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FEDERAL HIGHWAY ADMINISTRATION
BUREAU OF PUBLIC ROADS

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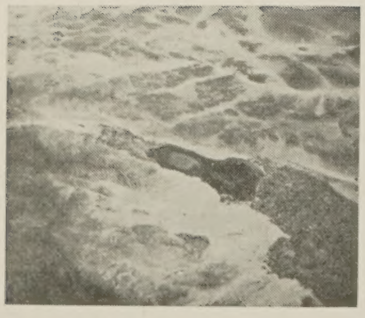

COVER

Satellite photograph obtained at an altitude of 110 nautical miles from Gemini V (Courtesy NASA). Applications of remote-photographic techniques to highway problems are discussed in the first article.

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Remote Sensing Applications to Highway Engineering

Y THE OFFICE OF
ESEARCH AND DEVELOPMENT
UREAU OF PUBLIC ROADS

Reported by[1] HAROLD T. RIB
Highway Research Engineer

In recent years, the availability of new remote sensors—radar, infrared, multichannel—has initiated a new era in the application of interpretation techniques in highway engineering. The data provided by the many types of sensors furnish information previously unobtainable, or available only at great expense. In this paper, the areas of possible applications of remote sensors in the highway field are discussed. Several examples are included to demonstrate the value of remote sensors in various aspects of highway engineering. Also included is a discussion of the Public Roads research program in remote sensing.

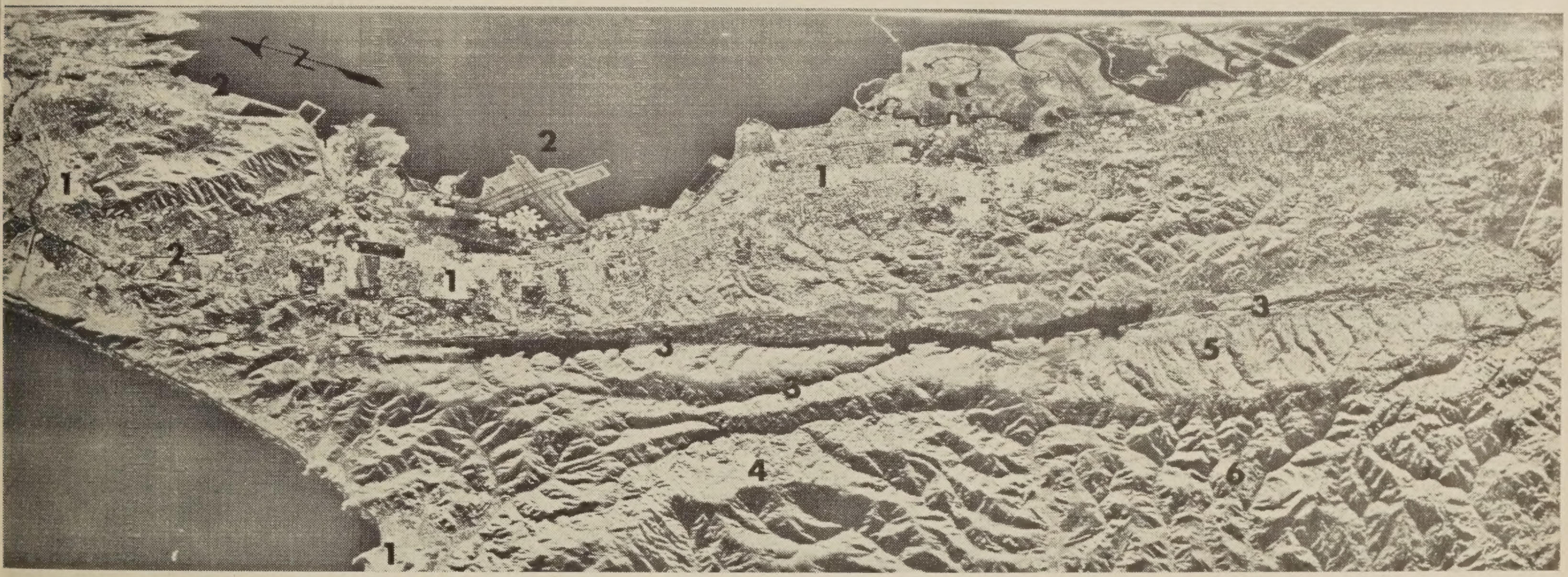

Figure 1.—Radar image of portion of San Francisco peninsula illustrating regional view obtained by side-looking radar and its ability to distinguish numerous features important to highway planning. Numbered items are discussed in text.[2]

Introduction

THE HIGHWAY field has entered a new era in the application of aerial reconnaissance techniques, now referred to as aerial remote sensing. This era has been ushered in by the availability of new sensors to civilian organizations and the potential to obtain broad regional coverage from satellite platforms. The new sensors include infrared, radar, and multichannel and multiband instruments. In addition, the improvement and availability of aerial film types, including natural color, color infrared, and color negative, and the development and use of special film-filter combinations for image enhancement, have aided in promoting this new era. Preliminary studies in the application of the newer sensors and techniques have demonstrated that, individually or in combination, these newer systems procure information previously unobtainable, or available only at great expense.

To describe the applications of these newer aerial remote sensors to highway engineering, six major stages of highway engineering are differentiated in this article: Highway planning surveys; condition and inventory surveys; traffic surveys; highway location surveys; construction surveys; and maintenance surveys. For each of these stages, the major factors or data required are indicated; the potential applications of the newer sensors are discussed; and research projects in progress, with some examples demonstrating the applications, are included. Finally, there is a description of the Bureau of Public Roads' research program in remote sensing as well as a discussion of research in progress.

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[1] Presented at the Fifth Remote Sensing Symposium, University of Michigan, April 16–18, 1968.

[2] Photograph courtesy National Aeronautics and Space Administration.

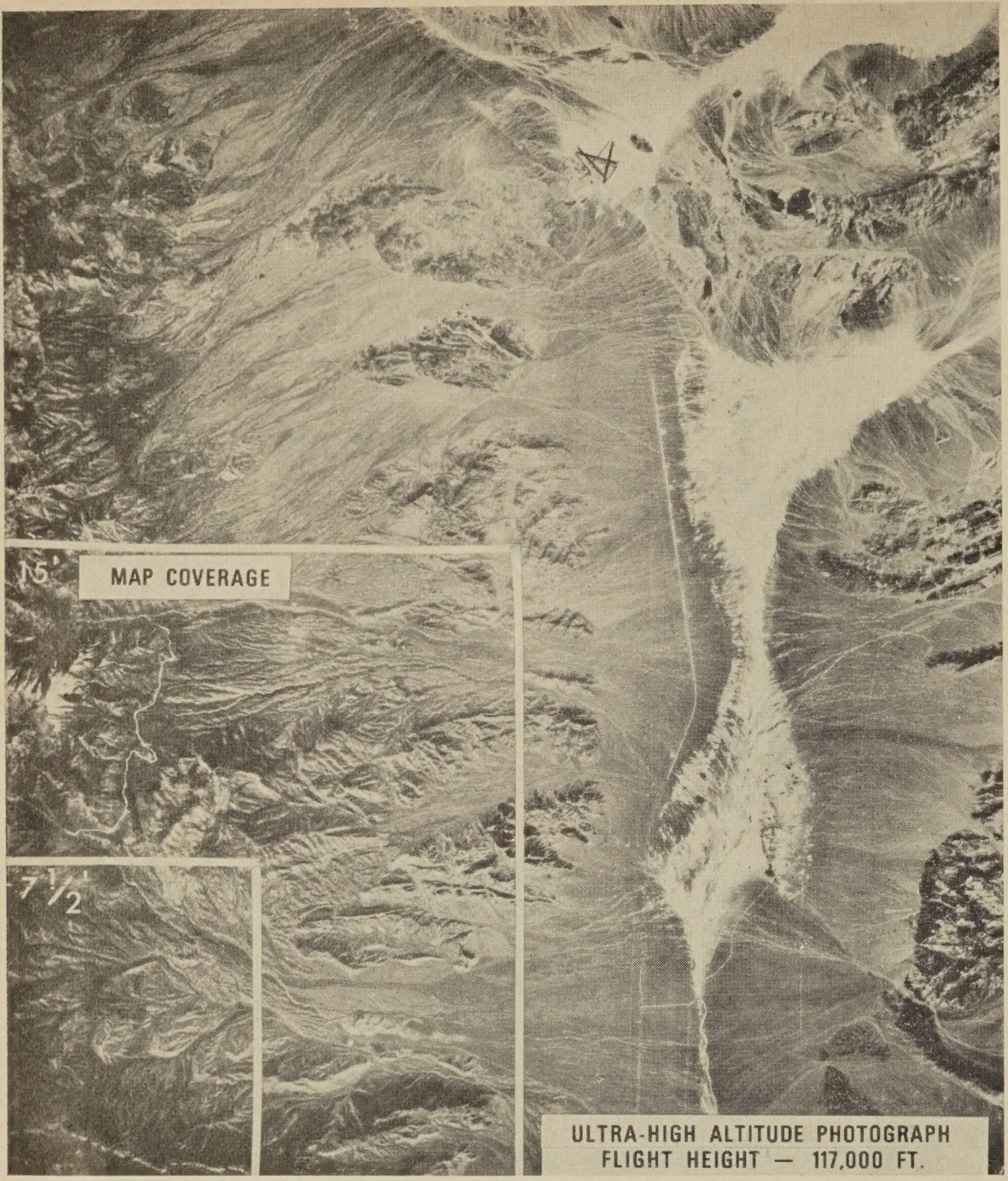

Figure 2.—High altitude photograph showing area of coverage compared to that of standard 7½ min. and 15 min. quadrangle sheets.[4]

Highway Planning

Highway planning is defined as ". . . the orderly and continuing collection of information about highways, including their history, condition, use, effects and needs, and the analysis of these data for the efficient and economic development of the highways systems" (*1*).[3] Proper highway planning must be comprehensive and coordinated. It should be part of an overall master plan for area or regional development, and should be coordinated with that of other agencies and organizations in the development of transportation facilities. The importance of these items is evident in recent planning trends. Comprehensive planning in larger communities required by law. Congress passed a bill r quiring all urban areas containing more tha 50,000 persons to have a comprehensiv transportation plan to receive Federal ai Coordinated planning is illustrated by th team concept in planning that is underwa in Baltimore, Md. In this program, a team architects, city planners, sociologists, econ mists, and others are working with highwa engineers on routing a section of Interstat highway through the city. The planners this highway corridor will also consider othe community needs, including replacemen housing, parking, recreational, commercia and other community facilities.[5]

Another important factor in planning that some studies contemplated today a of broad regional extent. Regional studi may include extensive transportation corrido that may even extend outside the boundari of a single State. An example of this is t study of transportation systems in the nort east corridor extending from Washington, D.C to Boston, Mass.

Remote sensing offers unique advantag in this area of regional planning and coord nation. Radar or satellite photography provid large regional coverage in which sufficie details for general planning purposes a obtained. For example, the side looking rad image in figure 1 shows the following importa features in highway planning: Populati centers—urban, rural, and other land u patterns (1); transportation systems—hig ways, railroads, airports (2); geologic stru ture and lithology—faults (3), difference rock types (4), (5), and (6). Drainage pattern and many other pertinent details also a evident. Similar regional factors can evaluated from satellite photography (s cover photograph) and from very hig altitude photography, as shown in figure The ability to judge the influence of the ma factors, which is possible through these for of remote sensing, makes the technique very valuable planning tool. Many of the

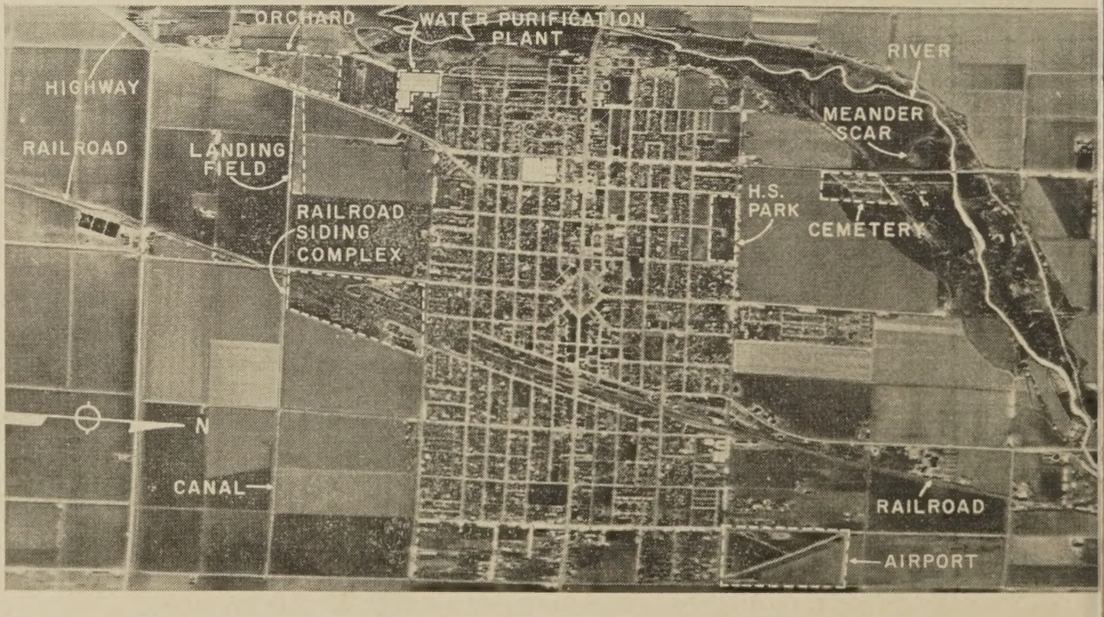

Figure 3.—Nighttime infrared imagery showing type of information obtainable fro views of populated areas.[6]

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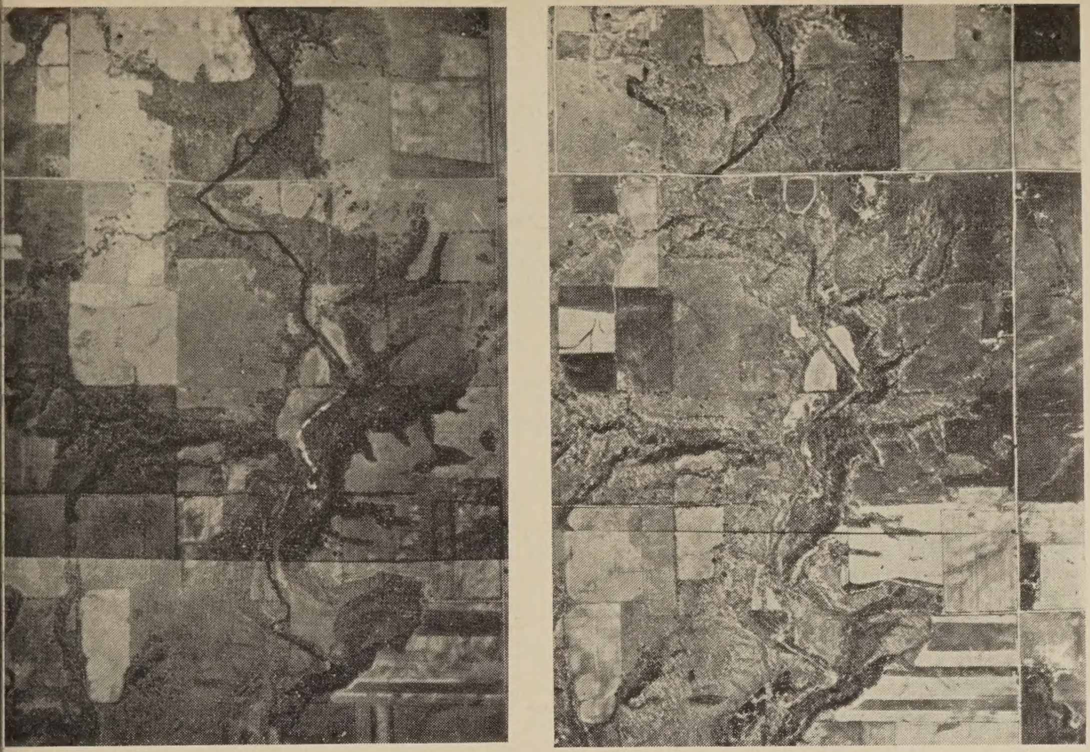
[3] Italic numbers in parentheses identify the references listed on page 36.

[4] Photograph courtesy U.S. Geological Survey.

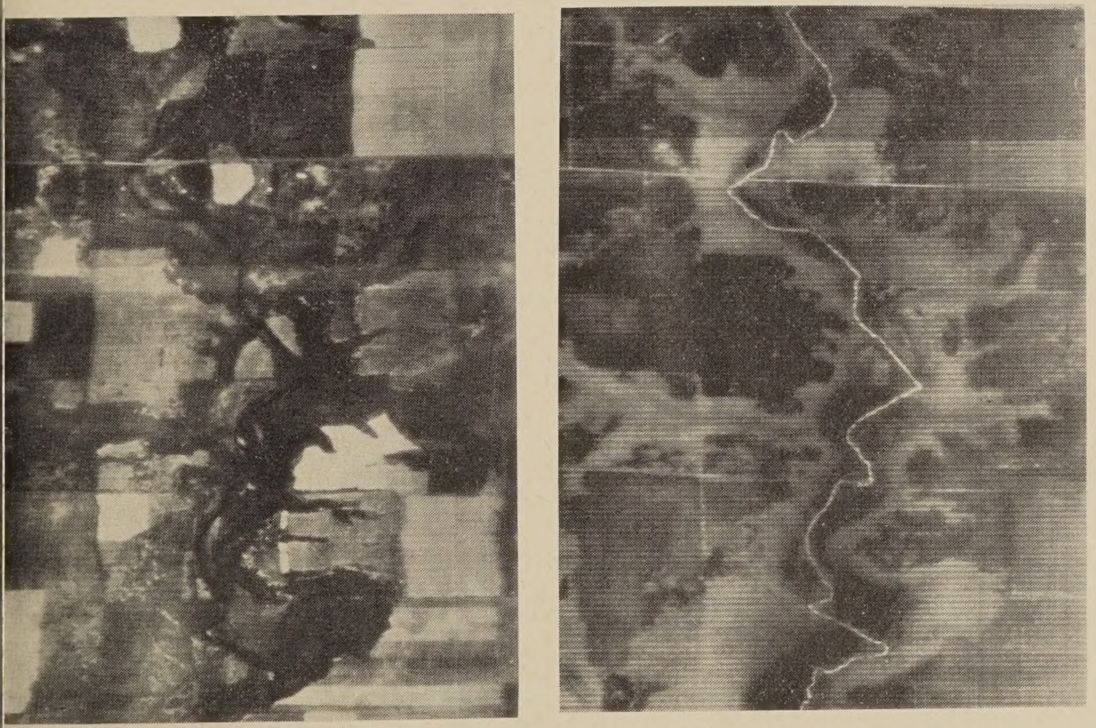
[5] From remarks by L. K. Bridwell before the Rubber Manufacturers Association (see acknowledgments).

[6] Photograph courtesy HRB-Singer Inc.



Black and white infrared.

Black and white aerial photography.



Infrared daytime.

Infrared nighttime.

igure 4.—Drainage patterns evident on various aerial views of photography and infrared imagery.

ctors, and much of the interplay between hem, cannot be evaluated rapidly or easily y other methods.

Radar offers a particular advantage in the ighway planning stage because coverage of rge areas can be obtained rapidly, regardless f weather or illumination conditions—day or ight, cloudy, raining, etc. Moreover, the dar mosaic has a fairly continuous tonal attern over the complete area, a character- tic that makes it easier to correlate various tems throughout the area. The ability to correlate tonal patterns over a photographic mosaic of an equivalent area is not always possible. Often the tonal differences present are not due to differences in objects alone. They can be due to differences of exposure and development between the individual photographs used to prepare the photographic mosaic.

Other items pertinent to highway planning include condition and inventory surveys and traffic surveys. These items are discussed as separate stages in this paper. In the final analysis, however, data determined from these surveys would be included in the long-range planning of a State highway system.

Condition and Inventory Surveys

Condition and inventory surveys are performed to compile statistics on: (1) mileage of the functional classifications of highways; (2) kind and number of structures; (3) road surface types, widths, and condition; (4) information on land uses bordering the highway; and (5) other data. Periodic evaluation and updating of highway conditions are required for the proper planning of a State highway system. Some of the detailed data needed in the inventory, such as sight distances, riding quality, superelevations, and clearances, can be determined only by field investigations. However, a good deal of the necessary data can be obtained by aerial remote sensing techniques.

The functional classification and mileage of the different surface types of roads—concrete, bituminous, gravel—are important items in inventory surveys. Multisensor coverage, or coverage in various spectral regions of the electromagnetic spectrum, offers a unique method to distinguish the road surfaces. This ability is demonstrated in table 1, in which tonal signatures are listed for various road surfaces in different regions of the spectrum. The values shown are average values, based on the analysis of photographic and imagery data collected over a 13-month period at an Indiana test site. Significant trends, as seen in the table are: (1) highway surfaces can be determined from multisensor coverage, and (2) at least three spectral regions have to be sampled for identification, that is, visible, photographic infrared, infrared. Figure 3 is a nighttime infrared image illustrating road detail and other information valuable to highway planning.

The results obtained indicate a great potential for the remote sensing approach in identifying various types of road surfaces. It is anticipated that with present day sensors, such as the University of Michigan's multichannel sensor, and present day electronic and computer equipment, a method can be developed to automatically map and classify highway systems. This is one of the items being investigated in Public Roads' remote sensing research program.

Remote sensing techniques can also be used to obtain information on numerous other items pertinent to condition and inventory surveys. Information such as road widths, road conditions, drainage conditions, kinds of structures, land use, rail crossings, etc., can readily be ascertained from natural or infrared color aerial photography. Many of the details can be determined on small scale photography (1:20,000–1:60,000), whereas, some would require medium scale photography (1:8,000–1:20,000).

The natural appearance of objects on natural color photography makes them easier to identify. On color infrared photography, road boundaries, road conditions (patching, break-up, etc.), and drainage features (drainage channels, seepage areas, sediment and pollution) are distinct. Studies by Rib (*2*) and Mintzer [7] have demonstrated that finer details and smaller objects can be more positively identified on color photography than on equivalent black-and-white photography at the same scale.

Considering the scope and amount of information needed for condition and inventory surveys, it would appear that the maximum amount of information could be obtained from aerial remote sensing flights simultaneously procuring multisensor imagery and aerial color photography.

Traffic Surveys

Information on traffic is an important factor in planning new highways and in evaluating the capabilities and need for improvement of existing highways. Factors required in traffic surveys include volume counts, classification (size, weight, vehicle type), speed, spacing, origin and destination data, as well as evaluation of regional land use for possible generation of traffic.

Many of the factors, including traffic density, speed, headway, occupancy, variation of traffic density with time, areas of congestion, and bottlenecks, have been evaluated from analysis of black-and-white photography. However, these have been evaluated only for specific cases because of limitations of the aerial photography. Weather and illumination conditions can effect the ability to gather data during critical periods of traffic flow such as the evening rush hour. In addition, the normal aerial photographic flights for traffic surveys are limited to the instantaneous area coverage obtained on each exposure. This limitation can be critical when considering the needs for accomplishing large regional corridor studies.

A potential solution for obtaining instantaneous, as well as periodic, coverage of large regional areas is the use of satellites. Photographs of large regional areas would show conditions that exist within major population centers at a given instant, or between major population centers within a fairly short period. Where weather or illumination conditions restrict procurement of photographic coverage, radar sensors might be used.

Some major limitations also exist in the use of satellites. These include: (1) resolution capabilities of sensors to distinguish small objects such as cars, (2) need to place the satellites in particular orbits to cover the regions of interest, and (3) cost of utilizing this technique. Nevertheless, the use of satellites needs to be investigated as it may prove to be the only practical way of obtaining simultaneous information of large regional traffic patterns.

Remote sensors also offer advantages for obtaining detailed traffic information over limited areas. Both infrared and radar sensors offer opportunities to obtain critical information at any time of day, and in the case of radar, in almost any type of weather condition in which an aircraft can fly. The use of lasers and television cameras are also fruitful areas to be investigated. The Bureau of Public Roads has contracted with private industry to determine the feasibility of the development of an area traffic surveillance and control system. This project is discussed in more detail in the section on Public Roads research.

Table 1.—Multispectral tonal signatures for typical highway surfaces

Highway surface	Tonal signatures [1]			
	Panchromatic (No. 12 filter)	Black-and-white infrared (No. 12 filter)	Infrared imagery (8–14μ)	
			Daytime	Nighttime
Concrete	Light	Medium	Medium light	Light.
Asphalt:				
Fresh	Dark	Dark	Light	Light.
Weathered	Medium light	Medium	Medium	Light.
Gravel	Light	Light	Medium	Medium light.
Cinders	Dark	Dark	Light	Medium light.

[1] Five tones distinguished—light, medium light, medium, medium dark, and dark.

Highway Location Surveys

Highway location surveys usually consist of four substages: (1) reconnaissances survey of an area to determine feasible routes; (2) reconnaissance survey of route alternatives to select a route; (3) preliminary survey of the selected route; and (4) location survey staking of the designed location on the ground. The type of information needed in these substages varies from small scale regional coverage in the first substage, in which general parameters are evaluated, to limited large scale coverage in the concluding substages in which numerous details such as location of property boundaries, selection of control points for targeting, etc., are needed. These extreme requirements have necessitated the use of two or more scales of photography for accomplishing highway location and design.

Some of the major items obtained by surveys and evaluated in highway location and design include: (1) land use—severances, costs, access, cultural items (archeological sites, cemeteries, scenic viewpoints); (2) geology—type of rock, topography, presence of faults and fracture zones; (3) soils and soil conditions—presence of poor soils, erodible soils, swamps, landslides, high water table, springs, and seepage zones; (4) drainage—drainage pattern, structure needs, watershed areas, flooding conditions; (5) traffic—control points, origin–destination, volume; (6) construction material—consolidated, unconsolidated, quality, quantity, proximity; and (7) plans for boring programs and field surveys. Aerial reconnaissance techniques received maximum use in the highways location survey stage in the past (*3*) and, similarly, is the stage where maximum application of the newer remote sensing techniques can b applied.

The value of remote sensors, used both individually and in combinations, has been reported by numerous investigators. The use of radar for area reconnaissance, specifically for determining geologic features and land use patterns, has been demonstrated by Barr and Miles,[8] Dellwig,[9] Morrain and Simonett (*4* and Sheridan.[10] The ability to observe large areas under uniformly illuminated conditions has enabled researchers to determine regiona structural and faulting patterns, as well a to differentiate certain rock formations tha were neither distinct nor interpretable by other methods. Analysis by satellite photography also has good potential application in this substage.

