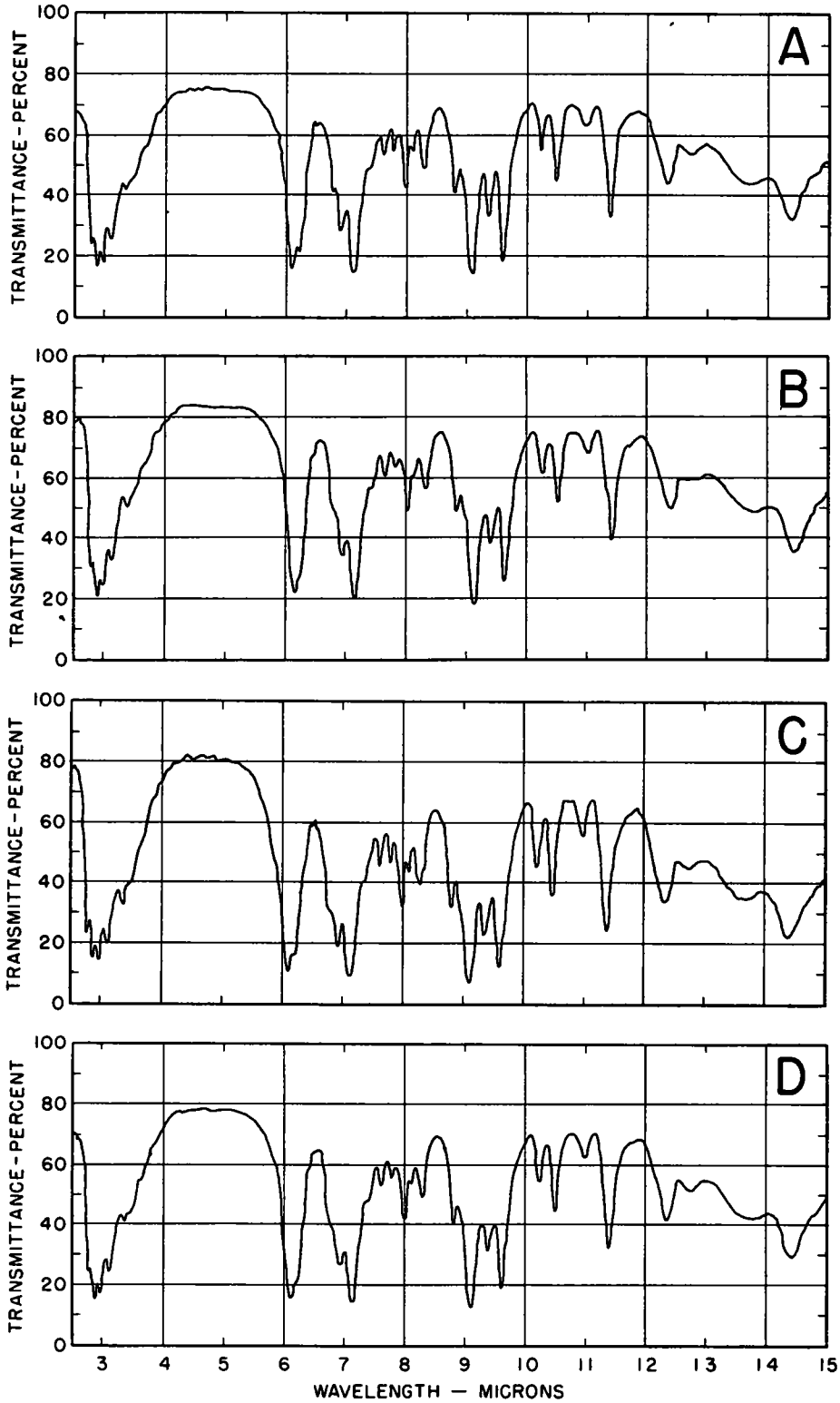


Figure 14. Infrared spectra of four different lots of the same trade name retarder (hydroxy-carboxylic type).

trade name. Each material had been obtained from a supplier by different State highway departments at different times ranging from 1954 (Fig. 13A) to 1958 (Fig. 13D). The general shape of the spectra are the same, with significant peaks occurring at the same wavelengths in each lot. This definitely established that in each case the materials were chemically the same. By analyzing the peak intensities at selected wavelengths and knowing the concentration of sample used in the infrared analysis, any material differences in composition of the retarder from batch-to-batch could be demonstrated. Here, the compositions were shown to be fairly uniform, thus establishing that no material alteration of differences existed between the lots submitted.

Figure 14 shows the spectra for an organic acid retarder, specifically, a hydroxycarboxylic acid salt in liquid form. Here again, each sample was obtained under the same trade name by different State highway departments at different times ranging from 1956 (Fig. 14A) to 1958 (Fig. 14D). The "fingerprinting" ability of infrared analysis once again determined the nature and concentration of the ingredients. The uniformity of the spectra shows that each lot was substantially the same.

COMPARISON OF METHODS OF ANALYSES AND CONCLUSIONS

Inasmuch as the major objective of this study was to develop procedures by which the composition of commercial retarders could be readily identified and determined so as to provide a basis for obtaining the necessary assurance that the composition would be uniform from batch-to-batch, it is noteworthy to compare the various methods of analyses.

Infrared spectral analyses offer the most promising and rapid means of clearly identifying and classifying retarder materials. This technique, by obtaining recorded spectral curves, "fingerprints" the unique and distinctive characteristics for each retarder.

