THE EVALUATION OF THE BAUSCH AND LOMB REFLECTANCE SPECTROPHOTOMETER FOR THE COMPARISON OF MINUTE PAINT SPECIMENS

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By

Theodore R. Elzerman

AN ABSTRACT OF A THESIS

Submitted to
Michigan State University
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1964

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ABSTRACT

THE EVALUATION OF THE BAUSCH AND LOMB REFLECTANCE SPECTROPHOTOMETER FOR THE COMPARISON OF MINUTE PAINT SPECIMENS

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Instrumentation is playing a very important part in the field of Forensic Science. The results of several supplementary tests of various properties showing similarities will make the comparison of evidence for purposes of establishing positive identification more convincing as to probable source or origin.

Paint and pigment specimens were measured in a wavelength range of 400 to 700 millimicrons. The reflectance curves were recorded on a graph.

Paint chip specimens were mounted on white card stock with double stick scotch brand adhesive tape and examined in the reflectance sphere of a Bausch and Lomb Spectronic 505 Recording Spectrophotometer. A specimen covering an area of 40 square millimeters (approximately 6 x 7 millimeters) of the illuminating beam was necessary to produce valid reflectance curves. Because a 40 square millimeter paint specimen is rarely encountered in the Forensic Science Laboratory, a procedure for diluting the paint specimen with a white pigment--lithopone--was investigated.

Using pure pigment smears, an area of 144 square millimeters (12 millimeters square) was necessary in the path of

the illuminating beam to produce valid reflectance curves. Pigment and paint specimens diluted with lithopone and mixed with linseed oil or polyvinyl acetate as vehicles were smeared on glass slides. The specimens thus prepared were examined in the reflectance sphere of the spectrophotometer.

The Spectronic 505 reflectance sphere has no value for directly examining paint chip specimens under 40 square millimeters in area. Diluting minute paint specimens with lithopone, making smears on glass slides and examining them in the reflectance sphere has limited value in the Forensic Science Laboratory. Concentrations of 0.1 per cent of a pure pigment mix, with a quantity of 10 milligrams of the mixture with lithopone as the diluent, were required for examination. Concentrations of 5 per cent of a light colored paint scraping and 1 per cent of a dark colored paint scraping with the same diluent required 10 milligrams of the mixture for examination. The paint specimen must be capable of being ground to a powder to produce repeatable results. Further, an area of 144 square millimeters with the diluted pigment and paint scrapings was required.

A modification of the reflectance sphere so that paint specimens smaller than the above may be examined without treatment, such as by condensing the illuminating beam onto the specimen, may give this instrument more application to the comparison of minute paint specimens in the visible wavelength range 400 to 700 millimicrons.

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CHAPTER I

INTRODUCTION

I. SCOPE OF THE PROBLEM

The fundamental problem of the forensic scientist is that of identifying an object which is held in evidence as having come from the same source as another object which is associated with a suspect.

Paint fragments are frequently obtained as evidence in cases where physical force or contact has been made. Burglaries, hit-and-run accidents and even homicides may involve paint as evidence. In many cases the circumstances are such that the amount of evidence available for analysis is in the form of trace smears.

With no standard quantity of paint to work with, methods of analysis and comparison will also vary, and any method which will give additional information will be useful.

II. SOME METHODS OF COMPARISON AND IDENTIFICATION

Only a few methods will offer absolute proof of origin. These methods include the fitting together of broken edges of paint chips or the matching of characteristic striated markings.[1] In some instances it is possible to identify the

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[1] P. Kirk, _Crime Investigation_ (New York: Interscience Publishers, Inc., 1960), p. 261.

make, model and year of manufacture of a car by microscopic examination of its paint flakes.[2]

These situations are not often found in actual practice, and in most cases no single examination will give a positive identification of one specimen with another. It is possible, through several types of examinations, to show similarities which may prove the source or origin of paint chips or smears.

The forensic scientist may conduct a visual or microscopic examination to determine paint layers and colors,[3] or density of the paint sample and pigment distribution.[4]

The paint sample may also be subject to microchemical,(5, 6, 7, 8) spectrographic,(9, 10, 11) infrared

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[2] C. F. Tippett, "The Identification of Make, Model and Year of Manufacture of a Car by an Examination of its Paint Flakes," Medicine, Science and the Law, IV (1964), pp. 22-25.

[3] J. G. Brewer and D. Q. Burd, "Paint Comparison, A Method for the Preparation of Cross Sections of Paint Chips," J. of Criminal Law and Criminology, XXXX (1949), p. 230.

[4] Kirk, op. cit., pp. 688-690.

[5] F. Klug, O. Schubert, and L. L. Vagnena, "A Microchemical Procedure for Paint Chip Comparisons," Journal of Forensic Science, IV (1959), p. 91.

[6] H. F. Payne, Organic Coating Technology, Volume II (New York: John Wiley & Sons, Inc., 1961), p. 870.

[7] N. W. Hanson, "Analyses of Paints, Lacquers, and Varnishes," Journal of the Oil and Colour Chemists' Association, XXXXI (1958), p. 210.

[8] C. P. A. Koppelmeier, Editor, Chemical Analysis of Resin-Based Coating Material (New York: Interscience Publishers, Inc., 1959).

[9] Klug, Schubert, and Vagnana, op. cit., p. 95.

[10] W. A. Cregeen, "The Spectrographic Examination of Small Samples by a Procedure Giving High Sensitivity," Journal of Forensic Science, V (1960), p. 226.

[11] C. E. O'Hara and J. W. Osterburg, An Introduction to Criminalistics (New York: The MacMillan Co., 1963), p. 598.

spectrophotometric,(12, 13, 14, 15) or X-ray diffraction (16, 17) examinations in determining its compositions and origin.

Neutron activation analysis is also under investigation and may prove to be a very important aid in the comparison and identification of minute paint chips to determine their origin.(18, 19, 20, 21)

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[12] "Infrared Spectroscopy. Its Use as an Analytical Tool in the Field of Paints and Coatings." Chicago Society for Paint Technology, 1960.

[13] T. R. Harkins, J. T. Harris and O. D. Shreve, "Identification of Pigments in Paint Products by Infrared Spectroscopy," <u>Analytical Chemistry</u>, XXXI (1959), p. 541.

[14] George L. Clark, Editor, <u>The Encyclopedia of Spectroscopy</u> (New York: Reinhold Publishing Corporation, 1960), p. 505.

[15] W. R. Heilman, "Nondestructive Infrared and X-Ray Diffraction Analyses of Paints and Plastics," <u>Journal of Forensic Science</u>, V (1960), p. 338.

[16] <u>Ibid</u>., p. 342.

[17] C. E. O'Hara and J. W. Osterburg, <u>op</u>. <u>cit</u>., p. 620.

[18] V. P. Guinn and C. D. Wagner, "Instrumental Neutron Activation Analysis," <u>Analytical Chemistry</u>, XXXII (1960), p.317.

[19] D. Gibbons, "Activation Analysis--An Aid to Forensic Investigation," <u>Forensic Science Society Journal</u>, IV (1963), p. 33.

[20] R. R. Ruch, <u>et</u>. <u>al</u>., "Neutron Activation Analysis in Scientific Crime Detection--Some Recent Developments," <u>Journal of Forensic Sciences</u>, IX (1963), p. 119.

[21] A. K. Perkons, <u>et</u>. <u>al</u>., "Further Development to Forensic Activation Analysis, <u>Proceedings of the Canadian Society of Forensic Science</u>, III (1964), p. 40.

With these thoughts in mind, reflectance spectrophotometry is evaluated as an additional method of comparison for identifying paint specimens which might be recovered at a scene of a crime.

III. HISTORY AND LITERATURE

The fundamental way to measure the color belonging to an area is to break it down into its component spectral parts, the radiant flux from that area, and to measure each of these parts of flux separately.[22] The spectrophotometer is an instrument designed to measure the intensity of the light transmitted or reflected by a substance and, when provided with an automatic recorder, a permanent record of the spectrum is rapidly obtained.

Spectrophotometers have been found useful in examining physical evidence[23] and one of the first spectrophotometers which employed a recorder was the Hardy or General Electric Spectrophotometer.[24] Since then, many recording spectrophotometric instruments have become available.

One of the more recent recording spectrophotometers available is the Bausch & Lomb Spectronic 505. When this

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[22] D. B. Judd, _Color in Business, Science, and Industry_ (New York: John Wiley and Sons, Inc., 1952), p. 29.

[23] "Use of a Recording Spectrophotometer in the Examination of Evidence," _F.B.I. Law Enforcement Bulletin_, XV (1946), p. 6.

[24] M. G. Mellon, _Colorimetry for Chemists_ (Columbus, Ohio: The G. Frederick Smith Chem. Co., 1945), p. 72.

instrument is equipped with a reflectance sphere it is capable of analyzing light reflected from an opaque object from 400 to 700 millimicrons.[25]

The literature on the use of absorbance (or transmittance) spectrophotometry for qualitative and quantitative purposes is voluminous, but in contrast, there are few accounts of similar applications of reflectance spectrophotometry.[26]

Reflectance spectrophotometry has frequently been employed in industry for the descriptive evaluation of colorants and pigments.(27, 28, 29, 30, 31, 32, 33,

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[25] Bausch and Lomb Bulletin on Specifications. Catalog Numbers D-2009, 0263., p. 10.

[26] H. Zeitlin and A. Niimoto, "Comparison of Transmittance and Reflectance Spectra of the 2, 4-Dinitrophenylhydrazones of Acetone and 4-Methyl-2-pentanone," Analytical Chemistry, XXXI (1959), p. 1167.

[27] J. Sendroy and W. C. Granville, "Application of Reflectance Spectrophotometry to Quantitative Microanalysis," Industrial and Engineering Chemistry, XIX (1947), p. 500.

[28] Committee on Colorimetry, Optical Society of America, The Science of Color (New York: Thomas Y. Crowell Co., 1953) p. 218.

[29] H. A. Gardner and G. S. Sward, Paint, Varnishes, Lacquers, and Colors, (Twelfth edition; Bethesda, Maryland: Gardner Laboratories, Inc. 1952) p. 13.

[30] D. B. Judd, Color in Business, Science and Industry (New York: John Wiley and Sons, Inc., 1952) p. 82.

[31] D. R. Duncan, "The Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry," Journal of the Oil and Colour Chemists' Association, XXXXV (1962) p. 300.

[32] G. Reimann, D. B. Judd, H. J. Hiegan, "Spectrophotometric and Colorimetric Determination of the Colors of the TCCA Standard Color Cards," Journal of the Optical Society of America, XXXVI (1946) p. 128.

[33] K. L. Kelley, K. Gibson and D. Nickerson, "Tristimulus Specifications of the Munsell Book of Color from Spectrophotometric Measurements," Journal of the Optical Society of America, XXXIII (1943) p. 355.

34, 35) It also has been used to study cobalt(II) salts[36] mecuric iodide[37] and other reactions resulting in the production of color[38] or the changing of colors.(39, 40, 41)

The examination of paints and other pigmented compositions by reflectance spectrophotometry has been studied by Duncan in detail.[42] While some workers feel that information which may be derived from reflectance curves without interpretation by means of color theory is limited, although in some cases valuable,(43, 44) others believe that no further

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[34] Mellon, op. cit., p. 104.

[35] C. A. Lermond and L. B. Rogers, "Differential Measurements of Reflectance," Analytical Chemistry, XXVII (1955) p. 340.

[36] L. I. Katzin, "Reflection Spectra of Some Solid Cobalt (II) Salts in the Visible Region," Journal of the American Chemical Society, LXXV (1953), p. 2830.

[37] G. Kortum, "DiffuseReflectance Spectra of Mercuric Iodide on Different Adsorbents," Transactions of the Faraday Society, LVIII (1962) p. 1624.

[38] Sendroy and Granville, op. cit.

[39] T. R. Griffiths, K. Latt, M. Symons, "Diffuse Reflectance Spectrophotometry in the Ultraviolet Using Powdered Salts," Analytical Chemistry, XXXI (1959), p. 1338.

[40] S. Wendlandt, et al., "High Temperature Diffuse Reflectance Spectroscopy," Analytical Chemistry XXXV (1963), p. 105.

[41] W. Wendlandt, "The Dynamic Reflectance Spectroscopy," Science, Vol. 140 (1963), p. 1085.

[42] Duncan, op. cit., p. 305.

[43] E. Atherton and D. Touch, "Aspects of Colorimetry Applied to the Colour Gamut of Pigments," Journal of Oil and Colour Chemists' Association, XXXX (1957), p. 115.

[44] Duncan, op. cit., p. 300.

reduction of spectrophotometric data is necessary if two objects have identical curves for given angular conditions of illumination and view.(45, 46)

Paint comparison in the forensic science field has been done utilizing reflectance data with the Beckman Model B. Spectrophotometer.[47] The instrument can handle a paint chip that is 3.2 by 4.8 millimeters (15.4 sq. millimeters), and can examine it in a wave length range from 350 millimicrons to 1000 millimicrons. In most instances the quantity of paint encountered is smaller than this and more often is nothing more than a smear.

IV. PURPOSE OF THE PAPER

In relation to color, the chief problem of the forensic scientist is the matching of colors. A procedure of matching colors from a collection of samples of various colored materials is unsatisfactory because of the inconsistency of the color of the sample due to aging.[48] Also, color sense varies with the individual and is influenced by other

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[45] Judd, op. cit., p. 94.

[46] W. F. Ulrich, F. Kelley, and D. C. Nelson, "Evaluation of Colorants by Spectrophotometric Methods," Paint Industry Magazine, LXXIV (1959) p. 15.

[47] J. F. Williams, "Examination of Paint Chips and Scrapings with the Spectral Photometer," Journal of Criminal Law, Criminology and Police Science, XXXXIV (1954), 647.

[48] "Reflectance Attachments Provide Data for Precise Calculation of Tristimulus Color Values," Beckman Application Data Sheet DK-78-MI. Beckman Instruments, Inc., Fullerton, California.

factors, such as the field surrounding the sample and the manner of observation.(49, 50) Color matching will vary too, with the quality of the light by which the comparison is made and the angle at which the samples are viewed with respect to the sample and illumination.[51] A method of objectively matching and specifying colors which overcomes the above problems involves the use of the spectrophotometer.(52, 53, 54)

The reflectance sphere on the Bausch and Lomb Spectronic 505 Recording Spectrophotometer is evaluated as a means of comparing and identifying minute paint chips and paint scrapings which may be encountered by the forensic scientist. Results of such tests could be used to supplement visual, microscopic, chemical and spectrographic examinations to show similarity or dissimilarity of color as well as composition.

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[49] Atherton and Tough, op. cit.

[50] E. A. Zahn, Scientific Paint Evaluation (Dayton, Ohio: Research Press, Inc., 1955), p. 265.

[51] E. I. Stearns, "Spectrophotometry and the Colorest," American Dyestuff Reporter, Vol. 33 (1944), p. 18.

[52] Duncan, op. cit., p. 300.

[53] Judd, op. cit., p. 82.

[54] Max Saltzman, "Color Matching via Pigment Identification," Dyestuffs, XXXXIII (1959), 57.

CHAPTER II

COLOR MEASUREMENT AND PAINT

I. COLOR MEASUREMENT

Substances are colored because of their selective absorption of white light. If absorption occurs uniformly at all wavelengths, the object appears to be gray or black. If the absorption is non-uniform, that is, if absorption is more pronounced at some wavelengths than at others, colors are perceived which are complimentary of those representative of the absorbed wavelengths.(1, 2)

The physical basis of color can be demonstrated by passing separate beams of white, red, green, and blue light through individual red, green, and blue filters. The red filter allows the red portion of the white beam and the red beam to be transmitted. The green filter allows the green portion of the white beam and the green beam to be transmitted. The blue filter allows the blue portion of the white beam and the blue beam to be transmitted. This may also be demonstrated by superpositioning yellow, magenta and cyan glasses which are employed in the printing of colored

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[1] W. F. Ulrich, F. Kelley and D. C. Nelson, "Evaluation of Colorants by Spectrophotometric Methods," Paint Industry Magazine, Vol. 74 (1959), p. 11.

[2] H. F. Payne, Organic Coating Technology (Volume II; New York: John Wiley & Sons, Inc., 1961), p. 695.

photographs. This phenomenon is illustrated in many articles.(3, 4)

Colored reflecting materials make selection from the spectrum in substantially the same manner. Colored materials rarely absorb or reflect all of any wave length that may fall upon them. The per cent reflectance for all wave lengths of the visible spectrum needs to be known for the measurement of the color of any object. The reflectance spectrophotometer is used for this purpose. The wavelengths of maxima and minima reflectances on spectrophotometric curves are highly characteristic of the materials of which the sample is composed. Such data on wavelengths is valuable for analysis and identification of paint specimens.

The visible spectrum is only a small part of the entire electromagnetic spectrum. It is the portion of the spectrum between 400 and 700 millimicrons. This is the portion of the spectrum for which the reflectance measurements in this report are made.

II. PAINT

Paint is defined in the ASTM Standards as "A pigmented liquid composition which is converted to an opaque solid film after application as a thin layer."[5] A pigment

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[3] Committee on Colorimetry, Optical Society of America, The Science of Color (New York: Thomas Y. Crowell Co., 1953), p. 220.

[4] W. D. Morgan, editor, The Encyclopedia of Photography (New York: Greystone Press, 1963), p. 802.

