NOTE TO USERS

This reproduction is the best copy available.

UMI

SOME FACTORS INFLUENCING THE REFLECTION OF ULTRA-VIOLET LIGHT BY PAINTS

A dissertation
submitted to the faculty
of the
INSTITUTE OF SCIENTIFIC RESEARCH
of the
UNIVERSITY OF CINCINNATI
in partial fulfillment
of the requirements
for the degree of
DOCTOR OF ENGINEERING SCIENCE
by

Donald Frederick Wilcock

B. S. in C. E. Harvard Engineering School 1934
M. E. S. University of Cincinnati 1938

Basic Science Research Laboratory
August 1, 1939

TABLE OF CONTENTS.

Foreword	1
I. Apparatus	2
1. Description	2
2. Testing	11
3. Reliability of Measurements	14
II. Development of Ultra Violet Paints	21
1. Reflection and Transmission of Paint Materials	21
2. Properties of Simple Paints: Two Component Systems	32
3. Properties of Simple Paints: Three Component Systems	51
4. Unpigmented Films	61
5. Milled Paints	65
6. Exposure Tests	74
7. Other Requirements	82
8. Other Factors Affecting Reflection Factor	83
III. Influence of Pigment Properties	86
1. Particle Size	86
2. Particle Structure or Aggregation	91
IV. Film Thickness and Hiding Power	101
1. Theoretical Relations	101
2. Experimental Results	110
V. Summary	131

References 124

Appendices 131

A. Theory of Integrating Sphere 132

B. Analysis of Transmission Cell 139

C. Calculation of Pigment Absorption 143

D. Derivation on Rhodes and Fonda's Assumptions 147

E. Film Thickness and Hiding Power 150

Foreword.

It is well known that irradiation by ultra-violet rays of wave lengths shorter than approximately 3200 Angstroms will prevent and cure rickets and possibly other diseases by production of vitamin D-3 in the skin. That such irradiation may produce beneficial effects other than those attributed to the formation of this vitamin is perhaps less certain. Irradiation with wave lengths shorter than 2800-2900 Angstroms is known to be harmful to the skin.

Luckiesh and Holladay[1] state: "Little is known definitely about the benefits of erythemal (2800-3200 A.) radiation to so-called healthy persons, but an impressive case can be constructed", and argue that an ultra-violet component in everyday lighting will provide "whatever beneficence there is in summer sunlight". The efficient use of such lighting will require interior paints with high ultra-violet reflectances, and Luckiesh has prepared casein paints with reflectances as high as 54 per cent.

This dissertation is an attempt to apply the methods of science to the study of ultra-violet reflecting paints, and describes paints of superior film properties which attain reflectances over 70 per cent. In this study, the importance of aggregates in producing high reflectivity from inert pigments became evident. Study of the reflection from paints of different thicknesses led to a functional relation between reflection and thickness which permits accurate evaluation of hiding power for visible as well as ultra-violet light.

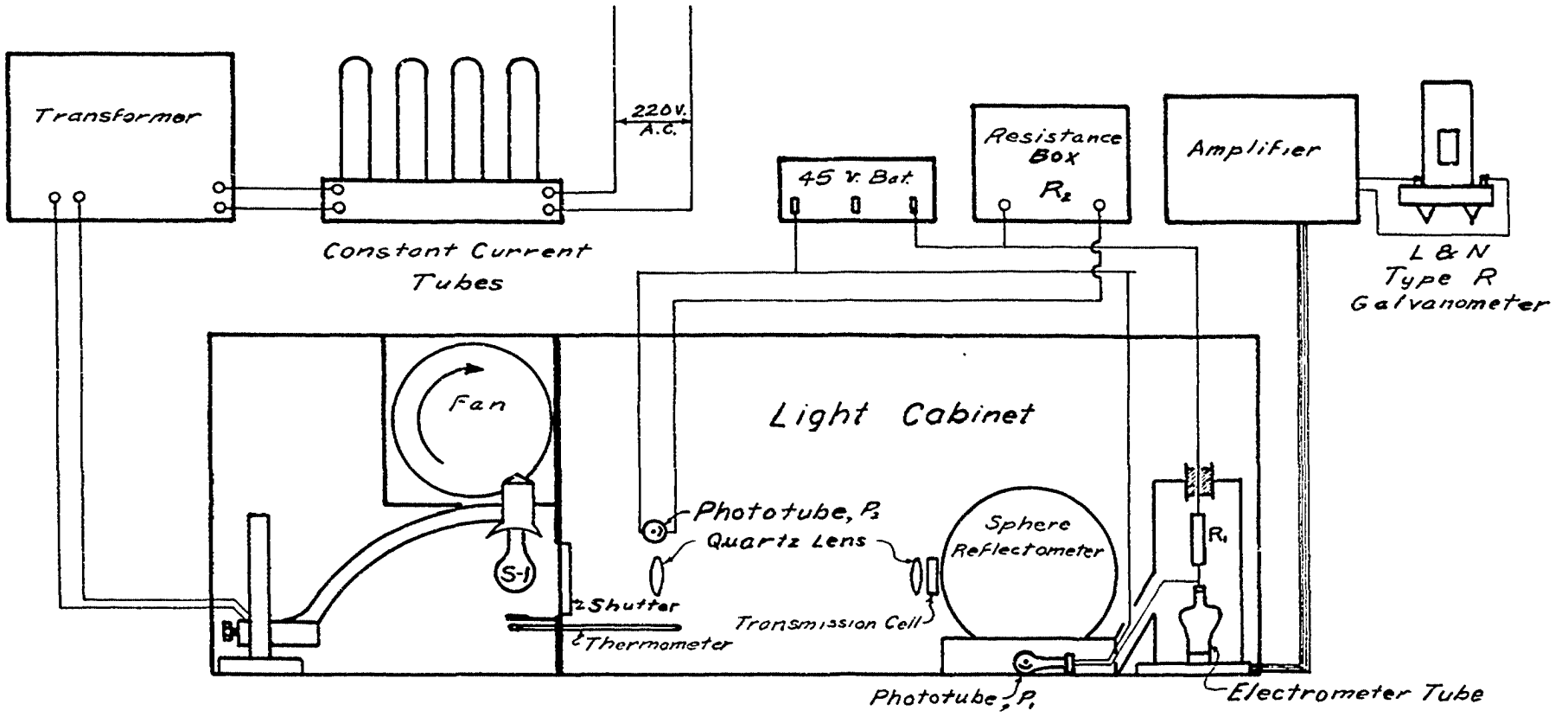
I. APPARATUS.

1. Description.

An apparatus was designed to measure the transmission coefficients of liquids and the integrated reflection factors of pigments and solid surfaces in the near ultra-violet band, 2800 to 3200 Angstroms. It is shown diagrammatically in Figure 1, and consists of an ultra-violet source with current and temperature regulation, a sphere reflectometer, phototubes with balancing circuit, and an amplifier.

The source is a General Electric S-1 Sunlamp. A clear Corex glass envelope encloses a tungsten filament and a mercury arc between tungsten electrodes. Since Corex glass does not transmit more than small amounts of radiation of wave length less than 2800 Angstroms, the envelope acts as a filter to provide the lower limit of the band of measurement. The current input to the Sunlamp is passed through a bank of RCA UV676 constant current tubes. A variable speed fan provides temperature control of the mercury arc in the Sunlamp, since its output is temperature sensitive.

Two quartz lenses are used to focus a beam of light from the Sunlamp on the window of the sphere reflectometer. The sphere integrates[2] all the light reflected from a sample, a property which is important in testing samples



Schematic Diagram of Apparatus

figure 1

which reflect diffusely. The inside surface of the sphere is coated with magnesium oxide, a substance with a very high reflection factor in the ultra-violet. A phototube, (P_1), placed at a window at the bottom of the sphere, measures the light intensity within the sphere. A reflection factor is determined by taking the ratio of the phototube currents when the light beam is directed on the sample, and when it is directed on the sphere wall.

The sphere reflectometer, as used in this apparatus, gives an absolute measurement of reflection factor; that is, the measurement does not depend on the reflection factor of the sphere coating or any other substance as a standard. The accuracy, therefor, is affected only by slight sources of error due to the construction of the sphere itself[3]. The accuracy of transmission measurements, although dependent on the reflection factor of the sphere coating, is not affected by it since the reflection factor is constant for magnesium oxide at 98 per cent from 2536 to 5461 Angstroms[4].

The theory involved in measurements with the sphere is that of the Taylor reflectometer[5,6] which measures diffuse reflection factors for light, and which has been applied by Taylor to ultra-violet measurements[3]. The theory applied to this equipment, together with an analysis of the errors to be expected, is presented in Appendix A.

The phototubes are General Electric PJ-135 cadmium alloy cells. They do not respond to light of wave length

greater than 3200 Angstroms[7], and thus provide the upper limit of the band of measurement.

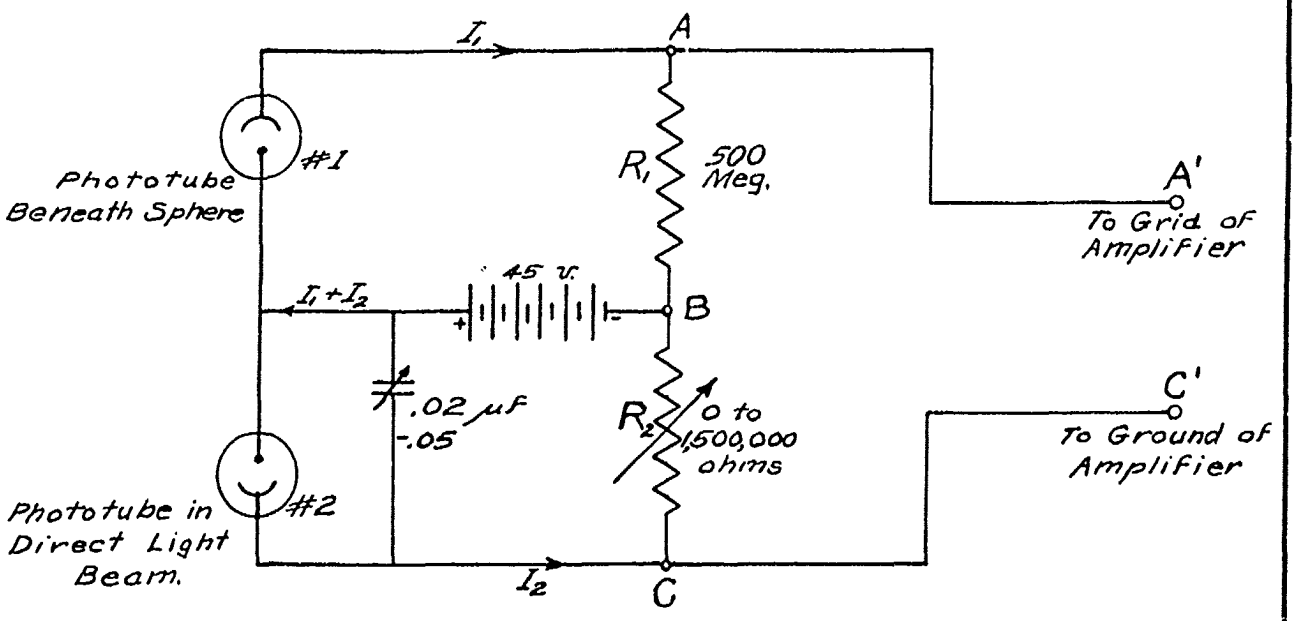
Despite the constant current input to the sunlamp, there are relatively rapid, irregular variations of several per cent in the output, and, since two consecutive readings are required for each measurement, it is important that the effect of these variations be eliminated. This is accomplished by using a second phototube, (P_2), so placed as to receive light directly from the source. By employing the ratio of the currents from both phototubes instead of the current from the single cell (P_1) beneath the sphere, it is possible to correct automatically for fluctuations in light intensity. The phototubes, of course, should have identical characteristics. Furthermore, it was found that the relation between them remains constant only when they are placed in nearly the same direction from and on the same side of the source.

A simple circuit is used (Figure 2) which gives the ratio between the two currents directly with only one reading. Points A and C are brought to the same potential by adjusting R_2. Then:

$$I_1R_1 = I_2R_2$$

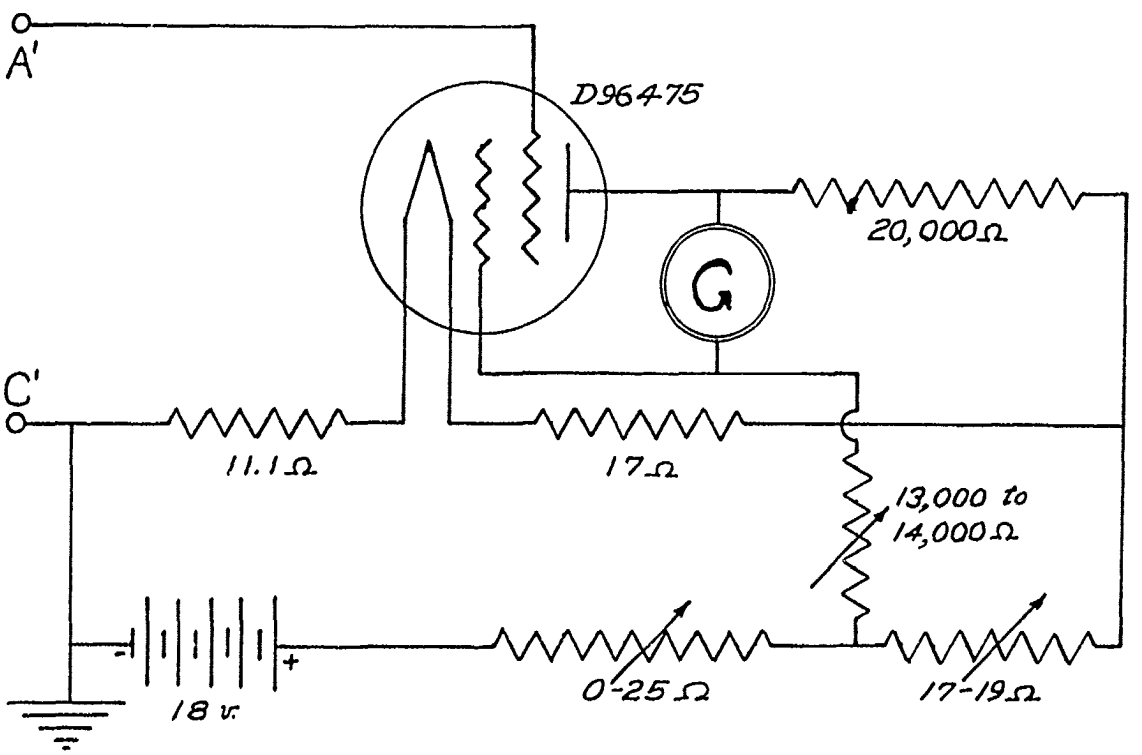
and since I_1 and I_2 are proportional to the light intensities Φ_1 and Φ_2 respectively, the ratio of Φ_1 to Φ_2 is:

$$\frac{\Phi_1}{\Phi_2} = \frac{K_1I_1}{K_2I_2} = \frac{K_1R_2}{K_2R_1}.$$



Phototube Circuit.

figure 2



Amplifier Circuit.

R_1 is a constant and cancels out in making a reflection factor measurement as follows:

$$\text{Reflection Factor} = \frac{\left(\frac{E_1}{E_2}\right)_{\text{sample}}}{\left(\frac{E_1}{E_2}\right)_{\substack{\text{sphere}\\\text{wall}}}} = \frac{\frac{K_1 R_{2s}}{K_2 R_1}}{\frac{K_1 R_{2sw}}{K_2 R_1}} = \frac{R_{2s}}{R_{2sw}}$$

The method described above applies to transmission measurements as well, since these also are made by taking two readings on the sphere wall, one with the sample in the light beam, and one without the sample.

For all transmission measurements, and for series of reflection factor measurements on the same sample, R_{2sw} remains constant, so that once it is determined only a single reading is necessary for each measurement. At first, the sphere had a large window three inches in diameter for the reflection sample, so that R_{2sw} varied for each sample due to its effect on the internal reflections of the sphere, and both R_{2sw} and R_{2s} had to be read to determine the reflection factor. Reducing the size of the sample window to one inch has made the variation in R_{2sw} from sample to sample negligible without impairing the accuracy.

Points A and C are brought to the same potential by a null method. That is, the amplifier galvanometer must show no deflection when I_1 and I_2 are started flowing by opening a shutter in the light beam. Switches cannot be used in

the circuit because of contact potentials.

The maximum potential drop across BC is about $1x10^{-2}$ volts. To measure this with an accuracy of 0.1 per cent requires the detection of $1x10^{-5}$ volts potential difference between A and C. Such a potential is easily measured with a galvanometer in a low resistance circuit, but is possible in a high resistance circuit only if an amplifier is used.

The amplifier circuit (Figure 3) is a modification of the Soller balanced circuit[8,9,10], using a Western Electric Electrometer vacuum tube (No. D96475), and a galvanometer of $1x10^{-10}$ amperes per mm sensitivity. The vacuum tube has a very high grid resistance and is well adapted to measurements in high resistance circuits. All power for the amplifier is supplied by one battery and the circuit balances out the effect of variation in battery voltage. The amplifier works well with the main part of the circuit unshielded, but it is necessary to shield the electrometer tube and all leads in the phototube circuit with grounded shields. Plate I shows the electrometer tube in its shield can, placed close to the phototube beneath the sphere, so that the capacitance to ground of the grid lead will be as low as possible. Due to this capacitance, it takes a small but finite time for the voltage across AB to build up; a longer time than for the voltage across BC. Thus there is a voltage difference during the transient state which gives the galvanometer in the amplifier a kick,

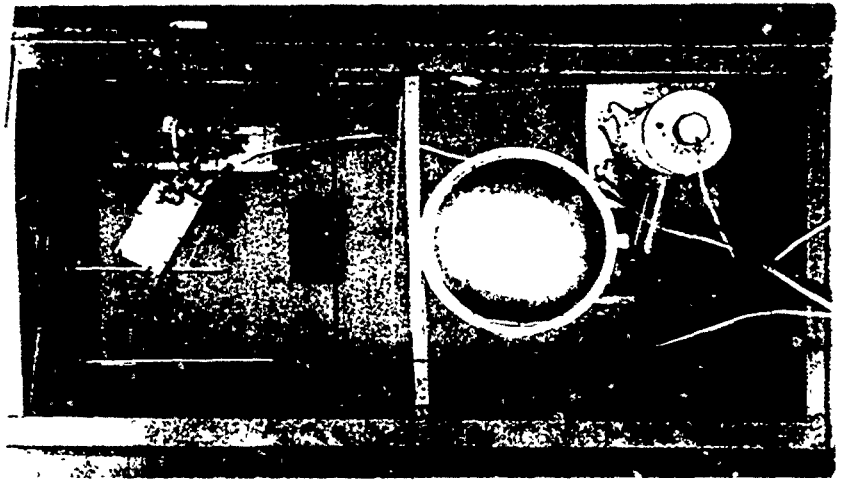


PLATE I

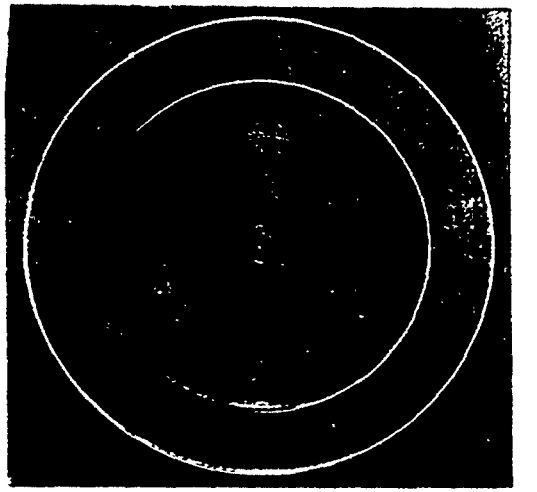


PLATE II

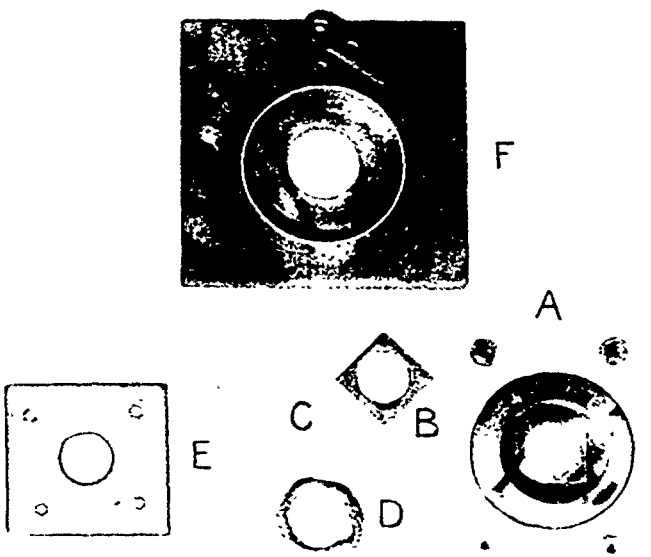


PLATE III

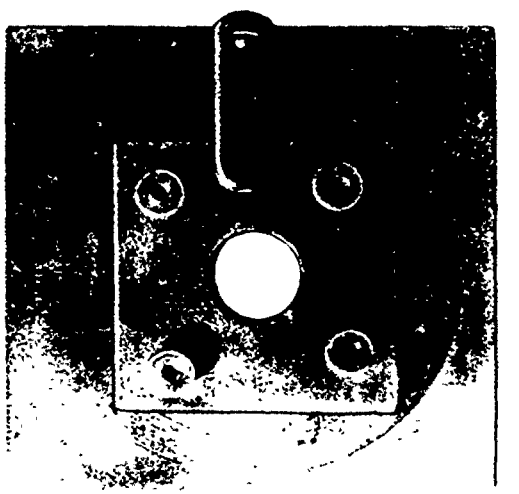


PLATE IV

making it difficult to obtain an exact balance across AC. The condenser placed across phototube No. 2 (Figure 2) tends to equalize the transient states in both phototube circuits and greatly reduces the amount of kick.

This method of measurement has three principal advantages. First, by essentially making simultaneous readings of reflected intensity and total light intensity, the effect of fluctuations in the source output is eliminated. Second, by measuring directly the ratio of these two intensities, the error in making simultaneous readings is avoided. Third, by balancing the two phototube currents before they are amplified, variations in the amplification factor of the amplifier do not affect the measurements.

In operating the apparatus, it is necessary to allow an hour for the electrometer tube to reach thermal equilibrium before the amplifier is sufficiently steady for accurate readings. A better method is to run the tube continuously, which is feasible since it draws only 0.27 amperes.

The S-1 Sunlamp reaches an approximately steady output in about half an hour. A thermometer placed close to the lamp but shielded by asbestos from its direct rays gives the air temperature near the lamp. The lamp is cooled and kept at a constant temperature by a low speed

fan. This is necessary since not only does the total output of the Sunlamp vary with temperature but the spectral distribution of the radiated energy shifts to some extent due to the change in vapor pressure with temperature of the mercury within the lamp[11]. This shift in spectral distribution affects the measured reflection factor. Figure 4 shows the reflection factor of a particular sample, measured at several lamp temperatures. The usual ambient temperature is 47°C.

2. Testing.

Pigments are tested dry by packing them in a shallow steel cell (Plate II). Aluminum bronze could not be packed in the cell, and was tested by coating a small panel with a rapid drying damar resin solution and dusting it over with the dry pigment. Tests made on basic carbonate white lead by both methods differed by only 2 per cent in reflection factor.

Liquids are measured in a specially constructed vitreosil cell. Vitreosil, or fused silica, is, like quartz, transparent to ultra-violet light. The cell (Plate III) consists of a steel body, A, in which a 1"x1"x1/32" polished vitreosil plate is cemented with sodium silicate; a copper spacer, B, 0.027" thick, which

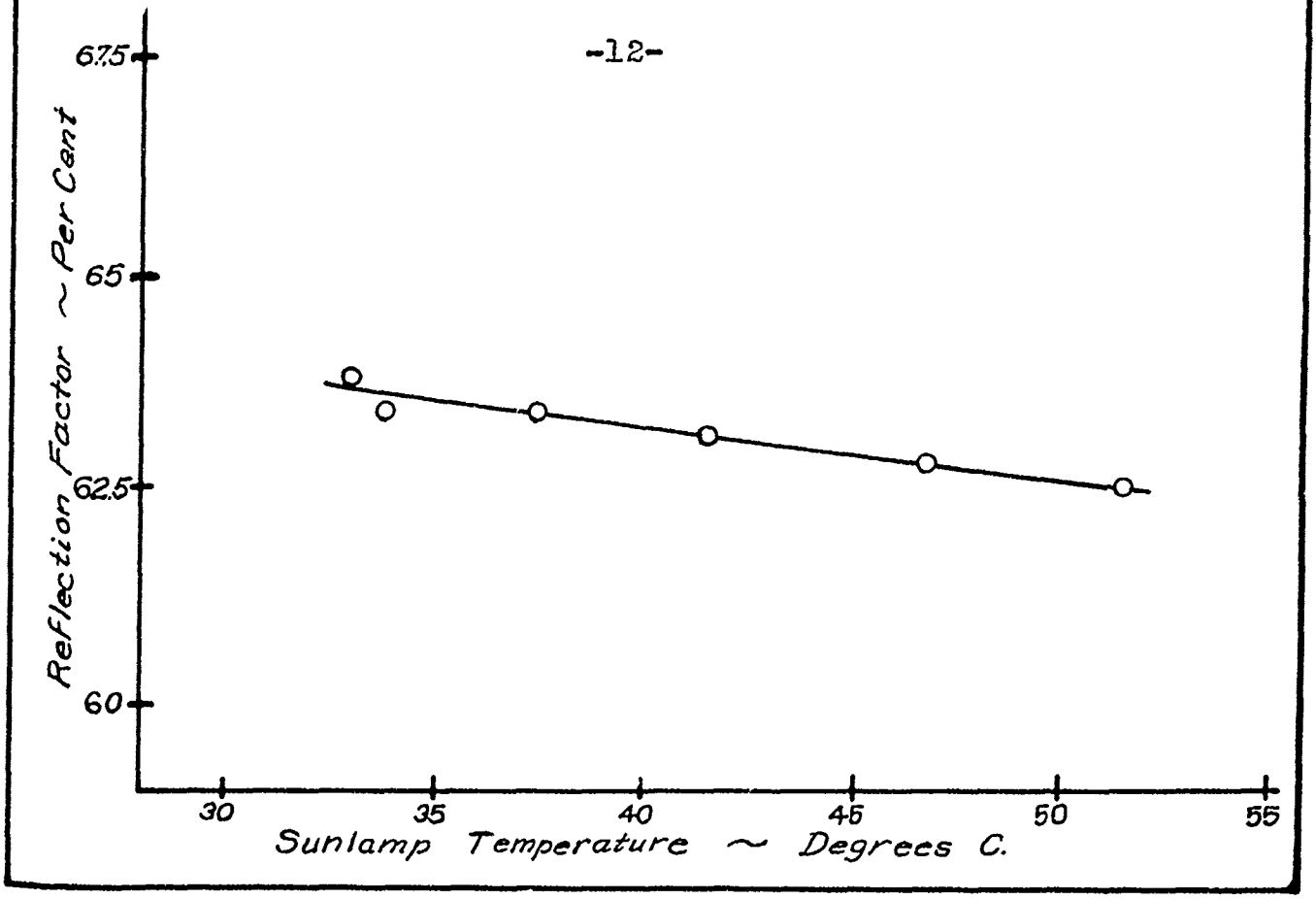
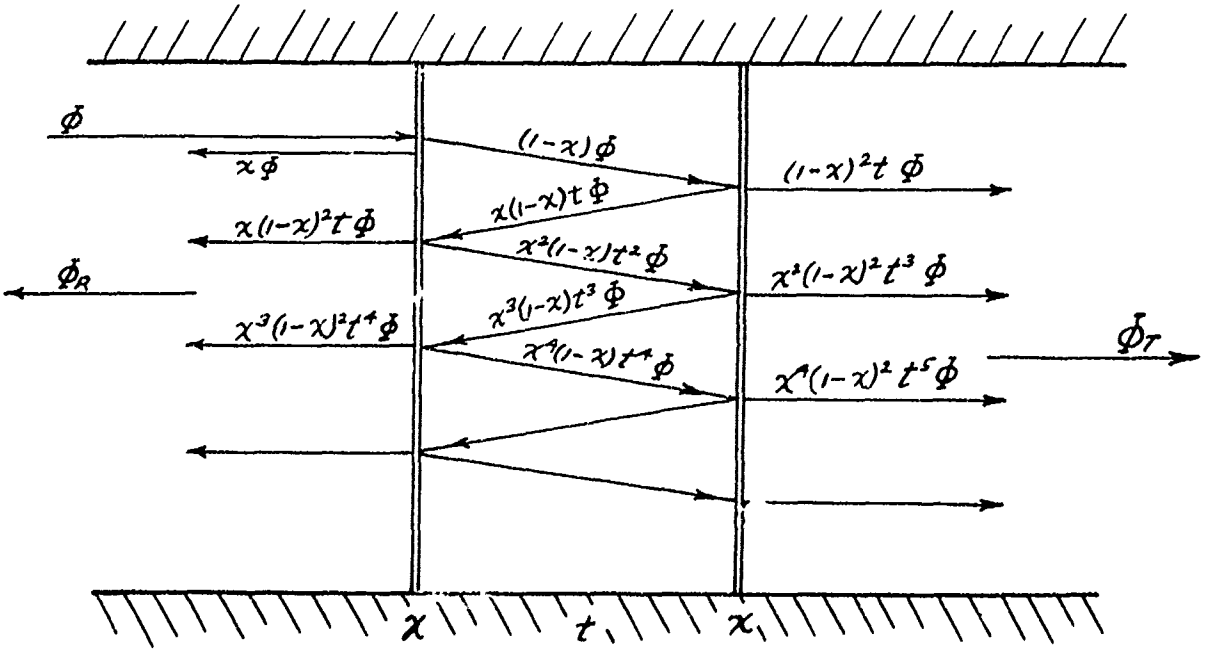


figure 4



Multiple Reflections
from
Two Parallel Surfaces

provides space for the liquid; a second vitreosil plate, C, 1"x1"x1/8"; a rubber washer, D; and a steel top plate, E, with which the entire assembly is clamped together. There is a clear light path through the cell 3/4" in diameter.