All three types of retarders could be distinguished from each other on the basis of infrared spectra. Although the lignosulfonate retarders had the same general infrared spectrum regardless of the type of salt present or the source of supply, in many instances, specific commercial lignosulfonates could be identified or differentiated by spectral differences caused by the manufacturing process or the presence of other ingredients. As to organic acids and carbohydrates, specific trade products could be distinguished from each other.

Infrared analyses can also be used to assure the purchaser that the nature and concentration of each lot of retarder for specific field projects has not been materially altered from that of the original material. The time required for the analysis is only 20 to 30 min as compared to a week or more by conventional methods of chemical analysis.

Ultraviolet techniques were also found to be of value in identifying lignosulfonates and in establishing the concentration of the major active ingredient. However, specific commercial lignosulfonates were not as easily differentiated by ultraviolet spectra as compared to their infrared spectra. Ultraviolet as well as visible spectral analyses were not found suitable for identifying other types of retarders.

The determination of the quantitative amounts of inorganic constituents can be most conveniently and precisely determined by conventional chemical methods. However, while useful, the conventional procedures were tedious and time-consuming, and often yielded empirical or doubtful results for certain organic constituents. This was found to be particularly true among the lignosulfonate and organic acid retarders.

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A Field Investigation of Water-Reducing, Set-Retarding Admixtures in Concrete Pavement and Bridge Superstructures

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The test sections of reinforced portland cement concrete pavement and decks in this investigation were placed to evaluate and compare the properties of portland air-entraining cement concrete containing water-reducing, set-retarding admixtures with those of regular air-entraining portland cement concrete from the standpoint of their desirability for use on highway projects. The behavior of each admixture was studied with regard to the workability of the mix in placing and finishing including time involved, reduction in water-cement ratio, retardation of setting-time, and the effect of weather conditions on setting-time.

●THE investigation covers the use of the lignosulfonic acid type and the hydroxylated carboxylic acid type of water-reducing, set-retarding admixtures in highway concrete pavement and bridge superstructure wearing courses. The amount of each admixture used per sack of cement remained the same throughout the investigation. Data on actual placement of the pavement and bridge decks under typical Ohio field conditions only are presented.

The test pavement consists of six sections containing the admixtures and three control sections. These sections were placed intermittently throughout the project for a total distance of 1.6 mi of 9-in. reinforced concrete pavement, 24 ft wide.

The two bridge decks were divided into two sections each. A water-reducing, set-retarding admixture was added to the concrete mix of one section of each deck, the other section being designated as the control.

Previous to the placing of the experimental sections in the field, preliminary tests were made in the laboratory using admixtures, cements, and aggregates from sources to be used on the project. Each water-reducing, set-retarding admixture studied performed sufficiently well with respect to retardation of set, reduction in water-cement ratio, and increase in compressive strength to make it desirable to continue the study of the admixtures under actual field conditions.

It was desirable for test purposes to place the control and test sections under similar weather conditions, particularly with respect to ambient temperature. However, it was not always possible to realize this aim.

A progressive record covering each 50 lin ft of test pavement as a unit was maintained. This information included the customary field tests relative to consistency and density plus the elapsed time to various operations from the placing of the concrete on the subgrade to the spraying of the curing membrane on the finished pavement. The temperature of the concrete when spread is also included. The record of daily weather conditions covers air temperature, wind velocity and direction, amount of evaporation of water during the placing of the test sections, and condition of the sky. Similar observations, but in limited number, were recorded while placing the bridge sections.

A set of three 6- by 12-in. cylinders was made from the concrete of determined consistency and density for each 50 lin ft of pavement and tested in compression at 7, 28, and 90 days.

Rate-of-hardening tests were performed in a field laboratory according to the Tentative Method of Test for Rate of Hardening of Mortars Sieved from Concrete Mixtures by Proctor Penetration Resistance Needles (ASTM Designation: C-403-57T). The Proctor penetration resistance apparatus was based on plans furnished by the Bureau of Public Roads, Physical Research Branch, Washington, D.C. Needles with $\frac{1}{10}$- and $\frac{1}{30}$-sq in. bearing areas were used to perform the tests.

The cement factor for the structural concrete mix was 6.5 sacks per cu yd with 38.5 percent natural fine aggregate. The coarse limestone aggregate was used in the proportion of 50 percent No. 4 ($\frac{3}{8}$ - 1 in.) and 50 percent No. 3 ($\frac{3}{4}$ - 2 in.). The cement factors for the pavement sections were 6.5 sacks per cu yd and 5.75 sacks per cu yd with 33 percent natural fine aggregate and gravel coarse aggregate in the proportion of 45 percent No. 4 ($\frac{3}{8}$ - 1 in.) and 55 percent No. 3 ($\frac{3}{4}$ - 2 in.). The 5.75-sack mix was introduced to provide additional compressive strength data. Seventy and five-tenths pounds of No. 4 and No. 3 were added in these proportions to the coarse aggregate in the 5.75-sack mix to compensate for the difference in batch weights. The aggregate gradings remained reasonably constant throughout the project and no proportional change in the amounts of fine and coarse aggregate was necessary.

BRIDGE SUPERSTRUCTURES

Ready-mixed concrete was used for the structures. The air-entraining portland cement conformed to the requirements of ASTM Designation C-175 Type IA.

