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

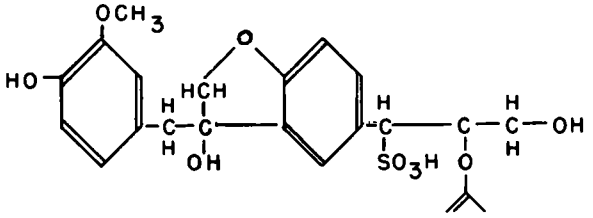
The retarders investigated were found to be of three general chemical types: lignosulfonates, salts of organic hydroxy-carboxylic acids, and carbohydrates. A general discussion of the origin and characteristics of these major types of retarders studied is given in the following paragraphs.

Lignosulfonates

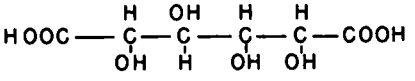
With one exception, the lignosulfonate materials studied were derived from spent sulfite liquor obtained in the acid process of wood pulping. The single exception was derived from the Kraft (alkaline) process. Materials were supplied as the calcium, sodium, or ammonium salts, and either as a powder or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

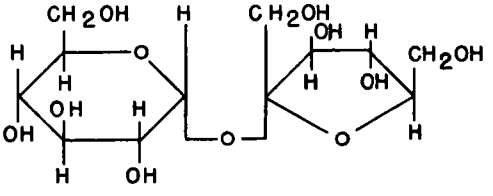
Many commercial lignosulfonates also contain varying amounts of reducing sugars. A typical analysis showed the following percentages of wood sugars based on total



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	Solubility in[d]: 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	I	0	0	0	0	-
3	Solid	Olive	30118	Woody	-	7 2	S	I	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	I	10	7	4	1 5	Mold growth
8	Solid	Pink	30313	None	-	7 6	I	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	I	2	2	1 5	1	Mold growth
11	Solid	Light brown	20400	Woody	-	6 8	S	I	I	I	4	2	0	0	Mold growth
12	Solid	Mustard	30266	Woody	-	6 7	S	I	PS	I	0	0	0	0	-
13	Solid	Medium brown	30117	Woody	-	9 4	PS	I	I	I	1	0 5	0	0	-
14	Solid	Tan	31643	Woody	-	4 6	S	I	I	I	5	4	3	1 5	-
15	Solid	Olive	30009	Woody	-	7 4	S	I	I	I	11	8	4 5	2	-
16	Solid	Tan	31643	Woody	-	7 3	PS	I	PS	I	9	6	2 5	1	-
17	Solid	Light brown	20400	Woody	-	3 8	S	I	S	I	1 5	1	0 5	0	Mold growth
18	Solid	Tan	31643	Woody	-	7 4	S	I	I	I	3 5	2	1	0 5	-
19	Solid	Light brown	20400	Woody	-	6 6	S	I	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	I	5	2 5	1	0 5	-
23	Solid	Medium brown	10091	Woody	-	9 5	S	I	I	I	0	0	0	0	-
24	Solid	Tan	31643	Woody	-	7 8	PS	I	I	I	1	1	0 5	0	-
25	Solid	Tan	31643	Woody	-	4 6	PS	I	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]			Lignosulfonate (Proctor-Hirst test)[c] (5)	Chloride ($AgNO_3$ test) (6)	Sulfate ($BaCl_2$ test) (7)	Carbonate (acid effervescence) (8)	Calcium (oxalate test) (9)
	Original Material (2)	Alcohol-insoluble Fraction (3)	Alcohol-soluble Fraction (4)					
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		Hydroxy Acids (di-naphthol test) (14)	Complexing Agents ($CuSO_4$+NaOH test)[f] (15)	Melting Point of Phenylhydrazine Derivative, °C[f] (16)
		Ammoniacal[d] (12)	Albuminoid[d] (13)			
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. [f]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 $CaCl_2$		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]			B_2O_3[e]	
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]	Lignosulfonate (cinchonine method)[b]	Lignin, Calculated from Methoxyl[c]	Total Carbohydrates, as Glucose[d]	Reducing Sugars, as Glucose[e]	Sucrose (AOAC method)[f]	Anionic Sulfonated Synthetic Detergent[g]	Phenol[h]	Nitrogen			
										Total (as N)[a]	Ammoniacal (as NH_3)[a]	Albuminoid (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	78 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	6 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