The cell is constructed to be as thin as possible on the side which is next to the sphere. For reflection measurements, the adapter plate, F, coated on its inner face with magnesium oxide, holds the cell in position on the sphere. For transmission measurements, the cell is slid into steel ways which hold it in the light beam directly in front of the sphere window.

It is customary to use these transmission cells in such a way that the transmission of the cell containing a solution is compared to the transmission of the cell containing pure solvent, thus eliminating the effect of the cell. In testing oils and solvents this cannot be done. Furthermore, with certain liquids in the cell, the per cent transmission is greater than for the empty cell. These liquids, being almost completely transparent to the ultraviolet, and having an index of refraction greater than that of air, reduce the amount of light reflected from the vitreosil-liquid interfaces and so increase the overall transmission of the cell. This extreme case shows the necessity of analysing the effect on transmission measurements of the multiple reflections from the four surfaces

of the cell.

It can be shown (Appendix B) that the transmission coefficient, t, of the material in the cell is:

$$t = -\frac{(1-R)^2-T^2}{2T} + \sqrt{\left[\frac{(1-R)^2-T^2}{2T}\right]^2+1}$$

where R and T are the measured overall reflection and transmission coefficients of the filled cell. Calculations on many samples have shown that t is usually about 10 per cent larger than T. Lambert's Law, $t=e^{-kd}$, is used to obtain the coefficient "k" which is characteristic of the liquid and independent of the thickness of the test sample.

Paints are tested by brushing or spraying on 4"x4" steel panels which can then be placed in the sample position on the sphere.

5. Reliability of Measurements.

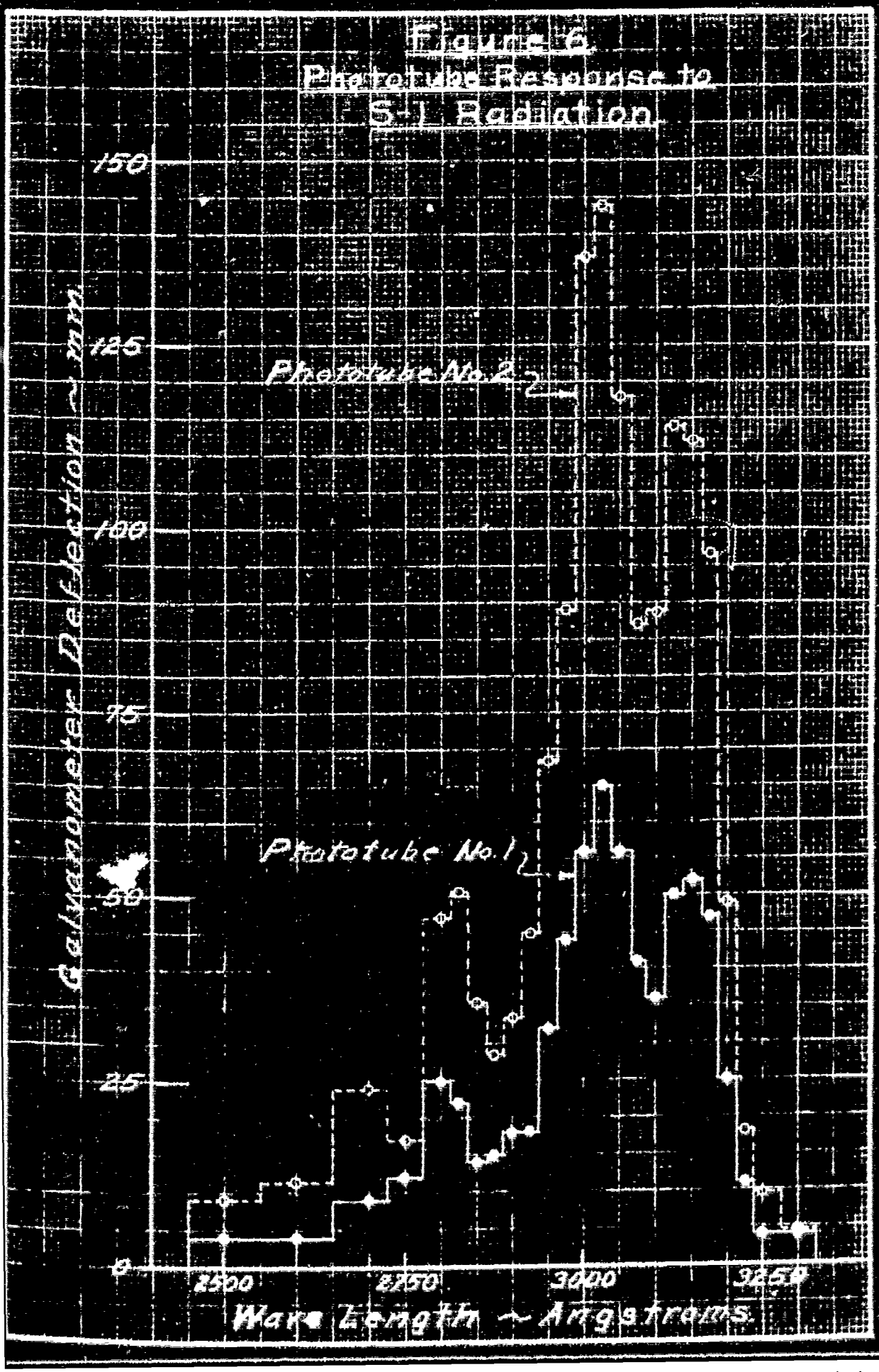
For a series of tests on successive days of the same sample, the reproducibility attainable with the apparatus was found to be within 0.2 per cent based on the incident light. Since the measurements are made in a band 400 Angstroms wide containing several strong mercury lines and since most materials are selective in absorption and reflection in the ultra-violet, the energy distribution in the band will have an effect on the measured reflection factors.

The characteristics of the measured energy in the band

were determined by measuring the response of each of the two phototubes at different wave lengths to the light from the S-1 Sunlamp, using a quartz monochromator. The Soller circuit with an input resistance of 14,000 megohms was used to measure the phototube currents. The results (Figure 6) show that their characteristics are similar, but that one phototube has about twice the current response of the other. The maximum measured energy in the band is at 3024 Angstroms, with the "center of gravity" of measured energy at about the same wave length.

The data shown in Figure 6, together with the data by Barnes[15] for the energy output of the S-1, enable the sensitivity curves of the two phototubes to be determined. Barnes measured the energy output perpendicular to the plane of the leads for the lamp running vertically in the open, which was its position for the measurements for Figure 6. Table I gives the calculated sensitivities for the two phototubes, and Figure 7 shows the agreement between these calculated results and the sensitivity curve furnished by the maker for Phototube No. 2.

As an independent check on the results furnished by this apparatus, Dr. A. H. Taylor of the Nela Park Laboratories of the General Electric Company was kind enough to measure the reflectances of several panels at 3024 Angstroms



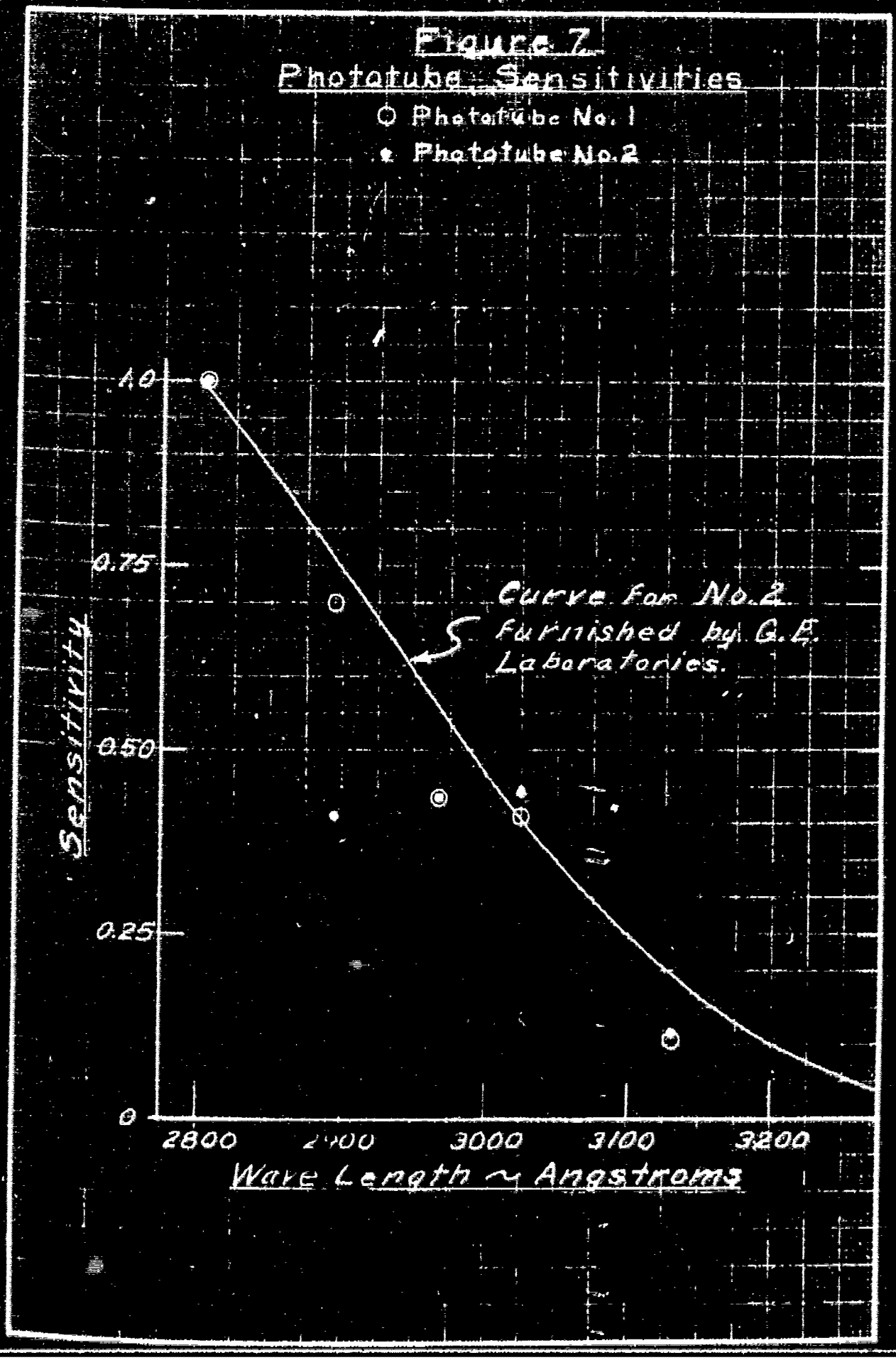


Table I.

Phototube Sensitivity.

Wave-length	Relative Energy, S-1	Galv. Reading	Relative Sensitivity	Reduced Sensitivity
		Phototube No. 1		
3130	13.5	52	3.85	0.105
3024	4.4	65	14.8	0.41
2967	2.54	40	15.8	0.435
2894	0.71	18	25.4	0.70
2804	0.69	25	36.2	1.00
		Phototube No. 2		
3130	13.5	114	8.45	0.115
3024	4.4	144	32.7	0.442
2967	2.54	82	32.2	0.435
2894	0.71	33 (est.)	30.3	0.41
2804	0.69	51	74.0	1.00

which is the most intense mercury line in the band measured by this apparatus. Dr. Taylor used a 4 inch integrating sphere, a quartz spectrograph and a quartz sodium photoelectric cell[5]. Table II is a comparison between the reflectances obtained by Dr. Taylor and the reflectances obtained with the apparatus described herein. The agreement is excellent when it is considered that one measurement is for a single spectral line and the other

Table II.

Comparison of Reflectances.

Panel	Reflectance for band 2600-3200 A.	Reflectance at 3024 A.
G-5a	54.7	53.
H-5	41.1	42.
H-8	41.6	43.
H-10	41.2	45.

for a 400 Angstrom band. The higher reflectance for G-5a, and the lower reflectances for the H series panels, obtained for the band are probably the result of differences in the spectral absorption curves of these paints.

A further check was provided by duplicating an ultra-violet paint described by Luckiesh and Holladay[16], their Paint "C". They give its reflection factor as 54.0, and the value obtained for the duplicate with this apparatus was 55.9.

The reflection factors obtained for pigments are subject to an additional error besides that inherent in the apparatus due to the fact that the manner of packing them into the cell and leveling off the surface is not entirely reproducible. Barytes, for example, exhibited a variation of 1.5 per cent when several successive determinations were made on freshly prepared samples. Consequently, the results

for the reflectances of pigments are given only to the nearest per cent.

II. DEVELOPMENT OF ULTRA-VIOLET PAINTS.

1. Reflection and Transmission of Paint Materials.

A systematic investigation of the possibilities of making paints with high ultra-violet reflectances requires a knowledge of the ultra-violet behaviour of the materials of which such paints might be made. To this end, the reflection factors of white and colored pigments and the transmission coefficients of oils, resins and thinners were measured. All materials are of commercial grade and purity unless otherwise indicated.

In Table III are listed the reflectances for the white pigments. They agree qualitatively with the data which Pfund[14], Stutz[12], Luckiesh[15,16] and Goodeve[17] have obtained for the more common pigments. This is satisfactory when it is remembered that the results in Table III are for the band 2800-3200 Angstroms (Figure 6) whereas the data in the literature with the exception of some by Luckiesh[16] are for individual lines of the mercury spectrum.

Pfund points out that there is an inverse relationship between the reflection factor and opacity (i.e. light absorption) of a pigment, and observes that "The inerts, as a class, are much less opaque, particularly in the short wave length region". From a brief study of Table III, it is evident that magnesium, zirconium, silicon, aluminum, lead, calcium, and barium pigments do not absorb erythemal

Table III.

White Pigments.

Pigment	Chemical Composition	Per Cent Reflection
Lead Free Zinc Oxide	ZnO	3
35% Leaded Zinc Oxide	$PbSO_4$, ZnO	4
Zinc Sulfide	ZnS	6
Titanox B	25% TiO_2, $BaSO_4$	6
Lead Titanate	$PbTiO_3$	6
Titanium Dioxide	TiO_2	7
Titanox C	TiO_2, $CaSO_4$	7
Lithopone	26% ZnS, $BaSO_4$	8
Antimony Oxide	Sb_2O_3	17
Zirconium Oxide, Com'l.	ZrO_2	41
Celite	SiO_2, Silicates	45
Basic Sulfate White Lead	$PbSO_4$, 16% PbO, 9% ZnO	48
China Clay	$Al_2Si_2O_7 \cdot 2H_2O$	54
Aluminum Oxide	Al_2O_3	55
Basic Carbonate White Lead, Carter Process	75% $PbCO_3$	59
Surfex	$CaCO_3$	61
Basic Carbonate White Lead, Dutch Process	75% $PbCO_3$	62
Commercial Whiting	$CaCO_3$	66
Aluminum Hydroxide	$Al_2O_3 \cdot H_2O$	67
Asbestine Pulp	Mg Silicate	67
Barytes	95% $BaSO_4$	68

Table III (Continued).

Pigment	Chemical Composition	Per Cent Reflection
Silica	SiO_2	71
Magnesium Oxide, heavy, (Squibb)	MgO	74
Zirconium Oxide, C.P.	ZrO_2	78
Aluminum Bronze	Al	80 (est.)
Magnesium Carbonate, U.S.P., (Mallinkrodt)	$MgCO_3$	81
Magnesium Carbonate, Com'l.	$MgCO_3$,$Mg(OH)_2$	81
Magnesium Oxide, light, (Squibb)	MgO	82
Magnesium Oxide, C.P., (Baker)	MgO	83
Magnesium Carbonate, U.S.P., (Coleman & Bell)	$MgCO_3$	85
Magnesium Oxide, U.S.P., (Eimer & Amend, E-75)	MgO	90
Magnesium Oxide, freshly smoked	MgO	98

ultra-violet appreciably, whereas zinc, titanium, and antimony pigments absorb it to a large extent. Zirconium oxide has a refractive index of 2.2, higher than that of any of the high reflecting pigments, so that if it can be obtained in a purer state commercially, it should be the best covering pigment that can be used in an ultra-violet paint. A surprising fact is the small but definite

superiority in reflection of the Dutch process over the Carter process white lead, since the Carter process pigment is white and the Dutch process pigment has a decided yellow-gray cast.

Table IV shows the results for colored pigments. Although not complete, the list is representative of the chemical groups found in colored pigments. The results agree well with those of Stutz[12] for 3024 Angstroms.

Table V lists the absorption coefficients for oils, thinners, driers and other liquids, resins, and plasticizers. Since the surface reflection from a liquid-air interface is negligible up to an angle of incidence of 50° from the normal, it is evident that any liquid or resinous material to be used in a paint, other than volatile thinner, must have a low absorption coefficient in order that light may be reflected by the pigment without undue absorption by the vehicle. In practice, it has been found that a coefficient less than 60 to 70 is fairly satisfactory. From Table V-A, it is evident that no oil will be satisfactory. Refined castor oil is possibly an exception, but, when made into a drying oil by dehydration, it is unsatisfactory.

Table V-B shows that the common driers cannot be used except in minute amounts. However they need not be used at all since the oils themselves are unsatisfactory. Many of the common solvents have low absorption coefficients, so that they can be used to test resins in solution. Casein is

Table IV.

Colored Pigments.

Pigment	Per Cent Reflection
Solfast Sky Blue	1
Chinese Blue (A Prussian Blue)	2
C. P. Para Toner Dark	2
Toluidine Toner	2
Lt. Para Toner	2
Copper Carbonate	3
Graphic Red H (Lithol Red Toner)	2
Mapico Yellow Lemon	3
Chrome Yellow Med.	3
Molybdate Orange	3
Cadmium Sulfide	3
Zinc [illegible]omate	3
C. P. Chrome Orange Dark	5
Chromium Oxide	5
Rose Lake	5
Alizarine Lake	5
Persian Gulf Oxide (Iron Oxide)	5
Litharge	6
Sublimed Blue Lead	10
Ultra Marine Blue	20

Table V-A

Ultra-Violet Absorption of Oils.

Material	Absorption Coefficient (in^{-1})
Oiticica Oil	Infinite
China Wood Oil	1.6×10^2
Heat Bodied Linseed Oil	1.6×10^2
Refined Perilla Oil	1.6×10^2
Alkali Refined Linseed Oil	1.5×10^2
Heat Bodied Perilla Oil	1.5×10^2
Special Dehydrated Castor Oil	1.2×10^2
Alkali Refined Soya Bean Oil	1.2×10^2
Dehydrated Castor Oil	95
Castor Oil, Com'l.	74
Refined Castor Oil	62

Table V-B

Ultra-Violet Absorption of Thinners Driers and Other Liquids.

Material	Absorption Coefficient (in^{-1})
6% Cobalt Nuodex	Infinite
6% Manganese Nuodex	Infinite
24% Lead Nuodex	1.8×10^2
Acetone	1.3×10^2
Sulfate Wood Turpentine	76
Casein Solution	57
Mineral Spirits	44

Table V-B (Continued).

Material	Absorption Coefficient (in^{-1})
Solvesso No. 2	28
Commercial Xylol	24
Toluene	9.5
Butanol	9.2
Ethylene Dichloride	3.9
Glycerine	3.5
Absolute Alcohol	1.1
Distilled Water	0.4

found to be only moderately absorbent. Luckiesh[16] has prepared paints with reflectances as high as 54 per cent with casein as binder.

The resins were tested in solution. In calculating the absorption coefficients of the resins from the coefficient for the solutions, a modification of Beer's Law was used. It was assumed that the absorption coefficients are additive in proportion to the relative volume of each component, and that the volumes of resin and solvent are additive in solution. These assumptions are as accurate as the data warrant, since the thickness of the material in the cell is known only to two figures. Table V-C shows that the natural resins have very high absorption coefficients. Of the synthetic resins, urea formaldehyde,

Table V-C.

Ultra-Violet Absorption of Resins

Material	Solvent	% by Wt.	S.G.	Absorption Coeff.(in^{-1}) Sol'n.	Resin
B. R. 8963 Bakelite	Toluene	20	1.12	230	1.4×10^{3}
Amberol F7 Lt.	Toluene	20	1.10	230	1.4×10^{3}
801 Amberol	Toluene	20	1.15	215	1.3×10^{3}
Limed Rosin	Toluene	20	1.1	215	1.3×10^{3}
V-13005 Lt. Stable Phenolic Resin	Toluene	66.8	1.10	215	1.3×10^{3}
Kopol 500 (Fused Congo-Glycerine Ester)	Toluene	20	1.06	230	1.2×10^{3}
Ester Gum A.V. 5-7	Toluene	20	1.10	184	1.1×10^{3}
550 Durez	Toluene	20	1.12	164	1.0×10^{3}
XR4056 Bakelite	Toluene	20	1.04	161	8.6×10^{2}
XR820 Bakelite	Toluene	20	1.20	152	8.1×10^{2}
2000 Super Beckacite	Toluene	20	1.05	124	6.8×10^{2}
Cumar G 1/2	Toluene	20	1.02	119	6.3×10^{2}
Batavia Demar	Toluene	20	1.05	108	5.8×10^{2}
Varcum 250-F	Toluene	20	1.1	94.5	5.3×10^{2}

Table V-C (Continued).

Material	Solvent	% by Wt.	S.G.	Absorption Coeff. (in^{-1}) Sol'n.	Resin
4X Manilla	Abs. Alcohol	20	1.07	70.2	4.5×10^2
Nevillite (a vinyl resin)	Toluene	20	1.02	47.3	2.3×10^2
Glyceryl-Phthalate Varnish B	1/3 Xylol 2/3 Solvesso No.2	65	1.37	131.	2.2×10^2
Glyceryl-Phthalate Varnish A	1/4 Xylol 3/4 Solvesso No.2	65	1.37	102.5	1.7×10^2
L-2786 Neofat Alkyd Resin Sol'n.	½ Xylol ½ Solvesso No.2	65	1.02	97.4	1.4×10^2
Ethyl Cellulose B	.8 Toluene .2 Alcohol	10	1.14	71.2	75
Rezyl No.227-8 Sol'n.	½ Toluene ½ Butanol	50	1.02	34	64
Urea-formaldehyde Resin Sol'n.	.6 Xylol .4 Butanol	50	1.19	32	52
Methyl Methacrylate	Toluene	18.3	1.19	15.0	48.8
Urea-formaldehyde Resin		100	1.1		46
Ethyl Methacrylate	Toluene	20	1.11	14.6	40.5
Nitro-cellulose Lacquer Sol'n.		25		40	
Acryloid B-7	Ethylene Dichloride	20	1.15	9.6	30

Table V-C (Continued).

Material	Solvent	% by Wt.	S.G.	Absorption Coeff. (in^{-1}) Sol'n.	Resin
Urea-formaldehyde Resin Sol'n. (V-7746)	½ Xylol ½ Butanol	50	1.19	20	25
Propyl Methacrylate	Toluene	20	1.06	12.1	24.6
Butyl Methacrylate	Toluene	20	1.05	11.6	21.8
Isobutyl Methacrylate	Toluene	19.6	1.03	11.3	20.0
Vinylite AV-AA	Toluene	17.8	1.19	11.0	20

Table V-D.

Ultra-Violet Absorption of Plasticizers.

Material	Solvent	% by Wt.	S.G.	Absorption Coeff. (in^{-1}) Sol'n.	Plasticizer
4,4 dichloro-diphenyl	Toluene	4.5	1	82	1.9×10^3
Methyl Abietate		100			2.3×10^2
Hydrogenated Methyl Abietate		100			1.6×10^2
Dow Plasticizer No. 6		100			1.2×10^2
Dow Plasticizer No. 5		100			1.2×10^2

Table V-D (Continued).

Material	Solvent	% by Wt.	S.G.	Absorption Coeff.(in^{-1}) Sol'n.	Plasticizer
Benzyl Benzoate		100			1.8×10^2
Methyl Ricinoleate		100			1.0×10^2
Santicizer No. 8		100			60
Dibutyl Phthalate		100			49
Santicizer B-16		100			37
Butyl Stearate		100			37
Tricresyl Phosphate		100			30
Triphenyl Phosphate	Toluene	50	1.20	14.0	20
Dow Plasticizer No. 2		100	1.11		18
n-butyl d-tartrate		100			15
Dow Plasticizer No. 7	Toluene	41	1.07	9.0	8.1
Tripropionin		100			2.8

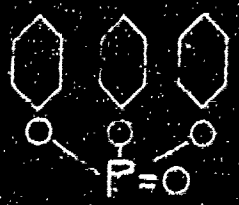
nitro-cellulose lacquer, ethyl cellulose, the methacrylate esters, and vinylite are low in absorption. Urea-formaldehyde, however, must be baked, and it is well known that nitro-cellulose deteriorates upon exposure to ultra-violet radiations.

Table V-D shows the absorption coefficients of plasticizers used with ethyl cellulose and the methacrylates. The results on the Dow Plasticizers are interesting in view of their structures (Figure 8). The substitution of tertiary butyl groups in para position on triphenyl phosphate decreases the absorption slightly. The substitution of one phenyl group by a diphenyl group increases the absorption tremendously, but the substitution of a second has no further effect. The explanation of this effect is a subject for further investigation, but has no direct bearing on this work.

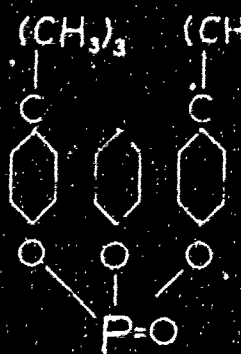
2. Properties of Simple Paints: Two Component Systems.

A typical paint formula is very complex, and may include several pigments and fillers, one or more oils or varnishes, driers and thinners. This complexity is the result of the modification of an originally simple formula in order to give the paint various desirable properties such as brushability, lack of settling, high hiding power, and so forth. Since this work is an investigation of the possibil-

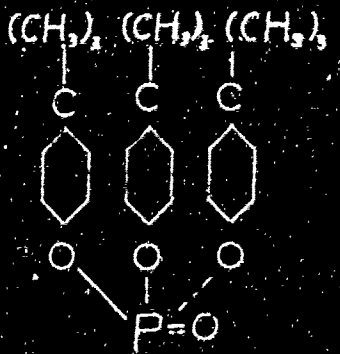
Figure 8.



