APPLICATION OF INSTRUMENTAL METHODS FOR EVALUATING HIGHWAY MATERIALS
(Infrared Spectroscopic Characterization of Paving Asphalts in Relation to Durability)

MICHIGAN
HIGHWAY
RESEARCH LABORATORY SECTION

MICHIGAN DEPARTMENT OF STATE HIGHWAYS

APPLICATION OF INSTRUMENTAL METHODS FOR EVALUATING HIGHWAY MATERIALS
(Infrared Spectroscopic Characterization of Paving Asphalts in Relation to Durability)

A Highway Planning and Research Investigation Conducted by
the Michigan Department of State Highways and Transportation
in cooperation with the U. S. Department of Transportation
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Research Laboratory Section
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Michigan State Highway and Transportation Commission
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John P. Woodford, Director
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The work described in this report is the combined effort of R. J. Matel, B. S. Shilling, and V. Troms, of the Spectroscopy Subunit of the Research Laboratory. The project was carried out under the general supervision of W. L. Frederick, Project Leader, and M. H. Janson, head of the Spectroscopy and Photometry Unit.

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SUMMARY

Six 60-70 penetration grade asphalts originally used in the Michigan Bituminous Experimental Road (1) in 1954, and ten 60-70 penetration grade asphalts representative of those asphalts available in Michigan in 1965 were characterized by infrared spectroscopy. The infrared data were correlated with: pavement performance (1954 test road samples only), weatherometer exposure (1965 samples only), a pellet tumbling test which gaged the durability of the asphalts as aggregate binders, and the crude oil sources of the asphalts. Identifications for all sixteen samples are given in Table 1. Physical characteristics of the asphalts are given in Table 2.

Infrared Spectrophotometric Data

Solution Data - Absorbance data are reported, for solutions of the asphalts in organic solvents, at wavelengths of 3.4, 7.3, 8.7, 9.7, 11.5, 12.3, and 13.9μ. A plot of absorbance at 3.4μ ($A_{3.4}$) vs. $A_{11.5} + A_{13.9}$ was found to separate the asphalts studied according to crude oil source.

Film Data - Asphalt films on sodium chloride discs were exposed in an oven at 212 F for periods up to 400 hours, with periodic measurement of absorbance at 5.9μ. Absorbance at 5.9μ increases as the asphalt reacts with oxygen and provides an index of oxidation susceptibility. All the asphalts reacted with oxygen to some extent, but asphalt S-2, from Venezuelan crude oil, and asphalt 4, from a blend of Venezuelan and Mid-Continent U.S. crude oils, had significantly higher oxidation rates than the other asphalts.

Other asphalt films on sodium chloride discs were used to measure the crystallinity of the methylene chain fraction of the asphalts. Absorbance measurements were made at 13.7 and 13.9μ at ambient temperature and after the films were cooled to approximately -100 F, to increase crystallinity. Non-crystalline methylene chains absorb mainly at 13.9μ and increasing crystallinity is evidenced by increased absorbance at 13.7μ. None of the asphalts was found to have sufficient crystallinity to adversely affect its performance as a pavement binder.

Weatherometer Exposure

Thin films of the ten 1965 asphalts (approximately 2 by 4 by 0.015 in.) were exposed on aluminum panels in a horizontal position in an Atlas Electrical Devices Twin Carbon Arc Weatherometer. The following exposure schedule was used in 20-hour cycles.

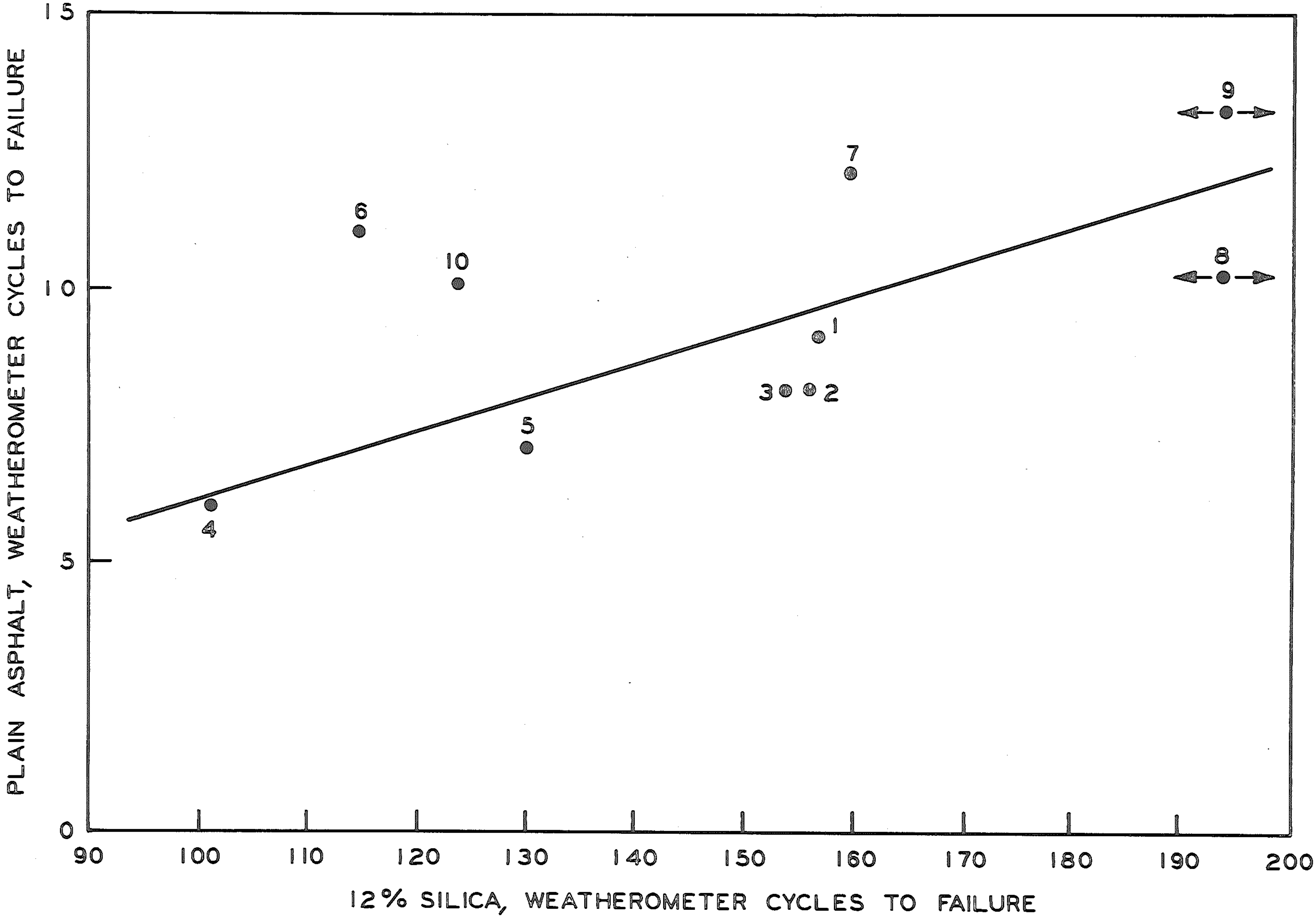

Figure 1. Correlation of weatherability of plain and silica filled asphalts.

49 minutes - light only, black panel temperature of 140 ± 5 F.
9 minutes - light, with water spray.
2 minutes - light, with a jet of compressed air directed to remove water droplets from the panel surfaces.

The films were inspected after each cycle and points of film failure were located by impressing a potential difference of 8,000 volts dc between a wire wand and the aluminum backing panel (ASTM 1670-62T). Arcing occurred whenever the wand passed over a discontinuity in the asphalt film. The failure point for a panel was reached when arcing occurred in 10 percent of the squares in a 220 square overlay grid, placed over a photographic record of the spark pattern for the panel. The averaged results of weatherometer runs ranked the asphalts as follows:

Asphalt No.	Weatherometer Cycles to Failure
4	6
5	7
2, 3	8
1	9
8, 10	10
6	11
7	12
9	13

In spite of the horizontal exposure position the asphalt films flowed somewhat to form a pattern of mounds and valleys, which hastened their failure. Accordingly, additional single panels were weathered using 12 percent by weight of colloidal silica in the asphalt as a stabilizer. The asphalt remained ductile but did not flow. In every case, the weatherability increased by a factor greater than ten, as shown in Figure 1. Weatherometer exposure was terminated even though samples 38 and 39 had not failed.

The correlation between weatherability of plain and silica-filled asphalts is good, except for asphalts 6, 7, and 10 which would have to weather considerably longer when filled with silica to correlate with the results obtained without the silica filler added. The results for plain asphalt are believed more reliable since they are based on duplicate runs, and the asphalts were not subjected to the elevated temperature necessary to incorporate the colloidal silica.

Pellet Tumbling Durability Test

A pellet abrasion test was adapted to rate the asphalts studied. A mix made up of 4 g of asphalt and 175 g of 30 to 40 mesh glass spheres was molded into cylindrical pellets of 0.5 in. diameter by 0.5 in. high. These pellets were weighed, then tumbled for 500 revolutions at 90 rpm in a square style 16-oz glass bottle which was rotated in a horizontal position. The pellet was then reweighed to determine weight loss. Low weight loss correlates with good durability as a binder. The average of pellet tumbling test results ranked the asphalts as follows:

Asphalt	Weight Loss, percent
S-4	5.3
S-6	9.1
6	9.4
S-5	12.0
7	14.6
9	20.6
10	22.3
5	24.2
2	27.1
S-1, 1, 8	27.8
S-3	28.8
3	28.9
4	31.4
S-2	35.0

Pellet tumbling and weathering test results for the 1965 asphalts compare as follows:

Decreasing Durability

Pellet Tumbling Rank	Weatherometer Rank
6	9
7	7
9	6
10	8, 10
5	1
2	2, 3
1, 8	5
3	4
4	

In comparing the weathering and pellet tumbling test results for the 1965 asphalts, it is seen that asphalt 6, 7, 9, and 10 rank highest in both groups. Asphalts 1, 2, 3, and 8 occupy intermediate positions in both groups. Asphalt 4 ranks lowest in both groups. Only asphalt 5 changes markedly in position, dropping from mid-range in pellet tumbling test results, to next to the bottom in the weathering results.

Test Road Performance

Inspection of the six sections (S-1 through S-6) of the bituminous experimental test road after 16 years of exposure to traffic yielded rankings of the six asphalts as follows:

	Asphalt
Decreasing Durability ↓	S-3, S-4, S-5
	S-1, S-6
	S-2

Sections S-3 (Wyoming crude oil), S-4 (West Texas crude oil) and S-5 (Arkansas crude oil) were in good condition. Some random cracking and one small pothole was observed in each of these sections. Section S-6 (East Texas crude oil) exhibited more fine cracks than Sections 3, 4, and 5, so it was judged to be slightly more deteriorated than the three best sections. Section S-1 (Wyoming crude oil) was also judged to be slightly more deteriorated than Sections 3, 4, and 5. Section S-2 (Venezuelan crude oil) was in much poorer condition than the other five sections. Larger cracks and a greater number of potholes were found. Many small potholes had been previously filled with patching material.

Correlation of Infrared and Durability Data

Absorbance data for asphalt solutions at other wavelengths than those included in the durability index (below) showed little correlation with durability data:

3.4μ - Asphalt S-2, with poor durability ratings had the lowest absorbance, by a small margin, of the 16 sample group.

8.7μ - Data at this wavelength were recorded for the 1965 asphalts only. No correlations were observed.

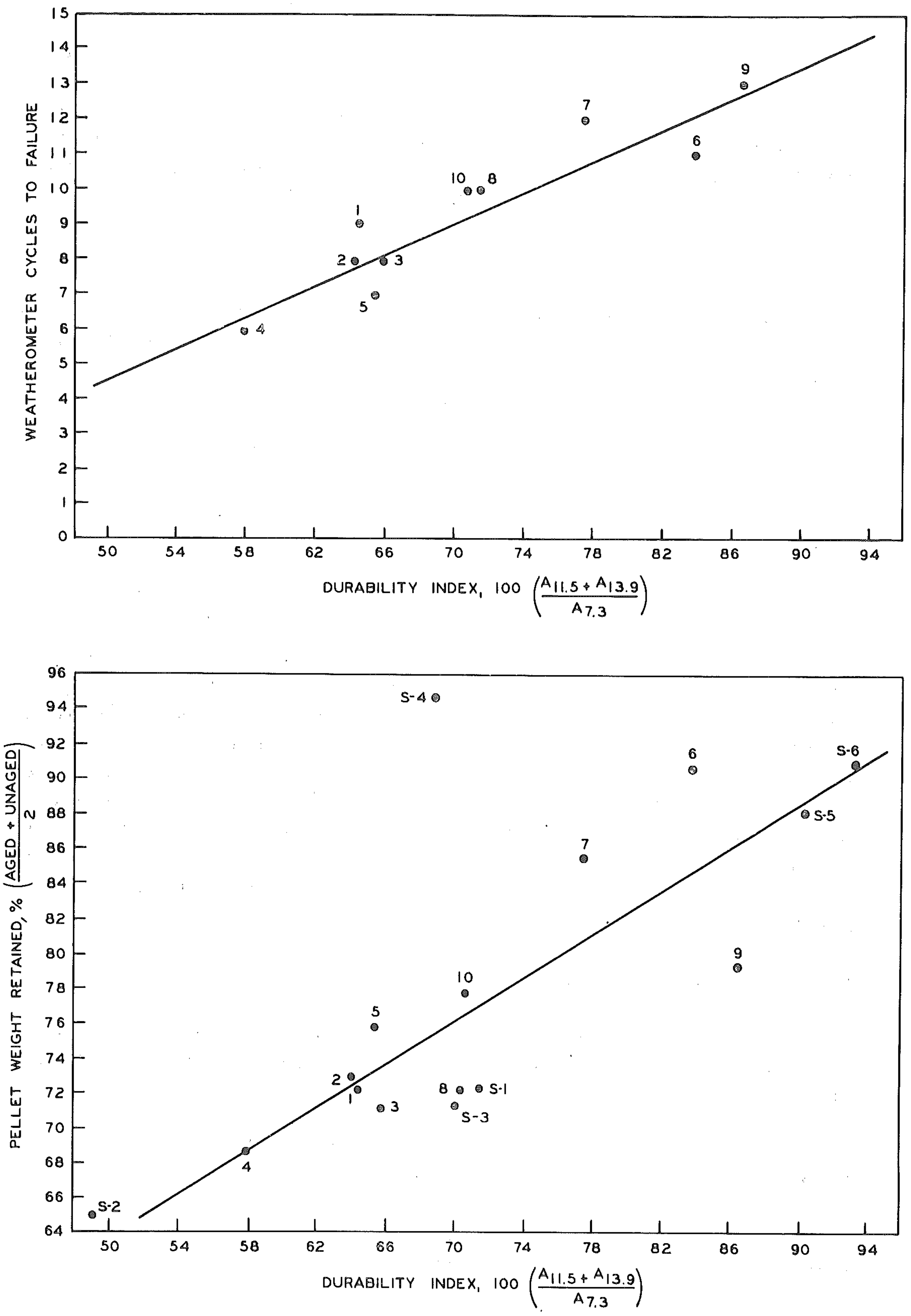

Figure 2. Correlations of infrared absorbance data and weatherometer data (above) and pellet test data (below).

9.7μ - Data were recorded for the ten 1965 asphalts only. The only correlation observed is that asphalt 4, with the poorest durability of the group, has significantly lower absorbance than the other nine asphalts.

12.3μ - The only correlation noted at this wavelength is that asphalts 4, and S-2, which rate poorest in durability, had the two lowest absorbance values.

The best combination of infrared absorbance data for correlation with durability ratings involved absorbance values obtained for asphalts in solution, at wavelengths of 7.3, 11.5, and 13.9μ. An "Infrared Durability Index," $100\frac{(A_{11.5} + A_{13.9})}{A_{7.3}}$, is plotted vs. weatherometer and pellet tumbling test data in Figure 2. The maximum deviation from the correlation line for weatherometer data is about ± one cycle, which is within the repeatability of weatherometer runs on the same asphalt.

This Infrared Durability Index correctly predicts that:

Asphalt 4, from a blend of Venezuelan and Mid-Continent U.S. crude oils, has the lowest weatherability of the new asphalts.

Asphalts from Wyoming crude oil (1, 2, 3, 5) group together with better weatherability than the asphalt from Venezuelan and Mid-Continent U.S. crude oils.

Asphalts from a blend of Wyoming and Texas crude oils (8, 10) have better weatherability than asphalts from straight Wyoming crude oil.

Asphalts 6, 7, and 9 form a group with the best weatherability of the 1965 asphalts. Asphalt 6 is from Arkansas crude oil. Asphalt 7 is from a blend of U. S. crude oils, and asphalt 9 is alleged to have come from the same supplier as asphalt 7.

The correlation of the Infrared Durability Index and pellet tumbling test data is good for 15 of the 16 asphalts studied. Asphalt S-4, however, performs considerably better in the pellet tumbling test than predicted by the infrared data. Even so, the infrared index rates this asphalt as good in relation to the group of asphalts studied.

It is interesting that the ten 1965 asphalts occupy similar relative positions in the plots of weatherability and pellet tumbling test data vs. the Infrared Durability Index. Two different types of properties--resistance to chemical and physical changes under the stress of environmental exposure, and the ability of an asphalt to function as a binder for aggregate particles--are apparently affected or controlled by the same chemical groups.

The Infrared Durability Index also correctly predicts that asphalt S-2 will produce a pavement lower in durability than the pavement produced by the other five test road asphalts. The Infrared Durability Index for asphalt S-2 is 20 units below the value obtained for asphalts that were in much better condition after 16 years of pavement service. The infrared index, however, does not correlate with test road durability beyond separating asphalt S-2 from the other five asphalts.

Conclusions

The general agreement among the infrared data, the pellet tumbling test results, weatherometer results, and the test road observations indicates that infrared spectroscopic methods can be used to help predict the potential durability of an asphalt in pavement. Problems related to subbase and paving practices, however, could still cause early pavement failure, even though a quality asphalt had been used.

The infrared data correlation methods used here may not apply to asphalts from other crude oil sources.

It will often be possible to identify the crude oil source of an unknown asphalt, providing that infrared reference data are available for asphalts from the same crude oil source. Some inferences as to crude oil source appear possible for asphalts refined from mixed crude oils.

INTRODUCTION

This report is submitted as the final part of a Highway Planning and Research Project, sponsored by the Michigan Department of State Highways and Transportation in cooperation with the Federal Highway Administration, U.S. Department of Transportation, entitled, "Application of Instrumental Methods for Evaluating Highway Materials." This report completes the last phase of the project and is devoted to the characterization of paving asphalts in relation to their durability by means of infrared spectroscopic methods.

The overall purpose of this HPR project (63 G-124) was "...to develop and apply instrumental methods for the evaluation of materials used in the construction and maintenance of highways." It's Objectives section stated that the Research Laboratory would attempt to: "1) determine those highway materials which are suitable for analysis by techniques of absorption spectroscopy and vapor chromatography, 2) develop methods for characterizing or identifying these materials, 3) relate known characteristics with performance, quality, or specification requirements of the materials, and 4) correlate these relationships and apply these correlations to systems used for quality control standards and procedures."

This project proposal was submitted to the FHWA in February 1963, and the work on the project, after Federal approval, commenced in July 1964 as a Highway Planning and Research project. In addition to this report, final reports have been issued on four phases (five reports) of the project: "Application of Instrumental Methods for Evaluating Highway Materials: Determination of Amount of 'Plastiment A' Retarder in Hardened Concrete" (MDSHT Research Report No. R-586, 1966); "Application of Instrumental Methods for Evaluating Highway Materials: Detection and Determination of Ground, Cured Scrap Rubber in Hot-Poured Joint Sealers" (MDSHT Research Report No. R-641, 1967); "Application of Instrumental Methods for Evaluating Highway Materials: Pyrolysis Gas Chromatography" (MDSHT Research Report No. R-666, 1968); "Application of Instrumental Methods for Evaluating Highway Materials: Pyrolysis Gas Chromatography II)" (MDSHT Research Report No. R-727, 1970); and "Application of Instrumental Methods for Evaluating Highway Materials: Use of Infrared Spectrophotometry in Acceptance Testing of Membrane Curing Compounds for Concrete" (MDSHT Research Report No. R-744, 1971).

The work described in this report is the result of a research program carried out by the Research Laboratory of the Michigan Department of State Highways and Transportation in cooperation with the Federal Highway Administration. The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification or regulation.