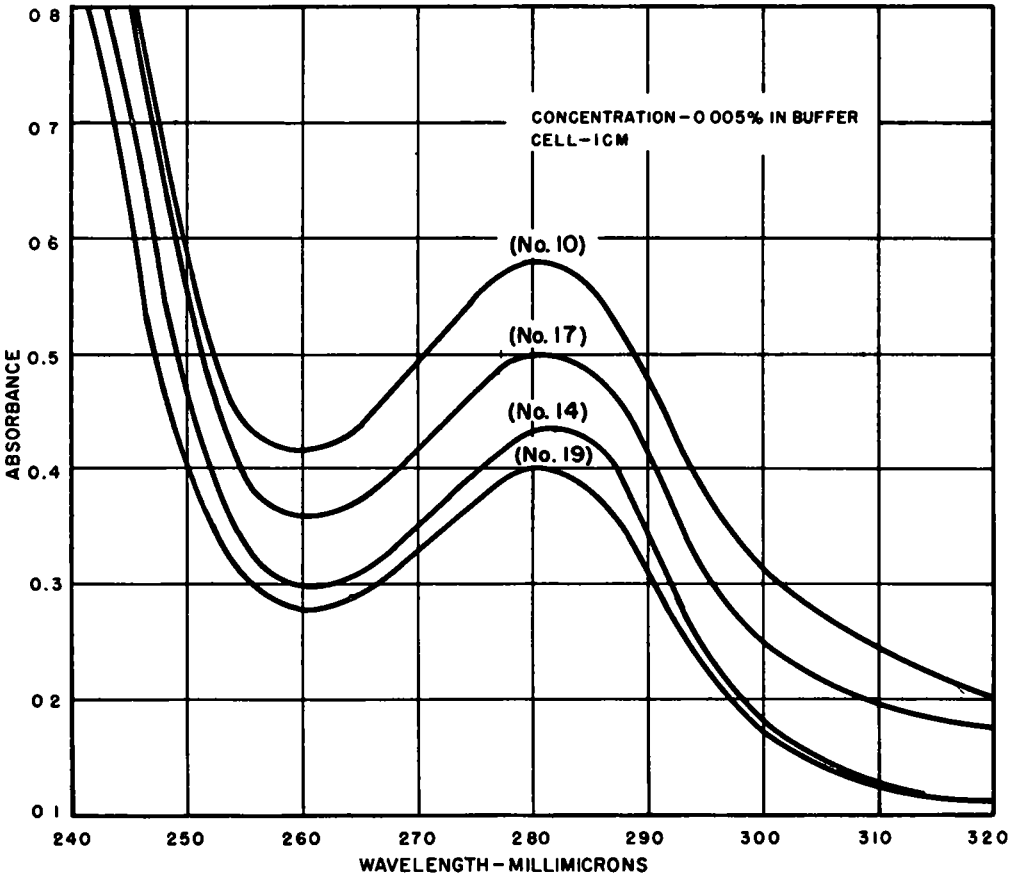


Figure 2. Typical ultraviolet spectra of lignosulfonates.

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 $\log_{10} I_O/I$, where I_O 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

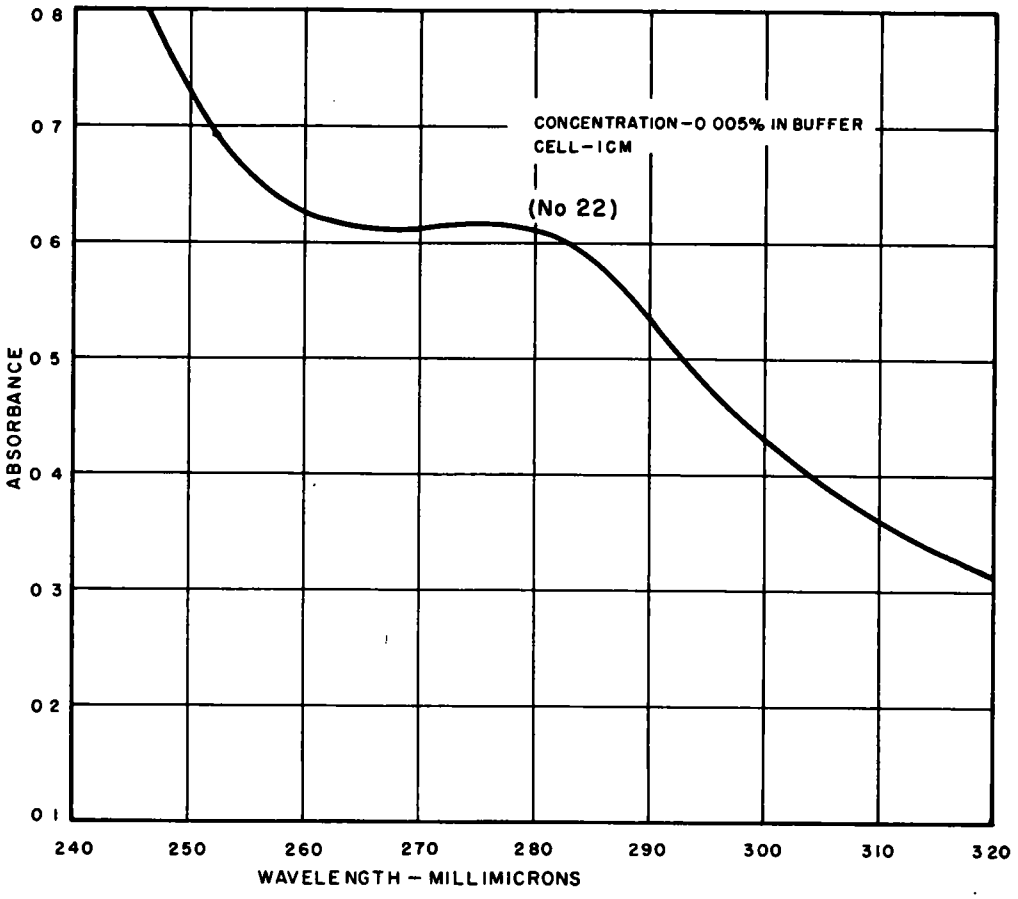


Figure 3. Ultraviolet spectrum of lignosulfonate from Kraft process.

