

APPLICATION OF INSTRUMENTAL METHODS  
FOR EVALUATING HIGHWAY MATERIALS  
Use of Infrared Spectrophotometry in  
Acceptance Testing Membrane Curing Compounds for Concrete

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MICHIGAN DEPARTMENT OF STATE HIGHWAYS

APPLICATION OF INSTRUMENTAL METHODS  
FOR EVALUATING HIGHWAY MATERIALS  
Use of Infrared Spectrophotometry in  
Acceptance Testing Membrane Curing Compounds for Concrete

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Progress Report on a Highway Planning and Research Investigation  
Conducted in Cooperation with  
The U.S. Department of Transportation--Federal Highway Administration

Research Laboratory Section  
Testing and Research Division  
Research Project 63 G-124  
Research Report R-744

Michigan State Highway Commission  
Charles H. Hewitt, Chairman; Wallace D. Nunn, Vice-Chairman;  
Louis A. Fisher; Claude J. Tobin; Henrik E. Stafseth, Director  
Lansing, June 1971

## INFORMATION RETRIEVAL DATA

**REFERENCE:** Frederick, W. L. Application of Instrumental Methods for Evaluating Highway Materials; Use of Infrared Spectrophotometry in Acceptance Testing Membrane Curing Compounds for Concrete. Michigan Department of State Highways Research Report No. R-744. Research Project 63 G-124.

**ABSTRACT:** The use of infrared spectra may greatly reduce the number of tedious, lengthy water retention tests (ASTM C-156) that are currently performed on white pigmented membrane curing compounds for concrete. Based on samples from five different producers over a three-year period, a reduction in water retention tests from 293 to 64 was predicted. A similar reduction in the number of drying time and reflectance tests would be expected, in most cases. The infrared spectra are used to show that the resin and pigment of acceptance samples have the same composition as the resin and pigment of reference samples of known performance. The infrared method is recommended for acceptance testing transparent membrane curing compounds as well.

**KEY WORDS:** acceptance tests, concrete curing, curing agents, membrane curing, infrared spectrophotometry.

## FOREWORD

This report is submitted as partial fulfillment of a Highway Planning and Research project, sponsored by the Federal Highway Administration, entitled "Application of Instrumental Methods for Evaluating Highway Materials." This report completes the phase of the project devoted to acceptance testing of membrane curing compounds by means of infrared spectrophotometry.

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." Its 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."

In addition to this report, final reports have been issued on three phases (four reports) of the project: "Application of Instrumental Methods for Evaluating Highway Materials: Determination of Amount of 'Plastiment A' Retarder in Hardened Concrete" (MDSH Research Report No. R-586, November 1966); "Application of Instrumental Methods for Evaluating Highway Materials: Detection and Determination of Ground, Cured Scrap Rubber in Hot-Poured Joint Sealers" (MDSH Research Report No. R-641, August 1967); "Application of Instrumental Methods for Evaluating Highway Materials: Pyrolysis Gas Chromatography" (MDSH Research Report No. R-666, August 1968); and "Application of Instrumental Methods for Evaluating Highway Materials: Gas Chromatography (II)" (MDSH Research Report No. R-727, July 1970).

## INTRODUCTION

Initial infrared spectroscopic work was done in the Research Laboratory on white pigmented membrane curing compounds for concrete in order to detect prohibited waxy materials in the resin fractions of samples that exhibited characteristic soft, slippery films during the water retention test. The infrared method was found to be fast and effective for detecting waxy material. The present study explores the feasibility of extending the use of infrared spectral data to greatly reduce the number of tedious, lengthy water retention tests that are currently performed as acceptance tests for concrete curing compounds. In many cases, drying time and reflectance tests could also be eliminated.

We have successfully employed an infrared comparison method for acceptance testing of traffic paints for over ten years. Infrared spectra are used to show whether the resin and pigment of test samples have the same composition as the resin and pigment used two and three years previously in paints whose durability was established by field tests with transverse test stripes on pavement. Field tests are no longer made each year so the same infrared reference spectra are used for two years. No accepted sample has failed to render satisfactory field performance.

It is also accepted industrial practice to use infrared spectra for comparing batches of incoming raw materials, and for quality control of outgoing lots of the product. At least one state is including infrared spectra as part of a materials specification for epoxy resins; requiring that an infrared spectrum of the acceptance sample match the reference spectrum in the specification.

### Specification Requirements

The specification requirements for white pigmented curing compounds pertinent to this study are:

- 1) The non-volatile matter content shall be not less than 60 percent by weight, as determined by ASTM D 154.
- 2) The vehicle shall contain no waxy compounds. (Waxy compounds interfere with adhesion of traffic paint.)
- 3) Moisture loss shall be not more than  $0.055 \text{ g/cm}^2$  when tested by ASTM C 156, "Method of Test for Water Retention Efficiency of Liquid Membrane Forming Compounds and Impermeable Sheet Materials."

4) Under the conditions used for the water retention test (hereafter referred to as WRT), 100 F at 32 percent relative humidity, the compound shall dry to touch within four hours.

5) The luminous directional reflectance shall be not less than 70 percent, relative to magnesium oxide, upon completion of the WRT.

#### Water Retention Test

The water retention test procedure is tedious and lengthy, requiring approximately 74 hours elapsed time. Triplicate samples are required. Briefly, the test is conducted by placing weighed pans of fresh mortar (6 by 12 in. ), coated on the surface with curing compound, in a curing cabinet at a temperature of 100 F and at a relative humidity of 32 percent for 72 hours. The pans are reweighed at suitable intervals to determine moisture loss.

Examples of the tedious parts of the test method are:

- 1) Mixing the mortar in a carefully prescribed manner.
- 2) Filling the pans with fresh mortar, using a specified regimen of tamping and screeding.
- 3) Determining the proper condition of initial surface dryness of the mortar.
- 4) Forming a groove 1/8 in. deep, 1/16 in. wide, in the mortar around the edge of the pan.
- 5) Sealing the groove with a resinous liquid. (A crucial step if accurate results are to be obtained).
- 6) Weighing the pan of mortar and immediately applying the curing compound at a specific rate of application (spray or brush) from a tared container. A uniform coating must be quickly applied with minimum loss, such as overspray.
- 7) Coating a tared metal plate having the same area as the mortar specimens with the same quantity of curing material used on the mortar specimen. The volatile matter content thus determined is used to correct the weight of liquid curing compound applied to the mortar specimen. Overspray may cause erroneous results here, as well.

## Basis for Using Infrared Spectra

It may be possible to replace most of these 74-hour WRT procedures with an evaluation process requiring approximately four hours to process four samples. Once a string of samples was started one could be finished about every fifteen minutes. Only the resin and pigment from the original liquid curing compound remain in the dried film on the concrete surface. If it can be shown that a proven resin and pigment combination is being provided in correct relative amounts in batch after batch of a given producer's curing compound, it would no longer be necessary to run the WRT package (WRT, drying time, and reflectance tests). An infrared spectrum can be used to identify a chemical compound much as a fingerprint identifies a person. If the infrared spectra of two samples of resin or pigment are the same, it follows that they have the same composition. Thus, infrared spectra have been used in this study to compare the composition of different batches of a product.

### PROPOSED OPERATION OF THE INFRARED-BASED PROCEDURE

To put the instrumental method into use, obtain the following data for the early samples of each formulation of various producers until three batches of the same composition are approved:

- 1) Lot or batch number
- 2) Infrared spectra of resin and pigment (automatic wax detection)
- 3) Non-volatile matter content
- 4) Pigment content
- 5) Resin content
- 6) Water retention efficiency (moisture loss)
- 7) Drying time
- 8) Reflectance, relative to magnesium oxide.

These three initially approved samples then serve as references with which subsequent batches are compared. On all subsequent samples, then, it would not be necessary to run the WRT package (water retention, drying time, and reflectance tests) if:

- 1) The sample meets the non-volatile matter requirement
- 2) Infrared spectra show the resin and pigment have the same composition as references

3) The resin and pigment are present in proportions similar to the references.

If three initial samples of a given composition were rejected by WRT, subsequent samples with the same composition and proportioning would be rejected without the WRT package.

Two additional steps not taken in the present study, due to the low incidence of excessive drying time or low reflectance, could be employed as additional checks on curing compound samples:

1) Measure reflectance, when the WRT is not run, by applying the curing compound to mortar blocks or grey cardboard by doctor blade.

2) Monitor the composition of the solvent fraction by gas chromatography. The vehicle portion of a centrifuged sample (care taken to avoid water globules) can be analyzed by a rapid, simple procedure developed for direct gas chromatographic analysis of unfractionated paint. The procedure is described in MDSH Research Report No. R-727.

The following order of tests on subsequent batches is recommended:

- 1) Non-volatile matter content
- 2) Pigment content
- 3) Calculate resin content
- 4) Infrared data
- 5) WRT package (if used).

The simplest test is performed first so that any cause for rejection can be discovered with minimum testing. The pigment determination also yields the fractions for obtaining infrared spectra. After a small sample of curing compound is centrifuged to remove the pigment, a few drops of the supernatant vehicle (resin solution) are evaporated on a sodium chloride plate to form a film of dried resin. This sodium chloride plate is placed in the sample beam of an infrared spectrophotometer to obtain the resin spectrum. The pigment is then washed free of resin and dried. About 1 mg of pigment is ground thoroughly with 500 mg of pure potassium bromide and the mixture is pressed into a 13 mm diameter disc which transmits infrared radiation so that a pigment spectrum can be obtained. See Appendix I for details of infrared sample preparation.

If the producer used a different resin or pigment or markedly altered the relative amounts of component ingredients, while still meeting other specification requirements, a complete test program would be run on one

to three samples to establish the suitability of the new formulation. Then, the WRT package would not be run on either formulation.

For samples which contain resin and pigment of the same composition as reference batches but in different relative proportions (all other requirements are met) the following considerations apply:

Approve - Sample contains larger proportion of resin than reference samples; or a somewhat smaller proportion of resin might be allowed if the moisture loss values of the reference samples were well below the specification limit. The arbitrary permissible decrease in resin content used in this study is 10 percent of the reference sample resin content above the 10 percent resin content level and 5 percent of the reference sample resin content below 10 percent. Obviously, if the moisture loss values for the reference samples were near the specification limit, no reduction in resin content below the resin content of the lowest reference sample could be tolerated without running the WRT. To date, no sample has failed the WRT when the resin content was above 15 percent, indicating that wide latitude in resin content is reasonable above the 15 percent resin content level.

Run WRT, Resample, or Reject - Sample has resin content below guideline limits described above. If the resin content indicates a reasonable expectation of satisfactory performance, run the WRT. For example, no further tests would be recommended for a sample containing only 3.7 percent of a resin which had failed the WRT in another sample at a resin content of 7.5 percent. Extremely low resin content for a single batch may indicate a non-representative sample. Resampling should be considered before rejection.

Actual composition and physical property data for white pigmented curing compounds received over a three-year period (1966-68) are given in the next section.

## SAMPLE DATA AND DISCUSSION

Table 1 summarizes test results for all samples studied. The different resin types in Table 1 are based on infrared spectra presented later. Those samples listed under "Other Failures" did not meet either the non-volatile matter or reflectance requirements of the specifications.

TABLE 1  
SUMMARY OF OBSERVED (Obs.) TEST RESULTS (ASTM METHODS)  
AND PREDICTED (Pred.) TEST RESULTS USING INFRARED SPECTRA<sup>1</sup>

Producer	Year	Resin Type	Number of Samples	Water Retention Failures		Other Failures		Reduction in. W. R. Tests
				Obs.	Pred.	Obs.	Pred.	
1	1966	A	12	2*	2	0	0	from 12 to 5 41 to 4 27 to 5
		B	41	0	0	0	0	
		C	27	0	0	0	0	
1	1967	B	5	0	0	2	2	5 to 0
		C	12	6*	0	0	0	12 to 0
		D	45	0	0	0	0	45 to 7
1	1968	C	10	1*	0	0	0	10 to 0
		D	15	2	2	0	0	15 to 1
		E	19	1	1	0	0	19 to 6
		F	8	0	0	0	0	8 to 3
			194	12	5	2	2	194 to 31
2	1966	G	26	0	0	11	2	26 to 4
2	1967	H	14	3	3	0	0	14 to 7
2	1968	H	24	13**	12	0	0	24 to 9
			64	16	15	11	2	64 to 20
3	1966	I	5	0	0	1	1	5 to 3
3	1967	J	6	0	0	1	1	6 to 3
3	1968	J	3	0	0	1	1	3 to 0
			14	0	0	3	3	14 to 6
4	1966	K	4	0	0	0	0	4 to 3
5	1967	L	9	0	0	0	0	9 to 4
5	1968	L	8	0	0	2	2	8 to 0
			17	0	0	2	2	17 to 4
6	1966	M	1	0	0	1	1	not run
6	1967	N	1	0	0	1	1	not run
			2	0	0	2	2	
COLUMN TOTALS			295	28	20	20	11	293 to 64

(1) In every case, samples that were predicted to fail were samples that had been observed to fail the indicated test.