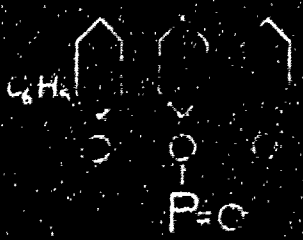
Triphenyl Phosphate
(k=20)



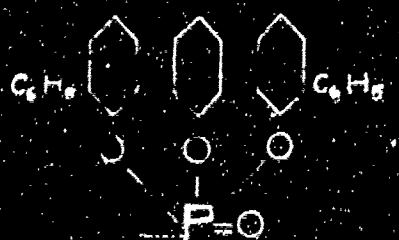
Dow Plasticizer No. 2
(k=18)



Dow Plasticizer No. 7
(k=8)



Dow Plasticizer No. 5
($k=1.2 \cdot 10^2$)



Dow Plasticizer No. 6
($k=1.2 \times 10^5$)

ity of new types of paint which will reflect ultra-violet, and since in complex systems it is difficult to distinguish the properties of the individual components, the simplest possible systems of pigment and vehicle were studied first.

Since surface reflection at the vehicle-air interface can account for but a small part of the reflection of a paint, reflection must result chiefly from repeated reflection and refraction of the light by the pigment particles with the final result that that light which is not absorbed emerges from the paint film as reflected light. It is evident then that, among other properties, it is desirable that both pigment and vehicle possess low absorption in order that the maximum amount of light may be returned from the film. Neglecting the effects of refractive index and particle size, a high reflecting pigment will have a low absorption coefficient.

Therefor it was decided to prepare a number of preliminary simple paints to test the truth of the above conclusions; also, in slightly more complicated systems, to observe the effect of varying one component at a time. From these tests the combinations of pigment and resin which would prove satisfactory were determined. Then, after satisfactory plasticizer composition and content had been determined for each resin, trial paints were milled and compared, and the correct pigment volume per cent determined.

The preliminary paints were ground by hand in a mortar and pestle with an appropriate thinner, and brushed to a heavy film on steel panels. No effort was made to control exactly the pigment volume per cent, as its effect and correct value were not known, and only the general effects of pigment and vehicle were desired. Table VI is a complete tabulation of the paints ground by mortar and pestle.

The combinations of a single pigment with a single oil or resin show that both a high reflecting pigment and a vehicle with a low absorption coefficient are necessary in order to produce a paint with a high reflection factor. This is clearly shown in Table VII which shows the relation of reflection factor to vehicle absorption and pigment reflection, and which is a retabulation of part of Table VI. Another fact, not so obvious, is illustrated by this table, namely that those white pigments which are used as inerts and fillers in paints reflecting visible light, behave in somewhat the same manner in paints reflecting ultra-violet light. In other words, "inert" pigments, which are materials with refractive indices for visible light so close to those of most oils and resins that their particles are inefficient reflectors and refractors, also have refractive indices in the ultra-violet comparable to those of the resins. Thus, dry silica powder reflects 71 per cent, but immersed in a urea-formaldehyde resin reflects only about 25 per cent; whereas dry white lead reflects 62 per cent and immersed in

Table VI.

Preliminary Paints.

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-1	Silica	Acryloid B-7	90.0	58	Brittle
P-2	Aluminum Bronze	Acryloid B-7	80.5	79	Brittle
P-3	B. C. White Lead	Acryloid B-7	91.5	55	Tough
P-4	Leaded Zinc Oxide	Acryloid B-7	89.0	4	
P-5	Zinc Oxide	Acryloid B-7	87.2	4	
P-6	Silica	Nitro-cellulose Lacq.	82.0	37	Fairly tough
P-7	Silica	V-7746 (urea-form.)	74.7	21	
P-8	Silica	Glyceryl Phthalate Varnish A.	67.0	9	Tough
P-9	Silica	Linseed Oil	75.3	6	
P-10	Silica	Rezyl #227-8	78.3	27	
P-11	Silica	Neofat Alkyd Resin L2786	66.8	6	
P-12	Silica	V-13005 Lt. Stable Phenolic Resin	67.5	7	

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film.	Refl. Factor	Comment
P-13	B. C. White Lead	V-13005 Lt. Stable Phenolic Resin	74.1	12	
P-14	Barytes	Acryloid B-7	86.3	18	
P-15	Magnesium Oxide	Acryloid B-7	54.6	46	
P-16	Basic Sulfate White Lead	V-7746 (urea-form.)	75.5	33	
P-17	Aluminum Bronze	Rezyl #227-8	59.8	70	
P-18	Basic Sulfate White Lead	Rezyl #227-8	63.3	34	Tough
P-19	Aluminum Bronze	V-7746 (urea-form.)	65.2	72	Soft
P-20	B. C. White Lead	V-7746 (urea-form.)	71.8	42	Tough
P-21	B. C. White Lead	Rezyl #227-8	83.5	46	Hard,peels
P-22	Barytes	Acryloid B-7	89.2	22	Very tough
P-23	Magnesium Carbonate	Acryloid B-7	66.8	69	Baked,brit.
P-24	Magnesium Carbonate	Acryloid B-7	78.5	74	Soft
P-25a	Magnesium Carbonate	V-7746 (urea-form.)	50.0	63	Soft
P-25b	Magnesium Carbonate	V-7746 (urea-form.)	50.0	55	Baked,soft

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film.	Refl. Factor	Comment
P-26	B. C. White Lead	Acryloid B-7	91.2	53	Tough
P-27	80% B. C. White Lead 20% Aluminum Bronze	Acryloid B-7	89.4	51.5	Soft
P-28a	Magnesium Carbonate	Urea-form. Resin Sol'n.	43.7	38	Brittle
P-28b	Magnesium Carbonate	Urea-form. Resin Sol'n.	43.7	30	Baked, blistered
P-29	60% B. C. White Lead 40% Aluminum Bronze	Acryloid B-7	90.0	62.9	Soft
P-30	30% B. C. White Lead 70% Aluminum Bronze	Acryloid B-7	90.4	73.2	Soft
P-31	Aluminum Bronze	Acryloid B-7	84.8	76.1	Soft
P-32	95% B. C. White Lead 5% Aluminum Bronze	Acryloid B-7	90.5	45.8	Soft
P-33	Magnesium Carbonate	Urea-form. Resin Sol'n.	62.8	51	Baked, soft
P-34	98% B. C. White Lead 2% Aluminum Bronze	Acryloid B-7	90.6	45.5	Tough
P-35	Magnesium Oxide	V-7746 (urea-form.)	58.5	42	Tough
P-36	Commercial Whiting	Acryloid B-7	88.2	24	Tough

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-37	Asbestine Pulp	Acryloid B-7	83.1	32	Tough
P-38	Surfex	Acryloid B-7	88.1	45	Tough
P-39	China Clay	Acryloid B-7	83.3	59	Tough
P-40	Celite	Acryloid B-7	73.0	57	Soft
P-41	Antimony Oxide	Acryloid B-7	82.0	12	Tough
P-42	B. C. White Lead	Nitro-cellulose Lacq.	89.5	53	Soft
P-43	B. C. White Lead	V-7746 (urea-form.)	57.2	44.3	Tough
P-44	75% B. C. White Lead 25% Magnesium Carbonate	V-7746 (urea-form.)	57.2	39.5	Tough
P-45	50% B. C. White Lead 50% Magnesium Carbonate	V-7746 (urea-form.)	44.5	34.9	Tough
P-46	25% B. C. White Lead 75% Magnesium Carbonate	V-7746 (urea-form.)	39.7	31.6	Tough
P-47	Magnesium Carbonate	V-7746 (urea-form.)	56.4	22.9	Tough
P-48	B. C. White Lead	Acryloid B-7	76.9	49.2	
P-49	99% B. C. White Lead 1% Ultra Marine Blue	Acryloid B-7	76.9	44.2	

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-50	95% B. C. White Lead 5% Ultra Marine Blue	Acryloid B-7	76.9	52.8	
P-51	90% B. C. White Lead 10% Ultra Marine Blue	Acryloid B-7	76.9	25.7	
P-52	80% B. C. White Lead 20% Ultra Marine Blue	Acryloid B-7	76.9	16.5	
P-53	98% B. C. White Lead 2% Chrome Yellow Med.	Acryloid B-7	76.9	27.1	
P-54	95% B. C. White Lead 5% Chrome Yellow Med.	Acryloid B-7	76.9	20.1	
P-55	90% B. C. White Lead 10% Chrome Yellow Med.	Acryloid B-7	76.9	15.0	
P-56	Magnesium Carbonate	Acryloid B-7	58.1	64.0	
P-57	98% Magnesium Carbonate 2% Ultra Marine Blue	Acryloid B-7	50.0	50.3	
P-58	95% Magnesium Carbonate 5% Ultra Marine Blue	Acryloid B-7	50.0	52.4	
P-59	Aluminum Bronze	Ethyl Cellulose	61.9	71.5	
P-60	B. C. White Lead	Ethyl Cellulose	86.2	46.6	Peeled

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-61	Magnesium Carbonate	Ethyl Cellulose	45.5	59.9	
P-62	Magnesium Oxide	Ethyl Cellulose	64.7	43.6	
P-63	Silica	Ethyl Cellulose	80.5	47.9	
P-64	Aluminum Bronze	Cellulose Acetate	92.5	72.0	
P-65	B. C. White Lead	Cellulose Acetate	81.6	- -	Peeled
P-66	Magnesium Carbonate	Cellulose Acetate	44.2	51.9	Peeled
P-67	Magnesium Oxide	Cellulose Acetate	62.8	48.7	Peeled
P-68	Silica	Cellulose Acetate	80.1	52.3	Peeled
P-69	B. C. White Lead	Acryloid B-7	90.5	54.0	Tough
P-70	75% B. C. White Lead 25% Magnesium Carbonate	Acryloid B-7	78.6	59.2	Tough
P-71	50% B. C. White Lead 50% Magnesium Carbonate	Acryloid B-7	69.7	64.0	Tough
P-72	25% B. C. White Lead 75% Magnesium Carbonate	Acryloid B-7	62.7	65.3	Soft
P-73	Magnesium Carbonate	Acryloid B-7	56.7	67.4	Soft

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-74	99% B. C. White Lead 1% Rose Lake	Acryloid B-7	90.5	42.7	Tough
P-75	98% B. C. White Lead 2% Rose Lake	Acryloid B-7	90.5	39.9	Tough
P-76	95% B. C. White Lead 5% Rose Lake	Acryloid B-7	90.5	30.7	Tough
P-77	90% B. C. White Lead 10% Rose Lake	Acryloid B-7	90.5	22.9	Tough
P-78	99.5% B. C. White Lead 0.5% Rose Lake	Acryloid B-7	90.5	45.3	Tough
P-79	Magnesium Carbonate	Acryloid B-7	52.5	64.0	Tough
P-80	98% Magnesium Carbonate 2% Aluminum Bronze	Acryloid B-7	52.6	61.0	Soft
P-81	95% Magnesium Carbonate 5% Aluminum Bronze	Acryloid B-7	53.8	59.5	Soft
P-82	75% Magnesium Carbonate 25% Aluminum Bronze	Acryloid B-7	58.3	51.1	Soft
P-83	60% Magnesium Carbonate 40% Aluminum Bronze	Acryloid B-7	61.8	50.6	Soft
P-84	30% Magnesium Carbonate 70% Aluminum Bronze	Acryloid B-7	70.9	61.7	Soft

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-85	Aluminum Bronze	Acryloid B-7	85.5	79.4	Soft
P-86	98% Magnesium Carbonate 2% Rose Lake	Acryloid B-7	52.7	55.9	Soft
P-87	97% Magnesium Carbonate 3% Rose Lake	Acryloid B-7	52.7	54.4	Tough
P-88	93% Magnesium Carbonate 7% Rose Lake	Acryloid B-7	52.7	46.9	Soft
P-89	85% Magnesium Carbonate 15% Rose Lake	Acryloid B-7	52.7	51.7	Tough
P-90	99% Magnesium Carbonate 1% Persian Gulf Oxide	Acryloid B-7	52.7	55.5	Tough
P-91	98% Magnesium Carbonate 2% Persian Gulf Oxide	Acryloid B-7	52.7	50.4	Tough
P-92	95% Magnesium Carbonate 5% Persian Gulf Oxide	Acryloid B-7	52.7	44.0	Soft
P-93	90% Magnesium Carbonate 10% Persian Gulf Oxide	Acryloid B-7	52.7	36.8	Soft
P-94	Magnesium Carbonate	Acryloid B-7	76.9	75.5	Soft
P-95	Magnesium Carbonate	Acryloid B-7	68.8	73.2	Soft

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-96	Magnesium Carbonate	Acryloid B-7	62.3	70.6	Soft
P-97	Magnesium Carbonate	Acryloid B-7	45.6	52.0	Tough
P-98	Magnesium Carbonate	Acryloid B-7	35.9	29.1	Tough, brit.
P-99	98% Magnesium Carbonate 2% Chrome Yellow Med.	Acryloid B-7	52.7	47.6	Tough
P-100	95% Magnesium Carbonate 5% Chrome Yellow Med.	Acryloid B-7	52.7	43.4	Tough
P-101	90% Magnesium Carbonate 10% Chrome Yellow Med.	Acryloid B-7	52.7	28.5	Tough
P-102	80% Magnesium Carbonate 20% Chrome Yellow Med.	Acryloid B-7	52.7	15.5	Tough
P-103	B. C. White Lead	Acryloid B-7	94.5	60.5	Tough
P-104	B. C. White Lead	Acryloid B-7	91.2	57.3	Soft
P-105	B. C. White Lead	Acryloid B-7	69.5	50.5	Tough
P-106	B. C. White Lead	Acryloid B-7	80.7	49.1	Tough
P-107	99% B. C. White Lead 1% Persian Gulf Oxide	Acryloid B-7	90.3	40.4	Tough

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-108	98% B. C. White Lead 2% Persian Gulf Oxide	Acryloid B-7	90.3	35.1	
P-109	95% B. C. White Lead 5% Persian Gulf Oxide	Acryloid B-7	90.3	26.0	
P-110	99.5% B. C. White Lead 0.5% Persian Gulf Oxide	Acryloid B-7	90.3	42.0	
P-111	Surfex	Acryloid B-7	89.3	32.7	Tough
P-112	75% Surfex 25% B. C. White Lead	Acryloid B-7	89.3	35.3	Soft
P-113	50% Surfex 50% B. C. White Lead	Acryloid B-7	89.3	39.1	Tough
P-114	25% Surfex 75% B. C. White Lead	Acryloid B-7	89.3	40.9	Tough
P-115	75% Aluminum Bronze 25% Ultra Marine Blue	Acryloid B-7	83.3	33.8	Soft
P-116	50% Aluminum Bronze 50% Ultra Marine Blue	Acryloid B-7	83.3	30.0	Soft
P-117	1/3 Aluminum Bronze 1/3 Ultra Marine Blue 1/3 B. C. White Lead	Acryloid B-7	83.3	40.6	Soft

Table VI (Continued).

Nbr.	Pigments	Oils or Resins	% Pigment by wt. in solid film	Refl. Factor	Comment
P-118	B. C. White Lead	85% Acryloid B-7 Sol'n. 15% of a 20% Nevillite Sol'n.	90.2	49.2	Tough
P-119	B. C. White Lead	Casein Sol'n.		51.0	Brit., Peeled.
P-120	B. C. White Lead	Casein Sol'n.		50.5	Brittle
P-121	Magnesium Oxide (Baker)	40% Dow No. 7 60% Ethyl Cellulose B	68.7	70.0	Soft
P-122	Aluminum Bronze	Rezyl 227-8	51.5	75.8	Baked
P-123	Aluminum Bronze	17% Dow No. 7 83% Rezyl 227-8	51.4	76.5	Baked, soft
P-124	Aluminum Bronze	17% Dow No. 7 83% Rezyl 227-8	30.7	49.6	Baked, filtered
				67.3	Baked, unfiltered
P-125	Aluminum Bronze	17% Dow No. 7 83% Urea-form. sol'n.	30.7	69.6	Baked
P-126	Aluminum Bronze	35% Dow No. 7 65% Ethyl Cellulose	36.2	64.2	

Table VI (Continued).

Nbr.	Pigments	Oil or Resin	% Pigment by wt. in solid film	Refl. Factor	Comment
P-127	Aluminum Bronze	12% Butyl Stearate 88% Isobutyl Meth-acrylate	38.8	69.0	
P-128	Magnesium Oxide, light (Squibb)	40% Dow No. 7 60% Ethyl Cellulose B	68.5	75.4	Filtered
P-129	Magnesium Oxide, heavy (Squibb)	40% Dow No. 7 60% Ethyl Cellulose B	68.5	58.6	Filtered

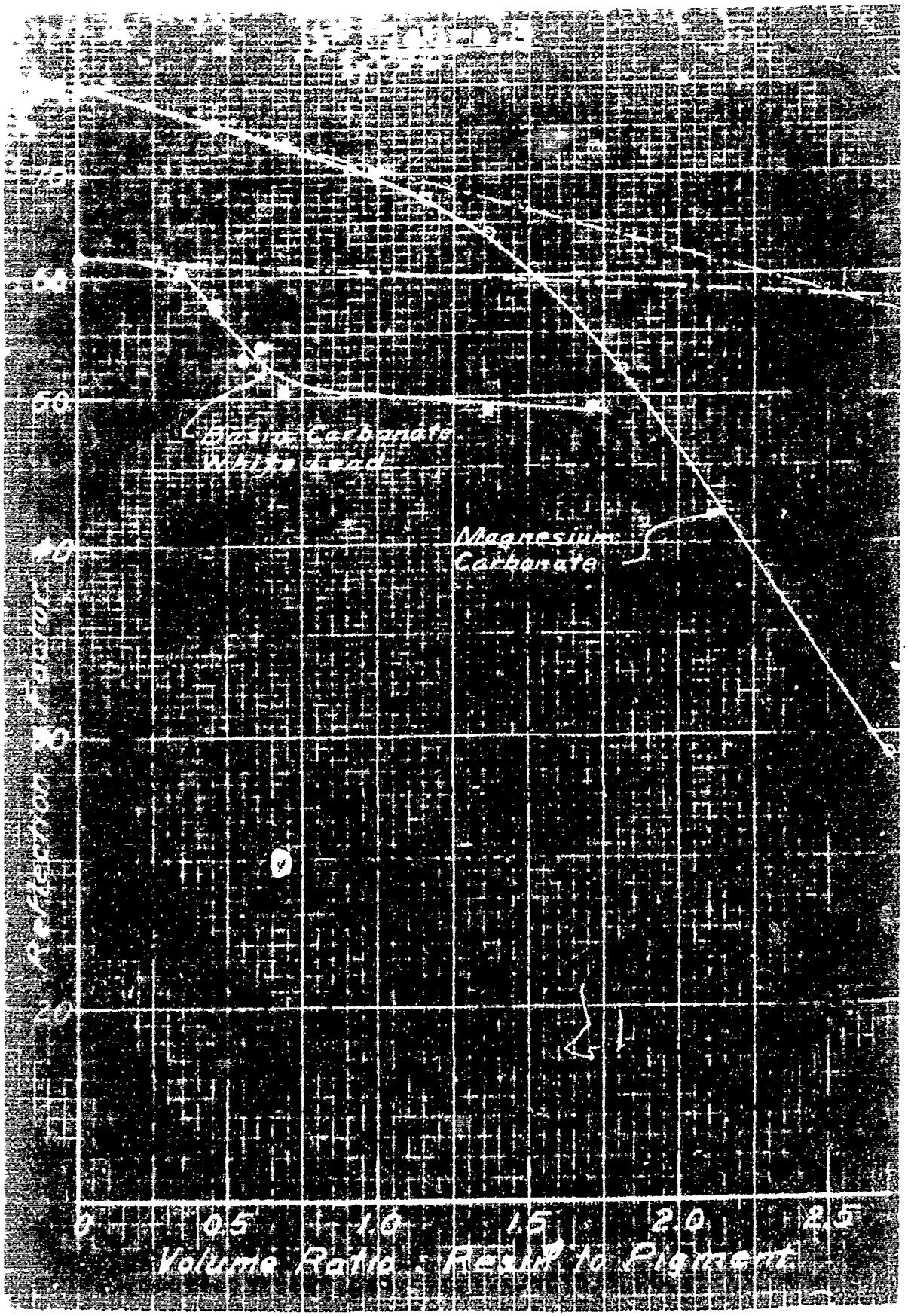
Table VII.

OIL OR RESIN / PIGMENT	Magnesium Carbonate (R=81)	Silica (R=71)	Commercial Whiting (R=66)	Aluminum Bronze (R=50)	Basic Carbonate White Lead (R=62)	Sulfur (R=61)	Zinc oxide (R=4)
V-7746 Urea-form. resin sol'n. (k=25)	65	21		72	42		
Acryloid (k=30)	74	58	24	79	55	45	4
Clear Nitro-cellulose lacquer. (k=40)		37			55		
Urea-form. resin sol'n. (k=52)	38						
Rezyl #227-8 (k=64)		27		70	46		
Ethyl Cellulose (k=75)	40	48		72	47		
Alkali Refined Linseed Oil (k=150)		6					
Glyceryl Phthalate Varnish A (k=170)		9					

urea-formaldehyde resin reflects about 45 per cent.

Most of the light reflected from a paint is not reflected from the surface, but has traveled a variety of paths of different lengths through the paint, a certain amount having been absorbed along each path before it emerges as reflected light. That light which does not appear as reflected light has been absorbed. A mean light path can be defined, such that if all the light traveled that path, the same fraction would have emerged as reflected light. Since the ratio of the refractive indices of the two materials at an interface determines the degree of bending of light rays passing through it, one would expect that the larger the ratio of refractive indices of pigment and vehicle, the sharper would be the average curvature of the light paths through a paint. Sharper curvature means shorter light paths, and consequently, for the same absorption coefficients, less total absorption and more reflection for larger refractive index ratios. A dry pigment can be thought of as a paint with no vehicle for these considerations of reflected light.

The effect on reflection of varying the relative proportions of pigment and resin was determined for basic carbonate white lead and for magnesium carbonate with Acryloid B-7 as vehicle (Figure 9). It can be shown (see Appendix C) that from these curves one can calculate very approximately the mean light path through the dry pigment, L_o, and the absorption coefficient of the pigment, k_p, provided one



knows the absorption coefficient of the resin. The mean light paths and absorption coefficients for the two pigments, calculated in this way, are given in Table VIII.

Table VIII.

Absorption of Pigments.

Pigment	Mean Light Path, L_o (in.)	Absorption Coefficient, k_p (in^{-1})
Magnesium Carbonate	0.01	20
B. C. White Lead	0.003	300

Magnesium carbonate paints attain half their maximum reflection factor at a thickness of about 0.001 inches. If the light paths are considered as semi-circles, this would correspond to a mean light path of about 0.005 inches for films of infinite thickness. Thus the calculated mean light path is of the right order of magnitude, since the actual light paths would be expected to be more irregular and longer than semi-circles.

5. Properties of Simple Paints. Three Component Systems.

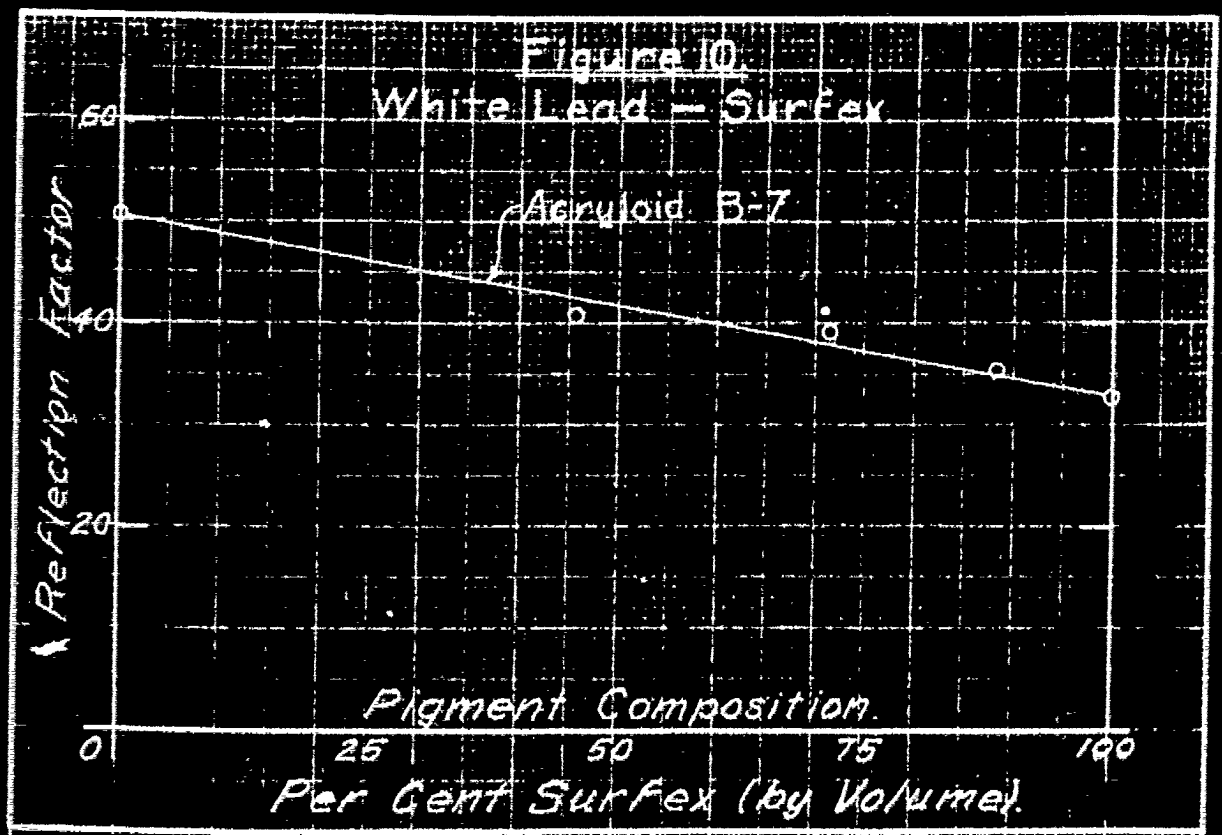
So far, only paints containing a single pigment have been considered. Since it is often desirable to incorporate more than one pigment in a paint either for economy, for improvement of film properties, or for tinting, three

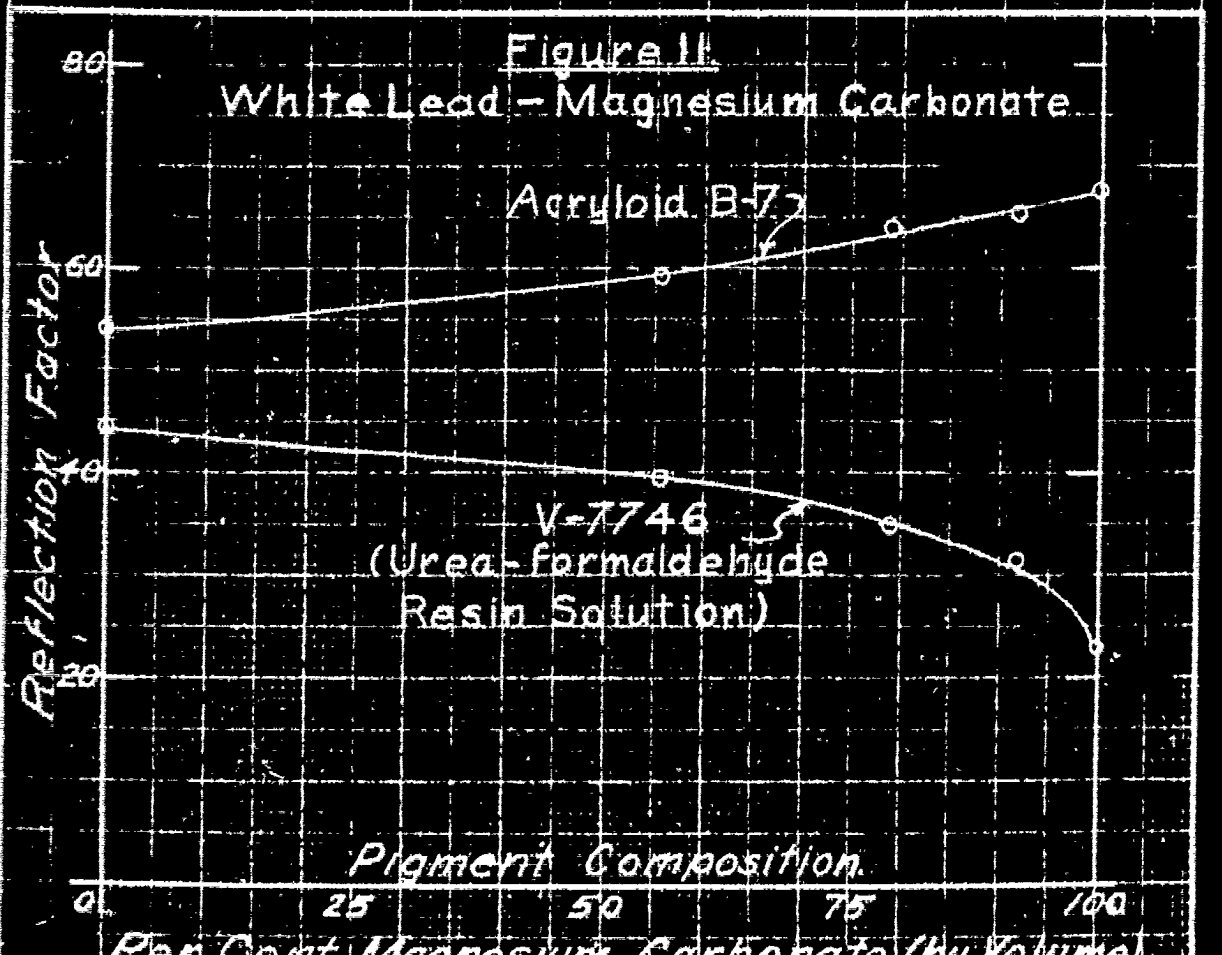
component systems were also investigated.