This report presents information obtained during a study aimed at finding correlations between durability of paving asphalts and differences in composition of the asphalts as shown by infrared spectrophotometric data.

Plan of Investigation

This study was conducted by compiling and correlating the following data, using 16 samples of asphalt.

1) Laboratory Physical Test Data

Standard physical tests were run on all the asphalts studied.

2) Durability Test Data

a) Pellet tumbling test
b) Weatherometer exposure (10 of 16 asphalts)
c) Performance of test road pavement over a 16 year period (6 of 16 asphalts).

3) Infrared Spectrophotometric Data

a) Quantitative infrared measurements at selected wavelengths made on solutions of the asphalts in organic solvents.

b) Quantitative infrared measurement of the increase in absorbance (due to oxidation) at 5.9μ on oven exposure at 212 F for asphalt films on sodium chloride discs.

c) Comparison of the crystallinity of asphalt films.

Asphalts Studied

Sixteen paving asphalts in the 60-70 penetration range were studied. Ten of the asphalts represent 1965 production of several suppliers of asphalt for paving projects. These are designated 1965 asphalts. Six of the asphalts were obtained in 1954 for use in a bituminous experimental road.

These are designated Test Road asphalts. Table 1 identifies the asphalt samples.

Data Obtained

Table 2 presents results of physical tests performed on the asphalts. Although the results tend to be quite similar, a few significant differences can be detected.

1) Test Road Asphalts

Asphalts S-2 and S-6 have similar viscosities, which are significantly higher than the viscosities of the other four test road asphalts both before and after the heat stability test.

Asphalt S-6 has much lower ductility than the other five asphalts; originally, and at five and seven-hour intervals in the BPR Thin Film Test. At 24 hours in the Thin Film Test asphalts S-2 and S-6 have the same ductility, which is lower than the ductility of the other four asphalts.

The ductility of asphalt S-5 decreases noticeably at seven hours in the BPR Thin Film Test, but at 24 hours its ductility is above the average for the six sample group.

Asphalt S-2 exhibits the lowest flashpoint and the greatest weight loss on heating during the BPR Thin Film Test. The weight loss on heating is more than ten times that observed for the asphalt with the next highest loss, after 24 hours of exposure at 163 C. The presence of low molecular weight material seems indicated.

Asphalt S-5 gained weight on heating, during the Thin Film Test, indicating probable reaction with oxygen.

2) 1965 Asphalts

The 1965 asphalts have fewer differences in physical properties than the Test Road asphalts. Asphalt 6 has a viscosity somewhat above the group average and asphalt 8 is somewhat lower in viscosity than the other samples.

Asphalt 10 has the lowest flash point and the highest loss on heating of the group, indicating that this sample has the largest fraction of low molecular weight material.

TABLE 1
IDENTIFICATION OF ASPHALT SAMPLES

	Identification Number	Crude Oil Source (according to supplier)	Supplier
1965 ASPHALTS	1	Wyoming	Ashland Oil and Refining Co., Ashland, Ky.
	2	Wyoming-Platte, negative Oliensis stream	Leonard Refining Co., Alma, Mich.
	3	Wyoming	Trumbull Asphalt Co., Detroit, Mich.
	4	Blend of Mid-continent U.S. and Venezuelan	American Bitumuls & Asphalt Co., Cincinnati, Ohio (Chevron Asphalt Co.)
	5	Wyoming	Berry Refining Co., Gary, Ind.
	6	Arkansas-Smackover	Lion Oil Co., El Dorado, Ark.
	7	Blend of Mid-continent Velma, Wyoming sour, and Cooke County	Sinclair Refining Co., East Chicago, Ind.
	8	Blend of 70% Wyoming and 30% West Texas	American Oil Co., Whiting, Ind.
	9	Obtained from Sinclair	Witco Chemical Co., Hammond, Ind.
	10	Blend of 70% Wyoming and West Texas with 30% East Texas	Seneca Petroleum Co., Toledo, Ohio
1954 TEST ROAD ASPHALTS	S-1	Wyoming	Leonard Refining Co., Alma, Mich.
	S-2	Venezuelan	American Bitumuls & Asphalt Co., Cincinnati, Ohio
	S-3	Wyoming	Trumbull Asphalt Co., Detroit, Mich.
	S-4	West Texas - Winkler	Standard Oil Co., Whiting, Ind.
	S-5	Arkansas-Smackover	Lion Oil Co., El Dorado, Ark.
	S-6	East Texas - Talco	American Liberty Oil Co., Mt. Pleasant, Texas

TABLE 2
PHYSICAL CHARACTERISTICS OF THE ASPHALTS STUDIED

Report Identification Number	1965 ASPHALTS[1]										TEST ROAD ASPHALTS[2]					
	1	2	3	4	5	6	7	8	9	10	S-1	S-2	S-3	S-4	S-5	S-6
Specific Gravity, 25/25 C	1.032	1.031	1.033	1.024	1.033	1.027	1.014	1.030	1.014	1.027	1.027	1.036	1.027	1.012	1.022	1.032
Flash Point, Cleveland Open Cup, C	310	308	305	308	299	366	323	328	320	287	320	282	326	316	356	300
Softening Point, R & B, C	49.0	50.5	49.5	49.4	49.7	49.1	49.1	48.0	47.2	49.3	48.9	51.8	48.1	50.7	49.0	51.2
Solubility in CCl_4, percent	99.94	99.98	99.96	99.87	99.98	99.97	99.97	99.97	99.99	99.84	99.99	99.97	99.95	99.82	99.88	99.99
Penetration, 0 C, 200 gm, 1 min, dmm	16	14	16	16	17	15	16	13	14	16	16	16	13	15	14	19
Penetration, 4 C, 200 gm, 1 min, dmm	20	23	21	20	22	19	20	20	20	24	21	21	20	24	21	26
Penetration, 15 C, 100 gm, 5 sec, dmm	20	19	20	19	22	22	20	19	17	21	22	21	22	23	21	23
Penetration, 25 C, 100 gm, 5 sec, dmm	63	65	62	62	65	63	66	65	66	64	63	60	67	60	61	65
Penetration, 25 C, 100 gm, 5 sec, dmm (1965)	--	--	--	--	--	--	--	--	--	--	58	57	58	53	52	61
Penetration, 35 C, 100 gm, 5 sec, dmm	180	183	167	180	179	173	188	192	208	190	173	154	186	151	144	141
Ductility, 4 C, 5 cm/min, cm	0	0	0	0	0	0	0	0	0	0	0	1	0	5	5	5
Ductility, 10 C, 5 cm/min, cm	25	33	73	100	43	21	39	59	94	94	18	25	14	10	12	8
Ductility, 15.6 C, 5 cm/min, cm	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	77
Viscosity, Saybolt Furol. 275 F, sec	220	214	222	233	210	272	232	184	205	211	192	313	197	217	276	337
Viscosity, Saybolt Furol. 275 F, sec (1965)	---	---	---	---	---	---	---	---	---	---	211	338	204	237	288	345
Viscosity, Saybolt Furol. 300 F, sec	118	110	116	120	110	143	119	93	108	107	101	170	105	128	150	172
Viscosity, Saybolt Furol. 325 F, sec	65	63	64	70	62	82	67	54	64	59	61	100	61	84	91	93
Heat Stability Test, 500 F, 100 gm, 2 hr																
Penetration, 25 C, 100 gm, 5 sec, dmm	58	63	58	58	61	61	62	62	62	63	58	57	66	63	56	61
Viscosity, Saybolt Furol. 275 F, sec	229	223	234	253	222	301	242	187	224	213	215	337	205	193	284	333
Viscosity, Saybolt Furol. 325 F, sec	70	65	66	73	65	83	71	55	66	61	68	108	61	59	88	109
1/8 in. BPR Thin Film Method																
Weight change on heating, 5 hr, 163 C, 50 gm, percent	+0.060	-0.070	-0.036	+0.010	-0.015	+0.102	-0.013	-0.050	-0.059	-0.101	-0.022	-0.132	-0.079	-0.091	+0.092	-0.016
Penetration of residue, 25 C, 100 gm, 5 sec, dmm	41	44	36	38	38	43	42	35	45	38	36	38	40	42	39	45
Ductility of residue, 25 C, 5 cm/min, cm	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	150+	77
Weight change on heating, 7 hr, 163 C, 50 gm, percent	---	---	---	---	---	---	---	---	---	---	-0.026	-0.142	-0.025	-0.050	+0.105	-0.054
Penetration of residue, 25 C, 100 gm, 5 sec, dmm	--	--	--	--	--	--	--	--	--	--	31	34	34	38	35	37
Ductility of residue, 25 C, 5 cm/min, cm	---	---	---	---	---	---	---	---	---	---	150+	150+	150+	150+	111	33
Weight change on heating, 24 hr, 163 C, 50 gm, percent	---	---	---	---	---	---	---	---	---	---	-0.048	-1.541	+0.046	-0.144	+0.239	-0.151
Penetration of residue, 25 C, 100 gm, 5 sec, dmm	--	--	--	--	--	--	--	--	--	--	16	16	17	22	21	22
Ductility of residue, 25 C, 5 cm/min, cm	---	---	---	---	---	---	---	---	---	---	6	4	6	7	6	4

[1] Values determined in 1965

[2] Values determined in 1954 unless otherwise noted.

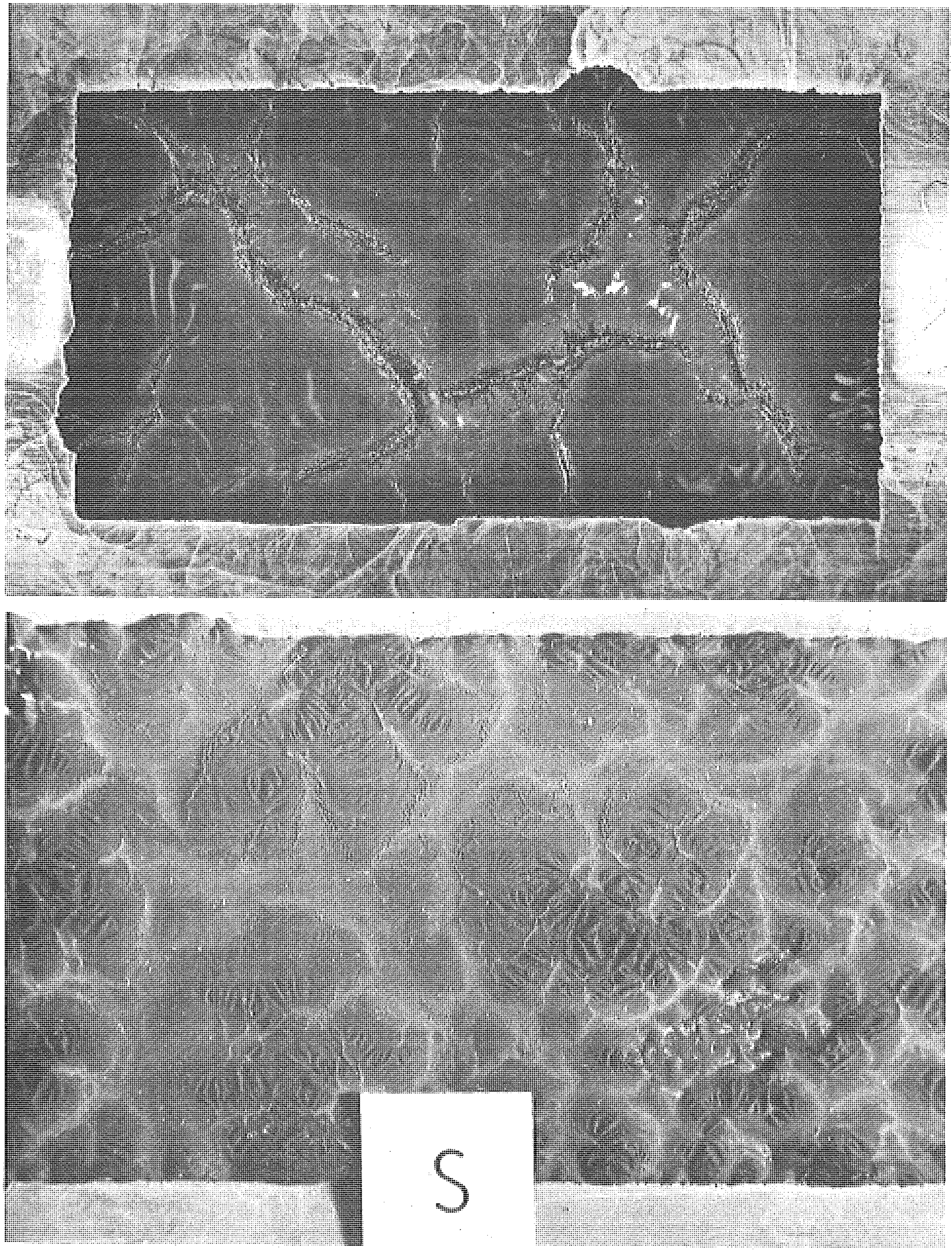

Figure 3. Appearance of typical panels after weathering. Note aluminum substrate showing through some of the valleys.

Asphalts 1, 4, and 5 increased slightly in weight during the Thin Film Test, while the other seven asphalts decreased slightly in weight.

ARTIFICIAL WEATHERING

Accelerated durability tests for the group of ten 1965 asphalts were run in an Atlas Electrical Devices Twin Carbon Arc Weatherometer. Films of asphalt were applied to aluminum panels according to a modification of ASTM D 1669-62 (Appendix A) and the failure end point was determined according to ASTM D 1670-62T. Exposure of the panels in the weatherometer was modified from ASTM D 529-62, "Accelerated Weathering Test of Bituminous Material." The test panels were exposed horizontally rather than vertically because these asphalts would flow on vertical exposure at a temperature of 140 F. The weatherometer platform carrying the samples rotated at 1 rpm and the panels were mounted on spindles which turned 1/6 revolution at each revolution of the platform, to insure even exposure of the panels to radiation from the carbon arcs. The following exposure schedule was used in 20 hour cycles.

49 minutes - light only (ventilation adjusted to maintain a black panel temperature of 140 ± 5 F)

9 minutes - light with water spray

2 minutes - light, with a jet of compressed air directed to remove water droplets from the panel surfaces.

In spite of the horizontal exposure position, the asphalts flowed to form a pattern of mounds and valleys. A thin crust formed on the asphalt surface, the surface lost its sheen and fissures opened in the crust. Film failure occurred in the thin spots in the valleys, rather than in the expected pattern of cracks over the surface of the panel. Figure 3 shows typical panels.

The failure end point was determined by impressing a potential difference of 8,000 volts dc between a wire wand and the aluminum backing panel (ASTM D 1670-62T). Arcing occurred whenever the wand passed over a discontinuity in the asphalt film. When a significant number of sparks were observed visually for a particular panel a record of the failure pattern was prepared by placing a piece of photocopy paper over the asphalt prior to the spark test. Each electrical discharge appears as a white spot on a black background when the copy paper is developed. An overlay grid of 220 squares was used to evaluate the photographic failure pattern. The failure point is reached when spots occur in 10 percent of the grid squares.

The results of two accelerated weathering runs are reported in the following table.

RESULTS OF ARTIFICIAL WEATHERING OF PAVING ASPHALTS

Cycles to Failure	Asphalt Number		
	Run 1	Run 2	Average
5	--	4	--
6	4	5	4
7	5	2, 3	5
8	3	--	2, 3
9	1, 2	1, 8	1
10	10, 8	6	8, 10
11	--	7	6
12	6	9	7
13	7, 9	--	9
14	--	--	--
15	--	--	--
16	--	--	--
17	--	10*	--

*Result considered non-representative, 10 cycles used to compute average.

Additional weathering of asphalt films containing colloidal silica to prevent formation of mounds is described later. Except for one panel of asphalt 10 which failed during the 17th cycle of run two, all the panels subjected to accelerated weathering failed by the 13th cycle. The tendency of the asphalt films to form mounds and thin spots during weatherometer exposure caused variations in results but trends were evident. Asphalt 4 consistently failed early in each run while asphalts 6, 7, and 9 were among the most durable. Asphalts 1, 2, 3, and 5 generally grouped together as having relatively low durability. Asphalt 8 tended to be slightly more durable than the 1, 2, 3, 5 group. Erratic results were obtained for asphalt 10 which ranged from good to outstanding in durability in the two runs.

The result for asphalt 10 in run two is considered questionable because it is the only case of an apparent increase in durability - all the other asphalts lasted for fewer weathering cycles than in run one. If the questionable failure point of 17 cycles for asphalt 10 in run two is disregarded, and the same failure point as run one is used (10 cycles) in computing average results, the asphalts rank in weatherability as shown in the average column of the table above.

Weathering of Silica Filled Asphalts

Weatherometer tests were also conducted using asphalt films containing colloidal silica[1], to counteract the tendency of the asphalt to flow into mounds. The long exposure times required for deterioration of the silica-bearing asphalts limited such testing to one panel of each asphalt. Colloidal silica was stirred into the molten asphalt, using a high-shear mixer, to prepare a stock mix from which weatherometer panels were prepared (see Appendix B for the experimental procedure).

Incorporation of the silica into a carbon disulfide (CS_2) solution of the asphalt, with subsequent removal of the solvent, produced consistent mixes at convenient temperatures, but it was found that the solvent altered the flow characteristics of the asphalt. This was determined by a flow test similar to Method 223.11 of Federal Specification SSR 406 C. Untreated asphalt and asphalt recovered from CS_2 solution without addition of silica were cast into 4 by 6 by 0.32 cm blocks on aluminum panels and allowed to stand at room temperature for 0.5 hour. The panels were then inclined at 75° from horizontal in an oven at 140 F. Asphalt recovered from solution always flowed more rapidly than its untreated control. Heating the recovered asphalt in a vacuum oven at 140 F for four hours did not change the results, so the direct blending process described above was adopted.

Preliminary weathering tests were conducted on asphalt films containing 4, 7, 13, and 20 percent silica by weight. The 4 and 7 percent silica mixes formed mounds. Mixes containing 13 and 20 percent silica remained ductile but did not form mounds, and their appearance after weathering was very similar. Figure 4 shows the appearance of asphalt films weathered with and without added silica. A silica content of 12 percent was chosen for further weathering tests.

Films of the 1965 asphalts containing 12 percent silica were applied to aluminum panels by the procedure described in Appendix A. Figure 5 shows these panels after 71 weathering cycles. The only effect noticed was that the surface appeared to have a powdery coating. The first significant deterioration occurred during the 106th cycle, when asphalt 4 changed from small surface cracks to the large cracks shown in Figure 6. Some of these

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[1] Cab-O-Sil M-5, produced by Cabot Corporation.