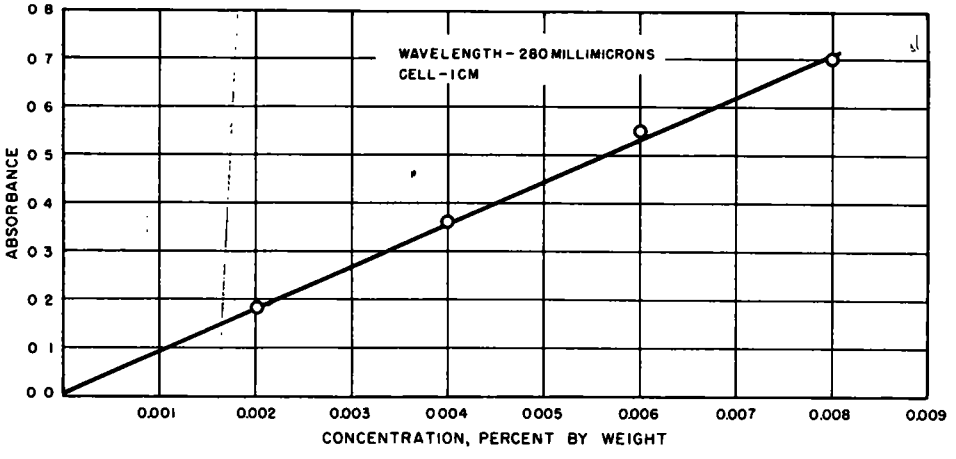


Figure 4. Relation between concentration and absorbance for lignosulfonate retarder.

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.

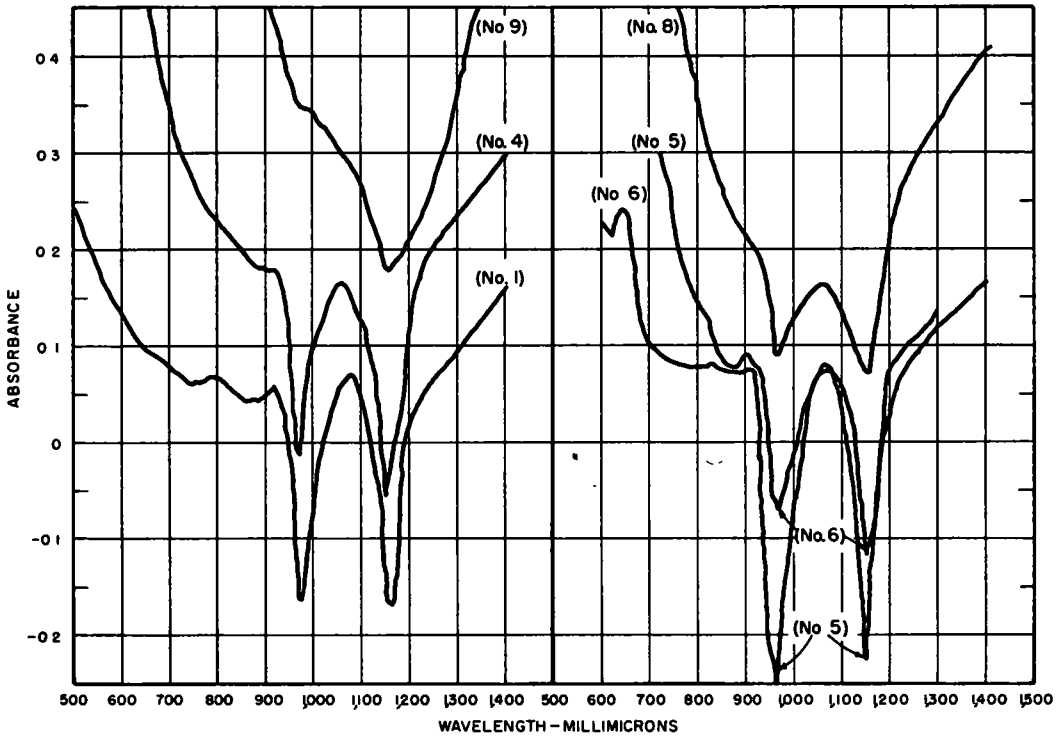


Figure 5. Visible spectra of retarders containing organic acids or carbohydrate.

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

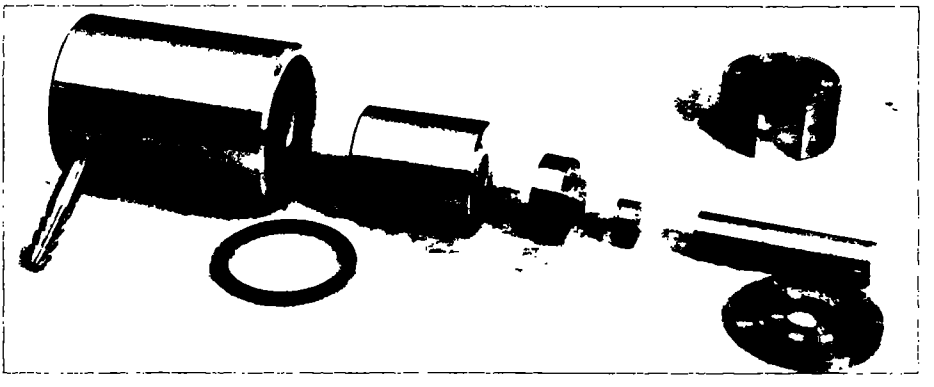


Figure 6. Evacuable die disassembled.