[5] A. S. T. M. Standards 1961. Part no. 8, Designation D16-59.

is defined as "The fine solid particles used in the preparation of paint, and substantially insoluble in the vehicle. The vehicle is the entire liquid portion of a paint which includes the pigment, binder or film-former, voltaile solvent, and anything that is dissolved in the liquid portion.[6]

Color and opacity in paints are imparted by the pigment, but it should also be noted that some pigments are not used to impart color or opacity but are merely extenders.

Pigmented paints are formulated from a wide variety of materials and have a broad range in usage. Consisting essentially of a pigment and vehicle, the paint's characteristics and functions are thus determined. Pigmented coatings include house paints, industrial automotive paints, red-lead paints, aluminum paints, colored lacquers, and water paints, as well as certain specialized products such as vinyl resin paints.

A wide variety of pigmented paints have been formulated to suit specific purposes. The vehicle that is most suitable for an outside wood paint is not desirable for an interior paint. Fade-resistant pigments are used in finish paints for machinery, while rust-inhibiting pigments are used in the priming paint. A gloss or semi-gloss paint is needed for walls and woodwork in kitchens, because of better washability, but a flat finish is usually desired for living room walls.

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[6] Payne, _op_. _cit_., p. 677.

Pigments may be classified as natural and synthetic and in each of these groups there are organic and inorganic types. There are hundreds of different types and makes, some of which will be described.(7, 8, 9)

Lead and zinc are terms frequently applied to paint pigments. In usage, they do not necessarily denote pulverized metals, but chemical compounds of the metals, such as lead carbonate, lead sulfate and zinc oxide. White lead is either basic lead carbonate or basic lead sulfate, or a combination of the two. Red lead, which is used in metal priming paint, is one of the lead oxides. Titanium indicates a pigment containing titanium dioxide and lithopone contains zinc sulfide.

These are all inorganic pigments, as are prussian blue, chrome green, zinc yellow, and the siennas, umbers and ochres. Synthetic organic pigments include the toluidines in reds and yellows, and the phthalocyanines in blues and greens.

Originally pigments were employed solely to impart color but now they are recognized as influencing many other properties of paint. Pigments are mixed to achieve different colors. Also to be considered are their effects on

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[7] Paint Manual. United States Department of the Interior, U. S. Government Printing Office, 1961, 2nd Ed.

[8] H. Gaertner, "Modern Chemistry of Organic Pigments," Journal of the Oil and Colour Chemists' Association, XXXXVI (1963), p. 14.

[9] George L. Clark, Editor, The Encyclopedia of Spectroscopy, (New York: Reinhold Publishing Corporation, 1960), p. 516.

hiding power, settling, workability, stability after exposure and ability to protect organic vehicle binders from the damaging rays of sunlight.

Most pigmented paints contain mineral fillers known as extenders. These are white or colorless pigments of low opacity. They contribute little to hiding power but because they are generally high in oil absorption properties, they act to minimize settling of pigments. They help control gloss and working consistency. Extenders used are magnesium silicate, barium sulfate, blanc fixe, barium carbonate, kaolin, calcium carbonate, diatomaceous silica and mica.

The amount of pigment in paint varies from as low as 10 per cent by weight in some vinyl resin paints to 80 per cent in some red-lead-in-oil-paints. House paints contain from 60 to 70 per cent pigment. The pigment content influences the gloss or shine of a dried paint film. Generally, the lower the pigment content, the higher the gloss.

The vehicle portion of the paint contains both volatile and non-volatile constituents, and is actually the film-forming part of paint. The volatile constituent facilitates the application and drying of the paint, but has no permanent part in the dried paint film. The non-volatile constituent is the binder, being an integral part of the paint film which binds the pigment particles together and insures adhesion of the film to a surface. The non-volatiles are substances such as linseed oil, vinyl resin, alkyd resin, nitrocellulose, and the synthetic resins of phenolic, epoxy, chlorinated rubber and various hydrocaron polymers.

CHAPTER III

THE SPECTROPHOTOMETER IN COLOR MEASUREMENT

I. THE SPECTROPHOTOMETER

The Spectrophotometer provides a precise measurement of the absorption or reflectance process at different wavelengths and can be employed to determine which portions of white light are absorbed by a substance and to what extent. In many instances it serves as a replacement for the human eye. It is valuable in the elimination of errors caused by the differing color responses of the human eye in various individuals. This instrument also detects metamerism and can perform a precise comparison faster than the human eye.[1]

The Spectrophotometer has several advantages over a colorimeter, which can also be used to measure reflectance. The essential difference between colorimetric and spectrophotometric measurement of color is the number of divisions into which the spectrum is divided when making reflectance or transmission measurements. Instead of three broad regions covered by the blue, green, and amber filters, the Spectrophotometer uses narrow bands over the entire visible spectrum.[2] The sample may be scanned in a few minutes and

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[1] W. F. Ulrich, F. Kelley and D. C. Nelson, "Evaluation of Colorants by Spectrophotometric Methods," _Paint Industry Magazine_, Vol. 74 (1959), p. 12.

[2] H. F. Payne, _Organic Coating Technology_ (Vol. II; New York; John Wiley & Sons, Inc., 1961), p. 695.

a permanent reflectance spectrum recorded on a chart when a recorder is attached to the spectrophotometer.

The essential parts of the Spectrophotometer include a light source, a prism or a grating to produce successive wave bands, a standard reflecting surface, and a receptor. These will be covered in more detail in the following discussion of the Spectronic 505.

II. THE BAUSCH AND LOMB SPECTRONIC 505 RECORDING SPECTROPHOTOMETER

The Bausch and Lomb Spectronic 505 Recording Spectrophotometer is capable of automatically recording spectra in the ultraviolet and visible wave lengths. When a reflectance sphere is attached to the instrument, it is limited to a wave length range of 400 to 700 millimicrons. The Spectronic 505 with reflectance sphere as employed in this study is shown in Figure 1. The Optical Schematic is illustrated in Figure 2.

The Spectronic 505 employs a light from a standard tungsten source (Source C) which is described in Section V. The beam is passed through a monochromator which uses two gratings and two sets of fixed slits set at five millimicrons. The beam then passes into a beam splitter. This provides two separate light paths, one for the sample and one for the reference. The beams pass into the reflectance sphere, one beam reflecting off the sample and one beam off the standard reference. The reflectance sphere is provided with two light traps set on the sides of the sphere. These

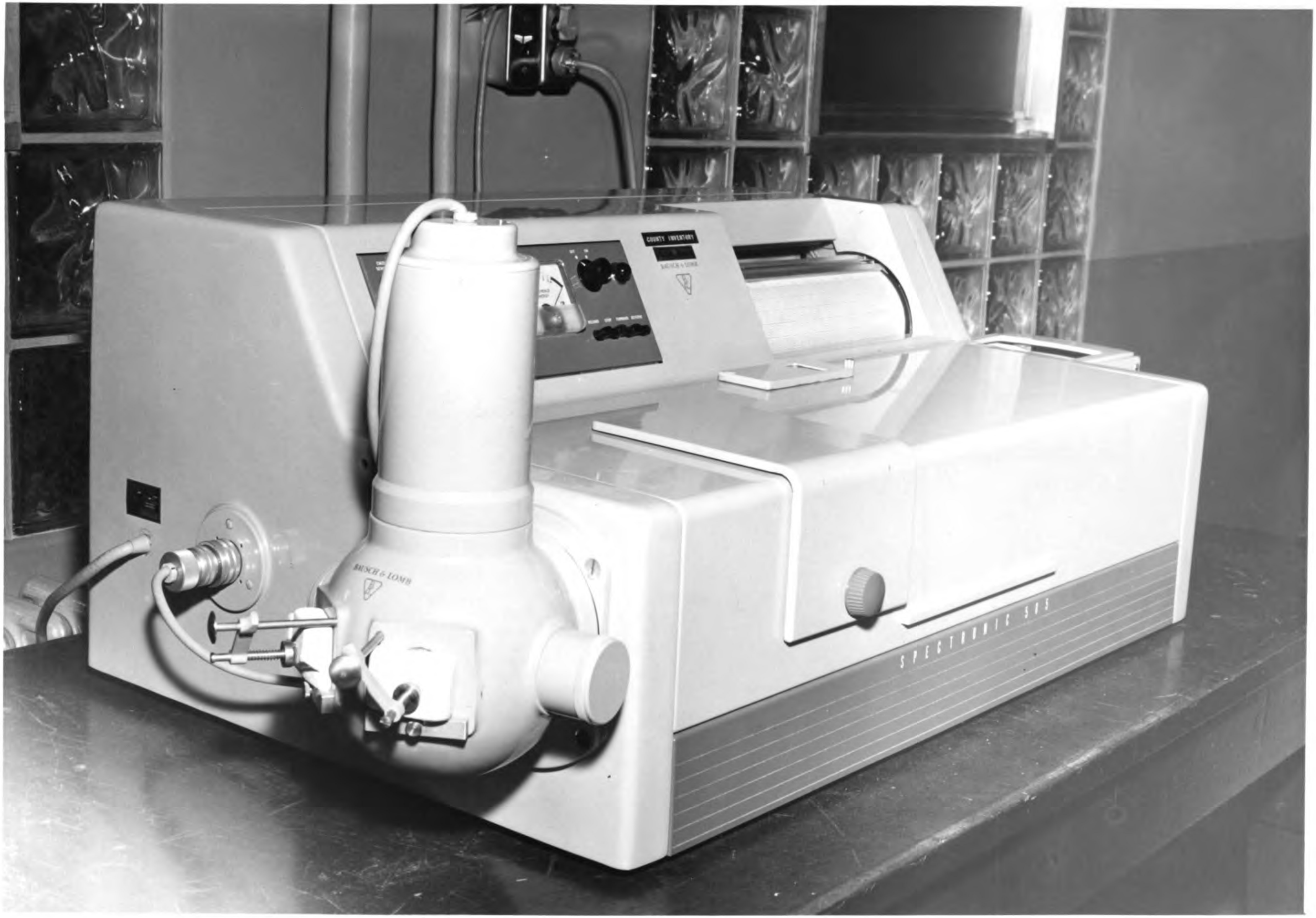

FIGURE I. THE BAUSCH & LOMB SPECTRONIC 505 RECORDING SPECTROPHOTOMETER

SPECTRONIC 505 OPTICAL SCHEMATIC WITH REFLECTANCE SPHERE

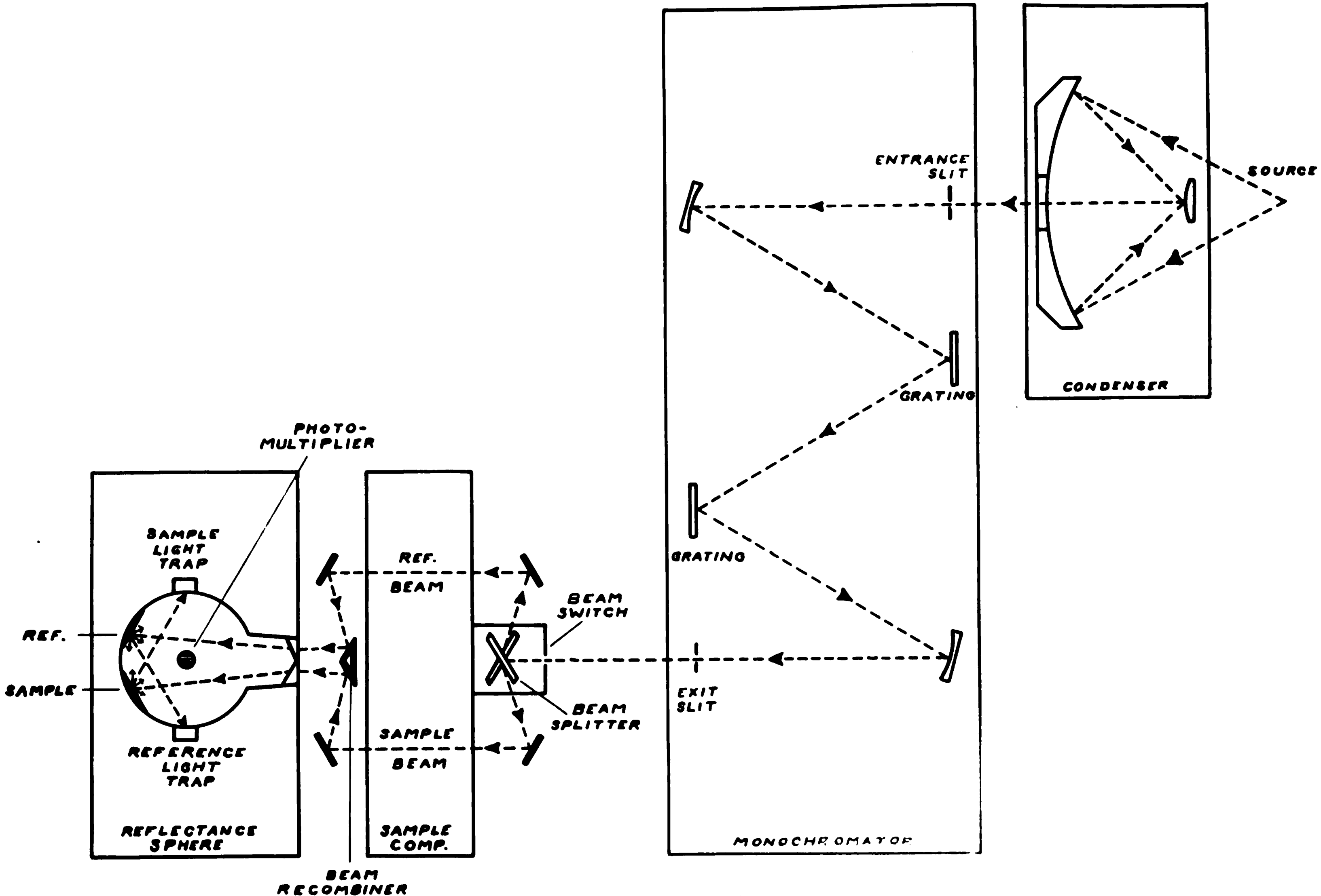

FIGURE 2

can be positioned to either remove or retain the specularly reflected components. The incident light beam has a size approximately 16 x 19 millimeters (304 square millimeters).[3] The interior of the sphere is covered with a white reflectance coating of barium sulfate. Barium sulfate was selected because of its even whiteness across the spectrum and for its excellent durability.[4] The spectral reflectance curve of a given sample is the ratio of the light reflected from the sample to that reflected by a white standard over the wave length range of interest.[5] A photo multiplier is mounted in the top of the reflectance sphere to detect the differences in the ratio of the light reflected. In the mode of irradiation employed with the Spectronic 505, beams are received simultaneously from the sample and the standard and compared directly. The system employs a sphere in which the sample and the standard simultaneously occupy openings in it. The alternately flickering beams permit the use of the same collection system for both the sample and the standard, thus fulfilling the requirement of equivalence. Reflectance spectral curves are recorded in the same manner as transmittance spectral curves.

III. REFLECTANCE MEASUREMENTS

A beam of light falling on an object is split into

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[3] Correspondence with Bausch and Lomb, Inc., Rochester 2, New York.

[4] Bausch and Lomb Bulletin on Specifications D-2009, 0263.

[5] J. D. Keller, Fundamentals of Spectrophotometry (Bausch and Lomb Booklet No. 1), p. 19.

three parts. Some of the light is reflected, some absorbed, and the balance transmitted.

Figure 3 indicates the beams of incidence (1), reflection (2), and transmission (4), and the portion of the beam absorbed (3) by a plate of glass.

For an opaque mat object the quantity to be measured is spectral reflectance--the ratio of reflected to incident flux for one part of the spectrum. All diffusing materials fail to be perfectly mat, that is, they exhibit more or less gloss. Part of the light incident on the surface is reflected in some more or less good approximation of an image-forming state. The remainder penetrates the surface, and, after suffering absorption, scattering, and multiple reflection beneath the surface, is re-emitted in a nearly diffused state.

Reflected light may be concentrated at an angle numerically equal to the angle of incidence, or scattered uniformly in all directions, or distributed between two extremes.[6] The extreme states are specular (mirror) illustrated in Figure 4-A and diffused illustrated in Figure 4-B. Specular reflection is produced by polished silver, while diffused reflection is produced by magnesium oxide (the smoke of burning magnesium deposited on a smooth surface). Figure 4-C illustrates part of the light reflected specularly

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[6] H. A. Gardner and G. G. Sward, Paint, Varnishes, Lacquers, and Colors (twelfth edition; Bethesda, Maryland: Gardner Laboratories, Inc., 1962), p. 25.