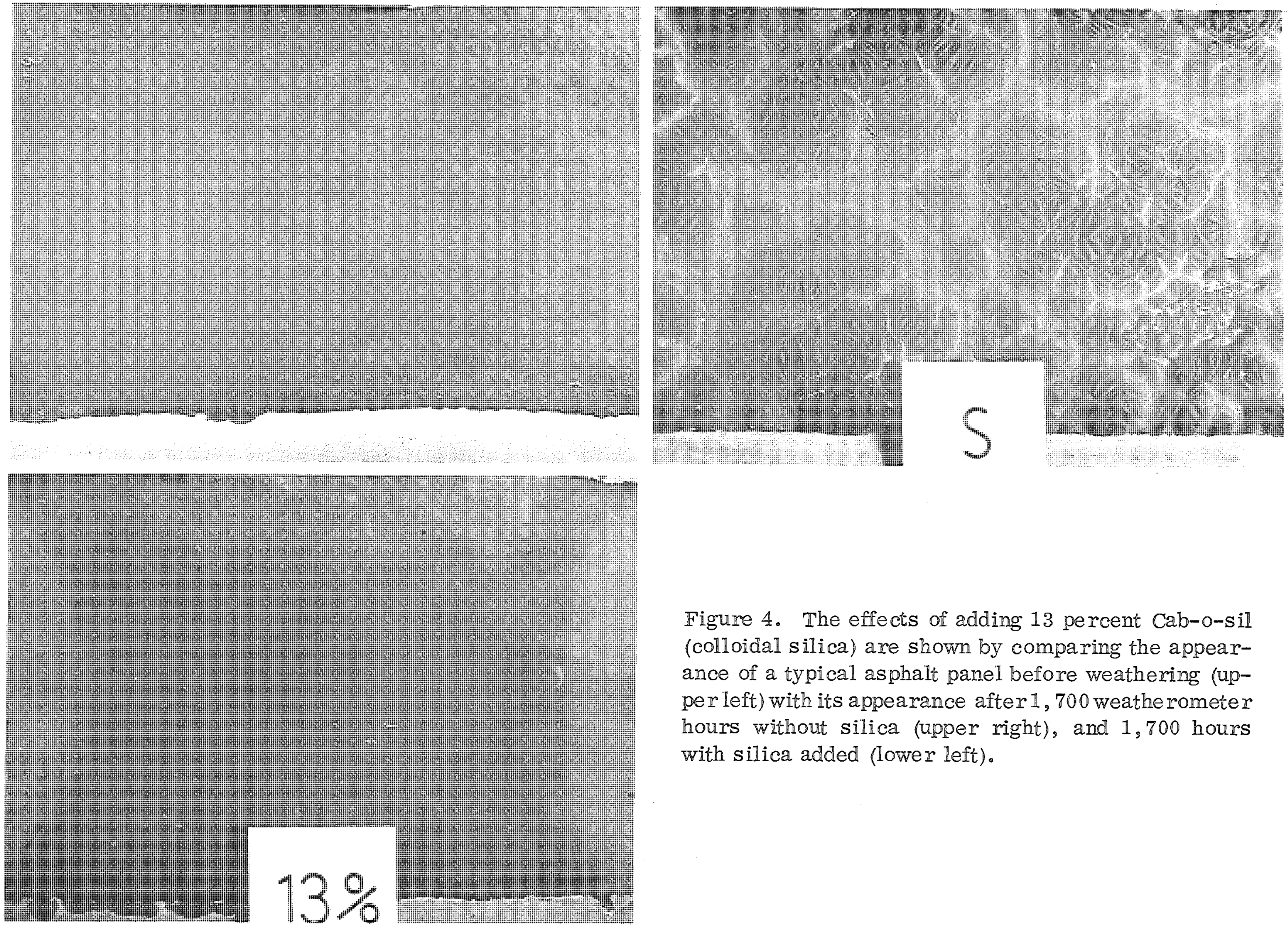


Figure 4. The effects of adding 13 percent Cab-o-sil (colloidal silica) are shown by comparing the appearance of a typical asphalt panel before weathering (upper left) with its appearance after 1,700 weatherometer hours without silica (upper right), and 1,700 hours with silica added (lower left).

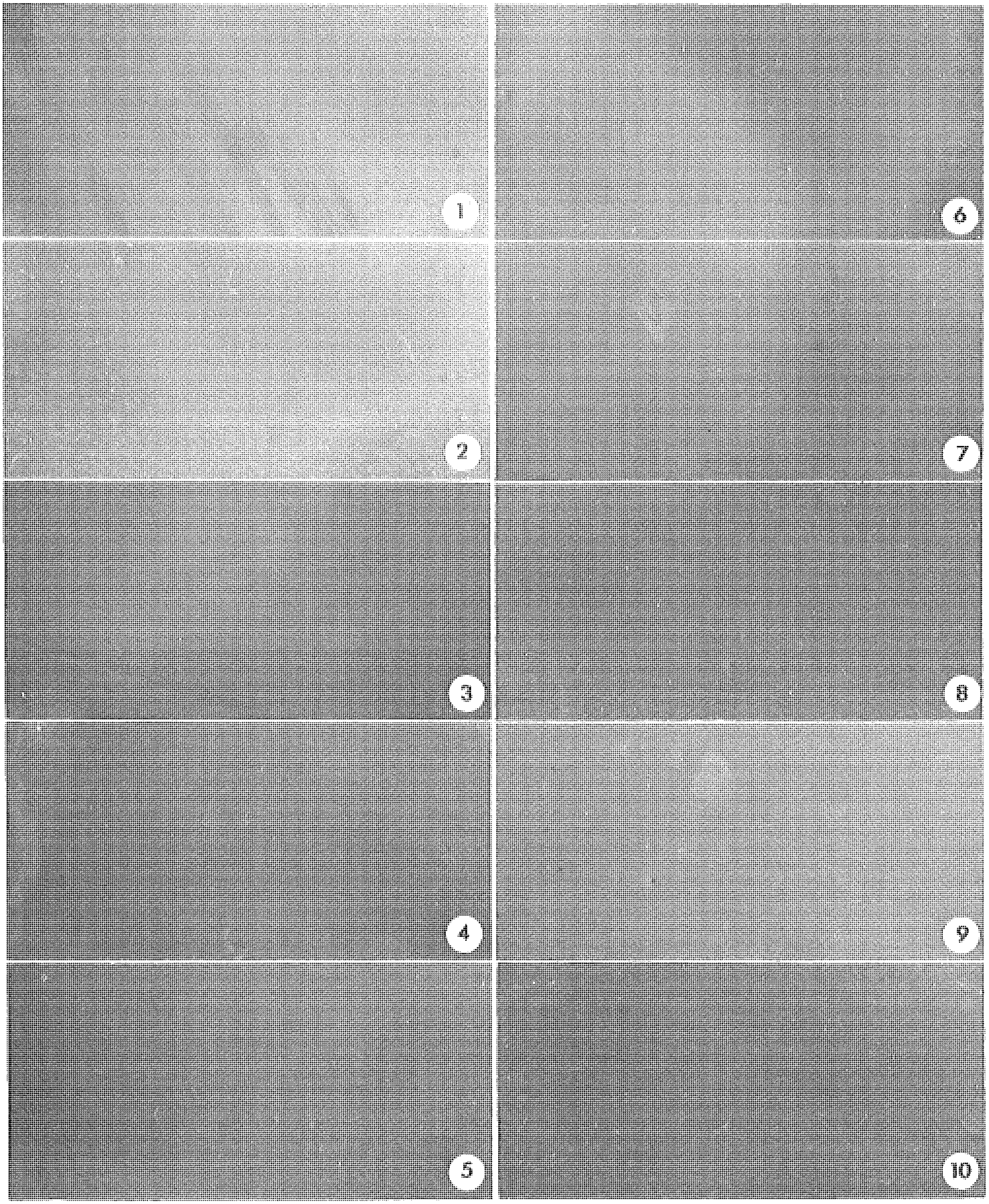


Figure 5. Appearance of films of asphalts 1 through 10, with 12 percent colloidal silica added, after 71 weatherometer cycles.

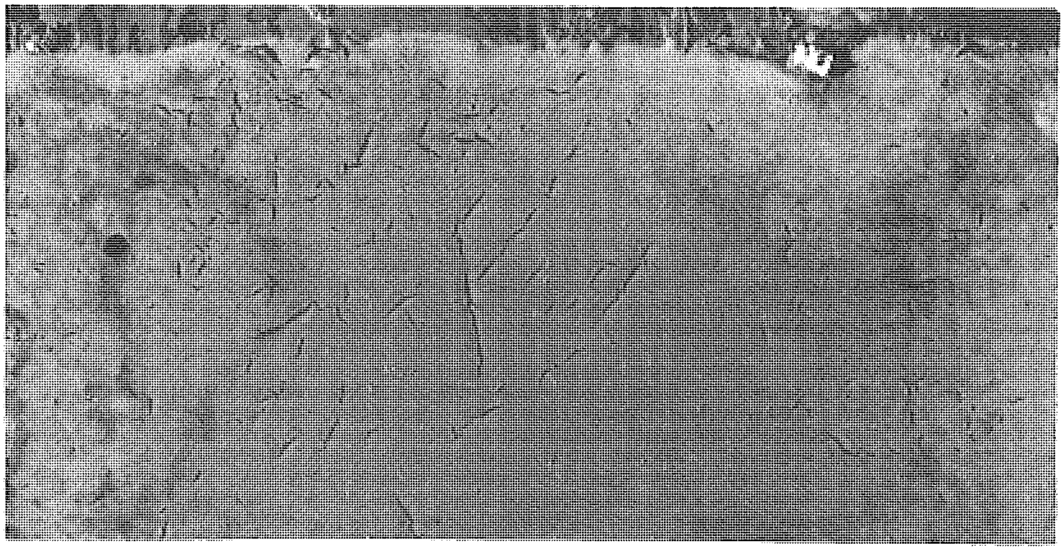


Figure 6. After 106 weatherometer cycles, asphalt 4 shows large surface cracks.

cracks penetrated to the aluminum backing. The other nine asphalts exhibited only minute surface cracks around the edges of the film. A number of additional cycles were required before cracks appeared in the central area of their test panels.

The following table ranks the ten 1965 asphalts according to weatherability when they are stabilized with silica. The reported number of cycles represents the same panel condition, determined visually, as that previously shown in the photograph of asphalt 4, except for asphalts 8 and 9 which had not cracked seriously when the test was stopped at 185 cycles. Figure 7 shows the appearance of all the panels at the end of the test.

Asphalt	Weatherometer Cycles	Cycles from Failure of Previous Specimen
4	106	--
6	120	14
10	129	9
5	135	6
3	159	24
2	161	2
1	162	1
7	165	3
8	185	Did not fail
9	185	Did not fail

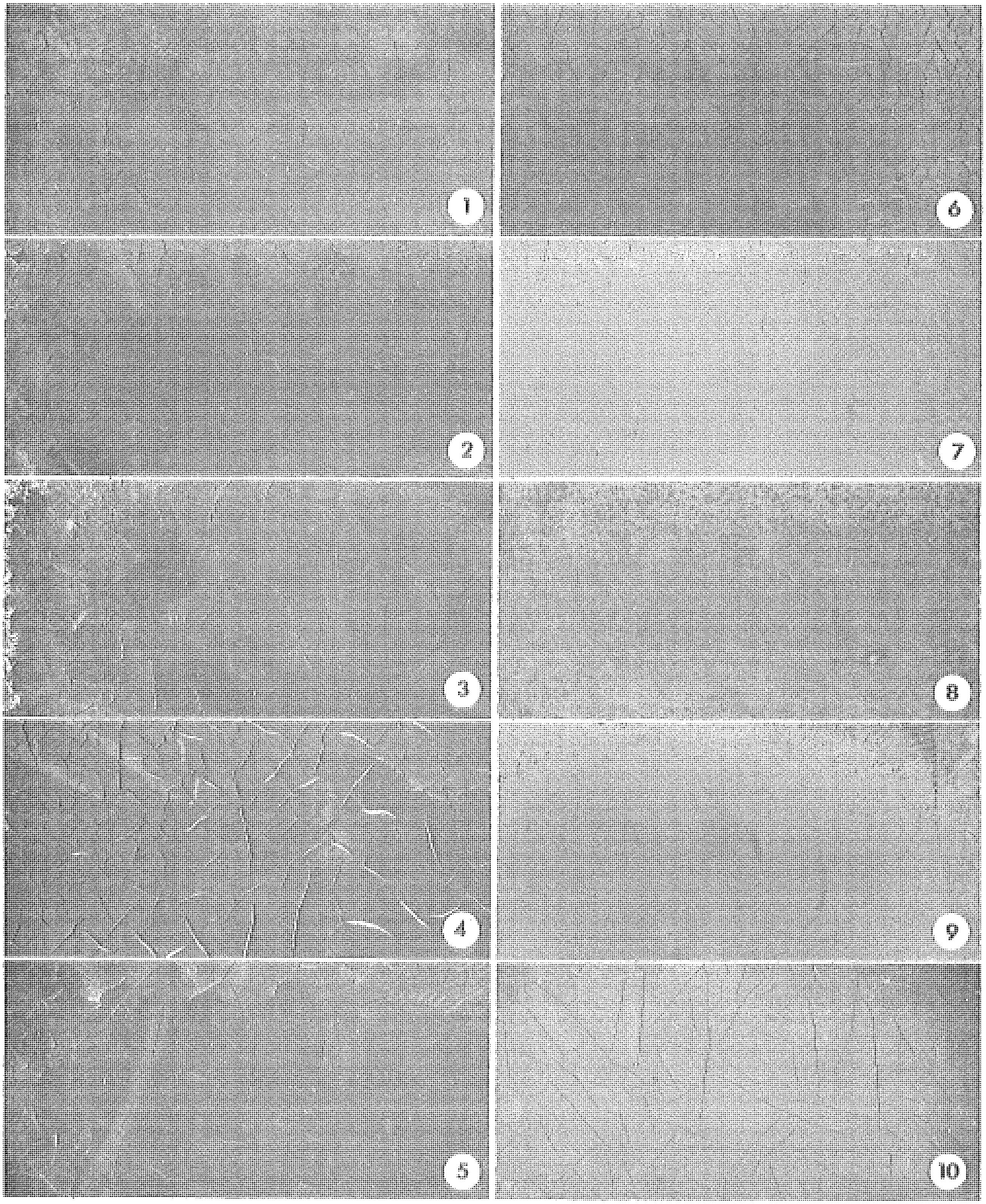


Figure 7. Appearance of films of asphalts 1 through 10, with 12 percent colloidal silica added, after 185 weatherometer cycles (termination of test).

The correlation of weatherability for plain and silica filled asphalts is reasonably good as shown in Figure 8. Asphalts 8 and 9 are plotted at an estimated failure point of 195 cycles for illustration only, since their failure points were not determined. Asphalts 6, 7, and 10 failed sooner than expected, based on results obtained without added silica.

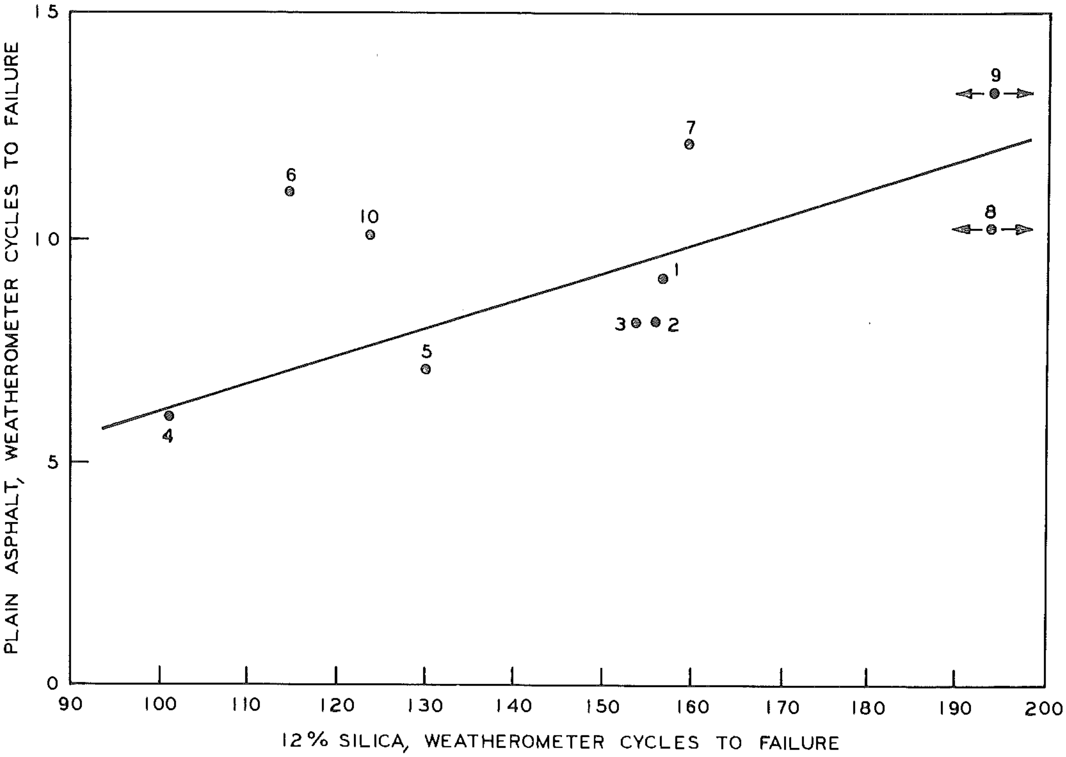


Figure 8. Correlation plot of weatherometer data for plain and silica filled asphalts.

This early failure may have been due to flaws in the single panel weathered, or asphalts 6, 7, and 10 may have been changed by interaction with the colloidal silica and/or the process used to incorporate the colloidal silica into the asphalt. The general agreement in weatherability ranking when the same asphalts are weathered plain and with colloidal silica added indicates that weathering results for the plain asphalts are valid even though the plain asphalts flowed into a pattern of mounds and valleys during weathering.

PELLET TUMBLING DURABILITY TESTS

A pellet abrasion test was used to rate the asphalts in this study. This test tumbled a pellet pressed from a mixture of asphalt and glass beads in a square glass bottle rotated in a horizontal position. The greater the weight loss of the pellet, the poorer the expected durability of a pavement constructed using the asphalt under test.

Asphalt-bead mixtures were prepared as described in Appendix C. Mix proportions were 4 g of asphalt to 175 g of 30 to 40 mesh glass beads. Portions of each mix were aged in shallow containers at 140 F for seven days. Both aged and unaged mixes were chilled to -20 F then crushed and stirred to improve homogeneity. Pellet size portions of mix (2.1 g) were stored at 77 F overnight. Pellets were pressed, weighed to ± 0.01 g, and cured at 77 F for two to five hours before tumbling. Unused mix was covered with aluminum foil and stored at -20 F to minimize change in asphalt properties.

Preliminary pellet tumbling runs did not yield reproducible results, so a reference asphalt system was adopted. Asphalt 5 was run with each group of asphalts tested and the average weight loss for the pellets from each asphalt were corrected by a factor based on results for asphalt 5. The corrected results for several runs of pellets from each asphalt were averaged to obtain a final value for use in ranking the asphalt.

Unaged mixes of the 1965 asphalts were run using six pellets for each of four different asphalts, plus six pellets for asphalt 5 (the reference) each day. Aged mixes of the 1965 asphalts and unaged and aged mixes of the Test Road Asphalts were run using four pellets for each of seven different asphalts plus four pellets for asphalt 5 each day. Asphalt 9 was rerun with the test road asphalts to check the consistency of results over a considerable time span. Average weight loss data for each run and corrected weight loss values for each run are presented in Appendix D.

There were considerable differences in weight loss for different runs of pellets from the same asphalt. The correction step based on asphalt 5 brought the results of different runs into good agreement. The reference values for asphalt 5 are based on the average of eight runs with unaged mixes (19.3 percent weight loss) and the average of five runs with aged mixes (29.2 percent weight loss). The comparison results obtained for asphalt 9 were 17.7 percent weight loss (average of three runs) when it was run with the unaged 1965 asphalts and 17.7 percent weight loss (average of five runs) when it was later run with the unaged Test Road Asphalts. Weight loss values of 23.4 percent and 23.6 percent were obtained for two comparison series of three runs each with aged mixes. This appears to confirm the validity of the correction procedure applied to the raw data.

Table 3 shows the ranking of the asphalts studied, based on pellet tumbling test results. The data can be divided into three groups as indicated. For the 1965 asphalts, 6 and 7 are rated highest in both aged and unaged runs. Asphalt 4 is rated lowest in both aged and unaged runs. Other asphalts changed relative ranking. Asphalt 2 moved above asphalts 1, 3, and

TABLE 3

RANKING OF ASPHALTS BY THE PELLET TUMBLING TEST

Durability	Unaged weight loss		Aged weight loss		Average of aged and unaged weight loss	
	asphalt	percent	asphalt	percent	asphalt	percent
BETTER	S-4	3.8	S-4	6.8	S-4	5.3
	6	5.8	S-6	9.1	S-6	9.1
	7	8.8	6	12.9	6	9.4
	S-6	9.1	S-5	13.0	S-5	12.0
	S-5	11.0	7	18.5	7	14.6
	10	17.0	9	23.4	9	20.6
	9	17.7	10	27.6	10	22.3
	5	19.3	5	29.2	5	24.2
	3	20.7	S-1	30.0	2	27.1
	8	20.9	S-3	32.1	S-1	27.8
	1	21.4	2	32.6	1	27.8
	2	21.6	1	34.0	8	27.8
			8	34.7	S-3	28.8
					3	28.9
	4	24.8	3	37.1	4	31.4
	S-1	25.6	4	38.2	S-2	35.0
	S-3	25.6	S-2	39.3		
POORER	S-2	30.8				

8 on aging. Asphalt 3 dropped below asphalts 1, 2, and 8 on aging. Other shifts of one position (relative to 1965 asphalts only) on aging, as noted for asphalts 1, 8, 9, and 10 were not considered significant. The Test Road Asphalts did not increase as much in pellet weight loss on aging as the new asphalts, nor did they switch ranks relative to each other. Results for asphalt S-6 did not change when aged and unaged mix was run. Apparently, this sample had already undergone changes similar to those caused by aging at 140 F, during storage at room temperature since 1954.