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

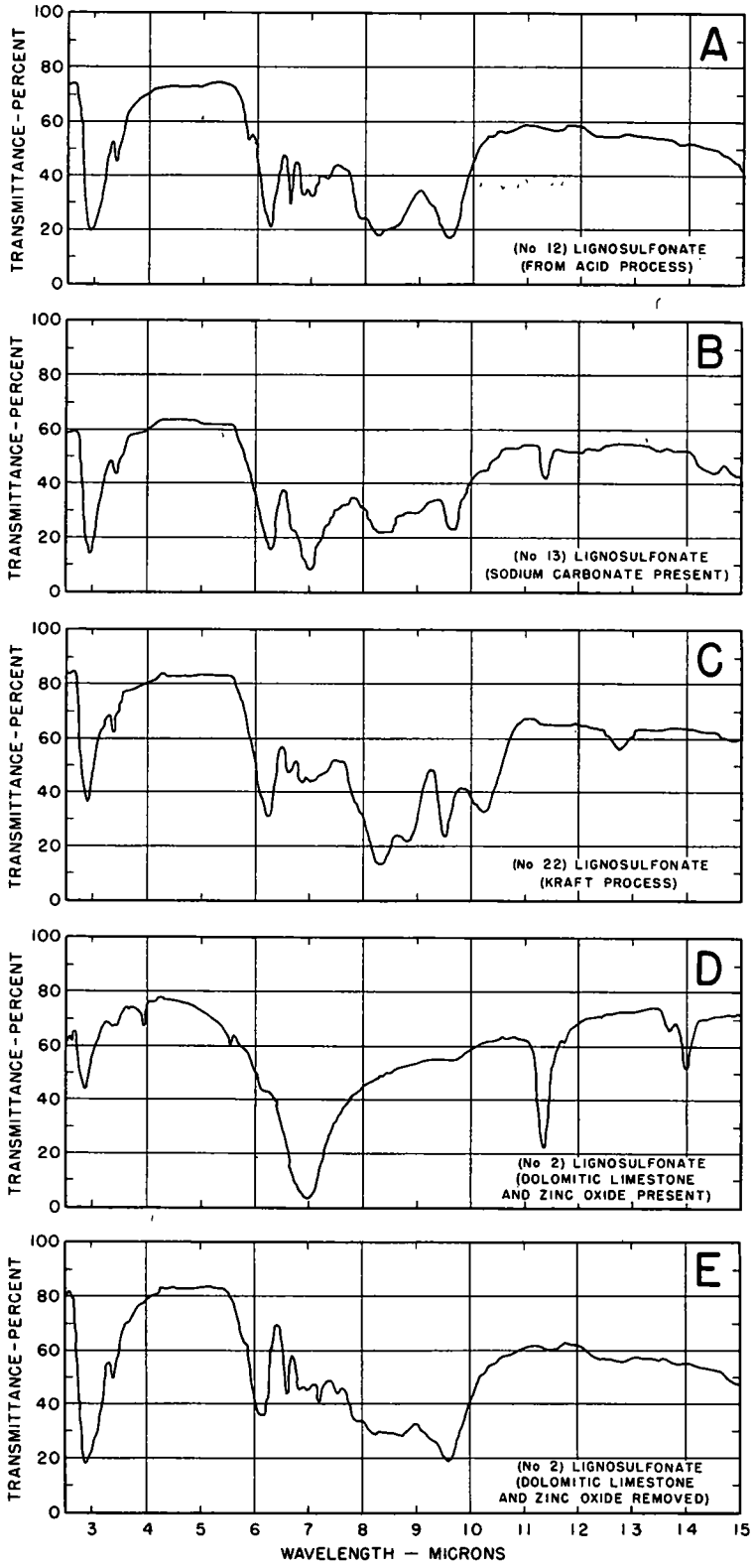


Figure 8. Typical infrared spectra of lignosulfonate retarders.