The ready-mixed concrete was batched from a non-automatic plant and delivered to the job site at an approximate rate of 50 cu yd per hr. Both types of admixtures were accurately measured and dispensed by automatic equipment furnished by the admixture producers. The liquid admixtures were added to the fine aggregate in the batch weigh bin. All coarse aggregate was maintained in the stock piles at a uniform moisture content not less than total absorption. It was occasionally necessary to add water to the batch at the job site to bring the concrete to the desired consistency. Accurate control of the mix is necessary if the desired results are to be obtained. Uniform slump can be difficult to obtain with ready-mixed concrete, but the addition of the admixtures apparently did not magnify this problem. However, it is important that the concrete control inspector realize that the slump or workability of the mix cannot be determined by observation. The admixtures improved the workability of the concrete with reduced water-cement ratios. The bridge decks were machine-finished full width and cured with a double thickness of wet burlap which was continuously water sprayed for 7 days. The plastic concrete containing Admixture "B" "pulled" to some extent under the finishing machine. However, the "pulling" did not present a serious finishing problem. No change was made in the mix design. A similar occurrence was at times noted by the pavement finishers during the straightedging of the pavement. Similar field reaction was encountered when air-entrained concrete was first introduced into Ohio. At times, concrete containing water-reducing admixtures may present a slight surface "pulling" effect or "stickiness" when being finished. This was attributed to the lower water-cement ratio used with these admixtures which gave a richer-appearing mix containing a smaller volume of paste.

After removal of the forms, the underside of the concrete containing the admixture presented a clean, smooth surface in contrast to the control or regular concrete section which was pock-marked with small surface voids caused by air bubbles. This condition is common in superstructures today where there is little clearance ($1\frac{1}{4}$ in.) between the reinforcing and the falsework. The difference in under-surface condition between the two sections of the slab may be attributed to the greater plasticity of the mix containing the admixture.

It may also be assumed that the bond between the concrete and the bottom of the reinforcing bars would be greater, because the greater mobility of the concrete containing the admixture results, under vibration, in easier and more complete envelopment of the reinforcement.

PAVEMENT

Nine pavement test sections were placed between May 9 and June 9, 1960. One each of the two main classes of water-reducing, set-retarding admixtures was used in six of the sections in predetermined quantity as recommended by the manufacturer and as previously used in the laboratory. Three sections were designated as control sections for comparison with the water-reducing, set-retarding sections.

Considerably more use has been made of water-reducing, set-retarding admixtures in the field of structural concrete than in pavement, and consequently there is more familiarity with this aspect of their use. Most of the advantages of the use of admixtures in structures apply equally to pavement concrete. In addition, there are advantages peculiar to paving operations. Efficient operation combined with speed and timing are essential for economical paving operations. Any changes in the mix which upset the timing or delay operations eventually raise the cost of pavement. Of course, there may be times when the value of a modification more than justifies the cost. In this instance there was concern as to whether the addition of the admixtures would delay operating procedure at the batch plant, the paving operations, or the sawing of the transverse and longitudinal joints.

The lignosulfonic acid-type admixture is designated in this report as Admixture A. The hydroxylated carboxylic acid class of admixture is designated as Admixture B.

Another brand of air-entraining portland cement conforming to the requirements of ASTM Designation C-175 Type IA, was used in the pavement mix. The automatic batch plant was timed to weigh an aggregate batch every 7 sec. The accurate measuring and dispensing of the admixtures was accomplished in the allotted time by the automatic dispensing equipment furnished by the admixture manufacturers and installed at the batch plant. The admixtures were automatically added to the fine aggregate in the weigh bin. The fine and coarse aggregates were delivered daily to the batch plant by truck. Stock piles were kept small and an even moisture content was maintained throughout the paving operations.

The concrete was mixed for 1¼ min at the site in three dual-drum 34-E pavers at a speed of 16 rpm. A Heltzel Flex-plane was used in the screeding and finishing operation. Straightedging completed the finishing. After a suitable interval, the surface was burlap dragged, the pavement edged, and the slab sprayed with white waterproof curing membrane. The membrane was applied by means of an automatic mechanical sprayer. The retardation in setting time resulting from the addition of the admixture did not interfere with or delay these operations.

Atmospheric conditions prevailing at the time of the placing of each test section varied. Ambient temperatures ranged from a low of 72 F (Dyer Rd. bridge deck) to a high of 98 F (Big Run bridge deck). Pavement sections were placed with temperatures ranging between 75 and 88 F. Wind velocities ranged from 2 - 15 mph. Amount of evaporation of water during the placing of the test sections ranged from a low of 0.05 in. to a high of 0.14 in. These variations in weather conditions caused slight differences in the rate of hardening of the concrete, but may be considered insignificant insofar as affecting the placing and finishing operations. Change in water-cement ratio, providing other conditions remained constant, was the most dominant factor causing a change in the rate of hardening of the concrete.

On superelevated curves, the cohesiveness of the plastic concrete containing the admixtures was advantageous to finishing operations. There was less slippage of the plastic concrete from the elevated side of the pavement, thus eliminating any extra manipulation of the concrete by the finishers. The sawing of the transverse joints and the longitudinal joint was not delayed by the addition of the admixtures to the concrete. The transverse joints were cut approximately 8 hr after placement of the concrete and the longitudinal joint about 24 hr later. This schedule applied both to test sections and regular pavement.