\* The excessive moisture loss reported for these samples is not consistent with the composition data presented in Table 4.

\*\* The excessive moisture loss reported for three of these samples is not consistent with composition data in Appendix III.

TABLE 2  
TYPICAL CURING COMPOUND PROPERTIES

		Sample No.	Viscosity, Krebs Units	Pigment Dispersion, * mils	Water Content, wgt percent
1967	Producer No. 1	Passing			
		1964	49	4.0	18.8
		1071	49	4.0	18.8
		1098	51	3.5	19.1
		Avg.	49.7	3.8	18.9
		Failing			
		1067	50	3.0	18.8
	1068	45	3.0	19.1	
	1074	48	2.5	19.1	
	1075	47	4.0	18.9	
	1076	42	4.0	18.9	
	1077	48	3.5	18.8	
	Avg.	46.7	3.3	18.9	
	Producer No. 2	Passing			
1084		66	5.0	18.3	
1106		65	4.0	18.7	
1127		65	5.0	18.3	
Avg.		65.3	4.7	18.4	
Failing					
1085		76	5.0	18.2	
1086	79	5.0	17.9		
1111	63	4.0	18.1		
Avg.	72.7	4.7	18.1		
1968	Producer No. 2	Passing			
		141	65	5.0	----
		142	62	----	16.7
		143	65	----	----
		144	69	----	----
		145	72	----	----
		146	74	----	----
		176	82	4.2	14.2
		179	82	5.0	----
		193	77	4.2	17.5
		195	74	----	----
		196	75	5.0	----
		Avg.	73	4.7	16.1
	Failing	99	60	5.0	15.7
		100	59	----	----
		101	100	----	15.7
		102	63	----	----
		103	57	----	16.5
		107	60	4.2	----
		108	65	4.6	----
111	84	----	----		
113	92	----	----		
114	85	5.0	----		
115	95	----	16.4		
130	70	5.0	----		
194	75	----	----		
Avg.	74	4.6	16.1		

\* Determined according to ASTM D1210 "Fineness of Dispersion of Pigment-Vehicle Systems"

Whenever three or more samples from any producer failed the water retention test the following properties were compared for those samples and for representative groups of samples that passed the water retention test.

- 1) Viscosity, determined using Krebs-Stormer viscometer.
- 2) Pigment fineness, determined by ASTM D 1210, "Fineness of Dispersion of Pigment-Vehicle Systems."
- 3) Free water content, determined by the azeotropic method described in Appendix II.

Table 2 presents typical data. Analysis of these data was hampered by the limited number of samples failing the water retention test and variability arising from analyzing resamples (supplied by others) of larger samples that had been stored for periods ranging up to several months.

Viscosities varied considerably for samples from the same supplier. Failing samples from Producer No. 1 tended to have lower viscosity than passing samples. This trend was reversed for 1967 and 1968 samples from Producer No. 2. However, there was no firm correlation of viscosity with water retentiveness.

The fineness of pigment grind might also have a direct effect on the performance of resins in the film forming process. Smaller particles have greater surface area per unit mass to be coated by the resin than larger particles, and smaller particles could also pack more closely together in a dried film of curing compound.

For Producer No. 1, the pigment particles in samples failing the WRT were somewhat smaller than pigment particles in passing samples. The passing samples for comparison were chosen because they were received at about the same time as the failing samples. For Producer No. 2, in 1967 and 1968, there was no difference in pigment particle size for passing and failing samples. Pigment fineness was also not counted a definitive factor in water retentiveness.

Free water was present in five of the six producers' samples. Table 3 presents typical water contents. The water present in two rejected samples by Producer No. 6 was not quantitated. Water content data previously presented in Table 2 show that there is no significant difference in free water content for samples that passed the water retention test and those that failed.

**TABLE 3**  
**WATER CONTENT OF CURING COMPOUND SAMPLES**

Producer Number	Typical Water Content, weight percent
1	19
2	16
3	13
4	none
5	15
6	present, not quantitated

The characteristic or property of the curing compound samples which did correlate with water retention effectiveness was the chemical composition of the resin and the relative amount of the resin in a curing compound formulation. Table 4 (fold-out at back) summarizes composition and moisture loss data for all samples. Individual sample data are given in Appendix III.

The following WRT failures correlate with low resin content of the samples as shown by data in Table 4 and Appendix III. Sample numbers are from Appendix III.

Producer Number 1

(1968) - Resin Type D (two samples, 105 and 177). The resin content range for passing samples containing resin Type D in 1968 was 8.1 to 10.8 percent, but these two failing samples contained 3.7 and 7.5 percent resin.

(1968) - Resin Type E (one sample, 197). The resin content range for passing samples was 7.6 to 9.5 percent, but this sample contained only 6.4 percent resin.

Producer Number 2

(1967) - Resin Type H (three samples, 1085, 1086, and 1111). Resin contents for passing samples ranged between 9.1 and 15.5 percent (avg. 10.1). The three failing samples contained only 9.1 to 9.3 percent resin (avg. 9.2).

(1968) - Resin Type H (ten samples, 99 through 102 and 108 through 130). The resin content range for passing samples was 10.8 to 12.4 percent. Resin contents for the ten failing samples ranged between 8.8 and 9.1 percent.

Several other WRT failures are unexplained. Composition data indicate the samples would perform satisfactorily.

#### Producer Number 1

(1966) - Resin Type A (two samples, 829 and 849).

(1967) - Resin Type C (six samples, 1067, 1068, 1074, 1075, 1076, 1077).

(1968) - Resin Type C (one sample, 121). This sample had the highest resin content reported for any Type C sample in 1968.

#### Producer Number 2

(1968) - Resin Type H (three samples, 103, 107, and 194). Again, data obtained when the WRT was performed indicate that Sample 103 had the highest resin content for Type H resin in 1968.

Since correlation of composition data with test results was carried out at a different laboratory (without water retention test facilities) well after the initial water retention tests, no further work was done to discover the cause of the anomalous water retention failures. It is possible that this variation in water retention test results for samples of similar composition is due to droplets of free water which are not sufficiently dispersed before the curing compound is applied to the mortar used to test water retentiveness. Evaporation of such droplets of water during the test procedure would leave thin spots or pores in the resin-pigment film resulting in erroneously high moisture loss values.

### Resin and Pigment Composition - Application of Infrared Method

#### Producer Number 1

Producer No. 1, the largest supplier, has the lowest resin contents within each yearly period. The resin is probably the most expensive component of these products, so it is economically advantageous to formulate with the lowest resin content that will consistently meet specification requirements.

Composition data in Table 4 also indicate that it was necessary for different resin types from Producer No. 1 to be used at different concentrations. Resin Type A in 1966 was present at significantly higher concentration levels than Types B and C (9.9, 7.7, and 7.1 percent, respectively), yet the average moisture loss for samples passing WRT was 0.044, 0.036, and 0.038 g/cm<sup>2</sup>, respectively. Also note that except for one anomalous sample--No. 121 Resin Type C (1968)--no group of samples that averaged at least 8.5 percent resin content of resin Types C (1968), D (1967-68), E, or F, exceeded 0.030 g/cm<sup>2</sup> average moisture loss.

Infrared spectra of the pigment and six types of resin used by Producer No. 1 during the period studied are presented in Figure 1. The same pigment, a blend of calcium carbonate, calcium sulfate, and some titanium dioxide, was used in all samples. Three resin types, designated A, B, and C were found for 1966 samples. Types B and C were used again in 1967 along with a new resin, Type D. The 1968 samples contained resin Types C and D as well as two additional types, E and F. With the exception of Types D and E, it is readily apparent that there are differences in the pattern of peaks in the 13 to 15 $\mu$  (micron) region in the spectra of the various resins. The differentiation for Types D and E is in the relative depth of peaks at 11.0 and 11.5 $\mu$ . For Type D resins, the 11.5 $\mu$  peak is deeper than the 11.0 $\mu$  peak. The relative peak depths are reversed in Type E resins.

Further examination shows that Types A, B, and F have rather unique spectra compared to C, D, and E, which have similar spectra. Some other differences are:

5.8 $\mu$  region: Type A has an unshouldered peak which is closer to 6 $\mu$  than any other type. Type B also has an unshouldered peak. Types C, D, and E have peaks with higher wavelength shoulders (incompletely resolved peaks). Type F has a shouldered peak, at a slightly lower wavelength than any other type, and greater activity in three small peaks in the 5 to 5.7 $\mu$  interval.

6.7 to 7.0 $\mu$  region: Types A and B have little or no shouldering on 6.9 $\mu$  peaks. C, D, and E, have shouldered peaks, and F has two peaks in this region.

8 $\mu$  region: Only Type A has a single peak here, the others have two peaks.

9 $\mu$  region: Type A has less activity here than B, C, D, and E which have a broad double peak, and F has a triple peak at slightly lower wavelength than the others.

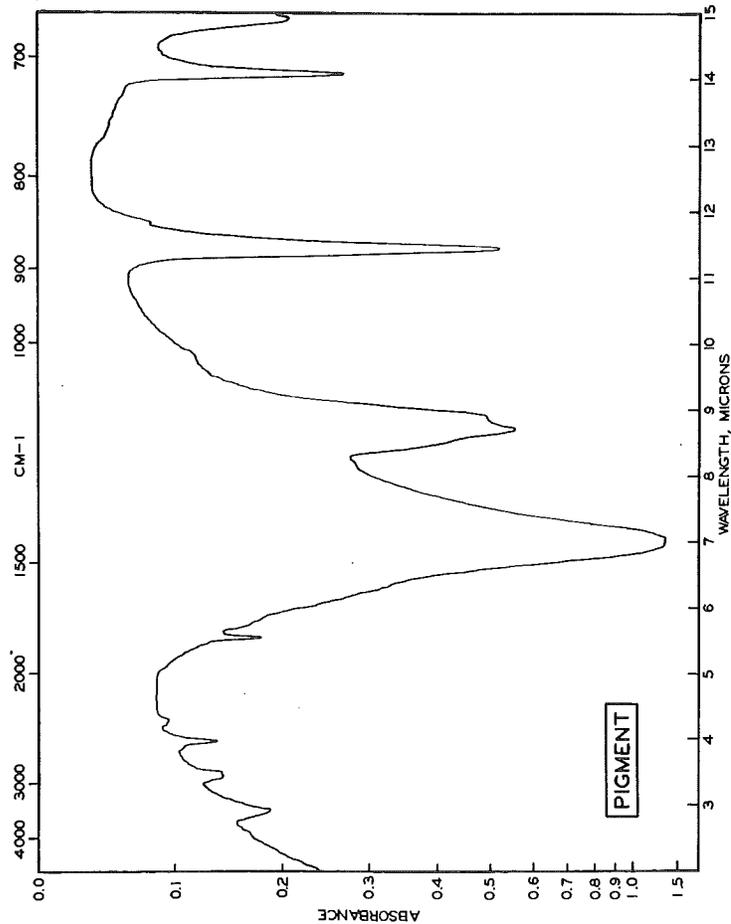
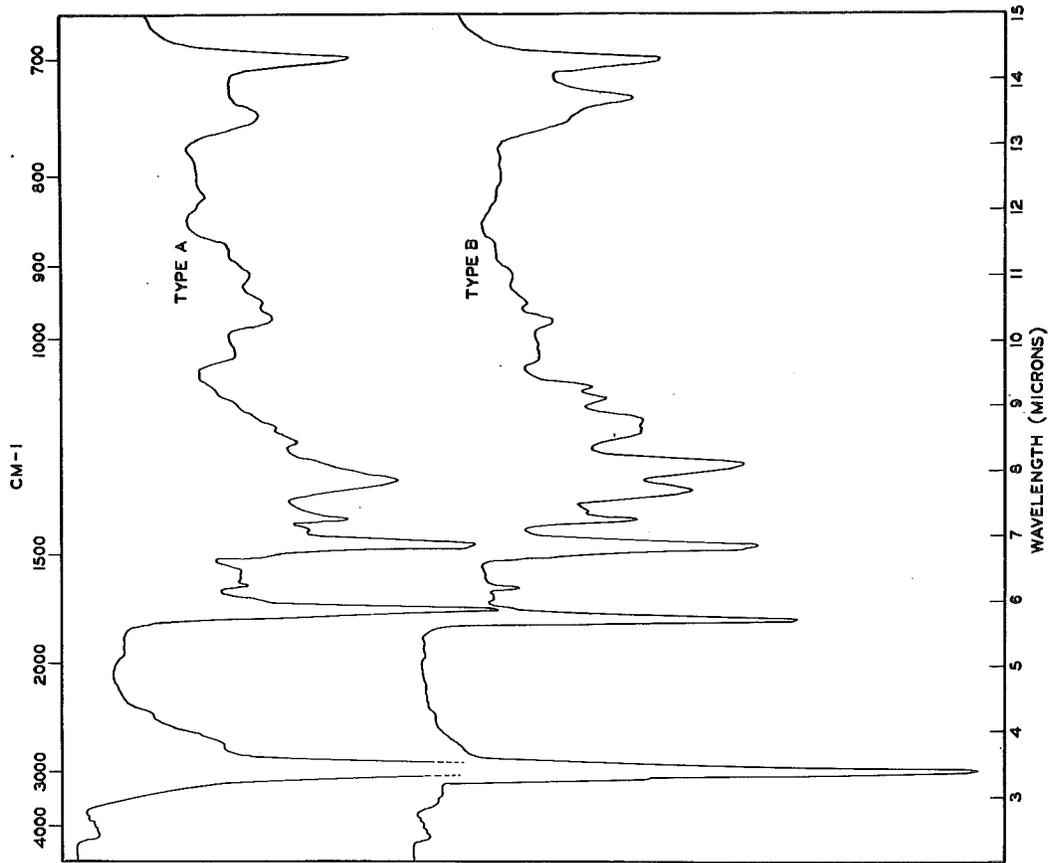