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

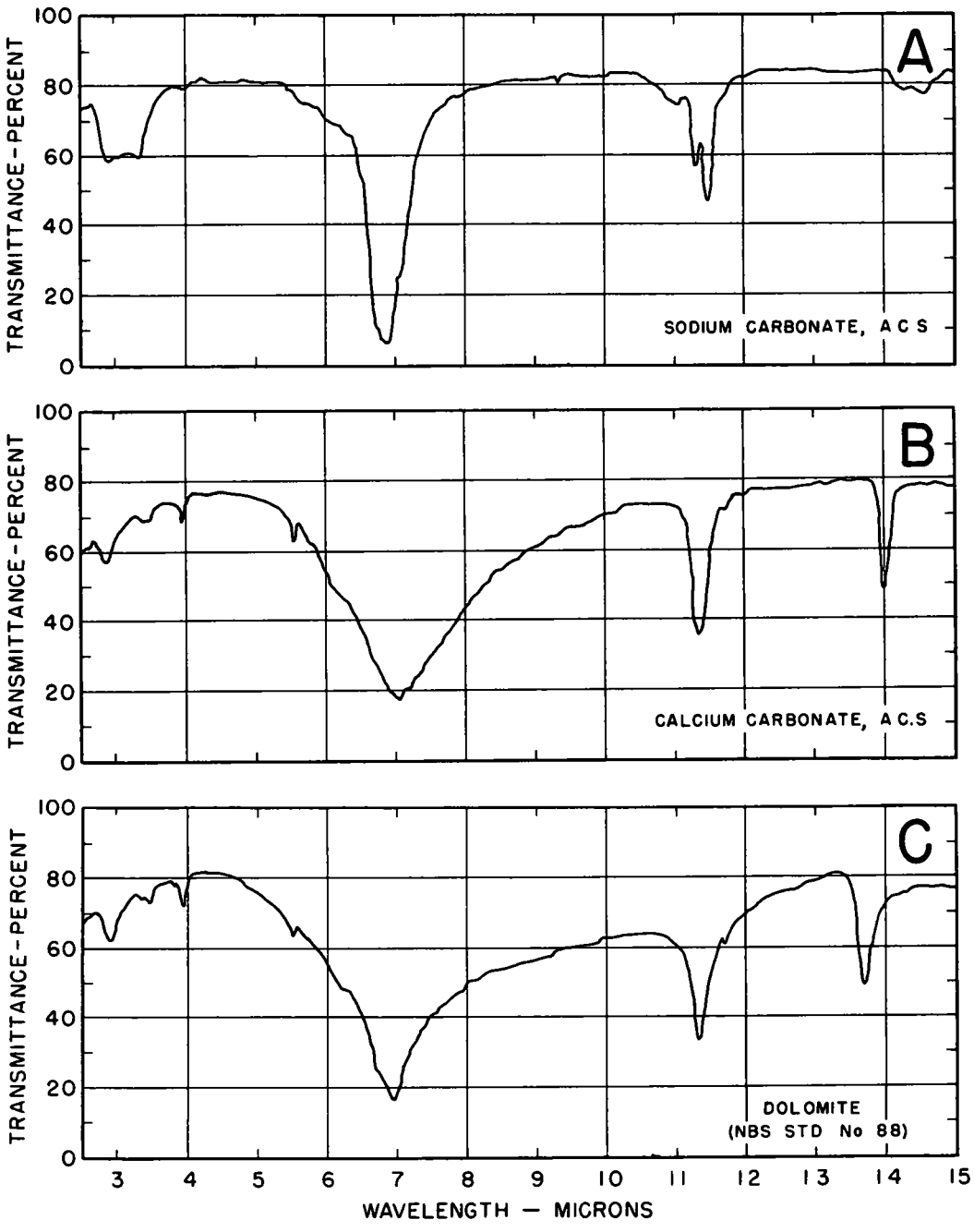


Figure 9. Infrared spectra of related inorganic carbonates.