For the reconnaissance survey of rout alternatives and for subsequent substages multichannel, multisensor, multiband an color photography have distinct applications Comparisons and evaluations of natural an infrared color photography with standar black-and-white photography have demonstrated the superiority of color. For determining soils and soil conditions, it has bee indicated (*2*) that natural color was the mos useful single film type. The natural colo tones of objects made them easier to identify Also, it was possible to distinguish betwee the various factors causing the tonal patterns—intrinsic soil color, composition of soi moisture content, vegetation and cultur effects. The advantages of color infrared wer better haze penetration and more accurat delineation of drainage conditions and vegetative growth. Also, as previously note finer details, identification of smaller object and greater accuracies were obtained fro color photography than from equivalen black-and-white photography at the sam scale. A further advantage of color photography was that special filters could be used i the viewing stereoscope to increase the contrast among features of interest. This made much easier to delineate and map so differences.

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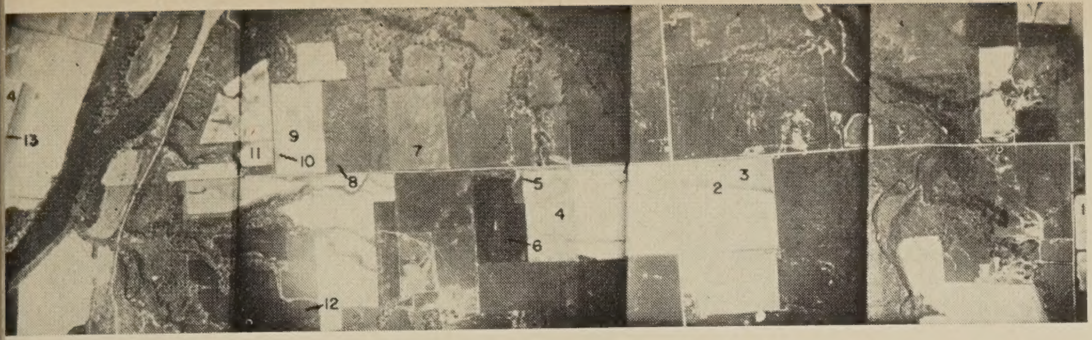
[7] O. W. Mintzer, Summary of *Report on Evaluation of Photo Interpretation Data from Phoenix, Arizona Test Site* (see acknowledgments).

[8] Paper by D. J. Barr and R. D. Miles, presented Highway Research Board (see acknowledgments).

[9] Report by L. F. Dellwig, presented at Highway R search Board (see acknowledgments).

[10] M. F. Sheridan's comments in NASA technical lett (see acknowledgments).



Point	*Soil or rock unit*	*Condition*
1.	Thick loess/glacial till	High position—bare
2.	Glacial till	High position—plowing in progress
3.	Glacial till	High position—recently plowed
4.	Glacial till	High position—plowed a few days ago
5.	Sandstone	Small exposure
6.	Glacial till	Covered with winter wheat
7.	Glacial till/sandstone	Pasture—sandstone exposed in places
8.	Glacial till/sandstone	Pasture
9.	Glacial till	High position
10.	Glacial till	Depression
11.	Glacial till	High position
12.	Glacial till	Covered with winter wheat
13.	Flood plain	Plowing in progress
14.	Flood plain	Recently plowed

Figure 5.—Location of points measured on multichannel imagery.

Mintzer (*5*), Chaves and Schuster (*6*), Anson (*7*), and others have similarly indicated the advantages of color photography. They have shown examples where many items of interest, such as soils and rocks, location of construction material, delineation of landslides and swampy conditions, and others, are more accurately delineated on color photography.

The use of radar and color photography, individually, are of great value in the highway location stage; however, the most promising of all the newer techniques is the multisensor approach in which several different regions of the spectrum are sensed simultaneously. In principle, each object is unique in its response throughout the electromagnetic spectrum. Therefore, it should be possible to delineate the different objects by their varying responses in the different regions. This principle is demonstrated by the examples illustrated in figures 4, 5, and 6.

In figure 4, several sensor forms illustrate the appearance of drainage patterns in different regions of the spectrum. The nighttime infrared image provides the clearest view of the stream and its intricate bends, but tributary creeks are difficult to delineate on this image. The most complete information on the drainage pattern is obtained by analyzing the images of all the sensor forms.

Figure 5 is an aerial photographic mosaic showing the conditions existing at the time the multisensor data were obtained. The location and description of the various terrain features are described in this illustration.

Figure 6 shows the normalized spectral response signatures developed from the multisensor data for the various terrain features noted in figure 5.

The multisensor data for developing the signatures were obtained wlth the multichannel sensor at the University of Michigan. This sensor simultaneously obtained up to 18 channels of data, ranging from the near ultraviolet to the far infrared regions. All the channels were at the same scale, resolution, and format. Thus, by making densitometric measurements of particular terrain features on each channel, and normalizing these to the darkest and lightest tones present, the spectral response signatures shown in figure 6 were developed.

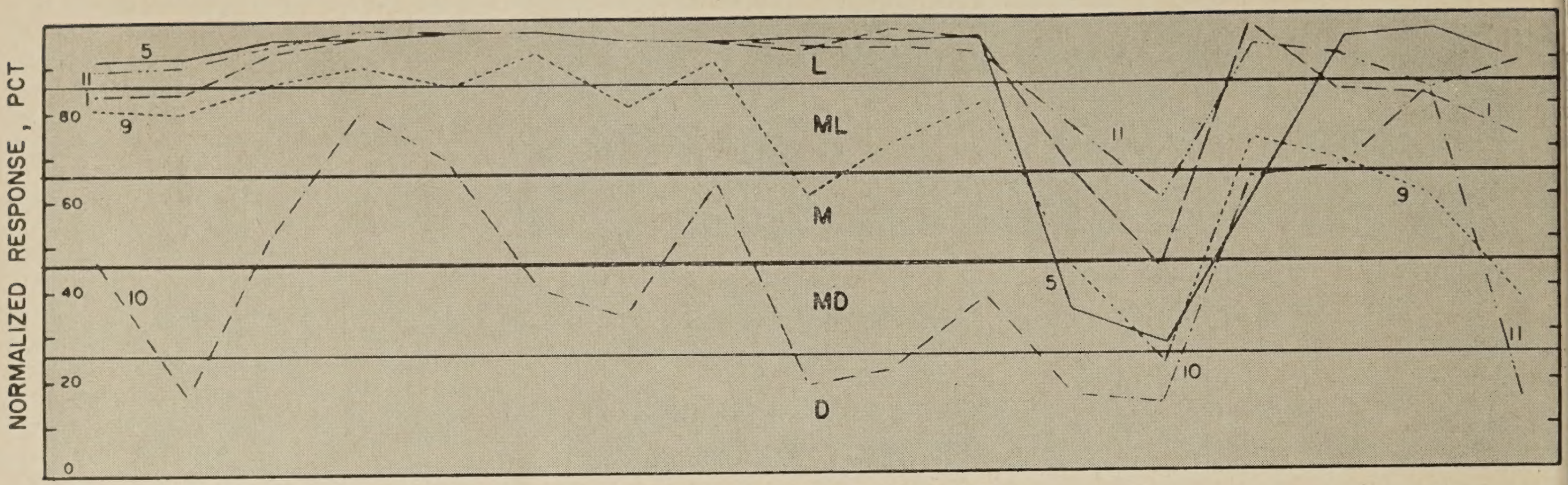
The curves in figure 6 are divided into three groups. Figure 6(a) includes spectral response signatures for bare soils and rock units; figure 6(b) includes spectral response signatures for bare soils, in which tones vary from those in figure 6(a) because of farming practices; and figure 6(c) includes spectral response signatures for various vegetation conditions present in the area. The five bands delineated in figure 6 (L) light, (ML) medium light, (M) medium, (MD) medium dark, and (D) dark are qualitative ratings. They were used to compare the relative tones of the multichannel imagery with those of other forms of photography and imagery for which comparative measurements were not possible.

The spectral response curves in figure 6(a) demonstrate the similarities and differences present for sandstone (curve 5); glacial till soils of various topographic positions, eroded slope (curve 9), depressional area (curve 10), high topographic position (curve 11); and glacial till soil overlain by 4–5 feet of loess (curve 1). All these units can be separated because of distinct differences in various portions of the spectral region. For example, curves 1, 5, and 11, are similar throughout the visible region, but curve 5 shows a darker tone than curves 1 and 11 in the photographic infrared region, whereas, curve 11 shows a darker tone than curves 1 and 5 in the far infrared region. Curves 9 and 10, similarly, have distinct differences to aid in separating them from each other and from the other units.

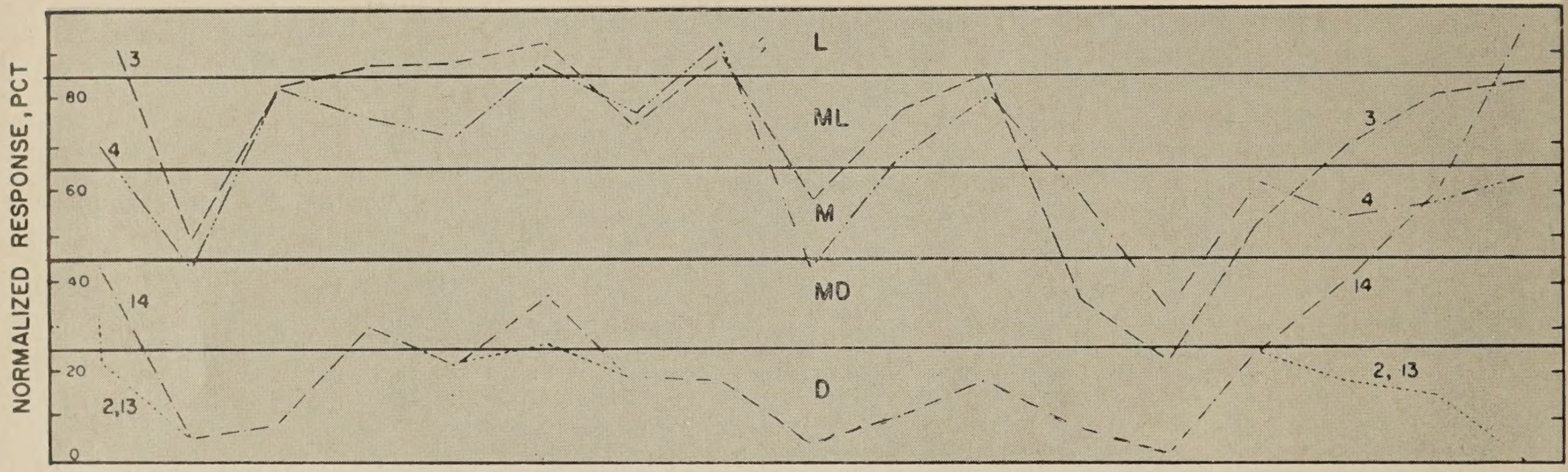
The effect of farm practices on the tones obtained in the different bands is demonstrated in figure 6(b). All these curves represent soils recently plowed. Curve 4 represents a field plowed a few days before the flight. Curves 3 and 14 represent fields plowed the morning of the flight; flight was performed in the afternoon. Curves 2 and 13 represent areas being plowed during the flight, or a very short time prior thereto. Soils represented by curves 2, 3, and 4, are glacial till soils predominantly in the high topographic position, and those by curves 13 and 14 are sandy soils of the flood plains.

The effects of the plowing are to expose, at the surface, the wetter and darker colored subsoils. When the soil is first turned over, the moisture effect is the controlling factor; tones are darker in all bands regardless of texture (curves 2 and 13). As these soils dry out, the effect of moisture is decreased and that of soil color becomes prominent (curves 3, 4 and 14). It can be noted that curves 3 and 4, drying ½ day and 2 days, respectively, are similar and both resemble curve 9, figure 6(a), the eroded glacial till soil in which the subsoils are exposed.

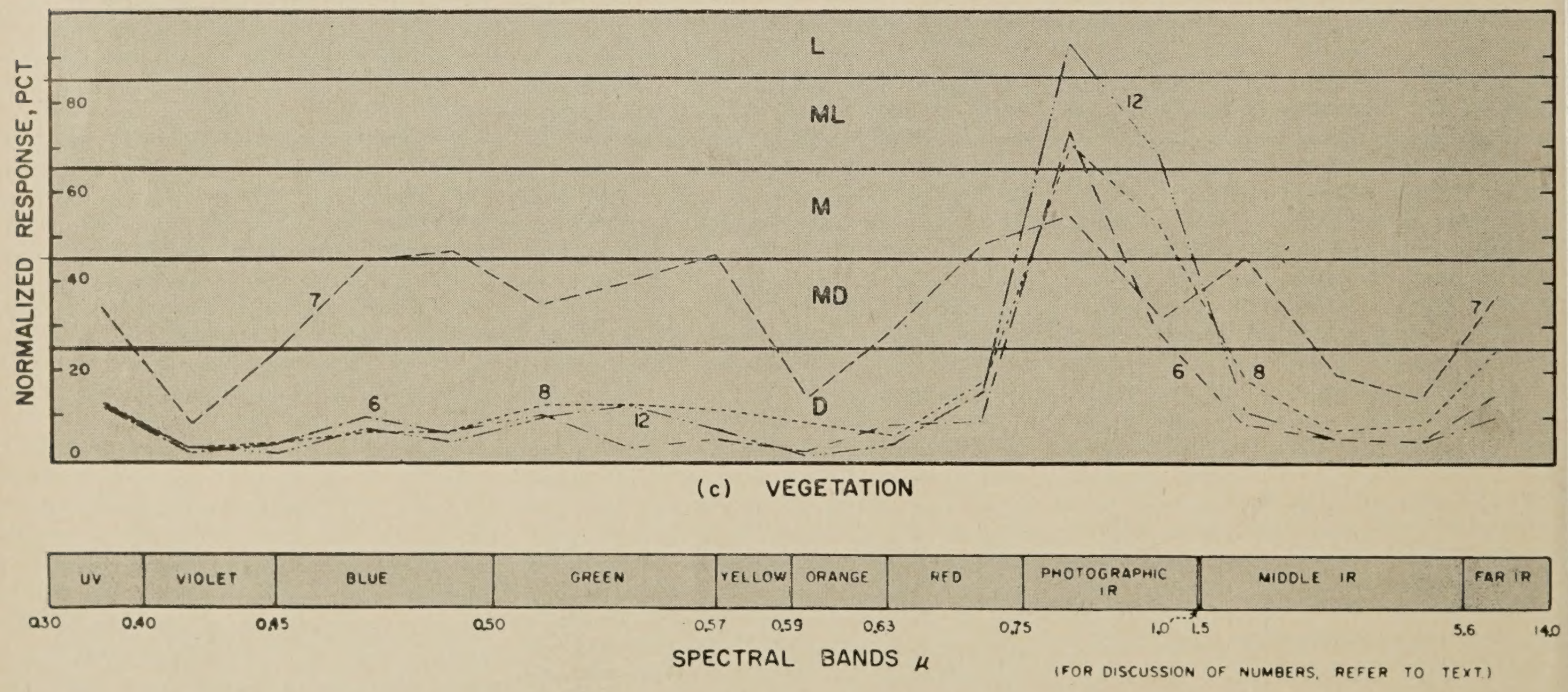
The last group of curves in figure 6(c) shows the differences in spectral responses signatures for various vegetation conditions. Curves 6 and 12 represent fields of winter wheat, and curves 7 and 8 represent pasture fields. It is noted that pasture fields can generally be distinguished from winter wheat by lower reflectance in the photographic IR (infrared) region. It is further noted that all the curves in this figure indicate that the presence of vegetation results in dark or medium dark tones in all bands except the photographic IR. Since the previous curves for soils indicate



(a) SOILS AND ROCK UNITS



(b) EFFECTS OF FARMING PRACTICES



(c) VEGETATION

Figure 6.—Spectral response signatures for various terrain features.

at soils have low response in the photo- raphic IR, this is an excellent band for dis- nguishing tonal effects caused by vegetation om those caused by soils.

The differences in response between the asture fields shown in curves 7 and 8 is that e field containing point 7 has bedrock close the surface, and its influence is indicated by e light streaks in the field (see fig. 5). This fects the overall tonal response, resulting in ightly lighter tones. The differences between e fields of winter wheat shown in curves 6 d 12 are a little more difficult to explain. hese curves are similar in all bands but the otographic IR. In that band, curve 6 is rker. From investigation of this phenomena the field, it was determined that field 6 was lanted 2 weeks earlier than field 12. In addi- on, it was discovered that in the previous ear this field had been planted in corn and eld 12 had been planted in a low cover crop. botanist suggested that the tonal patterns ay reflect vegetation differences because of arying nitrogen levels in the soils. This could ot be verified, but similar effects of previous lanting history on variations in tonal pat- erns, obtained for similar crops, has been eported by C. E. Olson.[11]

The example demonstrates the variety of errain features, important in highway loca- on, that can be interpreted from multisensor overage, particularly multichannel. The use f the multichannel sensor provides the poten- ial for development of a new technique for utomatic interpretation of terrain features, hich will be significant to highway engineer- g. Because the data collected on each hannel can be normalized to a common basis, is possible to compare the information on ll channels and arrive at typical tonal signa- ures for different objects.

The data shown in figure 6 demonstrate hat most of these features can be differ- ntiated by using just five broad tonal bands nd three to four spectral regions. Thus, most f these features could be differentiated when orking with 5^4 or 625 tonal combinations. y again using just five tonal bands and 15 hannels, the number of tonal combinations vailable is more than thirty billion. This hould be sufficient to distinguish among most bjects of interest. For these comparisons, omputers will have to be utilized. This ap- roach is being investigated by the Bureau of ublic Roads as well as by other research roups (*8*, *9*).

Construction Surveys

Remote sensing techniques are applicable to the construction stage for obtaining information to assist in the following operations: (1) estimation of contract quantities—clearing, rock excavation, haul distances; (2) determination of construction progress; and (3) ascertainment of damage caused by construction to adjacent property, vegetation, and drainage. As much detailed information is required in the construction stage and because it is necessary to distinguish between numerous items, the use of natural and infrared color photography and multisensor imagery offer the best approach. The color enables one to discriminate and positively identify objects, while the multisensor imagery makes it possible to identify and delineate various items for estimation of quantities.

Maintenance Surveys

Maintenance surveys are performed to evaluate the existing condition of the highway system and facilities, and to determine what corrective measures are needed to bring the system up to the original or an acceptable condition. Included in this stage are surveys determining damage caused by water, wind, landslides, or subsidence.

As in the previous stage, detailed information is required about particular sites, and general information and quantities are needed for large regional areas. For example, information is needed on areas damaged by floods, as well as on details of damage occurring at particular sites. The remote sensors most applicable to this stage include the use of natural and infrared color photography and multisensor imagery. These sensors should provide the detailed information along selected sites, in addition to general and quantitative information for regional areas.

Summary and Costs

In the discussion of the potential applications of remote sensing techniques to the various stages of highway engineering, it is apparent that no single technique, or even combination of techniques, is applicable to all stages. In addition, the information obtained in one stage is not always applicable to other stages. Where large regional areas are to be evaluated, satellites, radar, and other sensors providing broad coverage, are applicable. Where details, quantities or delineation of objects, materials, soils, geology, etc., are needed, a combination of multisensor imagery and color photography appears to be more fruitful. As both regional and detailed information are needed in almost every stage of highway engineering, it is apparent that combinations of these two groups of coverage will be required to completely evaluate all the pertinent factors. In addition, to meet the requirements for each stage, periodic coverage is important. These requirements raise the important question of cost.

The cost of multisensor flights has been estimated at $1,000, or more, an hour. However, there is little information in the literature showing actual cost figures. Information is also lacking on comparisons of costs for performing surveys by remote sensing techniques and by conventional methods. Although remote sensing techniques might provide more information and more accurate information, it would not be applied if the cost becomes prohibitive or is much greater than conventional methods. To determine this cost factor, more research is required.

Public Roads Remote Sensing Research

The Bureau of Public Roads has developed a research program to promote investigation of the use of aerial remote sensing techniques to highway engineering, in general, and to identify natural materials, in particular. The program is entitled *Optimizing Utilization of Natural Materials by Means of Remote Sensing Techniques* and is a part of the *National Program for Research and Development in Highway Transportation.* Investigations in this research program are to be conducted in three principal areas: identification of natural materials by aerial remote reconnaissance techniques; identification and evaluation of natural materials by field remote reconnaissance techniques; and automatic identification of natural materials.

The goal of this program is to establish test sites in several areas of the United States representing different environmental conditions. Attempts will be made to develop diagnostic characteristics and patterns for various natural materials, both locally and on a regional basis. The research in these three areas is to be conducted by a combination of staff research, contract research, and cooperative research between State highway departments and the Bureau of Public Roads' Highway Planning and Research Program (HP&R). In the overall research program, Public Roads also hopes to cooperate with other Federal and private research organizations interested in remote sensing, so as to further the knowledge in this field and avoid costly duplication whenever possible.

Several HP&R studies, in which aerial remote sensing techniques are being evaluated, are in progress. A study entitled *Annotated Aerial Photographs as Master Soils Plans* is underway at Purdue University. Color photography and multisensor imagery are being evaluated in this study for soils mapping. Phase A of the study indicated that the optimum combination of sensors for detailed soils mapping in Indiana was natural color photography and multichannel imagery (*2*). In arriving at this conclusion, five different types of aerial film (three scales), two different infrared sensors, two different radar sensors, a multichannel sensor, and a multiband camera were evaluated over a 13-month period. In Phase B of this study, the optimum combination is being evaluated further along a 70-mile route location in Indiana. As part of this second phase, cost comparisons of the remote sensing technique versus standard field methods for determining soil and soil conditions pertinent to highway location and design are being evaluated.

Cooperative HP&R studies, evaluating the use of color photography for various highway applications, are in progress in Maine, Florida, and Ohio. A study is also in progress in California, where infrared imagery is being evaluated to determine information on types and identification of soils as a suitable source for construction material.

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[11] Paper by C. E. Olson, Jr., presented at the American Association for the Advancement of Science meeting (see acknowledgments).

The Public Roads staff research in remote sensing is concentrating on the problem of automatic identification. Based on multichannel data and color photography, investigations are underway to develop techniques for identifying various soils and soil conditions, and for automatic identification of various road surfaces. Work is also in progress on increasing the accuracy of arriving at standard descriptions of colors present in color photography by means of densitometric measurements. This method provides a means of automatically differentiating items which can be separated by color differences. This technique has been described by Gourley, Rib, and Miles (*10*) and Rib (*11*).

A research contract with industry to determine the feasibility of the development of an area traffic surveillance and control system is also in progress. The scope of this contract includes investigations into the feasibility of evaluating significant traffic parameters to specific tolerances—for example, speed in miles per hour ±0.5 m.p.h. per vehicle—from ground base systems, airborne systems and orbiting satellites.

ACKNOWLEDGMENTS

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D. J. Barr and R. D. Miles, *Techniques for Utilizing Side-Looking Ariborne Radar (SLAR) Imagery in Regional Highway Planning.* Unpublished report presented at the 47th Annual Meeting of Highway Research Board, January 1968.

L. K. Bridwell, Remarks made before the Rubber Manufacturers Association, New York, N.Y., November 16, 1967.

L. F. Dellwig, *What's New in Geology in Side Look Radar Imagery?* Unpublished report presented at the 47th Annual Meeting of Highway Research Board, January 1968.

O. W. Mintzer, *Summary of Report on Evaluation of Photo Interpretation Data From Phoenix, Arizona, Test Site.* Prepared for Geographic Systems Division, U.S. Army Engineer Topographic Laboratories, Fort Belvoir, 1966.

C. E. Olson, Jr., *Accuracy of Land-Use Interpretation From Infrared Imagery in the 4.5 to 5.5 Micron Band,* presented at American Association for the Advancement of Science Meeting, Berkeley, Calif., December 28, 1965.

M. F. Sheridan, *Preliminary Studies of Soil Patterns Observed in Radar Images, Bishop Area California.* Unpublished letter, U.S. Geological Survey Technical Letter NASA-63, November 1966.

REFERENCES

(*1*) *Highway Engineering Handbook,* edited by K. B. Woods, Editor-in-Chief, McGraw-Hill Book Company, New York, N.Y., 1960.

(*2*) *An Optimum Multisensor Approach for Detailed Engineering Soils Mapping,* by H. T. Rib, Joint Highway Research Project, vol. I and II, Report No. 22, Purdue University, December 1966.

(*3*) *Utilization of Photo Interpretation in the Highway Field,* by H. T. Rib, Highway Research Record No. 109, Photogrammetry and Aerial Surveys, 1966, pp. 18–26.

(*4*) *Vegetation Analysis With Radar Imagery,* by S. A. Morain and D. S. Simonett, Proceedings of the Fourth Symposium on Remote Sensing of Environment, April 12–14, 1966 University of Michigan, June 1966, pp. 605-622.

(*5*) *Photo Interpretation of Soils Using Colo Aerial Photography,* by O. W. Mintzer, Manu of Color Aerial Photography, The America Society of Photogrammetry, 1968, Chapter 1 (Soon to be published).

(*6*) *Use of Aerial Color Photography i Materials Surveys,* by J. R. Chaves and R. I Schuster, Highway Research Record No. 6 Color Air Photos, Soil Properties and Test 1964, pp. 1–9.

(*7*) *The Use of Color Aerial Photography i the Reconnaissance of Soils and Rocks,* b Abraham Anson, Materials Research an Standards, vol. 8, No. 2, February 1968, p 8–16.

(*8*) *Automatic Identification and Classific tion of Wheat by Remote Sensing,* by D. Landgrebe et al., Laboratory for Agricultur Remote Sensing, Purdue University, Researc Progress Report 279, March 1967.

(*9*) *A Spectrum Matching Technique for E hancing Image Contrast,* by D. S. Lowe ar J. G. N. Braithwaite, Applied Optics, vol. No. 6, June 1966, pp. 893–898.

(*10*) *Automatic Technique for Abstracti Color Descriptions from Aerial Photograph* by J. Gourley, H. T. Rib, and R. D. Mil Photographic Science and Engineering, v 12, No. 1, January–February 1968.

(*11*) *Color Measurements,* H. T. Rib, Manu of Color Aerial Photography, The Americ Society of Photogrammetry 1968, Sub-Chapt 1.2 (Soon to be published).

Kaolin-Lime-Water Systems
Part 1—Strength and Rheological Properties

Y THE OFFICE OF
ESEARCH AND DEVELOPMENT
UREAU OF PUBLIC ROADS

Reported by [1] W. C. ORMSBY, Research Chemist,
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The strength characteristics and flow properties of well-defined kaolin-water systems were evaluated in the study reported in this article. The systems contained different percentages of hydrated lime and were cured at room temperature for periods up to 15 days. Unconfined compressive strengths were measured, and flow properties were evalutated using a cone-plate viscometer operated over a range of shear rates.