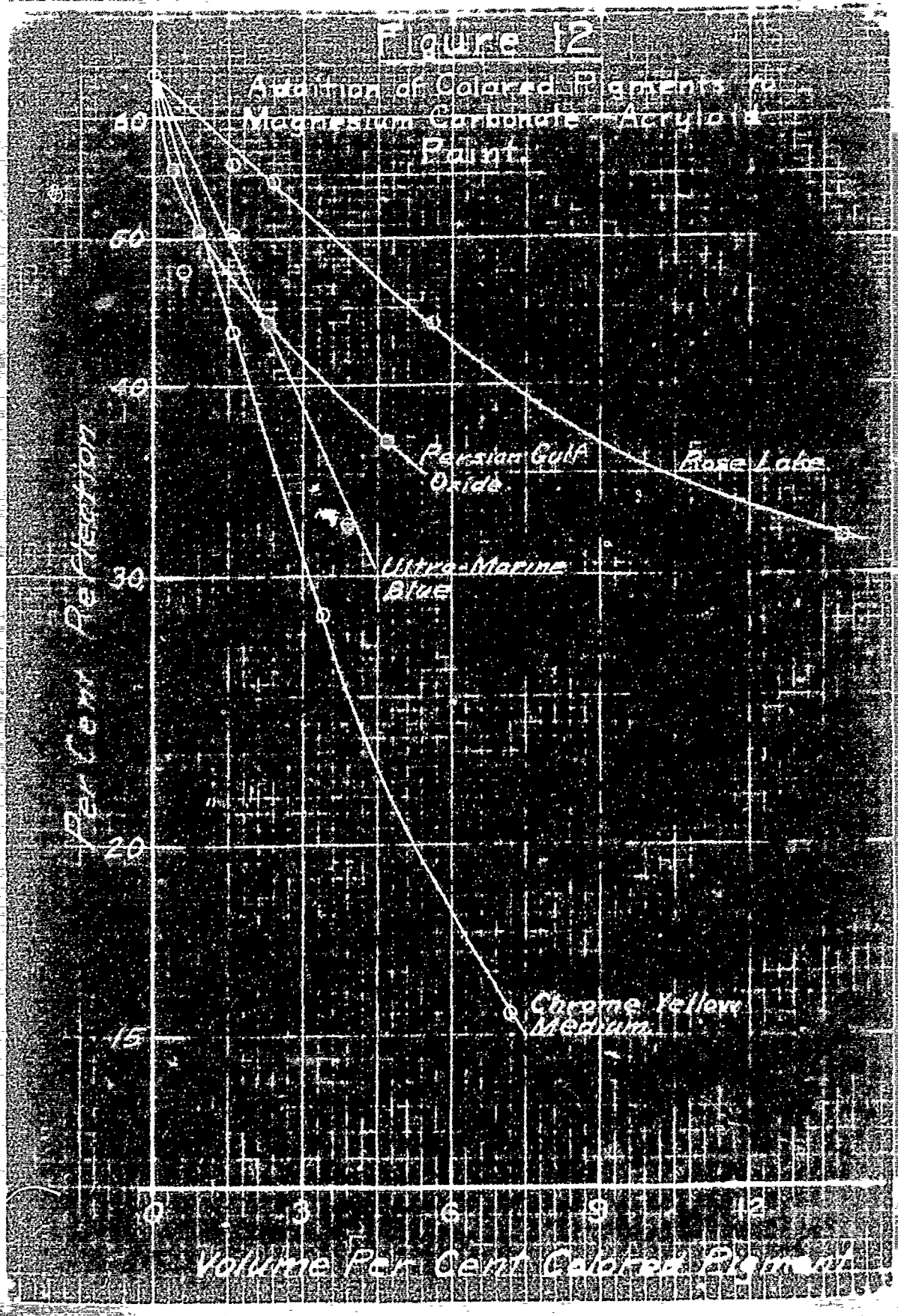
Figure 10 shows the effect on reflection of varying the proportions of an inert type pigment, sulfox, and a moderate hiding pigment, white lead, in an Aeryloid paint. Figure 11 shows the effect on reflection of different proportions of magnesium carbonate, also an inert type pigment, and white lead, in two different vehicles. The two vehicles, Aeryloid and V-7746, have about the same absorption coefficients. The separation between the two curves shows the effect of differences in total pigment concentration at each pigment composition, higher reflectances accompanying higher pigment concentrations.

Figures 12 and 13 show the effect of addition of colored pigments to magnesium carbonate and white lead paints. As would be expected from Table IV, small amounts of colored pigment depress the reflectance a great deal. The rate of depression is somewhat more rapid with the magnesium carbonate than with the white lead paints, and in the case of ultra marine blue it is much more rapid. This may be explained by the fact that due to the longer light path through magnesium carbonate paints, colored pigments can remove a larger amount of light in these paints than in white lead paints.

The effect of the addition of increasing amounts of aluminum bronze on the reflection factors of magnesium carbonate and white lead paints is illustrated in







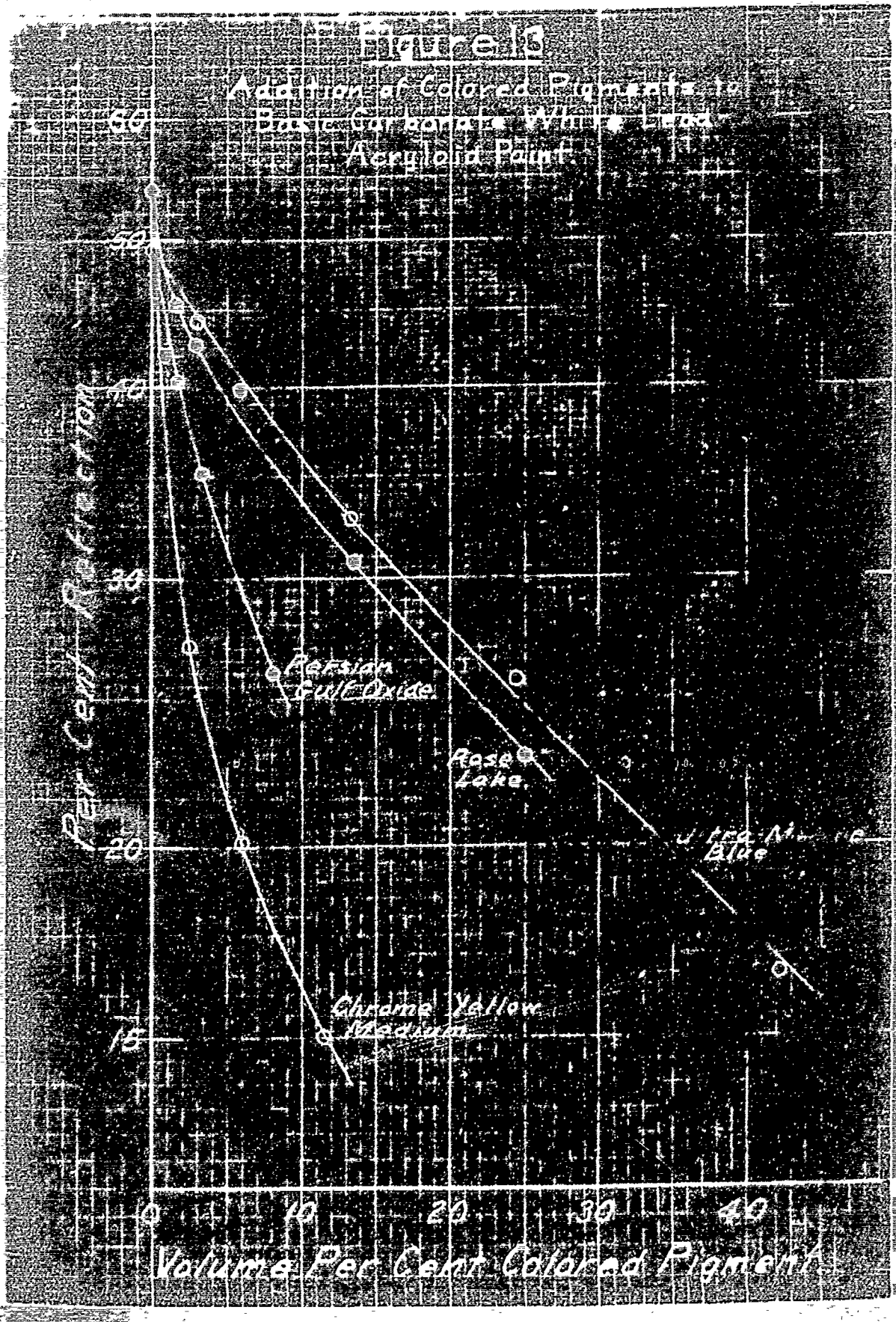
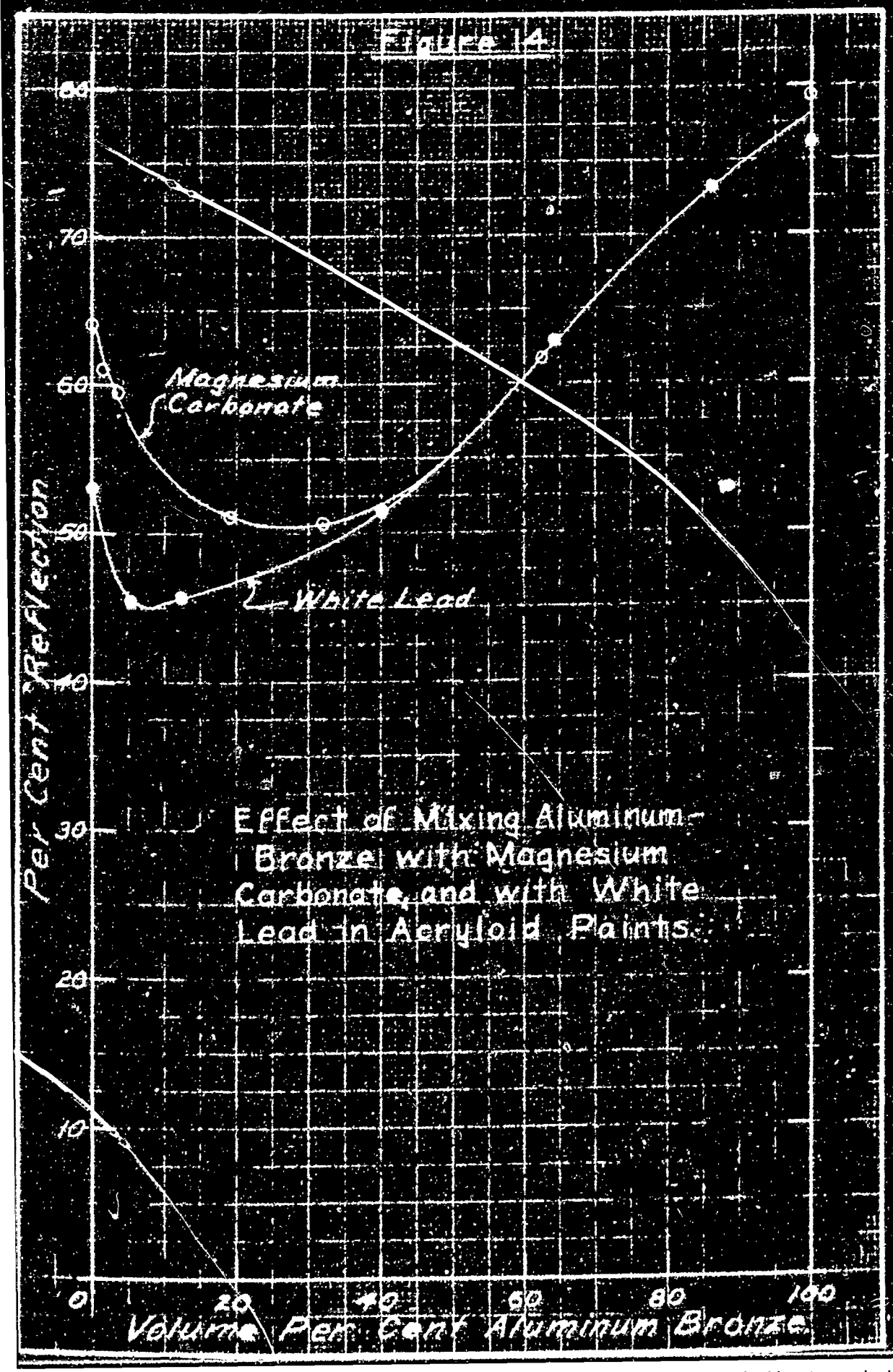
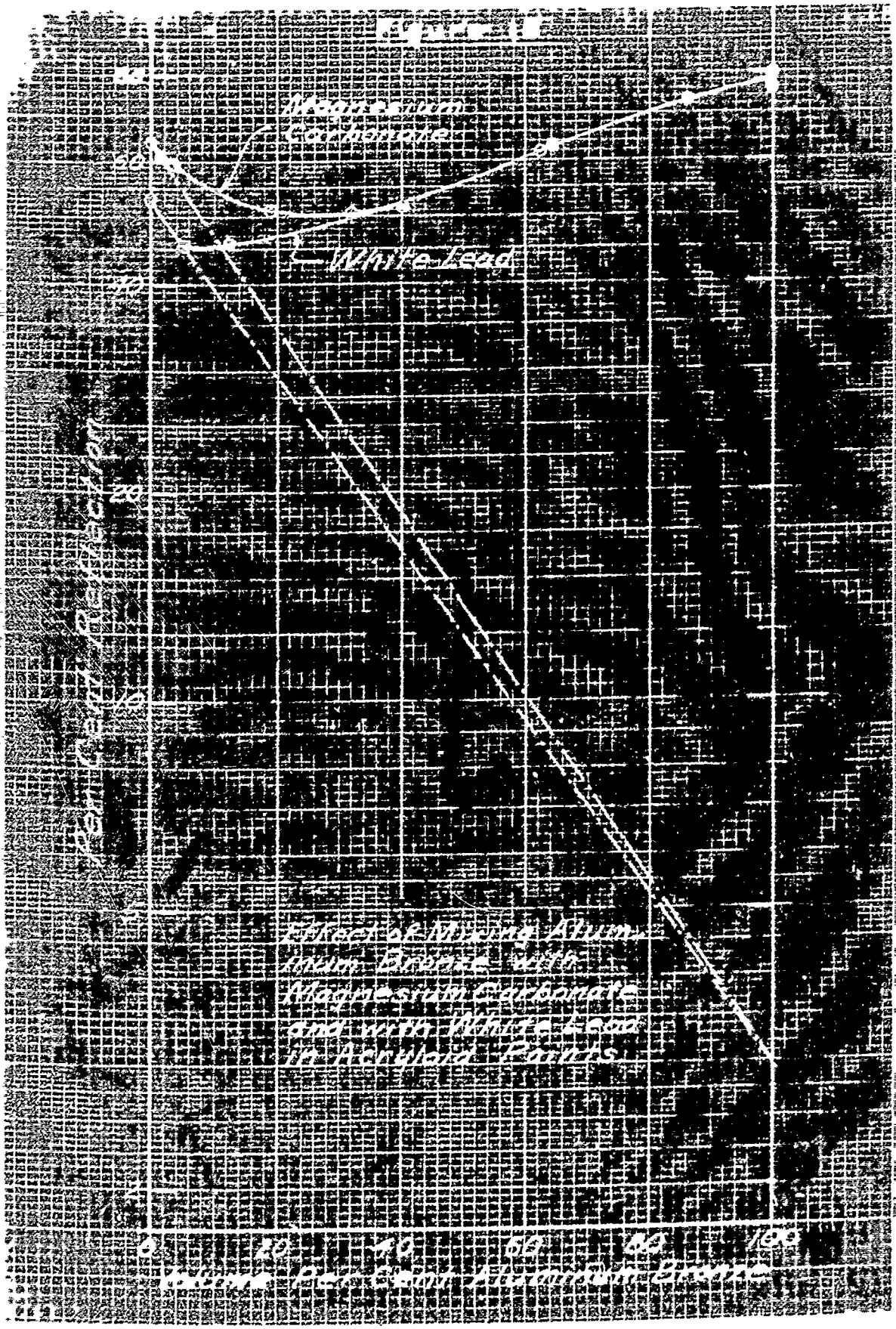


Figure 14. These curves indicate that the aluminum bronze first depresses the reflection factor, much as do the colored pigments, and then raises it again. The color of the paints ranges from white to a dull grey at the minimum; and beyond the minimum the paints become more and more metallic in appearance.

Aluminum bronze is a metallic pigment, with flat thin particles. It differs from the white pigments (Table III) in that each particle transmits practically no light, but reflects a large fraction, whereas each particle of a white pigment transmits a large fraction, but reflects only a small fraction of the light incident upon it. It appears, then, that the action of the aluminum bronze at low concentrations is due largely to the opacity of its particles, and at high concentrations is due principally to their metallic reflections.

In order to obtain a more definite picture of its action, assume that the aluminum bronze acts as a 100 per cent absorbing pigment mixed with the white pigment, deduct the effect of this mixture from the reflection of each paint, and ascribe the balance to metallic reflection from the aluminum bronze particles. Figure 15 shows the same curves replotted with log reflection factor as ordinate. The pigment mixture absorbs more light as the percentage of aluminum bronze is increased. This increase in absorption is exponential, due to Lambert's Law, so that the effect of



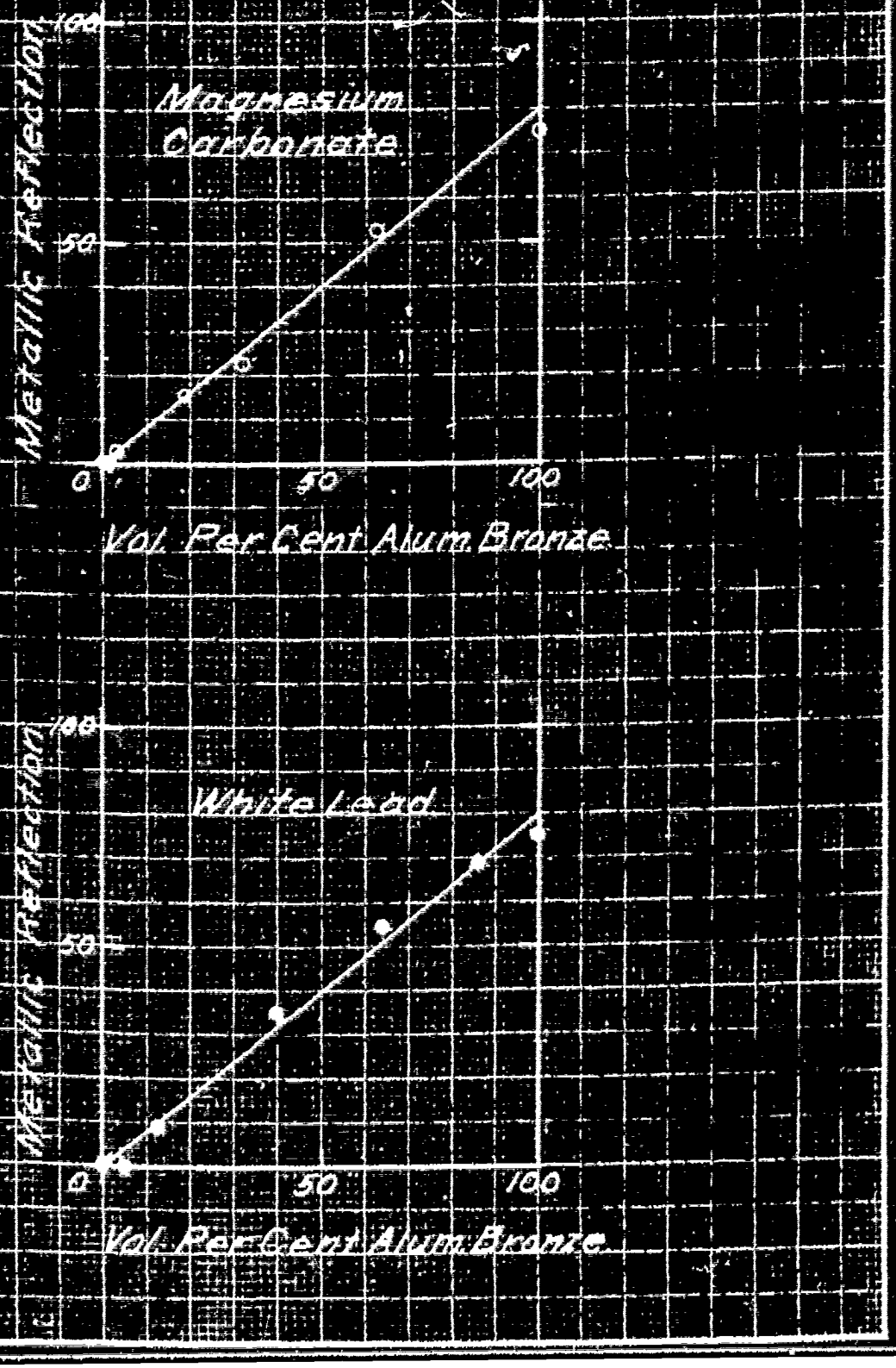


the mixture can now be represented by a straight line tangent to each curve at zero per cent aluminum bronze. Figure 16 shows the difference between each curve and its tangent plotted against per cent of aluminum bronze. Both curves can be approximated by the same straight line passing through the origin and the point 80 per cent reflection, 100 per cent aluminum bronze. This straight line represents the metallic reflection from the aluminum bronze. As one might expect, it is directly proportional to the volume per cent of aluminum bronze present in each paint, indicating direct reflection from the particles at the surface. Since it is the diffuse reflection factor which is being measured, it is not necessary that these particles be oriented parallel to the surface.

From the large decrease in reflection factor on addition of small amounts of colored pigment, it would seem that an ultra-violet paint will have to be either dead white, or at most a very light tint. Aluminum bronze, however, provides an interesting exception. The left branch of each curve provides a series of grays with a fairly high reflection factor and without the objectionable metallic lustre of an aluminum paint. This suggests addition of colored pigments to these grays to produce subdued colors together with moderate ultra-violet reflectance.

Paints P-115 and P-116, which represent the combination of 25 and 50 per cent ultra marine blue respectively to

Figure 16



aluminum bronze, show very little color and little loss of metallic lustre. Paint P-117, however, which is a mixture of aluminum bronze, ultra marine blue and white lead, is a sky blue with practically no metallic lustre. The presence of the aluminum bronze is indicated by a slight sparkle in the surface and by the high ultra-violet reflection factor of 40 per cent. Thus it appears that a colored ultra-violet paint containing both aluminum bronze and white pigments can be produced with a moderate ultra-violet reflectance.

4. Unpigmented Films.

The general behaviour of pigment-resin combinations with regard to reflection has been investigated, but little attention has been paid to the physical properties of the film produced, except for the rough observations that a film is brittle, tough, hard or soft, adheres well or peels. The properties of its film are important for a practical paint. They are principally dependent on the properties of the vehicle and on the proportion of pigment to vehicle. Hence it is logical to study the properties of unpigmented films, before proceeding further with the study of ultra-violet paints.

The possible resins for use in an air drying paint for ultra-violet service have been shown to be ethyl cellulose, vinylite, and the methacrylates. Strain, Kennelly and

Dittmar[18] have determined the compatibilities of the methacrylates for a number of plasticizers. Information on plasticizers for ethyl cellulose and vinylite was furnished by the Dow Chemical Company. Daas and Kauppi[19] have also given valuable information on the action of several plasticizers on ethyl cellulose. Plasticizers with high absorption coefficients were eliminated from consideration by use of the data of Table V-D. Tricresyl phosphate was eliminated because of its toxicity.

The various possible compatible combinations of resin and plasticizer were made up in solution at several concentrations between 0 and 40 per cent plasticizer content and flowed out on steel panels. After thorough drying, they were examined for toughness, hardness, brittleness, and adhesion. The combinations examined were: ethyl cellulose with triphenyl phosphate, tripropionin, Dow Plasticizer No. 2, Dow Plasticizer No. 7, and vinylite; methyl methacrylate with triphenyl phosphate, n-butyl d-tartrate, and tripropionin; isobutyl methacrylate with tripropionin, butyl stearate, n-butyl d-tartrate, triphenyl phosphate, Dow Plasticizer No. 2, Dow Plasticizer No. 7, and vinylite; and vinylite with Dow Plasticizer No. 7. Vinylite, although a resin, air dries to a soft film, and acts as a plasticizer in ethyl cellulose with which it is compatible up to about 30 per cent vinylite.

All methyl methacrylate films peel readily. Of the re-

maining combinations, four give good films. They are: ethyl cellulose with 40 per cent Dow Plasticizer No. 7; ethyl cellulose with 20 per cent vinylite; isobutyl methacrylate with 13 per cent butyl stearate; and isobutyl methacrylate with 35 per cent Dow Plasticizer No. 8.

5. Milled Paints.

The above four combinations of resin and plasticizer produce satisfactory unpigmented films. Their action when combined with pigment, and the best proportion of pigment to vehicle must next be considered. Although preliminary observations of hand-ground paints indicated that the reflection factor of a combination of two pigments did not exceed that of the better of the two, combinations of pigments were used because of possible desirable effects of mixed pigments on film properties.

For these studies, paints were milled in a ball mill so that a better and more uniform grinding of the pigment into the vehicle would be obtained. The mill used was a 6 inch diameter porcelain ball mill with 5/8 inch porcelain balls. It was rotated at 90 r.p.m. The composition and reflection factors of the several paints thus ground are listed in Table IX. The thinners used were toluene for the methacrylates and an 80-20 toluene-alcohol mixture for the ethyl cellulose. Unless otherwise indicated, all paints

Table IX.

Milled Paints.

Nbr.	Pigments	Resin and Plasticizer	% Pigment by vol. in solid film	Refl. Factor	Comment
G-1	Magnesium Carbonate	Acryloid B-7	44.8	36	
G-2	B. C. White Lead	Acryloid B-7	61.6	51	
G-3	50% B. C. White Lead 50% Magnesium Carbonate	Acryloid B-7	43.4	52	
G-4	60% B. C. White Lead 40% Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	50.0	62.1	
G-5	60% B. C. White Lead 40% Magnesium Carbonate	80% Ethyl Cellulose 20% Vinylite	50.8	61.6	
G-6	60% B. C. White Lead 40% Magnesium Carbonate	65% Isobutyl Meth. 35% Dow No. 2	50.0	54.5	
G-7	60% B. C. White Lead 40% Magnesium Carbonate	88% Isobutyl Meth. 12% Butyl Stearate	50.0	60.8	
G-8	60% B. C. White Lead 40% Magnesium Carbonate	50% Ethyl Cellulose 40% Dow No. 7 10% Vinylite	45.0	56.5	
G-9	Magnesium Oxide (Baker)	60% Ethyl Cellulose 40% Dow No. 7	40.0	47.3	
G-10a	Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	40.0	31.6	Grd. 70 hrs

Table IX (Continued).