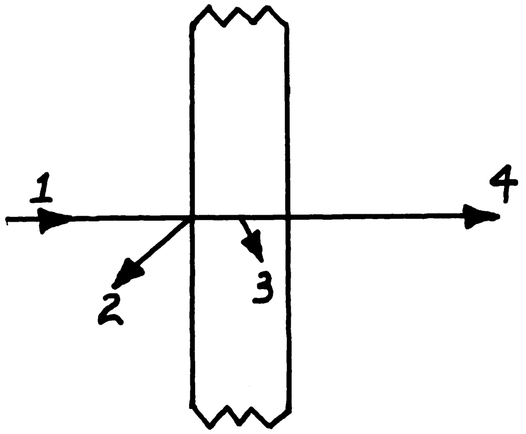
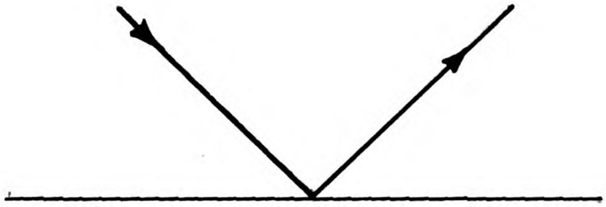


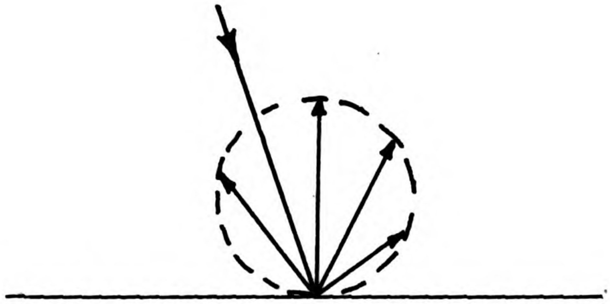
FIGURE 3

EFFECTS UPON A BEAM OF LIGHT

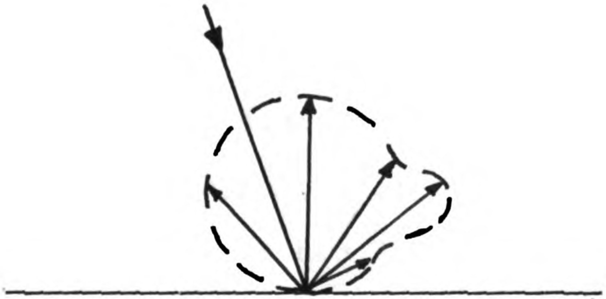
PASSING INTO A PLATE OF GLASS



A. Specularly Reflected--mirror



B. Diffused reflection uniformly--MgO



C. Part of light reflected specularly and part diffused--many paint surfaces

FIGURE 4

DIFFUSE REFLECTION TYPES

and part diffused as occurs on many paint surfaces.

The surface flux must be separated from the flux re-emitted from the body of the object. This may be done by illuminating the surface with essentially unidirectional light (at 45°) and viewing it along directions nearly perpendicular to the surface. Thus the viewing is separated by many degrees from the angle of mirror reflection. This is the recommendation of the International Commission on Illumination (I. C. I., 1931), and has been set up as a standard method.[7] It does not matter if the illuminating and viewing directions are interchanged. The standard in this method is not the incident flux, but instead the flux reflected by the ideal perfectly diffusing, perfectly reflecting surface illuminated and viewed along the same directions and to the same extent as the specimen. The ratio of these two fluxes is called directional reflectance.

Thus far the discussion has been limited to perfectly diffused reflection. This type of reflection is defined as that described by Lambert's Law.[8] The flux reflected per unit solid angle is proportional to the cosine of the angle measured from the normal to the surface. Since the projected area varies inversely as the cosine of this angle, the radiance of a perfect diffuser is independent of the viewing angle.

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[7] A. S. T. M. Standards 1961, Part No. 8, Designation D97-55.

[8] Committee on Colorimetry, Optical Society of America, The Science of Color (New York: Thomas Y. Crowell Co., 1953), p. 178.

The above case is ideal and may be demonstrated with a magnesium oxide reference standard. Actually, reflection at a painted surface is always partly specular and partly diffused (Figure 4-C), and in general the specification of the behavior of reflecting surfaces requires the measurement and statement of reflectance for several conditions of irradiation and collection.

Although conditions as recommended by the International Commission on Illumination and A. S. T. M. D-97-55 are desirable in principle, and have been employed, such conditions have not proved to be practical for spectrophotometers because of the relative inefficiency of the optical systems designed in accordance with the specifications.[9]

It has been found that if an incident beam employed is normal to the surface of the sample, over 99 per cent of the diffusely reflected energy is collected with uniform efficiency. Unfortunately, some indefinite fraction of specularly reflected energy is also collected. This indefiniteness is serious, however, only when glossy samples are measured. The indefiniteness is remedied by a modification of the collecting sphere.(10, 11) The modification employed in the Spectronic 505 is such that the incident light strikes

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[9] Ibid., p. 218.

[10] A. S. T. M. Standards 1961, Part No. 8, Designation D307-44.

[11] A. S. T. M. Standards 1961, Part No. 9, Designation D791-61T.

the sample at 25 degrees from the normal. The specularly reflected energy can be completely collected or completely eliminated by replacing with a light trap the position of the sphere wall on which the specularly reflected beam is incident.

IV. REFLECTANCE STANDARD

Magnesium oxide is not only an almost perfect diffuser, but is also the most diffused reflector that can be reproduced. The surface of magnesium oxide, prepared as described above, is a widely used and recommended standard.[12]

The problem with the magnesium oxide standard is that it is time-consuming to prepare and easily damaged. Magnesium Carbonate is another commonly used standard.(13, 14) It is a non-selective white which is convenient to use in compressed block form. It is necessary to clean the reflecting surface regularly. It has a slight preferential absorption in the blue region, but if it is used routinely as a standard, this presents no problem.

V. STANDARD ILLUMINANTS

Since the quality of the light transmitted or absorbed

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[12] A. S. T. M. Standards 1961, Part No. 8, Designation D986-50.

[13] A. J. Seavell, "Colorimetry in Paint Industry," Journal of the Oil and Colour Chemists' Association, XXXX (1957), 87.

[14] A. S. T. M. Standards 1961, Part No. 9, Designation D791-61T.

by a substance varies with the illuminant, it is important that a standard illuminant be used. The International Commission on Illumination designated three standard illuminants.[15] Source A is incandescent light, source B is noon sunlight, and source C approximates average daylight. Source C is normally used in spectrophotometers. Tables are available which list the relative spectral energy of each source.[16] If one desires to specify a color by trichromatic coefficients this may be done by multiplying the reflectance by relative spectral energy at a given wave length which, in turn, is multiplied by the tristimulus value at that wave length. Tables are available which list the relative spectral energy times the tristimulus value at selected wave lengths.(17, 18, 19) All that is needed is the reflectance of the sample at the given wave length. The procedure is still time consuming. Bausch and Lomb, Inc. has prepared a form which simplifies the specification of a color by trichromatic coefficients.[20] It is not within the scope of this thesis to calculate the tristimulus color values of the spectrophotometric data acquired.

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[15] A. S. T. M. Standards 1961, Part No. 8, Designation D307-44.

[16] Ibid.

[17] D. Judd, Color in Science, Business, and Industry (New York: John Wiley & Sons, Inc., 1952), pp. 108-120.

[18] M. G. Mellon, Colorimetry for Chemists (The G. Frederick Smith Chem. Co., 1945), pp. 106-109.

[19] "Reflectance Attachments Provide Data for Precise Calculation of Tristimulus Color Values," Beckman Application Data Sheet, DK-78-MI.

[20] Bausch and Lomb Trichromatic Coefficient Computing Form for Illuminant C, Catalog No. 33-29-12.

VI. THEORY OF REFLECTANCE MEASUREMENTS

The use of transmission spectra for identification and quantitative determination of substances in solution is now a common analytical method and involves the use of Beer-Lambert laws, which have been known for over a hundred years and are simple to apply.

The use of reflectance spectra for identification and determination of pigments in pigmented compositions involves the use of more complicated laws which have been known for only about twenty years.

Schuster[21] showed that the optical properties of scattering materials could be expressed in terms of two parameters, the coefficient of absorption (α), and the coefficient of scatter (δ), which were independent of thickness of a layer but varied with the wave length of light.

While Schuster was interested mainly in the visibility of astronomical bodies and that of terrestrial objects through fogs, the expressions that he deduced are of general applicability to scattering materials, although very complicated mathematically.

Kubelka and Munk[22] set up an equation based on Schuster's work to predict the manner in which the transmittance and reflectance of materials such as paint, varied

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[21] K. Schuster, "Radiation from Self-luminous Foggy Atmosphere of a Star," Astrophysics Journal, XXI (1905), 1.

[22] P. Kubelka and T. Munk, "Opacity of Translucent Materials," Z. Tech. Physics, XII (1931), 593.

with thickness.

The radiation reflected by paint consists of two components: a diffused part, the radiation penetrating into the interior of the layer and re-emerging to the surface after being scattered many times, and a regular part arising from the reflection at the surface of the paint.

The Kubelka-Munk expression thus derived is:

$$R_\infty = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{\alpha}{\delta}$$

where R_∞ is the relative spectral diffuse power of reflection. Since the scattering coefficient (δ) turns out to be nearly independent of the wavelength, the expression becomes:

$$\begin{aligned} \log (R_\infty) &= \log\alpha + \text{constant} \\ &= \log E + \log C + \text{constant} \end{aligned}$$

with E being the extinction coefficient and C the concentration.

If the log (R_∞) is plotted against the wavelength, the color curve of the specimen is obtained which coincides with the true absorption spectrum except for the additive constant.[23]

This relation can be applied to fine-grained light absorption powders when diluted in appropriate standardized substances like magnesium oxide or barium sulfate.[24]

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[23] G. Kortum, "Diffuse Reflectance Spectra of Mercuric Iodide on Different Adsorbents," Transactions of the Faraday Society, Vol. 58 (1962), p. 1626.

[24] G. Kortum and G. Schreyer, "Validity of the Kubelka-Munk function for reflection spectra with powders," Z. Mateerforsch, Vol. 114 (1957), p. 1018.

Duncan[25] has shown that the coefficient of absorption of a pigmented system could be treated as a simple additive function of coefficients of absorption assigned to the constituent pigments, and similarly that the coefficient of scatter of the system was the sum of the coefficients of scatter of these pigments, weighted in each case in accordance with the proportion of each pigment present. The expression deduced for the reflectance (R) of a paint film of hiding thickness is

$$\Theta = \frac{(a\alpha A + b\alpha B + c\alpha C + \cdots)}{(a\delta A + b\delta B + c\delta C + \cdots)}$$

where $\Theta = \frac{(1-R)^2}{2R}$ which also may be written $R/2 + 1/2R - 1$. R is expressed as a fraction of the light reflected under the same conditions by a perfect diffuse reflector. "a" is the concentration of a pigment A, "b" is the concentration of a pigment B, and so forth.

The direct use of reflectance curves for the qualitative identification of pigments is mainly of value with compositions containing no white pigment. If only one pigment is present, and it is not too dark in color, the form of the reflectance curve often serves to identify it or to indicate that it is one of a very limited range of pigments which then may be distinguished by chemical tests.

In most situations the presence of other pigments

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[25] C. R. Duncan, "The Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry," Journal of the Oil and Colour Chemists' Association, XXXXV (1962), 300.

modifies the reflectance curves. It may still be possible to recognize sufficient characteristics to identify a pigment from inspection of reflectance curves.

Many paints are based on white pigments tinted with colored pigments or yellow pigments tinted with small proportions of dark pigments.

Duncan has applied the use of Θ (theta) curves rather than the reflectance curves for identification. By application of the Θ curve method to a reflectance curve of white pigment (lithopone) tinted with the pigment or paint in question an identification of the pigments present is possible.[26]

Lermond and Rogers[27] examined mixtures of colored solids by differential spectrophotometric measurements. Their study consisted of adding adulterants such as ferric oxide, cupric oxide, and barium chromate, to barium sulfate and comparing this reflectance against magnesium carbonate and against barium sulfate with one or two of the adulterants present. Qualitative detection of substances by this method was limited without interpretation of the effects of the base material, barium sulfate, on the spectrum. The authors did find that the method was good for quantitative analysis by plotting the data using the log of concentration

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[26] Ibid., p. 306.

[27] C. A. Lermond and L. B. Rogers, "Differential Measurements of Reflectance," Analytical Chemistry, Vol 27 (1955), p. 341.

versus $(I-R)^2/2R$.[28]

Duncan,[29] Ulrich,[30] Lermond and Rogers,[31] and Judd[32] state that the spectrophotometric reflectance curves can be used for comparison purposes if the specimens being examined are treated in a like manner.

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[28] *Ibid*., p. 345.

[29] Duncan, *op. cit*., p. 306.

[30] Ulrich, *et al*., *op. cit*., p. 15.

[31] Lermond and Rogers, *op. cit*., p. 344.

[32] Judd, *op. cit*., p. 94.

CHAPTER IV

EXPERIMENTATION

I. INTRODUCTION

The size of the paint specimen received by the forensic science laboratory often dictates the type of examination to be made. Instruments are now available to compare specimens which heretofore were too minute to be compared successfully by microscopic and wet chemical means.

With these thoughts in mind, the use of the reflectance sphere on the Bausch and Lomb Spectronic 505 Recording Spectrophotometer is evaluated as one of the methods for comparison of paint specimens in the 400 to 700 millimicrons wavelength region. The sample opening of the reflectance sphere is 30 millimeters in diameter, but the illuminating beam at the opening is approximately 16 x 19 millimeters (304 square millimeters).[1] Since a sample size of 16 x 19 millimeters is impractical in this type of examination, an investigation was made to determine just what sample size could be adequately analyzed with the reflectance sphere.

II. REFLECTANCE EXAMINATION OF PAINT CHIPS

A total of 18 paint chip specimens removed from nine automobiles listed in Table I were examined in the reflectance

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[1] Correspondence with Bausch and Lomb, Inc., Rochester 2, New York.

TABLE I

AUTOMOBILE PAINT CHIPS EXAMINED

Specimen	Make of Automobile	Year	Location Removed	Manufacture Color Designation
1a	Ford	1963	Hood	Rangoon Red
1b	Ford	1963	Right front fender	
2a	Dodge	1961	Hood	Vermilion
2b	Dodge	1961	Left front fender	
3a	Chevrolet	1961	Right front fender	Honduras Maroon Metallic
3b	Chevrolet	1961	Right front door	
4a	Chevrolet	1961	Right front fender	Seafoam Green
4b	Chevrolet	1961	Hood	
5a	Ford	1962	Hood	Oxford Blue Metallic
5b	Ford	1962	Left front fender	
6a	Chrysler	1963	Right front fender	Holiday Turquoise Metallic
6b	Chrysler	1963	Hood	
7a	Ford	1963	Hood	Acapulco Blue Metallic
7b	Ford	1963	Left front fender	
8a	Chevrolet	1963	Right rear fender	Monoco Blue Metallic
8b	Chevrolet	1963	Left front door	
9a	Buick	1962	Right rear trunk	Cadet Blue Metallic
9b	Buick	1962	Right rear fender	

sphere. These chips were mounted on white card stock with double stick Scotch Brand tape. White card stock with the same area size double stick Scotch Brand tape was used in the reference beam. The purpose of this procedure was to determine what size of paint sample would provide sufficient area for the illuminating beam to produce a reflectance curve which would give valid data. Graphs 1 and 2 serve to illustrate a portion of the results of the examination.

Graph 1 illustrates the reflectance curves of a Rangoon Red paint specimen of varying area coverage (6 square millimeters to 225 square millimeters) removed from a 1963 Ford. It has been found that for reflectance curves to be of value, the curves should lie between the 10 and 90 percentile.[2] Curves 5 and 6, representing an area of 45 and 80 square millimeters respectively, fall in this range. Curve 7 represents an area of 225 square millimeters. From the information on this graph, it appears that a specimen filling the illuminating beam in excess of 30 square millimeters would be required to receive valid data from reflectance curves.