Figure 1. Infrared spectra for the pigment and six resins, Types A through F, (continued next page) used by Producer 1. In the pigment spectrum: the small peak near  $4\mu$  is spurious; the peak near  $3.5\mu$  is due to residual resin. Peaks near  $7$ ,  $11.4$  and  $14\mu$  are due to calcium carbonate. Peaks near  $9$  and  $15\mu$  are due to calcium sulfate. The increase in background absorbance beyond  $13\mu$  is indicative of titanium dioxide.

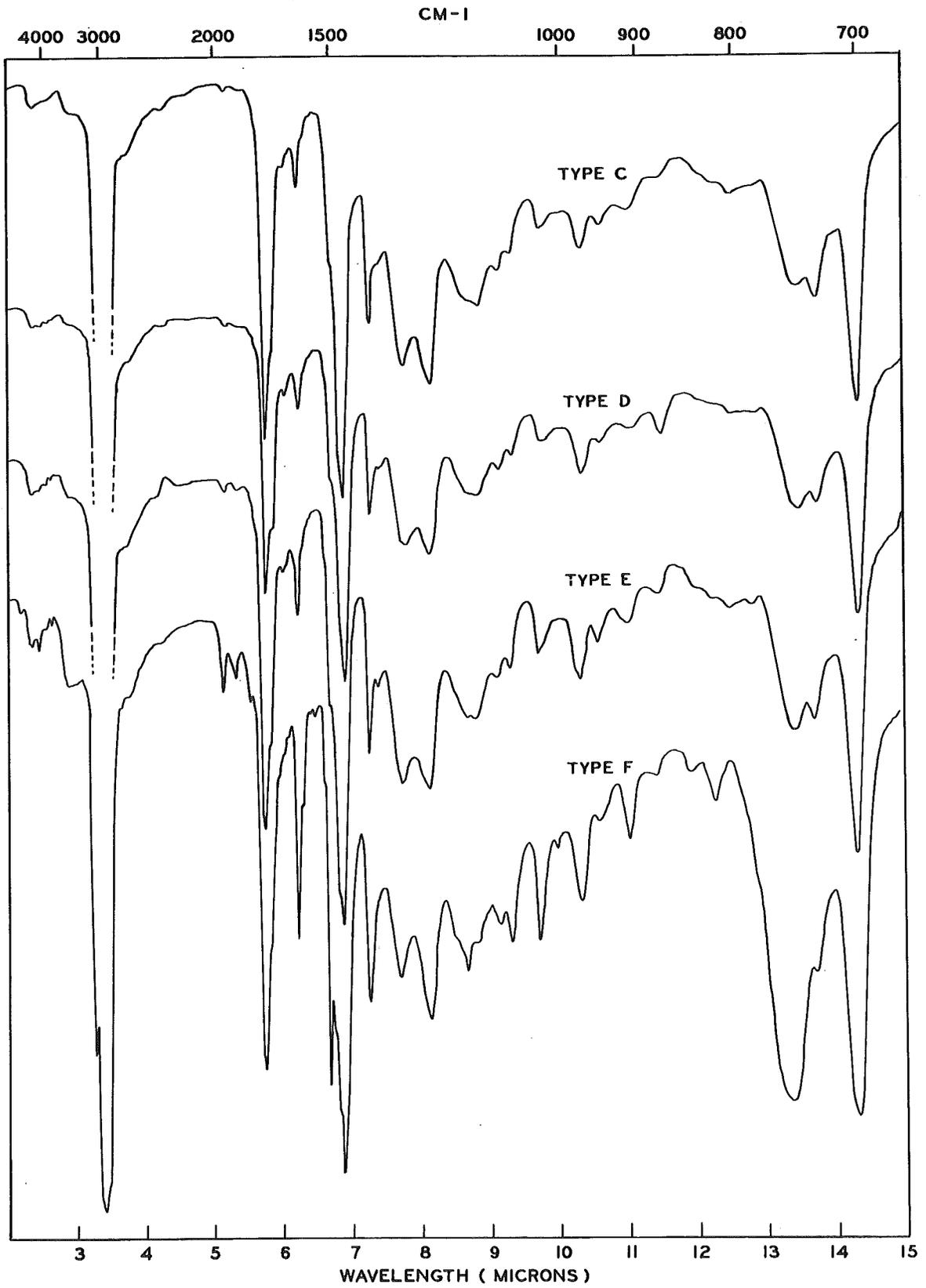


Figure 1. Continued from previous page.

10 to 13 $\mu$  region: This region is one of low absorption for all the resins. The A through E spectra are quite similar in overall pattern in this region, but F has a unique pattern of stronger peaks.

#### Infrared Method - Application to Producer Number 1

Resin Type A (1966 only) - Run all standard and instrumental tests on the first three samples (refer to Appendix III and proceed down the sample number column for Type A resin). Reject Samples 829 and 849 for excessive moisture loss. Run all tests on Samples 850 and 851 and approve them. Samples 830, 850 and 851 now become the reference samples for comparison of subsequent samples. The remaining samples have resin contents as high or higher than the reference sample average (9.3 percent) and meet other specification requirements, so they would be accepted without running the WRT, drying time, or reflectance tests (WRT package).

Resin Type B (1966) - Run all tests on the first three samples and approve them. Approve samples through 856 without the WRT package. They have resin contents higher than the lowest reference sample resin content and meet other specification requirements. Note that the moisture loss (0.037 g/cm<sup>2</sup>) for the reference sample is well below the specification limit of 0.055 g/cm<sup>2</sup>. Run the WRT on Sample 857, because of its lower resin content, before approving. Approve the remaining samples without running the WRT package.

Resin Type B (1967) - Approve the first three samples without the WRT package, since this same resin and pigment performed satisfactorily with the same proportioning in 1966. Reject Sample 1117, running only the non-volatile matter test. Reject Sample 1141 with no testing because it is blue instead of white. See note under reflectance in Appendix III for this sample.

Resin Type C (1966) - Run all standard and instrumental tests on--and approve--the first four samples. The fourth sample (927) is included because of its lower resin content. The moisture loss for Sample 927 is well below the specification limit so approve subsequent samples of higher resin content, through 964, without the WRT package. Run the WRT on Sample 965, due to lower resin content, before approval. Approve Sample 966 without the WRT package.

Resin Type C (1967) - Approve all samples without the WRT package. This formulation performed satisfactorily the previous year. The excessive moisture loss reported for six of these samples is not consistent with the composition data.

Resin Type C (1968) - Approve all samples without the WRT package. This same resin and pigment formulation has previously performed satisfactorily. Again, the high moisture loss for Sample 121 is not consistent with the composition data.

Resin Type D (1967) - Run all standard and instrumental tests on the first three samples and approve them. Approve samples through 1105 without the WRT package. Run the WRT on Sample 1112 because of lower resin content and approve it. Approve Samples 1121 and 1122 without the WRT package since their resin contents are higher than the two previous samples that passed the WRT. Sample 1124 has a new low resin content, so the WRT must be run before approval. Since the moisture loss for Sample 1124 at 7.4 percent resin is very low, Sample 1125 can be approved at 7.3 percent resin without the WRT package. Approve the remaining 18 samples without running the WRT package.

Resin Type D (1968) - Approve through Sample 97 without running the WRT package. This same resin-pigment formulation performed satisfactorily the previous year. Run the WRT on Sample 105 because of lower resin content and reject it. Approve samples through 156 without running the WRT package. The very low resin content, 3.7 percent, of the last sample (177) may be due to a non-representative sample. If a resample confirms the low resin content, rejection without further tests would be recommended.

Resin Type E (1968) - Run standard and instrumental tests on the first three samples and approve them. Approve Sample 109, since its resin content is as high as two of the reference samples. Sample 110 has a resin content below the 5 percent allowable decrease, so run the WRT before approval. Approve samples through 122 without running the WRT package. The lower resin content of Sample 124 requires running the WRT before approval. Approve through Sample 157 without the WRT package. Reject Sample 197 after running the WRT.

Resin Type F (1968) - Run standard tests and infrared spectra on the first three samples and approve all samples without further water retention tests.

Table 1 summarizes the predicted test results using the infrared method.

## Producer Number 2

Producer No. 2 used two basic resins but only one pigment (calcium carbonate with some titanium dioxide) during the period studied. The resin used in 1966 differed markedly from the resin used in both 1967 and 1968. Figure 2 presents infrared spectra of this producer's pigment and resins. Differences in the resin spectra are:

Type G has a small hydroxyl peak near  $3\mu$  which Type H does not have.

The 5 to  $7\mu$  region peak patterns are strikingly different.

Type H has two small peaks just below  $9\mu$  that are not present in Type G.

The 13 to  $15\mu$  region peaks have different relative heights in the two spectra.

The chemical composition of the resin shows up as an important factor in water retention effectiveness for this producer also.

All of the 1966 samples, containing resin Type G, passed the WRT (avg moisture loss  $0.036 \text{ g/cm}^2$ ) at an average resin content of 10.5 percent.

Three of fourteen 1967 samples, (resin Type H), failed the WRT. The average moisture loss of passing samples rose to  $0.051 \text{ g/cm}^2$  (near specification maximum) with an average resin content of 10.1 percent. Failing samples averaged only 9.2 percent resin content.

Thirteen of 24 samples (resin Type H) failed the WRT in 1968. The average moisture loss for passing samples was  $0.046 \text{ g/cm}^2$  at an average resin content of 11.9 percent. Failing samples averaged only 9.6 percent resin content.

## Infrared Method - Application to Producer Number 2

Resin Type G (1966) - Approve the first three samples after running all standard tests and infrared spectra (refer to Producer No. 2 samples in Appendix III). Approve samples through 883 without running the WRT package. Reject Sample 884, running only the non-volatile matter test. Approve Samples 919 and 928 without running the WRT package, since their resin contents are within guideline limits. The low resin content of Sample 929 requires performance of the WRT before approval. Approve samples through 935 without running the WRT package. Reject Sample 949, running only the non-volatile matter test.