Nbr.	Pigments	Resin and Plasticizer	% Pigment by vol. in solid film	Refl. Factor	Comment
G-10b	Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	40.0	64.0	Grd. without balls in mill
G-10c	Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	40.0	41.1	Grd. 39 hrs
G-10d	Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	40.0	56.5	Grd. 6 hrs
G-10e	Magnesium Carbonate	60% Ethyl Cellulose 40% Dow No. 7	40.0	48.9	Grd. 12.5 hrs
G-11	B. C. White Lead	60% Ethyl Cellulose 40% Dow No. 7	40.0	55.5	
G-12	Magnesium Carbonate (C.&B.)	Methyl Methacrylate	40.0	38.4	
G-13	Magnesium Carbonate (C&B)	Ethyl Methacrylate	40.0	24.6	
G-14	Magnesium Carbonate (C&B)	Propyl Methacrylate	40.0	35.6	
G-15	Magnesium Carbonate (C&B)	Butyl Methacrylate	40.0	32.0	
G-16	Magnesium Carbonate (C&B)	Isobutyl Meth.	40.0	30.8	
G-17	Magnesium Oxide, heavy, (Squibb)	60% Ethyl Cellulose 40% Dow No. 7	40.0	35.3	Cracks

Table IX (Continued).

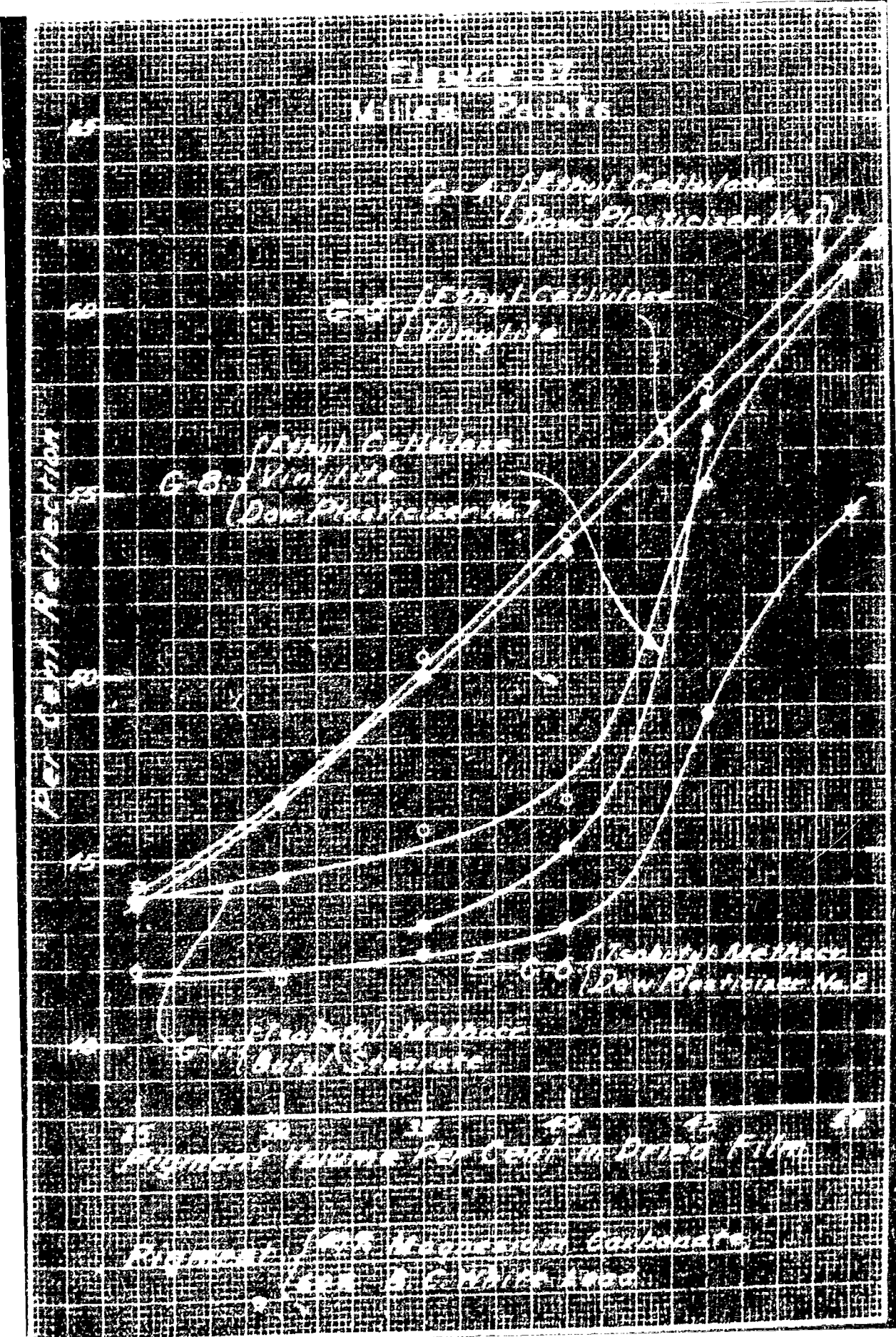
Nbr.	Pigments	Resin and Plasticizer	% Pigment by vol. in solid film	Refl. Factor	Comment
G-18	Magnesium Oxide, light, (Squibb)	60% Ethyl Cellulose 40% Dow No. 7	40.0	70.5	
G-19	35% Magnesium Oxide (Baker) 65% B. C. White Lead	60% Ethyl Cellulose 40% Dow No. 7	40.0	51.6	

were ground for 70 hours. After grinding, the paints were filtered through cloth and a portion was thinned and sprayed on 4"x4" steel panels to a heavy coat.

C-1, C-2, and C-3 show the effect on reflection factor of the more intimate grinding of the mill as compared with grinding by hand. If their reflection factors are compared with those in Figure 11 for 100, 0 and 79 per cent magnesium carbonate (by volume), it will be noted that the more thorough grinding of the mill produces a small decrease for white lead, a slightly greater decrease for the mixture of white lead and magnesium carbonate, and a very large decrease for magnesium carbonate.

In paints C-4 through C-7, a mixture of white lead and magnesium carbonate was used as the pigment in testing the action of the four good resin-plasticizer combinations when pigmented and the effect of varying the pigment volume per cent in the dried film. Each paint served as a base grind to which the proper amounts of resin-plasticizer solution were added to give pigment volume percentages ranging from 50 to 25.

Figure 17 shows the effect on the reflection factor of reducing the volume of pigment in the paint film. The reason for the difference between the curves for the ethyl cellulose paints and the curves for the isobutyl methacrylate paints is not clear, especially in view of the fact that the former resin-plasticizer combinations have higher



absorption coefficients than the latter. Then too, G-8, which is an ethyl cellulose paint containing both plasticizers present in G-4 and G-5, behaves like the methacrylate paints. Further, G-4 and G-5 are "flat" at all pigment volumes, whereas G-6, G-7 and G-8 are slightly glossy at pigment volumes below 40 per cent.

It is evident from Figure 17 that, whatever the reason may be, ethyl cellulose is somewhat superior to isobutyl methacrylate for the purposes of an ultra-violet paint, and that it is advantageous to keep the pigment volume per cent as high as possible. The limit to the pigment volume which can be used is set by the physical strength of the film; the weaker the film which can be tolerated, the higher is the pigment volume which can be used and the higher the reflection factor which can be attained.

Examination of the films showed that a pigment volume between 40 and 50 per cent would be satisfactory. The films adhered better and were tougher at 40 per cent; were less adherent and more brittle at 50 per cent. However the 50 per cent films compared favorably with standard interior wall finishes. The films containing ethyl cellulose were less brittle and more cohesive than those containing methacrylate. G-8, containing as plasticizer both vinylite and Dow Plasticizer No. 7, was no better than G-4 or G-5 in film quality, and lower in ultra-violet reflectance. Hence the more simple formulations were adhered to. Four reasons suggest

the choice of ethyl cellulose as the basic ~~vehicle~~ resin for ultra-violet paints: it gives higher reflectance films; it produces a truly "flat" finish; it produces a slightly better film; and it is also, at the present time, less expensive.

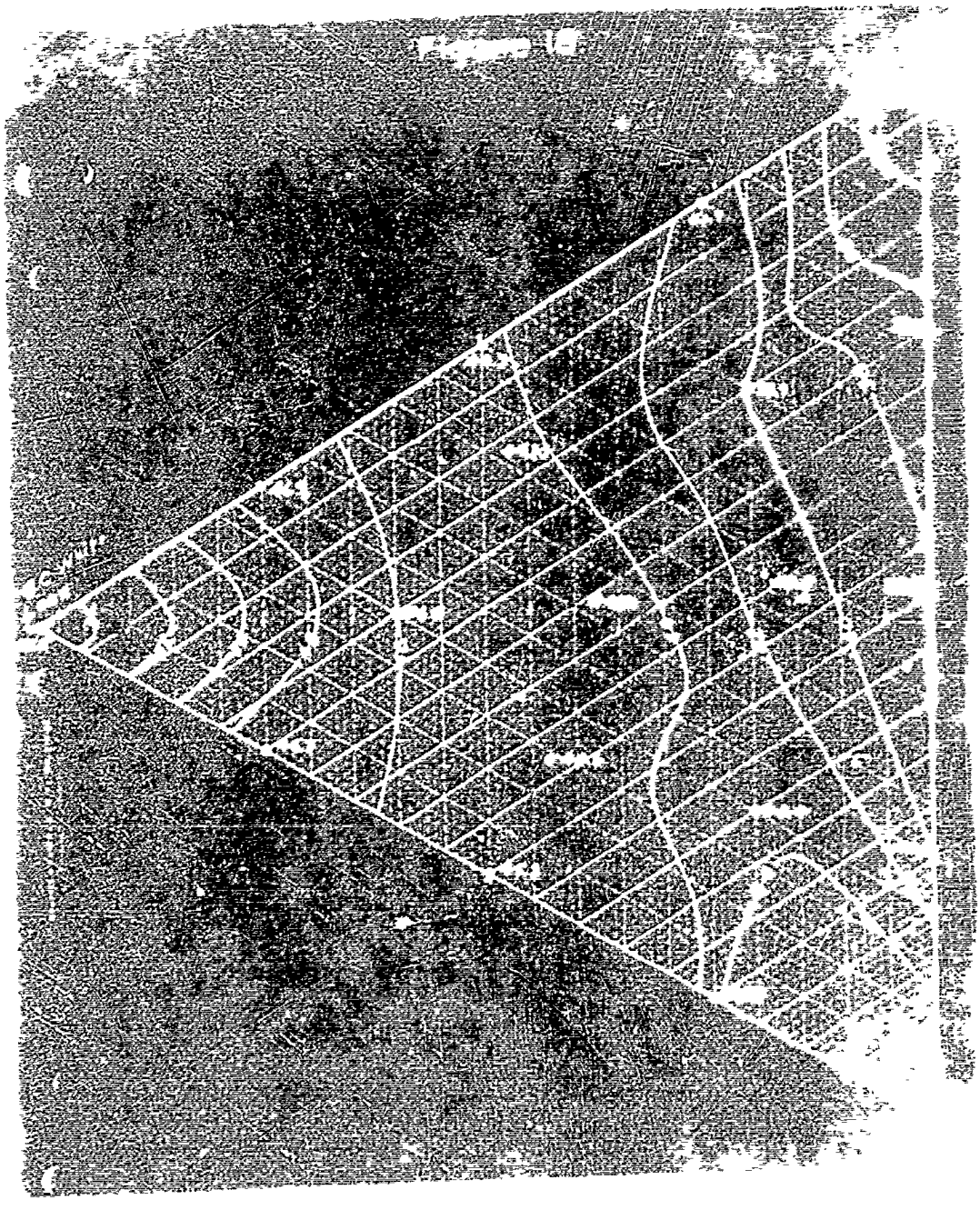
The determination of the optimum combination of pigments is not so simple as the choice of the best resin, since factors other than absorption are important; and the best combination has not yet been determined. White lead is the only pigment which has low ultra-violet absorption and which does not act as an inert; and consequently one should try to include it in any formulation because of its reduction of the thickness necessary for hiding. Zirconium oxide would be still better because of its high refractive index and low absorption, if it could be procured commercially in a more pure state and at a reasonable cost.

As a beginning of a more careful study of pigment combinations than was made with the preliminary paints, three ethyl cellulose paints were ground with white lead, magnesium oxide and magnesium carbonate, respectively, as pigment (G-9, G-10, G-11: Table IX). These three paints were mixed in the proper proportions to produce known volume ratios of the three pigments. The total pigment volume per cent remained constant, since all three paints were formulated at 40 per cent pigment volume. These mixtures were thinned and sprayed to a thick coat on steel panels, and their reflection factors measured. The results are

presented in Figure 18, a triangle diagram with the constant reflection contours sketched in. A surprising result is the low reflectance of the magnesium oxide paint, and the decrease in reflectance on addition of white lead to magnesium oxide. In amounts up to 55 per cent by volume, magnesium carbonate and magnesium oxide are equivalent in their effects on the reflection of white lead paints.

There is a difference in reflection between points of the same composition in Figures 17 and 18. The volume percentage of magnesium carbonate in the pigment in G-4 is 71.5 per cent. At 40 per cent total pigment volume, G-4 has a reflectance of 53.6 (see Figure 17), which compares with a reflectance of 42 for a paint of the same composition according to Figure 18. Similarly, G-19, with 50 per cent magnesium oxide, has a reflectance of 51.6, which compares with a reflectance of 45 per cent for a paint of the same composition according to Figure 18. These differences are much larger than the possible errors in reflection measurements. Therefor, for these three pigments, a higher reflection is produced when two pigments are ground together into a paint than when each pigment is ground into a separate paint and the paints mixed.

There are several possible reasons why these differences occur. It is shown later (III.2) that these paints consist in part of clusters or aggregates of particles, and that these clusters are the more effective portion of the pigment



in reflecting light. Paints ground separately and then mixed would contain two types of cluster each made up from but a single type of pigment particle. It may be that in grinding two pigments together, clusters containing both pigments are formed and that these complex clusters are more effective in reflecting light than the simple clusters. Another possibility is that no complex clusters are formed, but that the simple clusters are destroyed to a greater extent when only a single pigment is ground at a time than when two are ground together. The correct explanation is unknown. Its determination is a problem in itself, and was not considered in this study.

Another important fact brought out by the paints comprising Figure 18 is that paints containing mixtures of two pigments form films with better physical properties than single pigment paints. Thus, the magnesium oxide and magnesium carbonate paint films crack on drying, whereas white lead paint films show a tendency to peel. The mixtures of white lead with either magnesium oxide or carbonate formed paints which neither cracked nor peeled.

These results indicate that a pigment formulation of about 50 per cent by volume of white lead and the balance a mixture of magnesium carbonate and magnesium oxide, with 45 to 50 per cent pigment by volume in the dried film should be satisfactory.

6. Exposure Tests.

An ultra-violet reflecting paint will, in service, be submitted to prolonged exposure to ultra-violet radiation. It must, therefor, be designed to maintain its high reflectivity as long as possible. Although that light which is reflected from a paint cannot affect it, the 30 to 50 per cent which is absorbed may be converted into heat and passed off without further effect, or it may cause a photochemical reaction with a possibly deleterious action on the paint film or its reflectivity. Hence exposure tests are necessary in order to ascertain the behaviour of the paints under the conditions of use.

The four types of paint, G-4, G-5, G-6, and G-7, representing the four satisfactory resin-plasticizer combinations, and also G-9, G-10, and G-11, representing a single resin-plasticizer combination milled with three different pigments, were exposed to a strong ultra-violet source. Duplicate panels of each paint were kept in an envelope as a control. The panels were placed 12 inches from a Cooper-Hewitt mercury arc rated at 0.4 amperes at 200 to 250 volts. Since the Cooper-Hewitt arc has a quartz envelope, each panel was protected with a sheet of 1/16 inch Corex D glass so that the radiation reaching the paint corresponded approximately to that emitted by the S-1 Sunlamp, particularly in the absence of radiation less than 2800 Angstroms in wave length. The Corex glass sheets were separated from the panels by a

cardboard spacer around the edge, with a small vent left open to provide ventilation.

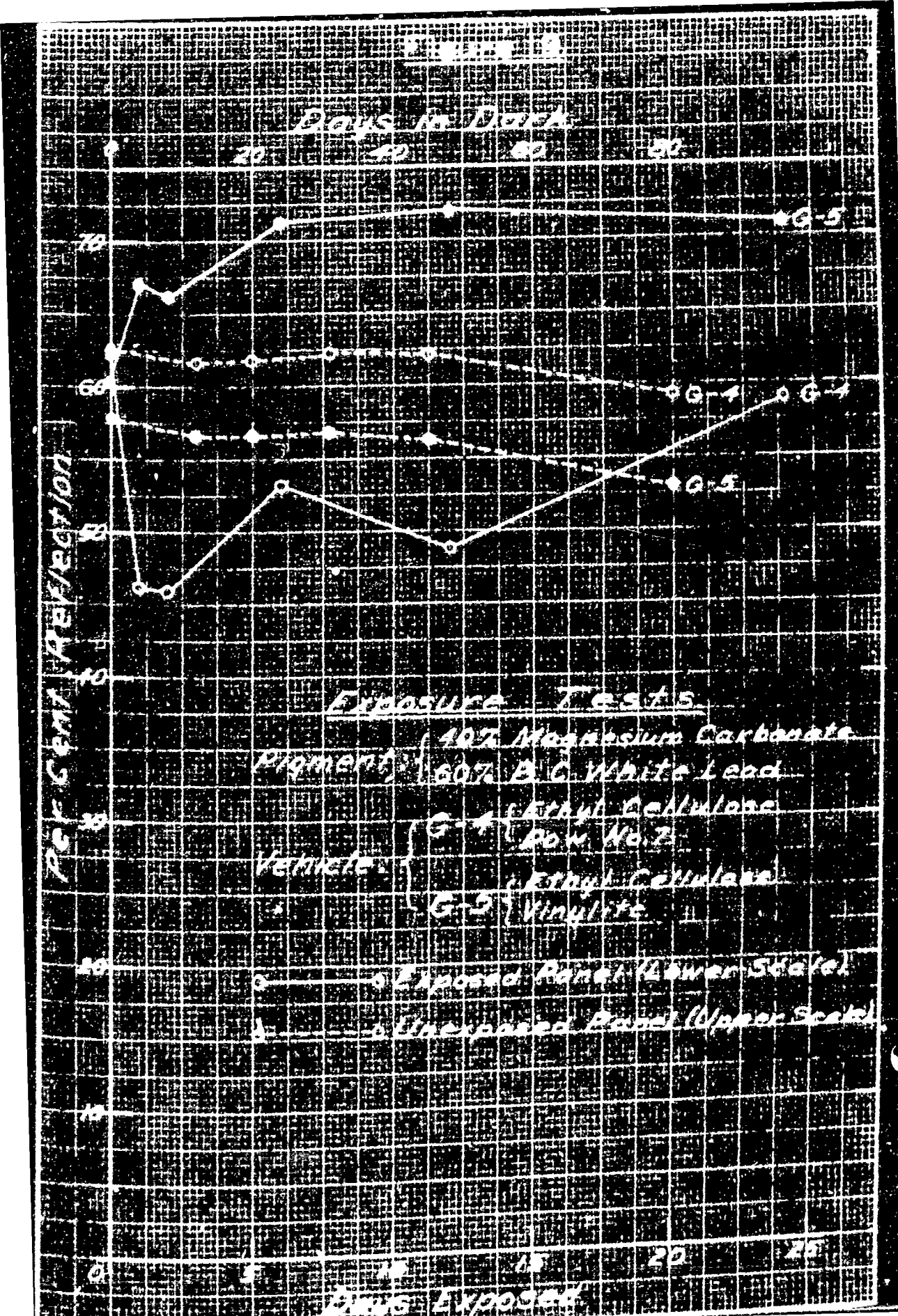
Table X is a comparison of the energy output of the Cooper-Hewitt arc and the S-1 Sunlamp, in microwatts per cm^2 at a distance of 30 cm (12 inches). The data on the output of the Cooper-Hewitt arc are by McAllister[20], roughly corrected to a distance of 30 cm by the inverse square law. The data on the output of the S-1 Sunlamp running open are by Barnes[13], similarly corrected to a distance of 30 cm. The data on the S-1 Sunlamp in its reflector are by Taylor[21] and have been converted from the ratio of energy output in reflector to energy output in open, using Barnes' data. The intensities of the ultra-violet lines from the Cooper-Hewitt arc are 10 to 20 times the intensities of the lines from the S-1, so that the 24 day exposure in these tests is approximately equivalent to a year's service one foot from an S-1 Sunlamp.

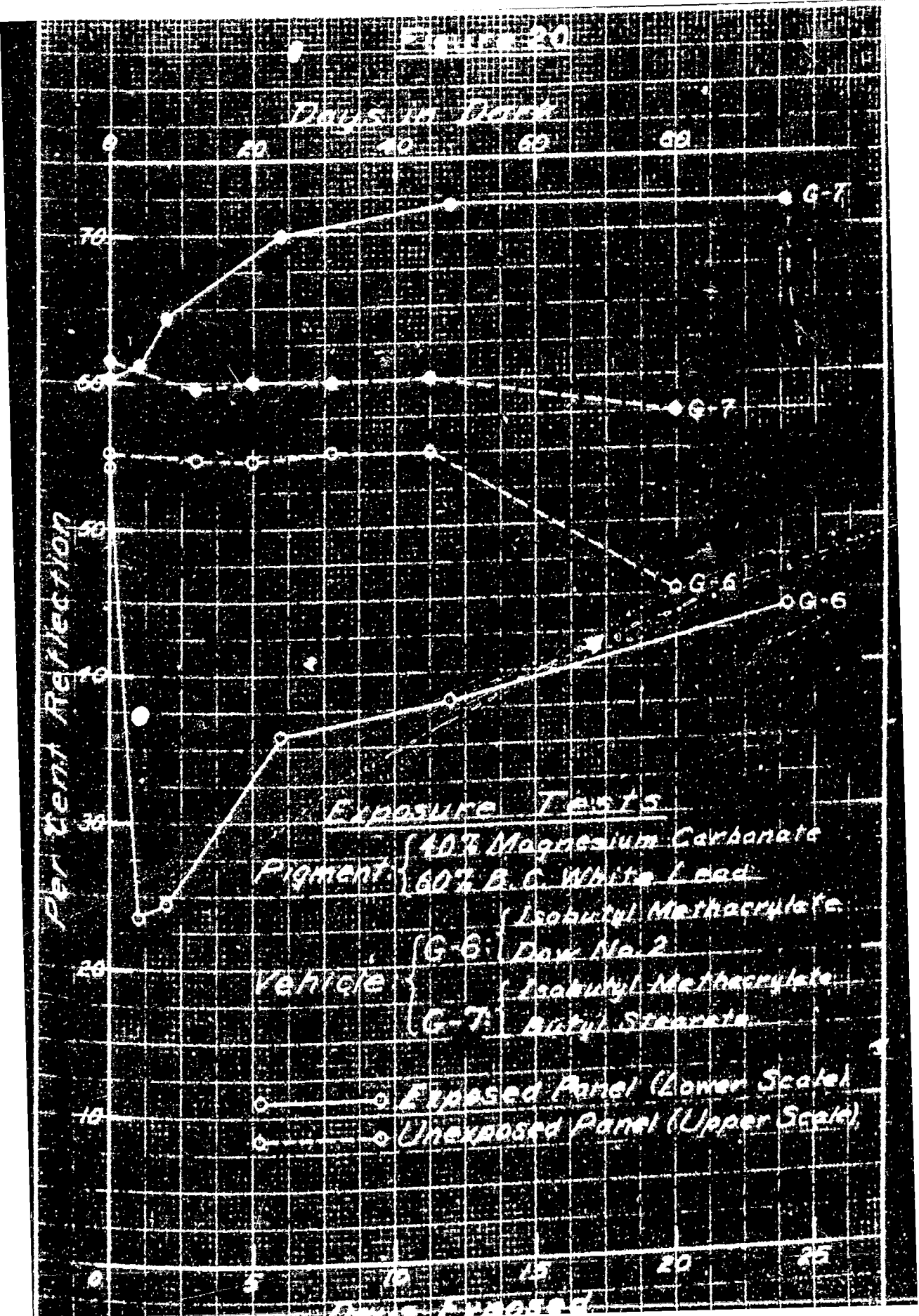
The effect of ultra-violet radiation on the reflection factors of the exposed panels and of aging without irradiation on the standard panels is shown in Figures 19, 20 and 21. The small initial differences in reflection between standard and exposed panels is due to the fact that some of these panels were not sprayed to effectively infinite thickness. Figures 19 and 20 show that both the ethyl cellulose and the isobutyl methacrylate paints which did not contain a Dow plasticizer increased almost 20 per cent in reflectance

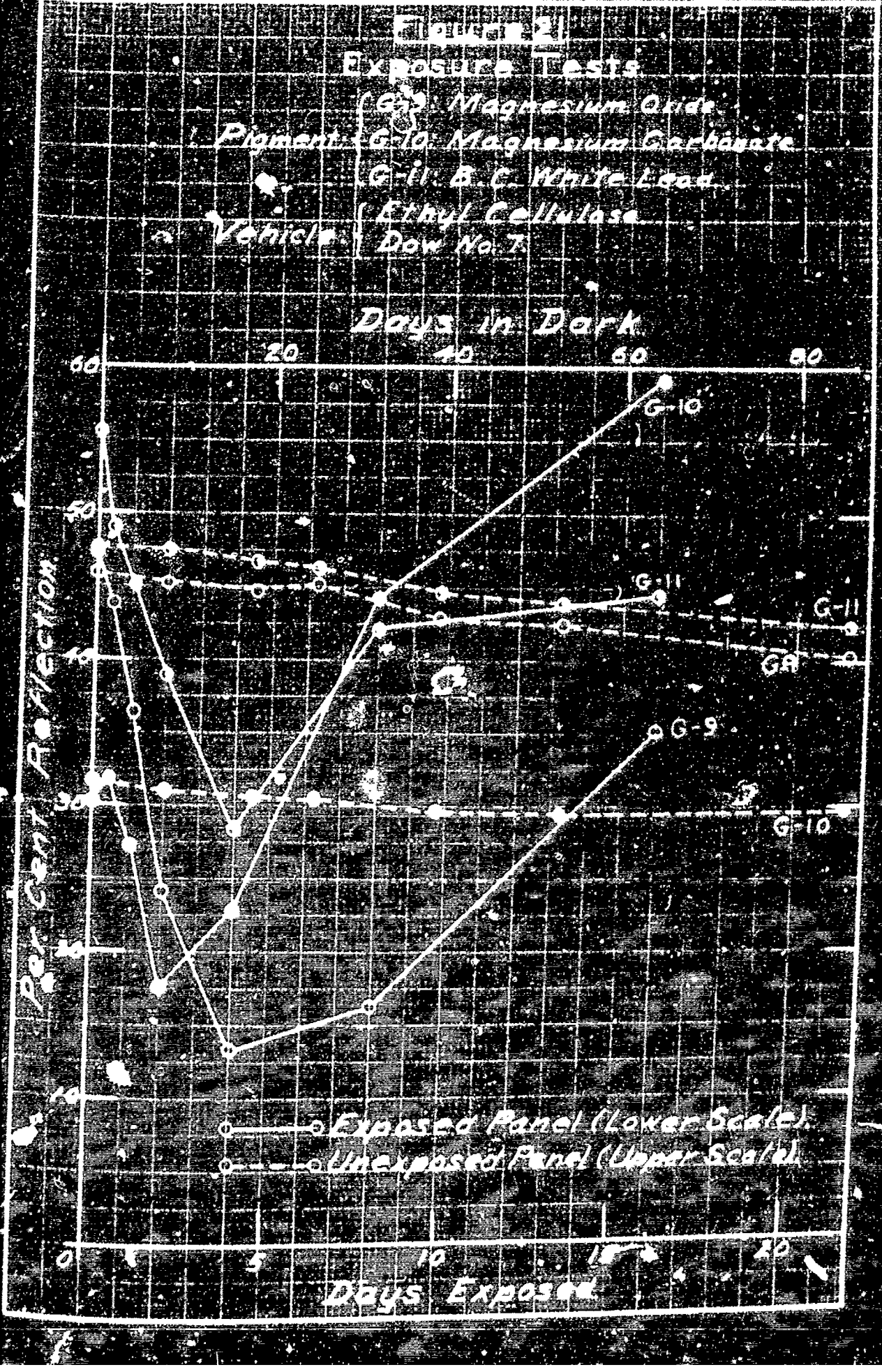
Table X.