Graph 2 illustrates the reflectance curves of an Oxford Blue Metallic paint specimen, of varying area coverage (3 square millimeters to 225 square millimeters), removed from a 1962 Ford. All but the specimen in curve 5 were taken from the left front fender of the automobile, specimen 5 was

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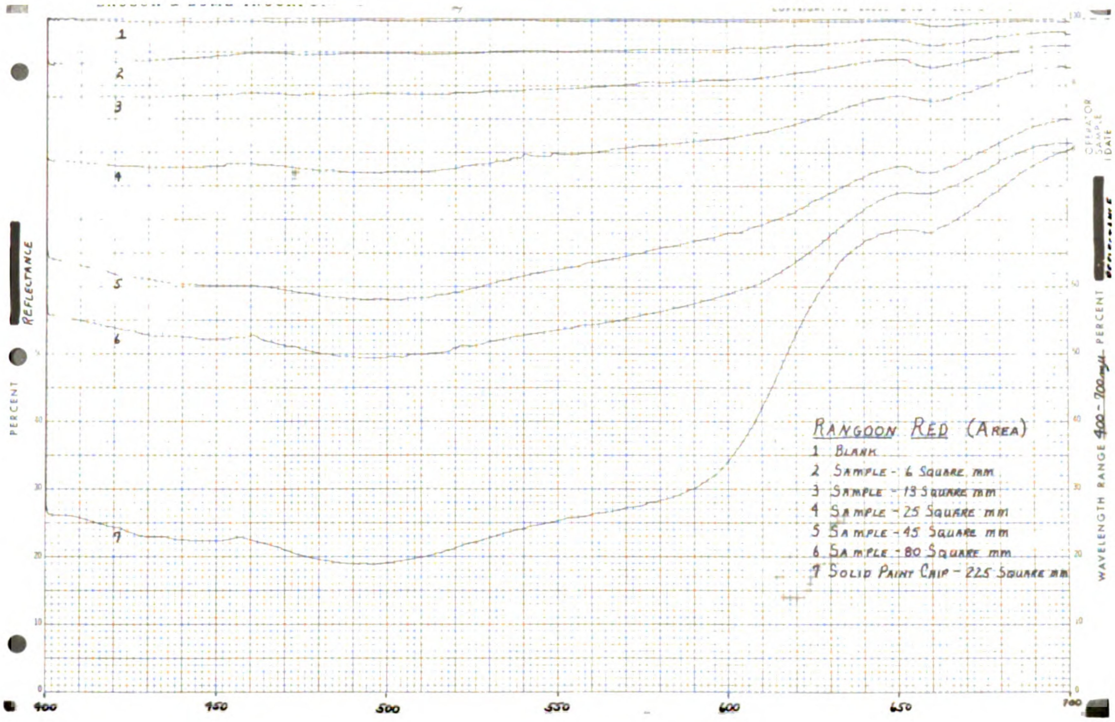
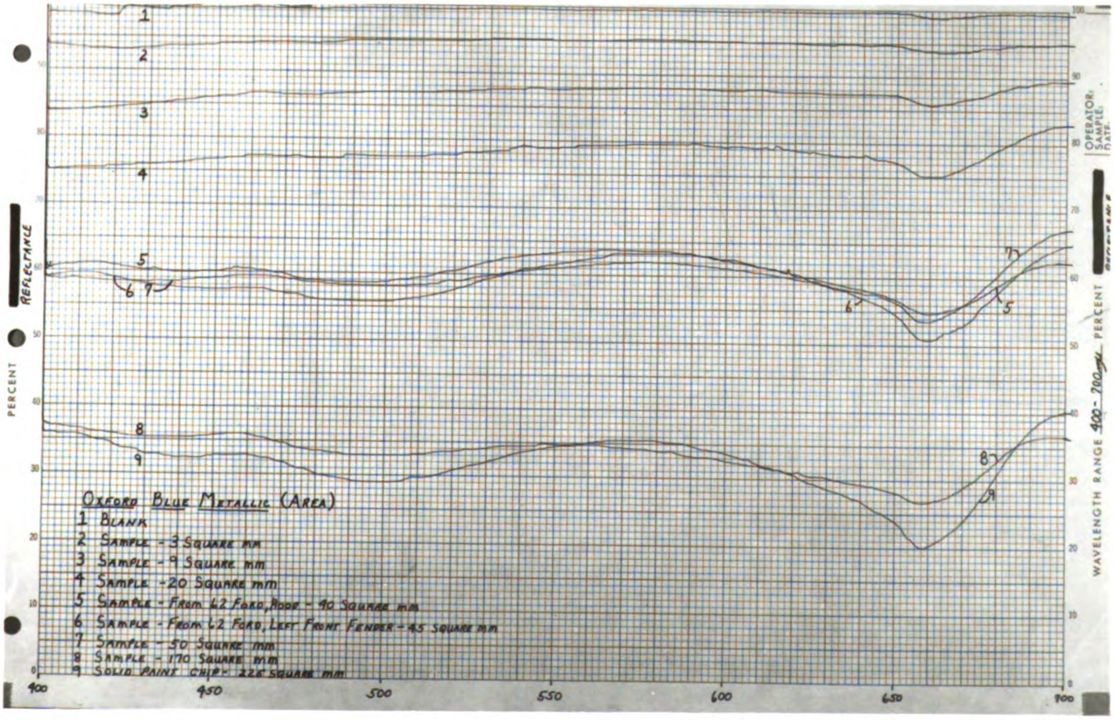
[2] M. G. Mellon, <u>Colorimetry for Chemists</u> (Columbus: The G. Frederick Smith Chemical Company, 1945), p. 115.



GRAPH I



GRAPH 2

taken from the hood. Curves 5, 6 and 7 are for 40, 45 and 50 square millimeter samples. A slight minimum between 470 and 520 millimicrons as well as the maximum between 520 and 610 millimicrons is not present in curve 4 for the 20 square millimeter sample. Though curve 4 as well as curve 3, for a 9 square millimeter sample, reflect less than 90 per cent of the illuminating beam, no valid data is present. Thus a specimen which would fill the illuminating beam in excess of 30 square millimeters would be required here also.

The solid paint chips used in Graphs 1 and 2 were whole chips cut to fill the illumination beam with 225 square millimeters of solid specimen while the samples were small chips placed on the adhesive portion of the tape to fill the illuminating beam to the areas indicated. The small spacings between each paint chip would have the effect of varying particle size resulting in deviations of the reflectance curves.[3]

Inspections of these reflectance curves as well as the other 14 paint specimen reflectance curves thus examined, revealed that when the illuminating beam area was covered with 40 square millimeters of paint specimen in the Bausch and Lomb Spectronic 505 Reflectance Sphere, valid curves for comparison purposes were received.

As a 40 square millimeter specimen of paint is rarely encountered in the Forensic Science laboratory, an

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[3] C. A. Lermond and L. B. Rogers, "Differential Measurements of Reflectance," Analytical Chemistry, Vol. 27 (1955), p. 346.

investigation was made to determine just what specimen size could be adequately analyzed with the reflectance sphere by diluting the specimen with a white pigment to cover a larger area of the illuminating beam in the reflectance sphere and thus obtain reflectance curves suitable for comparison.

III. SAMPLE PREPARATION

In this examination pure pigment smears were prepared using the pigment and linseed oil to determine the optimum area to be examined by the illuminating beam. The pure pigments used were secured from a pigment manufacturer and are those used in the manufacture of commercial paints.

A simple technique for preparation of small uniform paint smears was used.[4] This consisted of placing a piece of adhesive latex tape on a one inch by three inch glass slide, and cutting out a window of the desired size. The pigment-linseed oil mix was then spread out by drawing a glass slide over the window at a 45 degree angle. The angle, the speed of drawing, and the number of times the slide was drawn across was kept constant. After drying, the tape was removed from the slide, leaving the pigment film.

To prepare the pigment for this operation, fifty milligrams of pigment were placed in a mortar and moistened

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[4] H. Barnes and E. T. White, "A Simple and Inexpensive Technique for the Preparation of Small Uniform Areas of Paint Films of Graded Thickness," _Journal of Oil and Colour Chemists' Association_, XXXI (1948), 470.

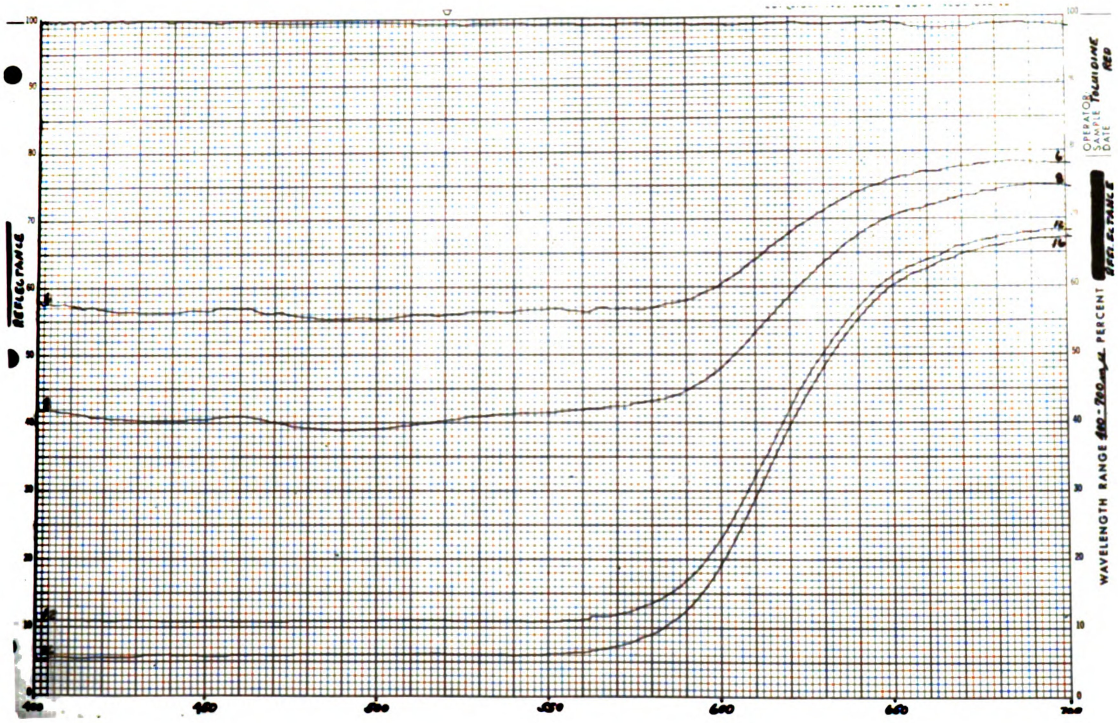
with sufficient linseed oil to make a blend mobile enough to smear. The amount of linseed oil varied with each pigment because some pigments required more to moisten them. However, each in the series of smears for a particular pigment-linseed oil mix was of the same concentration because each series was prepared from one batch of mix.

Enough of this mix was used in each window to cover it with a dried film 0.11 millimeters thick.

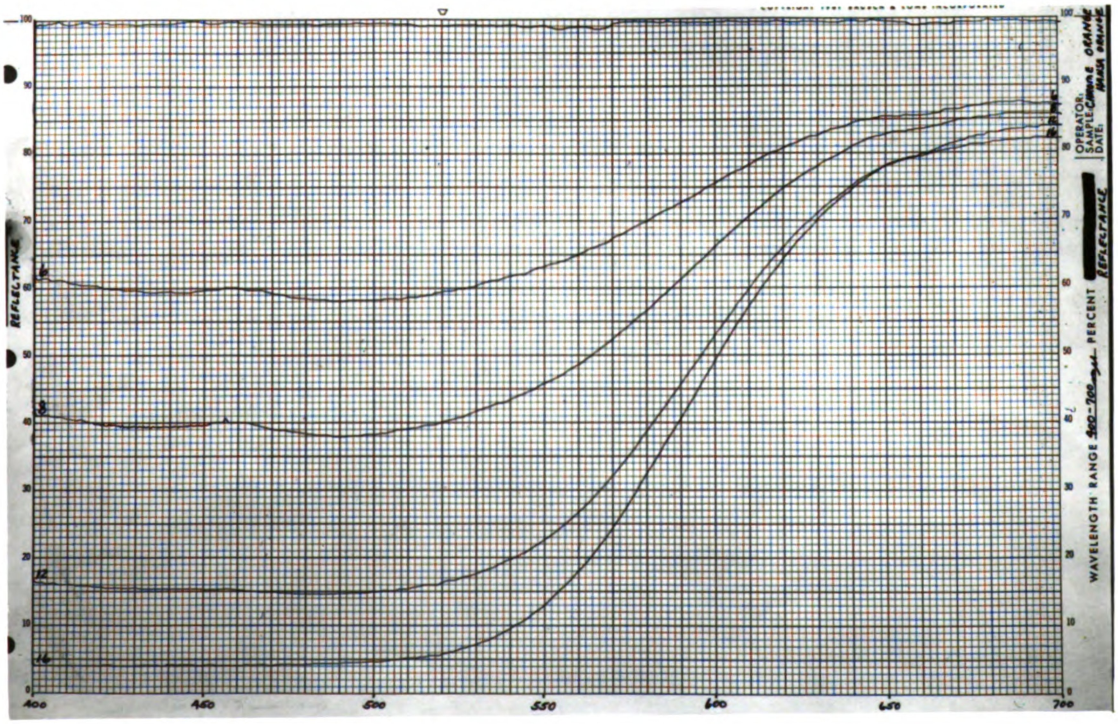
Five pigments were examined in this manner using a window size of 6 millimeters square, 8 millimeters square, 12 millimeters square, and 16 millimeters square. The reference used in this series was a block of magnesium carbonate. The background used behind the pigment smear on the glass slide was also a block of magnesium carbonate. The results are illustrated in Graphs 3 through 7. In all five cases there was considerable difference in the per cent reflectance between the 12 and 8 millimeter sized windows.

The increased difference in reflectance between the 12 and 8 millimeter sized windows was caused by the increased area of specimen being illuminated by the beam. The per cent reflectance increased when the specimen size was smaller than 12 millimeters square because of the increased blank area (reference) being illuminated behind the specimen. Because of this, a 12 millimeters square (144 square millimeters) specimen area was chosen as the size for preparing diluted samples to be compared.

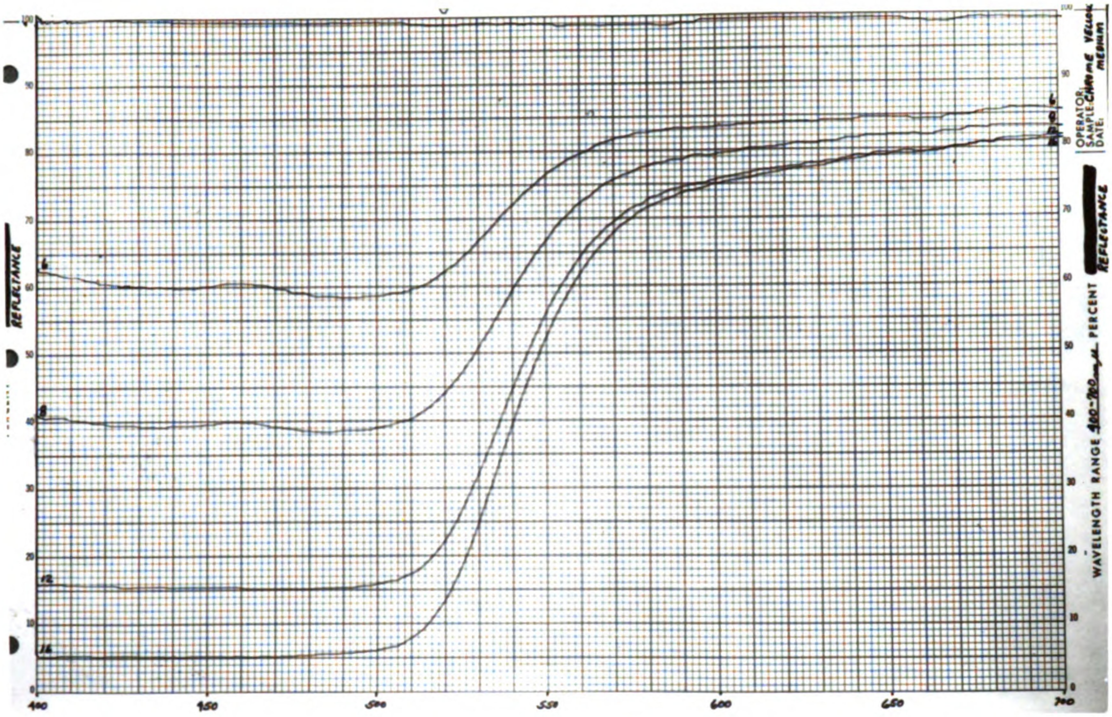
Of interest also was whether a white or a black