It was decided that the most meaningful ranking of the asphalts would be based on the average of aged and unaged results, as shown in the last column of Table 3.

PAVEMENT SERVICE OF TEST ROAD ASPHALTS

The Michigan Bituminous Experimental Road was placed over an existing 1931 vintage concrete pavement (US 10, north of Pontiac) in 1954. The test road project is described in a paper by Parr, Serafin, and Humphries, (1). Six 2,400-ft sections (S-1 through S-6) were each paved with a different asphalt, using the same aggregate source in all sections. From 1954 to 1961 the average daily traffic was near 11,000 vehicles with 17.3 to 22.3 percent commercial vehicles. Many of these commercial vehicles were large semitractor-trailer gravel trucks. Between 1962 and 1966, average daily traffic dropped to 7,300 vehicles with 13.7 percent commercial vehicles, due to completion of a parallel Interstate route. Traffic counts were not made after 1966.

A walking inspection of the test road in 1966 revealed that no serious deterioration had occurred. Sections 1, 3, 4, and 5 all exhibited a similar degree of random cracking in addition to the cracking quite obviously caused by faults in the underlying concrete pavement. Section 2 was similar in overall appearance to the previously described sections, but two irregular holes approximately 6 in. in largest dimension and 1-in. deep were also found. One of these holes may have been at the edge of a patched core hole. Section 6 had many fine cracks in a map-like pattern but no holes were found. Many of the cracks had been filled with molten asphaltic material which may have prevented further normal deterioration from occurring.

Section 2 was judged to be in the worst condition since it was the only area where holes were found. Because of the greater frequency of cracks, Section 6 was also thought to have deteriorated more than Sections 1, 3, 4, and 5.

A second inspection was made during March 1971. Sections 3, 4, and 5 were found to be in good condition. The random cracking noted in the previous inspection was found, along with one or two small potholes per section. Figure 9 shows a typical hole.

Section 6 still had many fine cracks, but only one small pothole was found. The earlier sealing of these cracks with molten asphalt may have prevented further deterioration .

Section 1 was also judged to be slightly more deteriorated than Sections 3, 4, and 5 because there were more potholes than had been found in the sections previously described.

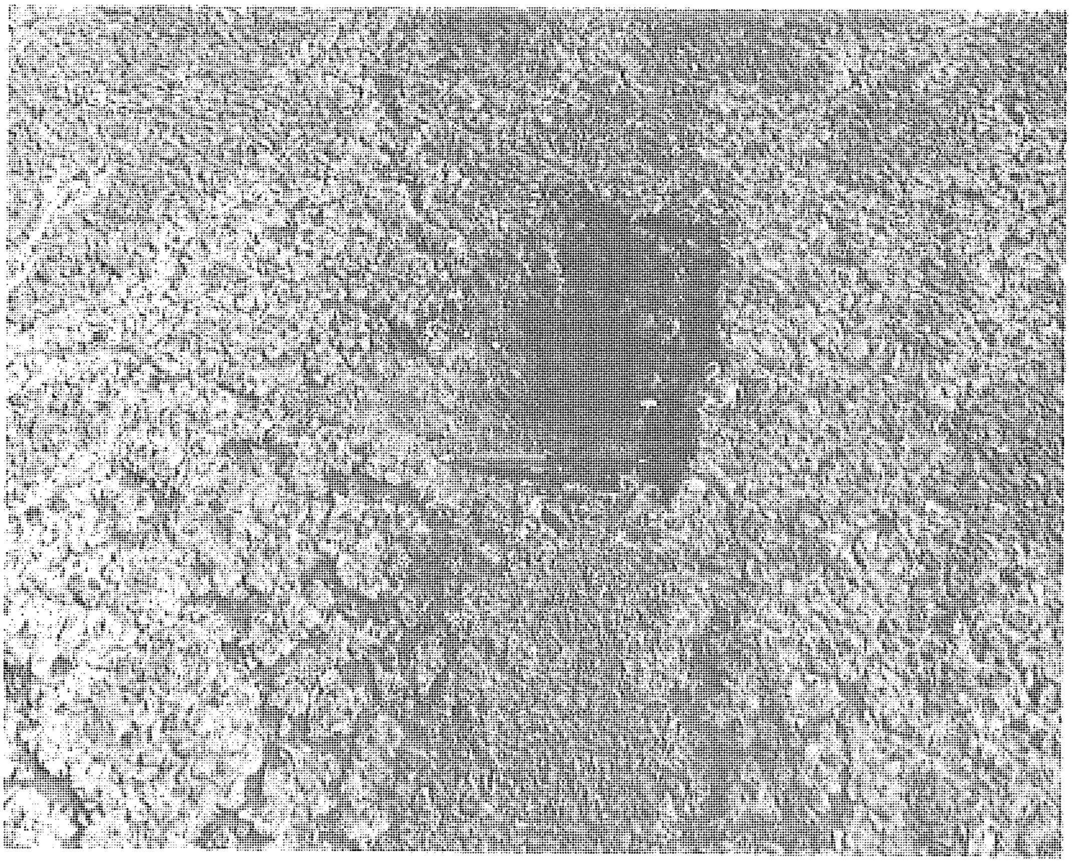


Figure 9. Small pothole, typical of those appearing in the test road sections at the 1971 inspection.

Section 2 was in much poorer condition than the other five sections. Cracks and potholes were much more in evidence. The edges of cracks were eroded, and many small potholes had been filled with patching material.

The relative durability of the six test road asphalts was judged to be as follows.

	Asphalt
Decreasing Durability ↓	S-3, S-4, S-5
	S-1, S-6
	S-2

QUANTITATIVE INFRARED SPECTROPHOTOMETRIC DATA

Asphalt Solutions

The relative amounts of certain chemical groups in the asphalts were compared by infrared spectroscopy of solutions.

The following solutions were used:

4 g of asphalt/liter of carbon tetrachloride - scanned from 2.7 to 4.5μ
40 g of asphalt/liter of carbon tetrachloride - scanned from 6.8 to 8.5μ
100 g of asphalt/liter of carbon disulfide - scanned from 7.5 to 15μ

Spectra were recorded the same day solutions were prepared to minimize possible changes in the asphalt on standing. A variable path length cell containing only solvent was placed in the reference beam of the spectrophotometer and its thickness was adjusted to compensate for absorption by the solvent in the sample solution. See Appendix E for experimental details.

Within each of the three wavelength ranges scanned, the asphalts were at the same concentration in solution when the infrared measurements were made, so the absorbance values are directly proportional to the relative amount of the chemical grouping in the asphalts which absorb at the wavelength being measured.

Wavelengths at which infrared absorbance is reported and the chemical structure assignments are as follows:

Wavelength, μ	Absorbing Structure
3.4	Aliphatic carbon-hydrogen bonds
7.3	$-C-CH_3$ (chain terminating)
8.7	No specific assignment
9.7	No specific assignment
11.5	Aromatic and paraffin structures
12.3	Aromatic structures
13.9	Hydrocarbon chains of four or more adjacent methylene ($-CH_2-$) groups.

Results of the quantitative infrared measurements are presented graphically in Figure 10, and tabulated in Appendix F.

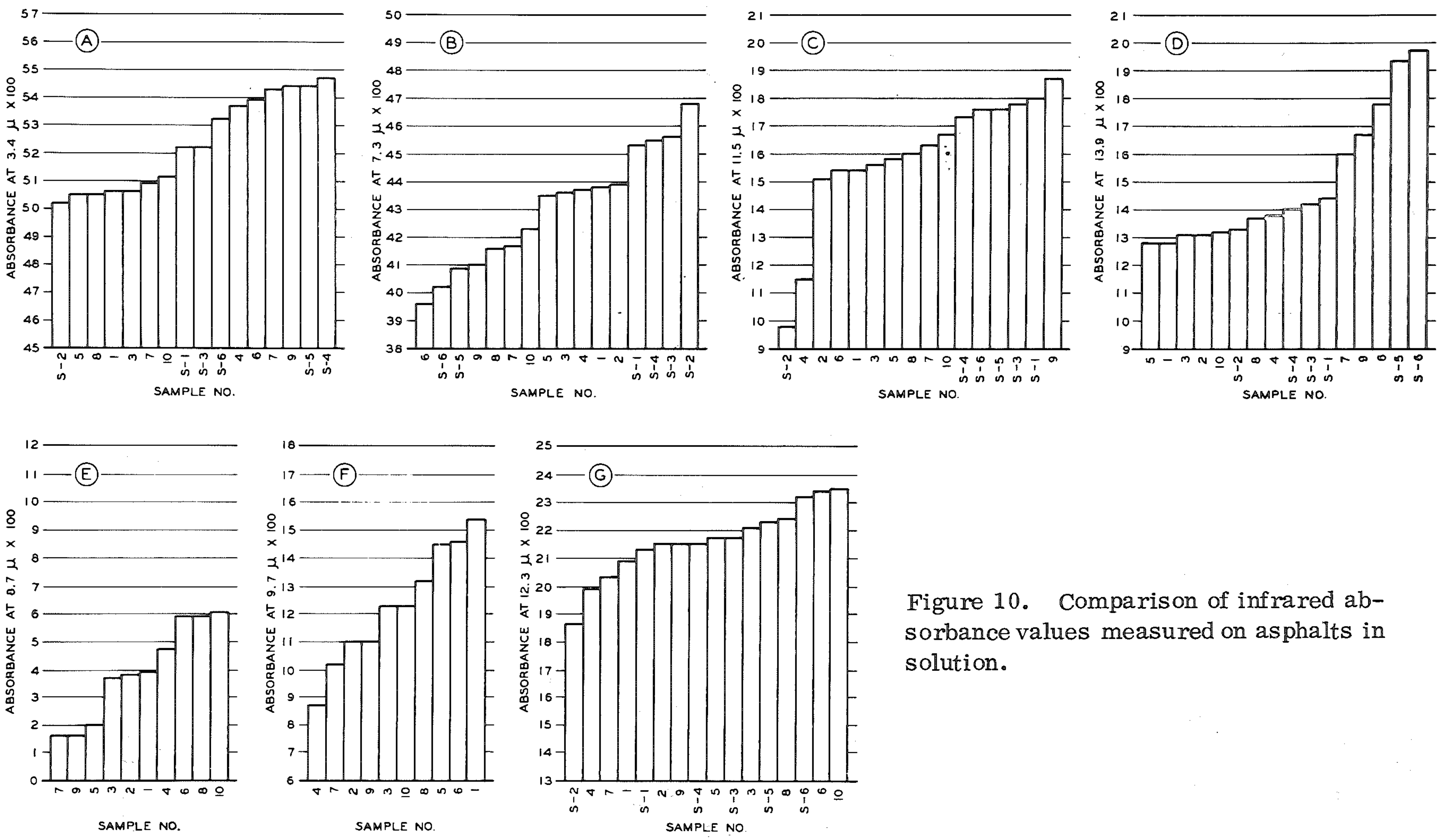


Figure 10. Comparison of infrared absorbance values measured on asphalts in solution.

Plots using data from four of the infrared absorption levels measured tend to separate the asphalts into groups according to crude oil source. Figure 11 is a plot of $\frac{A_{13.9}}{A_{7.3}}$ vs. $A_{3.4}$. This groups the asphalts from Wyoming crude oil together but does not give good separation of the other crude oil srouces. Figure 12 is a plot of $A_{11.5}$ vs. $A_{13.9}$. Asphalts from Venezuelan crude oil are isolated, and asphalts from Wyoming crude oil are again grouped in one area. The asphalt from West Texas crude oil falls in the same area as the Wyoming asphalts. East Texas and Arkansas asphalts also are not well separated.

The best separation according to crude oil sources was accomplished with a plot of $\frac{A_{11.5} + A_{13.9}}{A_{7.3}}$ vs. $A_{3.4}$ (Fig. 13). All of the known crude oil sources are separated to some extent, and the asphalts prepared from blends heavy in Wyoming crude oil are grouped in one area. The consistent moderate separation in all three of these plots between test road asphalts and new asphalts from Wyoming and Arkansas crude oils may stem from changes occurring during storage of the test road asphalts.

Asphalt Films

1) Oxidation Susceptibility - Infrared absorption by asphalt films applied to sodium chloride discs was measured at 5.9μ during oven aging and weatherometer exposure. Absorption at this wavelength is due to carbon-oxygen double bonding, and an increase in this absorption indicates that the asphalt has reacted with oxygen. Oxidation of an organic material generally results in decreasing strength and/or ductility.

Films of asphalt on sodium chloride discs were prepared using the procedure described in Appendix G. Asphalts 2, 8, and 10 were exposed in the weatherometer for 130 hours (light only). Asphalts 1, 2, 4, 5, 6, 7, 9, 10, S-2, S-3, and S-6 were exposed in an oven at 212 F for periods ranging up to 400 hours. Representative asphalts from all crude oil sources except West Texas were subjected to oven exposure.

The increase in absorbance at 5.9μ was nearly the same for oven and weatherometer exposure, so weatherometer exposure was discontinued. Figure 14 presents comparison results obtained during oven and weatherometer exposure for asphalts 2 and 10.

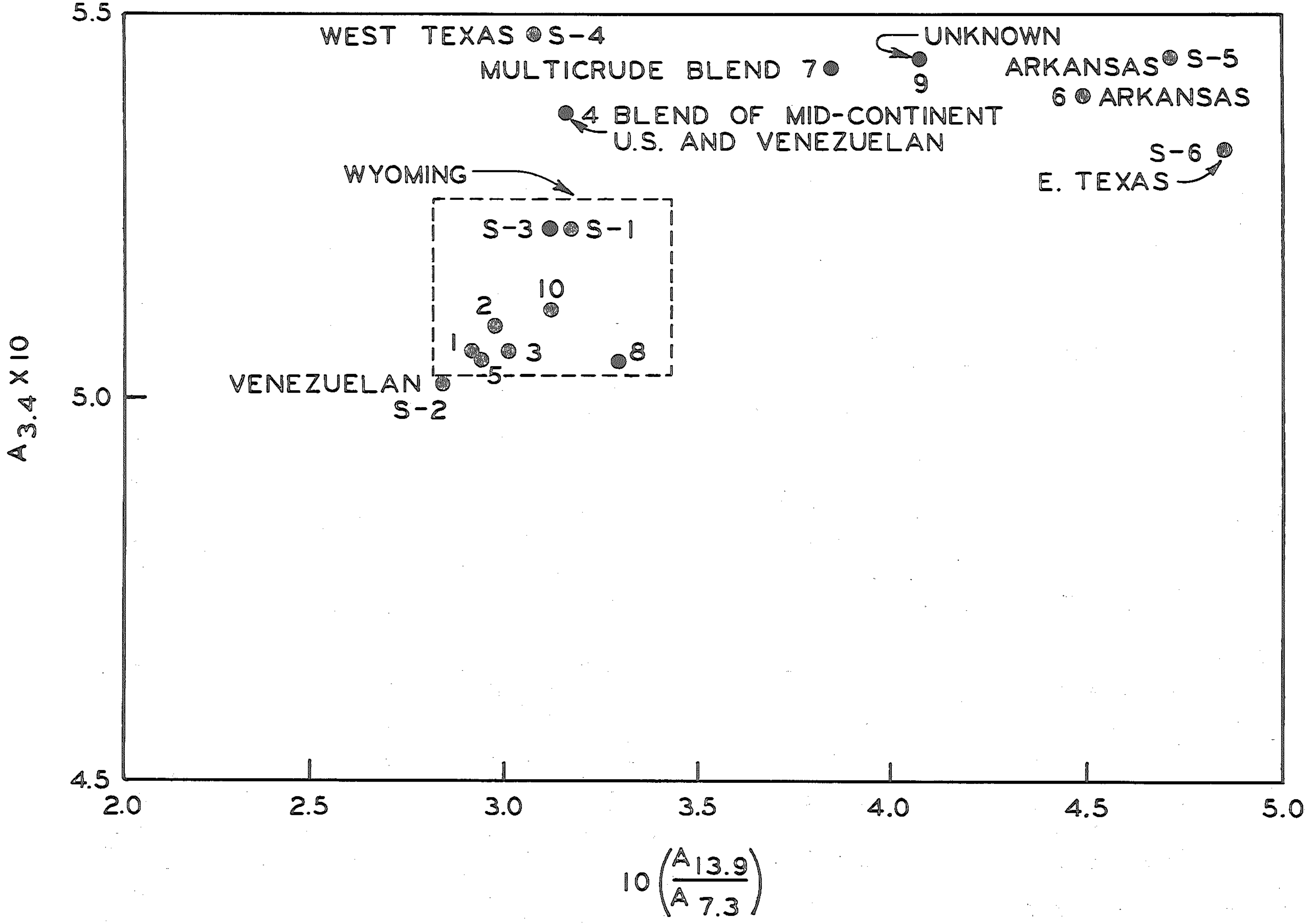


Figure 11. Separation of crude oil sources obtained by plotting $\frac{A_{13.9}}{A_{7.3}}$ vs. $A_{3.4}$.

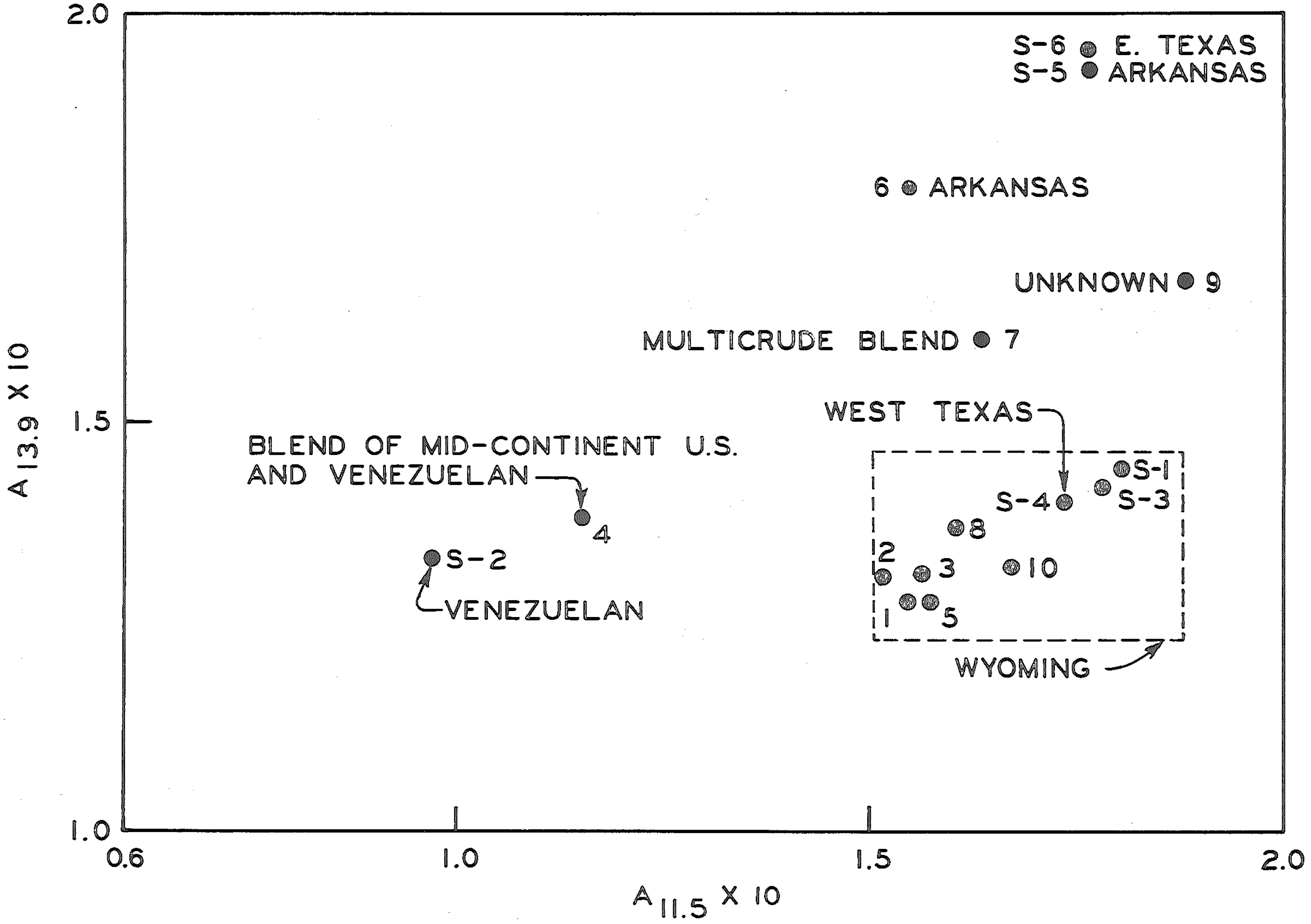


Figure 12. Separation of crude oil sources obtained by plotting $A_{11.5}$ vs. $A_{13.9}$.