Comparison of Cooper-Hewitt Arc and S-1 Sunlamp.

Wave-length	Energy Output (Microwatts per cm^2 at 30 cm). Vertical Cooper-Hewitt Arc	S-1 Sunlamp (Perpend. to leads) In Open	In Reflector
6908	37		
6234	13		
5780	2240	108	
5461	1890	91	
4916	67		
4358	1610	100	
4047	955	64	
3906	40	4	
3654	2880	193	
3341	256	12	
3130	1770	150	795
3022	926	49	288
2967	479	28	151
2925	65		
2894	174	8	40
2804	368	8	37
2752	115		
	Continuous:		
2500-3200	Pract. none	7	
3200-4000	" "	58	
4000-7600	" "	2320	





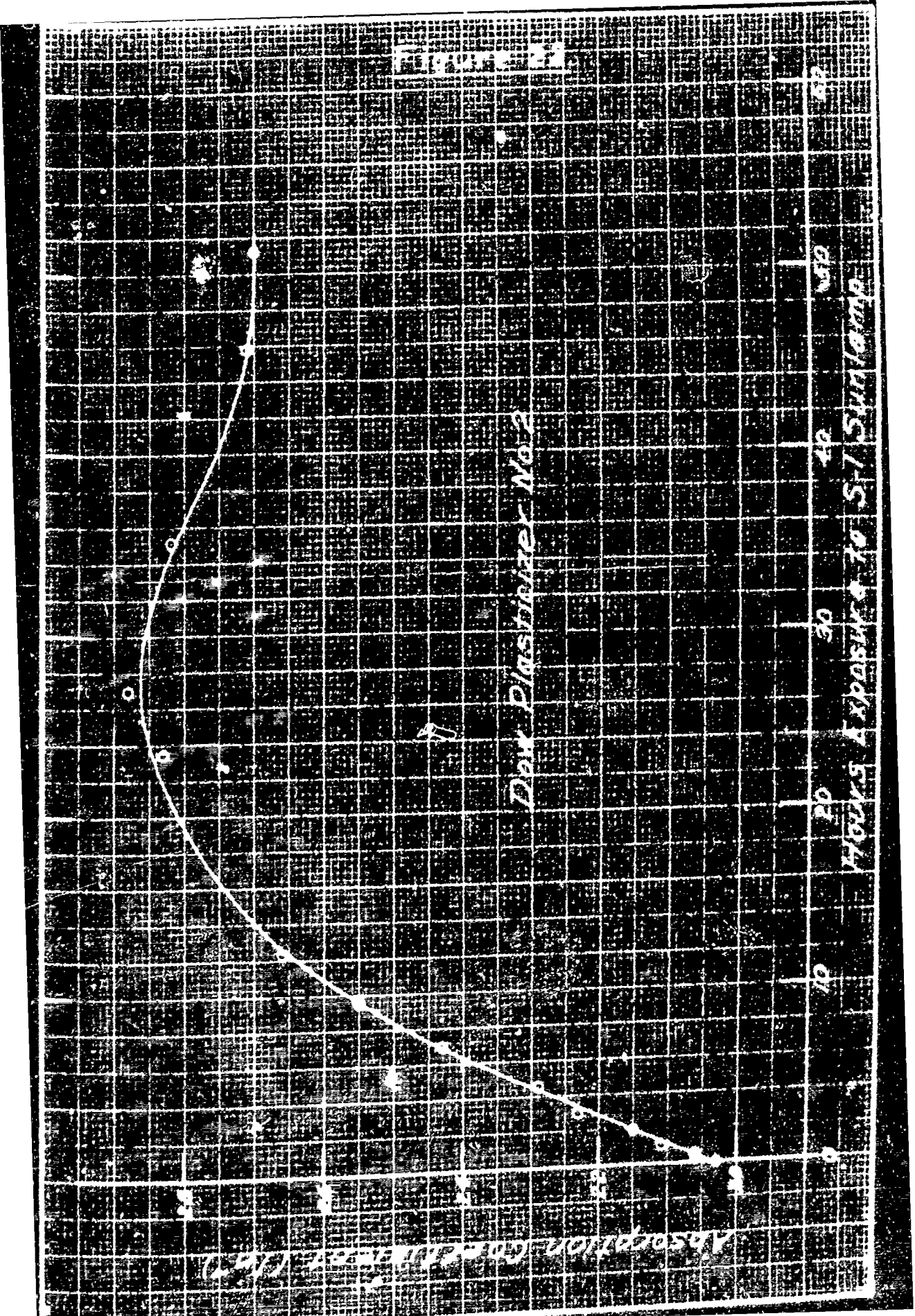


on exposure, whereas the paints containing either resin with a Dow Plasticizer decreased 25 and 50 per cent at first on exposure and then gradually increased to a reflectance almost as high as the unexposed standard panels. It is evident that it is the Dow Plasticizer which causes this transient deterioration.

The standard panels were kept in the dark in envelopes except for the five minutes necessary to determine each reflectance. They show a slight decrease in reflectance with age.

Figure 21 shows the influence of each of the three different pigments on the deterioration caused by Dow Plasticizer No. 7 in ethyl cellulose paints. The reaction occurs with all three and is greatest with magnesium oxide.

Evidently the Dow Plasticizers undergo a photochemical reaction when irradiated with ultra-violet. In order to make certain that this is the case, a sample of Dow Plasticizer No. 2 was placed in the vitreosil cell used for transmission measurements. The cell was then placed in the light beam in the apparatus and irradiated continuously with the S-1 Sunlamp for 52.5 hours. Its transmission was measured periodically. Figure 22 shows the variation in its absorption coefficient with duration of exposure. Its behaviour is quite similar to that of the paints: an initial rapid increase in absorption followed by a decrease.



Following its irradiation, the sample was left in the cell in the dark for three days. At the end of that time, its absorption was found to have decreased to 20.9 in^{-1}, almost its initial value.

The reaction of these Dow Plasticizers also causes paints containing them to yellow badly after, but not during, exposure, so that their use in any ordinary paint which may be occasionally exposed to ultra-violet, for example summer sunlight, is not advisable. Furthermore, it is not necessary, since the increase in reflectance of the paints not containing them is an unexpected effect very much to be desired.

7. Other Requirements.

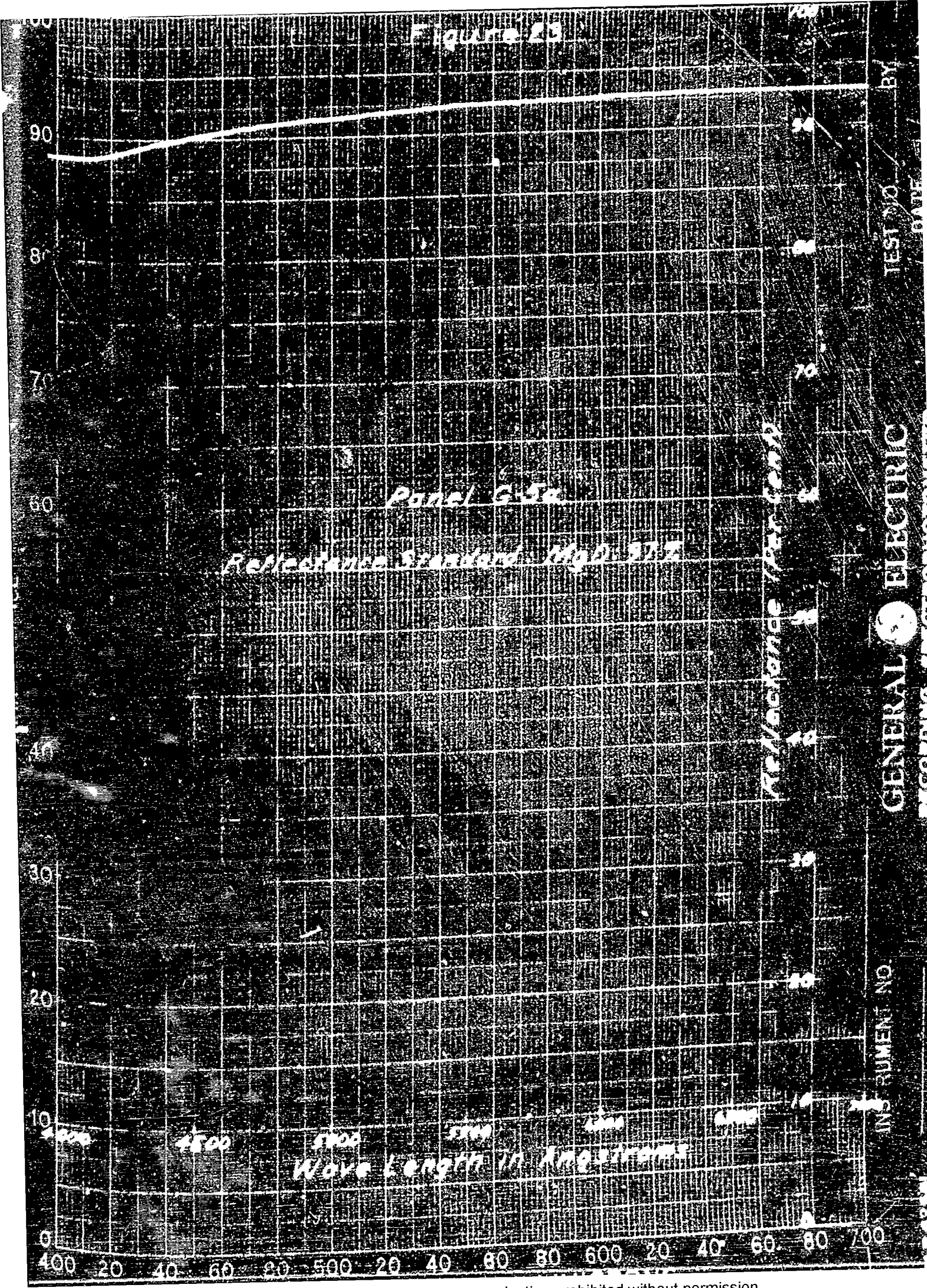
The studies so far indicate that a paint with good ultra-violet reflection can be made by using ethyl cellulose and vinylite as vehicle and white lead with some magnesium oxide and magnesium carbonate as pigment. The requirements of reflection and permanence which this type of paint has been designed to meet are the primary ones which any ultra-violet paint must fulfill and hence they were considered first. However there are added requirements which are important and should be mentioned. Thus a paint for interior use should have a high reflectance for visible light; should be cleanable, brushable, non settling and non-poisonous.

The requirement of high reflectance in the visible seems to be automatically satisfied by a good ultra-violet paint, since most materials with low ultra-violet absorption have low visible absorption and are non-selective. Figure 25 is a spectral reflectance curve for a panel of paint G-5 made on a Hardy Spectrophotometer through the courtesy of Dr. A. H. Taylor at the Nela Park Laboratories of General Electric. This same panel had an ultra-violet reflectance of 84.7 at the time the test was made.

An ultra-violet paint should be able to be cleaned in such a way as to remove any ultra-violet absorbing film of grease and dirt which may collect upon it, and so retain its high reflectance. Its solvent formulation should be adjustable so that it can be brushed or sprayed on a surface. Settling, which is rapid in these present formulations, should be overcome without impairment of ultra-violet reflectivity, in order to produce a stable product. And the use of white lead, because of its poisonous nature, should be carefully considered.

Other Factors Affecting Reflection Factor.

In this study of the possibility of making paints which reflect large percentages of incident ultra-violet light, attention has been focused chiefly on the two controlling factors, the transparency of the vehicle and of the pigment.



However, there have been indications that other factors may also be important. These are the physical properties of the pigment and the influence of the thickness of the applied film on reflection factor.

The importance of the ratio of the refractive indices of pigment and vehicle, in the dried film, has been pointed out already as being important, since it controls the possible bending of light by each particle and so is a factor determining directly the thickness of paint necessary for high reflection and the effect of addition of opaque pigments. The effects of the particle size of a pigment, its degree of wetting by the vehicle, and the particle arrangement within the paint may also be important. The relation between the reflection factor of a film and its thickness has a direct bearing on the hiding power and economy of a paint as well as the maximum reflectance obtainable from it. These factors are also of importance in paints designed for visible service, and will now be considered in more detail.

III. INFLUENCE OF PIGMENT PROPERTIES.

1. Particle Size.

The average size and the distribution of sizes of the particles of a pigment are important in determining the amount of light scattered by it and hence its reflecting power. This dependence of scattering on particle size is particularly critical when the particle diameter is approximately the wave length of the light being scattered.

Shoulejkin[22] has calculated the radial distribution of scattered light around particles of various diameters from the general form of Mie's equations for the scattering of electromagnetic waves by dielectric spheres. He finds that for particles very small compared to the wave length of the light the amount of light scattered back is equal to that scattered in the direction of the incident light; and that as the particle size is increased the amount scattered back decreases, until, for particles large compared to the wave length of the light, it is the amount calculated by the laws of optics. He concludes that "There is, therefor, a smooth continuous change from the scattering of light to its reflection and refraction".

Casperson[23], using Mie's and Shoulejkin's theories, has calculated the absorption coefficients and the intensities of the diffuse scattered reflection for various particle diameters, wave lengths of incident light, and ratios of

refractive indices of particles and dispersing medium. He finds that "...there is, for each particle radius, a wave length for which the absorption at constant concentration is a maximum. The position of these maxima is shifted more and more toward the long wave length spectrum for larger particle". At the maximum, the particle diameter is approximately two thirds the wave length.

The literature on the experimental relations between particle size and the scattering of light by smokes, sols, and dilute suspensions is extensive[24-27]. Agreement with Mie's and Rayleigh's theories is not found, as a rule. Nevertheless all results indicate that the particle size, in certain ranges, critically affects their ability to scatter and reflect light.

Three general means are available for determining the particle size and size distribution of pigments: the sedimentation method; the light absorption method; and the photomicrographic method. The sedimentation method has many variations, but all depend on Stokes' Law for the calculation of size. By the use of the ultra-centrifuge[28], very small particle sizes can be determined. Stutz and Pfund[29] use the percentage light transmission in the visible band by a suspension of fixed concentration to determine particle size, and Gamble and Barnett[30] use a similar method in the infra-red. The method is only applicable to fairly

uniform pigments with average particle size less than the wave length of light available. It is a relative method and requires a separate comparison with other methods for each pigment. The photomicrographic method is direct, but may involve sampling errors. Its lower limit is approximately the wave length of light used. Kuhn[31] describes a method using the Zeiss-Thoma blood corpuscle counting chamber. Green[32] describes an accurate method based on photographing the pigment after dispersing it on a glass slide, and points out the distinction between true particles and aggregates, and the importance of eliminating the latter by the proper dispersing procedure.

Because of the critical effect of the particle size on reflection and hiding power found with some pigments in the visible range, an effort was made to discover whether the particle size of the pigments used in ultra-violet paints has an important effect on their ultra-violet reflection. The photomicrographic method was used in examining the particles. Preliminary examination showed magnesium oxide to be the only pigment, of the three used, with many particles approaching the critical range in size. The difference in reflection between the commercial magnesium oxide powders and the smoked deposit (Table III) may be due to the existence of many more particles in the critical range in the smoked form, as well as to a lack of purity in the commercial form.

Two forms of magnesium oxide powder are available, "light" and "heavy", of which the light bulks much larger. In line with the reasoning above, the reflection factor measurements (Table III) suggest that the light form has the smaller particle size since it has the larger reflectance. Two paints were ground, G-17 and G-18 (Table IX), identical except that one contained the heavy and the other the light form of magnesium oxide. As might be expected, G-18 had a larger ultra-violet reflectance than G-17. Yet, photomicrographs of these two paints (Plate V) at first glance seem to indicate that G-18 has the larger particles.

This was first intimated by the fact that G-18 filtered through cloth slower than G-17 and also settled faster to a looser sediment. Closer examination of the photomicrographs shows that these large particles are actually clusters or aggregates of many small particles. Also, particles small enough to be in the critical range for ultra-violet scattering and reflection are just below the limit of visibility of a microscope using visible light, so that they do not appear on the photomicrographs. Hence it is uncertain whether the observed difference in reflection is due to particle size or to some other effect. In the case of paints G-1, G-2 and G-3, it was observed (p. 67) that the effect of grinding in the mill was to produce a reflection factor below that of paints of identical composition ground by hand, the difference

Plate V.

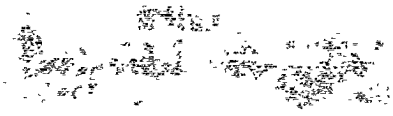
MgO, heavy, 10% dil. (×750)

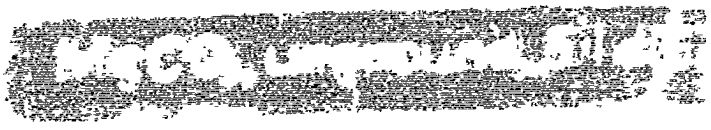
MgO, light, 10% dil. (×750)

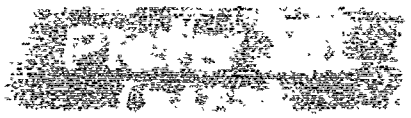
being greater the greater the proportion of magnesium carbonate to white lead. These differences cannot be due to differences in the particle sizes of the pigments, but must be due to the better dispersion obtained in the mill, so that it is likely that the difference between G-17 and G-18 is due to the different degrees of dispersion in the two paints as indicated by the many more large clusters of particles in G-18 as shown in the photomicrographs.

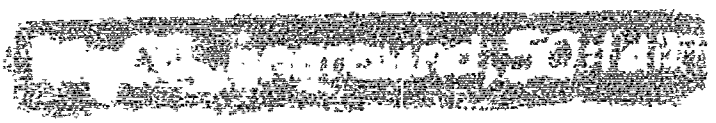
2. Particle Structure or Aggregation.

In order to compare the effect of particle structure alone (i.e. the clustering of a number of individual particles into an aggregate), examine the photomicrographs of the magnesium carbonate paints, G-10a, in the ground form, and G-10b, in the unground form (Plates VI and VII). These paints are identical except that G-10a was ground 70 hours as usual and G-10b was rotated in the mill for the same length of time, but without balls. Plate VI was made from the paints diluted 5:1 with a resin solution of the same viscosity and composition as that used in making the paints. Plate VII was made from the paints diluted 50:1 in the same way. Slides were prepared from the diluted paints by placing one drop on a clean slide, and spreading it out with the edge of another. This procedure was found to produce a uniform dispersion of the paint on the slide without









destroying the aggregate structure being investigated. The other photomicrographs presented here were similarly prepared from paints diluted as indicated. The photomicrographs were made by transmitted light.

The reflection factor of G-10a is 32 per cent, while that of G-10b, the unground form, is 64 per cent. The difference is evidently due to the difference in number and size of the aggregates as shown in the photomicrographs. Notice that some of the aggregates are perfectly black, indicating that they are reflecting practically all the light. Other smaller aggregates are less opaque and the fact that they are made up of a number of small transparent particles can be seen. Single particles are those with a clean line border and a clear center on the photographs.

That the difference in reflection is due to the presence of aggregates is very reasonable since in this case the paints are otherwise identical and the aggregates are dispersed on grinding. Figure 24 shows the decrease in reflection factor which occurs as the grinding time is increased and the aggregates are gradually dispersed by the action of the ball mill. Table XI shows the results of a count of the ratio of number of aggregates to number of single particles in the ground and unground paints, made on the photomicrographs. Such a count cannot be considered accurate since the very small particles do not show on the plates and are therefor not included; and because there are

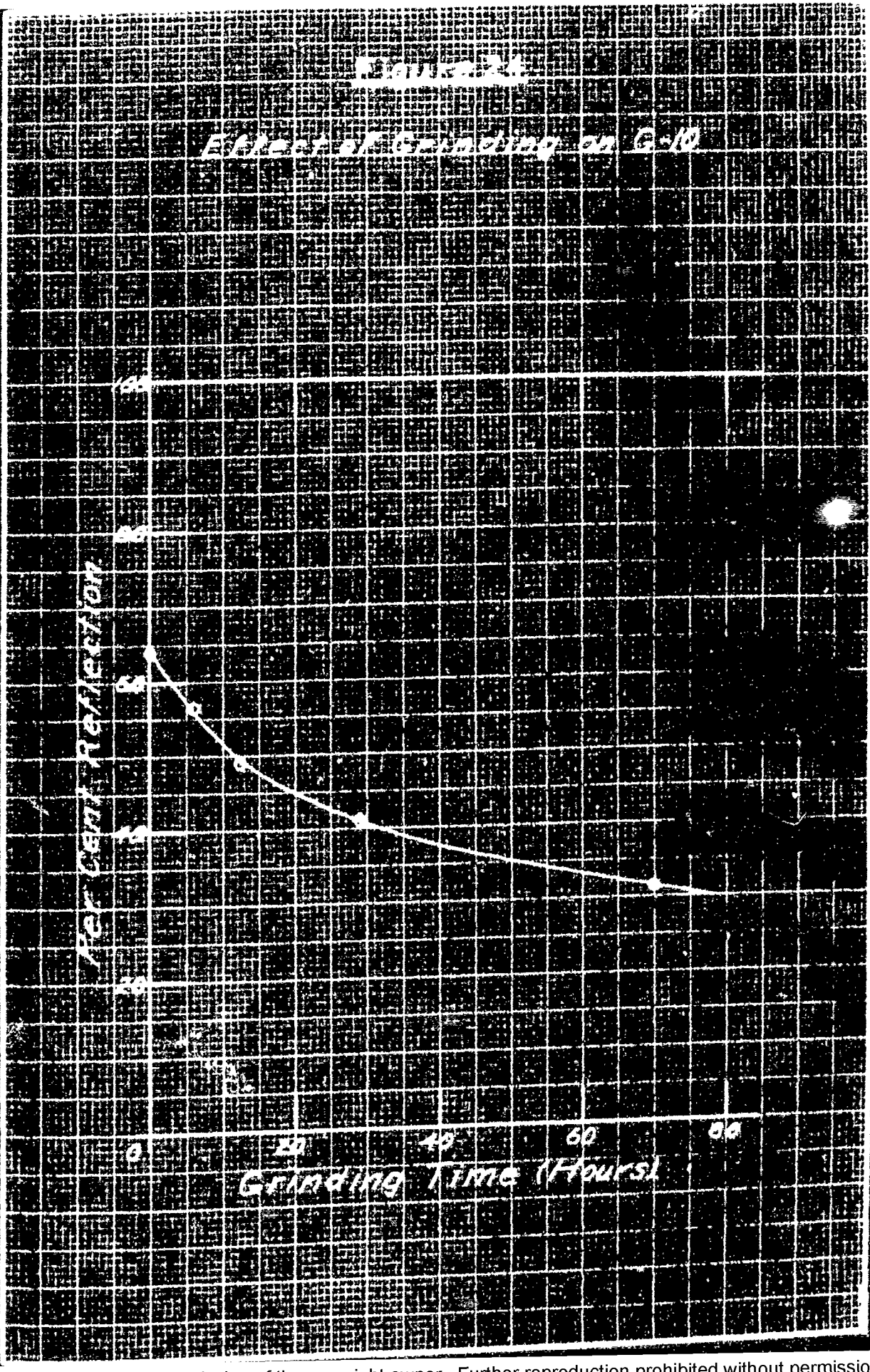


Table XI.

Aggregate Count.

Paint	Dilution	Aggregate Fraction: Less than 10 microns	Aggregate Fraction: Greater than 10 microns
G-10a	5:1	.03	.001
G-10a	50:1	.02	.0007
G-10b	5:1	.07	.007
G-10b	50:1	.04	.006

borderline cases where it is not definite whether a group of particles is an aggregate or a naturally occurring coincidence of particles. Nevertheless, it makes more quantitative the conclusions already reached. The large difference between the ground and unground paints is in the larger aggregates, and, as is evident from the photographs, they are the ones which are most effective in reflection. There appears to be a decrease in the aggregate count on dilution, but it is small and errors in the count and in sampling may account for it.

Plates V and VIII show that aggregate structure occurs also in magnesium oxide and white lead paints, suggesting the possibility that it may occur in all types of paint. The question naturally arises, then, whether the presence of aggregate structure will affect the light reflection from other paints as markedly as it does in the case of magnesium

Plate VIII

carbonate, because if it does it establishes the condition that dispersion of the pigment in paint manufacture should be kept to the minimum necessary to produce a smooth film.

A hint as to the answer is provided by paints G-1, G-2, and G-3, which, as had been pointed out, show an increasing drop in reflection factor from that of the hand-ground preliminary paints with increasing proportion of magnesium carbonate to white lead as pigment. Grinding or mixing with a mortar and pestle is approximately equivalent to long churning without balls in a mill, and in fact does not produce as smooth a product. Therefor these drops in reflection are similar to that described for G-10, and hereafter the hand-ground preliminary paints will be referred to as unground. Table XII shows the effect of grinding in relation to the approximate refractive indices of pigment and vehicle, for three pigments. The refractive indices are for visible light, and so are only approximate for comparison with ultra-violet reflection data. It is evident that, as the ratio of refractive index of pigment to vehicle increases above one, the effect of grinding on reflection factor decreases rapidly. Hence one will expect the presence of aggregate structure to be effective in increasing light reflection only in the case of inert type pigments which have low refractive indices comparable to those of the common vehicles. Thus, contrary to the usual manufacturing

Table XII.

Effect of Grinding on Different Pigments.

Pigment	Vehicle	Refractive Index Pigment	Refractive Index Vehicle	Reflection Factor Ground	Reflection Factor Unground
$MgCO_3$	Ethyl Cell. Dow No. 7	1.5-1.54	1.5	52	64
$MgCO_3$	Acryloid	1.5-1.54	1.5	56	66
MgO,C.P. (Baker)	Ethyl Cell. Dow No. 7	1.74	1.5	47	70
MgO,hvy. (Squibb)	Ethyl Cell. Dow No. 7	1.74	1.5	35	59
MgO, lt. (Squibb)	Ethyl Cell. Dow No. 7	1.74	1.5	70	73
B.C. Wh. Lead	Acryloid	2.0	1.5	51	52
B.C. Wh. Lead	Ethyl Cell. Dow No. 7	2.0	1.5	55	50-60 (est.)

procedure of dispersing the pigment as thoroughly as possible, inert type pigments may be made much more valuable by deliberately creating an aggregate structure within paints containing them, improving their light reflection and hiding power. Little decrease in reflection on grinding is observed in the case of light magnesium oxide, because, although ground at the same concentration in the same viscosity resin solution as the heavy magnesium oxide, it made a paint so viscous that the grinding action of the balls was destroyed.

What causes the effectiveness of aggregate structure, and in what ways it can be created or maintained within a paint, are questions which have not yet been answered satisfactorily. The importance of refractive index with respect to the effectiveness of aggregates, as shown in Table XII, suggests the explanation that there is some air within each aggregate, thus making the low refractive index pigments much more effective than if every particle were surrounded by vehicle, and making the higher refractive index pigments also more effective, but to a much lesser extent. Whether or not this explanation is correct is not yet known. Nevertheless, whatever the correct explanation may be, aggregates are important in promoting higher reflectances from paints containing inert pigments. It may be that aggregate structure is involved in the higher reflectances obtained when two pigments are ground together into a paint rather than separately. These questions deserve further study.

IV. FILM THICKNESS AND HIDING POWER.

1. Theoretical Relations.

Hiding power is defined as the area covered by a unit volume of paint when the paint film just obliterates a background of specified contrast, usually black and white of some specified brightnesses, and is obviously an important quantity, since it expresses the economic value of a paint, so far as hiding is concerned. Expressed as area per unit volume, it is readily converted into an equivalent film thickness, and measurements of hiding power are essentially measurements of the film thickness at which obliteration occurs. Obliteration occurs when the difference in the reflectances of the paint film over the contrasting areas becomes less than the minimum difference detectable by the human eye. The experimental determination of hiding power is difficult because the variation of reflection with film thickness is very slight at the hiding thickness, permitting considerable latitude in fixing the exact hiding thickness. Consequently a number of attempts have been made to derive a theoretical expression relating the light reflection of a film of light dispersing material to its thickness, so that the experimental determinations from which hiding power will be calculated can be made in regions where the film thickness is more critical.

