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SPECTROPHOTOMETRIC METHODS FOR ANALYSIS OF PAINTS

Identification of Alkyd Resin Acids  
by Infrared Analysis of Benzylamide Derivatives

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Research Laboratory Division  
Office of Testing and Research  
Progress Report No. P-83  
Research Project 53 G-65

Michigan State Highway Department  
John C. Mackie, Commissioner  
Lansing, June 1960

## SPECTROPHOTOMETRIC METHODS FOR ANALYSIS OF PAINTS

### Identification of Alkyd Resin Acids by Infrared Analysis of Benzylamide Derivatives

In 1953, a research project was established to find methods of qualitatively and quantitatively analyzing paint-type coatings, making maximum use of absorption spectroscopy. While, in general, the inorganic pigment component of paints and paint-like materials may be analyzed by classical chemical methods, there is no feasible way of similarly analyzing the vehicle portion. Paint vehicles are composed almost entirely of organic materials, such as oils, resins, and solvents, combined or blended in various proportions. The problem of analysis is complicated by the fact that the chemical constitution of the finished product is influenced by the method of processing and degree of control during manufacture, such as time and temperature of cooking, as well as the chemical nature of the original ingredients.

Absorption spectra have shown that different types of resins may be identified from an infrared spectrum of a dried film of resin. The infrared spectrum, however, does not reveal the specific substances which make up the resin of a given type. Schreve<sup>(1)</sup> has stated, "The infrared analytical technique affords no universal analytical panacea. Despite its great usefulness, problems of any complexity always require companion

techniques and various other physical and chemical methods of analysis." Analysis of paints is a complex problem. It has been necessary, therefore, to supplement absorption spectroscopy with chemical methods in attempting to solve this problem.

Infrared spectra of many materials used in paints have been recorded by the Research Laboratory Division for use as reference spectra. These materials include various oils, resins, driers, solvents, and pigments which might be used in traffic paints and other maintenance paints. Most paints dealt with here are formulated with one or more of four general types of resins--alkyd, epoxy, phenolic, and chlorinated rubber. There is an almost infinite variety of modifications of these resin types, either by other resins or by one or more oils.

During 1958, alkyd resins were more completely analyzed. This report is the first of a series on progress of the overall investigation and describes the results obtained from the use of a technique by which the dibasic acid component of an alkyd resin can be identified by infrared examination of the benzylamide derivative.

#### Materials and General Method

An alkyd resin is a polyester type of resin, the esterification product of one or more polyhydric alcohols with one or more dibasic acids and vegetable oil fatty acids. The most common type of alkyd has glycerol as a polyhydric alcohol, phthalic acid as the dibasic acid component, and

one or more nondrying, semidrying, or drying oils as the oil modifier. Alcohols other than glycerol and dibasic acids other than phthalic are coming into increasing use in such resins.

The present investigation was undertaken to identify and characterize alkyl resin dibasic acids by infrared examination of derivatives of these acids. Stafford<sup>(2)</sup> suggested that the benzylamides of paint resin acids were more characteristic derivatives than ethyl esters or potassium salts. Since these derivatives are easily prepared and purified it was decided to investigate them further in this laboratory.

The benzylamide derivatives of authentic samples of phthalic acid and maleic acid were prepared. Derivatives of five resins of known composition from the Reichhold Chemical Company were also prepared. The spectra of these derivatives furnished a library of spectra with which the derivatives of paint resins could be compared.

The derivatives of phthalic acid and maleic acid have characteristic infrared spectra by which they may be identified. The most useful absorption maxima for the maleic acid derivative occur at 3.9, 4.2, 6.0, and 11.7  $\mu$ . The useful absorption maxima for the phthalic acid derivative occur at 6.1 and 12.6  $\mu$ , and the maxima between 13.3 and 14.4  $\mu$  also have a characteristic shape. A small amount of maleic acid in a mixture of these two acids is difficult to detect since the phthalic acid absorption tends to mask the maleic acid maxima.

## Results

Table 1 lists the laboratory numbers of paints from which the resins were separated for examination. In each case the spectrum of the resin derivative could be matched with a similar spectrum from the library of known spectra. It could then be assumed that the paint resin contained the same acid components as the known material. Phthalic acid was the only acid found in the resins examined. Rosin and its esters proved unreactive and no derivative of rosin was obtained.