Unconfined compressive strength was generally improved by lime additions; significant improvement was noted for even very small additions, such as one-half to 1 percent. For the two curing periods used, 3 days and 15 days, most of the strength had been developed by the end of the 3-day period.

The viscosity, or consistency, of the kaolin-water systems was markedly in creased by the addition of lime; additions as small as 0.8 percent effected considerable change. The effect was immediate and, as indicated by the rheological data, was complete in less than 10 minutes.

Introduction

BENEFITS DERIVED from treating soils, clays, and other materials with lime ave been recognized for many years. The use lime for soil stabilization, that is, to increase rength, durability, and resistance to deformation of native soil, has been the subject many laboratory and field investigations, e results of which have been summarized in umerous reports (*1–6*)[2], by Eades,[3] and by ateos (*7*). These reports include results of vestigations on the physical and chemical haracteristics of lime-stabilized soils and ays.

Mateos (*7*) emphasized the importance of e lime retention concept proposed by Hilt nd Davidson (*4*), wherein it is hypothesized hat a certain initial concentration of lime, ime retention value," must be exceeded before pozzolanic action can occur. In this concept, lime concentrations at and below this itial concentration ameliorate the soil by hanging properties, such as plasticity and hrinkage, without improving strength; rength development occurs after this initial ne requirement is satisfied.

In contrast to the lime retention concept, aldino [4] and Kiek (*8*) demonstrated that ronounced improvements in strength characteristics of some soils and clays can be fected by additions below their probable me retention values.

The study reported here was initiated to vestigate further the concentration of lime quired for strength development. Well-haracterized kaolin-lime-water systems were valuated with respect to the effects of lime dditions on strength and rheological properes. The percentages of lime used extended ver a considerable range of concentration, including amounts less than the potential lime retention values of the clays under study. Assuming that the lime retention concept is valid, little change in strength properties or flow behavior would be expected from additions of lime that are less than the critical amount.

Materials

Three kaolins previously (*9*) characterized as to mineral composition, cation-exchange capacity, surface area, and crystallinity, were selected for study. Sample designations B, H, and E are the same as those used by previous investigators (*10–12*). Properties of kaolins are listed in table 1.

Moisture-Density Relations

In order to approximate optimum conditions for the fabrication of specimens for strength tests, it was necessary to determine moisture-density relations for various clay-lime-water mixtures. As only a small amount of each of the three clays was available, the compaction tests were miniaturized and performed using kaolin B only. Because of the close similarity of the three kaolins, as shown by the data in table 1, it was assumed that the compaction

Table 1.—Properties of clays studied

Property	Kaolin		
	H	B	E
Surface area meters ^{2}/gram	12. 10	11. 70	11. 80
Crystallinity index [1] $02\bar{1}/060$	0. 24	0. 26	0. 19
Cation-exchange capacity m.e./100g.	2. 14	2. 24	2. 30
Indicated mineral composition:			
X-rays	Kaolinite	Kaolinite	Kaolinite
Electron micrographs	Kaolinite	Kaolinite	Kaolinite
pH $\left(\frac{\text{Clay}}{\text{Water}}=\frac{1}{20}\right)$	5. 3	5. 2	5. 2
Liquid limit	45	46	48
Plasticity index	14	15	18

[1] The crystallinity index is determined from the ratio of the intensities of 2 X-ray diffraction peaks. The $(02\bar{1})$ peak is affected by changes in crystallinity whereas the (060) peak is not.

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[1] Presented at the 70th annual meeting of ASTM, Boston, ass., June 1967.

[2] The italic numbers in parentheses identify the referenecs sted on page 43.

[3] J. L. Eades, *Reaction of Ca(OH)$_2$ with Clay Minerals in oil Stabilization*. Ph. D. Thesis, University of Illinois, 1962.

[4] J. D. Baldino, *Analysis of a Factorially Designed Experient on Lime Stabilized Pure Clay Minerals*. C. E. 440 Report, ritz Engineering Laboratory, Lehigh University, 1963.

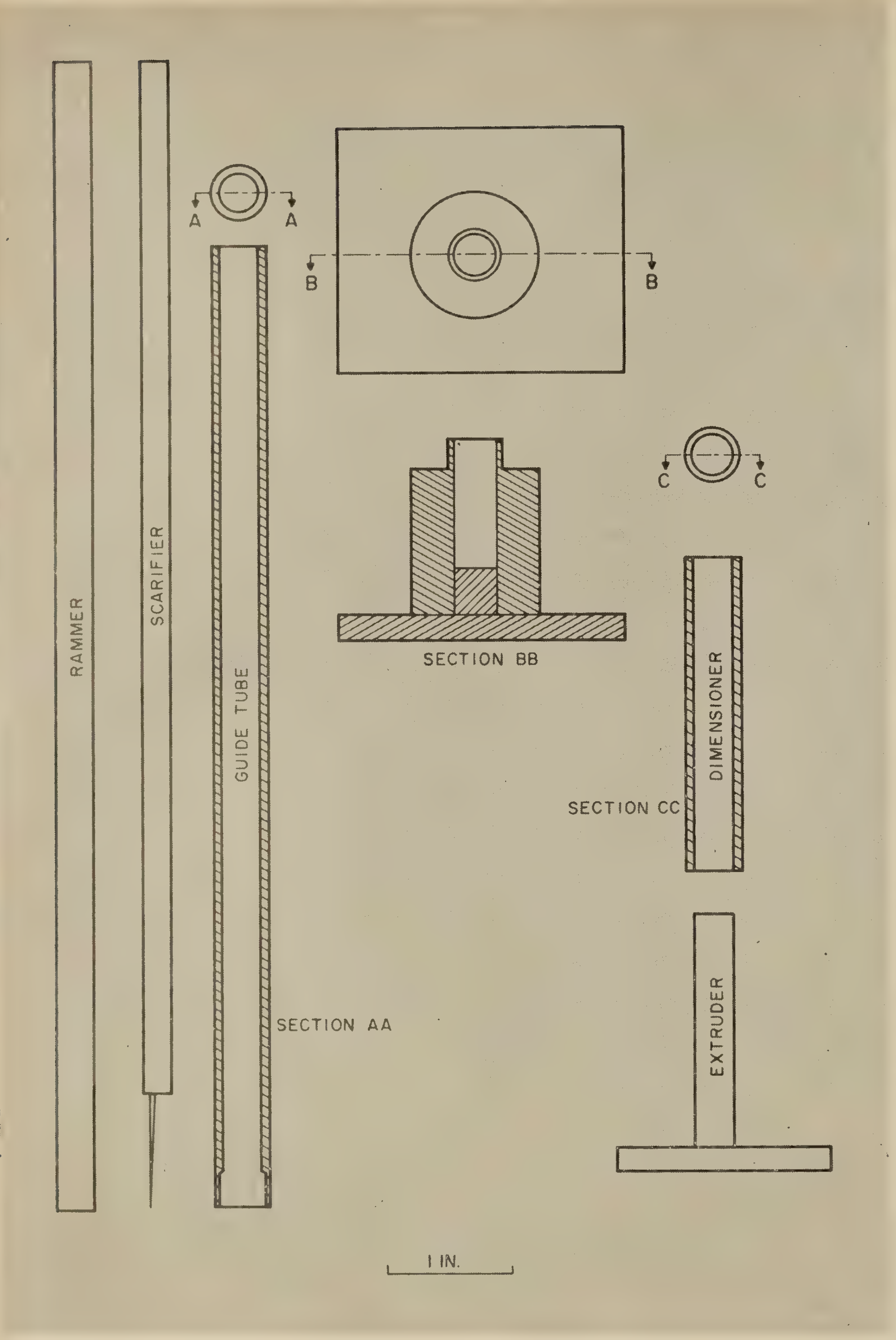


Figure 1.—Molding apparatus.

results for kaolin B would also be representative for kaolins H and E. Drawings of the molding apparatus and accessories are shown in figure 1. All parts of this equipment were made of brass except the mold which was made of teflon.

Clay for the compaction experiments was powdered to pass a No. 80 sieve and dried. For each composition, the required clay and $Ca(OH)_2$ were weighed, mixed on glazed paper, and placed in a small plastic bag. Distilled water was added, and the bags were sealed and thoroughly kneaded by hand. The mixture was immediately removed and compacted using three layers, which were each tamped eight times. This technique was satisfactory for determining optimum moisture content, and produced densities somewhat higher than Proctor densities obtained by Eades [3] for similar materials.

After fabrication, specimens were weighed and dried at 110° C., and densities were calculated from specimen weights and dimensions. Plots of density versus moisture content for different lime concentrations are shown in figure 2. As expected, the curves indicate a decrease in density with increasing lime concentration. A slight increase in optimum moisture content also occurred as the lime content was increased. On the basis of the results shown in figure 2, subsequent compositions for strength specimens were prepared to yield a measured moisture content of 22 percent, dry weight basis.

Strength Experiments

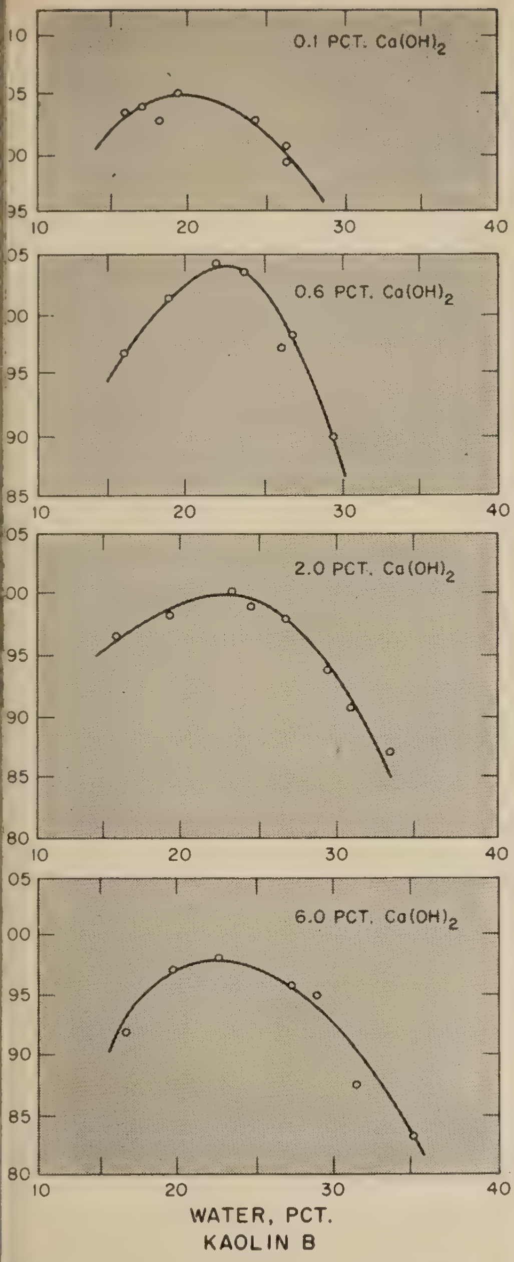
Strength experiments were performed on specimens prepared using kaolins H and E. Four replicate specimens of the following compositions were prepared: 0.0, 0.1, 0.2, 0.6 0.8, 2.0, and 6.0 percent lime on the dry weight basis. The required amounts of clay lime, and water were placed in plastic bags and were kneaded and compacted using the same molding equipment and compaction procedures that were employed for the moisture-density tests. Specimens were cured in a high humidity chamber at room temperature (23°-26° C.) for periods of 3 days and 15 days.

The compressive strength was determined using the apparatus shown in figures 3 and 4 Load was applied at a constant strain rate o 0.005 cm./min, and the chart speed was 0. cm./min. Loading sensitivity was ±10 grams The unconfined compressive strength was computed from the rupture load and the cross-sectional area of the specimen.

Viscosity Experiments

A cone-plate viscometer equipped with flow curve recorder was used in the viscosit experiments. The cone and plate arrangemen and sample positioning are shown schemat cally in figure 5. A photograph of the vi cometer with accessory apparatus is shown i figure 6. A truncated cone, 4 centimeters i diameter, was used in all of the experiment The cone was driven by a variable speed mot through an electrical torque dynamomet that measured the viscous traction caused b the sample. The amount of traction w indicated on an X-Y recorder where shear ra (proportional to the driving speed) was plott against torque (proportional to the she stress). Principles of operation of the vi cometer are fully described in the literatu (*13*, *14*).

Required amounts of kaolins H and E we screened to pass a No. 80 sieve and dried 110° C. Small portions of these clays we then weighed on glazed paper, and predete mined amounts of lime—concentrations 0.0, 0.1, 0.2, 0.6, 0.8, 2.0, and 6.0 percent the dry-weight basis—were added and mixe The mixtures were placed in small plas bags and distilled water was added to give concentration of 100 percent water, dry-weig basis. The bags were then sealed and stor under the same humidity and temperatu conditions as the strength specimens. For ea



gure 2.—Moisture-density relations for kaolin B.

Table 2.—Strength of clay-lime specimens

Concentration of $Ca(OH)_2$ added to clay specimens	Strength of clay specimens [1]				Average strength for all specimens at each lime concentration
	Kaolin H		Kaolin E		
	Cured 3 days	Cured 15 days	Cured 3 days	Cured 15 days	
Percent	*p.s.i.*	*p.s.i.*	*p.s.i.*	*p.s.i.*	*p.s.i.*
0	186	208	193	160	187
0.1	215	180	187	164	186
0.2	208	182	198	178	192
0.6	207	186	205	166	191
0.8	214	190	209	202	204
2.0	206	238	196	214	214
6.0	220	243	211	213	222

[1] Each strength value is the average of four replicates.

ty, two specimens were prepared at each ne concentration to provide separate speci- ens for each of the two curing periods of 3 ys and 15 days. After the prescribed curing, e sample bags were removed from the hu- dity chamber and thoroughly kneaded by nd. Each clay-lime-water mixture was then vided into two parts, one for a verification the moisture content, and the other for w property evaluation. The flow behavior as determined using a predetermined sched- e of shear rates and times. For most mixtures equilibrium curve was obtained after two three cycles, each cycle consisting of an tomatically-programed acceleration from ro to the maximum shear rate in a given me followed by a deceleration to zero in the me length of time. During the operation of e viscometer the specimen mixtures were aintained at a temperature of 25±0.2 grees C.

A separate series of specimens was prepared study the effect of short curing periods. These specimens, containing 2 percent lime and 100 percent water (dry-weight basis), were cured for periods up to 32 hours.

Results of Strength Tests

Results of the strength tests are given in table 2. An analysis of variance of the results in columns 2 to 5 was performed and is given in table 3. The interaction mean squares given in table 3 are of the order of magnitude to be expected from the variance computed using ranges of the individual determinations. Individual strength results, although not listed, were used to compute a standard error for

Figure 3.—Apparatus used in determining compressive strength.

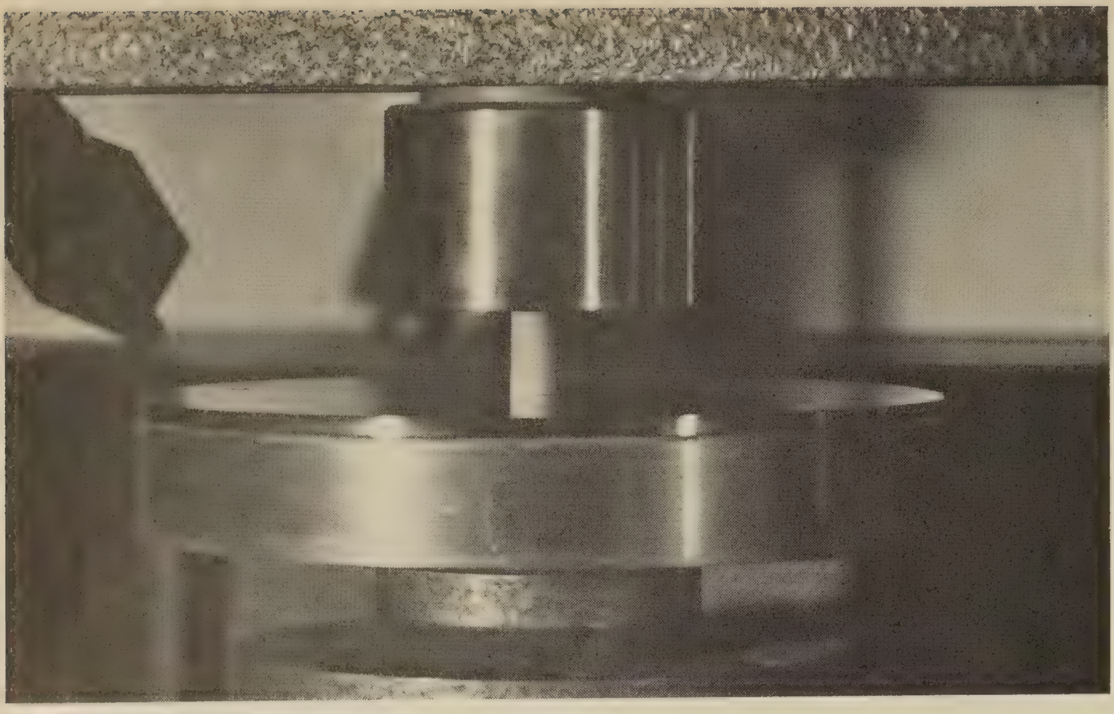


Figure 4.—Detail of loading arrangement showing sample positioning.

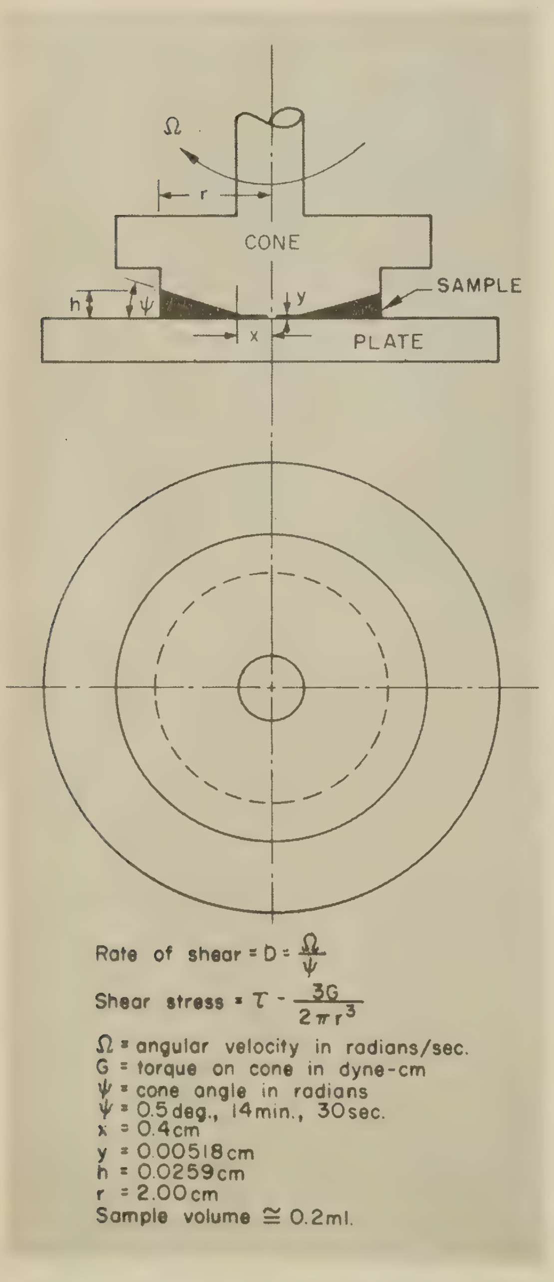


Figure 5.—Cone-plate viscometer details (not to scale).

means, and this standard error amounted to 13. This gives a variance of 169 for averages, which is in reasonable agreement with independent estimates of variance computed for various interactions in the analsysis of variance (table 3). The analysis indicates significant differences between clays and between lime concentrations and, importantly, shows that there are no significant interactions between clays and lime, between time and lime, or between clays and time. Therefore, because no interactions were detectable, one is justified in computing a concentration average in which the strengths at each lime concentration for the clays at both curing times are average. This average, based on 16 determinations, is given in column 6 of table 2.

To evaluate further the relationship between concentration of lime and strength, least-squares polynomials were fitted to the data (columns 1 and 6 of table 2). Results indicate a good fit for a second degree equation—$Y=186+18X-2X^2$, index of determination (r^2) = 0.95, standard error of estimate for $Y=3.86$ p.s.i. The curve calculated from this equation is plotted along with the experimentally determined points (open circles) in figure 7.

Higher degree equations were also fitted, but the fitting did not result in any improvement. Table 4 gives an analysis of variance for regression of the various equations fitted.

The results of the least-squares fitting and the analysis of variance indicate the following:

- An appreciable improvement in strength upon the addition of lime.
- Strength improvement begins at low concentrations of lime.
- Initial gain in strength is rapid but begins to taper off at about 2 percent lime.
- A second degree equation can adequately account for the variation of strength as the lime concentration is changed.

Viscosity Results

Flow curves for the different systems studied are given in figures 8–11. In general, these curves indicate an increase in the rigidity of the systems as the lime concentration is increased. This effect is evident from a comparison of the dynamic yield points which may be obtained by visually extrapolating the more or less straight-line portions of the curves back to zero shear rate. Increase of the yield points of the systems, as the percentage of lime is increased, indicates that lime produces a strengthening of the clay-water structure. Because of the difficulties in accurately drawing tangents to the curves, tangents were not used in calculating apparent viscosities instead, the flow curves were analyzed using the power law equation described later.

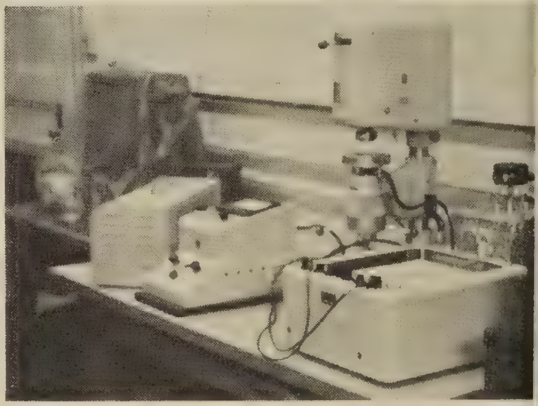


Figure 6.—Cone-plate viscometer with flow curve recorder used in viscosity experiments.

Table 3.—Analysis of variance—strength results

Source of error [1]	Sum of squares	Degrees of freedom	Mean square	*Test* degrees of freedom [2]	F ratio [3]
Clays	1249	1	1249	1/19	5.556*
Times	671	1	671	1/19	2.985 n.s.
C X T	153	1	153	1/6	0.955 n.s.
				1/18	0.688 n.s.
Lime	4707	6	784.5	6/18	3.429*
L X C	2072	6	345.3	6/6	2.155 n.s.
L X T	1085	6	180.8	6/6	1.128 n.s.
L X T X C	961	6	160.2		
Total	10898	27			
POOLED ERROR (1)	4118	18	228.77		
POOLED ERROR (2)	4271	19	224.79		

[1] C=Clays=2; L=Lime Concentration=7; T=Times=2; LTC=28.
[2] Test degrees of freedom indicates which error term was used in testing.
[3] *—Significant at 5% level; n.s.—not significant.

The curves for kaolin II (figs. 8 and 9) are om determinations made on an 80-second hedule; that is, 40 seconds to uniformly ccelerate the spindle driving the cone to the aximum r.p.m. of 1000, and 40 seconds to ecelerate to zero. The curves obtained during cceleration usually coincided with those obined during deceleration. This behavior inicates that the structure rapidly breaks own when the shear rate is increasing and, uring the deceleration portion of the cycle, forms at the same rate at which it was roken down, returning to the original structure at zero shear rate. Recycling of the pecimens produced curves that were almost lentical to the original.

The curves for kaolin E, shown in figures 0 and 11, were run on a 20-second schedule. /ith this clay, some hysteresis—slight openg up of the up-and-down curves—was obrved; this hysteresis is not evident in the gures, because only the downcurves are lustrated.

Figure 12 gives long-log plots of viscosity ata obtained for the various mixtures of aolin H that had been cured 15 days. These lots, which are typical for all of the systems udied, suggest a power law relation,

$$\tau = kD^N \text{ or } \eta_a = kD^{N-1}$$

/here,

$_a$ = apparent viscosity (poise)
= rate of shear (sec^{-1})
= shear stress (dynes/cm^2)
= power law constant
/ = power law exponent.

The constant k is proportional to the constency of the system, and N gives an indicaon of the departure from Newtonian behavior. 'or $N = 1$, $N > 1$ and $N < 1$, one obtains Vewtonian, dilatant, and pseudoplastic beavior, respectively. Results obtained for the ower law parameters, N and k, for kaolins I and E, are given in table 5.

The relations between the viscosity paramters k and percent lime are shown in figure 3 for the two clays. This figure indicates hat:

Viscosity is increased at relatively low conentrations of lime.

For kaolin H, the increase of viscosity rogresses fairly regularly up to 6 percent me; for kaolin E, the viscosity increases airly regularly up to 2 percent lime, then emains essentially constant upon further dditions.

The degree of crystallinity of the clay may nfluence the viscosity to a considerable egree, as the more poorly crystallized clay E has a much higher viscosity than kaolin II.