The first attempt was made by Mallett[33]. He does not

define his use of the term hiding explicitly, but appears to mean the ratio of the reflection of a paint film at a given thickness to its maximum reflection (at infinite thickness). He observed that if a paint had a hiding of 50 per cent at a certain thickness, it had a hiding of about 75 per cent at twice the thickness, 87.5 per cent at three times the thickness, and so on. He then assumes that the paint film is divided into a series of unit layers of unspecified thickness and that hiding is a geometrical function of thickness. These assumptions lead to the equation:

$$S = 1 - (1-a)^n \qquad (1)$$

where S is the hiding of n unit layers and a is the hiding of a single layer.

Rhodes and Fonda[34] assume the paint film to be divided into layers of thickness equal to the average diameter of the pigment particles, and that each layer transmits a fraction T of the light incident on it and reflects a fraction R. Then, considering the multiple reflections of the light between the first two and subsequent layers, they derive the expression:

$$B_u - B_n = (B_u - B_1)\left[\frac{T}{1-R^2}\right]^{2(n-1)} \qquad (2)$$

where B_u, B_n and B_1 are the brightnesses (reflectances) of an infinite thickness, of n layers, and of one layer respectively.

Hallett's equation can be put in the form:

$$B_n = B_u - B_u(1-a)^n, \qquad (3)$$

since B is defined as B_n/B_u. Rhodes and Fonda's equation differs essentially in the small correction term B_1 for the reflection from the surface layer. Their equation (2) can be rewritten:

$$B_n = B_u - (B_u-B_1)e^{-k(n-1)} \qquad (4)$$

This is a relatively simple equation which fits reflection-thickness data fairly well. However, their derivation is in error in the handling of multiple reflections beyond the first two layers. A correct derivation, based on the same assumptions, is given in Appendix D. The correct analysis does not give a summable finite series, as was obtained by Rhodes and Fonda, but gives a recursion formula which can be solved. The solution, not corrected for surface reflection, is:

$$B_n = \frac{B_u(1-e^{-kn})}{1-B_u^2e^{-kn}} \qquad (5)$$

This equation, which neglects surface correction, differs from (4) essentially in the additional term in the denominator, giving larger values of B_n for the same value of B_u.

Pokrowski[35] assumes that light flux is diminished exponentially with penetration into a body, in deriving an expression relating the reflection factor of a mixture of powders (at infinite thickness) to the reflection factors

of the component powders at infinite thickness. However he gives no justification for this assumption. His expressions, if integrated for a finite rather than an infinite thickness, give a dependence on thickness similar to equation (5), but with different constants.

Smith[36] assumes that the transmission and reflection of light by diffusing films is independent of the angle of incidence. By considering the symmetrical case of light sources on both sides of the film, and using matrix algebra, he obtains expressions involving the reflection and transmission of the film and hyperbolic functions of the film thickness. These expressions can be transformed into an equation to the decrease in light intensity through the film is

$$R = \frac{r(1-e^{-2kt})}{1-r^2e^{-2kt}} \qquad (6)$$

where R is the reflection of a film of thickness t, k is a characteristic constant of the material and r is the maximum

where R is the reflection of a film of thickness t, k is a

v

characteristic constant of the material and r is the maximum

r

value of R. If the number of layers, n, in equation (5) be (6) are identical. The importance of this derivation is the simplicity of the assumptions involved: no layer structure of the paint film is required, and no assumption as to the decrease in light intensity through the film is necessary.

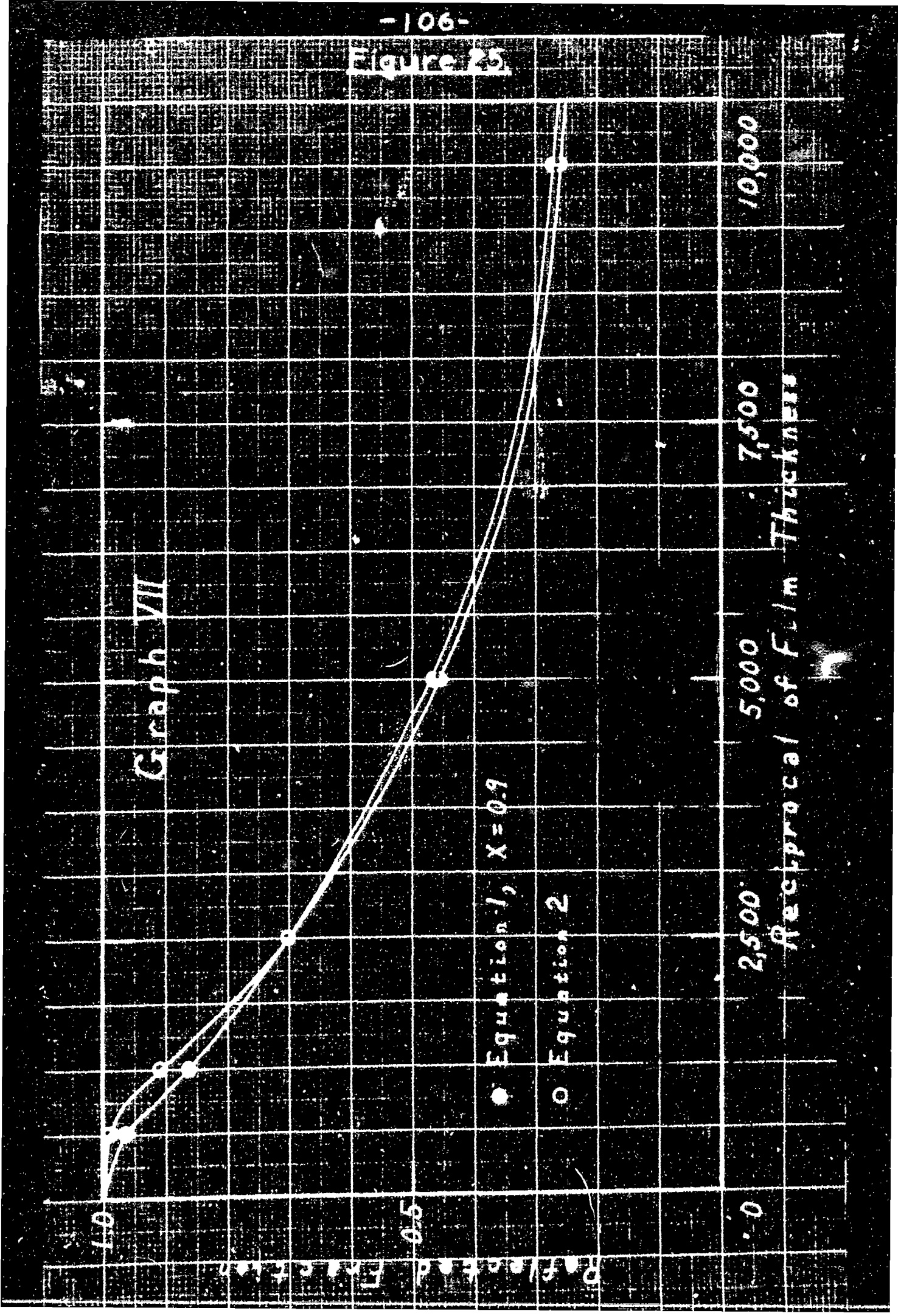
Smith goes on to derive an expression for the "absolute hiding power" of a film, which he defines as

$$\frac{J_1+J_2}{J_1-J_2}$$

where J_1 and J_2 are the reflection factors over contrasting areas of reflection factor 1 and 0 respectively. To do this, he regards the background as a source of light at the back side of the film of relative intensity equal to the product of the transmission of the film and the reflection of the background, and proceeds as in his first analysis. However this is only a first approximation, since it neglects subsequent multiple reflections between the film and the background, and hence his results on hiding power are approximate.

Kewish[37] assumes uniform cubical pigment particles oriented in planes of thickness equal to the edge length of the particles, no light absorption by liquid or pigment, and light incident normally on the surface. By considering the probabilities, for a given number of planes n, that different numbers of particles will be lined up beneath each other, and applying the law of multiple reflections for a series of reflecting planes, he obtains an expression giving the reflection from a paint film n layers thick as a series of n terms. To date, it has not been possible to sum this series. However, he has shown (Figure 25) that it can be expressed approximately by equation (3) (his equation 2, Figure 25), but only when x, the reflection of the unit

Figure 45.



particle, is large. This is an interesting result, as it indicates that paints may follow the usually observed form of reflection-thickness curve only when the pigment particles are distributed in a non-uniform manner, so that the unit particle for the above type of derivation is really a cluster of particles with a large unit reflection. However too much weight should not be given this observation, since no light absorption is assumed and since the experimental curves are fitted by equations, such as Smith's, which are derived without reference to the distribution of the particles except that it be reasonably uniform.

The writer, with the aid of Dr. Taylor*, has derived a relation equivalent to (6) in a more direct fashion than Smith, by considering the requirements which any functional relation between reflection and thickness must satisfy. Only two assumptions need be made regarding the paint film, both of which are tacitly made in every derivation. One is that the film is uniform to the extent that any small, but finite, volume of it will contain pigment in the same concentration and behave toward light in the same manner as any other small volume. The other is that either the angular distribution of the light penetrating to any depth in the film is the same, or the action of the film on light is independent of the angular distribution. The detailed

* Dr. W. C. Taylor, Mathematics Dept., Univ. of Cincinnati.

derivation is presented in Appendix E-1. Briefly, the method is to divide the film arbitrarily into two layers by an imaginary plane, and consider the multiple reflections between them which make up the reflection from the entire film. The requirement is then imposed that the reflection must be the same whether the thinner or the thicker layer is on top. This leads to a linear fractional relation between the reflcetion factor of the film and the reflection factors of the two layers. A special linear fractional transformation then transforms this relation into one whose solution is readily seen. The result, not corrected for surface reflection, is:

$$R = \frac{r(1-e^{-at})}{1-r^2e^{-at}} \qquad (7)$$

where R is the reflection factor at a film thickness t, r is the maximum value of R, and a is a characteristic constant.

The two assumptions involved in this derivation obviously cannot hold exactly for very thin films of the order of one pigment particle thick, and hence equation (7) cannot be expected to be correct for thin films. However Tolman[34] has found, for smokes and silica suspensions, a strict proportionality between the strength of the Tyndall beam and the concentration over a wide range of concentration; and Kowish has shown[37] that for very thin films the light reflection should be proportional to the thickness, neglecting

correction for surface reflection. With this in mind, it is interesting to observe that the relation (7) also gives a reflection proportional to thickness for small thicknesses, and so is probably valid over the entire range of thicknesses.

In Appendix E-2, the necessary corrections are made for reflection at the surface of the film, and the equations and constants are arranged for fitting to experimental data.

The brief survey herein of the literature on reflection-thickness relationships indicates a wide range in the meaning attached to the term hiding power. In Appendix E-3, hiding power is defined in accordance with the A. S. T. M. definition, and the related quantity hiding thickness is also defined. The correct method for determining the hiding thickness from the reflection-thickness relation is outlined, and it is shown that it depends on the reflectances of the contrasting background it is desired to hide and on the value chosen for the photometric sensibility of the eye. The hiding thickness is found to vary inversely as the curvature constant a, and to be a function of $1/r$, the reciprocal of the maximum possible reflection from a film.

Hanstock[58] states without derivation the approximate relation

$$T = \sqrt{\frac{k \alpha}{R - \alpha}} \qquad (8)$$

for the transmission at the hiding thickness, where k is

the least perceptible contrast, R and α are the reflectances of the contrasting areas to be hidden, and α is also the maximum reflectance of the paint. This equation neglects all multiple reflections.

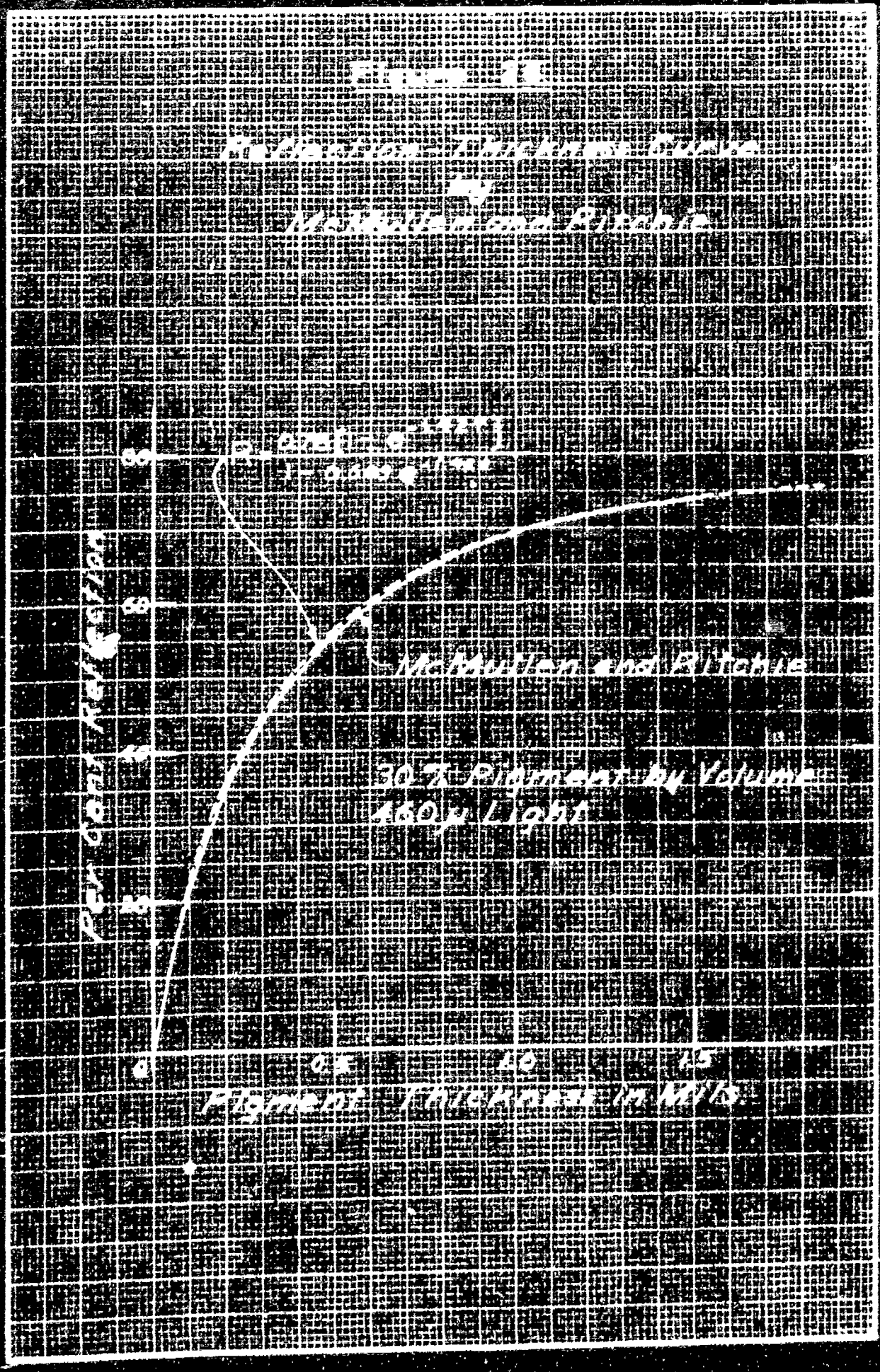
2. Experimental Results.

Rhodes and Fonda[34] obtained reflection-thickness curves for paints made from a number of white pigments and inerts ground with linseed oil. They found good agreement with their formula, equation (2), except for zinc oxide paints. Zinc Oxide gave higher values for intermediate thicknesses than could be fitted with their formula, and they attributed this to the agglomeration of the zinc oxide particles. The exact equation (7) should fit this case better, and at the same time give fair agreement with their other results.

Rhodes and Starr[39] found the reflection-thickness relation, (2), also valid for paints made by adding small amounts of carbon black, prussian blue and aluminum powder to white linseed oil paints.

Hellullen and Ritchie[40] give a reflection-thickness curve obtained with a recording spectrophotometer, but make no attempt to fit an equation to it. Figure 26 shows the fit which can be obtained with equation (7) to their curve.

Meacham[41] has measured the transmission of paint films on glass plates at various thicknesses. Although he did



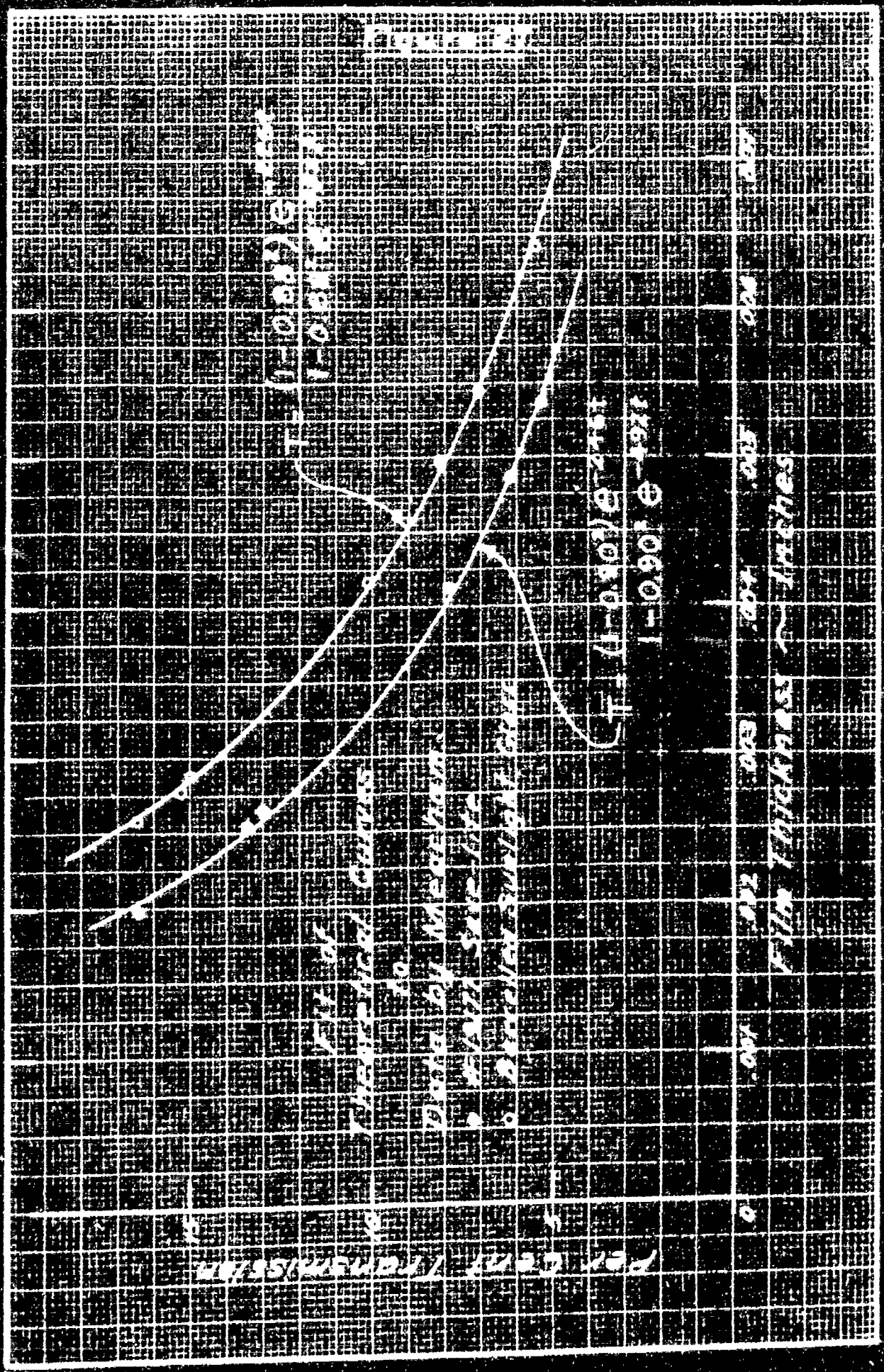
not use a sphere to gather all the diffusely transmitted light, he obtained most of it by placing his cylindrical photoelectric cell so that it touched the back of the plate. Equation (13), Appendix E, expresses the transmission of the film in terms of the same constants which are used in the reflection relation. This equation is:

$$T = \frac{(1-r^2)e^{-at/2}}{1-r^2e^{-at}} \qquad (9)$$

One would expect it to fit Meacham's results, and Figure 27 shows the fit of this equation to his data for two different white paints.

It is evident that the functional relations derived in Appendix E fit the experimental data well for reflection of visible light. Two questions then arise. Do these relations hold for ultra-violet reflection? And what are the relations between the constants a and r and the properties of the individual materials comprising the film? From practical experience, one would expect that both a and r would increase with increase in the ratio of refractive indices of pigment and vehicle, and that increase in the absorption coefficient of pigment or vehicle would decrease r. The nature of these relationships is not known, and experimental work to discover them would be worth while.

The scope of such work is so great that the solution of only a small part of the problem could be attempted here. It was decided to investigate the effect of the absorption



coefficient of the liquid, and by making reflection factor readings in the ultra-violet to determine whether the reflection-thickness curves follow the same law in the ultra-violet as in the visible region. Magnesium carbonate was chosen as the pigment for these tests because its long mean light path should make the effect of vehicle absorption larger and because it requires a relatively thick film to reach maximum reflection, thus making the measurements of thickness more accurate. The series of methacrylate ester resins was chosen for the series of vehicles because their physical and chemical properties are similar and they differ chiefly in their ultra-violet absorption coefficients.

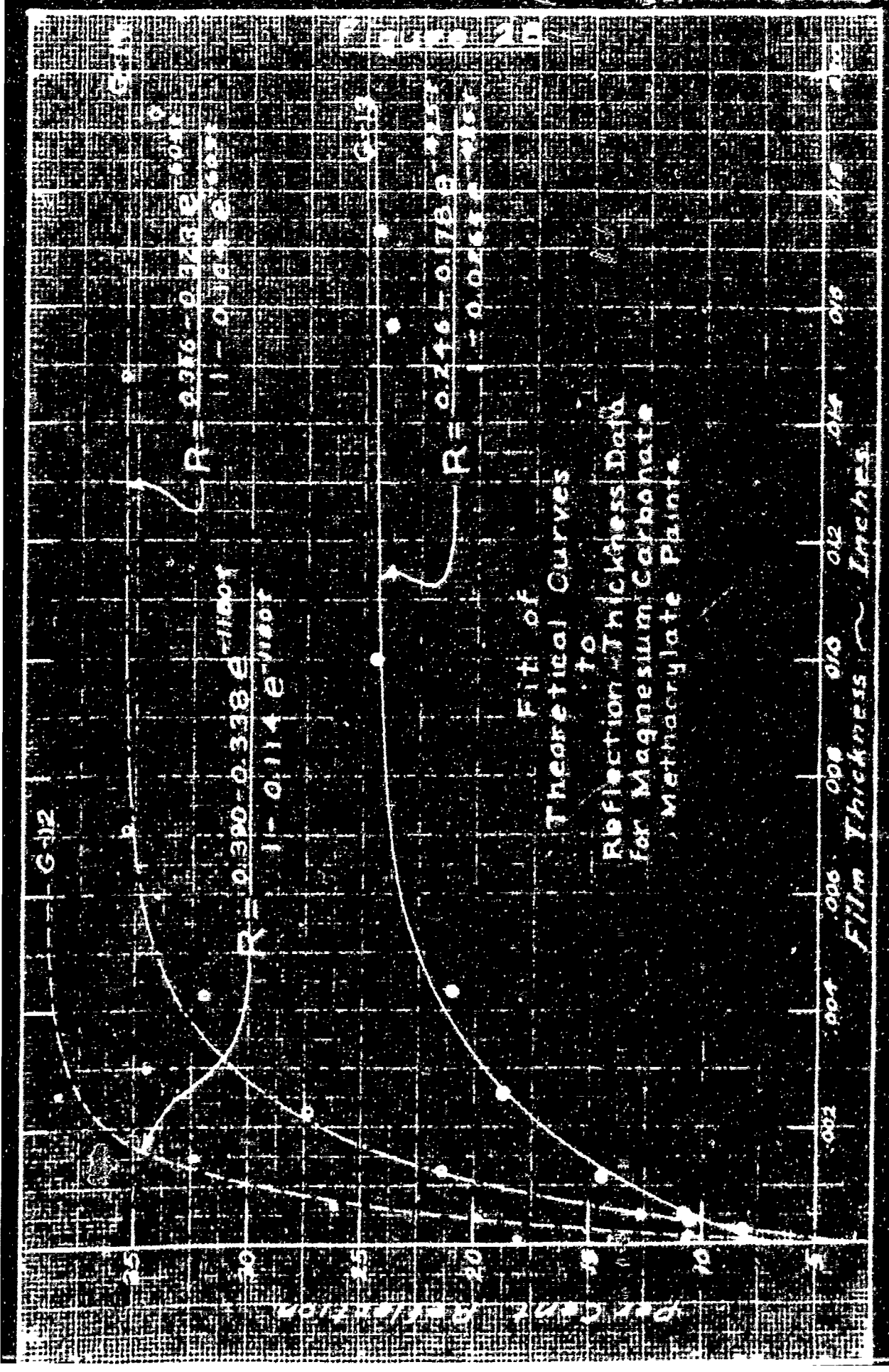
The series of paints, C-12 to C-16, was ground, each at 40 per cent pigment volume. The pigment for each was taken from the same sample of magnesium carbonate. The resin of each was dissolved in the same amount of solvent. Each paint was ground 24 hours at 90 r.p.m. in the same mill with the same set of balls.

The paints were sprayed on steel panels coated with a baked black finish, whose solid vehicle has a refractive index very nearly that of the methacrylates, so that reflection from the background would be negligible. The panels were masked during spraying so that only an area 1 1/2 inches square would be covered, and a more uniform film would be obtained. The weight of paint applied was obtained

by weighing the panels before spraying and after the paint had dried, and from this weight a relative film thickness was calculated from the specific gravities of the component materials.

The results obtained for each paint are displayed graphically in Figures 28 and 29 together with the curves, of the form derived in Appendix E-2, which have been fitted to the results for each paint. The results for G-12 scatter badly and cannot be fitted accurately with a curve. This is due to the fact that the resin of G-12, methyl methacrylate, although apparently well dissolved in its solvent, which was toluene and cellosolve, tended to form an air emulsion in the spray gun and to leave the gun in fibrous cobweb-like strands. Thus much air was trapped in the applied films with the effect of increasing their reflection factors due to the increased bending of light at the vehicle-air interfaces created within the film. This effect is quite similar to that suggested as the explanation for the effectiveness of aggregates with inert pigments, and might possibly be developed as a means of improving the reflection from paints containing inert pigments. Since the amount of air trapped in this way in the G-12 panels will vary for each panel sprayed, the reflection factors of such panels may differ widely.

For G-14 the last point, at a film thickness of 0.02



inches, is low. This is due to the fact that films as thick as this dry very slowly so that the pigment has a chance to settle, creating a film with a non-uniform composition. Thus the principal assumption in the derivation of the reflection-thickness relation is violated, and a different reflection factor is the result. This condition is almost impossible to avoid in spraying thick films with paints of the lacquer type, since each succeeding coat tends to redissolve the film already applied.

The fit of the calculated curves to the results indicates that the derived reflection-thickness relation also holds in the ultra-violet region. The constants a, R_0, and r employed in fitting curves to the results for the five paints, together with the absorption coefficients of the resins, and their densities and refractive indices as given by Strain[18], are tabulated in Table XIII.

Table XIII.

Reflection-Thickness Curve Constants.

Paint Nbr.	Surface Refl., R_0	Maximum Refl., r	Curvature Constant a (in^{-1})	Resin Abs. Coeff.	Resin Refr. Index	Resin Density
G-12	.06	.390	1180	48.8	1.490	1.19
G-13	.07	.246	425	40.5	1.485	1.11
G-14	.036	.356	605	24.8	1.484	1.06
G-15	.04	.320	628	21.8	1.483	1.05
G-16	.05	.308	642	20.0	1.477	1.02

Excluding the values for G-12, for the reasons given above, the curvature constant is found to decrease with increase in absorption coefficient of the resin and with decrease in the refractive index ratio of pigment and resin. The maximum reflection, r, however, does not vary in a uniform manner with any of the indicated variables, absorption coefficient, refractive index or density. Since it has been shown to what a large extent aggregates can affect the reflection factor of magnesium carbonate paints, it is possible that this factor was the controlling one in these tests, obscuring the effects of resin absorption. The differences in viscosity between the resin solutions used in G-13 to G-16 are negligible, so that viscosity differences probably did not affect the dispersion in the mill. But differences in the wetting of the particles by each resin could affect the degree of dispersion of the aggregates by the mill, especially if the view is taken that aggregates contain entrapped air. In this connection, it may also be pointed out that the differences between ethyl cellulose and isobutyl methacrylate paints shown in figure 17 may be due to better wetting of the pigment by the latter resin. Should wetting measurements substantiate this supposition, it would account for the difference in gloss which was noted, since it has been shown that addition of wetting agents to vehicles which wet the pigment poorly can improve the gloss.[42] Poorer wetting of the pigment by the ethyl cellulose would

provide the opportunity of occluding some air in the film, particularly since the pigment volumes are high, with the result of higher reflection because of the refractive index effect. Although the presence of air in the paint film is only definitely known in the case of the sprayed G-12 panels, which showed higher reflection factors, it is interesting that it also provides a consistent explanation of the case above and of the effectiveness of aggregates as well. This explanation, however, is entirely speculative and further research on this particular subject should be valuable.