TABLE 1  
LABORATORY NUMBERS OF PAINTS EXAMINED

Performance Test Paints		Acceptance Test Paints	
White	Yellow	White	Yellow
56 PR 93	56 PR 99	58 PR 5	58 PR 46
56 PR 100	56 PR 118	58 PR 6	58 PR 50
56 PR 102		58 PR 7	58 PR 53
56 PR 104		58 PR 8	
56 PR 106		58 PR 12	
56 PR 108		58 PR 16	
56 PR 110		58 PR 20	
56 PR 112		58 PR 24	
56 PR 120		58 PR 28	
		58 PR 32	
		58 PR 36	
		58 PR 40	
		58 PR 44	
		58 PR 54	
		58 PR 58	

Six illustrative spectra are attached (Figs. 1-6). Each group of three spectra is a unit illustrating one type of identification. Fig. 1 shows the

spectrum of the benzylamide of phthalic acid. Fig. 2 shows the spectrum of the benzylamide of maleic acid. Fig. 3 is the spectrum of a mixture of equal quantities of the benzylamides of phthalic and maleic acids. The identifying peaks for each acid are noted with the spectrum of the mixture to show that both acids may be identified. The second group of spectra (Figs. 4-6) illustrates the identification of phthalic acid in a traffic paint alkyd resin.

### Discussion

It is possible to identify an alkyd resin by its infrared spectrum. Infrared examination of the benzylamide derivative of an alkyd resin can be used to identify the dibasic acid component of the resin. Dibasic acids other than phthalic and maleic may be identified by this procedure if they are encountered. Rosin may interfere with maleic acid detection since rosin and maleic anhydride react during resin cooking. The infrared spectra of the amide derivatives can be used to get a rough quantitative determination of the composition of a mixture of the acids tested. Ultraviolet spectrophotometry can be employed for quantitative determination of alkyd dibasic acids, as described in ASTM Method D:1307-56. However, ASTM Methods D:1306-56 and D:1307-56 provide for quantitative determination of phthalic anhydride only. A correction may be applied for maleic and fumaric acids if known to be present, but no method for identifying these or other acids present is provided.

### Future Work

Paint vehicle characterization will be carried forward with two new investigations. An investigation has been undertaken to identify the polyhydric alcohols used in traffic paint alkyd resins. The Laboratory's vapor fractometer is being used to separate paint volatiles into fractions for subsequent analysis and characterization.

### Experimental Procedure

A paint sample is centrifuged to separate the vehicle from the pigment. The resin is separated from volatiles and thinners by precipitation with a nonsolvent such as petroleum ether. A 2-g sample is then refluxed for 2 hours with 6 ml of benzylamine and 0.2 g of ammonium chloride. The reaction mixture is poured into benzene, cooled to room temperature, and chilled to approximately 10 C in a refrigerator. The amide is filtered, using suction, and dissolved in the minimum amount of hot ethanol. This procedure yields a more crystalline product than the procedure of Stafford<sup>(2)</sup>, which involves pouring the ethanol solution into water to precipitate the amide. After cooling the mixture, the amide is filtered using suction, washed with benzene and water, and dried in a vacuum oven at 60 C for 1 hour.

The dry amide derivative is then incorporated in a potassium bromide pellet for infrared study. This involves mixing and grinding 2 mg of the amide with 500 mg of potassium bromide in a vibrator grinder which acts

like a miniature ball mill. The resulting powdery mixture is subjected to high pressure in an evacuated pellet die made by the Perkin Elmer Corporation. The pressure fuses the powder into a solid pellet with a diameter of 13 mm. The pellet is then placed in a holder which positions it in the sample beam of the Perkin Elmer Model 21 Infrared Spectrophotometer and the spectrum of the amide is obtained.

#### REFERENCES

1. Schreve, O. D., "Application of Infrared, Ultraviolet, and Roman Spectroscopy to the Analysis of Complex Materials." *Anal. Chem.*, 24: 1692 (1952).
2. Stafford, R. W., "Identification of Dicarboxylic Acids in Polymeric Esters." *Anal. Chem.*, 21:1454 (1949).
3. Schreve, O. D., and Heather, M. R., "Spectrophotometric Determination of the Total Phthalic Anhydride in Alkyd Resins and Other Phthalate Esters." *Anal. Chem.*, 23:441 (1951).
4. Stafford, R. W., Shay, J. F., and Francel, R. J., "Identification of Dicarboxylic Acids in Polymeric Esters." *Anal. Chem.*, 26:656 (1954).