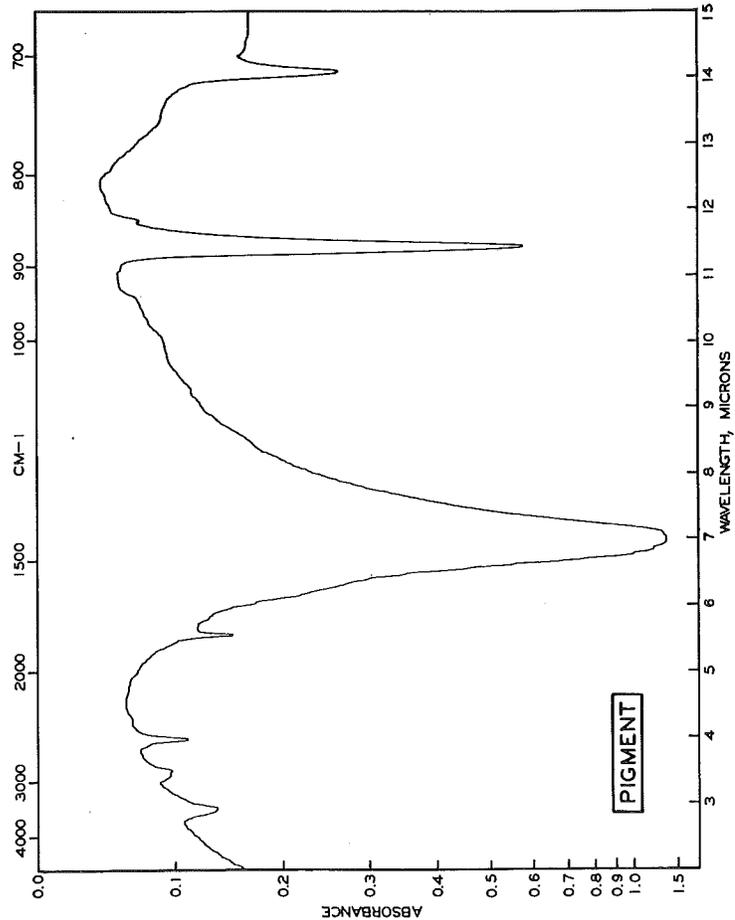
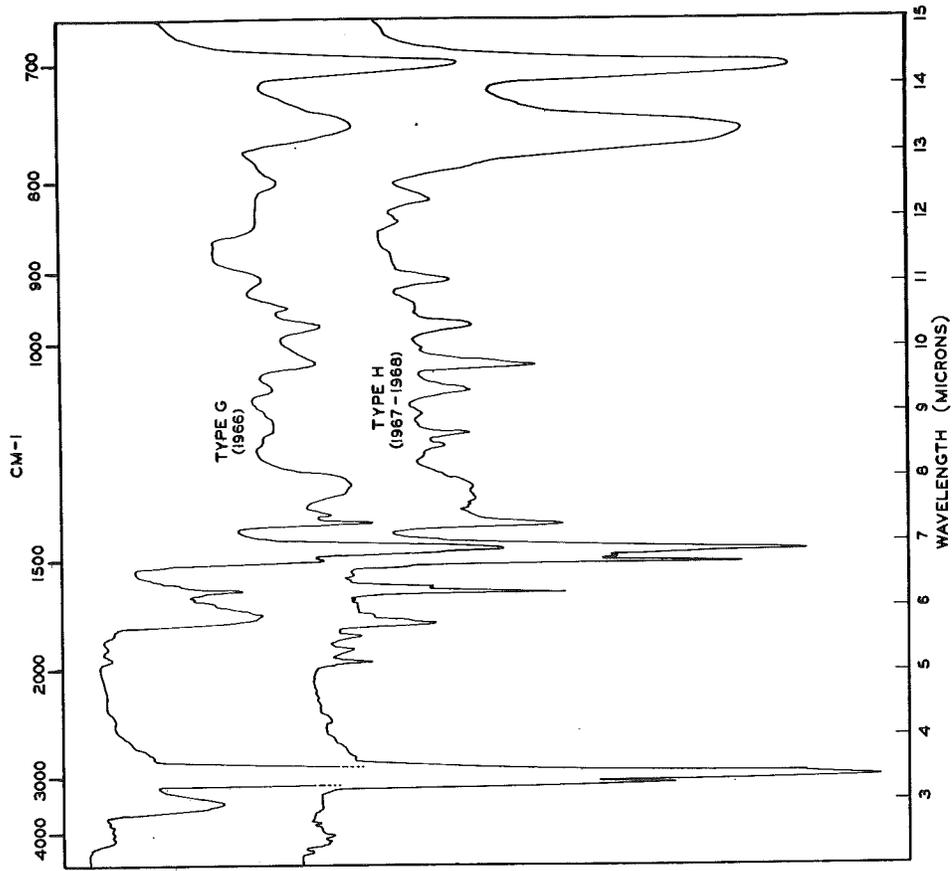


Figure 2. Infrared spectra for the pigment and two resins used by Producer 2. The small peak near  $4\mu$  in the pigment spectrum is spurious; the peak near  $3.5\mu$  is due to residual resin. The pigment is mostly calcium carbonate with some titanium dioxide added.

Reflectance values below the specification minimum of 70 percent were reported for ten samples in this group. One of these ten samples (884) also had low non-volatile matter content, and an eleventh sample (949) had low non-volatile matter content only. The two samples with low non-volatile matter content would be rejected by the instrumental comparison method used, but the other nine samples with reflectance values of 66 through 69 percent would be approved. When reference samples have reflectance values near the specification limit as they do for this formulation, measurement of the reflectance of subsequent samples may be desirable.

Resin Type H (1967) - Run all standard tests and infrared spectra on the first five samples. Reject Samples 1085 and 1086 for excessive moisture loss. Approve through Sample 1110 without running the WRT package. Run the WRT on Samples 1111 and 1127 due to borderline resin content. Reject Sample 1111, approve Sample 1127. Approve Sample 1123 without running the WRT package.

Resin Type H (1968) - Run a full battery of tests on the first three samples because of marginal performance of this formulation during the previous year, and reject for excessive moisture loss--as would be predicted from previous year samples by this producer at 9.0 or 9.1 percent resin content. Reject Sample 102 without the WRT package since it has the same composition as the first three samples. Run the WRT on Samples 103 and 107 and reject them. Reject Samples 108 through 130, which have resin contents below the level at which this formulation fails the WRT. Run the WRT on Samples 141, 142, 143, and approve, as would be predicted by their higher resin content. Approve Samples 144 through 176 without the WRT package. Run the WRT on Sample 179 due to decreased resin content, and approve. Approve Samples 193 through 196 without the WRT package. Although the reported moisture loss for Sample 194 was slightly high, it had the same composition as three passing samples (176, 195, and 196).

### Producer Number 3

This producer used one pigment, a calcium carbonate - calcium sulfate - titanium dioxide blend, and two resins. One resin type was used in 1966; the other resin type was used in both 1967 and 1968. The lack of water retention failures is attributed to the high resin content of the product. The lowest resin content measured was 22 percent. Although it is doubtful that the water retention test is sufficiently precise to permit a firm conclusion, the data indicate that the 1966 resin is not as efficient a moisture barrier as the 1967-68 resin. Compare an average moisture loss of 0.023 g/cm<sup>2</sup> at 29.2 percent average resin content in 1966 with an average moisture loss of 0.015 g/cm<sup>2</sup> at 27.5 percent average resin content in 1967.

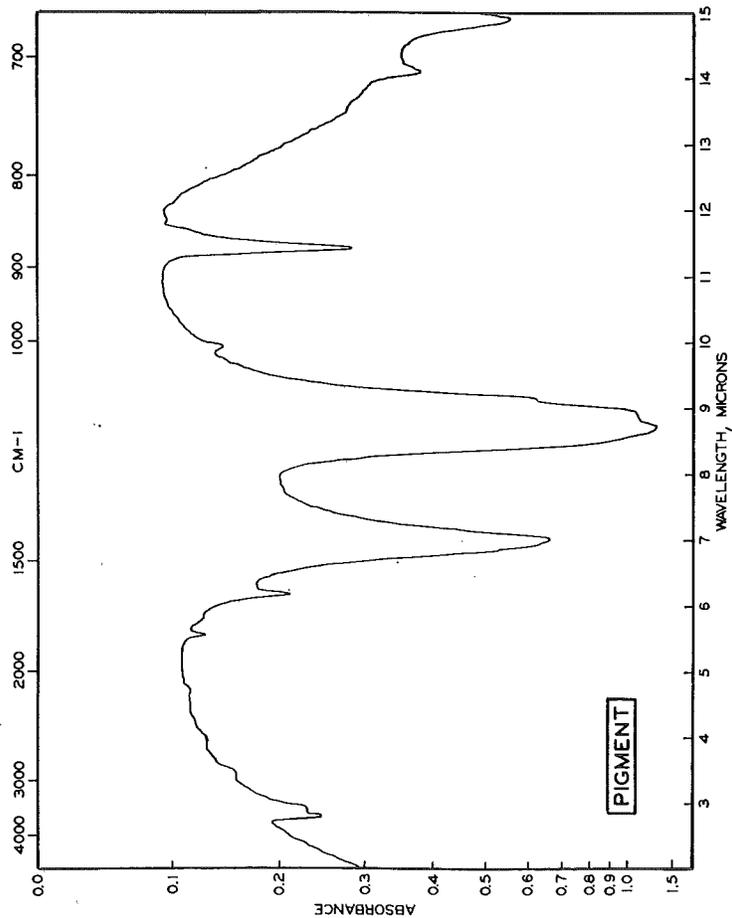
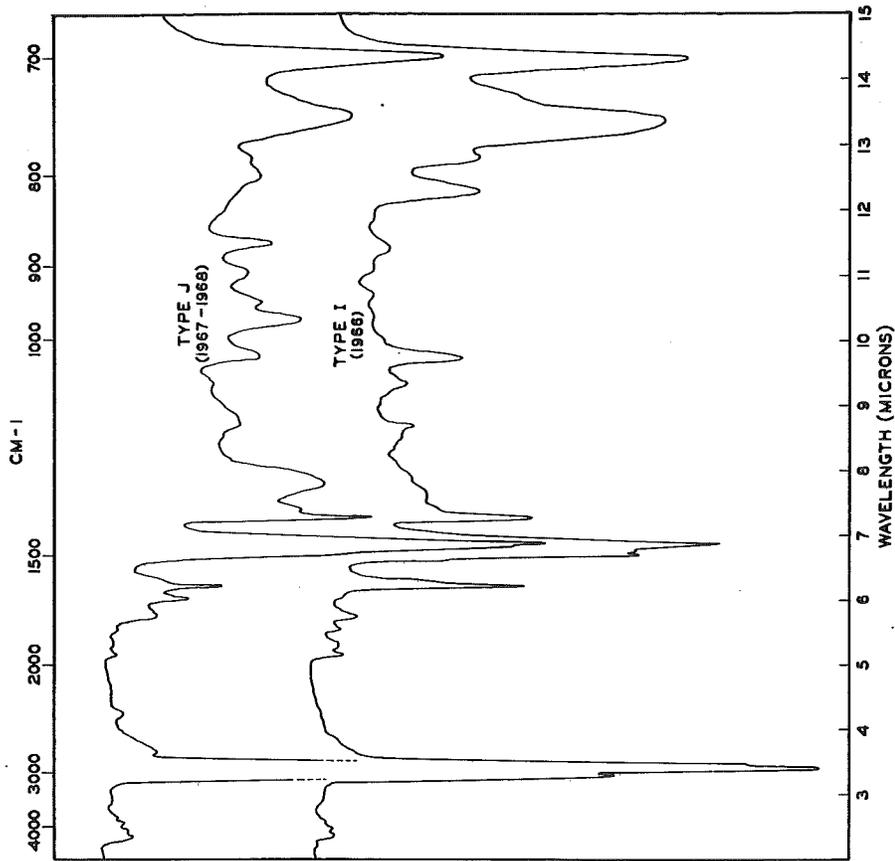


Figure 3. Infrared spectra for the pigment and two resins used by Producer 3. Peaks in the pigment spectrum near 7, 11.4, and 14 $\mu$  are due to calcium carbonate. Peaks near 9 and 15 $\mu$  are due to calcium sulfate. Increased background absorbance beyond 12 $\mu$  is due to titanium dioxide.

Figure 3 presents infrared spectra of this producer's pigment and resins. Differences in the two resin spectra are:

Type I has one medium peak at  $6.2\mu$ , Type J has two small peaks at  $6.0$  and  $6.2\mu$ .