Results of the experiments designed to letermine the effects of short curing periods re given in figure 14. The power-law paramters for the curves of figure 14 are given in able 6. It is noteworthy that the consistency parameter k for kaolin E with 2 percent lime s 1755, which is more than double that of the -day specimen of the same kaolin without ime (see table 5). It is thus clear, as far

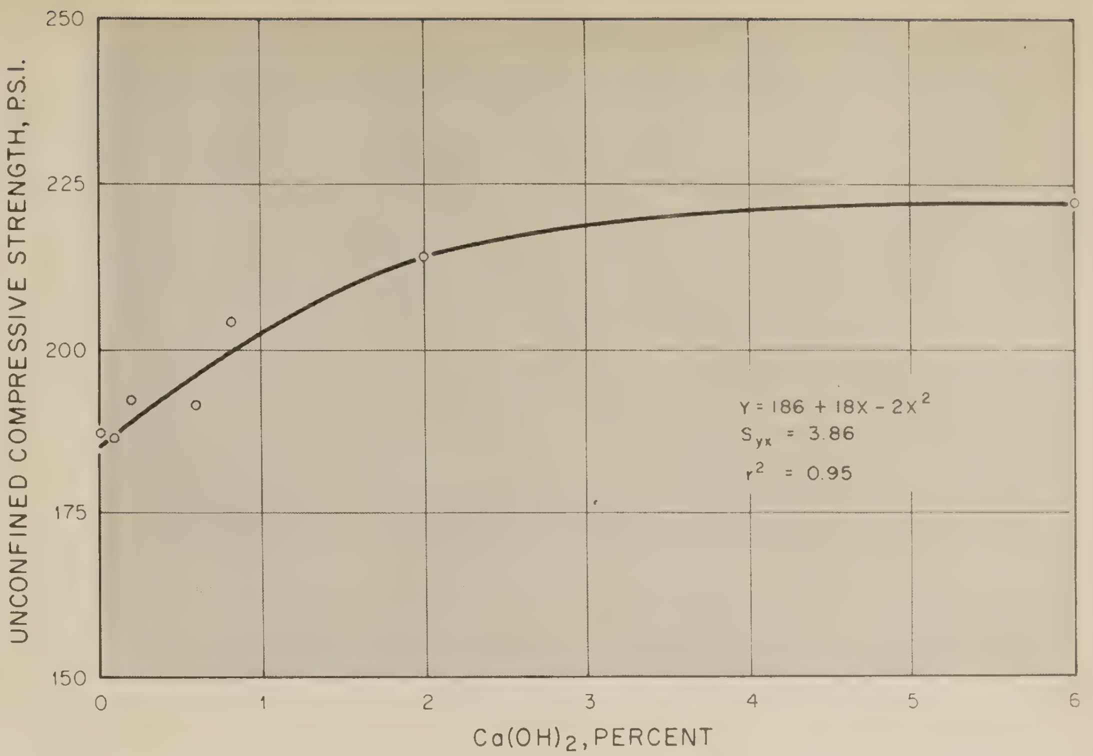


Figure 7.—Relations between unconfined compressive strength and percent lime for kaolins II and E.

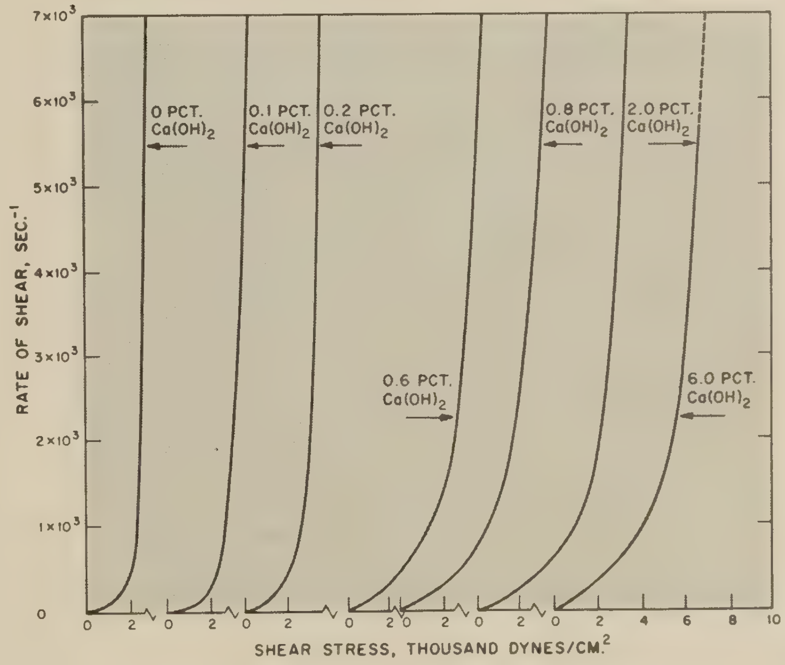


Figure 8.—Flow curves for kaolin II cured 3 days.

Table 4.—Analysis of variance for regression

Source of estimate	Sum of squares	Degrees of freedom	Mean square	F ratio [2]
Linear	931. 22820	1	931. 22820	62. 586**
2nd degree	212. 97250	1	212. 97250	14. 76*
3rd degree [1]	0. 06019	1	0. 06019	0. 00304 n.s.
4th degree [1]	10. 99475	1	10. 99475	0. 4375 n.s.
5th degree [1]	30. 77905	1	30. 77905	1. 7406 n.s.
Residual	17. 68261	1	17. 68261	
Total	1203. 71730			

[1] Variances for 3rd, 4th, and 5th degree were successively pooled with residual as they were non-significant when tested against residual or the appropriate pooled variances.

[2] **—Significant at 1 pct. level; *—significant at 5 pct. level; n.s.—not significant.

Table 5.—Viscosity parameters

Clay	Concentration of Ca (OH) $_2$	Power law parameters			
		Specimen cured 3 days		Specimen cured 15 days	
		Behavioral index, *N*	Viscosity index, *k*	Behavioral index, *N*	Viscosity index, *k*
	Percent				
Kaolin H	0.0	0.24	298	0.26	316
	0.1	0.26	377	0.32	197
	0.2	0.25	412	0.28	303
	0.6	0.26	614	0.28	303
	0.8	0.26	715	0.24	474
	2.0	0.27	644	0.28	632
	6.0	0.22	1016	0.24	954
Kaolin E	0.0	0.24	692	0.25	907
	0.1	0.20	695	0.22	646
	0.2	0.18	919	0.22	646
	0.6	0.24	1376	0.21	815
	0.8	0.21	2002	0.18	926
	2.0	0.18	2442	0.20	2302
	6.0	0.19	2440	0.20	2302

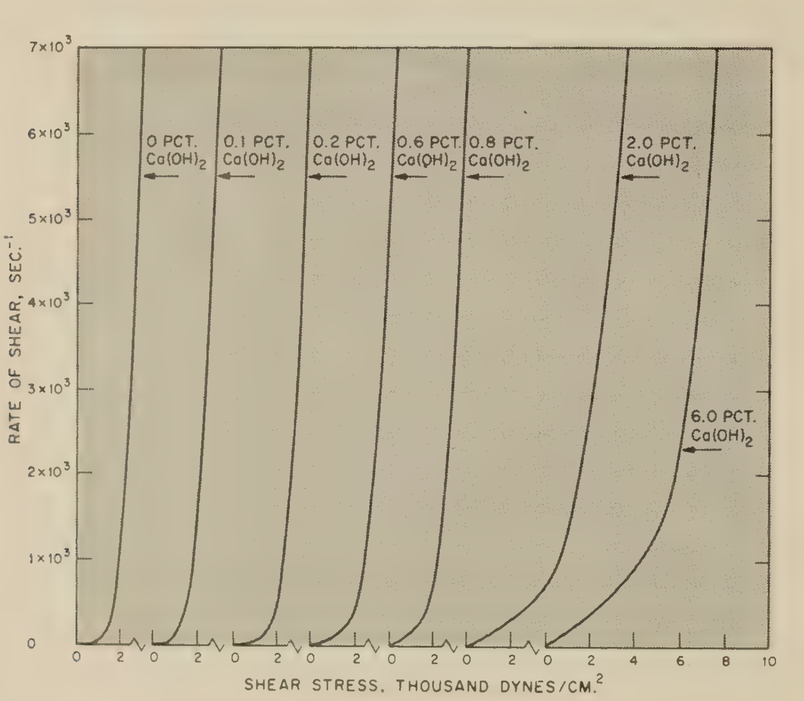


Figure 9.—Flow curves for kaolin H cured 15 days.

as viscosity increase is concerned, the effe of lime is almost complete in less than minutes.

Discussion

Previous work (*4*) suggests that the li retention value of kaolinite clays is usua about four or five times the cation-exchan capacity. In kaolins II and E this wou correspond to a lime retention value of near 0.4 percent. From the results described (f 7), it was determined that strength w developed at lime percentages of the order 0.1–0.2 percent, which are considerably le than the probable lime retention values of t clays.

As the clays were not calcium saturate prior to the addition of lime, some of the li added may have been used up in ion exchan before some additional increment becar effective in promoting the development strength. In other words, if the clays had be calcium saturated, an unequivocal streng response might have been noticed even wi lime contents as low as 0.1 percent.

Although cementitious phases were n unequivocally identified in systems containi very low percentages of lime, it seems like that such phases were present, as considerab interaction of clay and lime is indicated electron micrographs of replicas of specime containing only 0.8 percent lime (see Part

The relation between the viscosity para eter and the concentration of lime (fig. 1 indicates that lime has had a pronounc stiffening action. Viscosity increased wh even very small amounts of lime were adde At low concentrations of lime, the effect m be one of flocculation and aggradation similar to that produced in the consistency ceramic slips when they are cast in plas molds that have been treated with calci salts (*15*). Figure 13 also shows that fl properties may be affected by the degree crystallinity of the clay.

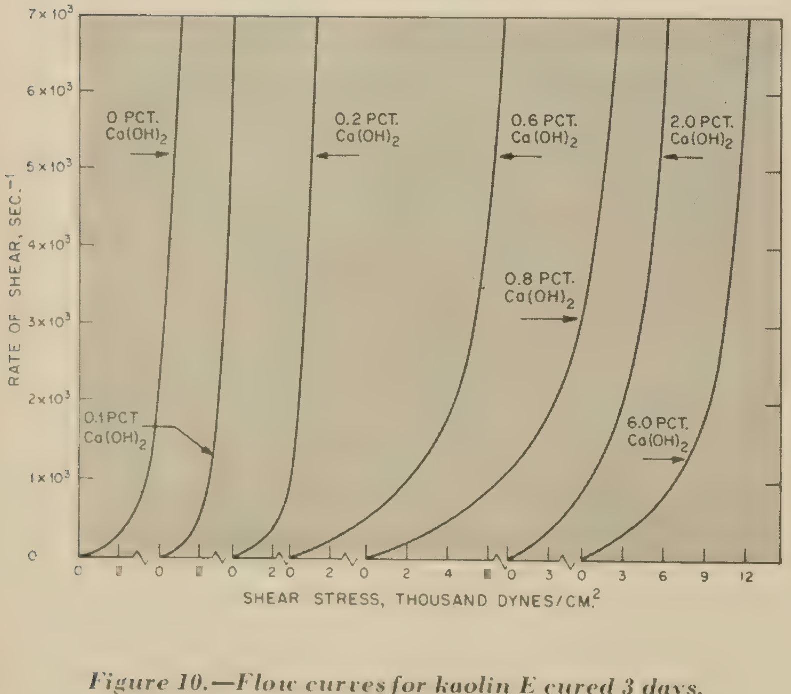


Figure 10.—Flow curves for kaolin E cured 3 days.

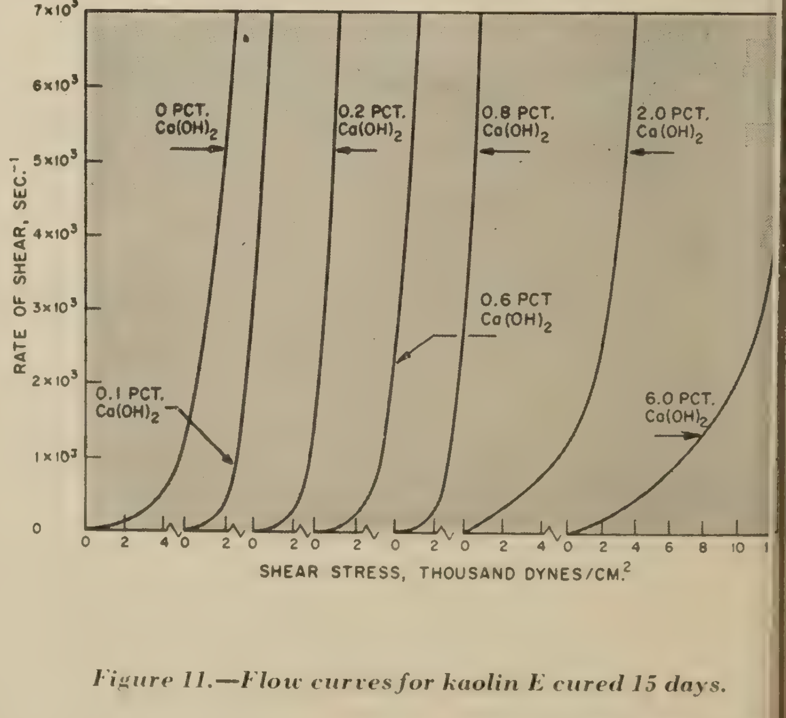


Figure 11.—Flow curves for kaolin E cured 15 days.

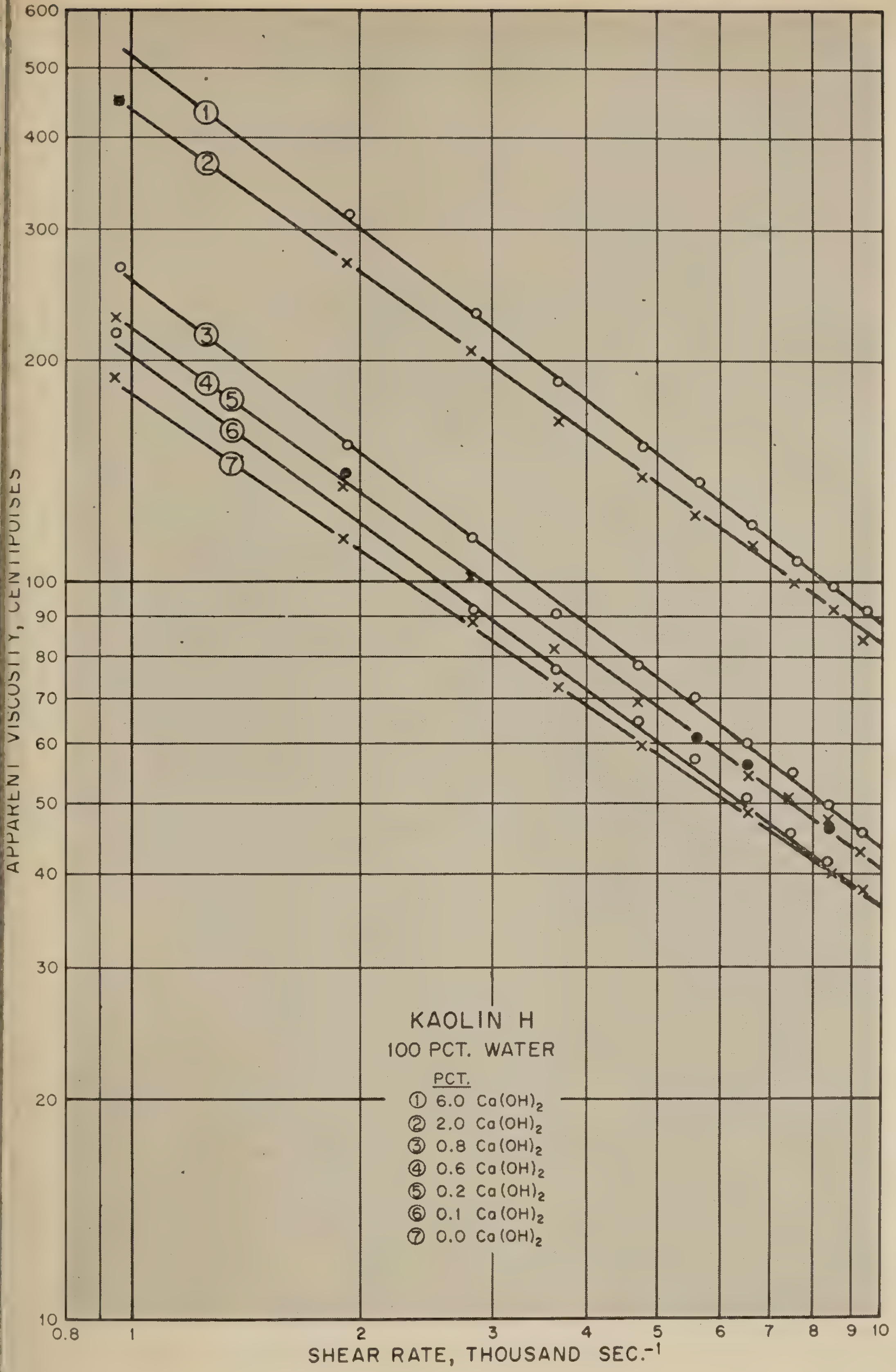


Figure 12.—Apparent viscosity-shear rate plots for kaolin H cured 15 days.

Summary

In the evaluation of strength characteristics and flow properties of kaolin-water systems containing various percentages of hydrated lime and cured at room temperature for periods up to 15 days, unconfined compressive strength of specimens was found to increase as the percentage of lime was increased.

Additions of modest amounts of lime—0.1 to 0.8 percent—produced an immediate increase in viscosity, or consistency; this effect was enhanced as the percentage of lime was increased. After the immediate viscosity increase, there was little further change during periods up to 15 days. For a given clay-lime-water composition the viscosity was higher for the more poorly crystallized clay.

The existence of a critical lime retention value, below which strength and viscosity effects would be minimal, was not revealed.

ACKNOWLEDGMENTS

The authors express their thanks to Sidney Diamond and Donald G. Fohs with whom valuable discussions were held.

The authors also express their appreciation to W. S. Brower, Jr., who assisted in the design and construction of apparatus used in the fabrication of specimens for compaction and strength experiments, to Sheldon Wiederhorn who made experimental facilities available, and to W. E. Worthy who determined liquid and plastic limits for the clays studied.

Clay samples were obtained through the courtesy of the Georgia Kaolin Company, Dry Branch, Georgia.

REFERENCES

(*1*) *Lime and Lime-Flyash Soil Stabilization*, Highway Research Board, Bulletin 193, 1958.

(*2*) *Lime and Lime-Flyash as Soil Stabilizers*, Highway Research Board, Bulletin 231, 1959.

(*3*) *Soil Stabilization With Asphalt, Portland Cement, Lime and Chemicals*, Highway Research Board, Bulletin 241, 1960.

(*4*) *Preconditioning and Stabilizing Soils by Lime Admixtures*, Highway Research Board, Bulletin 262, 1960.

(*5*) *Lime Stabilization: Properties, Mix Design, Construction Practices and Performance*, Highway Research Board, Bulletin 304, 1961.

(*6*) *Lime Stabilization: Mix Design, Properties and Process*, Highway Research Board, Bulletin 335, 1962.

(*7*) *Soil Lime Research at Iowa State University*, by Manuel Mateos, Journal of the Soil Mechanics and Foundations Division, Proceedings of the ASCE, vol. 90, No. SM2, March 1964, pp. 127–153.

(*8*) Discussion of the paper *The Application of Electrochemistry to Soil Stabilization*, by S. N. Kiek, Proceedings of the Third Australia-New Zealand Conference on Soil Mechanics and Foundation Engineering, 1960, p. 255.

(*9*) *Exchange Behavior of Kaolins of Varying Degrees of Crystallinity*, by W. C. Ormsby, J. M. Shartsis, and K. H. Woodside, Journal of the American Ceramic Society, vol. 45, No. 8, August 1962, pp. 361–366.

(*10*) *Correlation of Paper-Coating Quality with Degree of Crystal Perfection of Kaolinite*, by H. H. Murray and S. C. Lyons, Proceedings of the National Conference on Clays and Clay Minerals, National Academy of Sciences—National Research Council, publication 456, Washington, D.C., 1956, pp. 31–40.

(*11*) *Quantitative determination of Kaolinite by X-ray Diffraction*, by G. W. Brindley and S. S. Kurtossy, The American Mineralogist, vol. 46, Nos. 11–12, 1961, pp. 1205–1215.

(*12*) *Wettability of Kaolinite Treated With Ammonia, Methylamine, Ethylamine or their Corresponding Cations*, by Ayao Kitahara and W. O. Williamson, Journal of the American Ceramic Society, vol. 47, No. 7, July 1964, pp. 313–317.

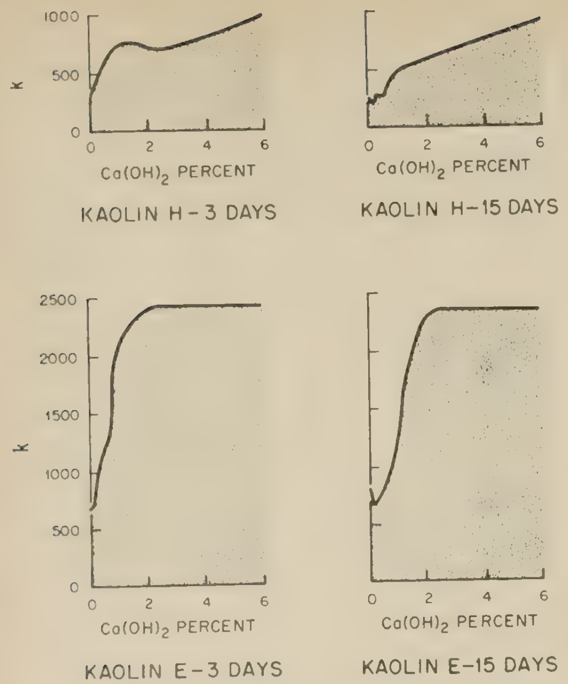


Figure 13.—Relations between viscosity parameter, k, and concentration of lime for kaolins H and E at different curing times.

(13) *The Influence of Viscometer Design on Non-Newtonian Measurements*, by Raymond McKennell, Analytical Chemistry, vol. 32, No. 11, October 1960, pp. 1458–1463.

(14) *Cone-Plate Viscometer, Comparison With Coaxial Cylinder Viscometer*, by Raymond McKennell, Analytical Chemistry, vol. 28, No. 11, November 1956, pp. 1710–1714.

(15) *Fundamental Study of Clay: III, Casting as a Base Exchange Phenomenon*, by A. L. Johnson and F. H. Norton, Journal of the American Ceramic Society, vol. 25, No. 12, August 1942, pp. 337–344.

Table 6.—Effect of curing time on the viscosity parameters of kaolin E +2% lime

Curing time	Behavioral index, N	Viscosity index, k
Uncured	0.21	1755
10 minutes	0.22	1703
30 minutes	0.22	1765
2 hours	0.22	1927
8 hours	0.20	1745
32 hours	0.18	1960

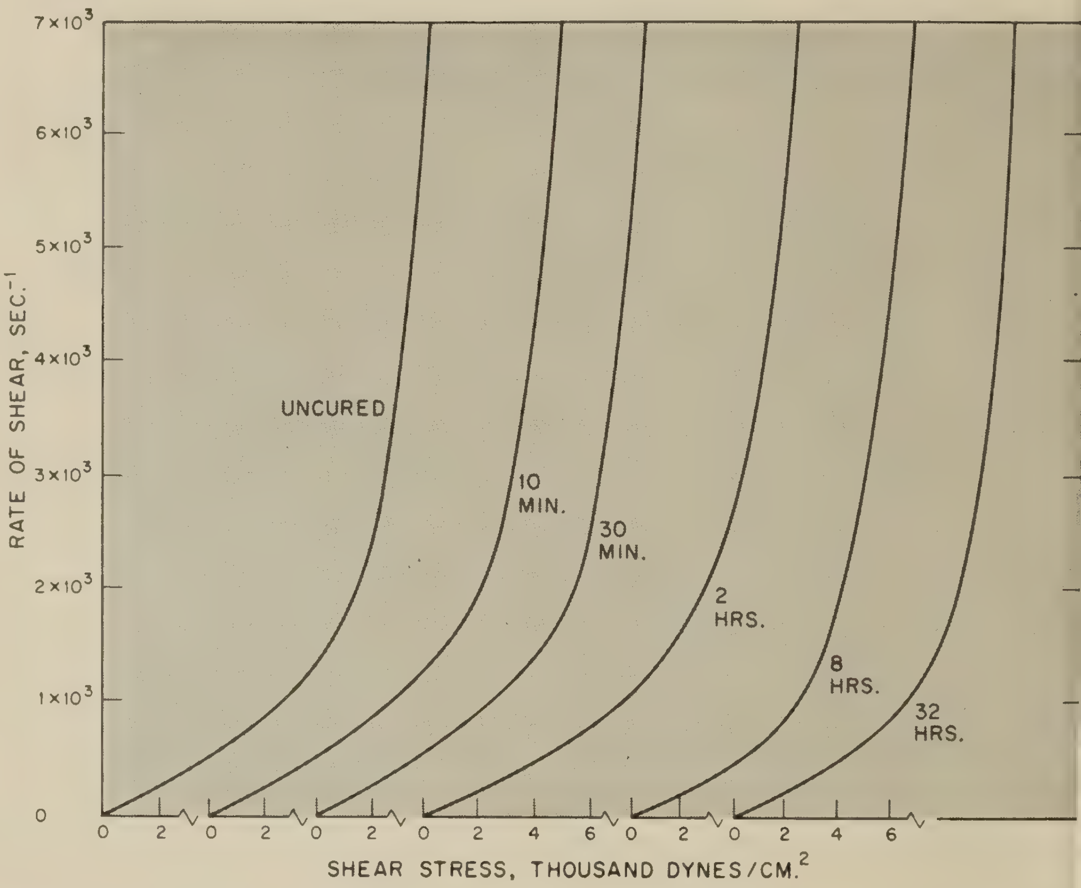


Figure 14.—Effect of curing time on flow behavior of kaolin E, 2 percent lime added.

Kaolin-Lime-Water Systems
Part 2—Electron Microscope Observations

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UREAU OF PUBLIC ROADS

Reported by[1] W. C. ORMSBY, Research
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L. H. BOLZ, Ceramic Engineer,
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Bureau of Standards

Electron optical investigations were made of kaolin-lime-water mixtures that had been cured for various periods. These mixtures, in the form of cylindrical compacts, were recovered from strength experiments. Considerable attack of kaolinite particles by hydrated lime was shown both in electron micrographs of replicas made from fracture surfaces of the compacts and in transmission electron micrographs of powdered compacts; attack occurred both on particle edges and basal surfaces. The formation of new phases—calcium silicate hydrates—was indicated by electron microscopy and confirmed by electron diffraction. The presence of these hydrates is undoubtedly responsible for the stabilizing effects (strength improvements) of lime reported in Part 1.

Introduction

EXAMINATION OF reaction products in clay-lime-water, soil-lime-water, and analogous systems is severely handicapped by the act that, generally, the products are poorly rystalline or amorphous, and occur in very mited quantities. These problems were recogzed by Eades and Grim (*1*)[2], and by Diamond t al., (*2*). In attempts to develop relatively rge quantities of reaction product of at ast moderate crystallinity, these researchers esorted to very high lime concentrations nd, in some instances, elevated curing temeratures. Under these conditions, certain nteresting reaction products were detectable y X-ray diffraction, and speculation about eactions at room temperatures and low lime oncentrations could be made. However, for ntensive study of systems that more nearly pproximate those encountered in practice, t is necessary to use a method of analysis ther than X-ray diffraction. Electron microsopy and electron diffraction have been used uccessfully by El Jack and Mitchell[3] in tudying soil-cement-water systems, and by loane (*3*) in studying clay-lime-water systems. ystems studied by Sloane contained a large xcess of water and did not closely approximate conditions that might be encountered n the practical application of lime as a soil tabilizing agent.

The study reported in Part 1 entailed investigation of the strength and rheological properties of kaolin-lime-water systems. The purpose of the investigation reported here was to examine, by electron microscopy and electron diffraction, the microtexture and composition of reaction products in the systems, using mixtures that were recovered from experiments on physical properties.