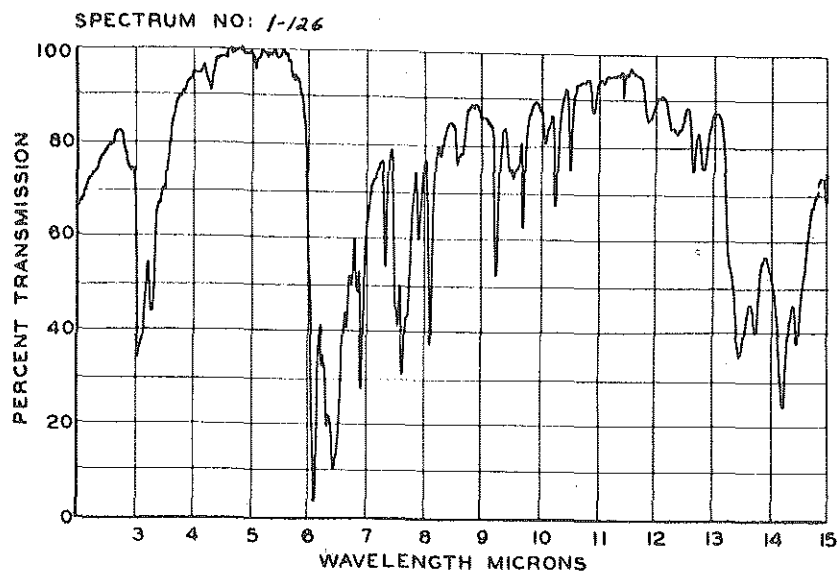


Figure 1. Spectrum of benzylamide of phthalic acid.

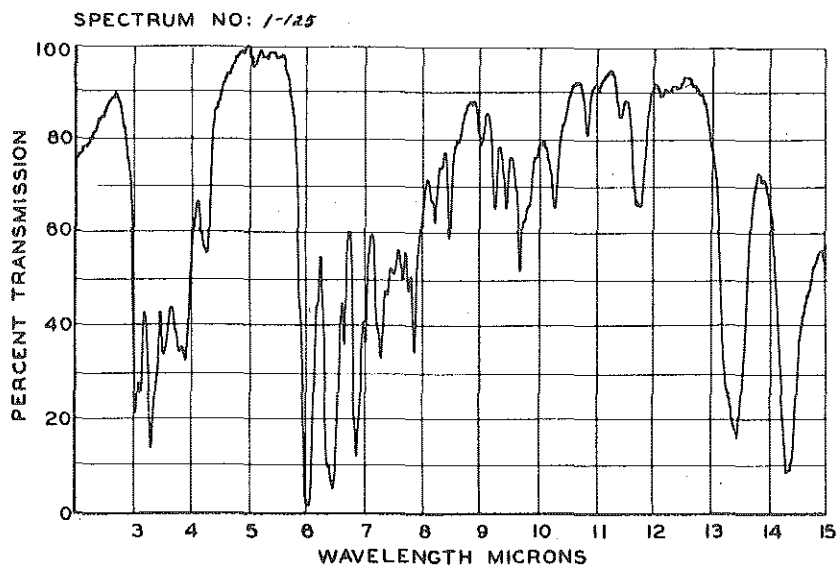


Figure 2. Spectrum of benzylamide of maleic acid.

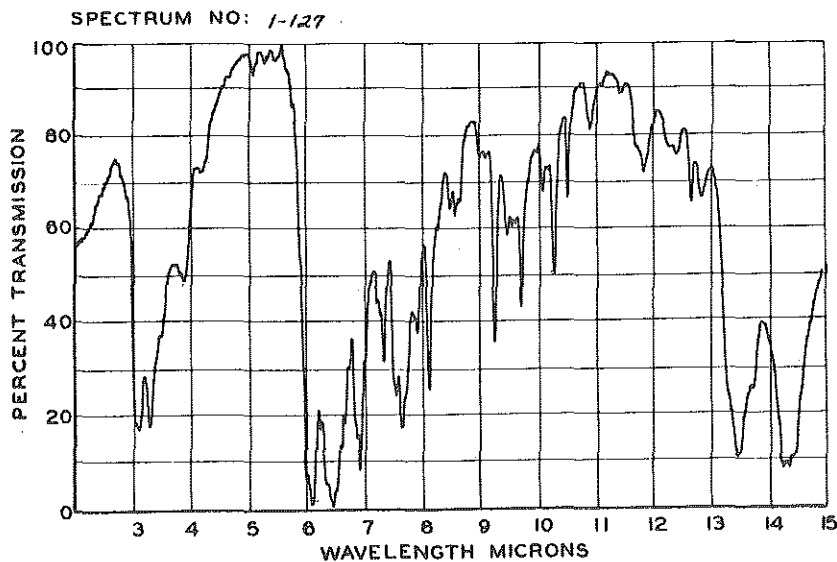


Figure 3. Spectrum of 1:1 mixture of benzylamides of phthalic and maleic acids. Maleic acid identification peaks occur at 3.9  $\mu$ , 6.0  $\mu$ , and 11.7  $\mu$ . Phthalic acid peaks occur at 6.1  $\mu$  and 12.6  $\mu$ .