Type I has a double peak with a maximum at  $6.9\mu$ , Type J has only poorly resolved shoulders on a  $6.9\mu$  peak.

Type J has a broad peak at  $7.8\mu$  which is absent in Type I.

Type I has a peak at  $12.3\mu$  which is absent in Type J.

The  $13$  to  $15\mu$  region peaks have different relative heights.

#### Infrared Method - Application to Producer Number 3

Resin Type I (1966) - Reject Sample 837, running only the non-volatile matter test (refer to Producer No. 3 samples in Appendix III). Run all tests on the next three samples, approving them. Approve Sample 886 without the WRT package.

Resin Type J (1967) - Run a full test program on the first, third, and fourth samples, approving them. Reject the second sample (1070) after non-volatile matter test only. Approve the two remaining samples without the WRT package.

Resin Type J (1968) - Reject the first sample after non-volatile matter test. Approve the two remaining samples without the WRT package, since this formulation was satisfactory the previous year.

#### Producer Number 4

This producer supplied samples during 1966 only, and used the same resin and pigment in all samples. The high resin content (20.4 percent minimum) resulted in a low average moisture loss of  $0.021 \text{ g/cm}^2$ . The absence of free water is also believed to aid in formation of a continuous membrane with low moisture permeability. Figure 4 shows infrared spectra of the resin and pigment used. The resin is similar to the resin used by Producer No. 2 in 1967-68. The pigment appears to contain calcium carbonate, calcium sulfate, kaolin clay, and titanium dioxide.

#### Infrared Method - Application to Producer Number 4

Run all tests on the first three samples and approve them. Approve the last sample without the WRT package.

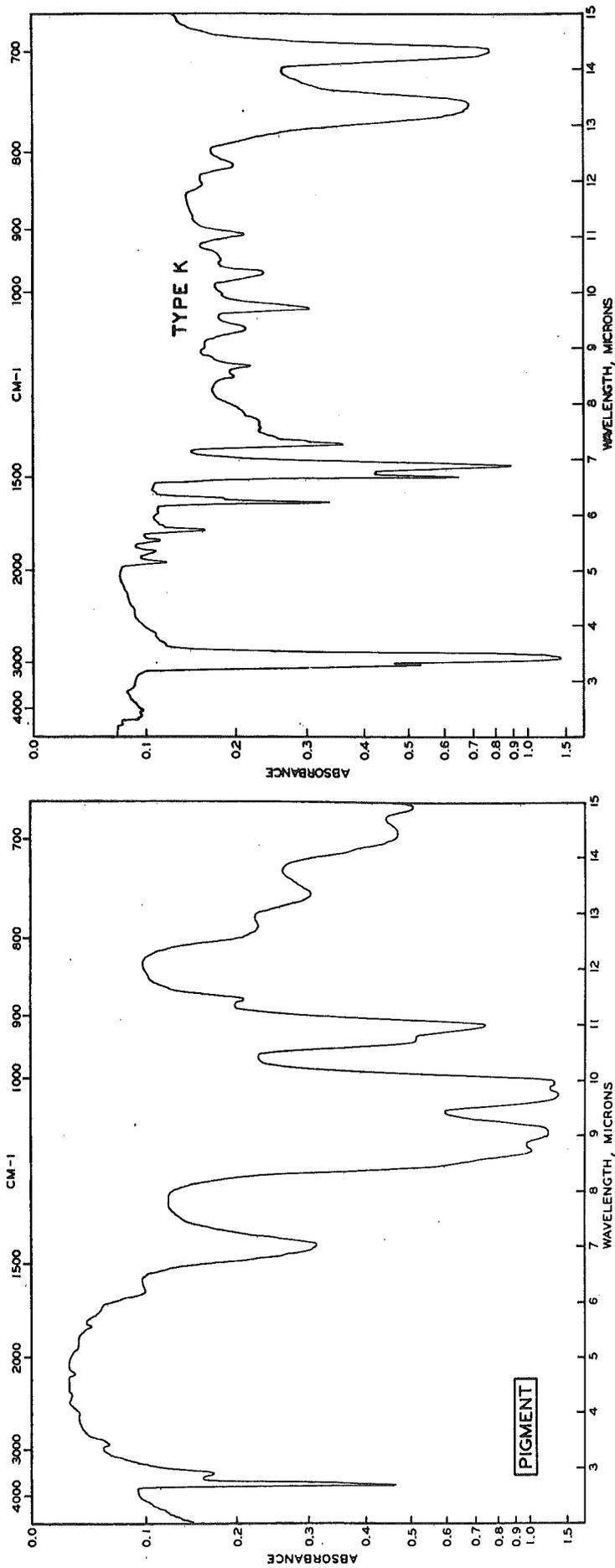


Figure 4. Infrared spectra of the pigment and resin used by Producer 4. This pigment appears to contain calcium carbonate (peaks near 7 and 11.4 $\mu$  and a shoulder near 14 $\mu$ ), calcium sulfate (peaks near 8.8 and 15 $\mu$ ), kaolin clay (remaining peaks in the 9 to 14 $\mu$  region), and titanium dioxide (indicated by generally rising background beyond 13 $\mu$ ). Peaks near 3 and 6.2 $\mu$  are due to bound water.

### Producer Number 5

Infrared spectra of the resin and pigment used by this producer are shown in Figure 5. The same basic resin was used for both 1967 and 1968. Two 1967 resins exhibited infrared peaks near  $13.9\mu$  which indicate the probable presence of waxy materials (long hydrocarbon chains). The dotted portion of the resin spectrum indicates the appearance of spectra not having the wax indication. This resin is similar to resin Type F used by Producer No. 1. The pigment consisted of calcium carbonate, calcium sulfate, and some titanium dioxide. One sample, which was rejected for low non-volatile matter content, contained an additional ingredient that added a peak near  $10\mu$  (dotted line) to the infrared spectrum of the pigment.

### Infrared Method - Application to Producer Number 5

Resin Type L (1967) - Run all tests on the first three samples and approve them. Approve the next two samples without the WRT package. The resin spectra for Samples 1157 and 1158 have two peaks just below  $14\mu$  indicating that wax might be present, so a solvent fractionation of the resin was carried out. The procedure for isolation of waxy material is detailed in Appendix IV.

The isolated material (14.2 and 9.9 percent, respectively of resin solids) was quite hard and did not have the characteristic slippery surface of wax. It softened somewhat, but did not melt when held at a temperature of 100 C. An infrared spectrum of the material exhibited two peaks in the  $13.7$  to  $13.9\mu$  region but there was also evidence that branched hydrocarbon chains and aromatic rings were present. The material could not be judged waxy. Accordingly, Sample 1157 would be run through the WRT (lower resin content) and approved. Sample 1158 has acceptable resin content, so approve it and remaining samples without the WRT package.

Resin Type L (1968) - Reject the first two samples, running only the non-volatile matter test. Approve the remaining samples without the WRT package since this same formulation was satisfactory the previous year.

### Producer Number 6

This producer submitted only one sample in each of 1966 and 1967. Both samples failed to meet drying time and non-volatile matter requirements, so no further tests were performed.

Infrared spectra for the pigments and resins used are shown in Figure 6. The pigment used in 1966 was calcium sulfate and titanium dioxide.

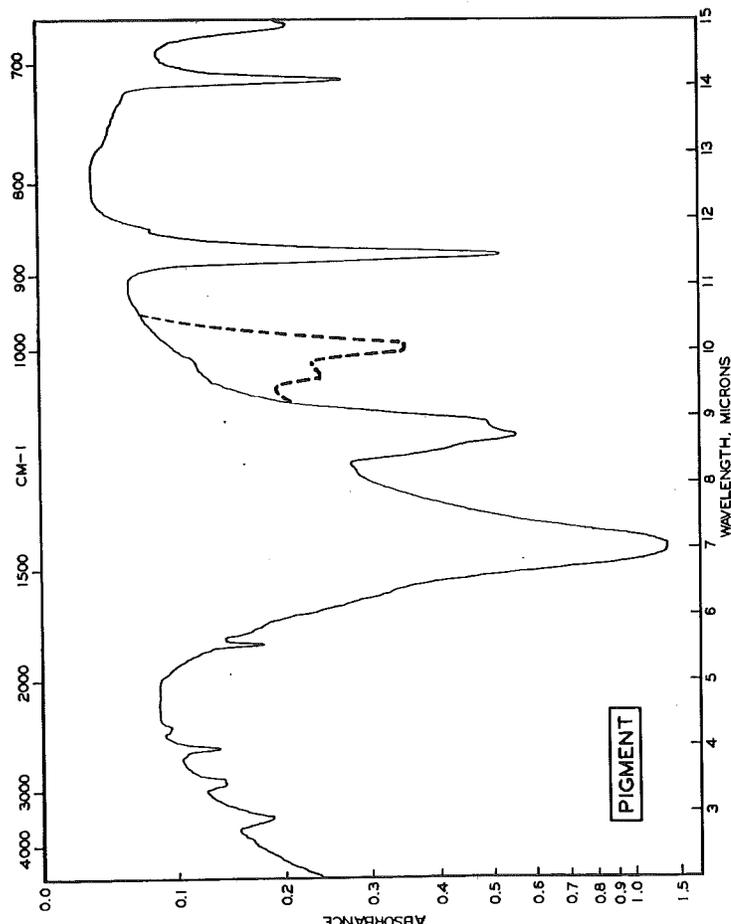
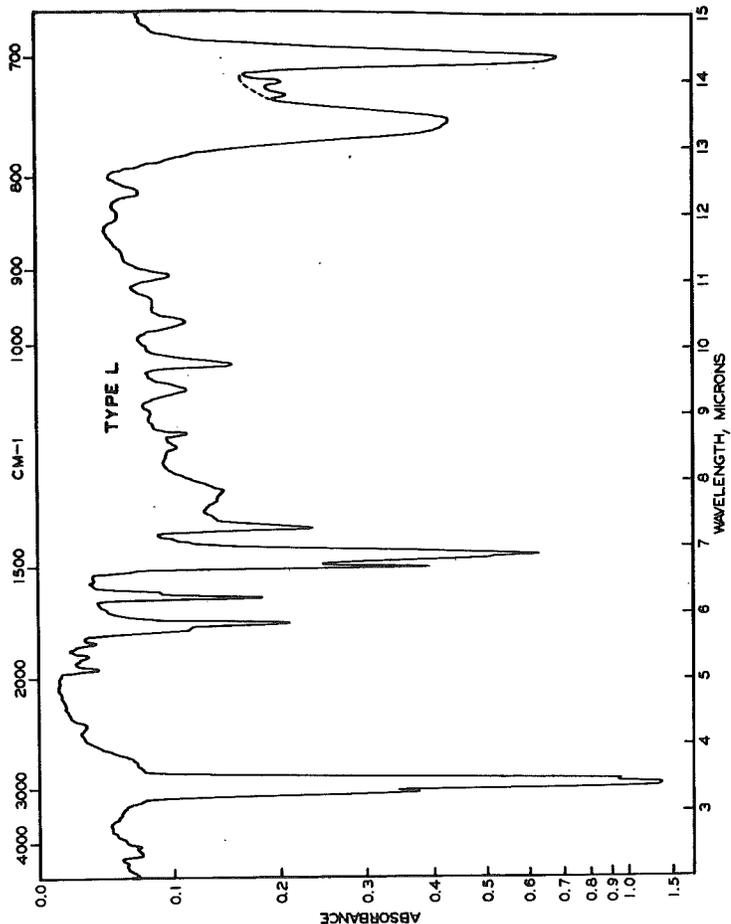


Figure 5. Infrared spectra of the pigment and resin used by Producer 5. In the pigment spectrum, the small peak near  $3.5\mu$  is due to residual resin and the small peak near  $4\mu$  is spurious. Peaks near  $7$ ,  $11.4$ , and  $14\mu$  are due to calcium carbonate. Peaks near  $9$  and  $15\mu$  are due to calcium sulfate. The increasing background absorption beyond  $13\mu$  indicates titanium dioxide is present. The dotted peak near  $10\mu$  was found in the spectrum of only one pigment sample. In the resin spectrum, two small peaks just below  $14\mu$  are typical of waxy materials.