Most of the test pavement was placed on days when the ambient temperature ranged from the middle seventies to the low eighties with winds of low velocity. Under these conditions, there was no realization of the benefits accruing from the use of these types of admixtures during hot weather concreting. However, when placing the deck on the

Big Run bridge under conditions of high temperatures, low humidity and with a drying breeze, the placing and finishing of the concrete was materially facilitated by the increased workability of the set-retarded, low water-cement ratio concrete.

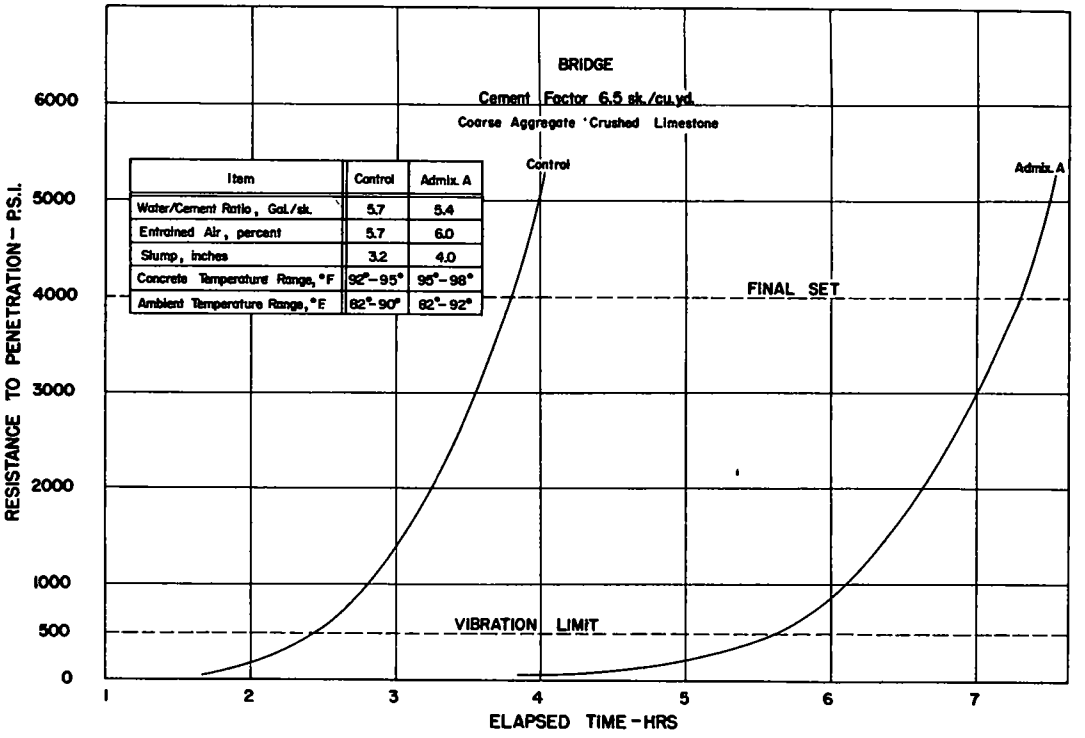
The elapsed time for placing and finishing operations for each 50-lin ft unit of pavement varied, but the differences were not caused by the inclusion of the admixtures in the concrete.

Roadsite operations were timed for one hundred and sixty-nine 50-lin ft units of which 60 were control sections. For the control sections, average elapsed time in minutes from the deposition of the concrete on the subgrade until the completion of the operations designated were: spreading—4, finishing—8, burlap drag—20. For the admixture concrete: spreading—4, finishing—10, burlap drag—24. In comparing these averages, consideration must be given to the fact that the control sections were closer to the batch plant and were placed on days when the weather conditions were what the paving contractors call "perfect finishing weather."

A reduction in water-cement ratio was maintained through the use of the admixtures, while the slump remained approximately the same as that of the regular concrete with a higher water-cement ratio. The average ratio for the control sections was 4.8 gal per sack in comparison with 4.5 gal per sack for the concrete containing the admixtures—a 6.25 percent reduction.

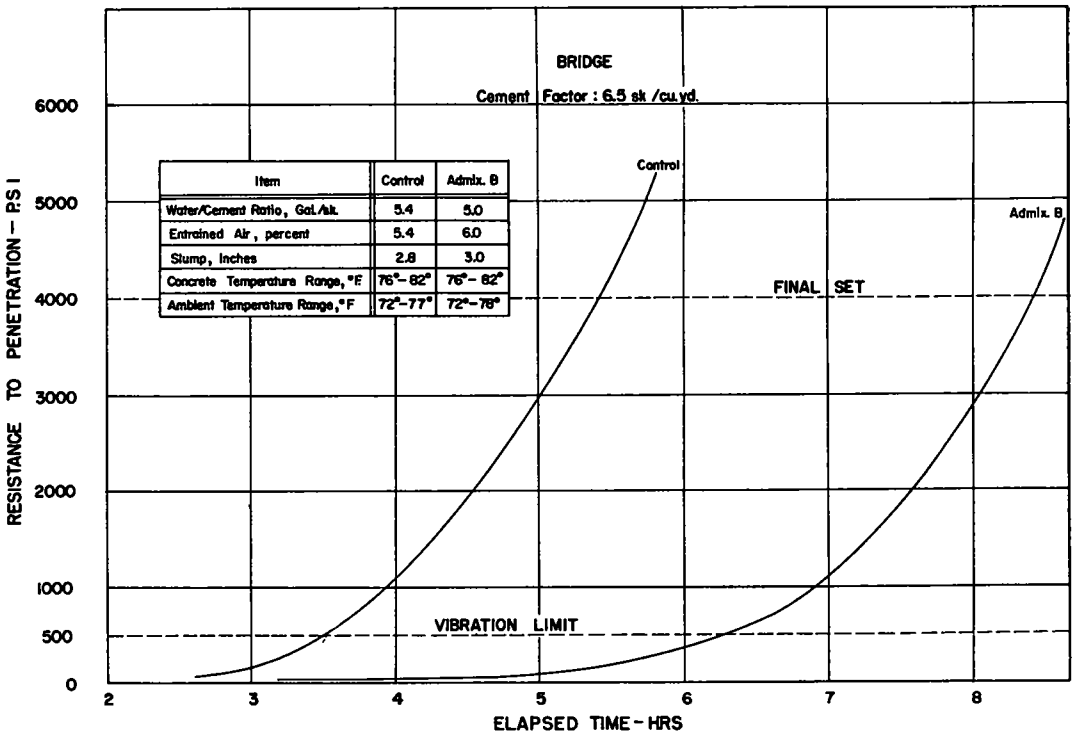
The average rate of hardening of the structural concrete is shown by the curves in Figures 1 and 2 which show similar relationship between the control and the retarded concrete. The approximate difference in time of retardation on the different days may be attributed mainly to the difference in ambient temperature.