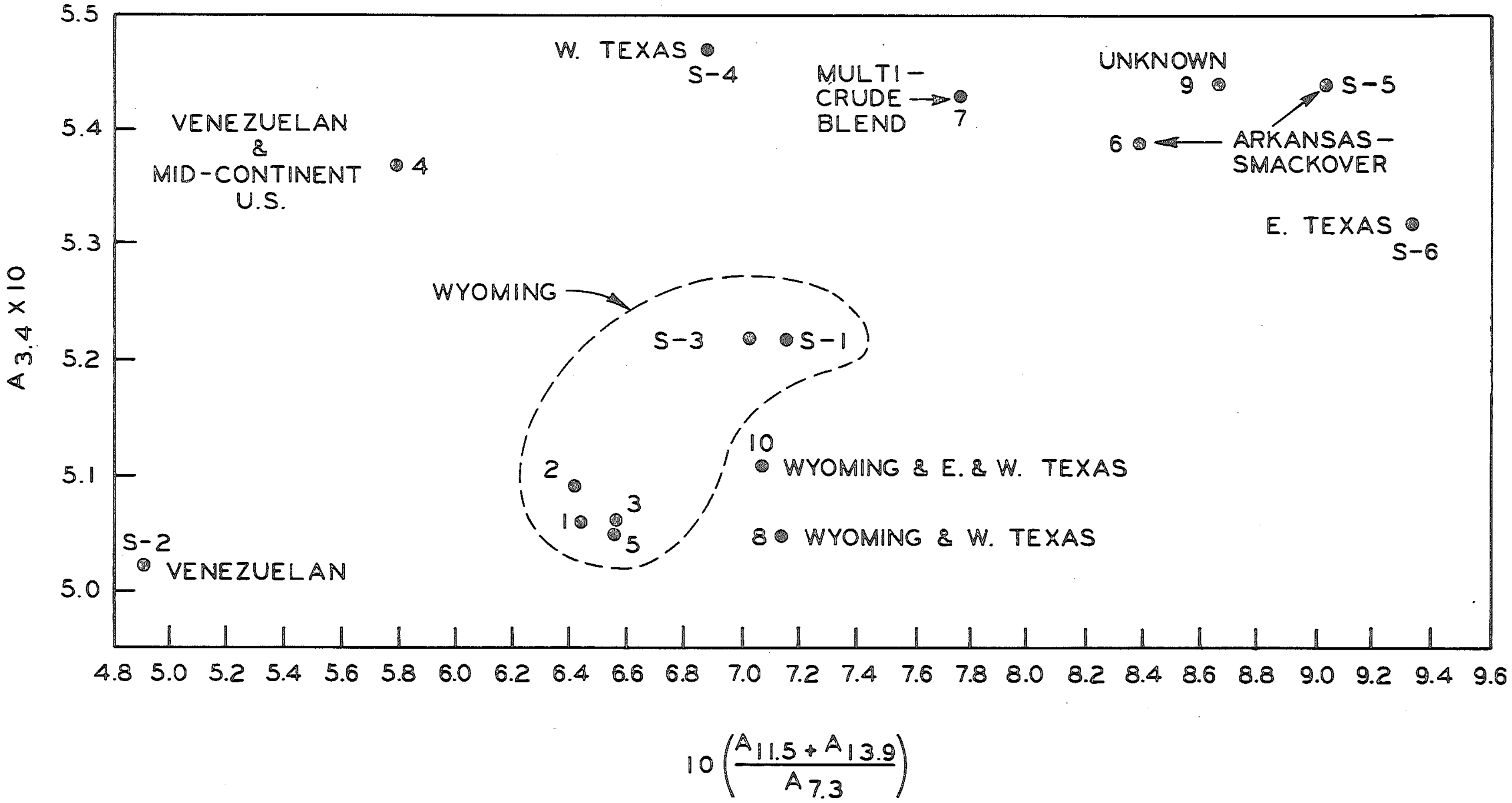


Figure 13. Separation of crude oil sources obtained by plotting $\frac{A_{11.5} + A_{13.9}}{A_{7.3}}$ vs. $A_{3.4}$.

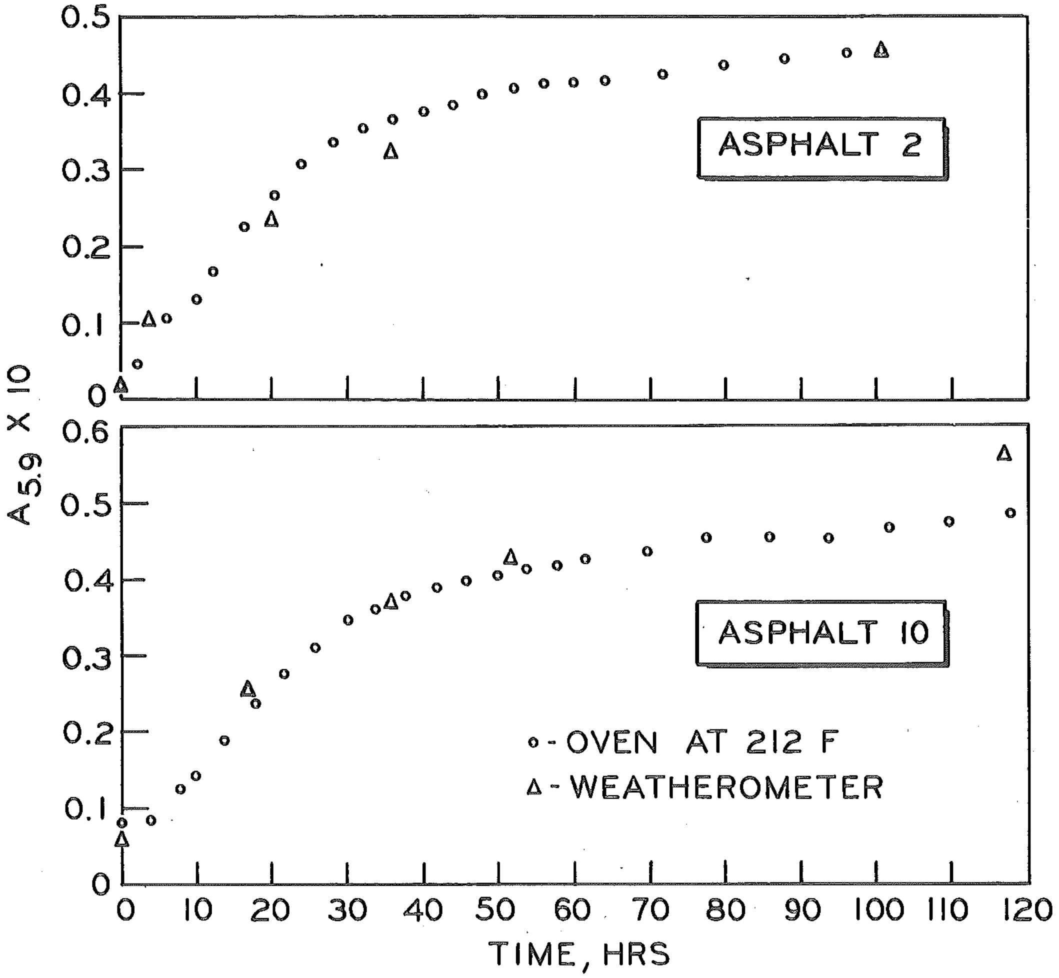
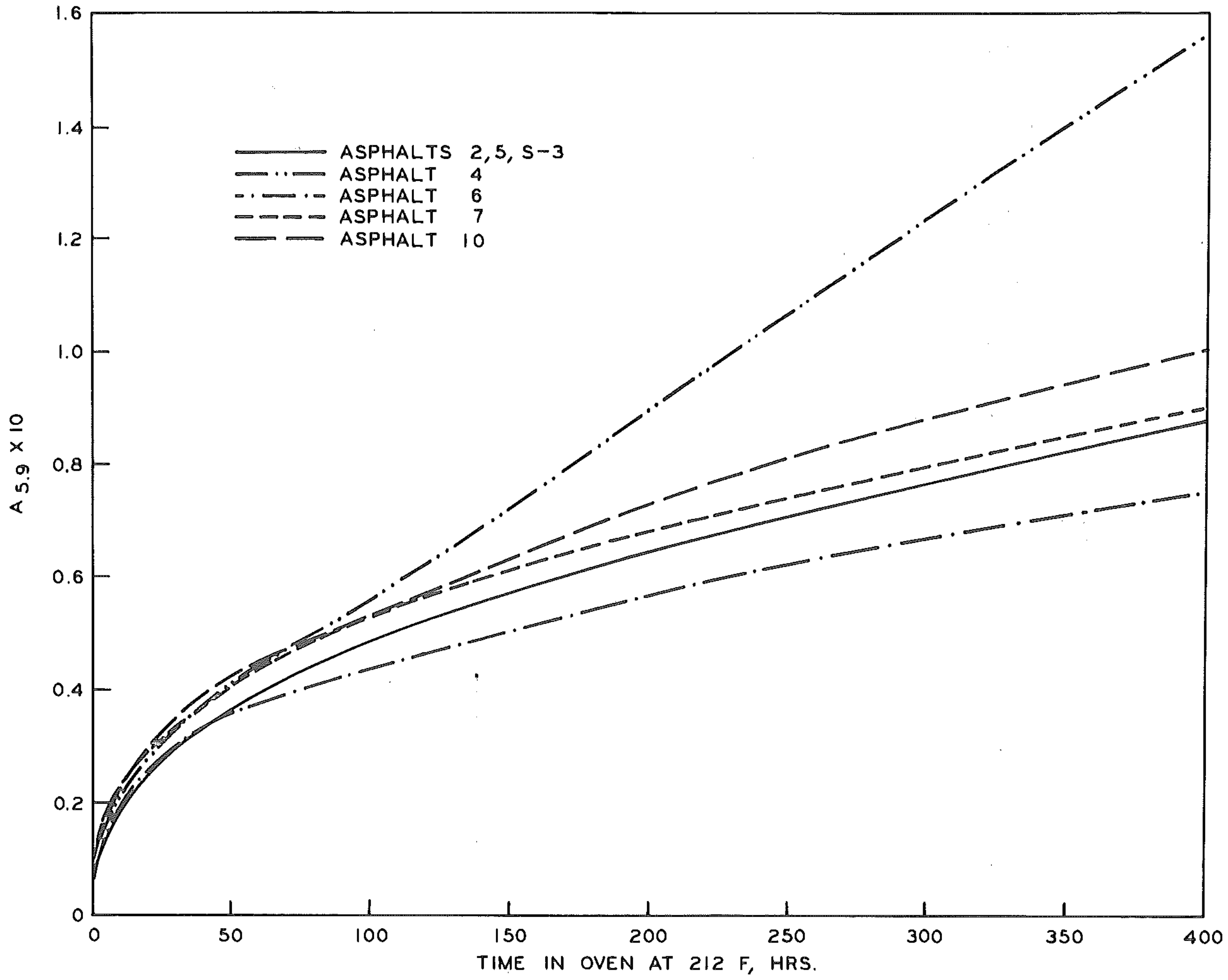


Figure 14. Comparison of increased absorbance at 5.9μ during weatherometer exposure and oven exposure.

The increase in absorbance at 5.9μ during oven exposure at 212 F is plotted in Figure 15. The first samples run (Group I) were terminated short of 200 hours because the background absorption became excessive. The Group II samples were run as thinner films, which permitted exposure time up to 400 hours. Asphalt 4 was run in both groups; Figure 16 shows the excellent agreement for the two runs. Absorbance data are tabulated in Appendix F.

With the exception of asphalt 9, which initially oxidized more rapidly than the other samples, oxidation rates were similar up to 100 hours exposure time. Beyond 100 hours, the oxidation rates of asphalts S-2 and 4, which are wholly or partly from Venezuelan crude oil, remained significantly greater than the remainder of the sample group.



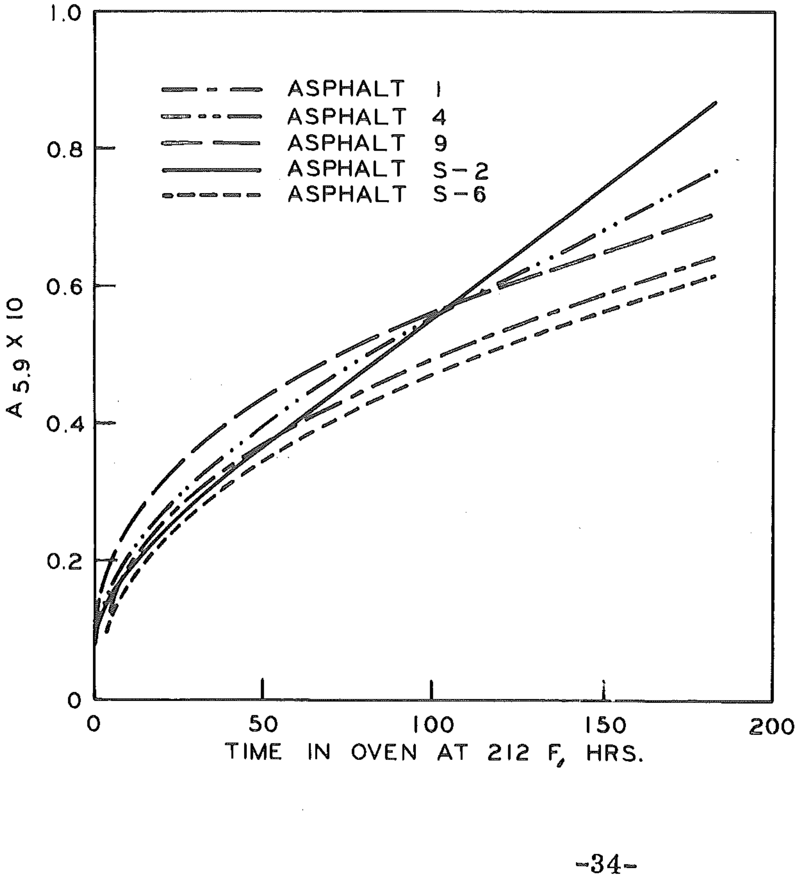


Figure 15. Increase in absorbance at 5.9μ during oven exposure at 212 F for asphalt groups I (left) and II (above).

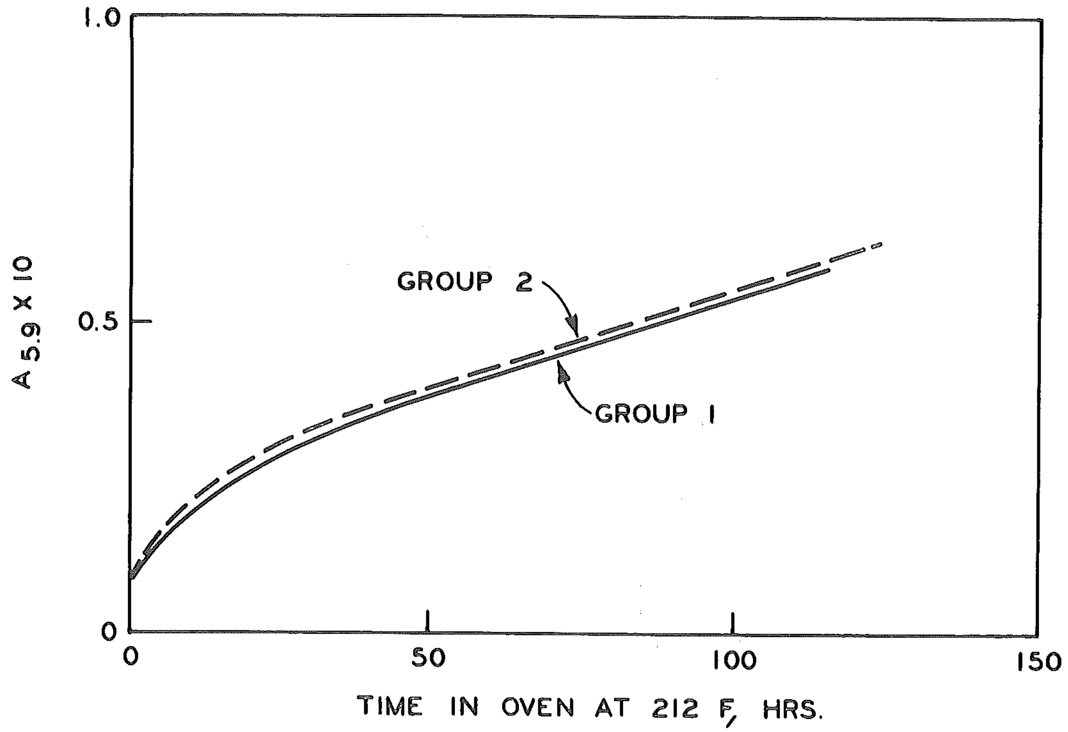


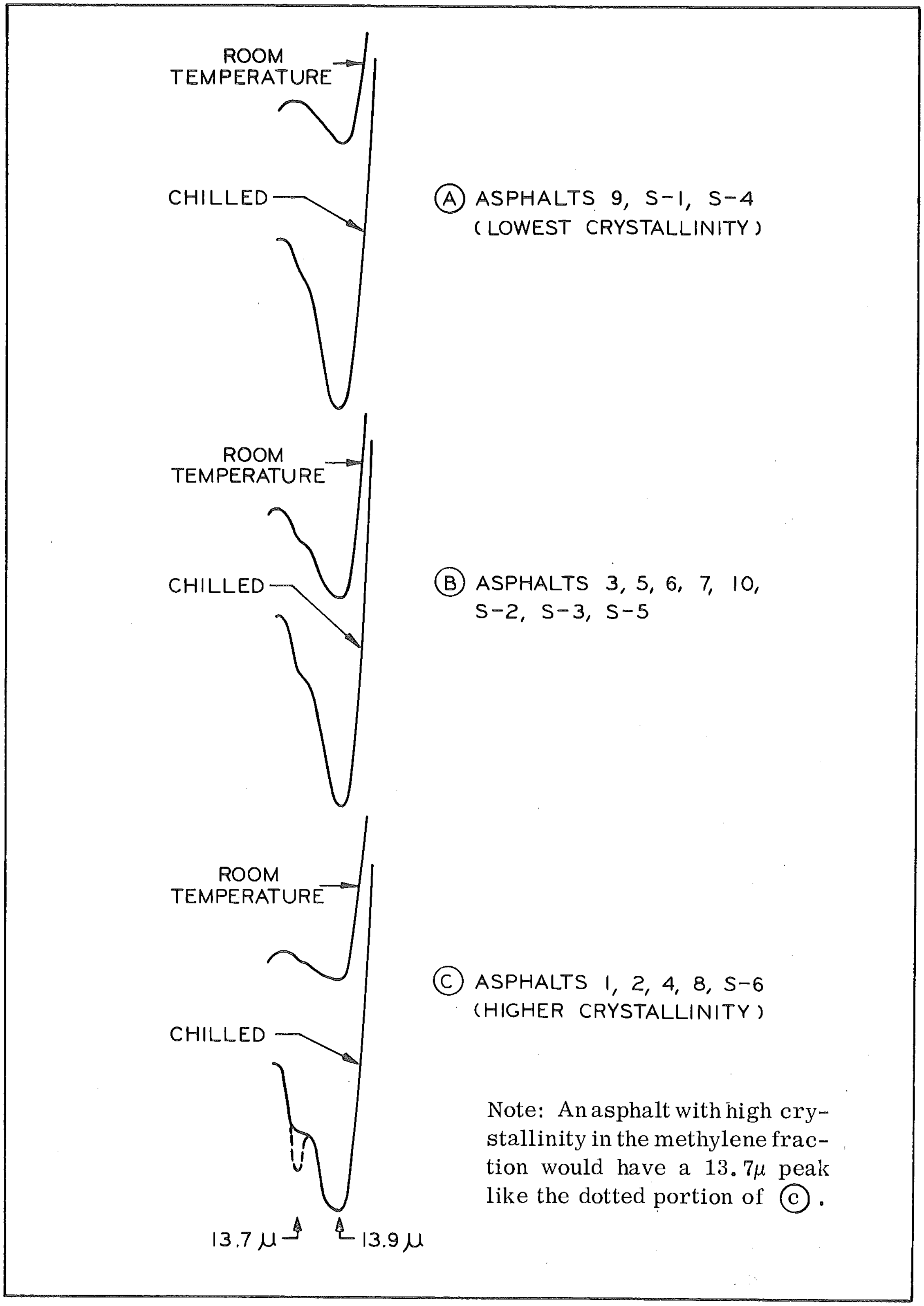
Figure 16. Comparison of two runs of oven exposure for asphalt 4.