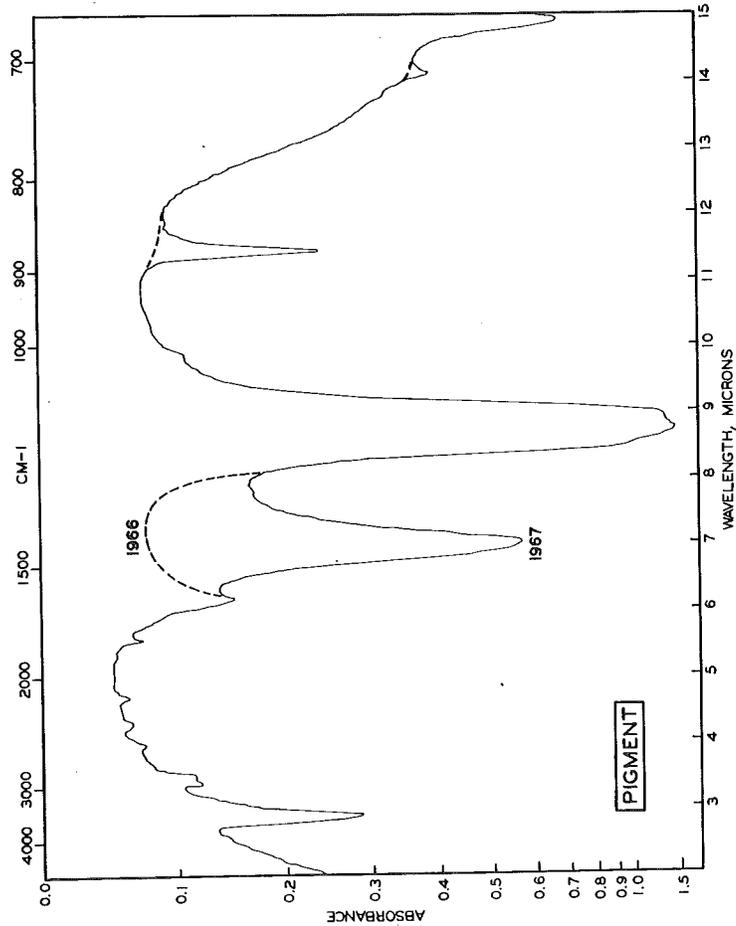
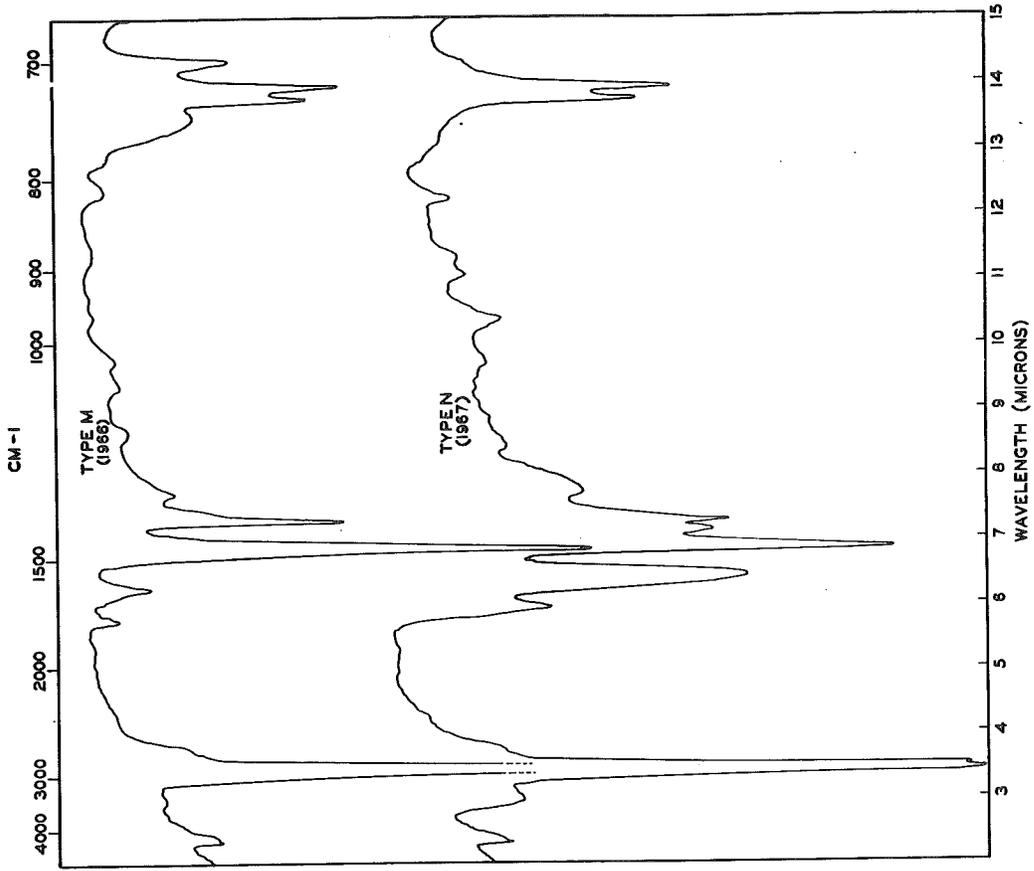


Figure 6. Infrared spectra of the pigments and resins used by Producer 6. The 1966 pigment was calcium sulfate and titanium dioxide. The dotted lines indicate the path of the calcium sulfate spectrum. The high background absorbance beyond  $12\mu$  is due to titanium dioxide. Peaks near 3 and  $6.2\mu$  are due to water bound to calcium sulfate. The peak near  $3.5\mu$  is due to residual resin. Peaks near 7, 11.4, and  $14\mu$  indicate that the 1967 pigment also contained calcium carbonate.

A blend of calcium carbonate, calcium sulfate, and titanium dioxide pigmented 1967 samples. Two resin types were used. Inspection reveals the following differences in the resin spectra:

Type M has small peaks near  $5.7\mu$  and  $6.2\mu$  while Type N has a medium peak near  $6.4\mu$  and a larger peak near  $6.5\mu$ .

Type M has a single peak near  $7.3\mu$ , Type N had a doublet in the  $7.1$  to  $7.3\mu$  range.

Type M has four peaks around  $14\mu$ , Type N has only two peaks in this area.

The sharp doublet just below  $14\mu$  is characteristic of waxy materials (long hydrocarbon chains). These samples failed to dry within four hours, a characteristic behavior noted for waxy curing compounds prior to this study.

#### Infrared Method - Application to Producer Number 6

Reject these samples after the non-volatile matter test. Record infrared spectra of the resins and pigments for information.

### SUMMARY

This study investigated the feasibility of applying infrared spectra to compare batches or lots of white pigmented membrane curing compounds for concrete, and thereby greatly reduce the number of water retention acceptance tests (ASTM C 156) presently performed. This follows successful application of infrared spectra to detect prohibited waxy materials in curing compound resins, and a very successful (over ten years) acceptance test program for traffic paints, based on comparison of infrared spectra of resin and pigment fractions of acceptance samples with the spectra of reference samples that were field tested. It is also widely accepted industrial practice to monitor the composition of both raw materials and finished products by their infrared spectra. At least one state stipulates that acceptance samples of epoxy resin yield an infrared spectrum which matches a reference spectrum that is part of the specification.

The proposed method would operate by comparing infrared spectra of the resin and pigment, and the resin and pigment contents (by weight) of acceptance samples with comparable data from three or more acceptable reference samples from the same producer. Prohibited waxy material in the resin fraction of any sample would be detected in the infrared spectrum. If the chemical composition of the resin and pigment are shown by their infrared spectra to be the same as the reference samples, and the proportioning of resin and pigment is correct, WRT package (water retention, drying time, and reflectance tests) would not be run. When proportioning or ingredients change, the WRT package would be run to evaluate the new formulation. If acceptable, the new formulation is used as a reference for subsequent batches.

Correlation of infrared spectra and physical test data was carried out for 295 samples of white pigmented curing compounds obtained from six different producers over a three-year period. The various products were found to be sufficiently consistent in chemical composition to compare batches successfully by infrared spectra. The largest supplier used three or four somewhat different resins with the same pigment during each production year. The other suppliers generally used the same resin and pigment for a whole production year. The same ingredients were used in two successive years by four of the five possible producers (one producer supplied samples for one year only). One resin and three pigments were used three successive years.

The greatest reduction in water retention, drying time, and reflectance tests would be achieved if one resin and one pigment were used year after year by each producer. Even though this ideal situation was not found, and one producer used six resin variations in three years, a large reduction in water retention tests (from 293 to 64) would still be possible.

Generally, there was a correlation between low resin content and failure of a sample to pass the water retention test. Other factors which did not correlate with water retentiveness were viscosity, pigment fineness (ASTM D 1210), and free water content. Water was found in products of five of the six producers, and ranged from 13 to 19.1 percent by weight. Twelve samples which had apparently satisfactory resin contents of an approved composition, however, failed the routine water retention test. The infrared and other correlation work was done at another laboratory (without water retention test facilities) some time after the routine tests and no further work was done to discover the causes of these anomalous failures of the water retention test.

## RECOMMENDATIONS

A suitable transition period where both the infrared comparison method and all standard tests are applied to every sample is recommended. The personnel involved in testing curing compounds would have the chance to gage the behavior of various products as the formulations varied and become accustomed to the method during this period.

The infrared comparison method should also be applied to acceptance testing the simpler system found in transparent membrane curing compound formulations. Gas chromatographic analysis of the solvent fraction may be desirable.

Additional information of interest to the curing compound consumer would be the threshold resin content below which samples will consistently fail the water retention test. This could be determined by systematically adding pigment to a curing compound to reduce the resin content, and running the water retention test. Such action would be justified only for suppliers submitting many samples, formulated with resin contents below 15 percent.

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The opinions, findings, and conclusions expressed in this publication are those of the author and not necessarily those of the Federal Highway Administration.

APPENDIX

## APPENDIX I

### INFRARED SAMPLE PREPARATION

#### Resin

Mix the curing compound sample thoroughly and place 2 or 3 ml in a 5 ml screw cap vial. Centrifuge the sample for 1 or 2 minutes to settle the pigment. Evaporate a few drops of the supernatant resin solution on a sodium chloride disc to obtain a film of resin with suitable thickness for recording an infrared spectrum. The thickness is checked by placing the air dried film in the sample beam of an infrared spectrophotometer and scanning a region of the spectrum expected to exhibit strong absorption. The  $3\mu$  to  $4\mu$  region is satisfactory for many samples. When a satisfactory thickness is achieved, dry the film in a vacuum oven at 60 C for 30 minutes. Record the infrared spectrum of the resin.

#### Pigment

Discard the supernatant resin solution remaining in the centrifuged sample. Wash the pigment once with acetone and twice with benzene by stirring the pigment with the solvent and recentrifuging. Discard the washings. Dry the pigment in an oven at 100 C for one or two hours, then grind the resulting lump with a mortar and pestle. The mortar should be of agate or other non-contaminating material. Prepare a potassium bromide disc, using 1 mg of pigment in 500 mg of spectroscopic grade potassium bromide. Record the pigment spectrum.