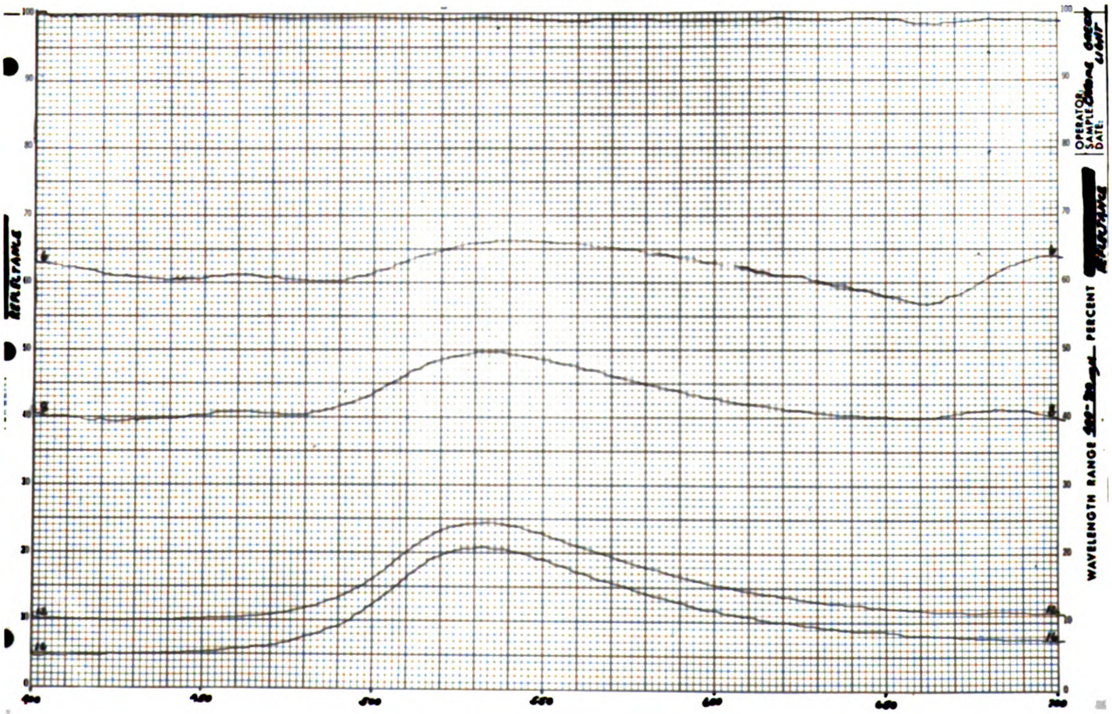
GRAPH 3



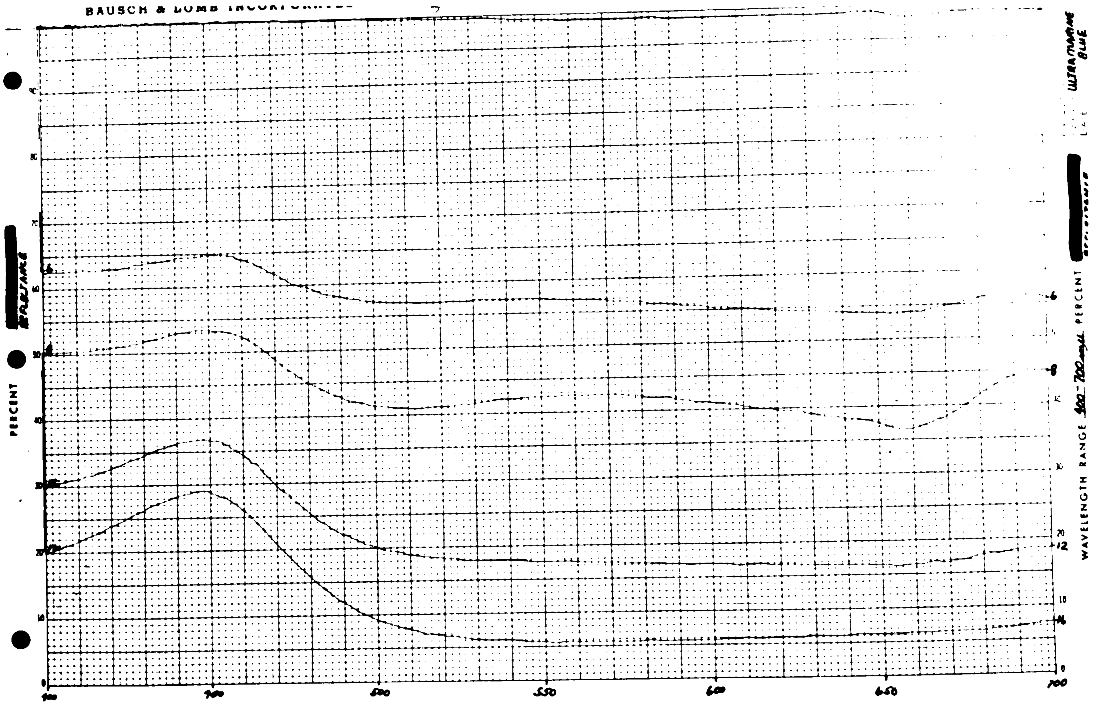
GRAPH 4



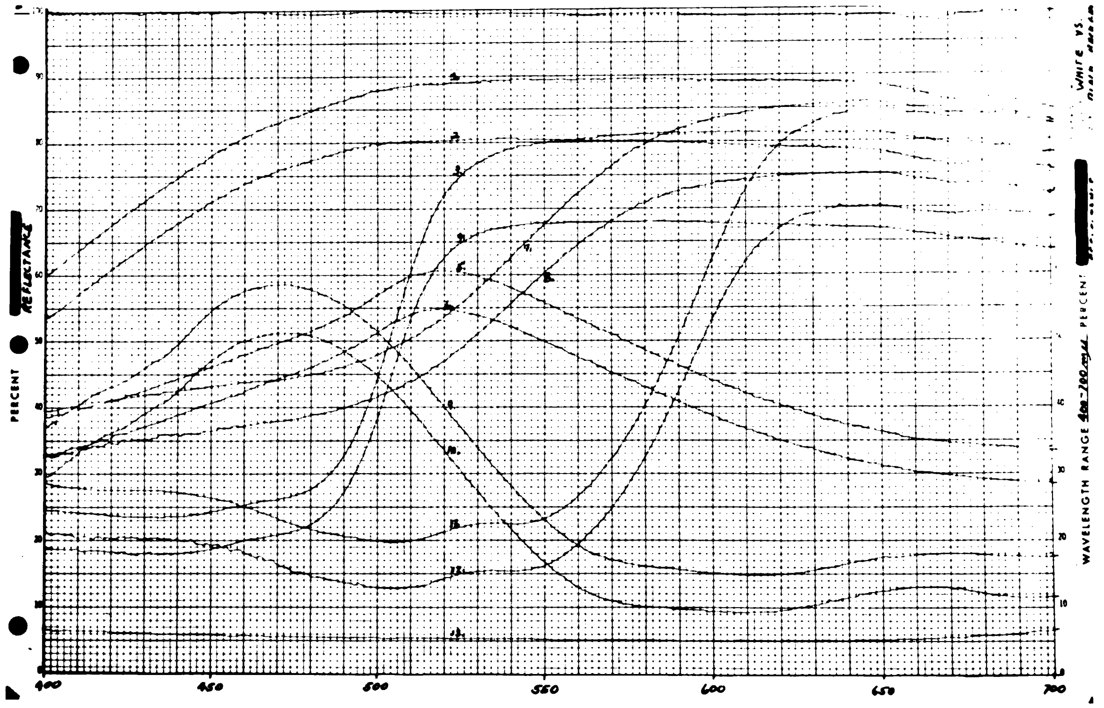
GRAPH 5



GRAPH 6



GRAPH 7



GRAPH 8

backing behind the sample would have any appreciable effect on the reflectance curve. Studies of this nature had been made using the G. E. Spectrophotometer,[5] and since the Spectronic 505 employs a different angle of illumination, the effect was examined with this instrument using a specimen size of 12 millimeters square. The excess of the illuminating beam not striking the specimen thus struck the black or white background.

Graph 8 illustrates the effect of the specimens as designated in Table II. The black backing employed gave a five per cent reduction in the reflectance curve.

According to Kelly, Gibson and Nickerson, the effect of black or white backing is noticeable at wave lengths greater than 550 millimicrons and reflectance greater than 60 to 65 per cent.[6] The differences observed are those shown in curves 3, 4, 7, 8, 11 and 12. No differences were observed in curves 5 and 6, 9 and 10, because they showed below 60 per cent reflectance between 400 and 700 millimicrons.

Graph 8 also illustrates that the lithopone-linseed oil blank has some absorption, particularly in the blue range (Curves 1 and 2). The absorption is apparently caused by the linseed oil which imparts a slight yellow

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[5] K. L. Kelly, K. Gibson and D. Nickerson, "Tristimulus Specification of the Munsell Book of Color from Spectrophotometric Measurements," _Journal of the Optical Society of America_, XXXIII (1943), 355.

[6] _Ibid_., p. 374.

TABLE II

WHITE VERSUS BLACK BACKING*

Spectice Number	Background	
1	White	lithopone-linseed oil blank
2	Black	lithopone-linseed oil blank
3	White	Toluidine Yellow
4	Black	Toluidine Yellow
5	White	Chrome Green, Medium
6	Black	Chrome Green, Medium
7	White	Chrome Orange
8	Black	Chrome Orange
9	White	Phthalo Blue G
10	Black	Phthalo Blue G
11	White	Toluidine Red
12	Black	Toluidine Red
13	Black background versus magnesium carbonate reference	

*The effects of white versus black backing upon the reflectance curves. The specimens are prepared by mixing one per cent of the pure pigment with lithopone and using linseed oil as the vehicle.

color to the mix. No correction was made for it in the reference window for this portion of the study.

If one were to compute the Tristimulus Specifications, the apparent differences caused by different backing is unimportant.[7] When employing the Spectronic 505 in reflectance measurements, the Reference Energy meter on the instrument should register at least 2 on the scale provided.[8] When the black backing was used, the reading on the scale did not reach 2 for the most part. There is a loss of energy, and for this reason, a loss in the per cent reflectance as illustrated in Graph 8 with the changing of backing using the same specimen.

From this examination a white background of magnesium carbonate for the specimen was selected for the remainder of the study.

IV. DILUTION AND EXAMINATION OF PURE PIGMENTS

The next problem considered was how dilute a specimen could still be measured with the Spectronic 505 reflectance sphere.

Ten pure pigments were weighed out and diluted with lithopone. Lithopone is a white hiding pigment consisting of about 28 per cent zinc sulfide and 72 per cent blanc

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[7] *Ibid.*, p. 374.

[8] Reference Manual for Spectronic 505 Spectrophotometer, Cat. N. 33-28-04, Bausch & Lomb Inc., Rochester 2, N. Y., p. 3-3.

fixe.[9] It is produced by precipitation from solutions of barium sulfide and zinc sulfate. The precipitate is then washed and strongly calcined to develop optimum pigment properties. The lithopone used was that passed through a 100 mesh sieve. The lithopone-pigment specimens were mixed in a Wig-L-Bug* Grinder-Mixer.

Ten milligrams of each pigment mixture were placed in the window of a glass slide and mixed with three drops of linseed oil. This pigment-lithopone-linseed oil blend was used to cover the window area of 12 millimeters square, resulting in a dry smear 0.11 millimeters thick.

After drying, the specimens were examined in the reflectance sphere, using magnesium carbonate as the reference. The results are illustrated in Graphs 9 through 18, with a pure pigment, a 10 per cent dilution (10 milligrams of pure pigment and 90 milligrams of lithopone), a 1 per cent dilution (10 milligrams of a 10 per cent dilution and 90 milligrams of lithopone), a 0.1 per cent dilution (10 milligrams of 1 per cent dilution and 90 milligrams of lithopone) and in some cases, a 0.01 per cent dilution (10 milligrams of 0.1 per cent dilution and 90 milligrams of lithopone) of the pigment being examined.

Graphs 9 through 11 illustrate three shades of blue, graphs 12 and 13 two shades of yellow, graphs 14 and 15

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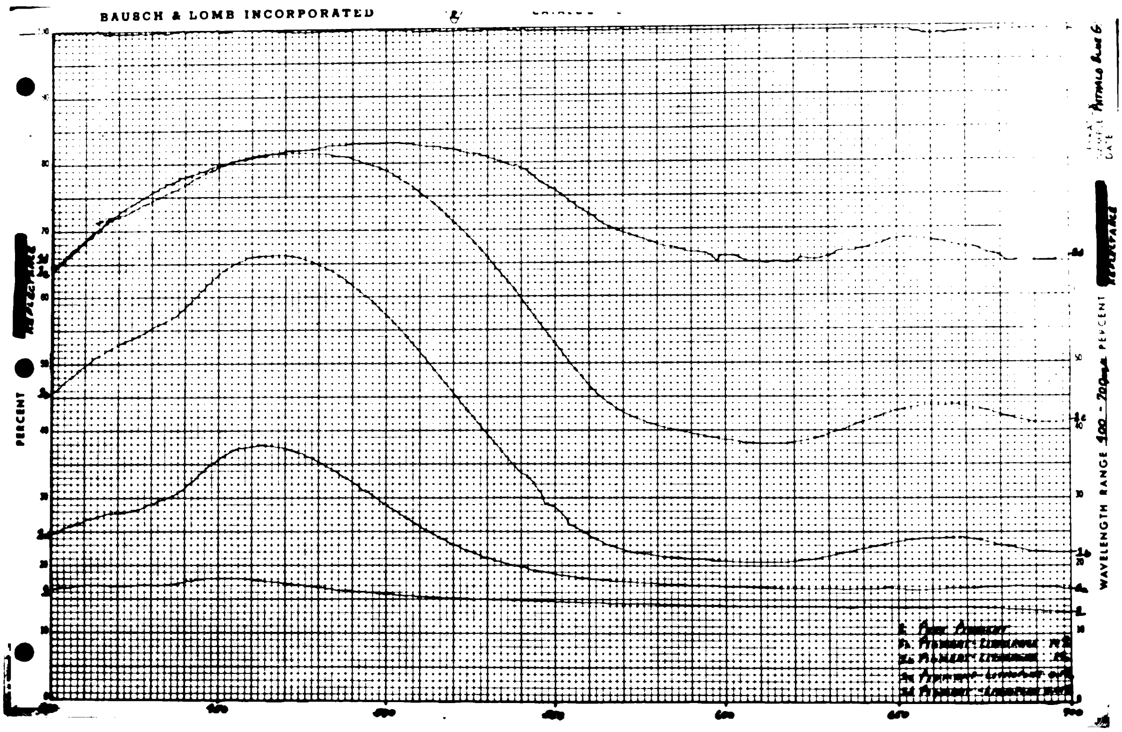
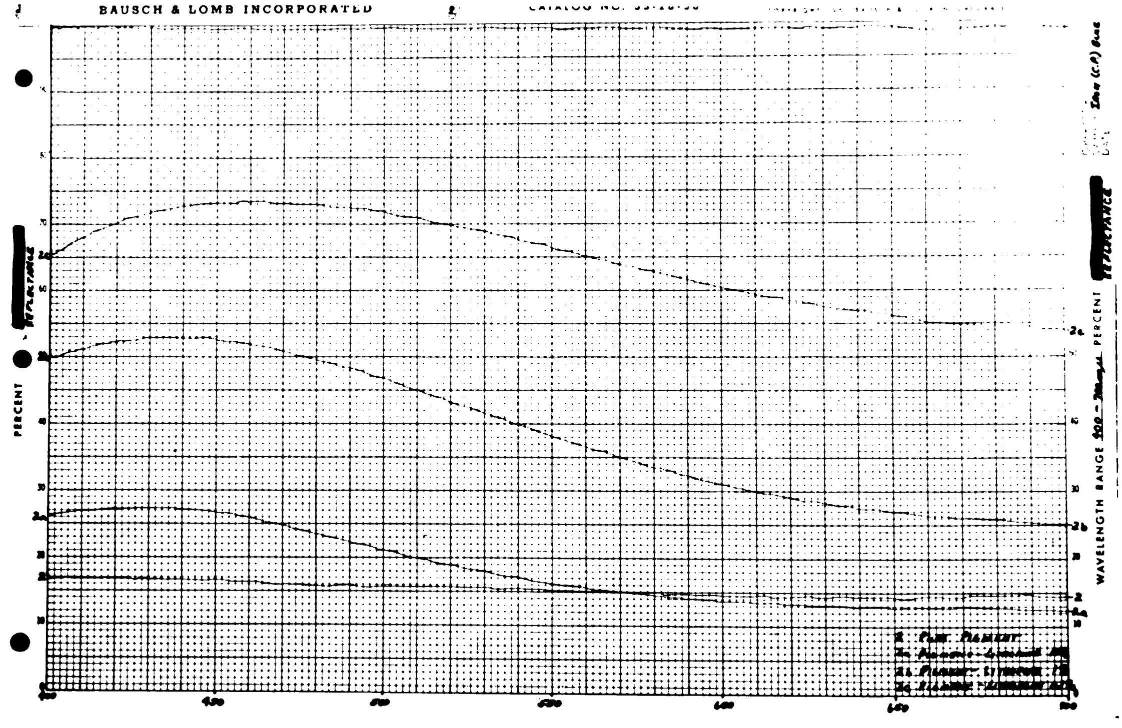
[9] Paint Industry Technical Yearbook and Materials Manual (Philadelphia, Pa.: Heckel Publishing Company, Vol. 5, 1960), p. 68.

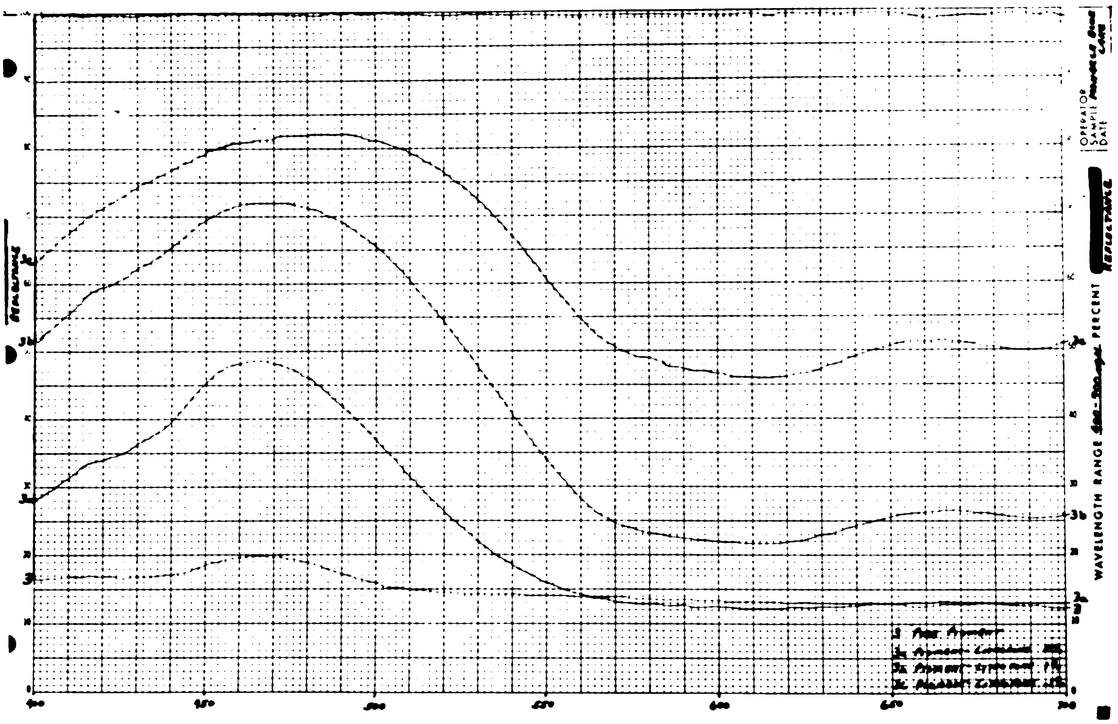
*Crescent Dental Supply, Chicago, Illinois.