Materials

Specimens recovered from strength experiments with two kaolins, H and E; were used in the studies; these kaolins are fully described in Part 1. The specimens, originally in the form of cylindrical compacts, 0.35 inches in diameter by 0.70 inches high, had been broken in unconfined compression, immediately dried at 110° C., and stored in airtight containers. For replica studies, a suitable unbroken portion of each specimen was newly fractured, and replicas were made of the fracture surfaces. For transmission electron microscopy and electron diffraction, the specimens were powdered to pass a No. 80 sieve and used as described herein.

Electron Microscopy

Replicas were made using a procedure similar to that outlined by Comer and Turley (*4*), which included the following steps:

(1) Strength specimens were fractured perpendicular to the altitude of the cylinder.

(2) Palladium was vacuum-evaporated onto the fractured surface at an angle of about 30° to the sample surface.

(3) A second palladium evaporation was made at an angle of approximately 30° to the sample surface from the opposite direction.

(4) Carbon was similarly deposited normal to the sample surface.

(5) Specimen was placed in distilled water with replica side up to allow the bulk of the clay sample to slake away.

(6) Replica was then placed in concentrated hydrofluoric acid to remove the last traces of clay; two treatments in hydrofluoric acid were usually necessary.

(7) Replica was washed with distilled water.

(8) Replica was picked up on an electron microscope grid and stored in a desiccator.

Replicas of true fracture surfaces were prepared from mixtures of kaolin E containing 0, 0.8, and 6 percent lime. Replicas were also prepared of pseudo-fracture surfaces and the lateral surfaces of some of the specimens. Pseudo-fracture surfaces are those formed when strength specimens are parted at a layer boundary. These layer boundaries resulted from the manner of specimen fabrication—that is, the specimens were molded using three layers of clay.

Specimens for transmission electron microscopy and electron diffraction were prepared from material passing a No. 80 sieve that had been picked up on the surface of a droplet of mercury. The material was then transferred to a collodion-coated microscope grid by first softening the collodion coating in amyl acetate vapor and then pressing the grid against the clay-coated mercury droplet.

Transmission electron micrographs and electron diffraction patterns were made of specimens of kaolins H and E containing 6 percent lime. An electron microscope, operated at voltages of 80 and 100 kv., was used for the examinations.

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[1] Part of the results reported here were published in the ournal of the American Ceramic Society, 49(7), 1966, pp. 64–366.

[2] The italic numbers in parentheses identify the references sted on page 49.

[3] Sid Ahmed El Jack and James K. Mitchell, *Electron Microscope Studies of Interactions Between Hydrating Port-and Cement and Soil Minerals.* Presented at the 44th Annual Highway Research Board Meeting, Washington, D.C., anuary 1965.

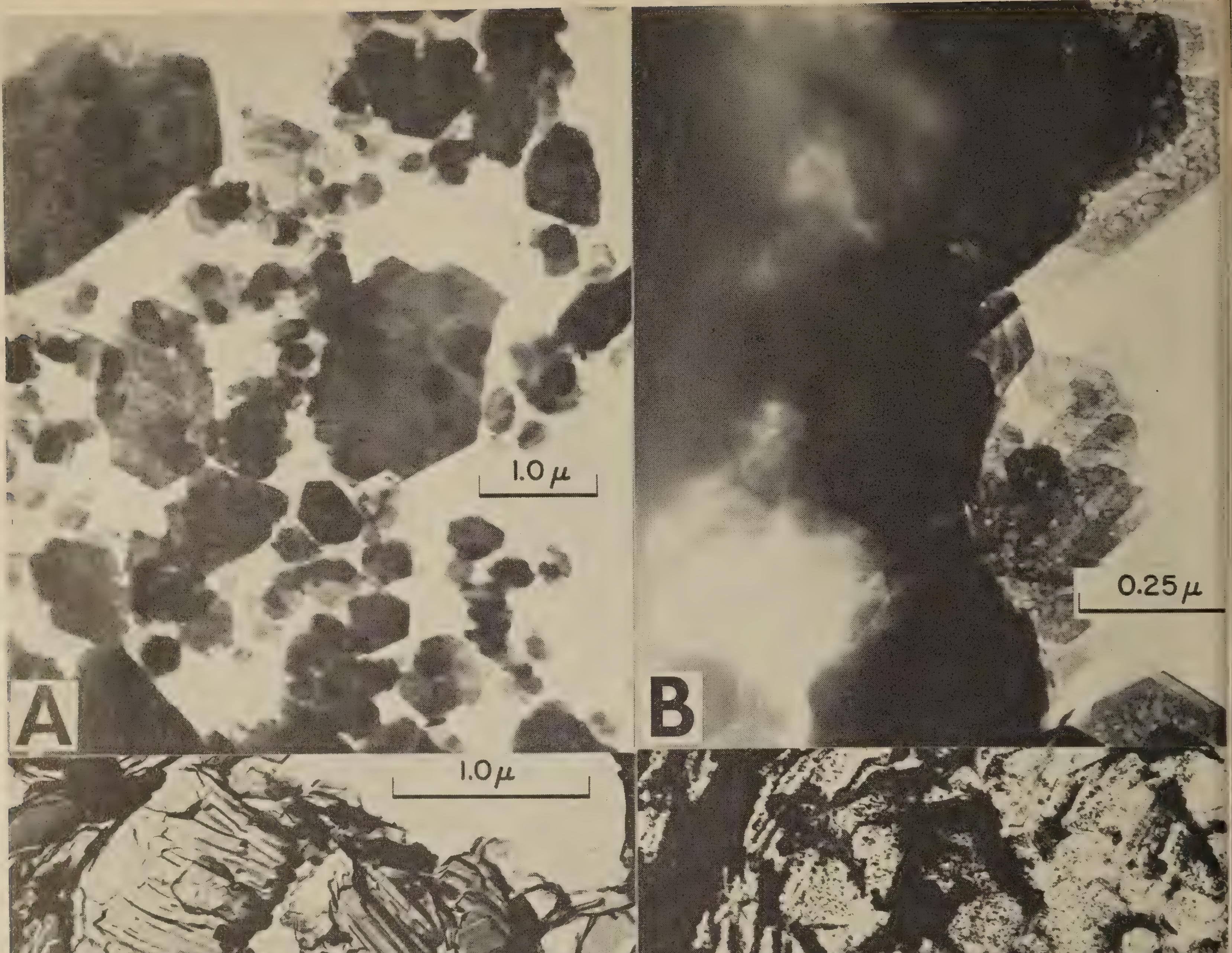

Figure 1.—Electron micrographs of (A) untreated kaolin E, (B) kaolin E plus 6 percent lime, cured 15 days, (C) replica of fracture surface untreated kaolin E, and (D) replica of fracture surface of kaolin E plus 6 percent lime, cured 15 days.

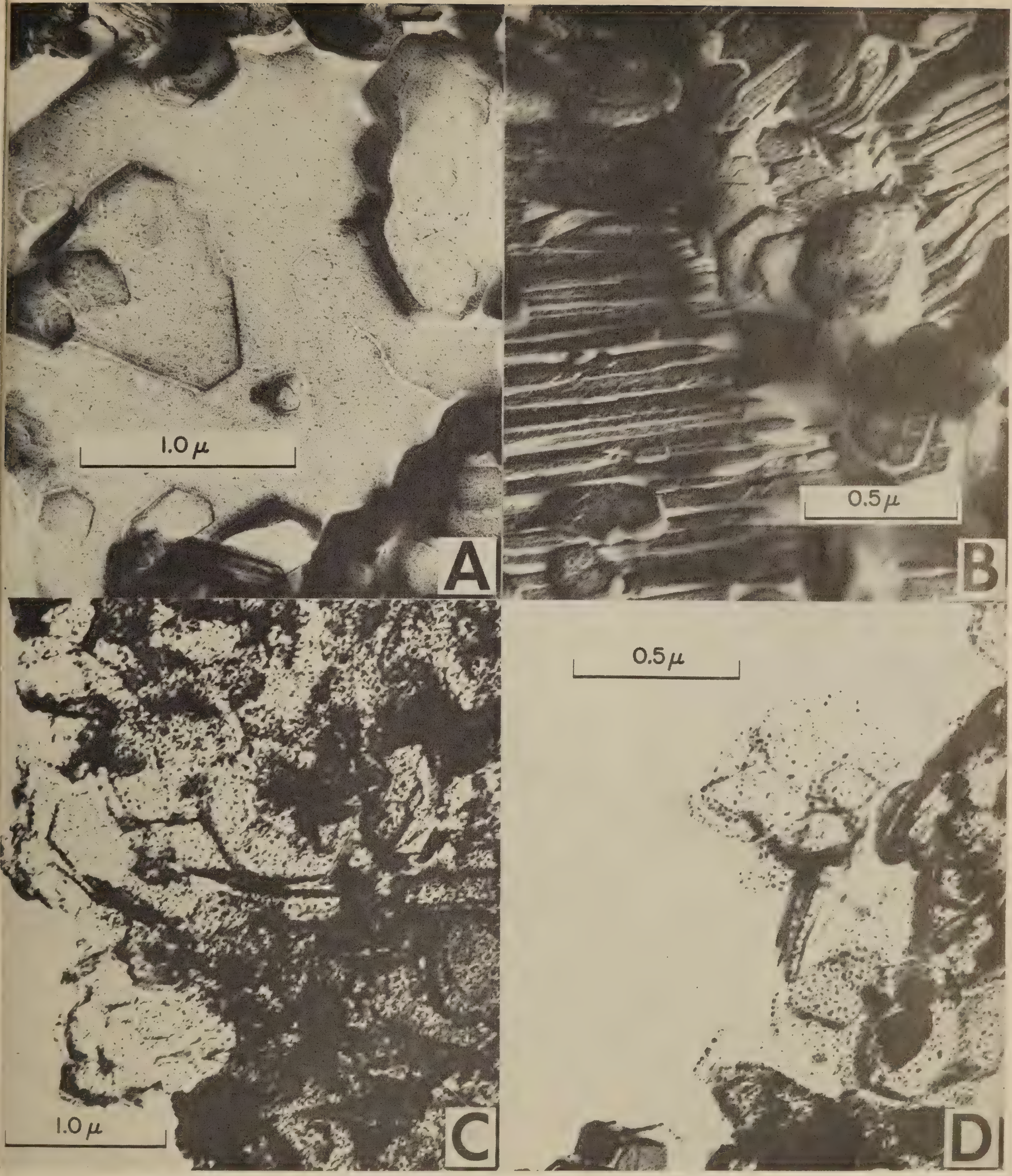

Figure 2.—Electron micrographs of (A) and (B) replicas of fracture surfaces of kaolin E (0.8 percent lime, cured 3 days), and (C) and (D) replicas of fracture surfaces of kaolin E (6 percent lime, cured 15 days).

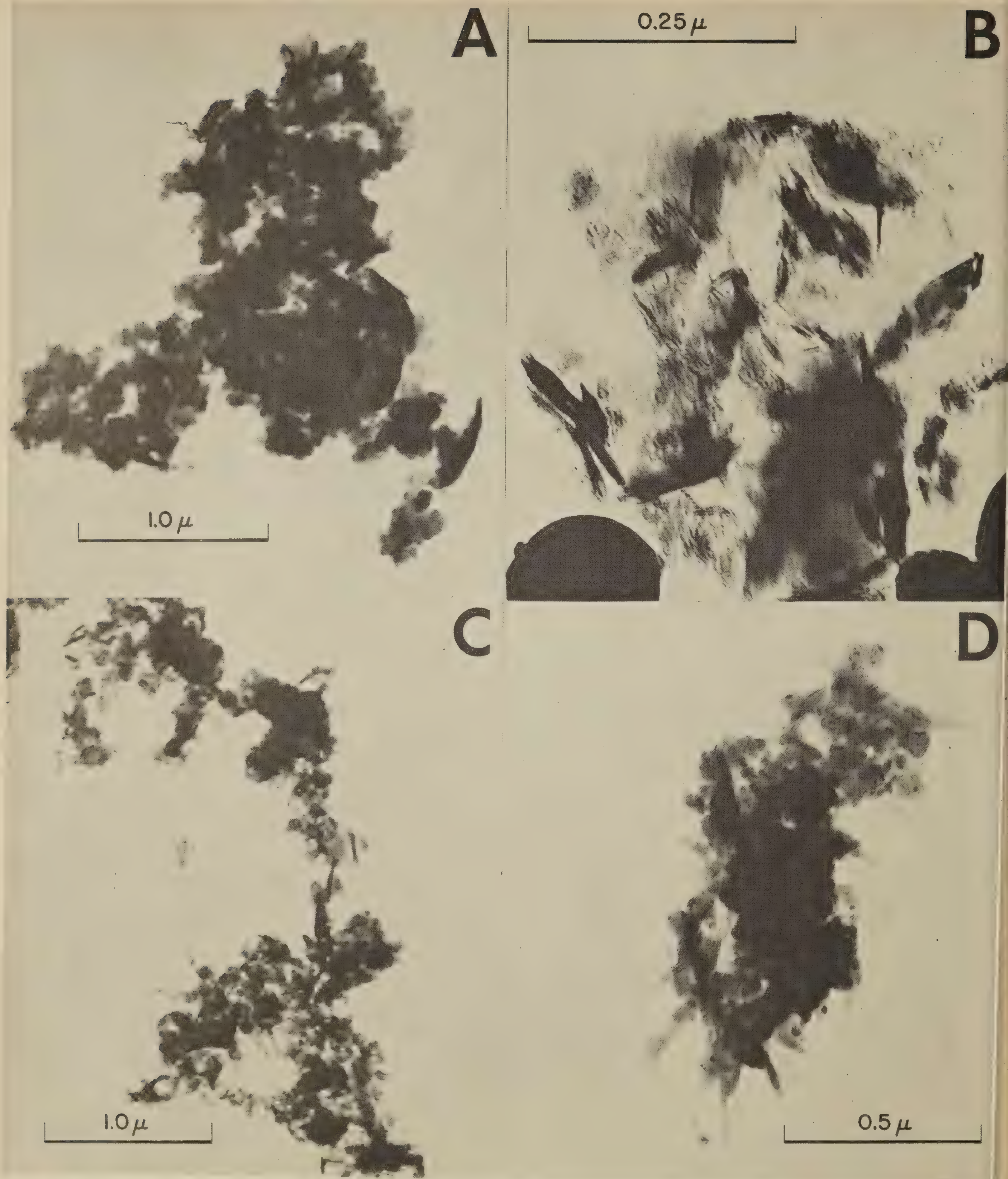

Figure 3.—Electron micrographs of (A) and (B) reaction product, kaolin E plus 6 percent lime, cured 15 days, and (C) and (D) reacti product, kaolin H plus 6 percent lime, cured 15 days.

Results and Discussion

Electron micrographs of morphological and xtural features of unreacted clay, of clay acted with lime, and of reaction products e shown in figures 1–3.

Hexagonal or pseudo-hexagonal shaped articles, typical for untreated kaolin E, are own in figure 1(A). Figure 1(B), a photo-aph of kaolin E treated with 6 percent lime ows kaolinite particles severely eroded and itted by the attack of the lime.

Photographs of replicas made from fracture rfaces of untreated and lime-treated kaolin are shown in figures 1(C) and 1(D). Figure (C), in which several kaolinite plates and ooks are shown, is typical of the untreated aolin. The plate and edge surfaces have a fine ranular texture, but no surface deterioration indicated. On the other hand, when the clay as been treated with lime, figure 1(D), basal rfaces and particle edges are severely eroded nd many particles have lost their sharp, exagonal outline. The opaque objects in gures 1(C) and 1(D) are from material that id not dissolve in the hydrofluoric acid used o remove the clay from the replica.

Figure 2(A) shows the fine structure of basal urfaces of kaolin E particles treated with 0.8 ercent lime and cured for 3 days. Small exagonal plates seem to be forming from rger plates as a result of surface attack. Progressive deterioration may result in the evelopment of cleavages and fissures perendicular to the basal surface and in the ragmentation of larger particles. Similar deerioration was observed by Oberlin and Tchoubar (*5*) in their study of the breakdown f kaolinite particles during $MgSO_4$ treatment. The process noted in the present study may, n the initial stages, be physically analogous o the effect produced by $MgSO_4$. In the experiment reported here, however, attack of he particle basal and edge surfaces may also esult in the loss of structural components (Si, Al) and in the formation of new compounds (calcium silicate and calcium aluminate hydrates), possibly by a through-solution mechanism.

Figure 2(B) is a replicated surface of a kaoin E specimen treated with 0.8 percent lime and cured for 3 days. This photograph shows he characteristic reticular structure noted for basal surfaces (fig. 2(A)), as well as similar features for edge surfaces, suggesting that the lime has had a considerable effect on the clay, attacking both basal and edge surfaces of particles.

Figures 2(C) and 2(D) are pictures of replicas of fracture surfaces prepared from kaolin E treated with 6 percent lime and cured for 15 days; they show further examples of the type of attack that occurs at relatively high lime concentrations. Pitting and eroding of particles is severe. The overall appearance of the surfaces suggests that nucleation of new phases is occurring. The nuclei are of the order of 200A in diameter and are similar in appearance to nuclei observed by Sloane (*3*), who studied compositionally analogous systems.

Transmission electron micrographs of reaction products in kaolin-lime-water systems are given in Figure 3. Figures 3(A) and 3(B) are photographs of reaction products of kaolin E treated with 6 percent lime and cured 15 days. Figures 3(C) and 3(D) are of reaction products of kaolin H treated with 6 percent lime and cured 15 days. The reaction products were commonly seen together with degraded kaolinite particles (fig. 1(B)). The reaction products assumed various shapes, including films, fibers, and laths. Phases of nondescript particle shapes were also common; such phases could represent material of very poor crystallinity, that is, amorphous or gel material.

The products of poor to intermediate crystallinity, when examined by electron diffraction, gave *d* spacings of 3.03, 1.84, and 1.52A, which correspond to the indices 220, 040, and 440, respectively, for calcium silicate hydrate phases.

Pseudo-fracture surfaces gave replicas with features typical of kaolinite, pictures of which were similar to those published by Stetson (*6*). Replicas of the lateral surfaces of cylindrical specimens gave pictures that had the appearance of replicas of kaolin-coated paper; photographs of this type have been published by Bates (*7*). In the replicas of both pseudo-fracture surfaces and lateral surfaces of cylindrical specimens, the kaolinite particles were very well oriented with basal plans parallel to the plane of the deposited film. The replicas of the pseudo-fracture surfaces showed slightly more contrast and a very fine granular texture.

Summary

Electron optical investigations were performed on fracture surfaces of strength-determination specimens of kaolin-lime-water and on the same specimens that had been powdered. Results of these studies showed the following:

- Reactions between clay and lime occur at early stages of curing and at relatively low levels of lime addition.
- Attack occurs on both particle prism and basal surfaces.
- Reaction products in the systems studied are poorly crystallized calcium silicate hydrates, which are assumed to be responsible for strength improvements in kaolin-lime-water mixtures.

ACKNOWLEDGMENTS

The authors gratefully acknowledge discussions with Sidney Diamond and E. B. Kinter, and the assistance of A. C. Bonanno in preparing photographs.

REFERENCES

(*1*) *Reaction of Hydrated Lime with Pure Clay Minerals in Soil Stabilization*, by J. L. Eades and R. E. Grim, Highway Research Board Bulletin 262, Preconditioning and Stabilizing Soils By Lime Admixtures, 1960, pp. 51–63.

(*2*) *Transformation of Clay Minerals by Calcium Hydroxide Attack*, by S. Diamond, J. L. White, and W. L. Dolch, Proceedings of the 12th National Conference, 1963, Clays and Clay Minerals, Pergamon Press, New York, N.Y., 1964, pp. 359–379.

(*3*) *Early Reaction Determination in Two Hydroxide-Kaolinite Systems by Electron Microscopy and Diffraction*, by Richard L. Sloane, Proceedings of the 13th Conference, of 1964, Clays and Clay Minerals, Pergamon Press, or New York, N.Y., 1966, pp. 331–339.

(*4*) *Replica Studies of Bulk Clays*, by J. J. Comer and J. W. Turley, Journal of Applied Physics, vol. 26, No. 3, 1955, pp. 346–350.

(*5*) *Etude en Microcopie et Diffraction Électroniques de l'Alteration de la Kaolinite Par l'Eau—Influence des Sels Dissous* (*Electron Microscope and Diffraction Study of the Alteration of Kaolinite by Water—Influence of Dissolved Salts*), by A. Oberlin and C. Tchoubar, Silicates Industriels, vol. 24, No. 4, 1959, pp. 197–202.

(*6*) *Note on Surface Smoothness of Kaolinite Flakes*, by Harold W. Stetson, Journal of the American Ceramic Society, vol. 38, No. 12, 1955, p. 462.

(*7*) *Electron Microscopy of Minerals*, by T. F. Bates, Encyclopedia of Microscopy, Edited by G. L. Clark, Reinhold Publishing Corp., 1961.

Direct Rapid Ultraviolet Determination of Phthalic Anhydride and Isophthalic Acid in Oil-modified Alkyd Resins and Paints

*BY THE OFFICE OF
RESEARCH AND DEVELOPMENT
BUREAU OF PUBLIC ROADS*

**Reported by LEONARD BEAN, Research
Chemist, and BERNARD CHAIKEN, Principal
Research Chemist, Materials Division**

Present standard procedures for determining the phthalic anhydride or isophthalic acid content of alkyd resins and paints, modified by drying oil, require prior chemical separation involving lengthy procedures. In this article a more rapid method is described by which these constituents can be determined directly in alkyd-resin paint vehicles within 2 hours, if other absorbing materials are known to be absent. The method is based on quantitative ultraviolet absorbance measurements of chloroform solution of the pigment-free vehicles after the original volatile solvents are removed, under vacuum, in a rotating flask evaporator. No prior chemical separations are required. Qualitative means for distinguishing alkyds, based on orthophthalic, isophthalic or terephthalic acids are demonstrated with infrared and ultraviolet spectra. This method is recommended for manufacturing process control, and especially purchase acceptance testing of alkyd and oil-alkyd paints. The method is generally applicable when the alkyd component is limited to any one of the three phthalate isomers and is not modified by other aromatics, unsaturated dibasic acids, or tung oil. Many of the coatings used in highways meet these requirements.

Figure 1.—Grating infrared spectrophotometer.

Introduction

ALKYD RESIN vehicles are commonly
used in highway traffic paints and in other
protective coatings for highway metal structures. For these uses alkyds are usually of th
glyceryl orthophthalate type modified wit
ordinary drying oils such as linseed or soya

Present methods published by the America
Society for Testing and Materials (ASTM)
for the determination of the phthalic an
hydride content of alkyd resin paint vehicle
require preliminary chemical separations tha
are relatively lengthy. All of the standar
methods require an initial saponification durin
a refluxing period that is followed by precipita
tion and washing of the phthalate component
Depending on the method used, these proce
dures are followed by re-solution and eithe
further precipitation or spectrophotometri
analysis (*1*, *2*, *3*).[1] A similar method for d
termining the isophthalic acid content
alkyd resins, now under consideration b
ASTM (*4*), also requires prior saponificatio
and other chemical manipulations an
separations.

In some of the larger State highway d
partments, the number of alkyd-type pain
analyzed each year may exceed 300. Cons
quently, the present methods of analys
require considerable time and effort.

A direct and simple instrumental procedu
to determine the phthalic anhydride or is
phthalic acid content of drying oil alk
resin paints, without resorting to prior che
ical separations, would be desirable and sa
considerable time. Shreve and Heether (
noted that phthalic acid and its esters sho
strong absorptions in their ultraviolet spectr
and that in some types of simple mixtures
should be possible to determine the phthala
ester content by direct ultraviolet absorpti
measurements of the mixture in a suita

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[1] The italic numbers in parentheses identify the referen
listed on page 58.

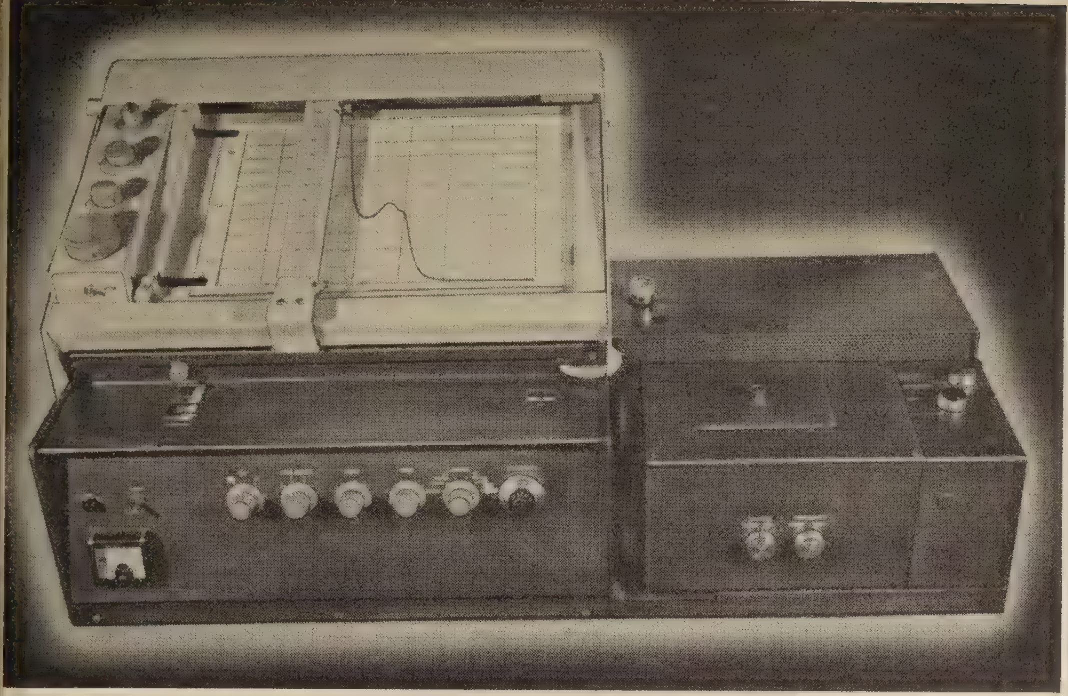

Figure 2.—Recording double-beam ultraviolet spectrophotometer.