## APPENDIX II

### PROCEDURE FOR WATER DETERMINATION

Mix the curing compound sample thoroughly, and accurately weigh approximately 25g into a single neck 200 ml round bottom flask. Add 100 ml of toluene to the flask. Place the flask in a heating mantle and attach a moisture test distilling receiver and a water cooled condenser. Pour toluene down the condenser to fill the distilling receiver. Supply water to the condenser, then reflux the toluene until no more water is entrained. Wash down the condenser with toluene to transfer droplets of water from the condenser to the receiver. Read the volume of water in the trap. Calculate water content as follows:

$$\text{Percent H}_2\text{O} = \frac{\text{Volume H}_2\text{O, ml X 100}}{\text{Sample Weight, g}}$$

**APPENDIX III**  
**Individual Sample Data**  
**PRODUCER NUMBER 1**

	Sample No.	Moisture Loss, g/cm <sup>2</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>	
				percent	size, mils				
Resin Type A	1966								
		829	0.059*	10.4	51.1	1.5	61.5	37	75
		830	0.055	9.2	53.3	1.5	62.5	35	75
		849	0.059*	9.4	51.2	2.0	60.6	57	72
		850	0.046	9.5	52.1	2.0	61.6	58	75
		851	0.046	9.1	52.6	2.0	61.7	50	73
		859	0.042	9.8	52.3	4.0	62.1	39	72
		874	0.047	10.5	51.4	1.5	61.9	25	73
		875	0.044	9.3	52.6	2.0	61.9	24	72
		885	0.036	10.4	52.1	1.5	62.5	41	71
		889	0.054	10.5	51.5	1.5	62.0	35	75
		890	0.038	10.4	51.5	1.5	61.9	35	75
	891	0.028	10.0	52.0	1.5	62.0	36	77	
Resin Type B	1966								
		831	0.041	7.9	53.5	1.5	61.4	34	81
		832	0.037	8.2	53.4	1.5	61.6	35	78
		833	0.037	7.0	54.0	1.0	61.4	33	78
		834	0.030	7.3	54.5	1.0	61.8	50	78
		835	0.044	7.5	54.4	1.5	61.9	45	77
		836	0.035	7.8	53.5	1.5	61.3	43	77
		838	0.032	7.8	53.7	1.0	61.5	45	77
		839	0.030	7.5	54.0	1.5	61.5	39	78
		840	0.039	7.5	53.6	1.5	61.1	42	78
		845	0.025	8.4	53.6	1.5	62.0	45	74
		846	0.037	8.7	53.3	1.5	62.0	40	79
		847	0.023	8.1	53.8	1.5	61.9	45	80
		848	0.034	7.6	54.1	1.5	61.7	35	78
		855	0.050	7.7	53.8	1.0	61.5	31	83
		856	0.036	7.9	53.7	2.0	61.6	30	85
		857	0.032	6.5	54.8	1.5	61.3	35	78
		858	0.056	7.2	54.6	3.5	61.8	35	83
		866	0.047	7.5	54.2	1.5	61.7	39	79
		867	0.037	7.8	54.4	1.5	61.8	43	80
		868	0.039	8.1	53.5	1.5	61.6	44	81
		869	0.044	8.2	53.8	2.0	62.0	38	78
		870	0.037	7.5	54.5	1.5	62.0	38	80
		871	0.036	7.4	55.0	1.5	62.4	40	81
		872	0.051	7.4	54.6	1.5	62.0	35	80
		873	0.039	7.6	54.3	1.5	61.9	33	80
	876	0.030	8.0	53.5	1.5	61.5	30	80	
	877	0.046	7.5	54.1	1.5	61.6	30	80	
	887	0.031	8.0	53.7	1.5	61.7	26	80	

(1) Magnesium Oxide = 100%

\* Sample failed to meet specification requirements for column indicated.

APPENDIX III (Continued)

Sample No.	Moisture Loss, g/cm <sup>2</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>
			percent	size, mils			
Resin Type B							
1966							
888	0.025	6.8	54.8	1.5	61.6	24	80
899	0.026	7.6	54.2	1.5	61.8	20	82
900	0.032	8.2	53.5	1.5	61.7	19	83
920	0.028	7.7	53.3	1.5	61.0	35	84
921	0.027	8.6	53.9	1.5	62.5	29	83
922	0.035	9.1	53.3	1.5	62.4	31	83
923	0.035	9.7	54.2	1.5	63.9	30	82
924	0.033	6.7	55.0	1.5	61.7	28	82
925	0.040	6.8	54.8	1.5	61.6	26	84
943	0.034	6.4	56.1	1.5	62.5	28	88
946	0.023	7.2	54.6	2.0	61.8	33	82
947	0.034	7.3	54.5	1.5	61.8	34	80
948	0.044	7.5	54.3	1.5	61.8	36	79
1967							
1063	0.043	7.3	54.9		62.2	35	79
1066	0.044	7.9	53.7		61.6	25	77
1101	0.026	7.3	54.6		61.8	30	82
1117	0.043	10.1	40.2		50.3*	15	73
1141	0.036	7.7	54.0		61.7	35	69*(lt. blue)
Resin Type C							
1966							
892	0.047	6.9	54.4	1.5	61.3	27	77
897	0.035	7.7	53.4	3.5	61.1	21	76
898	0.035	7.5	52.8	1.5	60.3	28	77
927	0.025	6.3	55.5	3.0	61.8	32	79
936	0.054	6.4	55.3	3.0	61.7	30	79
937	0.048	6.8	56.0	2.0	62.8	34	79
938	0.046	6.6	54.6	3.5	61.2	24	81
939	0.040	6.4	54.8	1.5	61.2	24	81
940	0.051	6.6	54.7	2.5	61.3	24	79
941	0.055	6.8	54.5	3.5	61.3	20	78
942	0.041	7.1	54.8	3.5	61.9	20	78
944	0.037	6.3	54.3	4.0	60.6	33	81
945	0.036	7.1	53.7	4.0	60.8	34	80
953	0.045	6.9	53.8	3.0	60.7	25	77
954	0.054	8.8	51.7	3.5	60.5	24	73
955	0.052	6.4	53.8	4.5	60.2	30	77
956	0.055	7.3	53.7	4.0	61.0	29	77
957	0.029	7.9	52.9	3.0	60.8	40	80
958	0.040	7.4	53.3	3.5	60.7	40	80
959	0.018	7.7	54.3	2.0	62.0	60	79
960	0.013	8.0	54.0	3.0	62.0	68	81
961	0.019	7.4	54.3	3.5	61.7	50	80
962	0.028	7.7	53.9	4.0	61.6	55	82
963	0.027	8.0	53.4	3.5	61.4	49	81
964	0.023	7.3	54.0	3.0	61.3	47	82
965	0.035	6.2	54.8	3.0	61.0	50	79
966	0.028	6.7	54.2	3.0	60.9	55	80

(1) Magnesium Oxide = 100%

APPENDIX III (Continued)

	Sample No.	Moisture Loss, g/cm <sup>2</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>
				percent	size, mils			
Resin Type C	1967	1064	0.050	6.9	54.5	61.4	75	79
		1067	0.071*	7.0	53.9	60.9	48	79
		1068	0.061*	7.5	54.0	61.5	60	79
		1069	0.043	8.6	53.0	61.6	53	79
		1071	0.031	7.9	53.6	61.5	40	81
		1072	0.049	7.5	54.3	61.8	45	81
		1073	0.055	7.4	53.6	61.0	50	80
		1074	0.059*	7.5	54.6	62.1	60	82
		1075	0.098*	7.5	54.4	61.9	60	80
		1076	0.080*	8.3	53.6	61.9	58	82
		1077	0.057*	7.5	53.4	60.9	19	79
		1098	0.040	7.0	54.4	61.4	20	78
		Resin Type C	1968	121	0.062*	10.9	50.2	61.1
137	0.019			8.8	54.0	62.8	45	77
138	0.024			8.7	53.9	62.6	30	78
139	0.014			8.6	54.3	62.9	40	80
140	0.024			9.1	54.0	63.1	25	79
147	0.020			8.4	55.0	63.4	45	79
148	0.020			8.2	54.9	63.1	35	80
149	0.021			8.5	54.1	62.6	45	79
150	0.022			8.3	54.1	62.4	35	83
151	0.050			8.0	54.2	62.2	30	77
Resin Type D	1967			1078	0.020	10.0	52.8	62.8
		1079	0.013	10.2	53.3	63.5	80	77
		1080	0.026	10.3	53.5	63.8	100	77
		1081	0.020	10.9	52.8	63.7	100	78
		1082	0.021	10.4	53.9	64.3	95	79
		1083	0.021	9.6	53.6	63.2	50	78
		1090	0.021	10.9	52.6	63.5	55	75
		1091	0.019	10.6	52.9	63.5	75	78
		1092	0.025	12.7	52.1	64.8	80	76
		1093	0.027	9.7	53.8	63.5	75	77
		1095	0.027	9.8	53.0	62.8	85	75
		1096	0.017	10.2	52.9	63.1	85	74
		1097	0.022	10.2	52.9	63.1	85	75
		1099	0.010	13.9	50.2	64.1	90	71
		1100	0.011	10.4	52.5	62.9	55	76
		1103	0.022	10.4	53.4	63.8	35	76
		1104	0.029	10.4	53.9	64.3	30	77
		1105	0.020	10.7	54.0	64.7	40	75
1112	0.044	8.8	54.9	63.7	30	79		
1113	0.037	8.8	53.5	62.3	25	77		
1114	0.041	8.9	53.3	62.2	35	77		
1118	0.019	9.6	52.3	61.9	60	78		

(1) Magnesium Oxide = 100%

APPENDIX III (Continued)

Sample No.	Moisture Loss, g/cm <sup>2</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>
			percent	size, mils			
Resin Type D							
1967							
1119	0.018	8.4	53.3		61.7	40	78
1120	0.014	7.8	53.5		61.3	40	79
1121	0.017	7.9	53.6		61.5	50	80
1122	0.014	8.2	54.2		62.4	45	82
1124	0.020	7.4	55.4		62.8	55	81
1125	0.025	7.3	55.6		62.9	50	82
1128	0.029	8.9	53.3		62.2	40	80
1129	0.026	9.4	52.6		62.0	25	79
1130	0.023	9.2	53.0		62.2	20	78
1132	0.015	8.5	54.2		62.7	45	80
1133	0.014	8.5	53.9		62.4	45	79
1134	0.013	9.3	53.3		62.6	40	78
1144	0.023	8.9	54.7		62.6	85	79
1145	0.017	8.0	54.7		62.7	85	79
1146	0.021	7.8	55.2		63.0	80	80
1147	0.010	7.7	55.3		63.0	80	79
1148	0.017	7.8	55.2		63.0	50	81
1149	0.016	8.1	55.0		63.1	50	82
1152	0.029	7.9	55.2		63.1	25	80
1153	0.032	8.1	55.3		63.4	35	81
1154	0.024	8.1	55.1		63.2	55	80
1155	0.021	8.8	55.0		63.8	45	81
1156	0.023	8.2	54.8		63.0	40	82
1968							
89	0.032	10.6	52.1		62.7	30	73
90	0.029	10.2	52.7		62.9	25	73
91	0.022	10.0	53.2		63.2	30	75
92	0.019	9.0	53.4		62.4	30	74
93	0.027	8.1	54.1		62.2	25	79
97	0.031	8.2	53.2		61.4	25	78
105	0.057*	7.5	55.0		62.5	30	80
106	0.027	8.6	53.3		61.9	35	76
118	0.042	8.9	53.9		62.8	25	80
123	0.040	8.7	53.2		61.9	20	79
129	0.040	10.8	52.2		63.0	35	76
154	0.030	10.2	52.6		62.8	28	75
155	0.028	9.5	53.6		63.1	31	77
156	0.029	9.5	54.3		63.8	39	76
177	0.109*	3.7	59.6		63.3	90	80
Resin Type E							
1968							
88	0.023	8.6	54.7		63.3	45	79
94	0.020	8.5	55.1		63.6	55	80
104	0.022	9.5	54.5		64.0	40	81
109	0.029	8.6	55.3		63.9	35	77
110	0.022	8.0	54.5		62.5	50	77
112	0.027	8.4	54.2		62.6	50	77
116	0.050	8.9	53.8		62.7	35	75

(1) Magnesium Oxide = 100%

APPENDIX III (Continued)

	Sample No.	Moisture Loss, g/cm <sup>3</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>	
				percent	size, mils				
Resin Type E	1968	117	0.036	8.3	54.3		62.6	25	78
		122	0.034	8.4	54.3		62.7	50	77
		124	0.027	7.6	55.1		62.7	45	78
		125	0.029	8.7	54.5		63.2	40	80
		126	0.023	8.5	54.4		62.9	55	80
		128	0.016	8.4	54.5		62.9	40	78
		131	0.020	8.9	53.0		61.9	45	74
		132	0.023	8.7	53.3		62.0	45	75
		133	0.031	9.2	51.7		60.9	40	72
		134	0.020	8.6	54.1		62.7	35	81
		157	0.031	9.4	55.2		64.6	51	78
197	0.082*	6.4	55.3		61.7	90	80		
Resin Type F	1968	158	0.020	8.8	53.1		61.9	55	76
		159	0.018	8.8	53.1		61.9	45	78
		160	0.018	8.7	53.2		61.9	55	78
		161	0.016	8.8	53.2		62.0	60	79
		162	0.019	9.5	52.5		62.0	60	80
		163	0.014	9.5	52.5		62.0	45	80
		164	0.029	8.9	53.1		62.0	50	81
		165	0.032	8.8	53.2		62.0	50	79