2) Crystallinity of Methylene Chain Content - Coating (roofing) asphalts with high non-crystalline methylene chain $(-CH_2-)_{N>4}$ content are reported to have good weatherability (2). In addition to detracting from weatherability, crystalline behaviour in paving asphalts would be detrimental in that it would cause them to be brittle and likely to crack under load, especially at low temperature.

The crystallinity of methylene chains can be estimated from infrared absorption at 13.7 and 13.9μ when the sample is in the solid state. A crystalline methylenic compound absorbs at 13.7 and 13.9μ, but a non-crystalline compound absorbs mainly at 13.9μ.

Films of the asphalts on sodium chloride discs were scanned between 12.5 and 14.5μ at room temperature and at approximately -100 F. Experimental details are in Appendix G. The low temperature runs were made to observe the relative susceptibility of the asphalts to crystallization (with attending brittleness) at low temperature.

Three representative portions of infrared spectra are presented in Figure 17 to illustrate the 13.7 and 13.9μ absorption by these asphalts at room temperature and at approximately -100 F. None of the 16 asphalts studied appears to have sufficient crystallinity in the methylene fraction to



Note: An asphalt with high crystallinity in the methylene fraction would have a 13.7μ peak like the dotted portion of Ⓒ.

Figure 17. Typical spectra obtained for comparing crystallinity of the methylene fraction of asphalts.

adversely affect its weatherability or performance as a pavement binder. An asphalt with a highly crystalline methylene fraction would absorb at 13.7μ as shown by the dotted portion of part (c), Figure 17. Absorbance data are in Appendix F.

CORRELATION OF INFRARED DATA WITH DURABILITY DATA

Some of the infrared data obtained for asphalts in solution showed little correlation with crude oil sources or durability tests.

8.7μ - Data at this wavelength were recorded for the 1965 asphalts only. No correlations were observed.

9.7μ - Data were recorded for the 1965 asphalts only. The only correlation observed is that asphalt 4, which has the poorest weatherability and pellet tumbling test durability for the 1965 asphalt group has significantly lower absorbance at this wavelength than the other nine asphalts.

12.3μ - The only correlation noted at this wavelength is that asphalts 4 and S-2, which rate poorest in weatherability and pellet tumbling test durability, had the two lowest absorbance values. Asphalt S-2 also had the poorest durability of the test road asphalts in actual pavement service.

Empirical combinations of the remaining infrared absorbance data were made and compared with weatherometer data, pellet tumbling test data, and test road observations in an effort to develop an "Infrared Durability Index." Thirty-five such combinations are listed in Appendix F. The data used in Appendix F include measurements made on: a) solutions of asphalts at wavelengths of 3.4, 7.3, 11.5, and 13.9μ; b) films of asphalt on sodium chloride discs at 13.7 and 13.9μ, to determine crystallinity of the methylene fraction; and, c) films of asphalt on sodium chloride discs, at 5.9μ, following oven exposure at 212 F to determine oxidation susceptibility.

It was previously stated that none of the asphalts studied appeared to have sufficient crystallinity in their methylene fractions to adversely affect their performance as pavement binders. This is supported by the fact that combinations of infrared data utilizing the 13.7μ data did not correlate generally with durability data.

The infrared data combination which was adopted as a "Durability Index" because it could be correlated with the largest number of durability tests is listed first in Appendix F. Figure 18 shows a plot of the durability index $\frac{A_{11.5} + A_{13.9}}{A_{7.3}}$ vs. weatherometer data for the 1965 asphalts and Figure 19 presents the same correlation for pellet tumbling test data on all 16 asphalts.

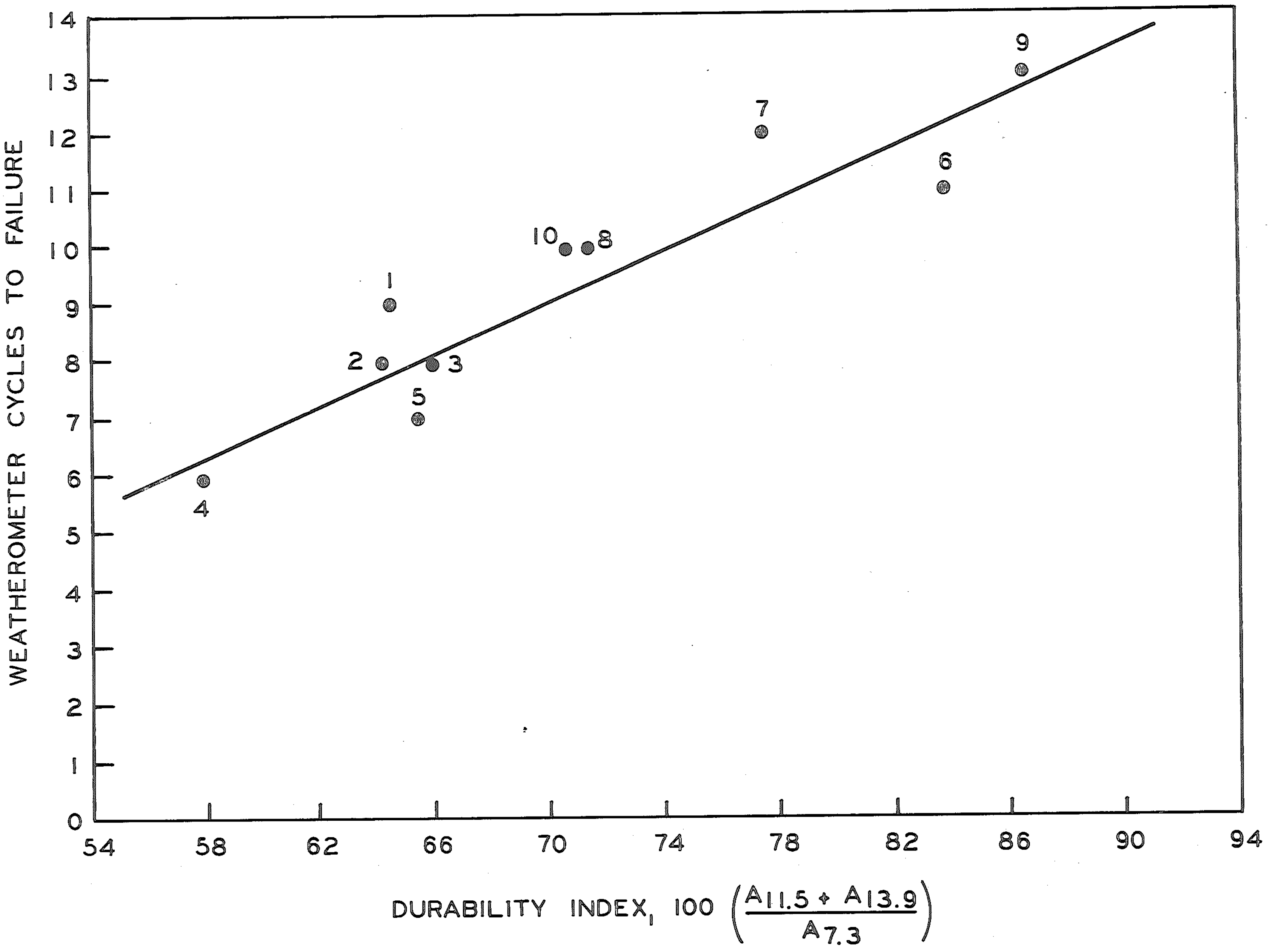


Figure 18. Correlation of weatherometer data and infrared absorbance data.

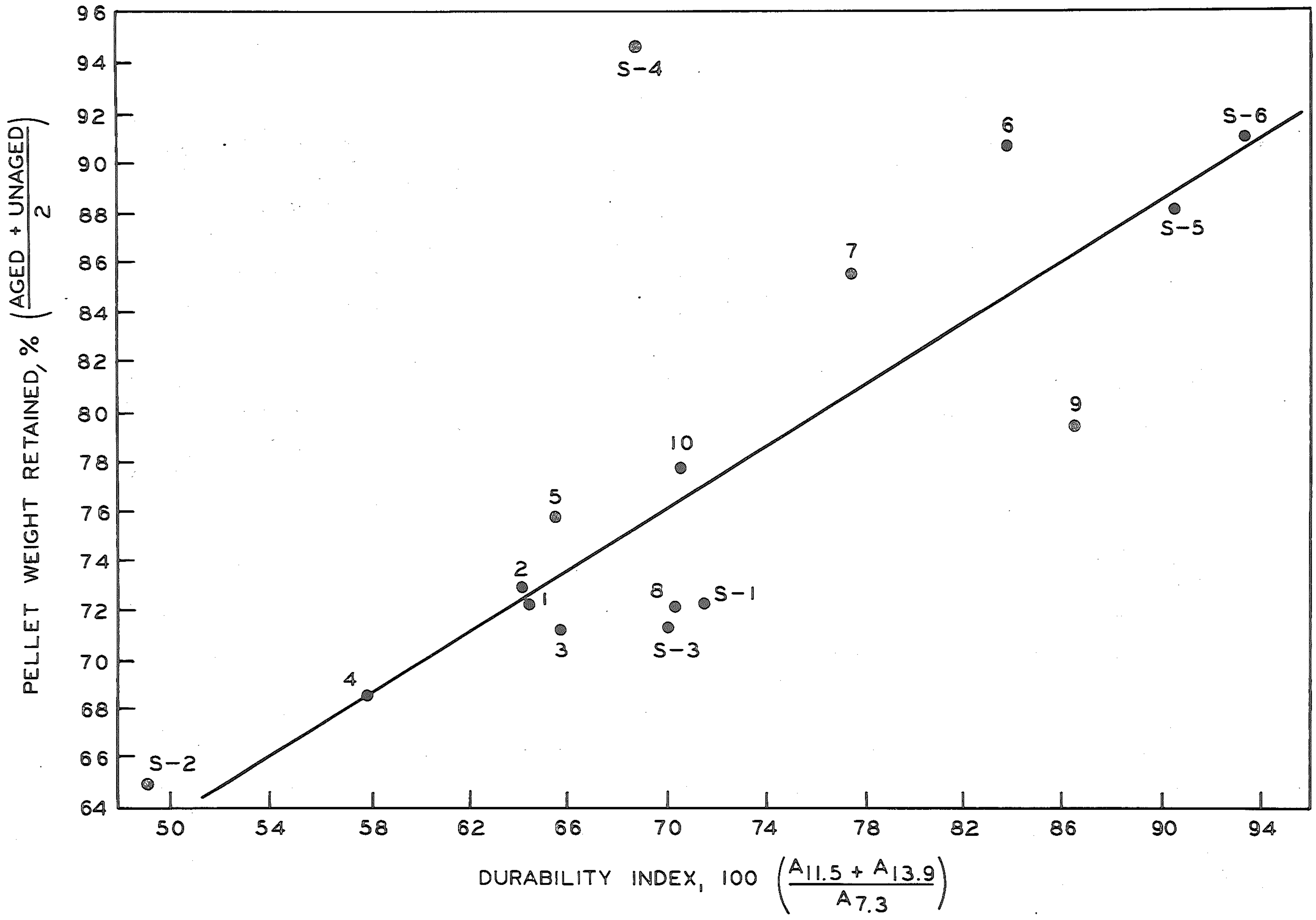


Figure 19. Correlation of pellet tumbling test data and infrared absorbance data.

Infrared data combinations 2 through 6 in Appendix F also yield rather good correlations with durability data, and representative plots are presented in Figures 20, 21, and 22. Data combinations 7 through 16 yield correlation plots similar to those already presented, with the various asphalts shifted relative to each other, so they are not shown. Data combinations 17 through 35 did not result in useful correlations with durability data.

It is readily apparent that high absorbance at 11.5 and 13.9μ correlates with good durability for asphalts from the crude oil sources studied, and that high absorbance at 7.3μ is indicative of poor durability. Oxidation susceptibility, as evidenced by increased observations at 5.9μ during oven exposure, also correlates with poor durability.

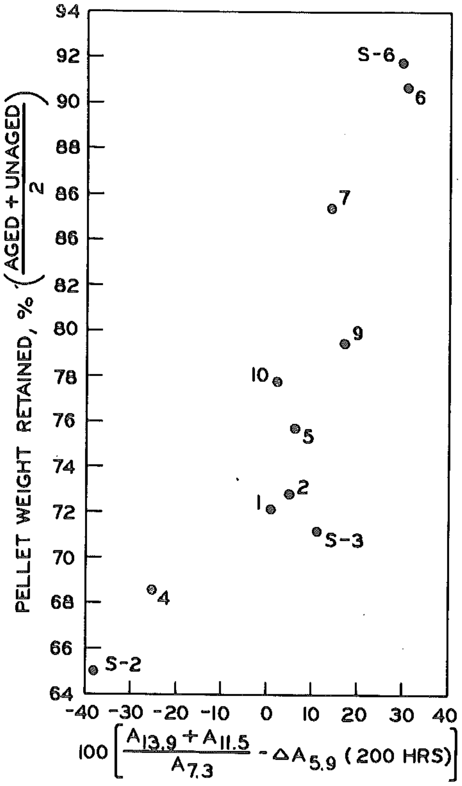


Figure 20. Correlation of infrared data (combination 2) and pellet tumbling test data. Data at 5.9μ available only for asphalts shown.

The agreement between averaged weatherometer data (1965 asphalts only) and the Infrared Durability Index (Fig. 18) is excellent. The largest deviation from the correlation line is about 1.5 weatherometer cycles. This deviation is comparable to the variation between repetitive weatherometer runs on the same asphalt. The infrared measurements are much more repeatable than the durability tests they are being correlated with. The asphalt from a blend of Venezuelan and Mid-Continent U. S. crude oils (asphalt 4) is correctly predicted by the Infrared Durability Index to have the poorest weatherability of the ten 1965 asphalts. The asphalts from Wyoming crude oil (asphalts 1, 2, 3, 5) are grouped together as having somewhat better weatherability than the asphalt from a blend of Venezuelan and Mid-Continent U. S. crude oil. Asphalts from a blend of Wyoming and Texas crude oils (asphalts 8, 10) are ranked close together with better weatherability than asphalts from straight Wyoming crude oil. Asphalts 6,

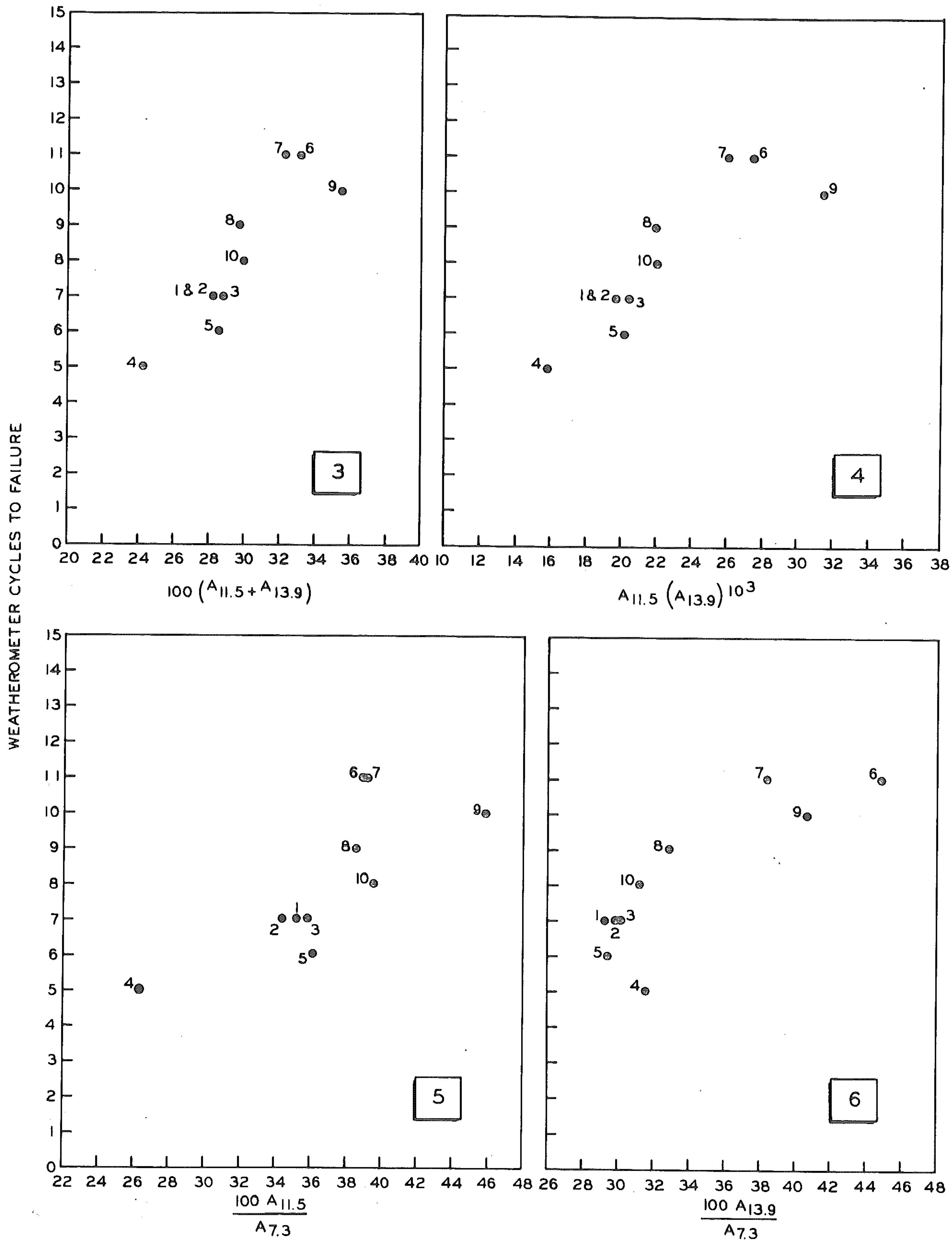


Figure 21. Plots of infrared data combinations 3 through 6 vs. weatherometer data.

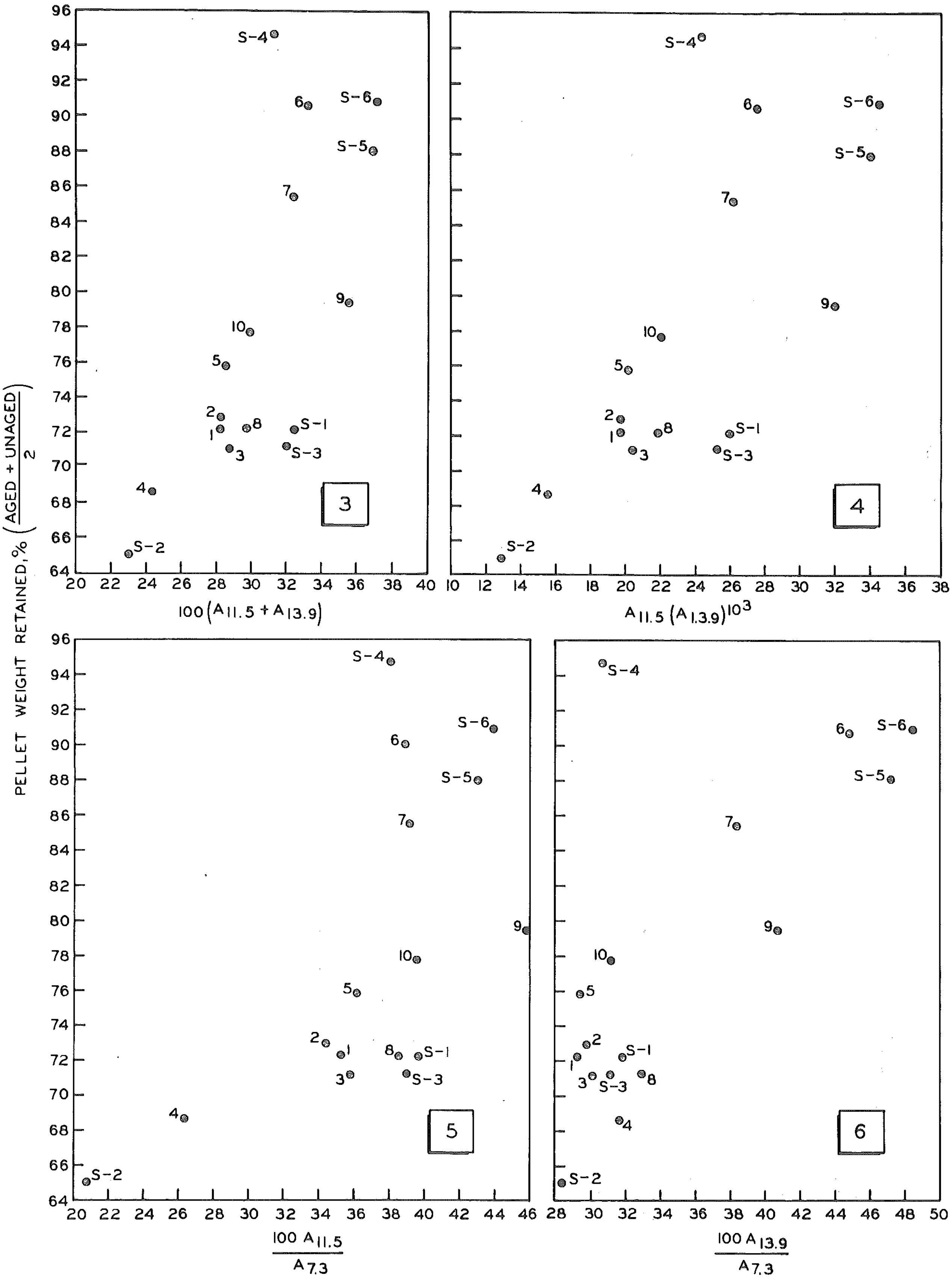


Figure 22. Plots of infrared data combinations 3 through 6 vs. pellet tumbling test data.