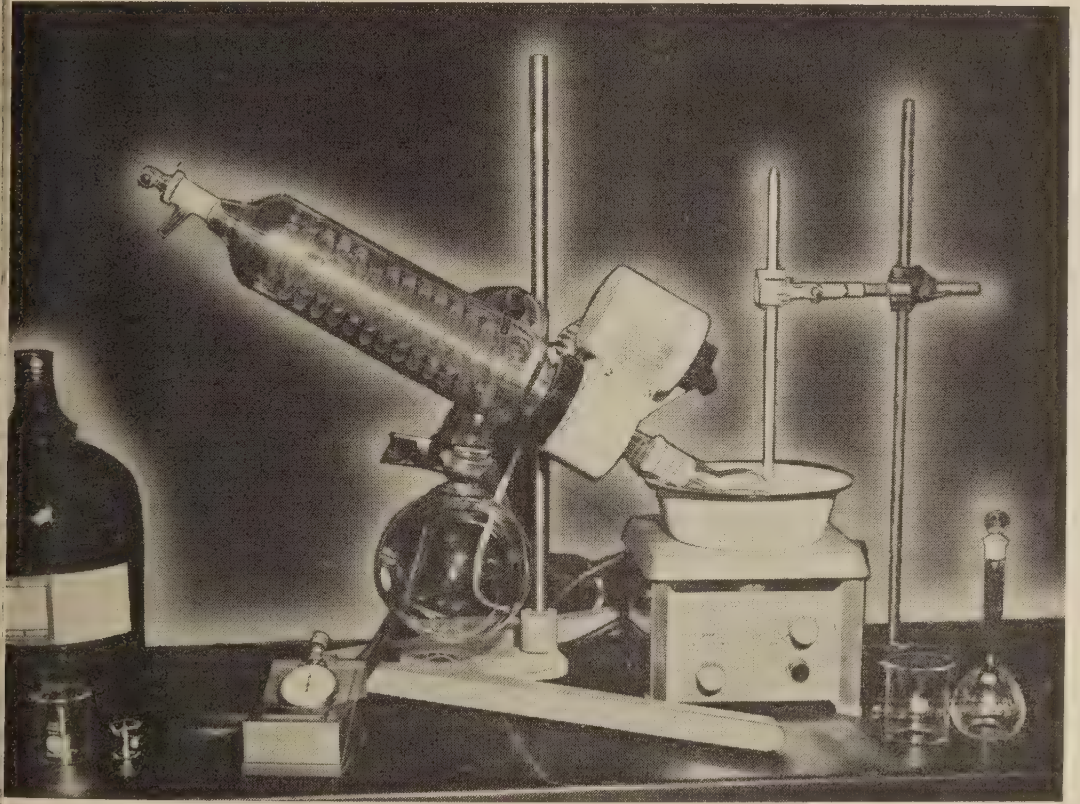

Figure 3.—Rotary-flask vacuum evaporator.

lvent. However, they reasoned that with aint vehicles and other types of coating aterials, "such a procedure would be imractical because the organic solvents, oils, nd other materials usually present would lmost invariably interfere" Their reported ork served as the basis of the present ASTM ethod for the spectrophotometric determinaon of phthalic anhydride in alkyd resins llowing preliminary chemical separations (*3*).

In a previous report (*6*, *7*), a procedure for determining possible adulteration of traffic paint vehicles was described. During that investigation we observed that possibilities existed for applying similar rapid and direct ultraviolet techniques to facilitate the quantitative determination of the phthalic content of drying-oil modified alkyd resin coatings. It is believed that some of the limitations of a direct ultraviolet procedure for actual coatings, noted by Shreve and Heether, could perhaps be obviated. Accordingly, an investigation was conducted to determine what general identifying and quantitative information might be obtained by use of ultraviolet and infrared spectroscopy, without resorting to lengthy chemical separations. As a result the method described in this article was developed.

Apparatus

A grating infrared spectrophotometer (fig. 1) was used to scan the region from 4000 to 200 cm.$^{-1}$ while being purged with compressed air from which most of the CO_2 and H_2O was removed by passing the air through an *H_2O–CO_2 Absorber Unit.* The samples were cast films supported on cesium iodide windows. The instructions for operating the spectrophotometer are contained in the instruction manual (*8*) supplied by the manufacturer of the instrument.

A recording double-beam ultraviolet spectrophotometer (fig. 2), together with 1-cm. matched silica cells, was used to obtain spectral curves and measure the ultraviolet absorbance. A hydrogen discharge lamp was used as a light source for most of the measurements, but when it became necessary to make a replacement, a deuterium lamp was installed. A photomultiplier tube was used as the detector and the instrument was operated at a scanning rate of about 20 millimicrons (nanometers) per minute. The instructions for operating the spectrophotometer are contained in the instruction manual (*9*) provided by the manufacturer of the instrument.

A rotary flask vacuum evaporator (fig. 3) was used to remove the original volatile solvents from the paint vehicle.

Materials Studied

A number of manufacturers cooperated by supplying samples of drying-oil-modified alkyd resins prepared with different percentages of either phthalic anhydride or isophthalic acid. One alkyd made from terephthalic acid was also supplied. Additionally, the pigments were removed, by centrifugation, from four samples of drying-oil-modified alkyd type paints so that these vehicles could also be studied. A general description of these vehicles, as well as quantitative information on their composition, is given in table 1.

Many of the raw materials used in the manufacture of alkyd vehicles were examined. These included various polyols, such as glycerol, ethylene glycol, and pentaerythritol. Drying oils, such as various types of linseed and soybean oil, and one tung oil were also examined.

Qualitative Infrared Examination of Oil-Alkyd Resins

Tests were made to determine whether infrared analysis could be used to establish the nature of the phthalic acid present. Differences were easily noted among the infrared

Table 1.—Description of oil-modified alkyd resins used in study

Alkyd resin	Laboratory number	Polyol	Percent phthalic anhydride or phthalic acid
			Percent phthalic anhydride: [1]
Orthophthalic type:			
Vehicle from oil-alkyd bridge paint primer	C 1929		7.8
Vehicle from oil-alkyd bridge paint primer	C 1836		7.8
Vehicle from oil-alkyd bridge paint primer	C 1908		14.5
Vehicle from oil-alkyd bridge paint primer	C 1837		15.0
Long linseed oil resin	C 1895	glycerol	23.0
Resin containing soybean oil	C 1858	glycerol and pentaerythritol.	28.2
Medium linseed oil resin	C 1892	glycerol	30.2
Medium linseed oil resin, 52% oil	C 1901	glycerol	32.6
Resin containing soybean oil	C 1860	pentaerythritol and ethylene glycol.	33.0
Resin containing 52% soybean oil	C 1817	glycerol	33.8
Short linseed oil resin, 48% oil	C 1902	glycerol	39.0
Soybean oil resin	C 1861	glycerol	41.7
Short linseed oil resin	C 1894	glycerol	41.6
			Percent isophthalic acid:
Isophthalic acid type: [2]			
A long soya oil resin, 74% oil	C 1932		19
A long soya oil resin	C 1916		24
A long safflower oil resin, 64% oil	C 1913		27
A long safflower oil resin, 61% oil	C 1933		27
A medium soya resin, 59% oil acids	C 1930		28
A medium soya oil resin	C 1917		33
A linseed oil modified resin, 50% oil, 8.8% para tertiary butylbenzoic acid.	C 1912		33.9
A short soya oil resin, 40% oil acids	C 1931		38
			Percent terephthalic acid:
Terephthalic acid type:			
A short soya oil resin, 40% oil, 14.7% benzoic acid (values furnished by manufacturer).	C 1945	glycerol	34.4

[1] The phthalic anhydride content was determined as described in ASTM Designation D 563–62, 1967 Book of ASTM Standards, Part 20.

[2] No information available concerning the polyol. Information on the isophthalic acid and oil contents was supplied by the manufacturer.

patterns of oil-modified alkyd resins made from either phthalic anhydride, isophthalic acid, or terephthalic acid, when approximately 15 percent or more of the phthalic constituent was present. White has observed *(10)* that *o*-phthalic esters have a characteristically sharp doublet (sometimes referred to as *rabbit ears*) in the vicinity of 1600 cm.$^{-1}$, which is probably due to aromatic skeletal in-plane $C=C$ vibrations. This absorption enables polymer chemists to spot *o*-phthalic alkyd resins at a glance.

In the infrared patterns of eleven *o*-phthalic resins examined in this study, the right *ear*, or band, at 1570 to 1580 cm.$^{-1}$, was always somewhat longer than the *ear* at 1595 cm.$^{-1}$, as shown in figure 4. In the infrared patterns of the two remaining vehicles, which contained less than 8 percent phthalic anhydride, the *rabbit ears* were not evident. In fact, the patterns of these two vehicles resembled that of linseed oil, the predominant constituent. On the other hand, in the patterns of all eight isophthalic resins examined, the doublet peaks shifted to approximately 1608 and 1585 cm.$^{-1}$, with the right *ear*, at 1585 cm.$^{-1}$, being much shorter than the left one at 1608 cm.$^{-1}$. This is illustrated in figure 5. In fact, in one isophthalic resin (fig. 6) the right *ear* had practically disappeared. In the pattern of the only terephthalic alkyd resin examined, the doublet peaks were at approximately 1600 and 1575 cm.$^{-1}$, with the right *ear* being somewhat shorter, as shown in figure 7. Thus, the exact wavelength positions and relative depths of the doublet peaks near 1600 cm.$^{-1}$, should easily indicate whether an orthophthalic, isophthalic, or terephthalic alkyd was the dominant material present in the oil modified resin. These criteria are quite useful in a qualitative evaluation of resins of unknown composition.

The region of 650 cm.$^{-1}$ was also investigated as a possibility for distinguishing between the types of phthalic acid present in an oil-alkyd resin. This band is attributed to the degenerate bending vibration of the ester group. It has been reported *(11)* that oil-modified alkyd resins, based on isophthalic acid, normally show a pair of bands near 650 cm.$^{-1}$, whereas *o*-phthalates have a single and sharp band. The spectra of most of the alkyds used in this study, as exemplified by figures 4, 5, and 6, failed to show these distinguishing characteristics. In fact, the bulk of both the orthophthalic and isophthalic alkyds showed similar and only single sharp bands at 650 cm.$^{-1}$. As shown in figure 7 the pattern of terephthalic resin examined showed no band at 650 cm.$^{-1}$.

Applicability of Ultraviolet Spectroscopy

Measurements were made, without prior chemical separations, to determine whether a correlation could be found between ultraviolet absorbance at definite wavelengths and the phthalic anhydride, or isophthalic acid, content of oil modified alkyd resins.

In general, the procedure used was that described in previous reports by the authors *(6, 7)*. The volatile solvents were removed at 56–60° C. from a weighed sample of the vehicle, using a rotating flask vacuum evaporator for 20 minutes. Then the remaining solid material was dissolved promptly in a solvent, diluted to volume, and aliquots were taken to provide suitable concentrations for ultra-

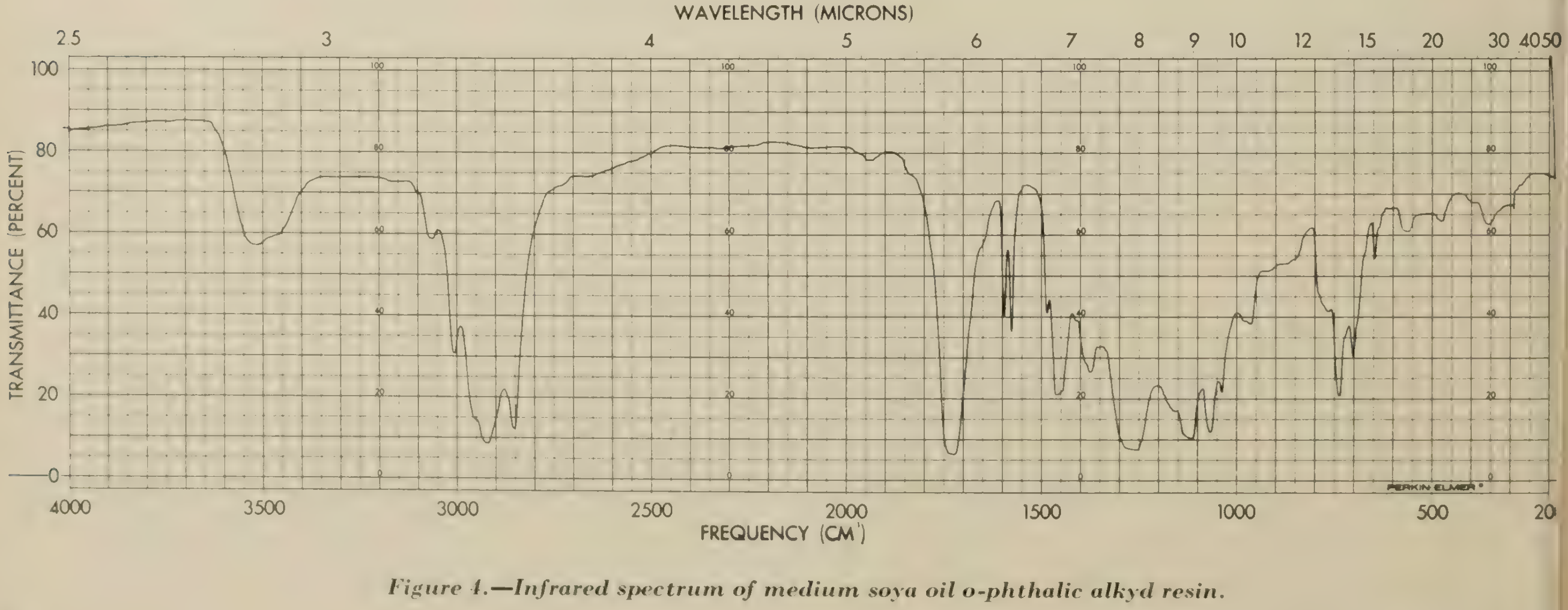

Figure 4.—Infrared spectrum of medium soya oil o-phthalic alkyd resin.

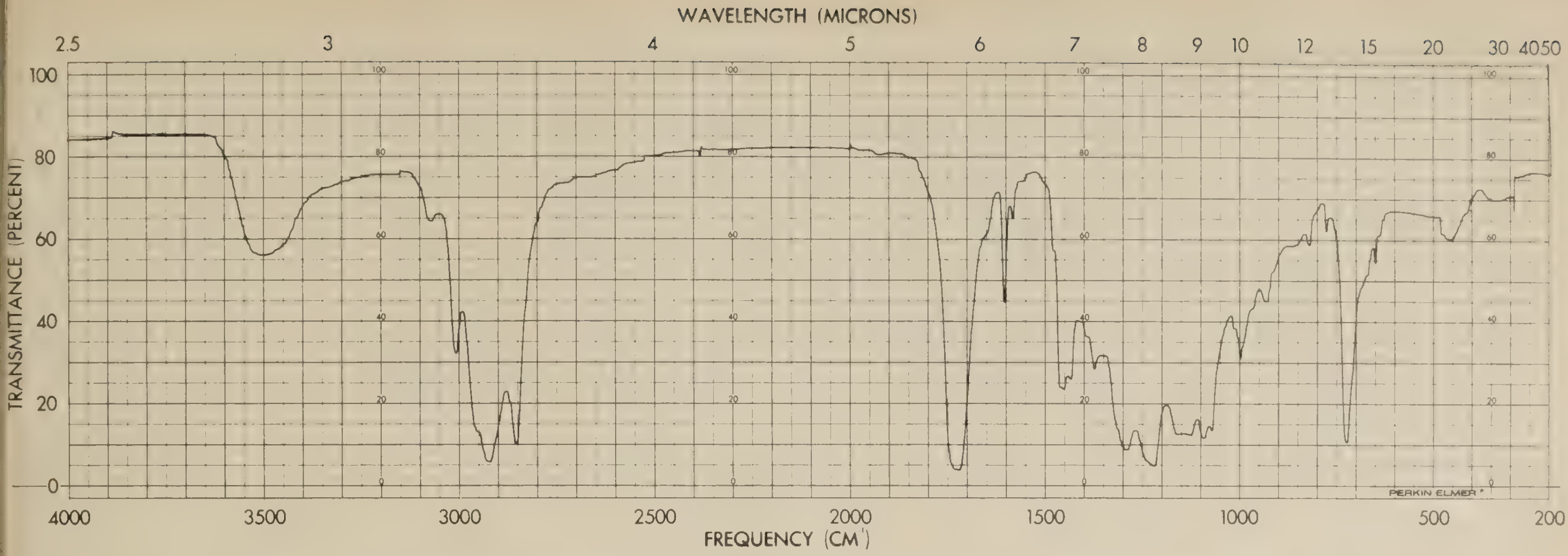

Figure 5.—Infrared spectrum of medium soya oil isophthalic alkyd resin.

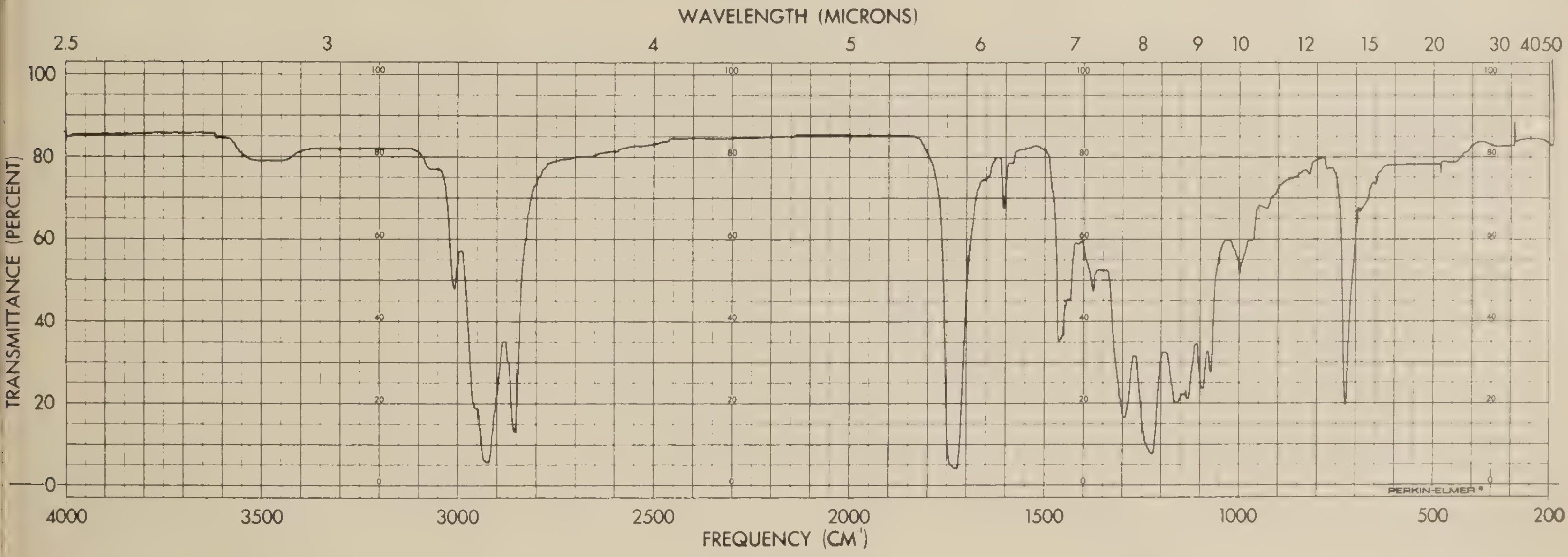

Figure 6.—Infrared spectrum of long soya oil isophthalic alkyd resin.

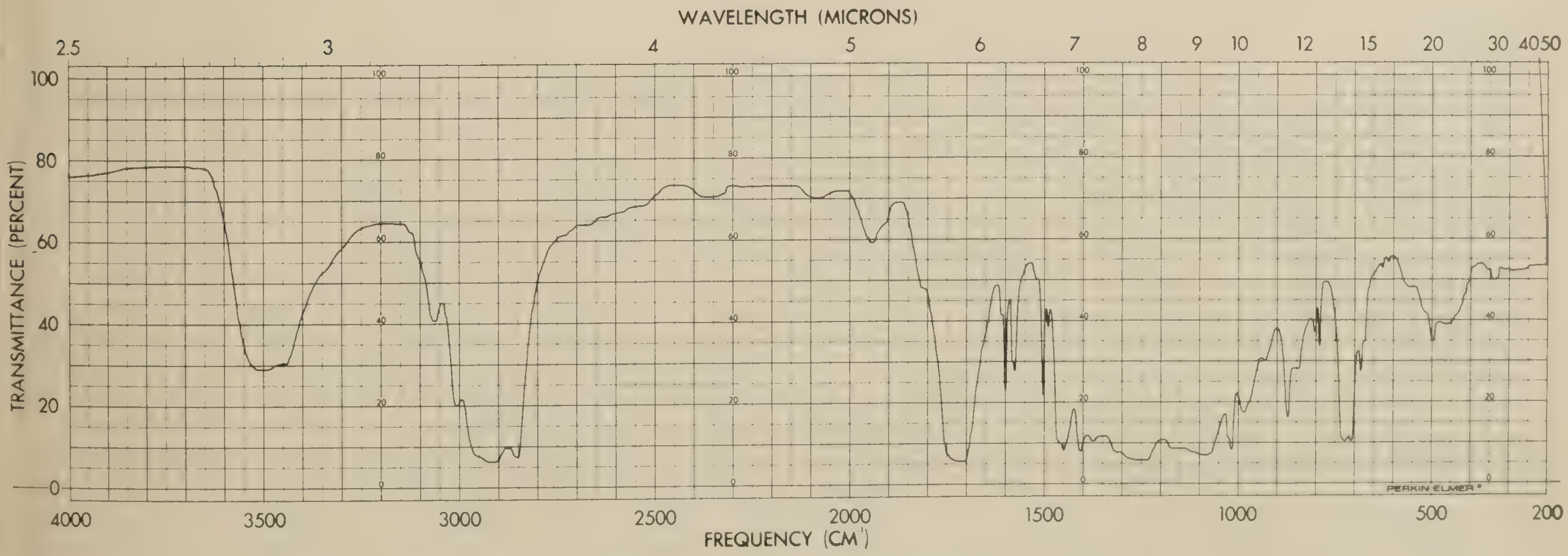

Figure 7.—Infrared spectrum of short soya oil terephthalic alkyd resin.

Table 1.—Description of oil-modified alkyd resins used in study

Alkyd resin	Laboratory number	Polyol	Percent phthalic anhydride or phthalic acid
			Percent phthalic anhydride: [1]
Orthophthalic type:			
Vehicle from oil-alkyd bridge paint primer	C 1929		7.8
Vehicle from oil-alkyd bridge paint primer	C 1836		7.8
Vehicle from oil-alkyd bridge paint primer	C 1908		14.5
Vehicle from oil-alkyd bridge paint primer	C 1837		15.0
Long linseed oil resin	C 1895	glycerol	23.0
Resin containing soybean oil	C 1858	glycerol and pentaerythritol.	28.2
Medium linseed oil resin	C 1892	glycerol	30.2
Medium linseed oil resin, 52% oil	C 1901	glycerol	32.6
Resin containing soybean oil	C 1860	pentaerythritol and ethylene glycol.	33.0
Resin containing 52% soybean oil	C 1817	glycerol	33.8
Short linseed oil resin, 48% oil	C 1902	glycerol	39.0
Soybean oil resin	C 1861	glycerol	41.7
Short linseed oil resin	C 1894	glycerol	41.6
			Percent isophthalic acid:
Isophthalic acid type: [2]			
A long soya oil resin, 74% oil	C 1932		19
A long soya oil resin	C 1916		24
A long safflower oil resin, 64% oil	C 1913		27
A long safflower oil resin, 61% oil	C 1933		27
A medium soya resin, 59% oil acids	C 1930		28
A medium soya oil resin	C 1917		33
A linseed oil modified resin, 50% oil, 8.8% para tertiary butylbenzoic acid.	C 1912		33.9
A short soya oil resin, 40% oil acids	C 1931		38
			Percent terephthalic acid:
Terephthalic acid type:			
A short soya oil resin, 40% oil, 14.7% benzoic acid (values furnished by manufacturer).	C 1945	glycerol	34.4

[1] The phthalic anhydride content was determined as described in ASTM Designation D 563–62, 1967 Book of ASTM Standards, Part 20.

[2] No information available concerning the polyol. Information on the isophthalic acid and oil contents was supplied by the manufacturer.

patterns of oil-modified alkyd resins made from either phthalic anhydride, isophthalic acid, or terephthalic acid, when approximately 15 percent or more of the phthalic constituent was present. White has observed (*10*) that *o*-phthalic esters have a characteristically sharp doublet (sometimes referred to as *rabbit ears*) in the vicinity of 1600 cm.$^{-1}$, which is probably due to aromatic skeletal in-plane C=C vibrations. This absorption enables polymer chemists to spot *o*-phthalic alkyd resins at a glance.

In the infrared patterns of eleven *o*-phthalic resins examined in this study, the right *ear*, or band, at 1570 to 1580 cm.$^{-1}$, was always somewhat longer than the *ear* at 1595 cm.$^{-1}$, as shown in figure 4. In the infrared patterns of the two remaining vehicles, which contained less than 8 percent phthalic anhydride, the *rabbit ears* were not evident. In fact, the patterns of these two vehicles resembled that of linseed oil, the predominant constituent. On the other hand, in the patterns of all eight isophthalic resins examined, the doublet peaks shifted to approximately 1608 and 1585 cm.$^{-1}$, with the right *ear*, at 1585 cm.$^{-1}$, being much shorter than the left one at 1608 cm.$^{-1}$. This is illustrated in figure 5. In fact, in one isophthalic resin (fig. 6) the right *ear* had practically disappeared. In the pattern of the only terephthalic alkyd resin examined, the doublet peaks were at approximately 1600 and 1575 cm.$^{-1}$, with the right *ear* being somewhat shorter, as shown in figure 7. Thus, the exact wavelength positions and relative depths of the doublet peaks near 1600 cm.$^{-1}$, should easily indicate whether an orthophthalic, isophthalic, or terephthalic alkyd was the dominant material present in the oil modified resin. These criteria are quite useful in a qualitative evaluation of resins of unknown composition.

The region of 650 cm.$^{-1}$ was also investigated as a possibility for distinguishing between the types of phthalic acid present in an oil-alkyd resin. This band is attributed to the degenerate bending vibration of the ester group. It has been reported (*11*) that oil-modified alkyd resins, based on isophthalic acid, normally show a pair of bands near 650 cm.$^{-1}$, whereas *o*-phthalates have a single and sharp band. The spectra of most of the alkyds used in this study, as exemplified by figures 4, 5, and 6, failed to show these distinguishing characteristics. In fact, the bulk of both the orthophthalic and isophthalic alkyds showed similar and only single sharp bands at 650 cm.$^{-1}$. As shown in figure 7 the pattern of terephthalic resin examined showed no band at 650 cm.$^{-1}$.