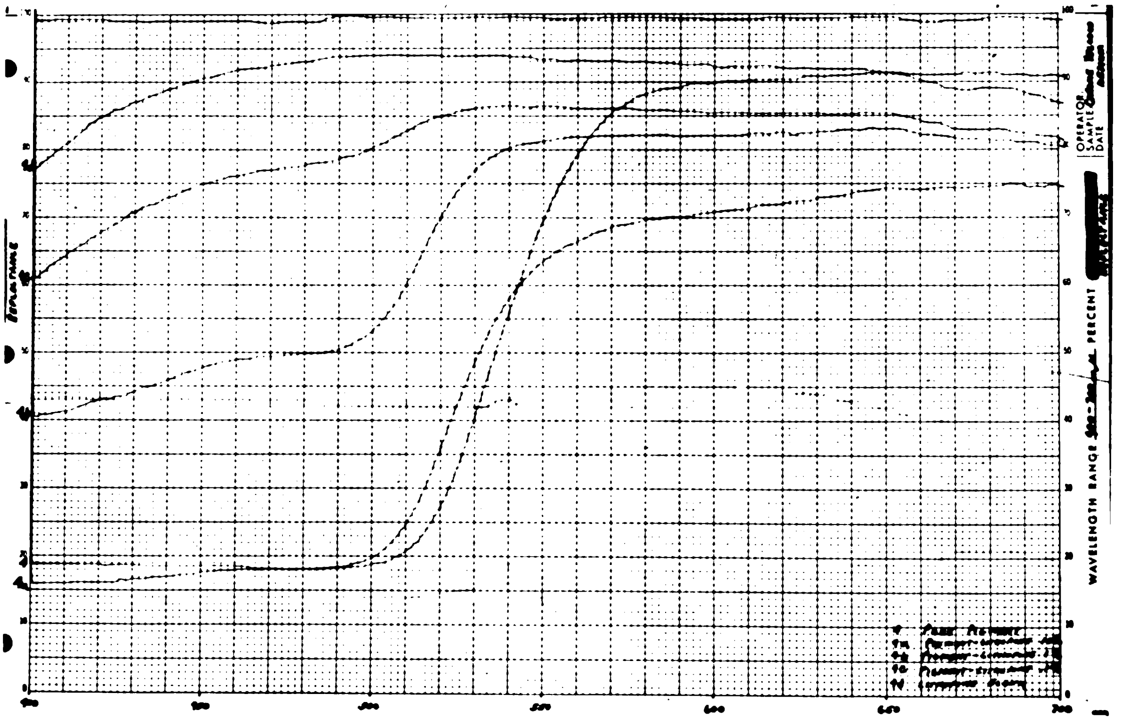
GRAPH 9



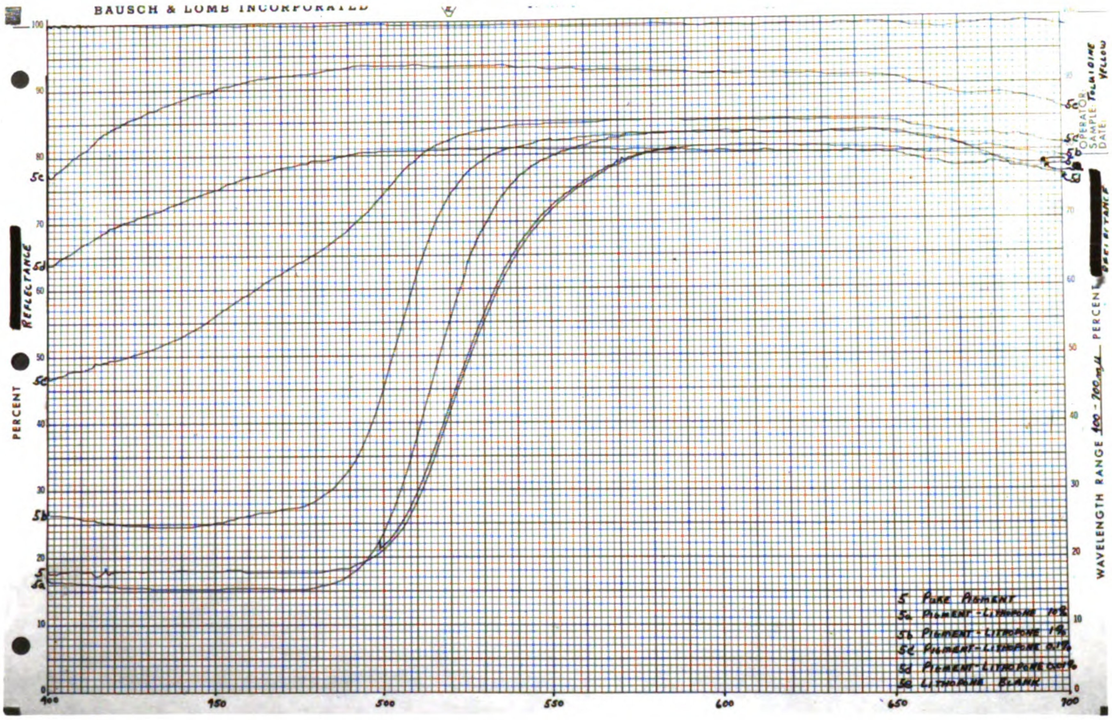
GRAPH 10



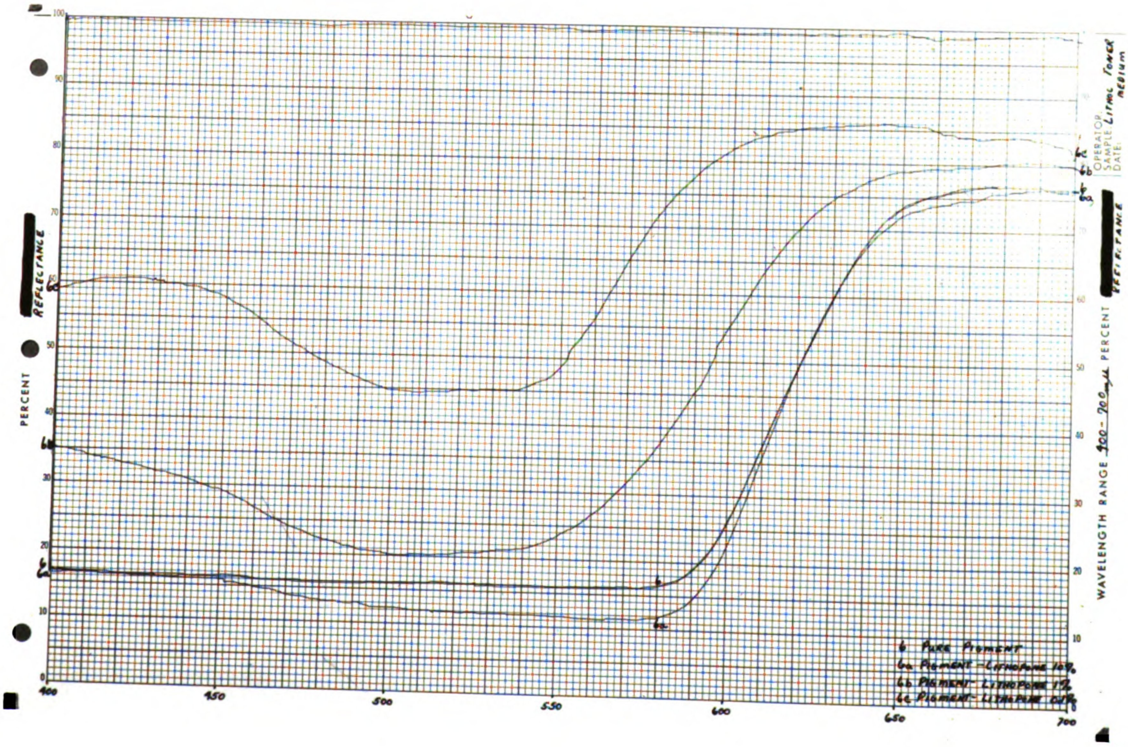
GRAPH 11



GRAPH 12



GRAPH 13



GRAPH 14

two shades of red, graph 16 a shade of orange, graph 17 a shade of green, and graph 18 a shade of maroon. They also illustrate that in most situations, a dilution over 0.1 per cent was of questionable value, particularly in the lighter colors. A dilution greater than 0.1 per cent results in a reflectance curve approaching that of lithopone and was affected less by the tinting pigment.

The pure pigment reflectance curves in graphs 9, 10, 11, 17 and 18 illustrate that a pigment which is too dark in color does not produce valid data and gives a reflectance curve similar to the curve of a dark gray pigment. Dilution of these dark colored pigments with a white pigment produces reflectance curves which offer information as to the type of pigment present.

The effect of dilution is a measure of the reflectance of the components present in the pigment sample. The change in reflectance caused by dilution is affected mainly by the predominant pigment.[10]

During this portion of the investigation, the weight of the sample as well as the percentage of dilution used in a single smear were also evaluated, to determine if the quantity of the sample had an effect on the reflectance curve. Graph 19 shows the reflectance curves of a duplicate series containing 5, 10, 15 and 20 milligram samples of

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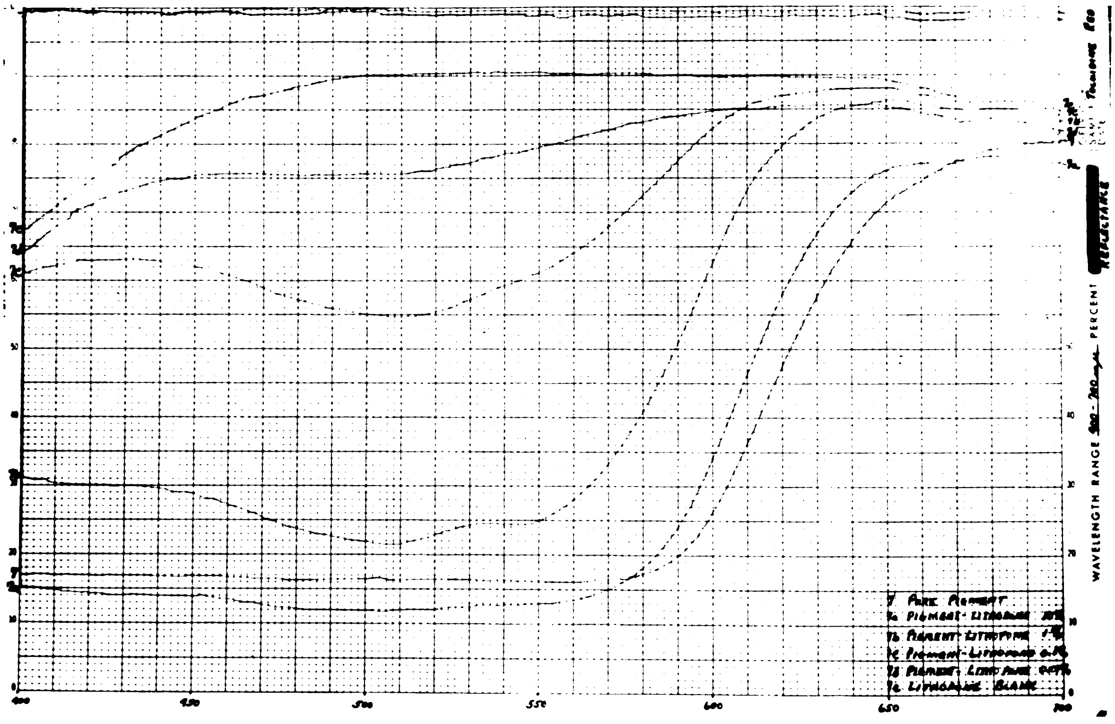
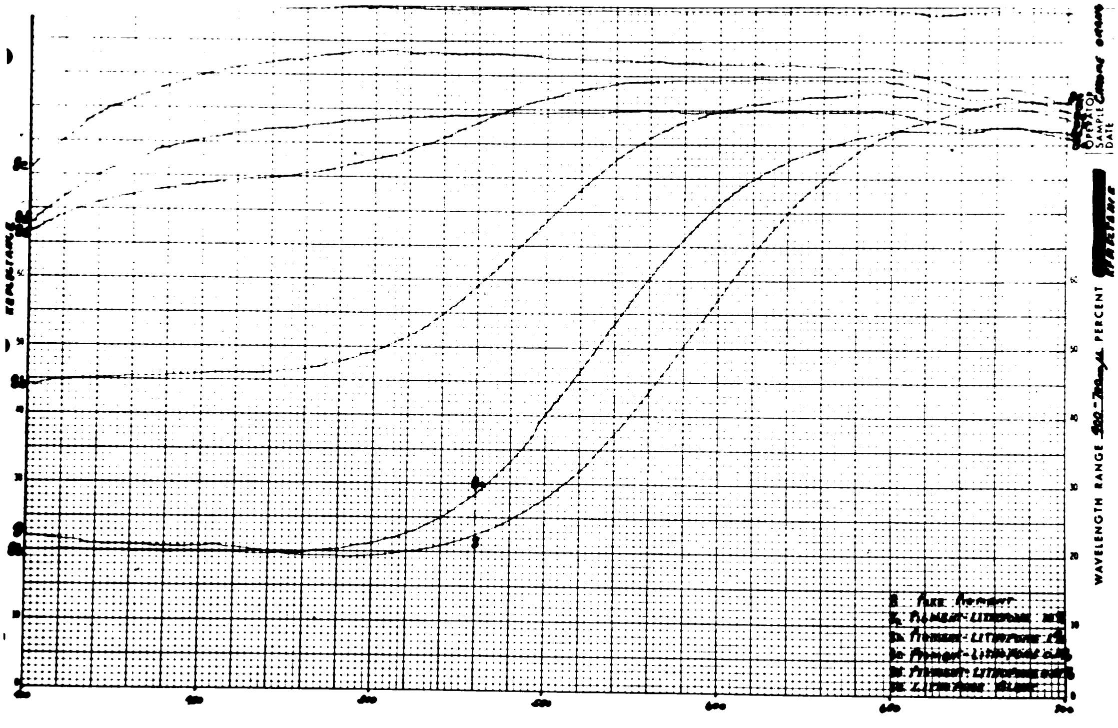
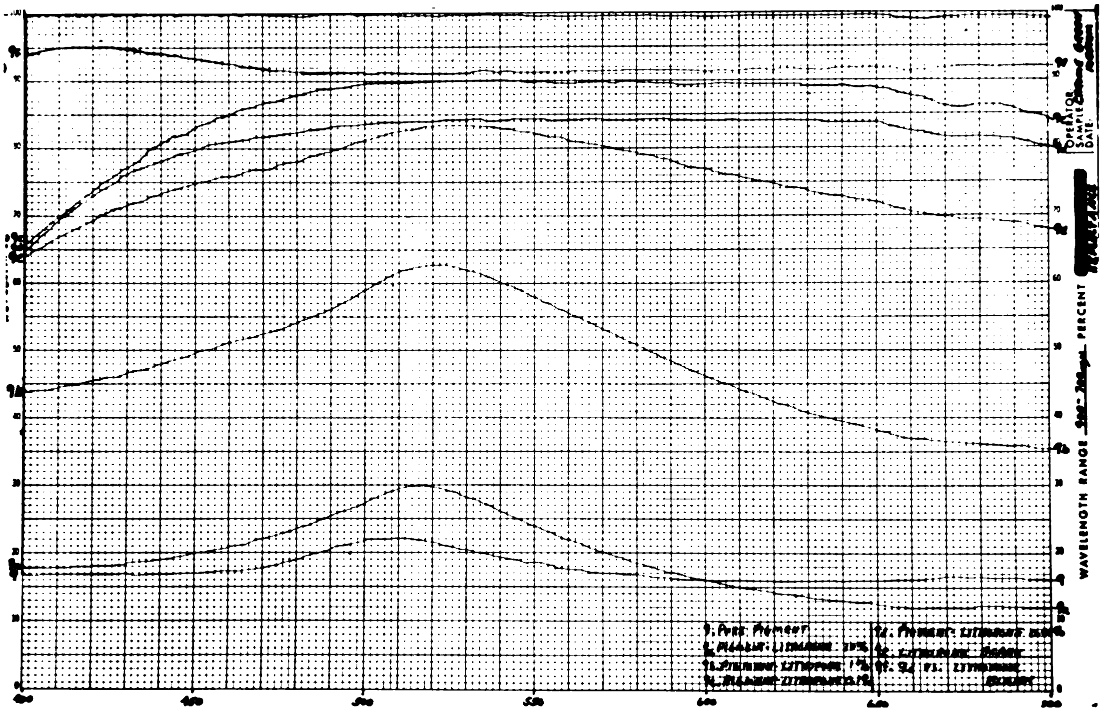
[10] D. R. Duncan, "One Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry," _Journal of the Oil and Colour Chemists' Association_, XXXXV (1962), p. 315.