7, and 9 form a group with the best weatherability of the ten asphalts exposed in the weatherometer. Asphalt 6 is from Arkansas crude oil. Asphalt 7 was prepared from a blend of U. S. crude oils. The crude oil source for asphalt 9 was not identified by the supplier, but this asphalt was allegedly obtained from the supplier of asphalt 7.

The agreement between the Infrared Durability Index and pellet tumbling test data (Fig. 19) is also very good. The ten 1965 asphalts are found in relative positions similar to those that previously correlated with weatherometer data. Asphalt S-2 from Venezuelan crude oil is correctly predicted by the infrared data to be of lowest durability, ranking even lower than asphalt 4, from a blend of Venezuelan and Mid-Continent U. S. crude oils. Again, asphalts from Wyoming crude oil (asphalts 1, 2, 3, 5) are rated higher in durability than the asphalts from Venezuelan crude oil and asphalts 8 and 10 from the Texas-Wyoming blend of crude oils have slightly better durability than asphalts from straight Wyoming crude oil. Test road asphalts S-1 and S-3, also from Wyoming crude oil, are grouped with the asphalts from a blend of Texas-Wyoming crude oils by the Infrared Durability Index. This may be due to chemical changes in the test road asphalts during storage. The pellet tumbling test, however, yielded similar results for all the asphalts from Wyoming crude oil. Asphalts 6, 7, and 9 again form a group with somewhat better durability than the asphalts from a blend of Texas and Wyoming crude oils. Test road asphalts S-5 (Arkansas crude oil) and S-6 (East Texas crude oil) rank highest in durability of the samples that correlate well with infrared data.

Asphalt S-4 (West Texas crude oil) is considerably above the correlation line. It performs much better in the pellet tumbling test than is predicted by the infrared data. Asphalt S-4 is also unusual in that it softens on heat aging, rather than hardening as did all the other asphalts studied. This asphalt has an original penetration of 60 dmm and a penetration of 63 dmm after two hours at 500 F.

The infrared index correctly predicts that asphalt S-2 will produce a pavement lower in durability than the pavement produced by the other five test road asphalts. The Infrared Durability Index for asphalt S-2 is twenty units below the value obtained for asphalts that were in much better condition after 16 years of pavement service.

The infrared index does not correlate with pavement durability in the test road beyond predicting that asphalt S-2 will be less durable than the other five test road asphalts, however.

REFERENCES

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APPENDIX

APPENDIX A
PREPARATION OF TEST PANELS FOR ARTIFICIAL WEATHERING OF PAVING ASPHALT
(Adapted from ASTM D 1669-62)

Preparation of Metal Panels

1. Wash the 3 by 5-in. by 0.025 to 0.075-in. thick aluminum or aluminum alloy panels in carbon tetrachloride. Rinse them in clean solvent and wipe each panel with a clean cloth. Do not allow the fingers to touch the panel surface to be coated with asphalt. Use panels the same day they are cleaned to prevent oxidation or other contamination of the faces.

2. Measure the thickness of all panels at six representative points, using a micrometer, and classify them into groups of identical thickness.

3. Fasten each panel to a 6 by 9-in. sheet of Kraft paper with masking tape. Mask a 1/2-in. wide strip across one end of the panel and a 1/4-in. strip along the remaining sides.

4. Preheat the mounted panels individually on a hot plate. A temperature of 200 F is used for plain asphalt. Silica-filled asphalt required 400 F. Do not prolong the heating as the masking tape becomes difficult to remove.

Pressing the Asphalt Film

1. Heat the platens (6 by 6 in. minimum) of a hydraulic press capable of applying a five-ton load, to 185 F. These platens must have smooth, flat faces which are parallel when the press is closed.

2. Prepare two sets of spacers equal in thickness to the aluminum panel, plus the desired thickness of the asphalt film (0.010 to 0.012 in.). The spacers are made by piling up feeler gauges or shim stock pieces that are 1/2 in. wide and 6 in. long. Place one set of spacers on each of two opposing sides of the bottom platen.

3. Melt the asphalt to be used on a hot plate thermostatically controlled at 370 F. Add the asphalt to the melt container in increments as the melting proceeds. Stir gently during the melting process to avoid localized overheating, or incorporation of air into the asphalt. (Melt silica-filled asphalt in an oven at 400 F.)

4. Pour approximately 1.25 times the quantity of asphalt needed onto the warmed panel. Tap the panel to dispel air bubbles, then cover the asphalt surface with a sheet of release paper ("Patapar Releasing Paper" manufactured by Paterson Parchment Paper Co., Bristol, Pa., was found satisfactory).

5. Place the panel in the hydraulic press between the spacers. The spacers must be under the Kraft paper but not under the masking tape.

6. Close the press slowly so that the asphalt may flow as pressure is applied to reach a final load of five tons, which is held for about 30 seconds. Remove the panel from the press and allow it to cool to room temperature.

Measurement

1. Measure the combined thickness of the panel, asphalt film, backing paper, release paper, and a 1-in. square metal plate which protects the asphalt film from denting, at six representative locations. Subtract the known thicknesses of the other components to find the asphalt film thicknesses. The film must have uniform thickness to within ± 0.001 in.

2. Remove the release paper from the asphalt surface and strip the masking tape from the edges of the panel.

3. Identify the panel by scratching with a stylus in the 1/2-in. margin. Start weathering the panels within 48 hours of preparation.

APPENDIX B
PROCEDURE FOR BLENDING ASPHALT AND COLLOIDAL SILICA

1. Weigh 62.8 g of asphalt into a 150 ml beaker, and 7.2 g of colloidal silica into another small container.

2. Heat the asphalt and colloidal silica in an oven at 400 F for 10 minutes, then remove from the oven and place on a small pre-heated hot plate covered with an asbestos pad. The hot plate should be adjusted to maintain a temperature of 400 F in the final blend.

3. Using a bunsen burner, pre-heat the blades and shaft of a counter-rotating mixer with a variable speed control (a Brookfield Model L 602 mixer was adapted to produce high shear with a minimum vortex formation by reducing the pitch of the blades and decreasing the distance between the blades).

4. Note the starting time and commence stirring the asphalt. Add the silica by sifting from a spatula as rapidly as it is incorporated into the blend. Agitate as rapidly as possible without entrapping air or losing sample. Advance the speed control on the mixer as the blend thickens, keeping the degree of agitation as constant as possible. Complete the addition of silica to the asphalt in eight to nine minutes.

5. Continue agitation at high speed for the remainder of an exact 10-minute period of agitation, but avoid vortex formation.

6. Return the blend to the 400 F oven for five minutes to allow trapped air to escape.

7. Remove the blend from the oven, stir it gently with a small stainless steel spatula, and pour it into aluminum moisture dishes, dividing the sample into three parts.

8. Prepare test panels by the procedure reported in Appendix A.

APPENDIX C

PROCEDURE FOR ASPHALT PELLET TUMBLING TEST

Preparation of Mix

1. Preheat 175 g of 30 to 40 mesh glass beads for 1 hr ± 10 min at 325 F.

2. Preheat 4 g of asphalt in a 600 ml beaker for six minutes at 325 F, in an oven.

3. Remove the beaker of asphalt from the oven and place it in a heating mantle coupled with a variable transformer adjusted to maintain the final mix at a temperature of 325 F.

4. Add the beads to the asphalt and mix with a spatula for six minutes.

5. At the end of the six minute mixing, pour the mix into a suitable container to cool. A 4-in. diameter ointment can lid is satisfactory. Material to be aged is set aside at this time.

Aging

1. Place a 1/2-in. level layer of mix (about 60 g) in a suitable flat dish, such as an ointment can lid.

2. Age the mixture in a vented oven at 140 F for the required time.

3. After aging stir the mix gently and transfer to a closed container for storage at a temperature of -20 F.

Homogenization and Sampling

1. Cool the mix to -20 F and crush it into 5 to 10 bead units maximum, using a chilled metal roller.

2. Place the crushed mix into a chilled container and cool to -20 F.

3. Stir the cold mix to achieve homogeneity and weigh out 2.05 ± 0.05 g portions. A flattened aluminum moisture dish is a good sample container. Store unused material at -20 F.

4. Store the weighed portions of mix at 77 F overnight.

Formation of Pellets

1. Condition the pellet die to 77 F. Pellets used were cylinders 0.5 in. in diameter by 0.5 in. high.

2. Transfer the mix to the die chamber and assemble the die.

3. Press the pellet with a force of 200 lb on the ram for one minute by stopwatch.

4. Weigh each pellet to 0.01 g.

5. Condition the pellets for at least one hour at the temperature at which they are to be tumbled.

Tumbling

1. Place a weighed, conditioned pellet in a 16 oz French-style, square glass bottle.

2. Rotate the bottle about its longitudinal axis in a horizontal position for 500 ± 10 revolutions at 90 rpm, in an oven controlled at 77 F.

3. After tumbling, carefully remove the largest piece of pellet from the bottle and weigh to 0.01 g.

4. Calculate the percent of pellet weight lost.

APPENDIX D

PELLET TUMBLING TEST DATA
(Aged and Unaged Mixes)

PELLET TUMBLING TEST DATA
(1965 Asphalts - 30-40 mesh glass bead mixes)
Unaged mixes

	Asphalt	Weight Loss, percent						Avg.	Adj. avg.
		Pellet 1	Pellet 2	Pellet 3	Pellet 4	Pellet 5	Pellet 6		
RUN 1	1	22.9	16.2	19.2	14.8	14.2	12.4	16.6	22.4
	2	19.2	21.0	15.4	16.0	16.7	11.9	16.7	22.5
	3	19.6	19.5	20.4	18.1	12.3	10.7	16.7	22.5
	5	15.1	15.2	14.5	12.9	14.6	13.6	14.3	(19.3)
	6	4.9	3.7	2.8	3.3	2.8	3.4	3.4	4.6
RUN 2	4	14.4	12.8	16.7	14.9	12.8	13.9	14.2	29.8
	5	10.6	9.1	8.4	10.0	8.8	8.5	9.2	(19.3)
	7	3.0	3.8	3.1	2.6	3.1	5.4	3.5	7.3
	8	12.2	13.3	10.1	11.0	10.8	7.8	10.8	22.6
	10	10.7	6.0	9.3	7.9	7.8	11.3	8.8	18.4
RUN 3	1	27.2	26.3	23.6	18.2	15.2	14.8	20.8	22.3
	3	30.8	30.4	19.0	18.5	17.1	11.8	21.2	22.6
	4	26.7	24.0	24.8	25.0	23.7	17.1	23.5	25.0
	5	25.1	25.0	20.0	16.6	14.6	12.2	18.1	(19.3)
	9	24.2	20.3	16.4	15.8	14.4	15.0	17.6	18.8
RUN 4	5	21.3	26.8	23.9	21.8	11.8	17.3	20.4	(19.3)
	6	5.6	12.8	7.9	6.3	4.9	3.8	6.8	6.4
	7	20.3	14.6	10.9	7.0	5.4	6.2	10.7	10.1
	9	28.9	23.6	21.2	14.3	14.0	12.7	19.1	18.1
	10	24.0	22.6	14.0	15.8	12.3	11.2	16.6	15.7
RUN 5	2	38.2	37.5	34.0	22.0	27.8	23.4	30.4	21.3
	3	35.0	34.5	29.8	31.1	22.5	20.9	29.8	20.2
	5	30.4	33.0	30.5	28.2	22.8	20.1	27.5	(19.3)
	8	33.3	33.6	---	31.3	27.3	24.2	29.9	21.0
	10	27.0	26.0	22.0	23.8	17.2	18.6	22.4	15.7
RUN 6	1	19.6	18.8	15.9	15.7	12.7	9.6	15.3	20.0
	5	20.5	18.5	13.1	14.5	10.9	11.5	14.8	(19.3)
	6	4.9	6.5	4.8	2.5	4.2	5.9	4.8	6.3
	7	10.4	5.3	5.0	5.8	5.0	3.8	5.8	7.6
	9	16.6	15.7	10.3	14.1	9.9	8.9	12.5	16.3
RUN 7	2	36.2	35.7	30.6	28.8	27.8	27.0	31.0	20.8
	3	33.2	31.5	28.5	19.8	22.2	22.1	26.2	17.6
	4	34.1	34.8	31.1	27.1	24.0	24.9	29.3	19.7
	5	35.0	34.1	26.8	28.1	---	19.6	28.7	(19.3)
	8	33.8	33.0	27.1	29.0	24.2	23.4	28.4	19.1
RUN 8	1	27.9	24.3	22.6	21.6	21.5	21.8	23.2	20.8
	2	25.1	25.8	22.4	23.1	24.6	25.4	24.4	21.9
	5	22.8	24.7	---	18.6	20.8	20.6	21.5	(19.3)
	7	15.6	13.2	11.7	12.4	7.9	9.2	11.6	10.4
	10	19.5	19.9	22.2	18.2	23.4	19.7	20.4	18.3

PELLET TUMBLING TEST DATA
(1965 Asphalts - 30-40 mesh glass bead mixes)
Mixes aged 7 days at 140 F

	Asphalt	Weight Loss, percent				Avg.	Adj. avg.
		Pellet 1	Pellet 2	Pellet 3	Pellet 4		
RUN 1	1	42.2	38.1	28.4	29.1	34.4	37.1
	3	39.7	36.0	29.1	29.2	33.5	36.2
	4	40.8	18.7	31.9	32.0	30.8	33.2
	5	33.6	32.7	21.5	20.4	27.0	(29.2)
	6	10.6	14.9	20.2	6.1	12.9	13.9
	7	21.6	19.7	12.4	14.7	17.1	18.5
	8	35.6	34.8	29.1	26.9	31.6	34.1
	9	25.5	23.7	17.6	17.6	21.1	22.8
RUN 2	2	20.2	25.3	18.5	20.7	21.1	31.4
	3	31.5	24.4	23.3	22.9	25.5	38.0
	4	36.7	26.3	31.9	27.8	30.6	45.6
	5	20.2	21.7	14.5	22.0	19.6	(29.2)
	6	5.8	7.7	4.0	4.3	5.4	8.0
	7	13.1	13.5	10.4	15.2	13.0	19.4
	8	29.0	24.6	26.8	29.8	27.5	41.0
	10	22.1	20.4	22.8	21.2	21.6	32.2
RUN 3	1	43.0	44.6	38.3	31.2	39.2	31.0
	4	47.1	---	41.3	40.2	42.8	33.8
	5	40.2	41.9	32.6	33.1	36.9	(29.2)
	6	25.0	23.1	15.2	11.2	18.6	14.7
	7	27.8	31.8	23.4	23.8	26.7	21.1
	8	42.1	45.9	33.6	32.8	38.6	30.5
	9	35.0	31.5	28.4	30.2	31.2	24.6
	10	33.2	28.8	27.9	30.0	30.0	23.7
RUN 4	2	45.3	42.1	34.1	34.2	38.9	33.8
	4	44.9	46.2	47.5	46.2	46.2	40.2
	5	38.2	38.6	28.6	29.2	33.6	(29.2)
	6	19.7	24.3	13.7	11.4	17.3	15.0
	7	32.5	27.8	21.6	22.2	26.0	22.6
	8	42.3	39.8	37.8	32.8	38.2	33.2
	9	31.8	29.6	21.4	21.8	26.2	22.8
	10	33.2	31.5	---	28.0	30.9	26.9

PELLET TUMBLING TEST DATA
(Test Road Asphalts - 30-40 mesh glass bead mixes)
Unaged mixes

	Asphalt	Weight Loss, percent				Avg.	Adj. avg.
		Pellet 1	Pellet 2	Pellet 3	Pellet 4		
RUN 1	5	29.6	36.5	16.2	20.9	25.8	(19.3)
	9	27.9	30.3	18.8	14.7	22.9	17.1
	S-1	41.6	36.4	25.8	24.2	32.0	23.9
	S-2	47.0	35.4	38.4	27.4	37.0	27.7
	S-3	39.7	38.8	23.9	24.5	31.7	23.7
	S-4	5.1	3.2	3.6	2.6	3.6	2.7
	S-5	20.9	15.9	10.8	8.2	13.9	10.4
	S-6	13.5	15.4	7.5	9.6	11.5	8.6
RUN 2	5	21.8	18.7	15.0	18.4	18.4	(19.3)
	9	13.0	17.9	14.4	11.7	14.2	14.9
	S-1	29.0	24.1	23.0	22.4	24.6	25.8
	S-2	35.9	33.8	39.2	35.5	36.1	37.9
	S-3	27.1	33.4	28.1	26.8	28.8	30.2
	S-4	3.6	3.2	3.8	3.1	3.4	3.6
	S-5	10.5	9.8	9.8	7.4	9.4	9.9
	S-6	8.3	7.5	5.2	9.2	7.5	7.9
RUN 3	5	32.2	34.2	23.7	25.8	28.9	(19.3)
	9	30.5	34.5	24.0	23.8	28.2	18.8
	S-1	46.5	44.3	34.7	31.4	39.2	26.2
	S-2	58.4	43.4	37.9	39.4	44.8	29.9
	S-3	40.1	42.3	35.2	31.5	37.3	24.9
	S-4	9.0	9.6	4.0	3.0	6.4	4.3
	S-5	21.8	19.6	12.7	12.4	16.6	11.1
	S-6	16.4	20.9	6.3	9.7	13.3	8.9
RUN 4	5	28.0	35.8	28.2	23.1	28.7	(19.3)
	9	31.4	30.2	18.5	23.7	26.0	17.5
	S-1	44.4	43.8	29.0	31.2	37.1	24.9
	S-2	44.8	45.9	40.8	38.6	42.5	28.6
	S-3	40.8	46.0	35.6	28.3	37.7	25.3
	S-4	8.9	7.2	3.9	4.2	6.0	4.0
	S-5	25.7	23.0	10.4	11.4	17.6	11.8
	S-6	15.5	20.7	9.5	10.9	14.2	9.5
RUN 5	5	31.5	27.5	21.9	23.6	26.1	(19.3)
	9	28.1	25.5	34.7	20.3	27.2	20.1
	S-1	40.0	38.7	34.7	32.5	36.5	27.0
	S-2	---	43.2	36.5	41.7	40.5	29.9
	S-3	35.5	33.0	33.9	26.3	32.2	23.8
	S-4	---	7.3	5.5	4.3	6.0	4.2
	S-5	17.0	19.9	13.0	13.1	15.8	11.7
	S-6	18.0	20.0	10.1	10.4	14.6	10.8

PELLET TUMBLING TEST DATA
(Test Road Asphalts - 30-40 mesh glass bead mixes)
Mixes aged 7 days at 140 F

	Asphalt	Weight Loss, percent				Avg.	Adj. avg.
		Pellet 1	Pellet 2	Pellet 3	Pellet 4		
RUN 1	5	53.5	56.5	47.2	48.7	51.5	(29.2)
	9	42.1	50.1	40.7	35.7	42.2	23.9
	S-1	52.3	57.8	47.4	44.2	50.4	28.6
	S-2	66.0	---	74.9	58.0	66.3	37.6
	S-3	58.9	54.6	48.4	45.1	51.8	29.4
	S-4	19.1	17.7	11.6	9.0	14.4	8.2
	S-5	32.2	27.2	18.9	23.2	25.5	14.4
	S-6	23.8	25.7	14.3	12.6	19.1	10.8
RUN 2	5	35.5	34.9	31.0	28.9	32.6	(29.2)
	9	26.4	27.4	20.8	22.4	24.2	21.6
	S-1	39.8	40.4	32.7	30.0	35.7	32.0
	S-2	47.7	48.2	48.7	48.2	48.2	43.1
	S-3	40.3	41.4	41.9	40.5	40.7	36.4
	S-4	8.5	6.2	4.9	6.0	6.4	5.7
	S-5	15.2	15.2	10.9	9.2	12.6	11.3
	S-6	9.7	7.6	7.6	6.1	7.8	7.0
RUN 3	5	53.0	48.0	37.5	33.9	43.1	(29.2)
	9	42.0	43.9	33.4	30.1	37.3	25.3
	S-1	50.4	51.7	36.4	35.6	43.5	29.5
	S-2	60.3	56.9	49.5	52.5	54.8	37.1
	S-3	46.3	49.4	46.0	39.0	45.2	30.6
	S-4	14.2	13.2	5.7	5.9	9.7	6.6
	S-5	25.5	23.6	17.2	11.9	19.5	13.2
	S-6	20.3	17.0	9.9	9.5	14.1	9.6

APPENDIX E
QUANTITATIVE INFRARED MEASUREMENTS ON ASPHALT SOLUTIONS

Preparation of Solutions

1. Weigh approximately the ideal weight of asphalt listed in the chart below into a 25 ml sample bottle equipped with a screw cap.