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

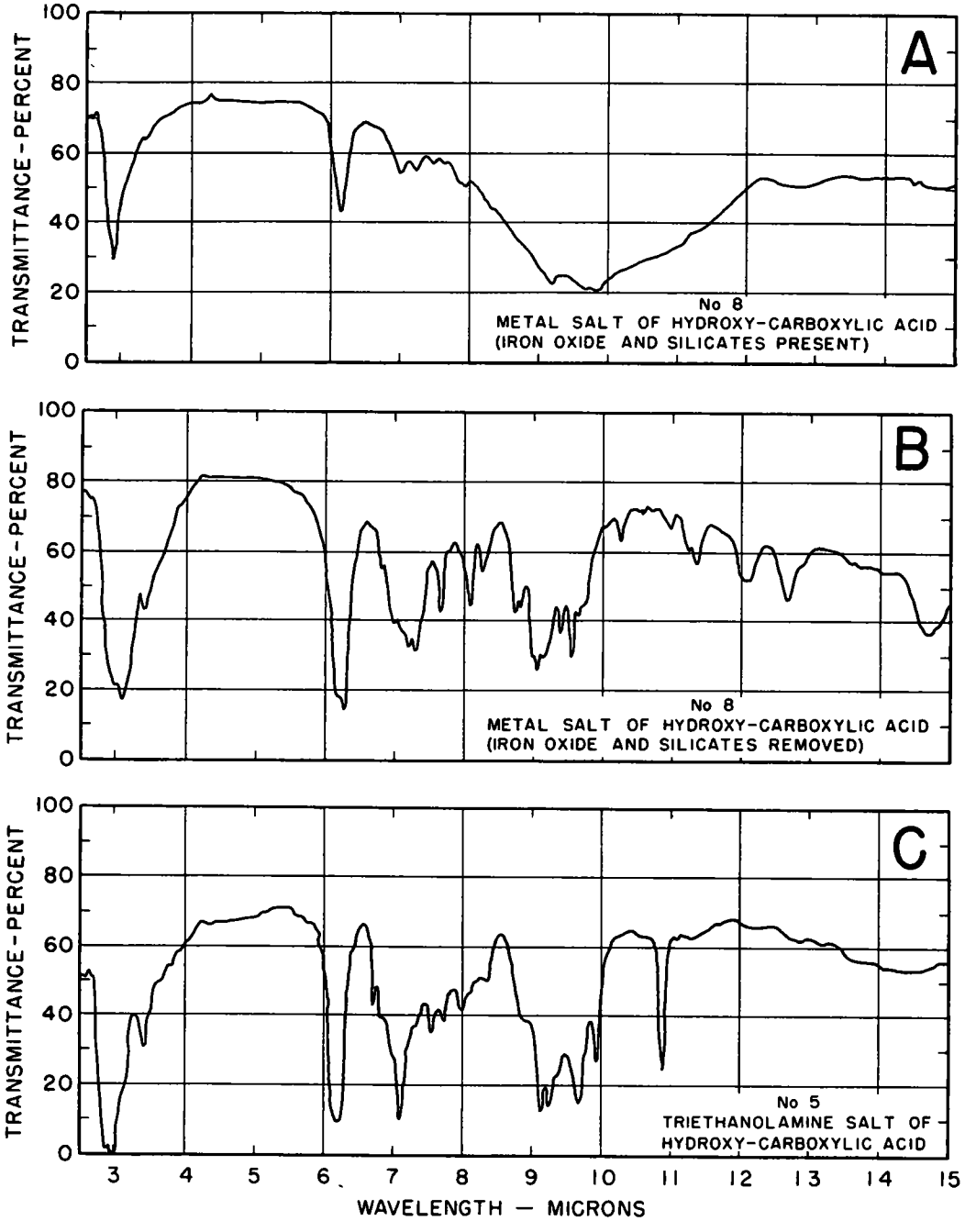


Figure 10. Infrared spectra of organic acid retarders.

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

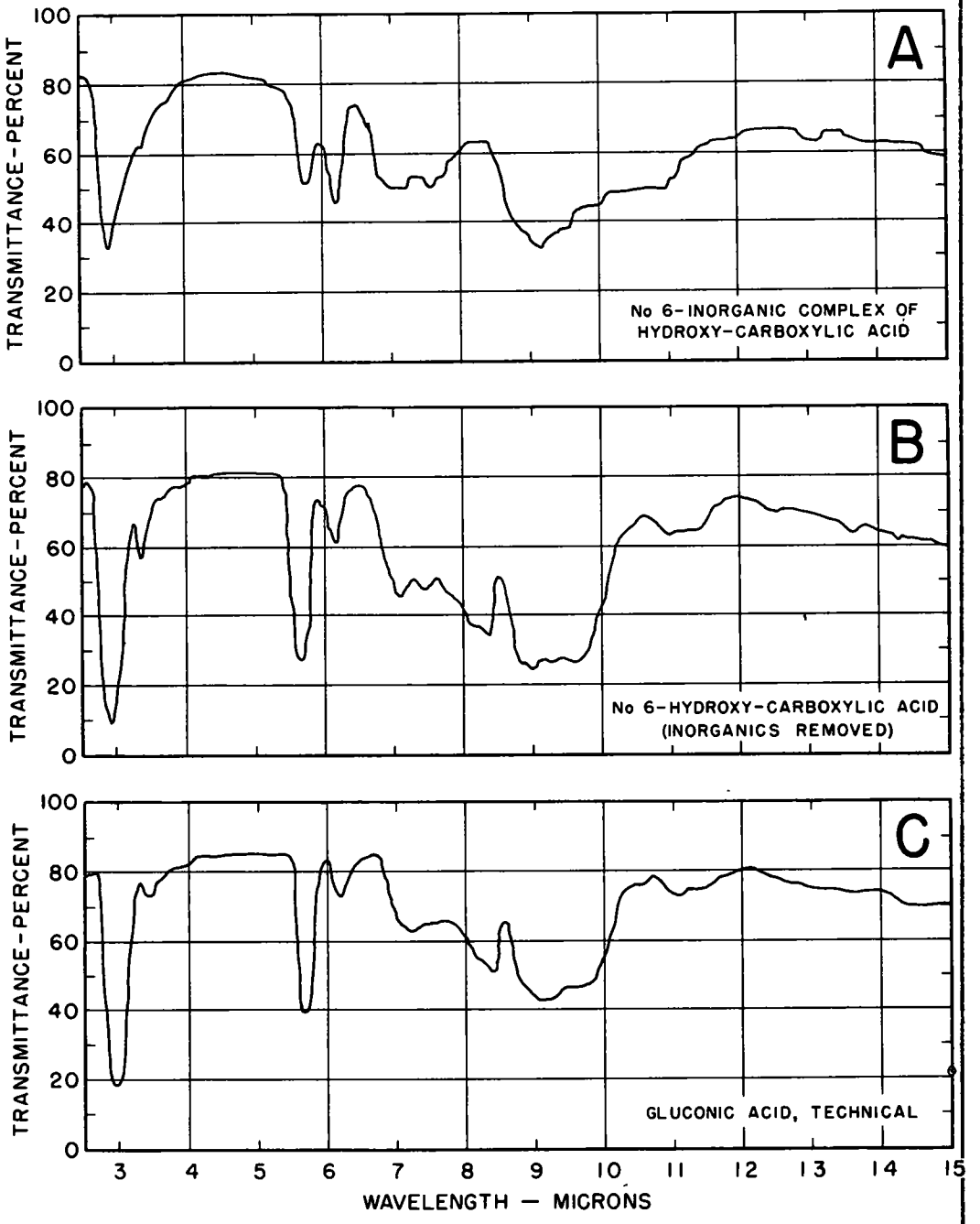


Figure 11. Infrared spectra of complexed organic acid retarder and gluconic acid.