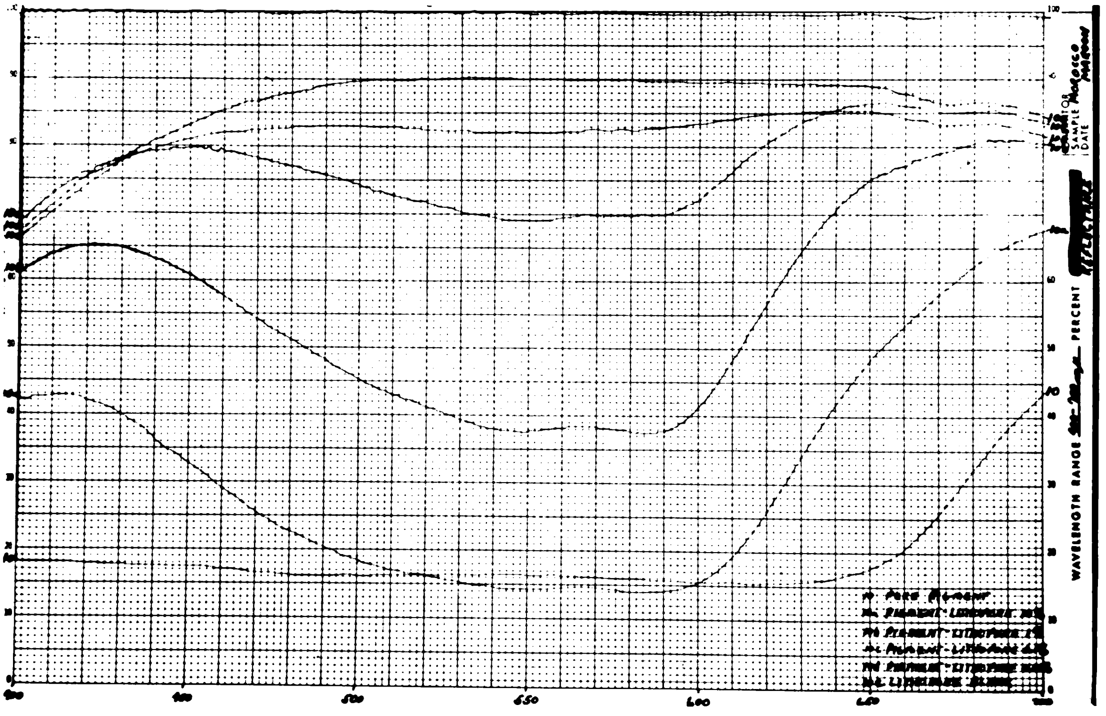
GRAPH 15



GRAPH 16



GRAPH 17

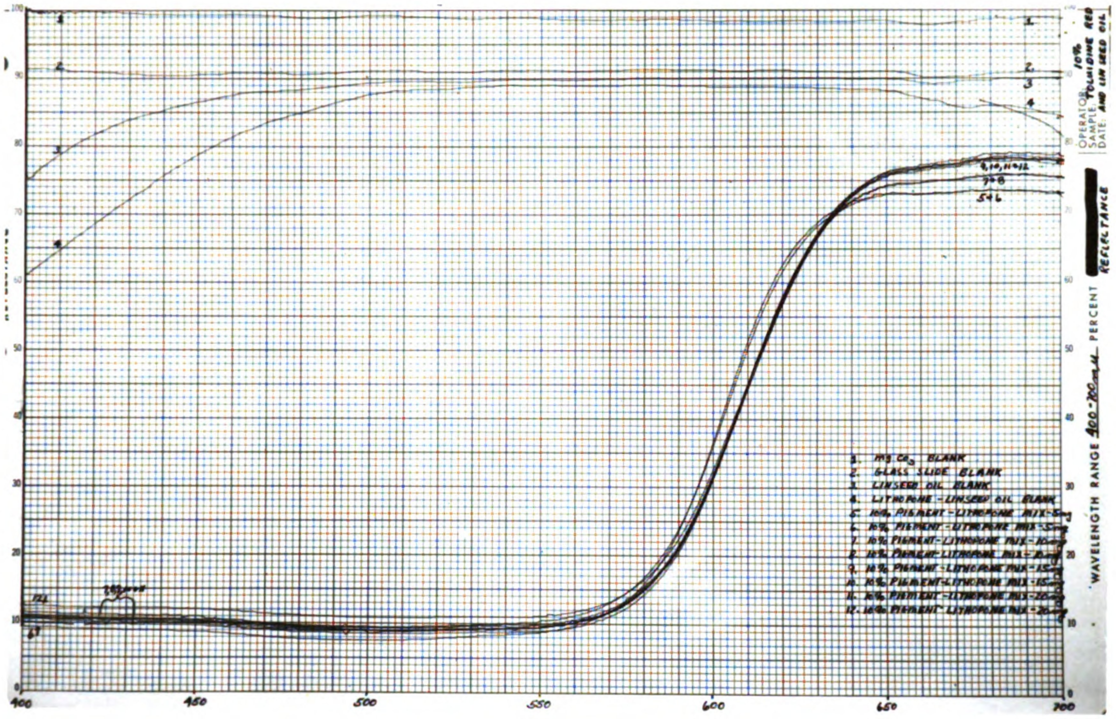


GRAPH 18

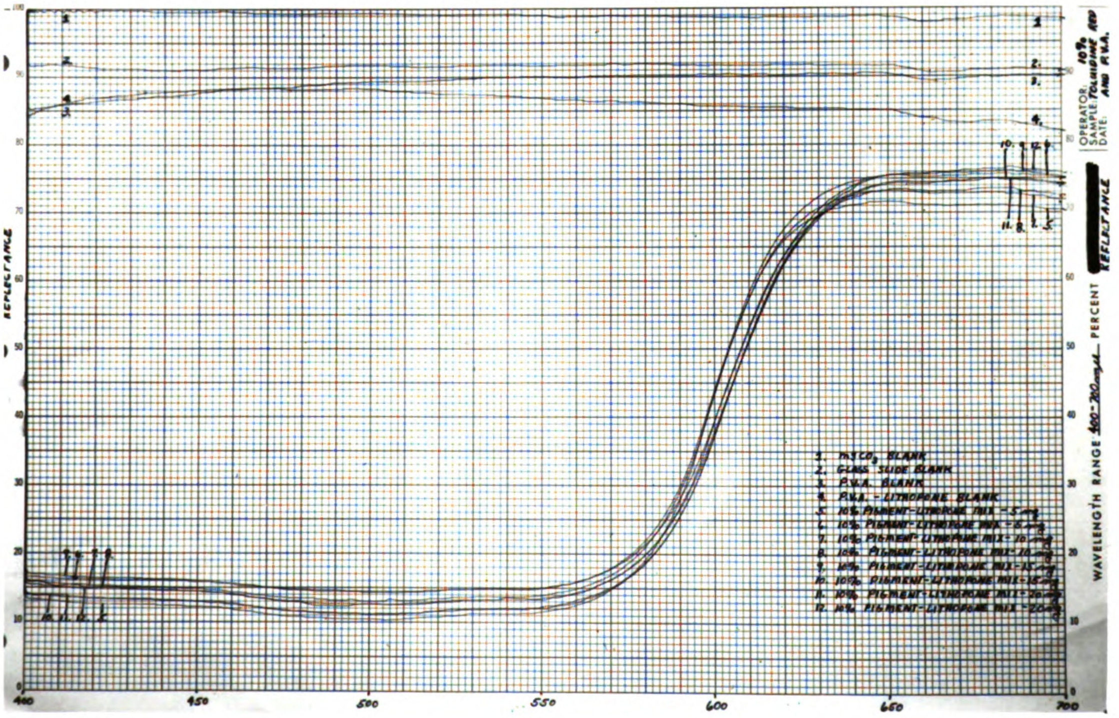
Toluidine Red pigment diluted to 10 per cent with lithopone and mixed with linseed oil. The repeatability of the curves is due to the uniform thickness and complete coverage of the window area. Slight variations are due to surface texture and particle size, rather than the quantity of specimen used.

Another vehicle was investigated to be used in place of the linseed oil. This vehicle is a copolymer of poly-vinyl acetate. Graphs 20 through 22 illustrate the curves of weighed duplicate samples of three concentrations (10 per cent, 1 per cent, and 0.1 per cent) of a Touidine Red pigment mixed with poly-vinyl acetate as the vehicle. Again, good repeatability is demonstrated at the three concentrations. Comparison of curves 3 and 4 on graphs 19 and 20 shows that linseed oil has much more absorption in the low wave length regions than does polyvinyl acetate. This does not affect the reflectance curves of pigment specimens which are dark in color, but would have an effect on the reflectance cuves of pigments which give a high percentage of reflectance at the low wave lengths. This results in a masking effect which would be overcome by using the vehicle-lithopone mixture on a glass slide with the same window size in the reference beam.

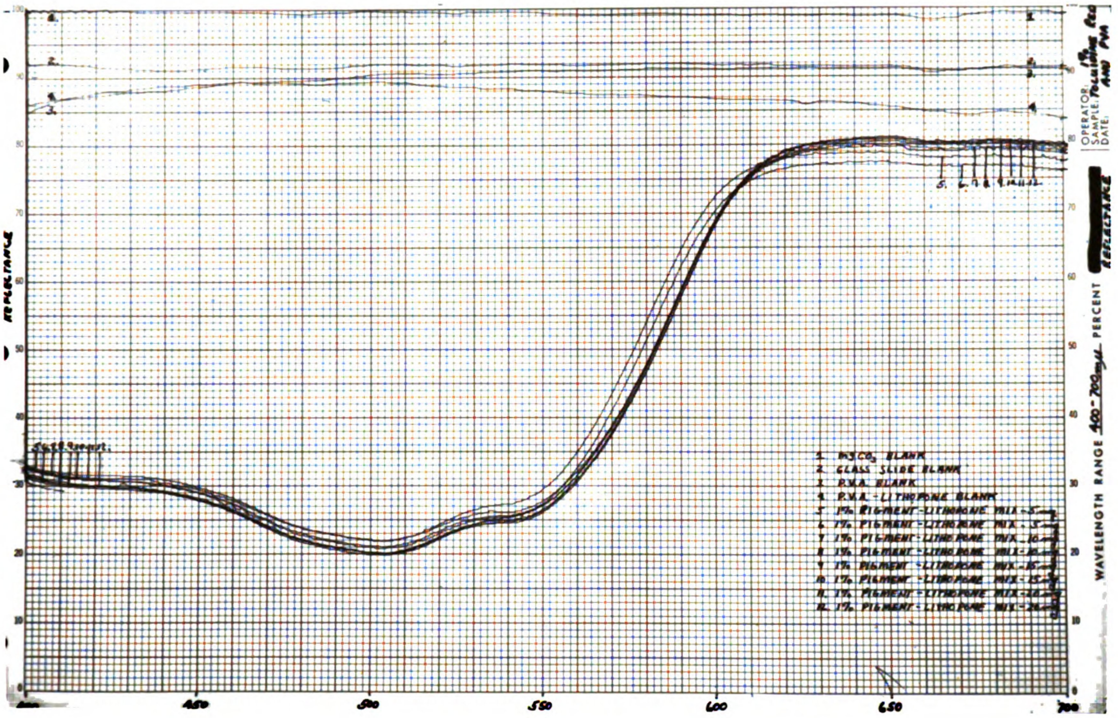
The effect of dilution is a measure of the reflectance of the components present in the pigment sample. The dilution causes a change in reflectance because the coefficient of scatter of the paint changes with wavelength and is



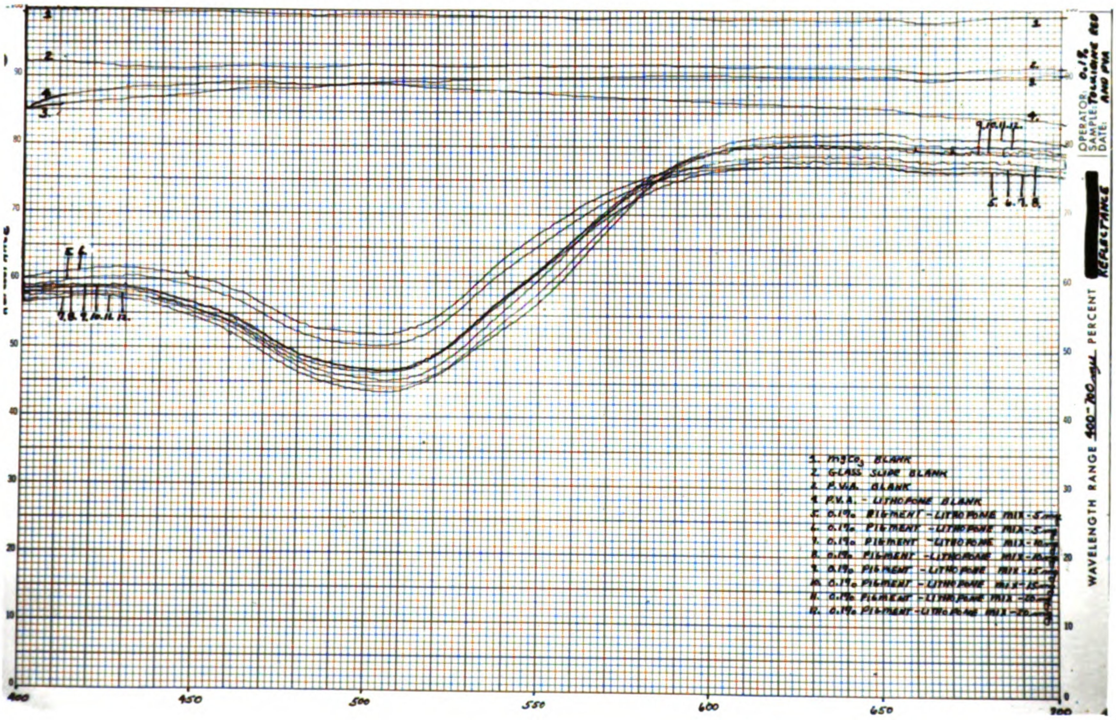
GRAPH 19



GRAPH 20



GRAPH 21



GRAPH 22

affected mainly by the predominant pigment[11] (which is white in the case of dilution). Particle size also affects the reflectance curve. A decrease in particle size will increase the intensity of the reflectance curve,(12, 13) with the region of the reflectance maximum being most pronounced.

In Graph 22 the greater variations of curves 5 and 6 are due to the poor coverage of the window area.

The polyvinyl acetate vehicle was found to be much easier to work with. This vehicle dried in the air in a matter of minutes while linseed oil required more than a week to dry. The specimens prepared with polyvinyl acetate were non-glossy, whereas those, particularly in colored pigment of dark colors, made with linseed oil were glossy. When working with polyvinyl acetate, the equipment was readily cleaned with water, while working with linseed oil, organic solvents were necessary in cleaning.

It was found that concentrations of less than 0.1 per cent of a pure pigment should not be used. The minimum quantity of mixture for a pigment dilution of 0.1 per cent should not be less than 10 milligrams to insure proper coverage of the window area 12 millimeters square (144 square millimeters), and to produce repeatable curves.

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[11] Ibid.

[12] Ibid., p. 305.

[13] G. Kortum, "Diffuse Reflectance Spectra of Mercuric Iodide on Different Adsorbents," Transactions of the Faraday Society, Vol. 58 (1962), p. 1625.

IV. EXAMINATION OF PAINT SCRAPINGS

In this section of the study, actual paint samples were ground and mixed with lithopone to test the proposed method of examining minute paint specimens with the Spectronic 505 with reflectance sphere.

Twelve painted panels, consisting of single layer automobile undercoats and finishes, were secured. These single layer samples eliminated the necessity of separating multi-layers of paint which would be commonly encountered. The panels were prepared by a paint manufacturer to determine paint flowing quality and no information was available about the pigment composition of the paint.

Five milligram and one milligram samples were scraped from the panels and mixed with lithopone to give five and one per cent dilutions. (A maximum sample of five milligrams of paint scrapings was used because larger amounts are rarely encountered by the forensic scientist, and could be compared directly as described in Section II earlier in this chapter.)

An attempt was made to grind the scrapings in a Wig-L-Bug Grinder-Mixer but met with limited success until lithopone was added. The lithopone apparently provided enough body to the mix to give a good grinding action.

Ten milligrams of the paint scraping-lithopone mixture were placed on a glass slide and wet with one drop of polyvinyl acetate. This blend was smeared to cover a window

12 millimeters square in area on the slide and allowed to dry. All samples in this section were prepared in this manner.

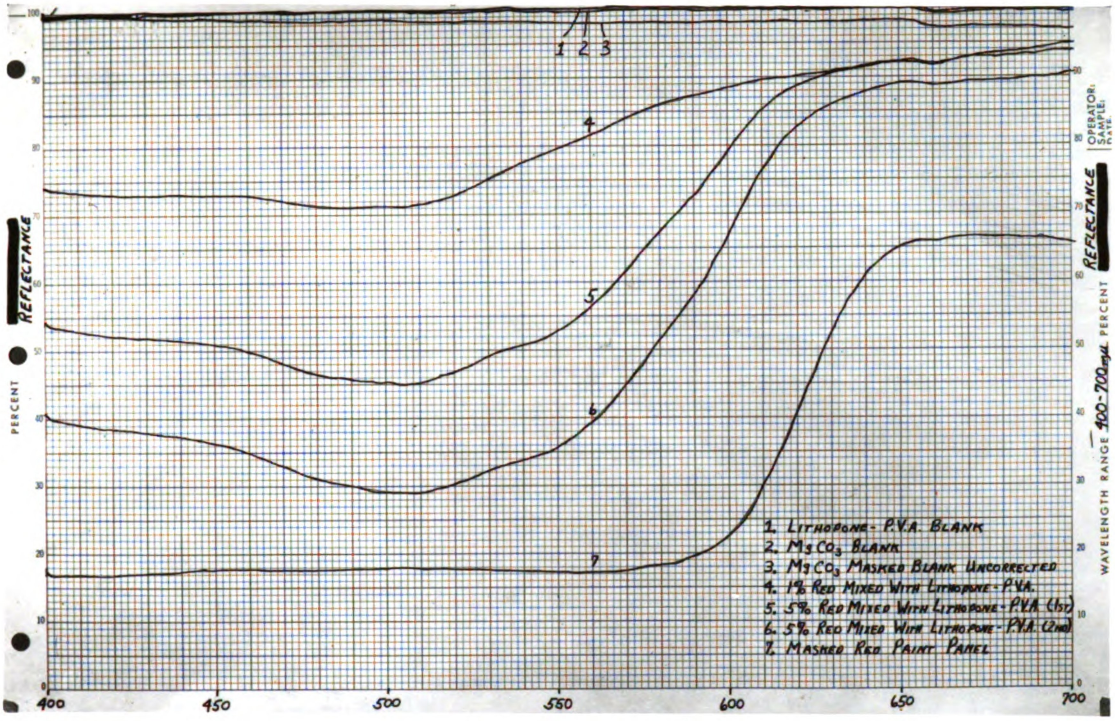
These samples were examined in the reflectance sphere, using a 12 millimeters square smear of lithopone-polyvinyl acetate in the reference beam. A magnesium carbonate block was used behind the glass slides in both the sample and reference beams.