The average compressive strength of the structural concrete (6.5 sacks per cu yd) is shown in Figure 3. Admixture A shows an increase in strength of 720 psi over the control concrete. Admixture B shows an increase of 990 psi over its control concrete. The compressive strength of the concrete containing Admixture B was lower than that



Item	Control	Admix. A
Water/Cement Ratio, Gal./sk.	5.7	5.4
Entrained Air, percent	5.7	6.0
Slump, inches	3.2	4.0
Concrete Temperature Range, °F	92°-95°	95°-98°
Ambient Temperature Range, °F	82°-90°	82°-92°

Figure 1. Average rate of hardening of concrete compiled from penetration test data determined in the field.



Item	Control	Admix. B
Water/Cement Ratio, Gal./sk.	5.4	5.0
Entrained Air, percent	5.4	6.0
Slump, Inches	2.8	3.0
Concrete Temperature Range, °F	76°-82°	76°-82°
Ambient Temperature Range, °F	72°-77°	72°-76°

Figure 2. Average rate of hardening of concrete compiled from penetration test data determined in the field.

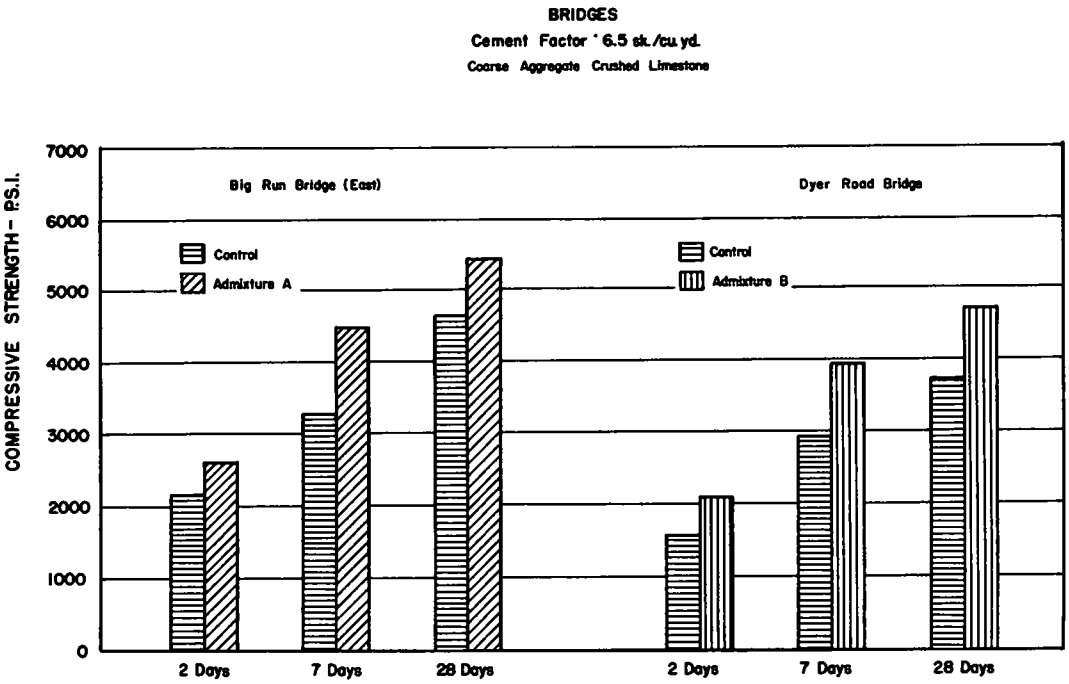


Figure 3. Average compressive strength—PSI.

of the concrete containing Admixture A, and a similar situation existed with the control concretes.

Pavement concrete placed on the same day as the Admixture B concrete and its control also developed lower-than-average strength.