Region	Solvent	Solution Concentration	Ideal Weight
7.5μ to 15μ	CS_2	100 g/liter	1.00 g
6.8μ to 8.4μ	CCl_4	40 g/liter	0.40 g
2.7μ to 4.5μ	CCl_4	4 g/liter	0.04 g

2. Calculate the volume of solvent needed to prepare a solution of the desired concentration by using the following relationship.

$$\text{Milliliters of solvent needed} = \frac{\text{actual weight of sample}}{\text{ideal weight of sample}} \times 10 \text{ ml}$$

3. Add the required volume of solvent to the sample bottle by means of a burette fitted with a teflon stopcock.

4. Immediately cap the sample bottle with a screw cap lined with aluminum foil.

5. Allow the asphalt to dissolve with occasional mild agitation.

Standardization of Infrared Spectrophotometer

1. Set up the spectrophotometer.

Control settings for a Perkin-Elmer Model 21 spectrophotometer were:

Resolution	984 (fairly wide slits)
Speed	50 sec/μ

Slight upscale drift on balance - 2 min for pen to travel from 50 to 80 percent transmittance.

2. Place a 1 mm pathlength cell filled with high purity benzene in the sample beam.

3. Scan the 3 to 6μ region using chart paper scaled in absorbance units.

4. Measure the baseline absorbance of bands near 3.76, 3.86, 4.19, 4.28, and 4.51μ.

5. Retain the data for reference.

6. Prior to running a series of asphalts, make an instrument check by repeating steps 1 to 4. Use the same cell and the same source of benezene as in (2) above.

7. Compare the results with the reference data.

8. If the data do not agree to within 0.002 absorbance units, make a minor adjustment in the slit program.

9. Repeat scans until the baseline absorbance at all five bands agrees with the reference data to within 0.002 absorbance unit.

Recording Sample Data

1. Fill a calibrated, fixed thickness cell (path length approximately 1 mm) with the asphalt solution. Position the cell in the sample beam.

2. Place a variable path length cell filled with the proper solvent in the reference beam and adjust the path length to balance out the absorption by the solvent in the asphalt solution.

3. Scan the region of interest, using chart paper scaled in absorbance units.

4. Measure the baseline absorbance of the peak of interest.

APPENDIX F
DATA COMBINATIONS USED FOR CORRELATING INFRARED AND DURABILITY DATA

Explanation of Notation:

A_N is absorbance at Nμ for an asphalt in solution, data reported in Table F-1 which follows. The values of N used here are 3.4, 7.3, 11.5, and 13.9.

$A_{13.7}$ r or c or $A_{13.9}$ r or c is absorbance at 13.7 or 13.9μ of the asphalt film used for crystallinity determination, corrected for film thickness. r = room temperature data, c = chilled film data. These data are reported in Table F-2 which follows.

$A_{5.9}$ (100 hr) is absorbance at 5.9μ of the asphalt film used for oven exposure at 212 F, corrected for film thickness, after 100 hr of exposure.

$A_{5.9}$ (200 hr) is the increase in absorbance at 5.9μ, corrected for film thickness, when an asphalt is exposed in an oven at 212 F for 200 hr. All 5.9μ data are reported in Table F-3 which follows.

1. $\frac{A_{11.5} + A_{13.9}}{A_{7.3}}$

2. $\frac{A_{11.5} + A_{13.9}}{A_{7.3}} - \Delta A_{5.9}$ (200 hr)

3. $A_{11.5} + A_{13.9}$

4. $A_{11.5} \left(A_{13.9}\right)$

5. $\frac{A_{11.5}}{A_{7.3}}$

6. $\frac{A_{13.9}}{A_{7.3}}$

7. $\frac{A_{11.5} \left(A_{13.9}\right)}{A_{7.3}}$

8. $\frac{A_{11.5}}{A_{7.3}} + A_{13.9}$

9. $\frac{1/2 \quad A_{11.5}}{A_{7.3}} + A_{13.9}$

10. $\frac{A_{11.5}}{A_{7.3}} + \frac{A_{13.9}}{2}$

11. $\frac{A_{13.9}}{A_{7.3}} + A_{11.5}$

12. $A_{11.5} + A_{13.9} - \frac{A_{7.3}}{10}$

13. $\frac{A_{11.5}}{A_{7.3}} + A_{13.9} - A_{13.7c}$

14. $\frac{A_{11.5} \left(A_{13.9}\right)}{A_{7.3}} - \frac{A_{13.7}}{2}$

15. $\frac{A_{11.5} \left(A_{13.9}\right)}{A_{7.3}} - A_{13.7}$

16. $\frac{100 \quad A_{11.5} \left(A_{13.9}\right)}{A_{7.3}} + \frac{A_{13.9r}}{A_{13.7r}} - \frac{A_{13.7c}}{A_{13.9c}}$

17. $\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9}$

18. $\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9} + A_{7.3}$

19. $\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9} + \Delta A_{5.9}$ (100 hr)

20. $\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9} + A_{7.3} + \Delta A_{5.9}$ (100 hr)

21. $A_{13.9} - \frac{A_{13.7c}}{A_{13.9c}} + \frac{A_{13.9}}{A_{7.3}}$

22. $A_{13.9} - \frac{A_{13.7c}}{A_{13.9c}} + \frac{A_{13.9}}{A_{7.3}} - \Delta A_{5.9}$ (100 hr)

23. $A_{13.9} - \frac{A_{13.7c}}{A_{13.9c}} - \frac{10 \quad A_{11.5} \left(A_{13.9}\right)}{A_{7.3}}$

24. $\frac{A_{13.9c} - A_{13.7c}}{A_{13.9c}} - \Delta A_{5.9}$ (100 hr)

25. $1 - \frac{A_{13.7c}}{A_{13.9c}} + \frac{A_{13.9}}{A_{7.3}}$

26. $1 - \frac{A_{13.7c}}{A_{13.9c}} + \frac{A_{13.9}}{A_{7.3}} - \Delta A_{5.9}$ (100 hr)

27. $10 \quad A_{13.9r} - \frac{A_{13.9c} - A_{13.9r}}{A_{13.9r}}$

28. $\frac{A_{3.4} \left(A_{13.9}\right)}{A_{7.3}}$

29. $\frac{A_{11.5} \left(A_{13.9}\right)}{A_{7.3}} - A_{13.7c} - \frac{1}{2} \Delta A_{5.9}$ (100 hr)

30. $1 - \frac{A_{13.7c}}{A_{13.9c}} - \Delta A_{5.9}$ (100 hr)

31. $\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9} + A_{5.9}$ (100 hr)

32. $A_{13.9} \left(x - \frac{A_{13.7c}}{A_{13.9c}}\right)$ where x = 2 to 5

33. $\frac{A_{13.9}}{A_{7.3}} \left(2 - \frac{A_{13.7c}}{A_{13.9c}}\right)$

34. $\frac{A_{13.9} \left(2 - \frac{A_{13.7c}}{A_{13.9c}}\right)}{A_{7.3} \left[A_{5.9} \text{ (100 hr)}\right]}$

35. $\left(\frac{A_{13.7c}}{A_{13.9c}} - A_{13.9}\right) A_{5.9}$ (100 hr)

TABLE F-1
BASELINE ABSORBANCE OF QUANTITATIVE SOLUTIONS

Asphalt	Wavelength, μ						
	3.4	7.3	8.6	9.7	11.5	12.3	13.9
1	0.506	0.438	0.039	0.154	0.154	0.209	0.128
2	0.509	0.439	0.038	0.110	0.151	0.215	0.131
3	0.506	0.436	0.037	0.123	0.156	0.221	0.131
4	0.537	0.437	0.047	0.087	0.115	0.199	0.138
5	0.505	0.435	0.020	0.145	0.157	0.217	0.128
6	0.539	0.396	0.059	0.146	0.154	0.234	0.178
7	0.543	0.417	0.016	0.102	0.163	0.203	0.160
8	0.505	0.416	0.059	0.132	0.160	0.224	0.137
9	0.544	0.410	0.016	0.110	0.188	0.215	0.167
10	0.511	0.423	0.060	0.123	0.167	0.235	0.132
S-1	0.522	0.453	---	---	0.180	0.213	0.144
S-2	0.502	0.468	---	---	0.097	0.186	0.133
S-3	0.522	0.456	---	---	0.178	0.217	0.142
S-4	0.547	0.455	---	---	0.173	0.215	0.140
S-5	0.544	0.409	---	---	0.176	0.223	0.193
S-6	0.532	0.402	---	---	0.176	0.232	0.197
Low Value	0.502	0.396	0.016	0.087	0.097	0.186	0.128
High Value	0.547	0.468	0.060	0.154	0.188	0.235	0.197

TABLE F-2
BASELINE ABSORBANCE AT 13.7 AND 13.9μ CORRECTED TO EQUAL FILM THICKNESS

Asphalt	Room Temp. Film		Chilled Film	
	13.7μ	13.9μ	13.7μ	13.9μ
1	0.075	0.157	0.169	0.351
2	0.081	0.171	0.170	0.362
3	0.064	0.165	0.142	0.351
4	0.071	0.172	0.161	0.374
5	0.076	0.163	0.168	0.360
6	0.068	0.203	0.180	0.469
7	0.057	0.181	0.136	0.369
8	0.060	0.162	0.184	0.379
9	0.056	0.190	0.119	0.411
10	0.065	0.160	0.145	0.376
S-1	0.070	0.161	0.148	0.349
S-2	0.066	0.150	0.138	0.316
S-3	0.071	0.167	0.155	0.357
S-4	0.038	0.123	0.111	0.328
S-5	0.090	0.197	0.186	0.428
S-6	0.103	0.222	0.263	0.509

TABLE F-3
BASELINE ABSORBANCE AT 5.9μ FOR ASPHALT FILMS HEATED AT 212 F, CORRECTED TO EQUAL FILM THICKNESS

	Asphalt	Exposure Time, hrs.				
		0	100	180	200	400
GROUP I	1	0.041	0.490	0.639	0.67*	---
	4	0.070	0.549	0.79*	0.86*	---
	9	0.087	0.555	0.735	0.78*	---
	S-2	0.068	0.548	0.886	0.94*	---
	S-6	0.016	0.470	0.617	0.65*	---
GROUP II	2	0.022	0.454	0.580	0.610	0.857
	4	0.073	0.550	0.828	0.892	1.574
	5	0.037	0.468	0.595	0.630	0.900
	6	0.043	0.435	0.551	0.572	0.754
	7	0.052	0.532	0.645	0.673	0.903
	10	0.058	0.528	0.712	0.742	1.003
	S-3	0.049	0.504	0.620	0.640	0.887

*Extrapolated values.

APPENDIX G
INFRARED STUDY OF ASPHALT FILMS ON SODIUM CHLORIDE DISCS

Preparation of Films

1. Place an aluminum panel (approximately 3 by 5-in. by 0.040-in. thick) on a hotplate adjusted to soften asphalt sufficiently for the subsequent procedure. Avoid overheating the asphalt.

2. Place two 1-in. diameter sodium chloride discs on the aluminum panel.

3. Place a 1/16 to 1/8-in. diameter ball of asphalt on one of the discs.

4. When the asphalt has softened, place the empty disc on top of the asphalt. Apply pressure to spread asphalt between the discs.

5. Slide the discs apart evenly and allow them to cool.

6. Check the thickness of the asphalt film by measuring its baseline absorbance at 2.35μ. Suggested Absorbance Values at 2.35μ:

Crystallinity Measurement	0.12 to 0.15
Oven Exposure	0.03 to 0.04
Weatherometer Exposure	0.07 to 0.08

Study of 5.9μ Absorbance During Weathering and Oven Exposure

1. Make appropriate settings on the spectrophotometer. Typical Settings for a Perkin-Elmer Model 21 Spectrophotometer were:

Resolution	984 (fairly wide slits)
Speed	50 sec/μ

2. Scan the 2 to 3μ region and the 5 to 7μ region.

3. Measure the baseline absorbance near 2.35 and 5.9μ.

4. Correct absorbances to be equivalent to a baseline absorbance of 0.075 at 2.35μ.

$$\text{Corrected absorbance} = \frac{\text{desired absorbance at } 2.35\mu}{\text{actual absorbance at } 2.35\mu} \times \text{measured absorbance}$$

5. Place specimens in weatherometer under single-arc operation without water spray, or in an oven at 212 F.

6. At appropriate intervals remove specimens and repeat the steps above.

Crystallinity Measurement

Assembly of Low Temperature Absorption Cell

1. Position the sodium chloride disc bearing the asphalt film in the copper sample holder, using a small amount of asphalt as an adhesive, Figure G-1.

2. Warm the male portion of the "Standard Taper" joint with a bunsen burner and apply a coating of "Apiezon W Black Wax" to the ground area.

3. Assemble the cell and heat the joint until the wax forms a complete seal. While the sealing wax is molten orient the asphalt film so that it is perpendicular to an axis passing through the sodium chloride windows of the cell.

4. After the assembly has cooled connect a vacuum pump to the cell and support the cell in the sample beam of the spectrophotometer.

Spectrophotometry

1. Set up the spectrophotometer. Typical settings for a Perkin-Elmer Model 21 Infrared Spectrophotometer were:

Resolution	940
Speed	1 min/μ

2. Position the cell to yield maximum transmittance and adjust a reference beam attenuator to set the pen at 90 percent transmittance at 2μ.

3. Scan the region from 2 to 3μ to obtain data for subsequent correction of results to constant film thickness. Baseline absorbance near 2.35μ should be 0.12 to 0.15.

4. Adjust the reference beam attenuator to set the pen at 98 percent transmittance at 10.8μ, a point of low absorbance. Interrupt the infrared beam to the sample.

5. Evacuate the cell, set the spectrophotometer to cycle from 12.5 to 14.5μ, open the sample beam and scan this region at room temperature.

6. After the first cycle add acetone and dry-ice to the reservoir in the absorption cell.

7. Add more dry ice as required, continue to scan the 12.5 to 14.5μ region until no further increase in absorption occurs. Place these repetitive scans in an unneeded area on the chart.

8. Add enough dry ice to maintain maximum temperature reduction, and interrupt the infrared beam to the sample for 15 minutes.

9. Open the infrared beam and scan the region from 13.4 to 14.5μ three times, closing off the infrared beam to the sample when the instrument runs back.

10. Remove the dry ice and acetone and allow the absorption cell to warm to room temperature before heating the joint for disassembly.

Examination of Spectra

1. Determine the baseline absorbance near 13.7 and 13.9μ for the room temperature and the final low temperature runs.

2. Construct a baseline for the absorption peak near 2.35μ and determine the absorbance at that wavelength.

3. To compensate for differences in film thickness, calculate corrected absorbances as follows:

$$\text{Corrected absorbance} = \frac{\text{desired absorbance at } 2.35\mu}{\text{actual absorbance at } 2.35\mu} \text{ x measured absorbance}$$

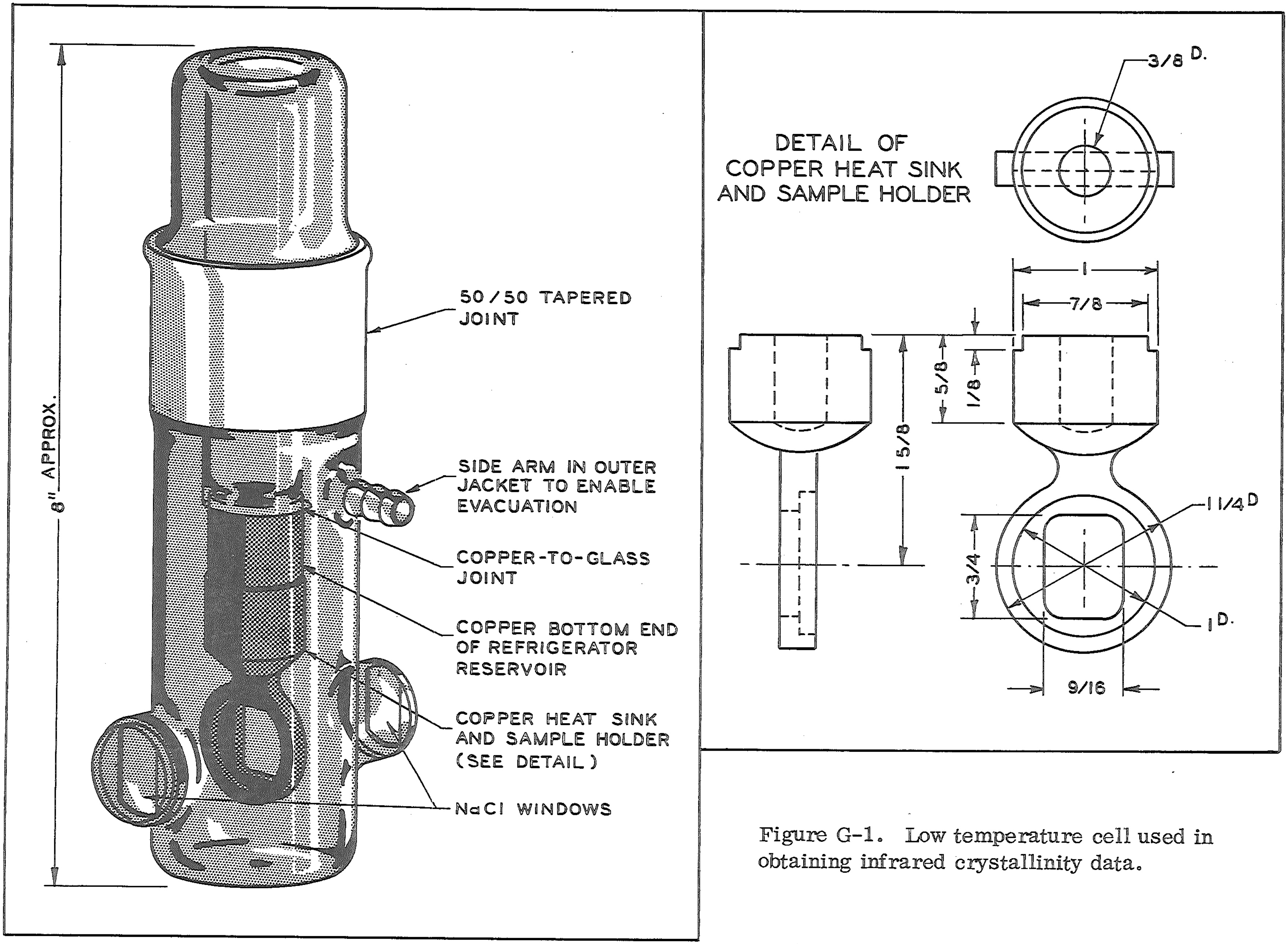

Figure G-1. Low temperature cell used in obtaining infrared crystallinity data.