Applicability of Ultraviolet Spectroscopy

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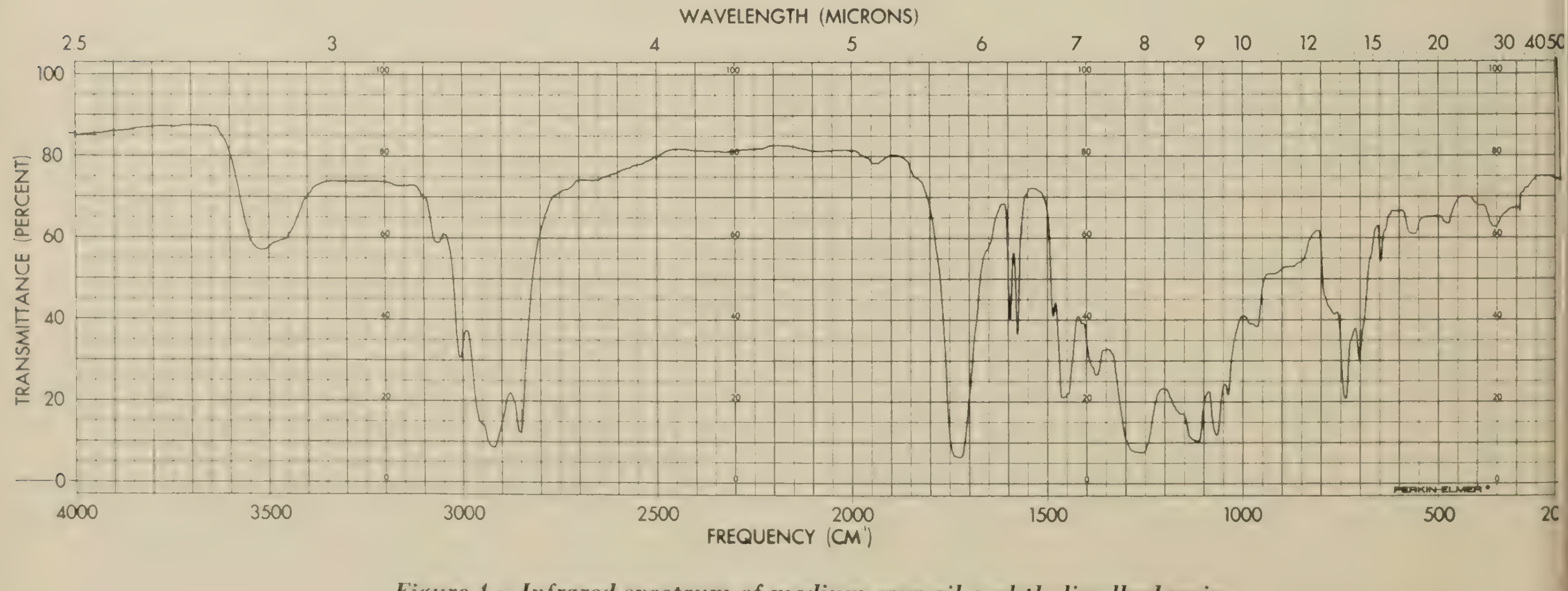

Figure 4.—Infrared spectrum of medium soya oil o-phthalic alkyd resin.

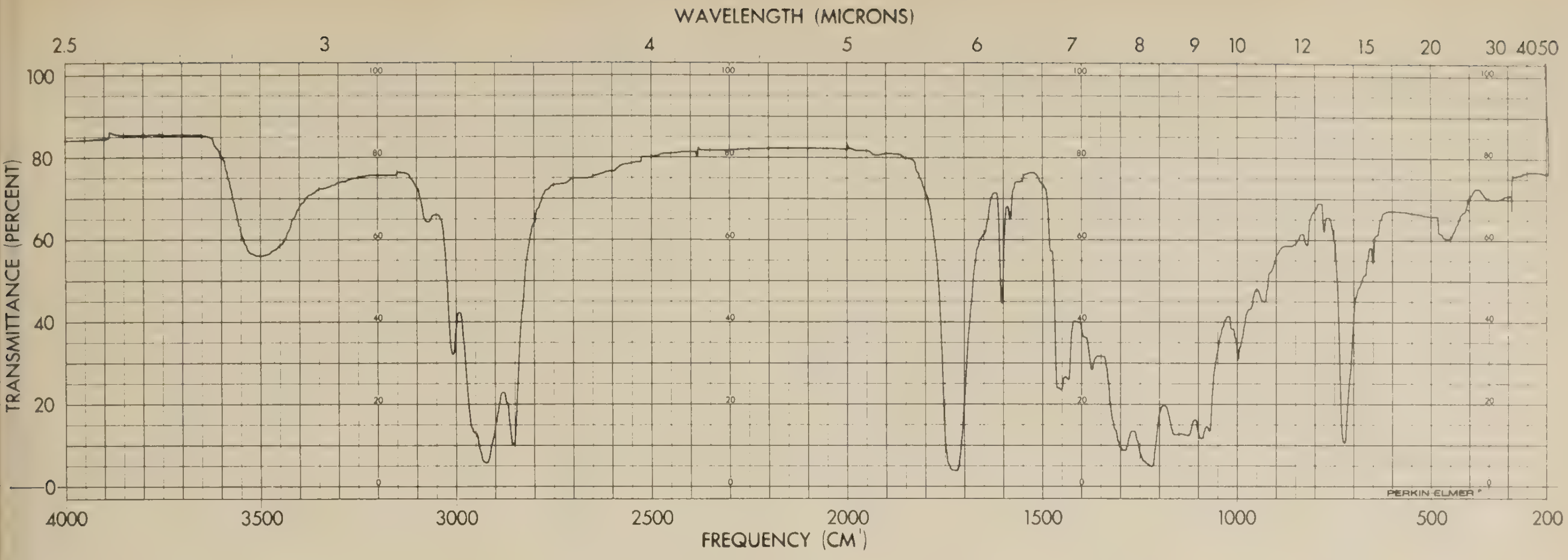

Figure 5.—Infrared spectrum of medium soya oil isophthalic alkyd resin.

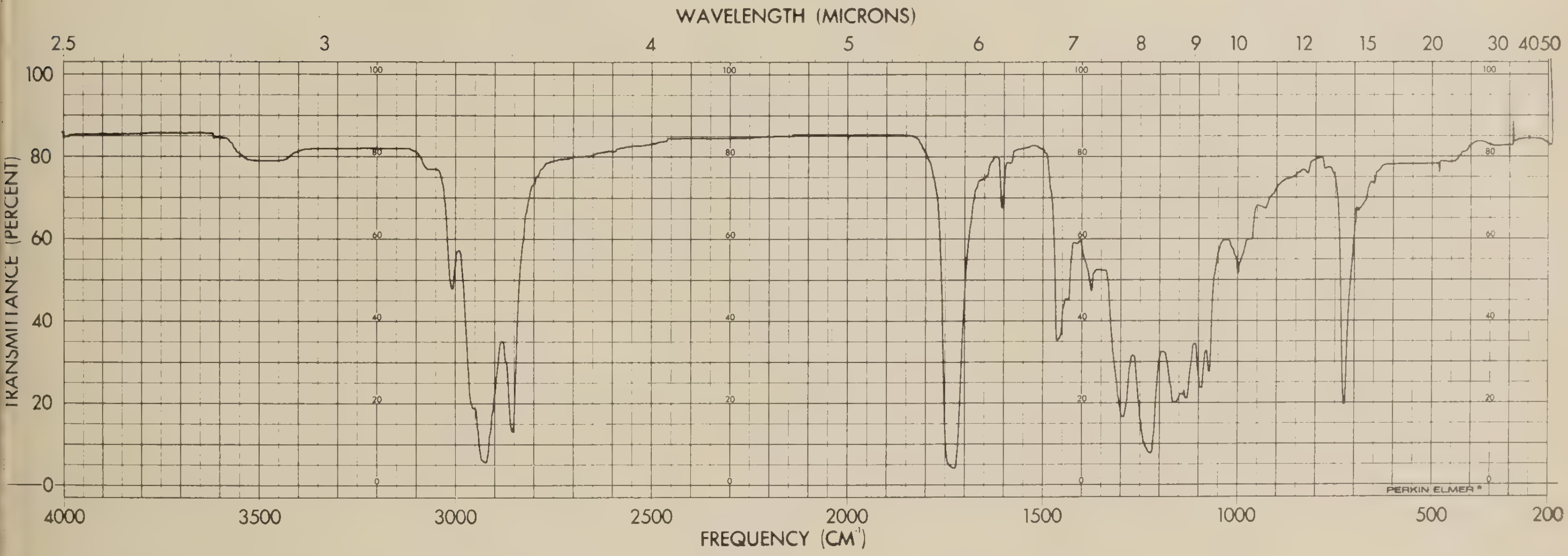

Figure 6.—Infrared spectrum of long soya oil isophthalic alkyd resin.

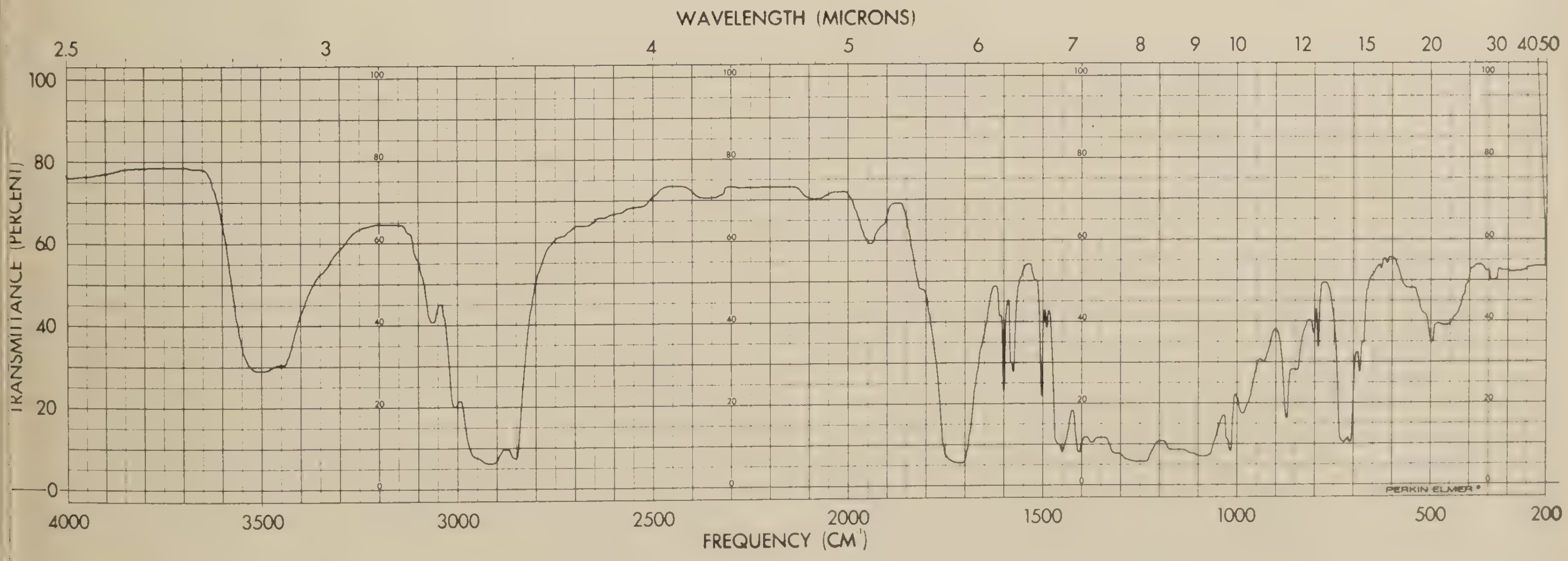

Figure 7.—Infrared spectrum of short soya oil terephthalic alkyd resin.

Figure 8.—Characteristic ultraviolet spectral curves of the three phthalate varieties of oil modified alkyds, 0.1 g/l concentration in $CHCl_3$.

violet absorbance measurements. For most of the measurements reported previously (*6*, *7*), cyclohexane was used as the solvent. This was fairly satisfactory as a solvent and could be used throughout the range of 220 to 360 millimicrons. Chloroform was used as a solvent for the oil alkyd resins studied in this investigation. Although this solvent is applicable only in the range from 240 to 360 millimicrons, it had, for our purposes, solvent properties superior to cyclohexane. In these experiments, solutions of the oil modified alkyd resins in chloroform remained clear indefinitely, whereas concentrated cyclohexane solutions of the resins became cloudy on standing.

Figure 8 shows typical ultraviolet absorption curves for solutions containing 0.1g/l of oil modified orthophthalic, isophthalic, and terephthalic acid alkyd resins in chloroform. All three materials produced characteristically different spectra. The orthophthalic resin was characterized by a peak at 276 millimicrons and a slight shoulder at about 284 millimicrons. These characteristics can be recognized clearly even in oil-resin mixtures containing less than 8 percent phthalic anhydride. In contrast, infrared spectra failed to indicate the phthalate characteristics at this low content of phthalic anhydride. As shown, three peaks at 291, 282, and 276 millimicrons are typical of an isophthalic resin. In some of the other isophthalics studied, the peak at 276 millimicrons is quite weak and is evident only as a shoulder. Terephthalic resin is distinguished by a peak at 283 millimicrons, a shoulder at about 298 millimicrons, and another slight shoulder at about 274 millimicrons. Similar distinguishing ultraviolet characteristics were reported by Kappelmeier (*12*) for the pure potassium salts of the various phthalic acids after they had been separated chemically from the parent oil modified alkyd resin. Thus, as a supplement to infrared analysis, it should be possible to determine qualitatively whether an alkyd resi was made from orthophthalic, isophthalic, o terephthalic acid, after the volatile solvent have been removed, by observing the patter of the ultraviolet absorbance curve of a pain vehicle without the necessity of prior chemica separations. Based on these results, the quantitative possibilities of a direct ultraviolet procedure appeared to have merit and wer therefore fully investigated, as reported i the following paragraphs.

Possible Interferences in a Direc Ultraviolet Procedure

Other than the phthalic acids or phthali anhydride, many materials used in the manu facture of alkyd resins will absorb ultraviole radiation (*5*). Therefore, measurements wer made on such materials to determine whethe their ultraviolet absorbances at the wave lengths of interest might interfere with quantitative evaluation of the content c phthalic anhydride or isophthalic acid.

Possible interfering materials to be con sidered include the following: the solvents the polyols (polyhydric alcohols)—glycol, gly erol, and pentaerythritol; dibasic acids oth than phthalates, such as, saturated types- succinic, adipic and sebacic, and monounsat rated types—itaconic, maleic, and fumari and the various drying oils.

Interference from the commercially use solvents, notably the aromatics, can be in mediately dismissed because the contemplat method involved the complete removal of t original solvent. The effect of the dibasic sat rated acids can also be disregarded, as th exhibit comparatively insignificant absorpti ity in the ultraviolet region under consider tion (*5*, *12*). Monounsaturated dibasic acids- itaconic, maleic, and fumaric—can possib interfere (*5*, *12*, *13*), but they are rarely us in highway coatings, so these potential effec were neglected in the investigation.

Consequently, this phase of the investig tion was limited to studying the possi interfering effects of various drying oils a polyhydric alcohols used in alkyd manufactu Ultraviolet absorbance measurements w made on appropriate solutions of various d ing oils including tung and fish oil; a ethylene glycol, pentaerythritol, and gl erol. Calculations were then made to det mine the absorptivity of these dissolv materials at the wavelengths of intere From these calculations it appeared that n of these materials, except tung oil, sho cause any measurable interference. For exa ple, fish oil, even if present to an extent 50 percent in an alkyd resin, will mer contribute an absorbance value of 0.009 a total solids concentration of 0.1 g/l, a therefore affect the results only slightly. T oil, however, absorbs strongly. An absorba value of 0.95 (equivalent to an absorptiv of 95) was obtained at 276 millimicrons a 0.01 g/l solution in chloroform. The spec interference of tung oil is produced by eleostearic acid component, which has a tr conjugated bond structure and is theref highly absorptive at 276 millimicrons (*14*,

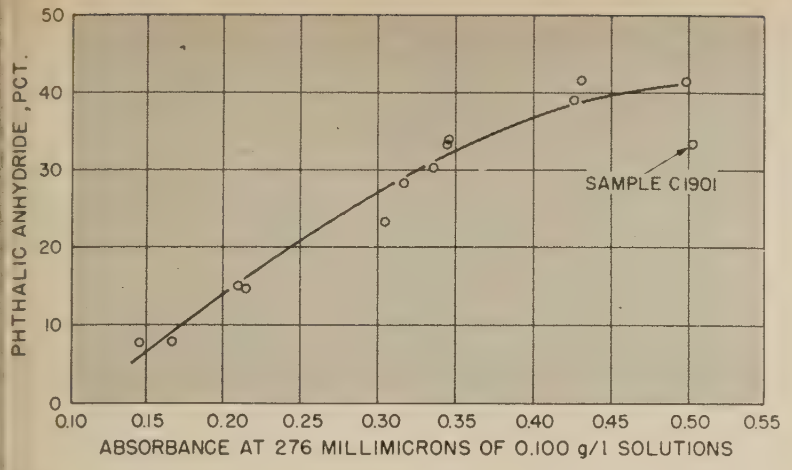

Figure 9.—Relation between phthalic anhydride content and ultraviolet absorbance of oil modified o-phthalic alkyd at 276 millimicrons, 0.1 g/l concentration in $CHCl_3$.

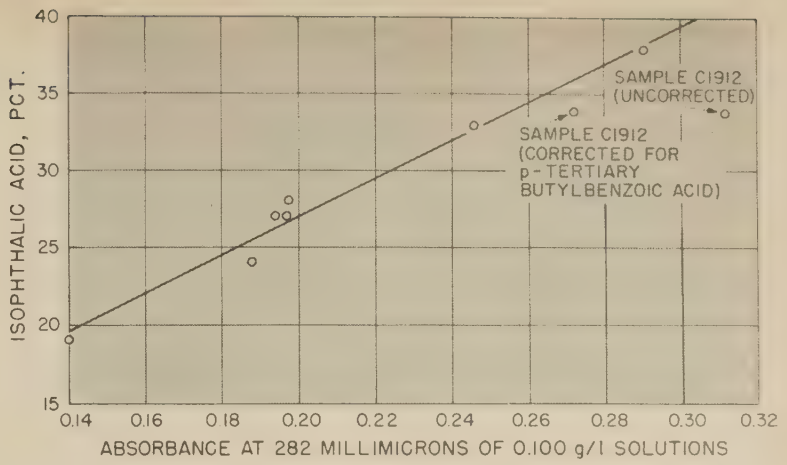

Figure 10.—Relation between isophthalic acid content and ultraviolet absorbance of oil modified isophthalic alkyd at 282 millimicrons, 0.1 g/l concentration in $CHCl_3$.

The type of conjugation may be determined by the location of the characteristic band maximum. In round numbers, a band near 230 millimicrons indicates diene conjugation, at 270 millimicrons—triene conjugation, and at 310 millimicrons a system of four conjugated bonds (*16*). Clearly then, the presence of any significant amounts of tung oil, which also has a high maximum absorbance at 276 millimicrons, would vitiate any attempts to correlate the amount of phthalic anhydride present with direct absorbance measurements made at 276 millimicrons.

Other workers have also pointed out[2] that other constituents of special alkyd resins would cause high absorption at 276 millimicrons. Among these are polystyrene, benzoic acid, vinyl toluene, epoxies, phenolic resins, coumarone-indene, chlorinated polyphenyl, and aromatic silicones. Such high absorption would occur when any aromatic adjunct is present in an alkyd, as the conjugated aromatic structure is highly absorptive in the ultraviolet region. Fortunately, such materials are not customarily incorporated in oil modified alkyds that are specified to be entirely of the *o*-phthalic or isophthalic type.

Quantitative Ultraviolet Measurements

Using the ultraviolet procedure described in detail in previous reports (*6, 7*), and given a condensed form under *Recommended Test Procedure*, quantitative absorbance measurements were made on the oil modified -phthalic and isophthalic alkyd resins and paints listed in table 1. Where necessary, the pigment was removed by centrifuging and the original solvent eliminated with the rotary vacuum evaporator. Chloroform solutions of the vacuum dried total solids were then prepared to contain exactly 0.100 g/l. Care was exercised to avoid undue exposure to the atmosphere.

Figure 9 shows the relation between the chemically determined phthalic anhydride content of oil modified *o*-phthalic alkyd resins and the absorbance value obtained at 276 millimicrons. In each case, the phthalic anhydride content plotted represented an average of two determinations. All but one point showed a fairly linear relationship throughout most of the range of values. These vehicles had been manufactured by seven different companies. The polyol constituent of the resins was either glycerol, ethylene glycol and pentaerythritol, or glycerol and pentaerythritol. Most of the resins contained glycerol. Linseed or soybean oil was present as the drying oil modification in each sample.

The plotted value for one sample, C1901, is far from the line drawn through the other points. Assistance in explaining the behavior of this sample was obtained from the Coating and Chemical Laboratory, Aberdeen Proving Grounds (A.P.G.). Their examination of the material showed that the high absorbance was caused by tung oil, present as an adjunct to the drying oil. The identification of the tung oil was made by extracting the oil acids following saponification and removal of unsaponifiable matter. The solvent-free oil acids were then dissolved in methanol and ultraviolet absorbance measurements made. The oil acids showed moderate absorption bands at 259, 269, and 280 millimicrons, the 269 band being the strongest. These bands are characteristic of tung oil eleostearic acids.[2] The A.P.G.'s findings were later corroborated in Public Roads' laboratory by a similar separation of oil acids and confirmation of the presence of bands of tung oil eleostearic acids.

A number of qualitative tests are recommended for the detection of the presence of tung oil in a mixture (*17*). Of these, the Wan Test gave a positive indication of tung oil.

Figure 10 shows the relation between isophthalic acid content, as provided by the producers, of drying oil modified isophthalic alkyd resins and absorbance at 282 millimicrons. All but one sample, C1912, indicate a fairly linear plot. The absorbance and peculiar behavior of sample C1912 are discussed in the succeeding paragraphs.

The ultraviolet absorbance of isophthalic alkyd solutions showed no evidence of changing with time or exposure to light, in contrast to the behavior of phthalic anhydride alkyds reported in an earlier paper (*6, 7*). Even an 89-hour exposure to an ultraviolet lamp caused no appreciable absorbance change in the isophthalic alkyds. Apparently, no special precautions must be observed when making absorbance measurements on isophthalic alkyds. A possible explanation for this difference in exposure behavior between *o*-phthalic and isophthalic acid is that the presence of minute amounts of quinones produces progressive changes in the absorbance of the *o*-phthalic resins. It has been reported that 1, 4-naphthoquinone may occur as an impurity in the manufacture of phthalic anhydride, and that although it absorbs ultraviolet radiation quite strongly, it is progressively oxidized and, thereby, its effect is reduced with time (*18*). Isophthalic acids are not known to contain such quinone impurities. This appears to account for the difference in exposure behavior.

Anomalous Absorbance of Sample C1912

One isophthalic alkyd, sample C1912, gave an unusually high absorbance at 282 millimicrons, as shown in figure 10. Information obtained from the manufacturer stated that 8.8 percent para tertiary butylbenzoic acid was used in the formulation of that resin. Ultraviolet absorbance curves were made of a *practical* grade of para tertiary butylbenzoic acid dissolved in chloroform 0.100 g/l. At 282 millimicrons the absorptivity was 4.27. When the absorbance of sample C1912 is corrected for the absorbance contributed by the presence of 8.8 percent para tertiary butylbenzoic acid, a corrected point, much nearer to the line drawn through the other points, is shown in figure 10.

A close examination of the ultraviolet absorption pattern for sample C1912 shows a

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[2] Private communications with M. H. Swann and G. G. Esposito, Coating and Chemical Laboratory, Aberdeen Proving Ground, U.S. Department of the Army, Aberdeen, Md.

Table 2.—Repeatability of absorbance measurements made on isophthalic resin sample C1917 [1]

Replicate runs	Absorbance value at 282 millimicrons
Determination number:	
1	0. 243
2	0. 250
3	0. 246
4	0. 246
5	0. 244
Average	0. 246
Range	0. 007

[1] In A. C. S. reagent grade chloroform at concentration of 0.1 g/l.

slight shoulder at about 302 millimicrons (see fig. 11). This shoulder was not present in the patterns of any of the other isophthalic alkyds examined, as exemplified by figure *8*. The isophthalic acid was isolated from this alkyd, sample C1912, by saponification and acidification (*4*), and an ultraviolet absorption curve was made on a methanol solution of it. The anomalous shoulder was still present, but in the free acid form it had shifted to about 298 millimicrons (see fig. 12). In this region, there was no comparable absorptivity shown in a spectral curve for a sample of para tertiary butylbenzoic acid. Thus, some additional unidentified interfering material appeared to be present.

Commercial isophthalic acid is known to contain some terephthalic acid. This is especially true if the isophthalic acid has been prepared from a mixture of meta and para xylene. To explore this possibility, an ultraviolet absorbance curve was made of a methanol solution containing 0.100 g/l of commercial terephthalic acid. At 302 millimicrons, this material had an absorptivity of about 1.20. Accordingly, the presence of some terephthalic acid could easily account for the shoulder that was present in the ultraviolet pattern of sample C1912. As can be seen from figure 8, such an impurity could produce a shoulder at about 302 millimicrons. If the chemical method of isolating the free isophthalic acid from this resin (*4*) failed to provide a perfect separation of isophthalic and terephthalic acids, the persistence of the shoulder in the ultraviolet pattern of the isolated free acids is thus explained. At 282 millimicrons, the absorptivity of the terephthalic acid solution was about 4.60. Therefore, any terephthalic acid present, in addition to isophthalic acid and para tertiary butylbenzoic acid, would contribute to the anomalous high absorbance value of sample C1912.

As further verification of the presence of these interferences, the infrared spectrum of the anomalous resin is shown in figure 13. Four sharp bands are noted by asterisks at 771, 1018, 1408, and 1500 cm.$^{-1}$. These bands are essentially absent in the other isophthali alkyds, as exemplified by figures 5 and 6.

From an examination of infrared pattern of para tertiary butylbenzoic acid, terephthalic alkyd (fig. 7), and terephthalic acid it was noted that these same four bands wer present in each. Thus the anomalous high absorbance value for this resin is clearly explaine by the presence of two other ultraviolet absorbing species in addition to isophthalic acid These findings serve to illustrate the value qualitative infrared and ultraviolet examinations preliminary to quantitative ultraviole analysis.

Repeatability of Quantitative Ultraviolet Measurements

General repeatability data were not obtained in this study; but some indication the precision of the method was obtained b making five independent measurements o freshly prepared solutions from one isophthal resin over a 3-day period. Measurements we made at 282 millimicrons on 0.1 g/l chlorofor solutions following the procedure describe above. The measured absorbance values a given in table 2. The calculated range absorbance of 0.007 represents a range percentage of isophthalic acid of 0.9 whe read from the curve shown in figure 10. Thu at this level of resin content, the repeatabili appears quite satisfactory.