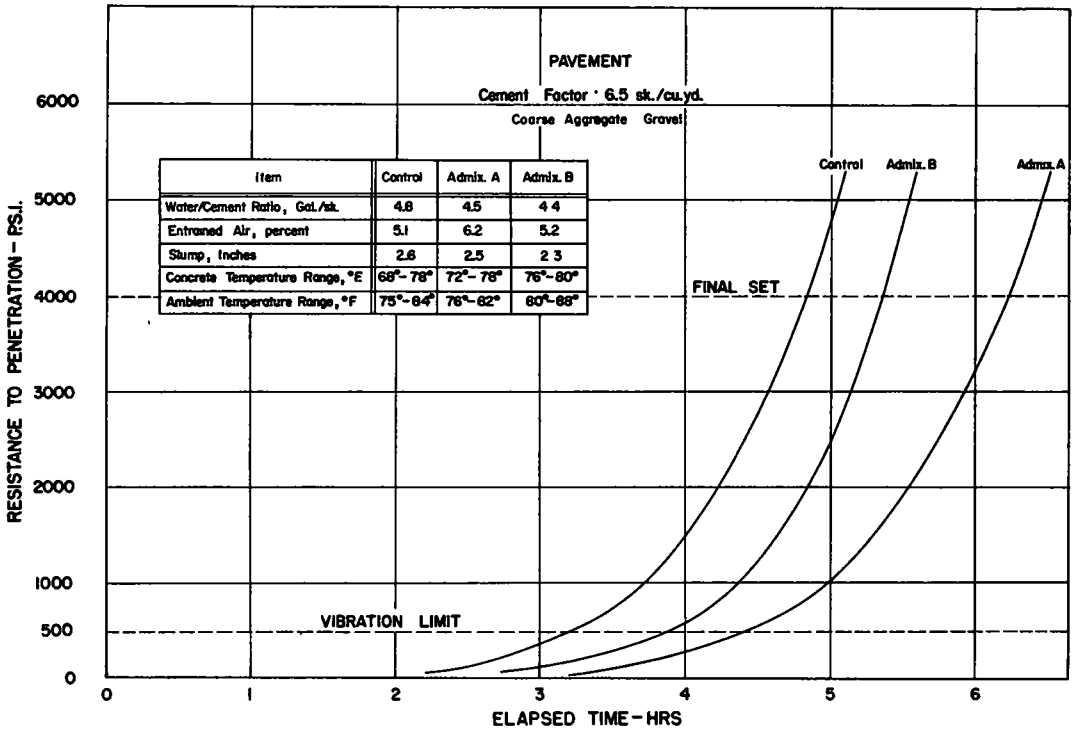
Figures 4 and 5 show average rate-of-hardening curves for the 6.5 sacks per cu yd and 5.75 sacks per cu yd pavement mix, respectively. In Figure 4 the average retardation is less for Admixture B than for Admixture A. No explanation is offered.

Pavement compressive strength averages by cement factor and admixtures are shown in Figures 6 and 7. Tests at 90 days show an average increase in compressive strength of 22 and 26 percent, respectively, for Admixtures A and B concretes over the 6.5 sacks per cu yd pavement mix without admixture. The admixture concrete with 5.75 sacks per cu yd shows an increase of 16 and 18 percent, respectively, at 90 days over the control for concretes containing Admixtures A and B.

OBSERVATIONS

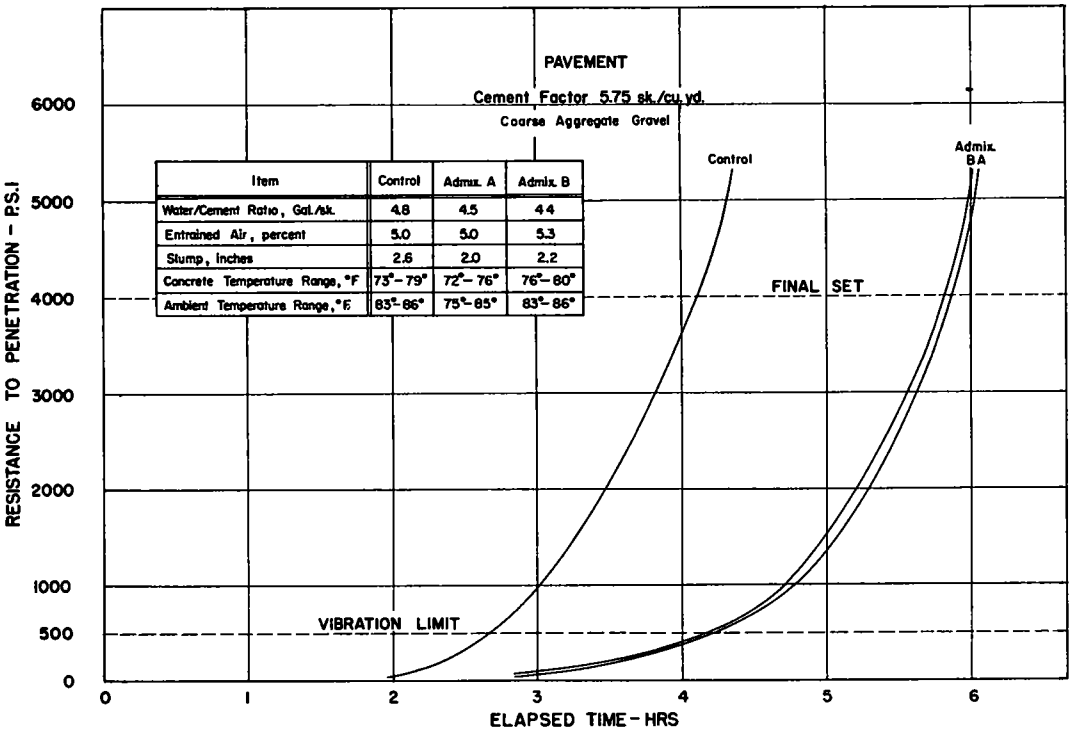
In conclusion, the following observations were made:

1. Both admixtures were apparently compatible with the cements, fine aggregates, and both the gravel and limestone coarse aggregates used on the project.
2. Many factors may influence the setting time of retarded concrete in the field, the most important of which is the amount of mixing water. In a lesser degree, the ambient temperature, wind velocity, humidity, intensity of the sunshine, and the temperature of the mix were observed to be determinants. Control by experienced inspectors is necessary to obtain desired results.
3. Admixture B apparently did not entrain air; that Admixture A entrained a slight amount is inferred from the fact that slightly less air-entraining agent was added to the mix in conjunction with Admixture A to obtain the same air content. It was not practical



Item	Control	Admix. A	Admix. B
Water/Cement Ratio, Gal./sk.	4.8	4.5	4.4
Entrained Air, percent	5.1	6.2	5.2
Slump, Inches	2.6	2.5	2.3
Concrete Temperature Range, °F	68°–78°	72°–78°	76°–80°
Ambient Temperature Range, °F	75°–84°	76°–82°	80°–88°

Figure 4. Average rate of hardening of concrete compiled from penetration test data determined in the field.



Item	Control	Admix. A	Admix. B
Water/Cement Ratio, Gal./sk.	4.8	4.5	4.4
Entrained Air, percent	5.0	5.0	5.3
Slump, Inches	2.6	2.0	2.2
Concrete Temperature Range, °F	73°-79°	72°-76°	76°-80°
Ambient Temperature Range, °F	83°-86°	75°-85°	83°-86°

Figure 5. Average rate of hardening of concrete compiled from penetration test data determined in the field.

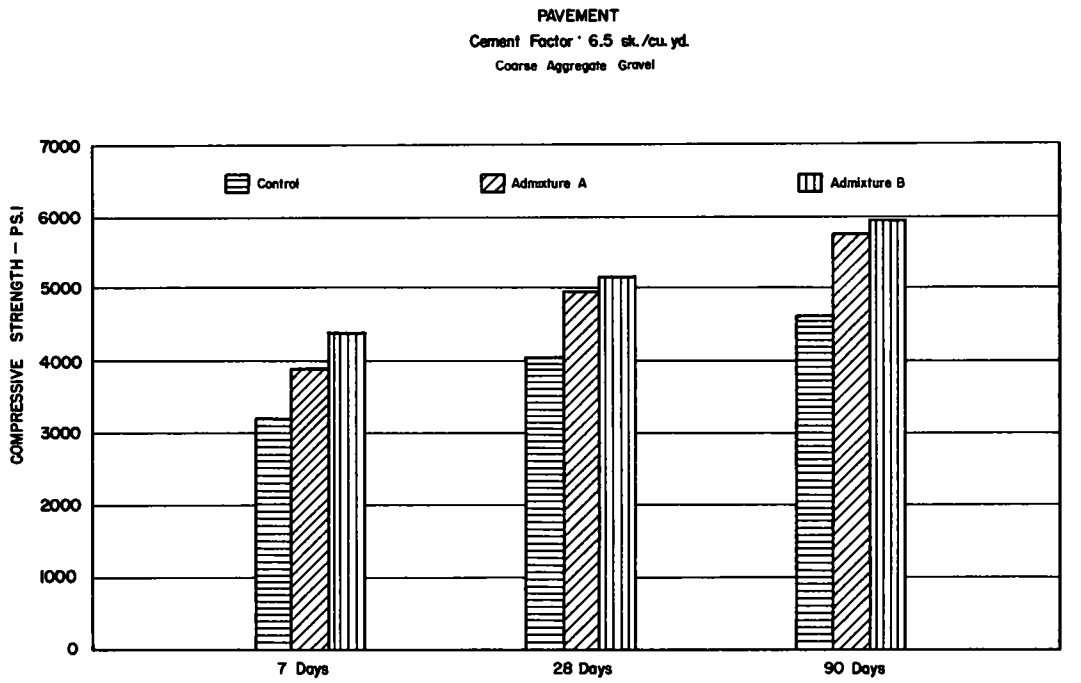


Figure 6. Average compressive strength—PSI.