To illustrate the difference between diluted and undiluted paints used in this portion of the study a reflectance curve of each painted panel, masked with white card stock to expose a 12 millimeters square to the illuminating beam, was made. White card stock with a 12 millimeters square exposing the magnesium carbonate was used in the reference beam.

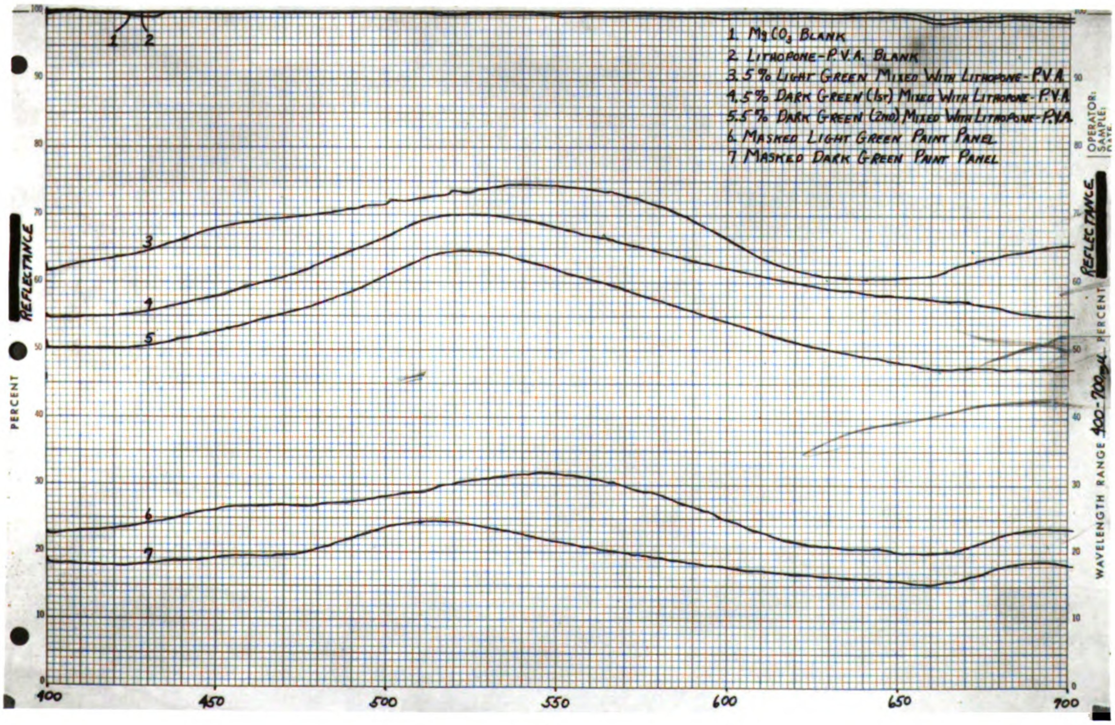
Although a 40 square millimeters area gives valid curves for comparison of undiluted paint specimens (see Section II earlier in this chapter), a 12 millimeters square area was used in this part of the study to keep the illuminated area constant in both diluted and the painted panels.

Some of the reflectance curves are illustrated in Graphs 23 through 26.

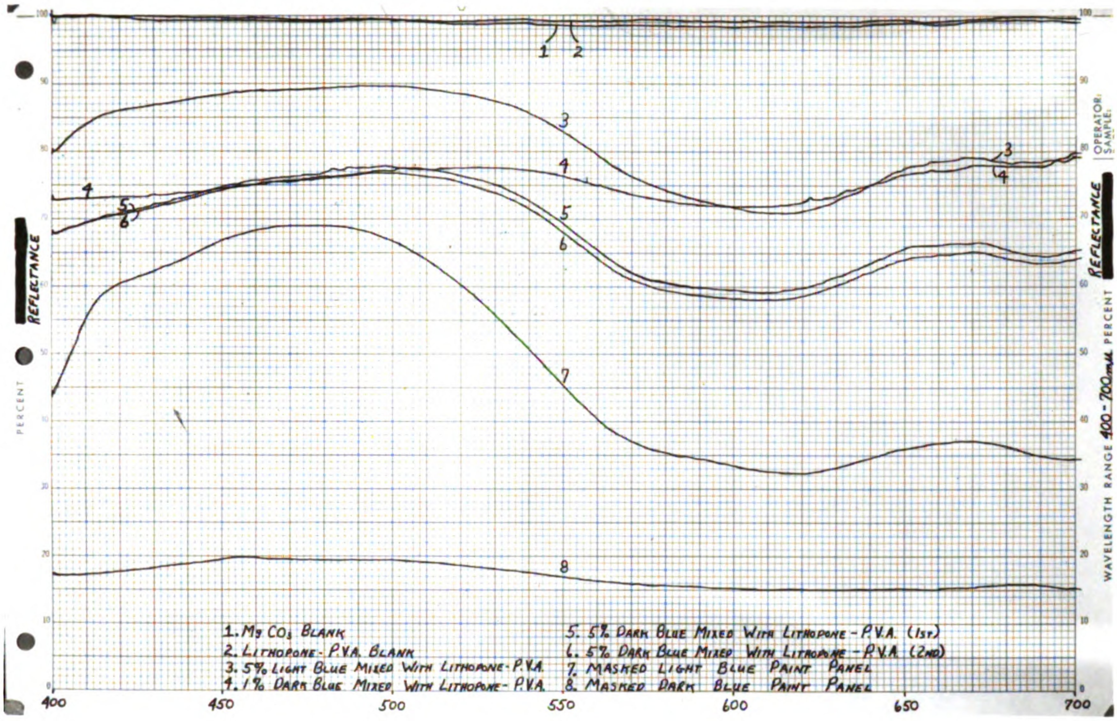
Curve 3 in Graph 23 is that of the masked blank before correction of the 100 per cent line with the optical density control. The 100 per cent line had to be rechecked between each run employing lithopone-polyvinyl acetate in the reference beam and the masked magnesium carbonate in the reference



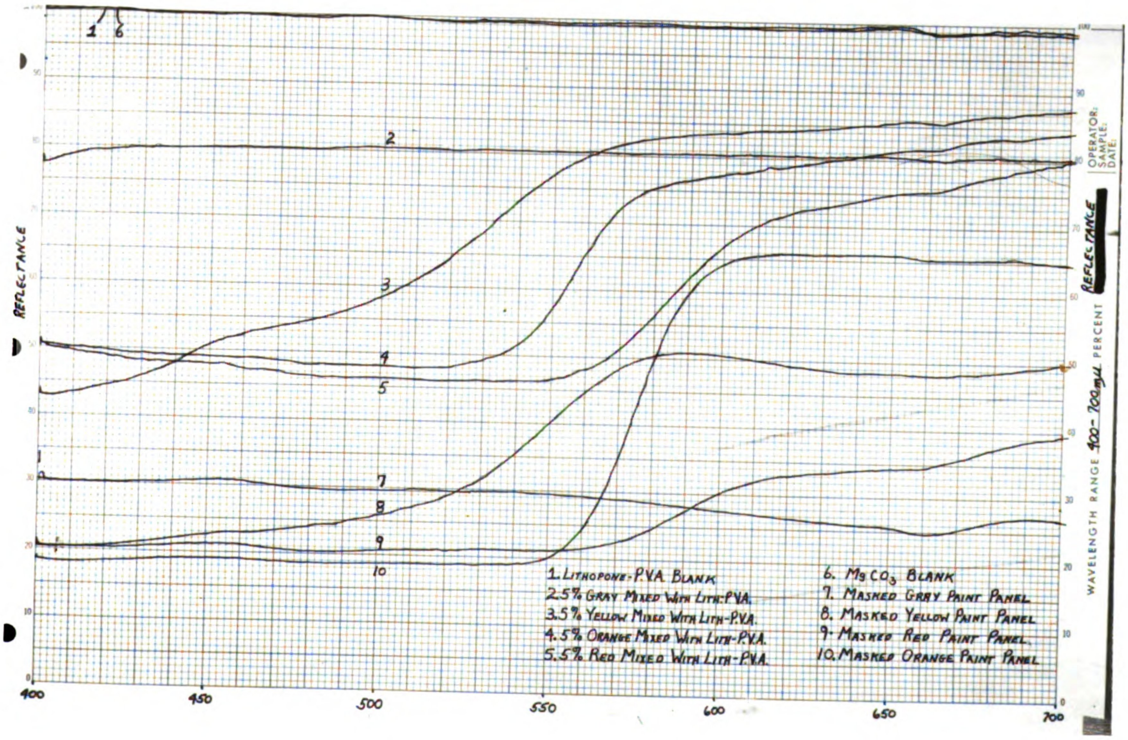
GRAPH 23



GRAPH 24



GRAPH 25



GRAPH 26

beam. This was necessary because the area illuminated outside of the lithopone-polyvinyl acetate in the reference beam was reflected from the magnesium carbonate block behind the glass slide. In the case of the masked magnesium carbonate in the reference beam, the area outside the 12 millimeters square was reflected from the card stock. (The illuminating beam size is approximately 16 x 19 millimeters.) The card stock has different reflectance qualities than does the magnesium carbonate.

Curves 5 and 6 of Graph 23 represent two separate preparations of a 5 per cent mixture of red paint scrapings and lithopone. The repeatability is poor, although the two have the same general curve. The 1 per cent paint-lithopone mix as represented by curve 4 may still be of value because there is a broad minimum between 480 and 510 millimicrons which indicates some absorption in the blue-green wavelength region.

Graph 24 illustrates the reflectance curves of two shades of green. Curves 4 and 5 represent two separate preparations of the 5 per cent paint-lithopone mix but again repeatability is lacking, although they do possess the same general curve across the wavelength scanned. It is also noted that the diluted specimens reflect the same general type of curves as do the masked paint panels from which the specimens were removed.

Two shades of blue are illustrated by the reflectance curves in Graph 25. Here curves 5 and 6 reflect much better repeatability indicating better grinding and mixing of the paint specimen with the lithopone. Curve 4, illustrating the reflectance of a 1 per cent paint-lithopone mix, is lacking in detail in the low wavelength region.

Curves 3 through 5 illustrate that 5 per cent dilutions of the paint specimens shown in curves 8 through 10, give valid reflectance curves. Curve 2 illustrates that dilution of a gray paint produces a straight reflectance curve, similar to the undiluted paint (Curve 7). The per cent reflectance is dependent upon the shade of gray.

Other samples were examined using a one per cent dilution but the reflectance curves are not included here because the reflectance was greater than 90 per cent and approached the reflectance of the blank.

If a light colored paint sample is diluted to less than five per cent with lithopone, it will not produce a valid reflectance curve. Therefore, the smallest amount of a light colored paint which could be validly examined by this method would be a 1 milligram sample (1 milligram paint and 19 milligrams lithopone to give a quantity of 5 per cent dilution which can be ground and mixed to recover the 10 milligrams necessary to cover a 12 millimeters square area).

Dark colored paint samples could be diluted to one per cent with lithopone and still produce a valid reflectance curve. Theoretically a dark paint sample weighing 0.2 milligram could be examined. Due to the mechanical limitations described below, this was not done.

Microscopic examination of the diluted paint smears showed that the grinding of the paint specimens was not uniform and in some cases, minute particles of paint, rather than a complete powder sample, were observed. The particle size of the paint and the lack of uniformity of the smear on the glass slide would have an effect on the repeatability of reflectance curves from individually prepared specimens because they affect the coefficient of absorption.(14, 15)

Additional samples were subjected to grinding with lithopone in the Wig-L-Bug for varying times. It was found that the paint specimens which were brittle, ground to a powder and produced an acceptable smear such as is illustrated in curves 5 and 6 of Graph 25. Paint which was somewhat soft and flexible did not grind to a powder and the smears made from these specimens were not acceptable because of the varying sized paint particles present.

Another problem is presented by multilayered paint specimens. Mechanical separation of paint layers is possible if they are not damaged or smeared. Because of the smallness of the paint specimens generally handled in the forensic science laboratory, mechanical separation of paint layers is impractical.

Selective solvent separation was also investigated. Although solvent separation of paint layers is acceptable in

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[14] Duncan, *op. cit.*, p. 305.

[15] Lermond and Rogers, *op. cit.*, p. 343.

some cases, again the small specimen size is a limiting factor because of the tendency of the solvent to creep during evaporation resulting in a loss of the paint specimen.

Relatively large paint specimens would be required for both mechanical separation of layers and a selective solvent procedure. Specimens sufficiently large for these two procedures could be examined by the method described under Section II earlier in this chapter.

CHAPTER V

SUMMARY

I. CONCLUSIONS

Several items should be considered before reaching any conclusions from the viewing of reflectance curves. No quantitative results should be attempted directly from reflectance curves of paint specimens. A mathematical interpretation, such as proposed by Duncan,[1] should be used for quantitative results. However, the wave lengths for maxima and minima of the curves should be similar for like specimens and are of value for qualitative measurements.[2] It is doubtful if these curves could be compared with known standards to identify the brand or manufacturer of the paint because of the unknown degrees of weathering to which the evidence specimens have been exposed.[3] It is common knowledge that if two panels are painted with the same paint and one panel is subjected to all weather conditions, a difference does occur because of the weathering. No examination

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[1] D. R. Duncan, "The Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry," Journal of the Oil and Colour Chemists' Association, XXXXV (1962), 300.

[2] D. B. Judd, Color in Business, Science and Industry (New York: John Wiley and Sons, Inc., 1952), p. 94.

[3] J. F. Williams, "Examination of Paint Chips and Scrapings with the Spectrophotometer," Journal of Criminal Law, Criminology, and Police Science, Vol. 44 (1954), p. 647.

of the weathering effect was made in this study.

In conducting reflectance measurement examinations, each case must be studied separately on its own merits, as well as running a number of controls. This, of course, is nothing new to the forensic scientist, as controls and blanks are required in most of the examinations in this field.

In this study, the reflectance sphere of the Bausch and Lomb Spectronic 505 Spectrophotometer in the wave length range of 400 to 700 millimicrons was evaluated for comparing minute paint specimens. The sphere would require paint chips covering an area of 40 square millimeters of the illuminating beam to produce valid reflectance curves. Because a 40 square millimeter specimen is rarely encountered in the Forensic Science Laboratory, a procedure for diluting the paint specimens with a white pigment and examining a smear, made on a glass slide, with the reflectance sphere was investigated.

Examining pure pigment specimen smears showed that an area 12 millimeters square (144 square millimeters) would provide sufficient area for the illuminating beam to produce valid reflectance curves. Pigments diluted to 0.1 per cent with lithopone would provide valid reflectance curves, with 10 milligrams of the mix necessary to provide adequate coverage of the window area.

Paint specimens diluted to 1 per cent with lithopone produced reflectance curves of little value for comparison purposes unless the paint specimens are of a sufficiently dark color. Light colored paint specimens required a 5 per cent concentration of the specimen-lithopone mix with 10 milligrams of the mix needed to provide adequate coverage of the window area. The paint specimen must be capable of being ground to a powder to produce repeatable curves.

Linseed oil and polyvinyl acetate were used as vehicles in this study to produce the specimen smears on glass slides. Polyvinyl acetate is more advantageous because it dries fast and has a relatively straight reflectance curve. Linseed oil takes a week to dry, has absorption in the shorter wavelength regions and yellows with age.

By grinding the paint chip specimens, certain surface characteristics due to aging and weathering are destroyed. These characteristics may be examined before grinding.

This study has shown that the reflectance sphere on the Spectronic 505 has limited value for the comparison of minute paint specimens even if the paint specimen is diluted with a white pigment to provide greater area of coverage required for the illuminating beam.

II. PROPOSED STUDY

Carl Zeiss, Inc., has recently developed a reflectance attachment for its spectrophotometer so that 1 square millimeter of paint can be examined.[4]

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[4] "Quick, Watson! The Gamma Spectrometer," The Clinical Laboratory, Vol. 31 (1963), p. 101.

A means of modifying the reflectance sphere of the Spectronic 505 to examine minute paint chip specimens without treatment would give this instrument more application in the Forensic Science Laboratory. Condensing the illuminating beam onto the specimen being examined may be one approach to such a modification.

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