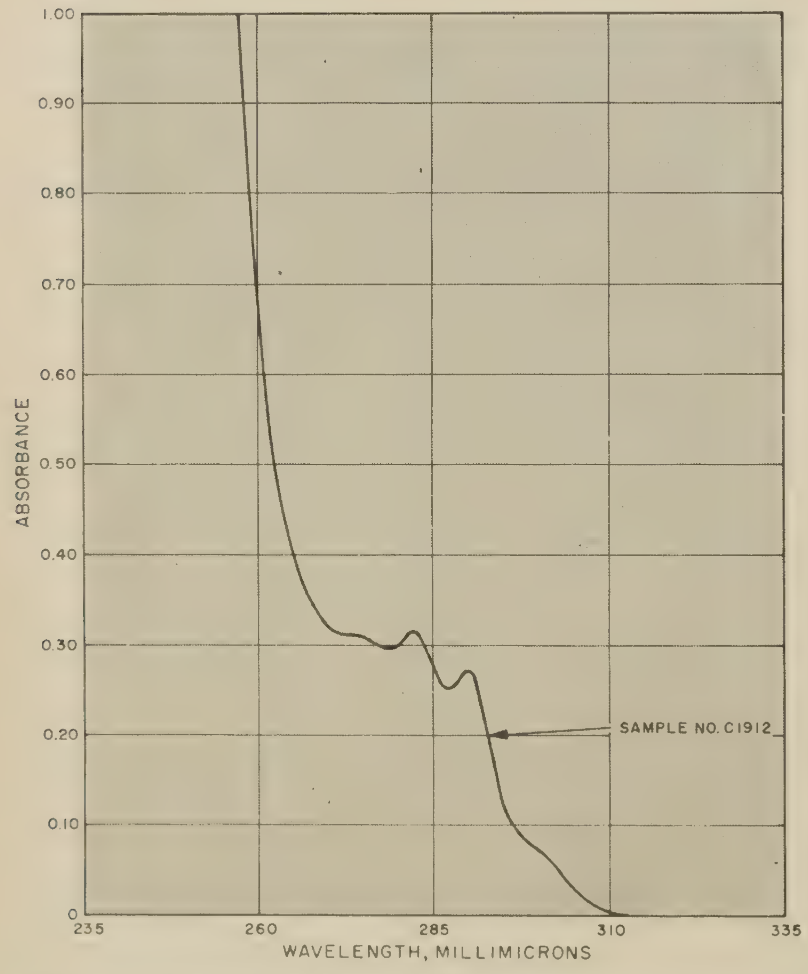


Figure 11.—Ultraviolet spectrum of oil modified isophthalic alkyd—sample C1912—that gave anomalous results, 0.1 g/l in $CHCl_3$.

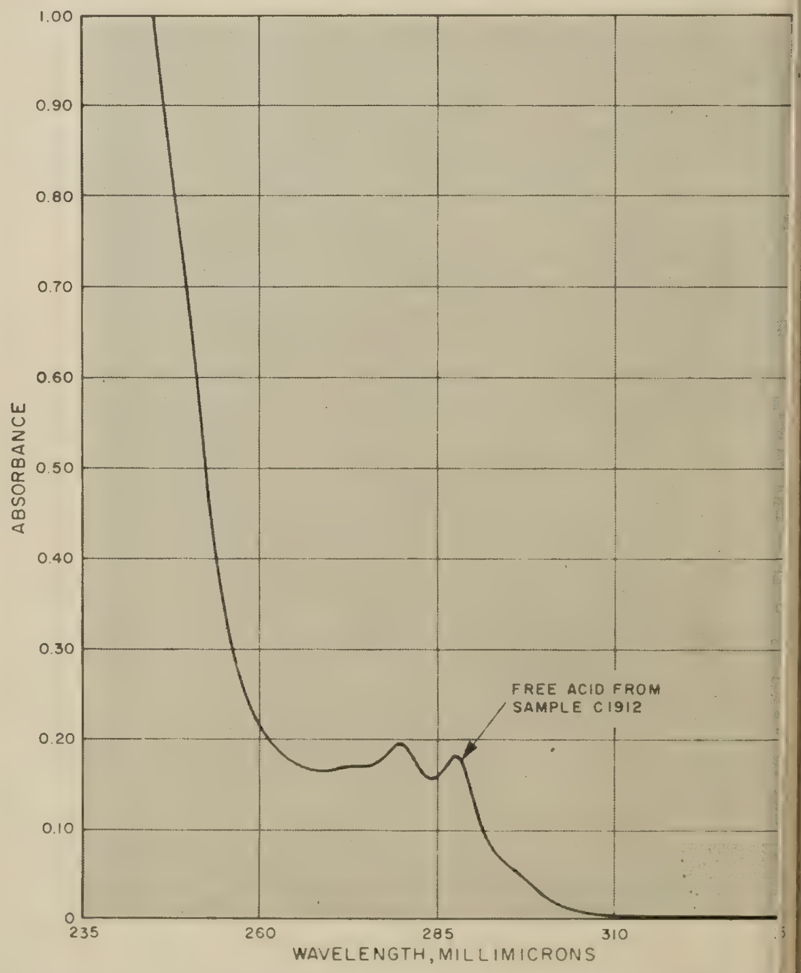
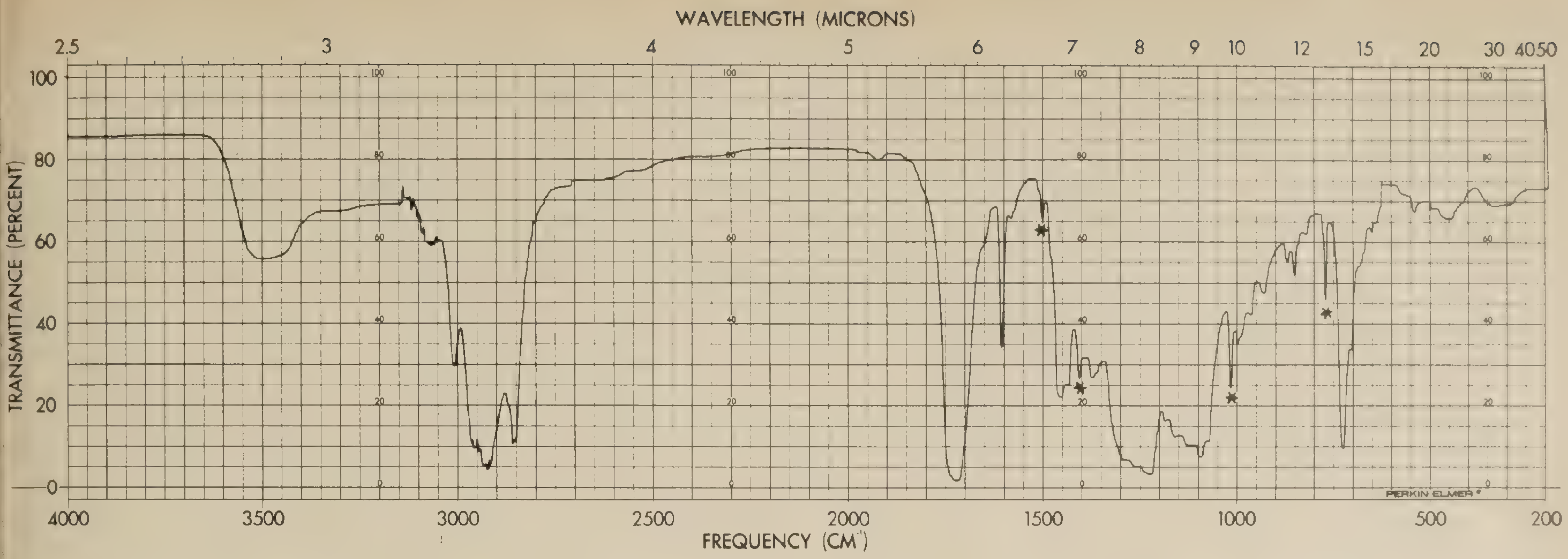


Figure 12.—Ultraviolet spectrum of isophthalic acid isola from parent alkyd material, C1912, shown in figure 11 CH_3OH).



igure 13.—Infrared spectrum of anomalous oil modified isophthalic alkyd, C1912. The four asterisks indicate bands that are essentially absent from spectra of the other isophthalic alkyds studied.

Repeatability measurements of the ultraviolet absorbance values were not made for he phthalic anhydride content of the oil modified orthophthalic alkyds used. Such measurements were available from a previous nvestigation (*6, 7*). Based on eight replicate measurements made in that study, it would ppear that the repeatability of the phthalic nhydride content determination by the ecommended procedure would be of an cceptable level, but somewhat less precise han for the isophthalic acid determination. The cause for this difference is explained by he previous discussion regarding quinone npurities and exposure changes.

Use of Cesium Iodide (CsI) Windows

Cesium iodide windows for infrared measrements throughout the range of 4000 to 00 cm.$^{-1}$ were used in the investigation. Cesium iodide is a very soft material that is asily scratched, bent, and corroded by water. single window (or plate) was used to obtain he infrared spectra of alkyd resins. A few rops of chloroform solution of the alkyd were laced on the window and dried at 60° C. in vacuum oven—a practice that was much impler than using two windows. When the esin was sandwiched between two windows, he windows could not be separated without njuring them.

On one occasion a CsI window became warped while it was drying in the vacuum ven at 60° C. To correct the warping, the window was placed between two steel plates with filter paper separating the steel and the window. Warping was eliminated after the ssembly was heated overnight, under vacum, at 60° C.

Frequent polishing and occasional grindng of the CsI windows were determined to be necessary. In fact, as a routine matter, the CsI window was nearly always polished after ach film had been removed with solvents. Thus, the transmittance of the window was satisfactory for use on the next sample to be examined, and grinding was seldom required. The following polishing technique was used [3]: A piece of chamois was stretched over the surface of a square glass plate. This was moistened with reagent grade 2-propanol and the CsI window polished with figure-eight motions. Plastic gloves were worn during polishing and grinding operations. Progress of the polishing operation was easily checked by placing the window in the sample beam of the spectrophotometer. A window that gave a transmittance of 83 to 86 percent at 4000 cm.$^{-1}$ was very satisfactory. This was approximately the transmittance of the windows when new.

A convenient method for grinding the windows when they became badly etched was to use a piece of number 600 waterproof silicon carbide abrasive paper placed on a flat surface. Then they were polished as described above. Other suitable procedures for grinding and polishing CsI windows have been published (*19, 20*).

Summary and Conclusions

The study reported here resulted in a demonstration of the usefulness of infrared and ultraviolet spectroscopy for the rapid qualitative and quantitative characterization of oil-modified alkyd resin paint vehicles that have not previously been separated chemically. A preliminary infrared examination will generally indicate whether a phthalate type alkyd is present and also provide evidence as to type—orthophthalate, isophthalate or terephthalate, or even mixtures of two of these. The type can also be substantiated by ultraviolet analysis. When the type is known, a suitable calibration curve can be used to determine the phthalic anhydride or isophthalic acid content by quantitative ultraviolet absorbance measurements using the procedure described under *Recommended Test Procedure*. The procedure requires no prior chemical separation; it requires only pigment separation, if necessary, and the removal of the original solvent under vacuum. Such determinations take about 2 hours, whereas about 5 hours are required to perform the necessary chemical separations and determine phthalic anhydride or isophthalic acid by ASTM and other available gravimetric and spectrophotometric methods. The more rapid procedure should be of considerable value to highway and other laboratories that conduct tests on a large number of alkyd resins and alkyd paint samples.

In the ultraviolet determination of isophthalic acid, a repeatability range for five determinations was obtained that represented 0.9 percent isophthalic acid. In connection with a previous, related investigation by the authors, it can be shown that the range for eight determinations represented 2.0 percent phthalic anhydride.

Reliance on the results of the test must be based on a knowledge of the absence of interfering substances. When tung oil is used as part or all of the drying oil modification, considerable error may occur. Such interfering substances may be detected by appropriate spot tests. Ordinarily, it would not be expected that the manufacturer would substitute tung oil when more economical drying oil modifications are specified for an alkyd.

The presence of other highly absorbing materials, such as terephthalic acid or para tertiary butylbenzoic acid, can also cause errors in the determination of isophthalic acid or phthalic anhydride by the method described. Use of the rapid method is not recommended when such adjuncts are known to be present or when qualitative infrared or ultraviolet information indicates the presence of such interferences.

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[3] Recommended in a private communication from J. L. Bernard, The Perkin-Elmer Corp., Silver Spring, Md.

The following recommended procedure should be useful in rapid acceptance testing of paints and in manufacturing processes to control the composition of batches or lots of alkyds or oil-alkyd vehicles. In manufacturing processes, in particular, the presence or absence of other absorbing materials would be known. It is reasonable to assume that quantitative measurements of terephthalic acid content, could be made in a manner similar to the procedures described for phthalic anhydride and isophthalic acid content.

Recommended Test Procedure

The test procedure given here is intended as a quantitative ultraviolet procedure for determining the phthalic anhydride or isophthalic acid content of alkyd resins without making any chemical separations. Absence of other high absorbance materials, at the wavelengths on which calculations are based, must be verified to use the method. The method is described for the phthalic anhydride determination; the procedure for isophthalic acid is the same except that absorbance at 282 millimicrons is used as the basis for evaluation.

Calibration

- Obtain 6 or more samples of paint or alkyd resin vehicles of the orthophthalic type in which the phthalic anhydride contents are known and cover the concentration range of interest. For paints, remove the pigments by centrifuging.
- Prepare infrared spectra of the alkyds. These may be obtained by diluting a small amount of the alkyd with chloroform, adding a few drops of the solution to the surface of a halide window, evaporating at 60° C. in a vacuum oven, and scanning with an infrared spectrophotometer. If unusual bands are evident in one sample do not attempt to use the subsequent ultraviolet procedure for that sample. Verify from the infrared spectra that these materials are typical orthophthalic alkyds.
- If the presence of tung oil is suspected, use of the Wan Test is helpful for identification. Do not use this ultraviolet procedure when tung oil, extraneous aromatics, or unsaturated dibasic acids are known to be present.
- Determine the nonvolatile solids content of each vehicle by heating it at 105° C. for 3 hours.
- Weigh accurately, by difference from a dropping bottle, an amount of vehicle sample equivalent to about 0.4 g of nonvolatile alkyd resin, and transfer to a 100-ml. round bottom flask with a standard taper neck that fits a rotating vacuum evaporator.
- Attach the flask to the rotating vacuum evaporator, evacuate, and start the rotation of the flask. Move a water bath at a temperature of 56–60°C. under the flask. Lower the flask until it is about one-half immersed in the water but does not touch the bottom of the bath. Allow evaporation to continue for 20 minutes, keeping the temperature of the water bath between 56° and 60°C.
- Turn off the vacuum connection and admit air to the assembly by removing the pressure tubing from the vacuum line. Reopen the vacuum line and turn the auxiliary ground-glass stopcock so that it is open to the air. Using a 5-ml. beaker, transfer about 45 ml. of chloroform (reagent grade) to the rotating flask. The transfer can be accomplished by repeatedly holding the 5-ml. beaker, filled with chloroform, under the glass inlet tube with one hand, and pushing the end of the pressure tubing against the vacuum-line stopcock opening with the other hand. This causes the chloroform in the beaker to be sucked through the center glass tube and into the evaporator. Shut off the vacuum line, leaving the pressure tubing disconnected. Continue rotating the flask in the water bath for 5 minutes more to insure complete solution of the residue in the flask.
- At the conclusion of the 5-minute period, raise the evaporator, dry the flask, and remove it and its contents. Transfer the contents of the flask quantitatively to a 100-ml. volumetric flask, rinse well with chloroform (under a hood), and collect the rinsings. After the flask has cooled to room temperature, dilute to the mark and mix thoroughly.
- From this stock solution, an appropriate concentration can be made by aliquoting into a 25-ml. volumetric flask and diluting this to the mark. A final concentration of 0.100 or 0.200 g/l will generally give useful absorbance values. To prepare 0.100 g/l, use:

$$\frac{0.100\times 25}{10\times \begin{matrix}\text{weight of}\\ \text{sample}\end{matrix} \times \begin{matrix}\text{nonvolatile}\\ \text{fraction}\end{matrix}} = \begin{matrix}\text{milliliters of}\\ \text{stock solution}\end{matrix}$$

- Obtain an ultraviolet absorbance curve with a recording spectrophotometer. Before each run, establish a baseline showing the relative absorbances of the two cells containing only chloroform.
- Record the value of the corrected peak absorbance at 276 mllimicrons (nanometers). The exact position of the peak may vary from instrument to instrument.
- Repeat this absorbance measurement for each one of the range of samples used.
- On suitable graph paper, plot the points obtained from each sample with absorbance as the abscissa and percent phthalic anhydride as the ordinate. Draw a smooth curve through the points obtained. This is the calibration curve which may be used indefinitely for subsequent test samples unless there is a significant change in instrumentation.

Test sample

- Repeat the above procedure for a test sample in which the phthalic anhydride content is unknown.
- Examine the appearance of the ultraviolet spectrum of the unknown sample. If the spectrum exhibits extra peaks or shoulders not shown in the spectra from which the calibration curve was obtained, it may be well to assume that the method described here may not give acceptable results.
- From the absorbance obtained at 276 millimicrons, read the percent phthalic anhydride of the unknown from the calibration curve.

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REFERENCES

(*1*) *Standard Method of Test for Phthalic Anhydride Content of Alkyd Resins and Resin Solutions*, ASTM Designation: D563–52, 1968 Book of ASTM Standards, Part 20, American Society for Testing and Materials, Phila., Pa., pp. 297–298.

(*2*) *Standard Method of Test for Phthalic Anhydride Content of Alkyd Resins and Esters Containing Other Dibasic Acids* (*Gravimetric*), ASTM Designation: D1306–56, 1968 Book of ASTM Standards, Part 20, American Society for Testing and Materials, Phila., Pa., pp. 579–581.

(*3*) *Standard Method of Test for Phthali Anhydride Content of Alkyd Resins and Ester Containing Other Dibasic Acids* (*Spectrophoto-metric*), ASTM Designation: D1307–56, 196 Book of ASTM Standards, Part 20, America Society for Testing and Materials, Phila., Pa. pp. 582–586.

(*4*) *Report of Committee D-1 on Pain Varnish, Lacquer, and Related Products*, Activ-ities of Subcommittee 33, American Societ for Testing and Materials, Phila., Pa., 196 Preprint, p. 16.

(*5*) *Spectrophotometric Determination of Tot Phthalic Anhydride*, by O. D. Shreve and M R. Heether, Analytical Chemistry, vol. 2 No. 3, March 1951, pp. 441–445.

(*6*) *Use of Ultraviolet Spectroscopy to Dete Adulteration of Traffic Paint Vehicles*, by Leo ard Bean and Bernard Chaiken, Materia Research and Standards, vol. 7, No. 2, Febr ary 1967, pp. 65–72.

(*7*) *Ultraviolet Spectrophotometric Detecti of Adulteration in Traffic Paint Vehicles*, Leonard Bean and Bernard Chaiken, Publ Roads, vol. 34, No. 12, February 1968, p 251–257.

(8) *Operating Instructions, Model 621 Spectrophotometer*, Perkin-Elmer Corp., Norwalk, Conn., April 1965.

(9) *Model DK–A Ratio Recording Spectrophotometers*, by E. F. Trujillo, Beckman Instructions 1220–A, Beckman Instruments, Inc., Fullerton, Calif., February 1963.

(10) *Handbook of Industrial Infrared Analysis*, by Robert G. White, Plenum Press, N.Y., 1964, p. 196.

(11) *Infrared Spectra of Polymers*, by D. O. Hummel, Interscience Publishers, New York, 1966, p. 43.

(12) *Chemical Analysis of Resin-Based Coating Materials*, by C. P. A. Kappelmeier, Interscience Publishers, Inc., New York, 1959, pp. 130–131.

(13) *Ultraviolet Spectrophotometric Determination of Styrene and Phthalate and Fumarate Esters in Polyester Resins*, by R. C. Hirt, R. G. Schmitt, and R. W. Stafford, Analytical Chemistry, vol. 27, No. 3, March 1955, pp. 354–356.

(14) *Fats, Oils, Fatty Acids, and Glycerides (Ultraviolet Spectroscopy)*, by Robert T. O'Connor, The Encyclopedia of Spectroscopy, edited by G. L. Clark, Reinhold Publishing Corp., New York, 1960, p. 35.

(15) *Application of Ultraviolet and Visual Spectrophotometric Data*, by E. I. Stearns, Analytical Absorption Spectroscopy, edited by M. G. Mellon, John Wiley & Sons, Inc., New York, 1950, p. 402.

(16) *Ultraviolet Absorption Studies of Drying Oils*, by J. Peter Kass, Protective and Decorative Coatings, vol. IV, edited by J. J. Mattiello, John Wiley & Sons, Inc., New York, 1944, pp. 381 and 387.

(17) *Paint Testing Manual, Physical and Chemical Examination, Paints, Varnishes, Lacquers, Colors*, by H. A. Gardner and G. G. Sward, 12th ed., Gardner Laboratory, Inc., Bethesda, Md., 1962, pp. 438–440.

(18) *Ultraviolet Absorption Spectra of Phthalic Anhydride and Related Substances*, by Hans Peters, Analytical Chemistry, vol. 31, No. 8, August 1959, pp. 1326–1331.

(19) *Chemical Infrared Spectroscopy, vol. 1—Techniques*, by W. J. Potts, Jr., John Wiley & Sons, Inc., New York, 1963, pp. 107–113.

(20) *Infrared Filters and Cells of Unpolished Salt Crystals*, by J. J. McGovern and R. A. Friedel, Journal, Optical Society of America, vol. 37, No. 8, August 1947, pp. 660–663.

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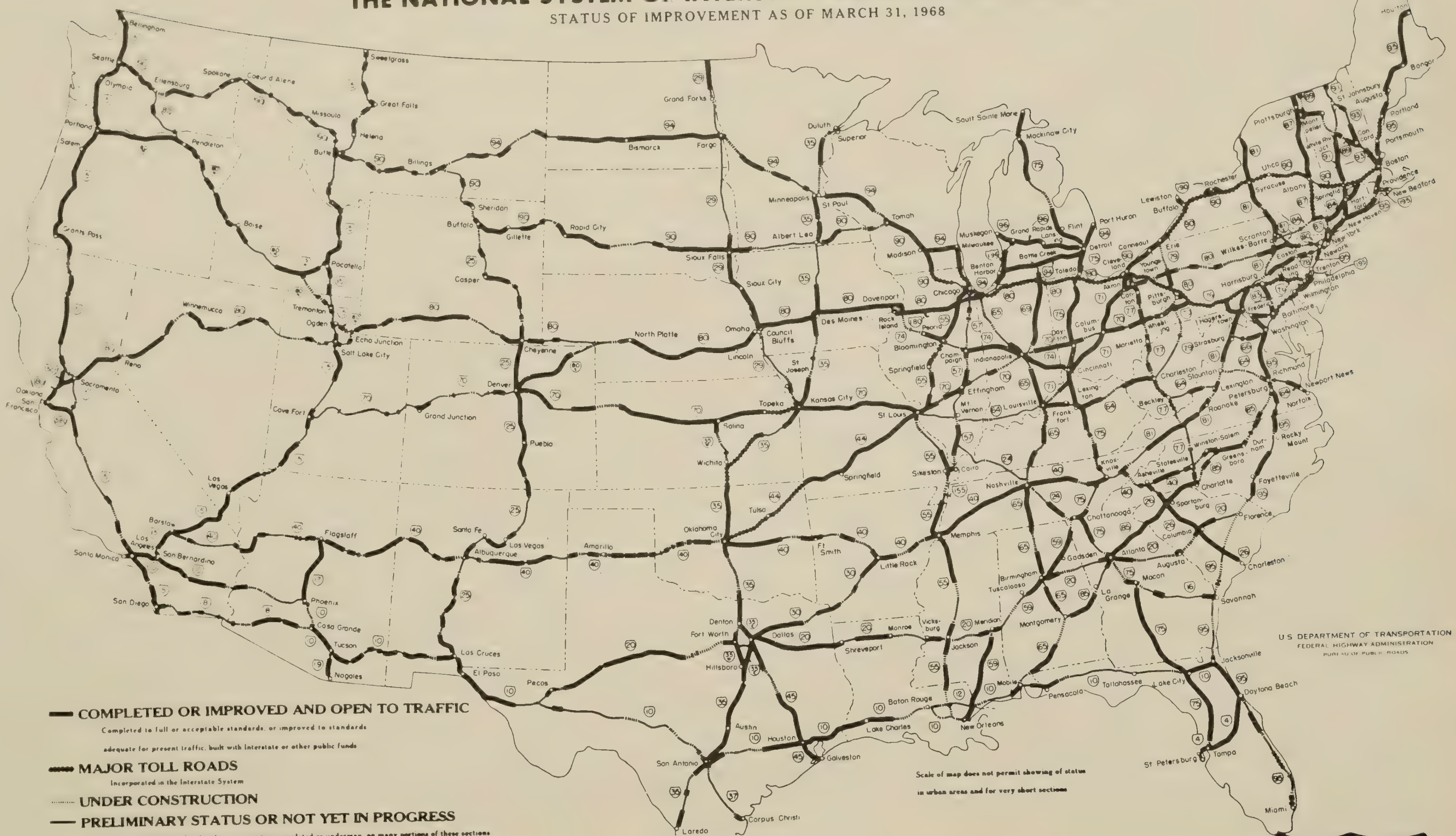

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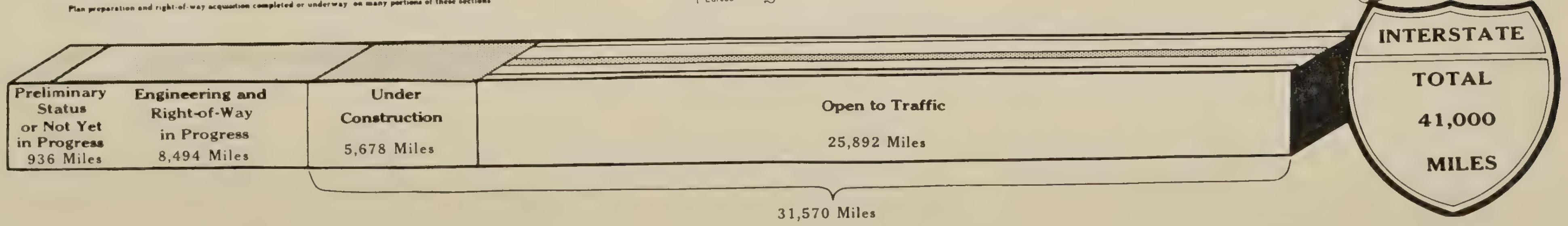

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