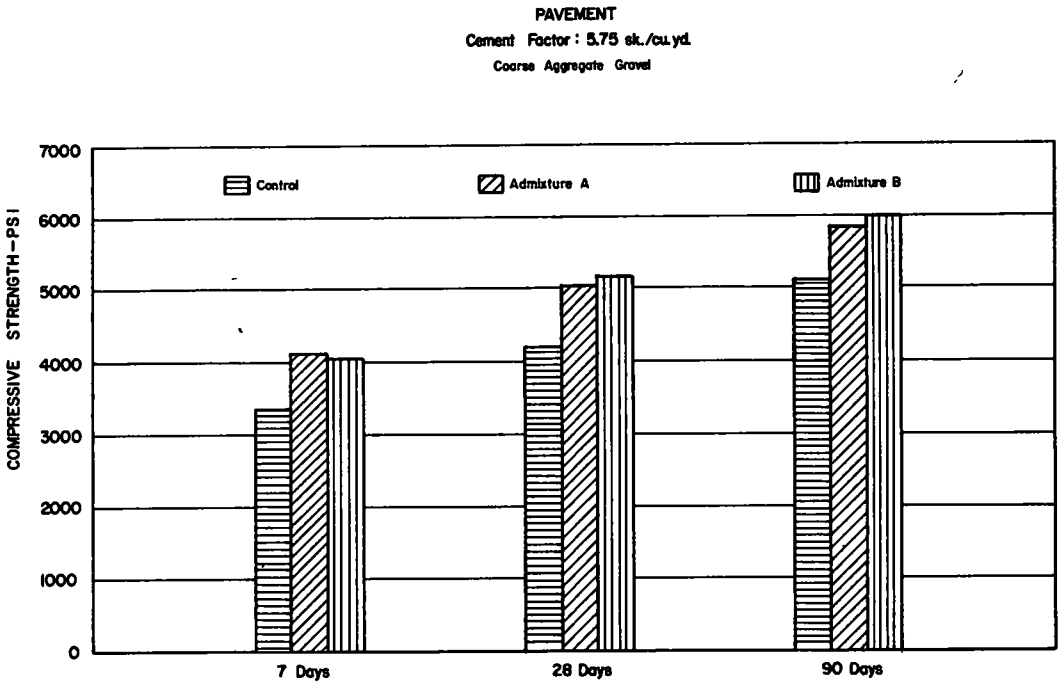


Figure 7. Average compressive strength—PSI.

to determine with precision the amount of air entrained by Admixture A, although it is estimated to be less than 1 percent.

4. An increase in compressive strength over the control mixes was obtained through the use of both admixtures with both cement factors at all ages. Tests were made at 2, 7 and 28 days on the structural concrete and at 7, 28 and 90 days for the pavement concrete.

5. Through controlled retardation of setting time, a bridge deck may be placed and finished in a continuous pour while the entire mass of concrete is still plastic. Cracks caused by the continually increasing deflection of the forms or girders due to the changing dead weight as the placing of the concrete progresses may thus be eliminated.

6. The paving concrete mixed at the roadsite was more easily controlled than the ready-mixed concrete.

7. After retardation has reached the "vibration limit," normal setting of the concrete may be expected.

8. The use of water-reducing, set-retarding admixtures did not delay, nor did it necessitate any change in normal paving operations.

9. This study indicates that economies may result from the use of water-reducing, set-retarding admixtures for one or more of the following reasons:

(a) Because with concrete containing these admixtures, bridge deck placing and finishing operations may be delayed beyond the time required to complete the same operations with ordinary concrete, fewer workmen may be required, and due to regulations governing labor compensation, a saving in wages may be effected.

(b) Not infrequently, ordinary concrete with low water-cement ratios "hangs up" in the concrete bucket on structural pours, with consequent loss of time in the placing of the concrete. No such difficulty was encountered with the admixture concretes.

(c) Because the concrete containing the admixtures gave greater strength than the ordinary concrete, it may be possible to obtain a specified strength with less cement where a minimum cement factor is not required.

10. Exactness in the dispensing of the admixture at the batch plant is vital to obtaining the benefits to be derived from their use. An increase may cause a "wet" batch and may excessively retard the set, whereas a decrease may lower the slump and require the addition of water to the mix, with resultant loss of strength through increase in water-cement ratio.

11. Until more data are accumulated as to what can be expected from the use of water-reducing, set-retarding admixtures, it is advisable to conduct a laboratory study prior to field use, employing the same aggregates and cement to be used in the field. Where such data already exist, the laboratory study can of course be omitted.

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THE NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL is a private, nonprofit organization of scientists, dedicated to the furtherance of science and to its use for the general welfare. The ACADEMY itself was established in 1863 under a congressional charter signed by President Lincoln. Empowered to provide for all activities appropriate to academies of science, it was also required by its charter to act as an adviser to the federal government in scientific matters. This provision accounts for the close ties that have always existed between the ACADEMY and the government, although the ACADEMY is not a governmental agency.

The NATIONAL RESEARCH COUNCIL was established by the ACADEMY in 1916, at the request of President Wilson, to enable scientists generally to associate their efforts with those of the limited membership of the ACADEMY in service to the nation, to society, and to science at home and abroad. Members of the NATIONAL RESEARCH COUNCIL receive their appointments from the president of the ACADEMY. They include representatives nominated by the major scientific and technical societies, representatives of the federal government, and a number of members at large. In addition, several thousand scientists and engineers take part in the activities of the research council through membership on its various boards and committees.

Receiving funds from both public and private sources, by contribution, grant, or contract, the ACADEMY and its RESEARCH COUNCIL thus work to stimulate research and its applications, to survey the broad possibilities of science, to promote effective utilization of the scientific and technical resources of the country, to serve the government, and to further the general interests of science.

The HIGHWAY RESEARCH BOARD was organized November 11, 1920, as an agency of the Division of Engineering and Industrial Research, one of the eight functional divisions of the NATIONAL RESEARCH COUNCIL. The BOARD is a cooperative organization of the highway technologists of America operating under the auspices of the ACADEMY–COUNCIL and with the support of the several highway departments, the Bureau of Public Roads, and many other organizations interested in the development of highway transportation. The purposes of the BOARD are to encourage research and to provide a national clearinghouse and correlation service for research activities and information on highway administration and technology.