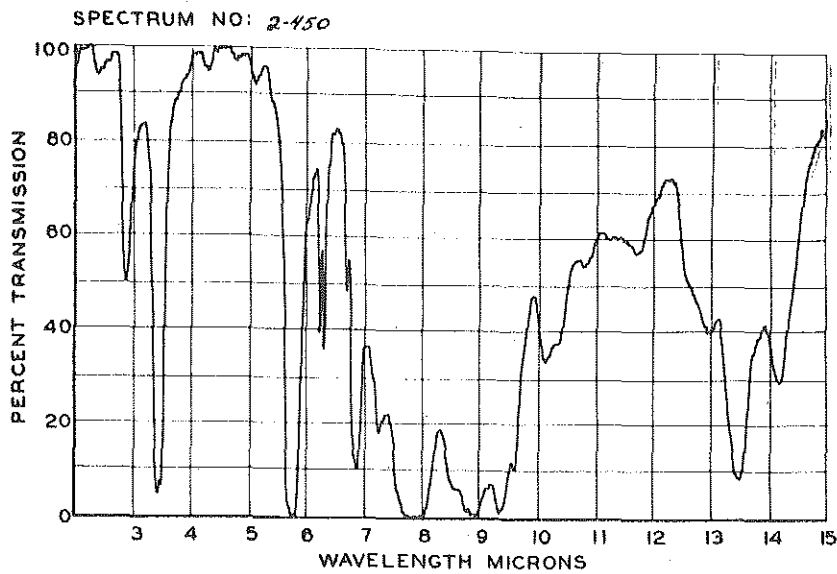


Figure 4. Spectrum of dried film of typical alkyd resin from a traffic paint.

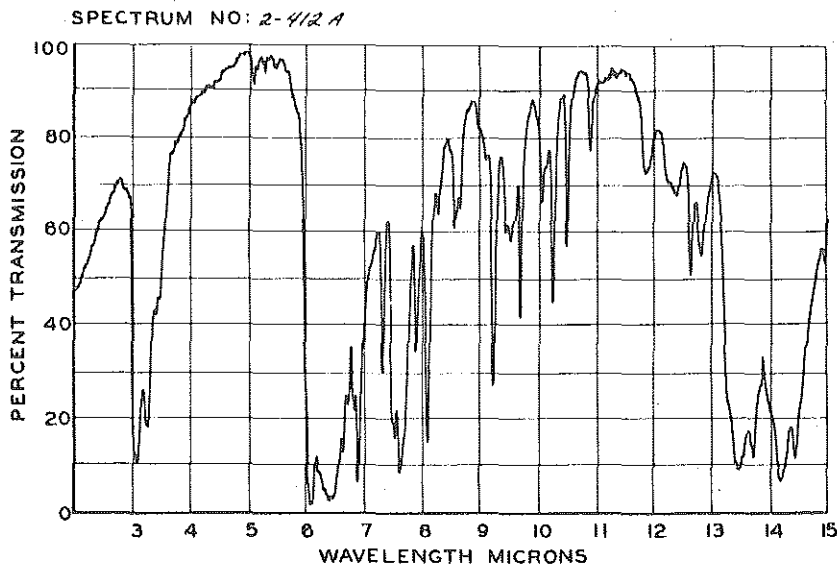


Figure 5. Spectrum of benzylamide derivative of the alkyd in Fig. 4.

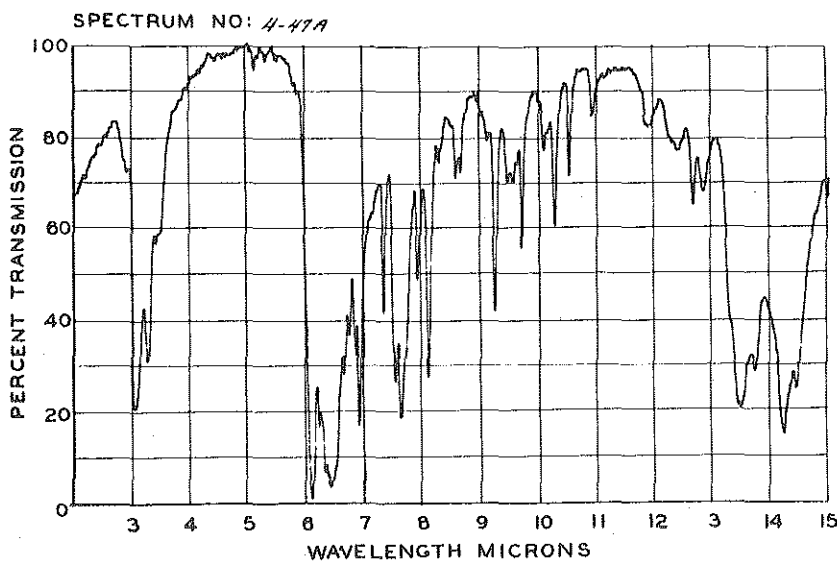


Figure 6. Spectrum of benzylamide derivative of alkyd resin known to contain only phthalic acid. Note close similarity to spectrum in Fig. 5.