PRODUCER NUMBER 2

Resin Type G	1966	841	0.023	10.7	51.9	4.0	62.6	24	71
		842	0.033	10.6	50.9	3.0	61.5	25	71
		843	0.031	10.8	50.6	3.0	61.4	16	71
		860	0.023	10.7	50.4	3.5	61.1	15	71
		861	0.032	10.5	50.5	4.0	61.0	12	73
		862	0.025	10.8	50.1	4.0	60.9	16	69*
		863	0.029	11.1	49.6	4.0	60.7	15	68*
		864	0.025	10.7	50.0	4.0	60.7	20	70
		865	0.027	10.9	49.8	4.0	60.7	20	68*
		878	0.040	11.2	50.4	4.0	61.6	23	68*
		879	0.046	11.1	50.3	5.0	61.4	28	67*
		880	0.039	11.2	50.5	4.5	61.7	26	69*
		881	0.031	11.2	50.1	5.0	61.3	30	66*
		882	0.050	11.2	50.3	5.0	61.5	26	67*
		883	0.035	11.1	50.5	5.0	61.6	26	69*
		884	0.027	9.0	49.3	5.0	58.3*	20	69*
		919	0.033	10.4	51.4	3.0	61.8	20	73
		928	0.040	10.6	53.8	5.0	64.4	42	75
		929	0.038	9.3	55.0	5.0	64.3	49	77
		930	0.042	10.5	54.1	5.0	64.6	39	75

(1) Magnesium Oxide = 100%

APPENDIX III (Continued)

	Sample No.	Moisture Loss, g/cm <sup>2</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time, min.	Reflectance, percent <sup>(1)</sup>	
				percent	size, mils				
Resin Type G	1966	931	0.048	10.1	53.8	4.5	63.9	37	73
		932	0.041	10.3	53.8	5.0	64.1	37	73
		933	0.041	10.1	53.9	4.5	64.0	54	73
		934	0.056	10.1	53.9	4.5	64.0	40	75
		935	0.052	9.8	53.8	5.0	63.6	36	70
		949	0.036	9.9	44.8	5.0	54.7*	30	70
Resin Type H	1967	1084	0.053	9.1	54.2		63.3	50	78
		1085	0.063*	9.1	54.2		63.3	40	78
		1086	0.064*	9.3	54.1		63.4	40	78
		1087	0.047	9.3	54.2		63.5	38	78
		1088	0.044	9.3	54.0		63.3	45	78
		1089	0.051	9.4	53.9		63.3	40	79
		1106	0.052	11.0	52.6		63.6	40	79
		1107	0.052	9.5	54.0		63.5	35	79
		1108	0.049	9.6	54.0		63.6	35	79
		1109	0.053	15.5	48.0		63.5	30	79
		1110	0.052	9.3	54.3		63.6	45	79
		1111	0.065*	9.2	54.3		63.5	40	79
		1123	0.054	9.8	54.4		64.2	30	78
		1127	0.050	9.2	55.1		64.3	----	80
Resin Type H	1968	99	0.068*	9.0	54.8		63.8	45	77
		100	0.064*	9.1	54.7		63.8	50	78
		101	0.067*	9.0	54.8		63.8	45	77
		102	0.070*	9.0	54.8		63.8	40	78
		103	0.065*	13.8	50.1		63.9	40	77
		107	0.068*	9.7	52.9		62.6	40	73
		108	0.071*	8.9	55.1		64.0	40	76
		111	0.059*	8.9	55.2		64.1	45	80
		113	0.068*	8.9	54.4		63.3	40	78
		114	0.064*	8.8	55.2		64.0	40	79
		115	0.070*	8.8	55.3		64.1	40	78
		130	0.059*	8.8	55.6		64.4	25	77
		141	0.036	12.1	48.7		60.8	40	72
		142	0.048	12.1	48.7		60.8	40	73
		143	0.038	12.1	48.7		60.8	40	70
		144	0.054	12.1	48.7		60.8	35	73
		145	0.038	12.2	48.7		60.9	40	71
		146	0.043	12.4	48.5		60.9	35	73
		176	0.053	11.8	48.9		60.7	40	75
		179	0.040	10.8	51.3		62.1	30	74
193	0.050	12.2	48.5		60.7	40	75		
194	0.058*	11.8	48.9		60.7	40	75		
195	0.055	11.8	48.9		60.7	35	73		
196	0.048	11.8	48.9		60.7	40	75		

(1) Magnesium Oxide = 100%

APPENDIX III (Continued)  
PRODUCER NUMBER 3

	Sample No.	Moisture Loss, g/cm <sup>3</sup>	Resin, percent	Pigment		Non-volatile Matter, percent	Drying Time min.	Reflectance, percent <sup>(1)</sup>	
				percent	size, mils				
Resin Type I	1966	837	0.015	29.0	29.8	1.5	58.8*	222	71
		844	0.016	29.1	32.3	2.0	61.4	135	74
		852	0.028	29.4	31.1	1.5	60.5	41	73
		854	0.035	28.4	31.2	3.5	59.6	29	72
		886	0.019	30.3	31.0	2.0	61.3	40	70
Resin Type J	1967	1065	0.018	27.8	34.5		62.3	80	74
		1070	0.019	22.0	36.6		58.6*	60	75
		1094	0.018	30.3	31.0		61.3	70	79
		1102	0.014	30.3	31.3		61.6	45	75
		1115	0.010	24.1	34.9		59.0	25	77
		1116	0.011	30.2	31.4		61.6	30	78
Resin Type J	1968	98	0.009	27.7	29.7		57.4*	90	67
		127	0.005	36.8	24.0		60.8	65	69
		178	0.021	33.9	28.0		61.9	60	74

PRODUCER NUMBER 4

Resin Type	Year	Sample No.	Moisture Loss, g/cm <sup>3</sup>	Resin, percent	Pigment percent	Pigment size, mils	Non-volatile Matter, percent	Drying Time min.	Reflectance, percent
Resin K	1966	893	0.022	20.4	39.0	2.0	59.4	27	70
		894	0.017	22.2	39.8	4.0	62.0	26	70
		895	0.019	21.2	39.3	4.0	60.4	26	72
		896	0.025	21.2	39.3	4.0	60.5	31	72

PRODUCER NUMBER 5

Resin Type	Year	Sample No.	Moisture Loss, g/cm <sup>3</sup>	Resin, percent	Pigment percent	Pigment size, mils	Non-volatile Matter, percent	Drying Time min.	Reflectance, percent
Resin Type L	1967	1131	0.055	10.5	52.6		63.1	35	84
		1142	0.054	10.6	51.1		61.7	38	83
		1143	0.052	10.7	51.0		61.7	36	82
		1150	0.053	10.6	52.0		62.6	55	83
		1151	0.052	10.3	49.6		59.9	30	85
		1157	0.039	9.2	52.5		61.7	55	87
		1158	0.046	9.2	52.5		61.7	55	86
		1228	0.050	11.5	57.3		68.8	35	84
		1229	0.046	11.5	57.3		68.8	40	83
Resin Type L	1968	95	0.053	8.3	48.9		57.2*	25	84
		96	0.069	8.0	49.4		57.4*	30	84
		119	0.055	9.8	52.5		62.3	35	85
		120	0.052	9.7	50.4		60.1	35	82
		135	0.050	9.7	52.8		62.5	30	85
		136	0.055	9.7	52.9		62.6	30	85
		152	0.044	9.9	52.1		62.0	90	86
		153	0.048	9.9	52.0		61.9	90	84

PRODUCER NUMBER 6

Resin Type	Year	Sample No.	Moisture Loss, g/cm <sup>3</sup>	Resin, percent	Pigment percent	Pigment size, mils	Non-volatile Matter, percent	Drying Time min.	Reflectance, percent
Resin Type N   M		926	Not Run	20.0	19.1		39.1*	fails	----
		1126	Not Run	22.1	11.9		34.0*	fails	----

(1) Magnesium Oxide = 100%

## APPENDIX IV

### PROCEDURE FOR ISOLATION AND ROUGH ESTIMATION OF WAXY MATERIAL

Place enough vehicle to yield about 1 g of solids in a tared beaker and evaporate the thinner on a steam bath. A stream of compressed air directed into the beaker speeds evaporation. Dry the sample for an additional ten minutes in an oven at a temperature near 100 C. Cool and weigh the beaker to determine the weight of vehicle solids present. Dissolve the solids in 10-12 ml of hot 1:1 benzene-ethanol (absolute). Transfer the solution quantitatively to a centrifuge tube and cool to approximately -5 C. Quickly transfer the tube to a centrifuge and centrifuge for four minutes. Immediately decant and retain the supernatant solvent. Dissolve the material remaining in the centrifuge tube in 10-12 ml of fresh 1:1 benzene-ethanol and repeat the cooling and centrifugation steps. Combine the solvent with that retained in the first isolation step and evaporate on a steam bath until a syrup or gel of the resin is obtained. Spread the resin on a sodium chloride plate to prepare a film suitable for recording an infrared spectrum. Dry the film in a vacuum oven at 60 C for 30 minutes before recording the spectrum. Check the spectrum for absorption at 13.7 and 13.9 $\mu$ . (Little or no absorption indicates satisfactory wax separation.)

Transfer the suspected waxy material remaining in the centrifuge tube to a tared container by dissolving it in a solvent such as trichloroethylene. Evaporate the solvent and reweigh the container to determine the weight of isolated material. Record an infrared spectrum of the isolated material spread on a sodium chloride plate. Examine the spectrum for indication of resin contamination and for further information about the chemical composition of the isolated material.

The isolated material must also meet the following criteria to be judged waxy: 1) melting point below 100 C, and 2) characteristic slippery sensation of wax when rubbed between the fingers.

TABLE 4  
SUMMARY OF COMPOSITION AND MOISTURE LOSS DATA

Producer	Year	Resin Type	Water Retention Test*		Avg. Moisture Loss g/cm <sup>2</sup>	Resin Content		Pigment Content	
			Samples Passing	Samples Failing		Range, %	Avg., %	Range, %	Avg., %
1	1966	A	10		0.044	9.1-10.5	9.9	51.4-53.3	52.1
				2	0.059	9.4-10.4	9.9	51.1-51.2	51.2
		B	41	0	0.036	6.4- 9.7	7.7	53.3-56.1	54.1
		C	27	0	0.038	6.2- 8.8	7.1	51.7-56.0	54.1
1	1967	B	5		0.038	7.2-10.1	8.1	40.2-54.9	51.5
				6	0.045	6.9- 8.6	7.6	53.0-54.5	53.9
		C	6	6	0.071	7.0- 8.3	7.6	53.4-54.6	54.0
		D	45	0	0.022	7.3-13.9	9.3	50.2-55.6	53.8
1	1968	C	9		0.024	8.0- 9.1	8.5	53.9-55.0	54.3
				1	0.062	----	10.9	----	50.2
		D	13		0.030	8.1-10.8	9.4	52.1-54.3	53.2
				2	0.083	3.7- 7.5	5.6	55.0-59.6	57.3
		E	18	1	0.030	7.6- 9.5	8.6	51.7-55.2	54.3
				1	0.082	----	6.4	----	55.3
		F	8	0	0.021	8.7- 9.5	9.0	52.5-53.2	53.0
2	1966	G	26	0	0.036	9.0-11.2	10.5	44.8-55.0	51.3
2	1967	H	11		0.051	9.1-15.5	10.1	48.0-55.1	53.5
				3	0.064	9.1- 9.3	9.2	54.1-54.3	54.2
2	1968	H	11		0.046	10.8-12.4	11.9	48.5-51.3	49.0
				13	0.065	8.8-13.8	9.6	48.9-55.6	54.0
3	1966	I	5	0	0.023	28.4-30.3	29.2	29.8-32.3	31.1
3	1967	J	6	0	0.015	22.0-30.3	27.5	31.0-36.6	33.3
3	1968	J	3	0	0.012	27.7-36.8	32.8	24.0-29.7	27.2
4	1966	K	4	0	0.021	20.4-22.2	21.3	39.0-39.8	39.4
5	1967	L	9	0	0.050	9.2-11.5	10.5	49.6-57.3	52.9
5	1968	L	8	0	0.051	8.0- 9.9	9.4	48.9-52.9	51.4
6	1966	M	----	----	not run	single	20.0	19.1	19.1
6	1967	N	----	----	not run	single	22.1	11.9	11.9

\*ASTM C 156.