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

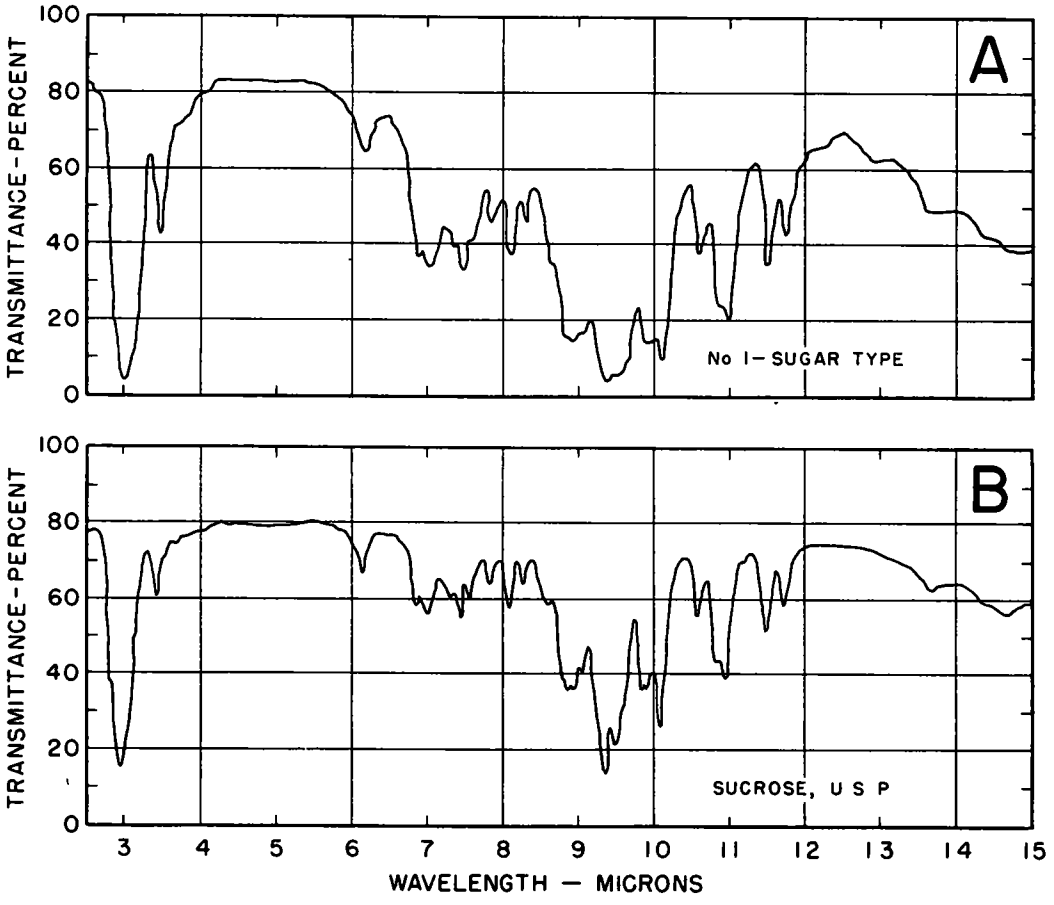


Figure 12. Infrared spectra of carbohydrate retarder and sucrose.

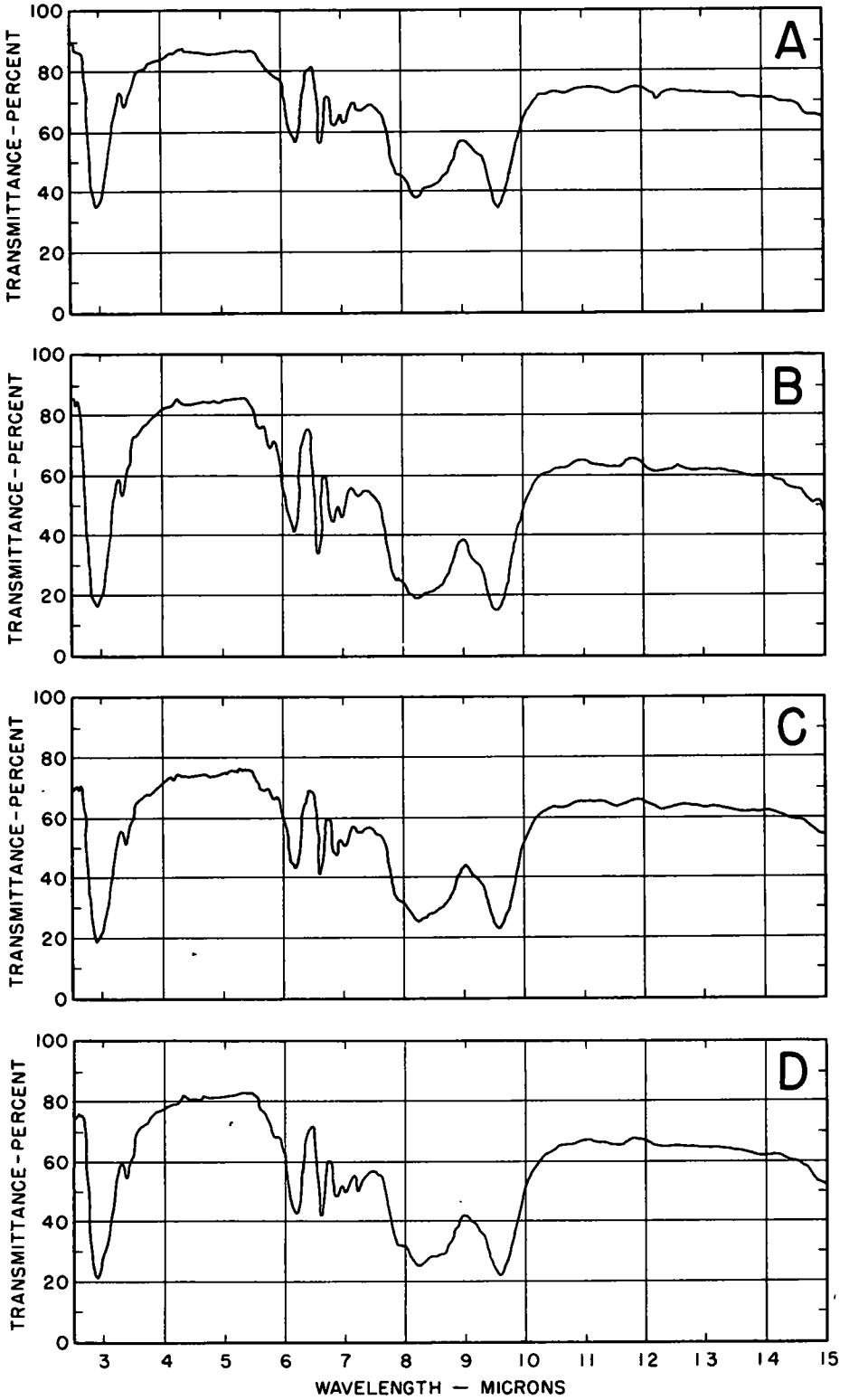


Figure 13. Infrared spectra of four different lots of the same trade name retarder (lignosulfonate type).

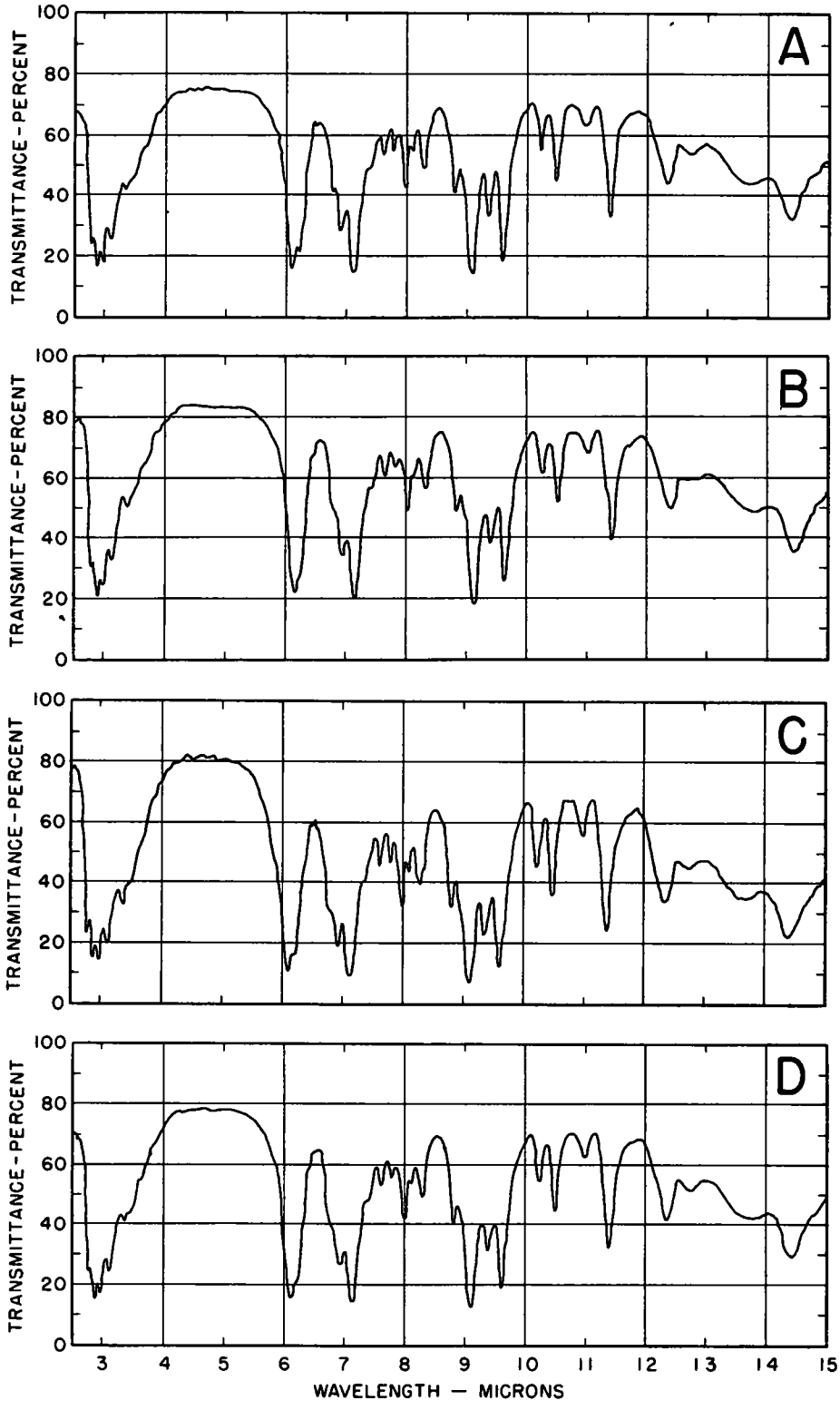


Figure 14. Infrared spectra of four different lots of the same trade name retarder (hydroxy-carboxylic type).

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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ACKNOWLEDGMENT

Acknowledgment is made to Raymond Cherwinski and L.B. Hayes, analytical chemists, for their assistance in carrying out the chemical and ultraviolet analyses.