This work on reflection-thickness curves is preliminary and shows the need of more experimentation of this type with careful control of all variables. For this, the choice of white lead, which is not so sensitive to the presence of aggregates, is indicated. The effect of refractive index, light absorption, particle size and particle structure of pigments on the constants a and r, as well as the effect of vehicle absorption, should be studied.

V. SUMMARY.

1. The development of paints reflecting up to 70 per cent in the ultra-violet is described. The four stages of development are (1) testing of reflection or transmission of all possible paint materials to select those suitable; (2) mixing and testing of the simplest possible combinations of pigment and vehicle to determine suitable combinations; (3) determination of low ultra-violet absorption resin-plasticizer combinations which form good films; and (4) accurate milling of the most likely paint formulations and testing them for reflection and deterioration.

2. For this purpose, an apparatus was developed which measures accurately the integrated reflection factors and the transmission coefficients of substances in the band from 2800 to 3200 Angstroms. This apparatus balances out fluctuations in source intensity, and its readings are independent of the amplification of its amplifier.

3. An exact method of taking into account the multiple reflections in an absorption cell is derived.

4. A method is derived by which approximate values for the absorption coefficient of a pigment and the length of the mean light path through it can be obtained from the variation in reflection with pigment concentration in paints, at very high pigment concentrations.

5. The effect of pigment properties and pigment

structure is discussed, and the great importance of an aggregate structure in improving the reflection of paints containing inert pigments is demonstrated.

6. The theoretical relation between the reflection and the thickness of a film is discussed in the light of the work of other investigators. A functional derivation of such a relation is made on the basis of two reasonable assumptions, and a beginning is made on the study of the connection between the constants of this relation and the physical properties of pigment and vehicle.

ACKNOWLEDGEMENT.

The writer is grateful for the counsel and advice of Dr. W. Soller, Dr. F. F. Heyroth and Dr. P. J. Flory of the Basic Science Research Laboratory and for the aid of Dr. W. C. Taylor of the Mathematics Department, University of Cincinnati. He is indebted to Professor E. E. Ware and Mr. J. A. Meacham of The Sherwin-Williams Company, and to Mr. D. A. Kohr, Mr. E. W. Fasig, Dr. J. H. Purdy and Dr. R. W. Kewish of The Lowe Brothers Company for their interested assistance and advice. The cooperation of Dr. A. H. Taylor of the Lighting Research Laboratory of the General Electric Company is appreciated.

Acknowledgement is due The Lowe Brothers Company for its sponsorship of the Cooperative Graduate Research Fellowship which has made this research possible.

REFERENCES.

1. Luckiesh, M. and Holladay, L. L., Fundamental units and terms for biologically-effective radiation, J. O. S. A. 23, 197 (1933).

2. Sumpner, Phil. Mag., 35, 81 (1893).

3. Taylor, A. H., The Measurement of Reflection Factors in the Ultra Violet, J. O. S. A., 21, 776 (1931).

4. Pfund, A. H., Some Optical Properties of White Paint Pigments in the Ultra Violet Spectrum, Proc. Am. Soc. Test. Mat., 23, II, 369 (1923).

5. Taylor, A. H., A Simple Portable Instrument for Measuring Reflection and Transmission Factors in Absolute Units, Trans. I. E. S., 15, 811 (1920).

6. Rosa, E. B. and Taylor, A. H., Theory, Construction and Use of the Photometric Integrating Sphere, B. S. Scientific Paper, No. 441.

7. Taylor, A. H., The Measurement of Erythemal Ultra Violet Radiation, J. O. S. A., 23, 60 (1932).

8. Soller, Walter, Balanced Electron Tube Circuits, U. S. Patent No. 2104211.

9. Soller, Walter, One Tube Balanced Circuit for D. C. Vacuum Tube Amplifiers of Very Small Currents, Rev. Sci. Inst. 3, 416 (1932).

10. Penick, D. B., Direct Current Amplifier Circuits for Use with the Electrometer Tube, Rev. Sci. Inst., 6, 115 (1935).

11. Forsythe, Barnes and Easley, Characteristics of a New Ultra Violet Lamp, J. O. S. A., 21, 30 (1931).

12. Stutz, G. F. A., Observations of Spectrophotometric Measurements of Paint Vehicles and Pigments in the Ultra Violet, J. Frank. Inst., 200, 87 (1925).

13. Barnes, B. T., Spectral Distribution of Energy Radiated from a New Type of Tungsten Mercury Arc, Physical Rev., 36, 1466 (1930).

14. Pfund, A. H., Some Optical Properties of White Paint Pigments in the Ultra Violet Spectrum, Proc. Am. Soc. Test. Mat., 25, II, 309 (1925).

15. Luckiesh, M., Spectral Reflectances of Common Materials in the Ultra Violet Region, J. O. S. A., and Rev. Sci. Inst., 19, 1 (1929).

16. Luckiesh, M. and Holladay, L. L., Paints for Reflecting Biologically-effective Radiation, J. Frank. Inst., 212, 787 (1931).

17. Goodeve, C. F., The Absorption Spectra and Photo-sensitising Activity of White Pigments, Trans. Faraday Soc., 33, 340 (1937).

18. Strain, D. E., Kennelly, R. G. and Dittmar, H. R., Methacrylate Resins, Ind. Eng'g. Chem. 31, 382 (1939).

19. Bass, S. L. and Kauppi, T. A., Evaluation of Ethyl Cellulose Plasticizers by Load-elongation Curves, Ind. Eng'g. Chem., 29, 676 (1937).

20. McAlister, E. D., Absolute Intensities in the Visible and Ultra Violet Spectrum of a Quartz Mercury Arc, Smithsonian Miscellaneous Collections, 87, No. 17 (1933).

21. Taylor, A. H., Ultra Violet Radiation from the Sunlight (Type S-1) Sunlamp, J. O. S. A., 21, 20 (1931).

22. Shoulejkin, Was., Scattering of Light by Very Big Colloidal Particles, Phil. Mag. 48, 307 (1924).

23. Caspersen, Torbjorn, The Optics of White Sols. I. Theoretical Derivation of the Absorption Coefficients, Kolloid Z., 60, 151-9 (1932); II. The Diffuse Scattered Reflection, Kolloid Z., 65, 162-70 (1933)

24. Tolman, Ryerson, Vliet, Gerke and Brooks, Relation Between the Intensity of the Tyndall Beam and Concentration of Suspensions and Smokes, J. Am. Chem. Soc., 41, 300 (1919).

25. Patterson, H. S. and Gray, R. W., The Scattering of Light by the Individual Particles of Smokes, Proc. Roy. Soc. (London), A113, 512 (1926).

26. Gurevich, Luckinskii and Mikhailov, The Dependence of the Scattering of Light in Aerosols on Particle Size and on Wave Length, Kolloid Z., 60, 24-34 (1932).

27. Tezak, D., The Relation Between Absorption and Scattering of Light by White Sols, Kolloid Z., 74, 16-22 (1936).

28. Colloid Symposium Monograph, Vol. III, p.260.

29. Stutz, G. F. A. and Ffund, A. H., A Relative Method for Determining Particle Size of Pigments, Ind. Eng'g. Chem. 19. 51 (1927).

30. Gamble, D. L. and Barnett, C. E., Scattering in the Near Infra-Red - a Measure of Particle Size and Size Distribution, Ind. Eng. Chem., Anal. Ed., 9, 310 (1937).

31. Kuhn, von Curt, On the Value of Counting Fine Grained Substances, Zeitschrift fur Angewandte Chemie, 28, 126 (1915).

32. Green, H., A Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments, J. Frank. Inst., 192, 637 (1921).

33. Hallett, R. L., Hiding Power of White Pigments, Proc. Am. Soc. Test. Mat., 22, II, 623 (1922).

34. Rhodes, F. H. and Fonda, J. S., Factors Determining the Brightness and Opacity of White Paints, Ind. Eng. Chem., 18, 130 (1926).

35. Pokrowski, G. I., On the Reflection Properties of Complex Systems, Z. Physik, 47, 898-905 (1928).

36. Smith, T., The Hiding Power of Diffusing Media, Trans. Optical Soc. (London), 33, 150 (1931-32).

37. Kovish, R. W., Reflection and Transmission of Light by Paint Films, Lowe Brothers T. R. 456, 4th supp., 4-14-39.

38. Hanstock, R. F., The Opacity of Paints, J. Oil Colour Chem. Assoc., 20, 5-34 (1937).

39. Rhodes, F. H. and Starr, J. V., Reflection Factors of White Paints, Ind. Eng. Chem., 21, 596 (1929).

40. McMullen, E. W. and Ritchie, E. J., New Uses for a Recording Spectrophotometer, Official Digest of the Federation of Paint and Varnish Production Clubs, 174, 117 (Mar. 1938).

41. Meacham, J. A., Light Reflection from Painted Surfaces, Am. Paint J., 23, 25 (Oct. 1938).

42. Pickett, C. F., The Effect of Pigment Concentration on the Gloss of Enamels, Official Digest of the Federation of Paint and Varnish Production Clubs, 187, 310 (Jun. 1939).

OTHER REFERENCES.

Apparatus.

Hardy, A. C., A New Recording Spectrophotometer, J. O. S. A., 25, 305 (1935).

Koller, L. R. and Taylor, A. H., Cadmium Magnesium Alloy Photo-tubes, J. O. S. A., 25, 184 (1935).

Reflection Measurements, Metals and Pigments.

Coblentz, W. W., Ultraviolet Reflecting Power of Aluminum and Several Other Metals, B. S. Jour. of Res., 189, Feb. 1950.

Hulburt, E. O., The Reflecting Power of Metals in the Ultra Violet Region of the Spectrum, Astrophys. J. 42, 205, (1915).

Preston, J. S., The Reflection Factor of Magnesium Oxide, Trans. Optical Soc. (London), 31, 15-35 (1929-30).

Stutz, G. F. A., The Testing of Paint Pigments for Transparency to Ultra Violet Radiation, J. Frank. Inst., 202, 89 (1926).

Taylor, A. H., Reflection Factors of Various Materials for Visible and Ultra Violet Radiation, J. O. S. A., 24, 192 (1934).

Taylor, A. H. and Edwards, Junius D., Ultra Violet and Light Reflecting Properties of Aluminum, J. O. S. A., 21, 677 (1931).

Transmission Measurements.

Davey, Duncan and Higgam, Absorption of Ultra Violet Light by Lacquer Films, Phys. Rev., 35, 1425 (1930); Ind. Eng. Chem., 25, 904 (1931).

Gamble, D. L. and Stutz, G. F. A., Ultra Violet Light Transmission Characteristics of Some Synthetic Resins, Ind. Eng. Chem., 21, 350 (1929).

Stutz, G. F. A., Absorption of Ultra Violet Light by Paint Vehicles, Ind. Eng. Chem., 19, 897 (1927).

Reflection of Paints.

Gamble, D. L., Light Reflecting Characteristics of Paints, Ind. Eng. Chem., 24, 875-81 (1932).

Gardner, H. A., Illumination from Paint, Paint, Oil and Drug Rev., 68, No. 23, 8 (1919).

Hallett, R. L., The Effect of Certain Paint Films on Ultra Violet Light, Proc. Am. Soc. Test. Lab., 23, II, 379 (1923).

McMullen, L. J., Ritchie, E. J. and Bullard, A. L., Determination of Hiding Power by the Spectrophotometer, Official Digest of the Federation of Paint and Varnish Production Clubs, 187, 272 (June 1939).

New, G. F., Radiation and Paint, J. Oil and Colour Chem. Assoc., 19, 156 (1936).

APPENDICES.

Appendix A.

Theory of Integrating Sphere.

1. Absolute Reflection Measurements. (After Sumpner, Taylor, and others).

Assume the inner surface of the sphere to be a perfect diffuser, so that light reflected from it obeys the cosine law. That is, (Figure 30-I),

$$\mathcal{L}_{AC} = \mathcal{L}_0 \cos \theta \qquad (1)$$

where $\mathcal{L}_{AC}$ is the intensity of light reflected in the direction AC, and $\mathcal{L}_0$ is the intensity of light reflected in the direction AO, when light is incident on the point A.

If $\mathcal{L}_0$ is the intensity of the light reflected normally, the intensity in the direction AC at C will be:

$$\frac{\mathcal{L}_0 \cos \theta}{\overline{AC}^2}$$

The intensity normal to the surface at C, due to reflection from A will be:

$$\mathcal{L}_C = \frac{\mathcal{L}_0 \cos \theta}{\overline{AC}^2} \cos \theta \qquad (2)$$

However,

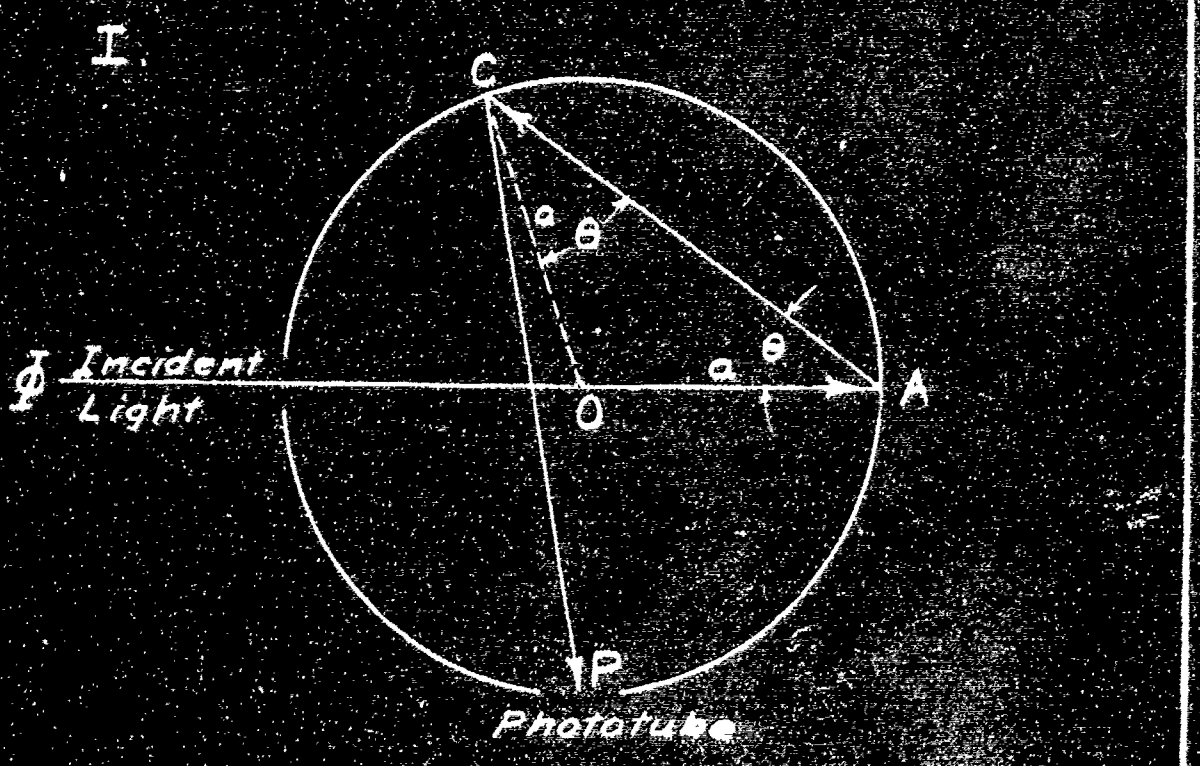
$$\overline{AC} = 2a \cos \theta \qquad (3)$$

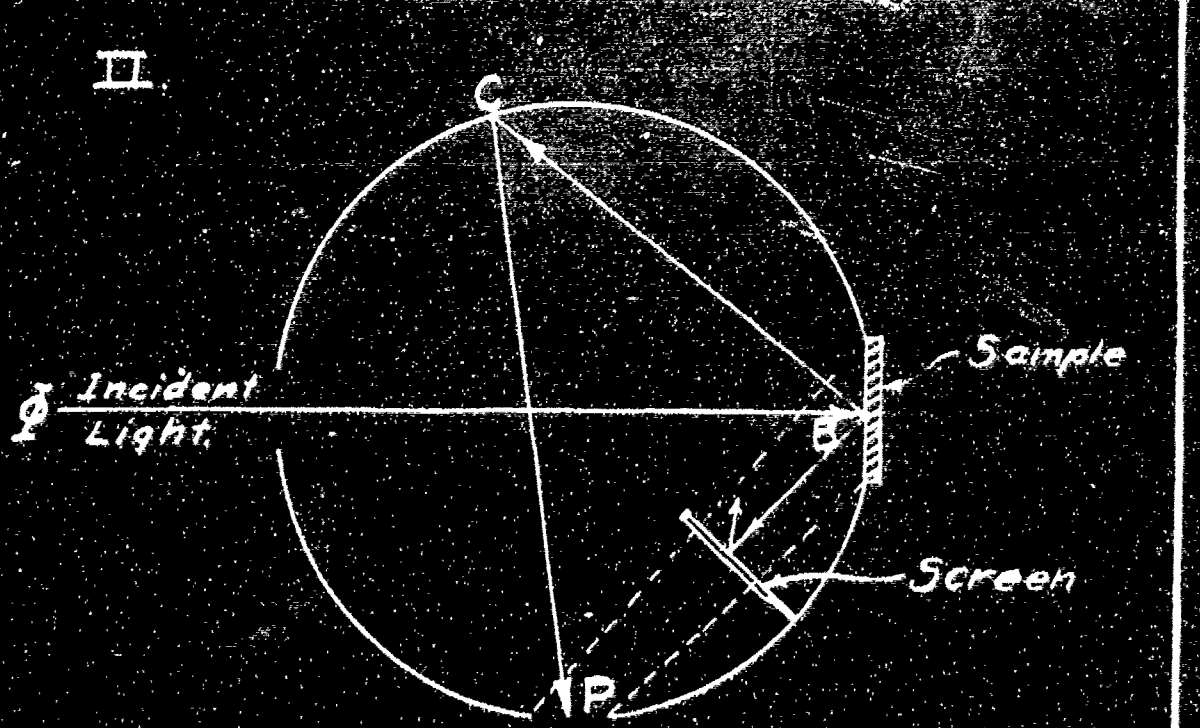
Hence

$$\mathcal{L}_0 = \frac{\mathcal{L}_0 \cos^2 \theta}{(2a \cos \theta)^2} = \frac{\mathcal{L}_0}{4a^2} \qquad (4)$$

Thus, since a is the radius of the sphere, and constant, the intensity at any point C inside the sphere due to the first

Figure 30.





reflection from A will be the same. In other words, each portion of the inner surface will illuminate uniformly each other portion.

Consider now the sphere reflectometer. The light beam enters the sphere through a small opening, and strikes either the sample or the sphere wall depending on how the sphere is turned. Let

r = reflection ratio of sphere coating, i.e. ratio of all reflected light to incident light.

R = reflection ratio of sample.

$4\pi a^2$ = area of sphere.

Consider first the case where the light is incident on the sphere wall (Figure 30-I). Due to the first reflection from A, the intensity at any point C on the sphere surface will be $\frac{\Phi r}{4\pi a^2}$, where Φ is the ~~intensity~~ flux of the incident light, since the sphere is equally illuminated from A. This will also be the intensity at P, due to the first reflection.

The second reflection from all points C to P can be evaluated as follows. From any unit area of the sphere, the intensity at P due to second reflection will be $\frac{\Phi r}{4\pi a^2} \cdot \frac{r}{4\pi a^2}$.

From the entire sphere surface, the intensity at P due to the second reflection will be $\frac{\Phi r}{4\pi a^2} \cdot \frac{r}{4\pi a^2} \cdot 4\pi a^2 = \frac{\Phi r}{4\pi a^2} \cdot r$

Similarly the intensity due to the third reflection will be: $\frac{\Phi r^2}{4\pi a^2} \cdot r$. Summing up all the multiple reflections, the total

intensity at P is:

$$\mathfrak{E}_p = \frac{\mathfrak{E}r}{4\pi a^2}\,(1 + r + r^2 + \cdots) \qquad (5)$$

Since r is less than one, the series can be summed, and

$$\mathfrak{E}_p = \frac{\mathfrak{E}}{4\pi a^2}\cdot\frac{r}{1-r} \qquad (6)$$

Now consider the case where the light is incident on the sample (Figure 30-II). It is not necessary to assume that reflection from the sample obeys the cosine law. Let θ and φ be polar coordinates with origin at B, and $f(\theta,\varphi)$ be the function representing the distribution of reflected light from the sample. Then the reflection ratio R is

$$R = \int_0^{\pi}\int_0^{2\pi} f(\theta,\varphi)\,d\theta d\varphi \qquad (7)$$

The intensity due to first reflection at any point C will be $\mathfrak{A}\,f(\theta,\varphi)\,d\theta d\varphi$. Due to the screen between B and P, this first reflected light does not reach P. The intensity due to the second reflection at P will be, because of equation (7): $\int_0^{\pi}\int_0^{2\pi} \mathfrak{A}\,f(\theta,\varphi)\frac{r}{4\pi a^2}\,d\theta d\varphi = \frac{\mathfrak{E}Rr}{4\pi a^2}$.

The intensity due to the third reflection at P will be

$$\frac{\mathfrak{E}Rr}{4\pi a^2}\cdot\frac{r}{4\pi a^2}\cdot 4\pi a^2 = \frac{\mathfrak{E}Rr^2}{4\pi a^2}\,.$$

Summing up all the multiple reflections, the total intensity at P is:

$$\mathfrak{E}'_p = \frac{\mathfrak{E}Rr}{4\pi a^2}\,(1 + r + r^2 + \cdots) = \frac{\mathfrak{E}R}{4\pi a^2}\cdot\frac{r}{1-r} \qquad (8)$$

Comparing equations (6) and (8), it is seen that

$$\frac{\mathfrak{E}'_p}{\mathfrak{E}_p} = R \qquad (9)$$

This is the ratio of intensities which is measured in an experiment by measuring the ratio of the phototube currents when the sphere is in the two positions. Equation (9) shows that such a reflection measurement is independent of the reflection factor of the sphere surface.

2. Error due to Holes and Sample.

In this derivation, the effects of holes in the sphere and of low reflection factor samples have been neglected. The error due to them can be found readily if the sample and sphere wall are assumed to obey the cosine law. Let b be the area of sample exposed in the sphere, and c be the area of holes in the sphere.

Considering first light incident on the sphere wall at A, the intensity at any point C due to the first reflection from A will be, as before, $\frac{dr}{4\pi a^2}$. The intensity at P due to the second reflection will, however, now be:

$$\frac{dr}{4\pi a^2}\left[\frac{r(4\pi a^2-b-c)+Rb}{4\pi a^2}\right] = \frac{dr^2}{4\pi a^2}\left[1-\frac{1}{4\pi a^2}\left(b+c-\frac{Rb}{r}\right)\right]$$

$$= \frac{dr^2\xi}{4\pi a^2} \qquad (10)$$

where $\xi = 1 - \frac{1}{4\pi a^2}\left(b + c - \frac{Rb}{r}\right)$ (11)

Similarly, the intensity due to the third reflection will be $\frac{dr^3\xi^2}{4\pi a^2}$. Summing up all the multiple reflections, the total

intensity at P is:

$$\Phi_P = \frac{\Phi r}{4\pi a^2}\left(1 + r\xi + r^2\xi^2 + \cdots\right) = \frac{\Phi}{4\pi a^2}\cdot\frac{r}{1-\xi r} \qquad (12)$$

Considering light incident on the sample, the intensity at any point C due to the first reflection from B is $\frac{\Phi R}{4\pi a^2}$. This first reflection does not reach P because of the screen. The intensity at P due to the second reflection is now: $\frac{\Phi R}{4\pi a^2}\left[\frac{r(4\pi a^2-b-a)+Rb}{4\pi a^2}\right] = \frac{\Phi R r\xi}{4\pi a^2}$. Similarly, the third reflection will give $\frac{\Phi R r^2\xi^2}{4\pi a^2}$. Summing up all the multiple reflections, the total intensity at P due to light incident on the sample is:

$$\Phi'_P = \frac{\Phi R r\xi}{4\pi a^2}\left(1 + r\xi + r^2\xi^2 + \cdots\right) = \frac{\Phi R}{4\pi a^2}\cdot\frac{r\xi}{1-r\xi} \qquad (13)$$

If one now takes the ratio of the intensities, from equations (12) and (13), one obtains:

$$\frac{\Phi'_P}{\Phi_P} = \xi R \qquad (14)$$

Thus the factor ξ, defined by equation (11), is the approximate correction for holes and for low reflectance samples. The correction factor ξ is unity (i.e. no correction) only when the sample has the same reflection as the sphere wall, and there are no holes in the sphere. Neither requirement can be achieved practically. Hence, in order to keep the correction factor as near one as possible, the area

of holes and the area of sample exposed must be kept as small as possible. The correction will always be larger for smaller values of sample reflectance, and the measured reflection factor will always be slightly ~~high~~ low.

Appendix B.

Analysis of Transmission Cell.

1. Transmission of Material in Cell.

The transmission cell is composed, essentially, of two vitreosil plates with space between for the material to be tested. The two surfaces of each vitreosil plate can be considered, for this analysis, as one composite surface, which reflects a certain percentage of the light striking it. The cell can then be represented (Figure 5) as an absorber transmitting a fraction "t" between two surfaces each reflecting a fraction "x". If we let

x = the fraction of light reflected from the two surfaces of each vitreosil plate,

R = the total reflection from the cell (measured),

t = the fraction of light transmitted by the material in the cell,

T = the overall transmission of the cell (measured),

we can write the total reflection from the cell as the infinite series:

$$R = \frac{\phi_R}{\phi} = x + (1-x)^2t^2x + (1-x)^2t^4x^3 + \ldots$$

$$= x + (1-x)^2xt^2\,(1 + x^2t^2 + x^4t^4 + \ldots)$$

This can be summed, since x^2t^2 is less than one, whence

$$R = x + \frac{(1-x)^2xt^2}{1-x^2t^2} = \frac{x(1 + t^2 - 2xt^2)}{1-x^2t^2} \qquad (1)$$

Similarly, we can write the overall transmission of the

cell as the infinite series:

$$T = \frac{\Phi_T}{\Phi} = (1-x)^2t + (1-x)^2x^2t^3 + (1-x)^2x^4t^5 + \ldots$$

$$= t(1-x)^2(1 + x^2t^2 + x^4t^4 + \ldots)$$

whence, since x^2t^2 is less than one,

$$T = \frac{t(1-x)^2}{1-x^2t^2} \qquad (2)$$

In order to eliminate x and solve for t, note that equations (1) and (2) can be combined to give:

$$R = x + xtT \quad \text{or} \quad x = \frac{R}{1 + tT} \qquad (3)$$

Substitute for x in equation (1) from equation (3):

$$R = \frac{R}{1 + tT} \cdot \frac{1 + t^2 - \frac{2Rt^2}{1 + tT}}{1 - \frac{R^2t^2}{(1 + tT)^2}}$$

Clear of fractions:

$$(1+tT)^2 - R^2t^2 = (1+tT)(1+t^2) - 2Rt^2$$

Multiply out and rearrange:

$$Tt^3 + (1-2R+R^2-T^2)t^2 + (T-2T)t = 0$$

Divide through by tT:

$$t^2 + \frac{(1-2R+R^2-T^2)}{T}t - 1 = 0$$

Whence, solving for t:

$$t = -\frac{(1-R)^2-T^2}{2T} + \sqrt{\left[\frac{(1-R)^2-T^2}{2T}\right]^2 + 1} \qquad (4)$$

2. Refractive Index of Material in Cell.

Let us consider in detail a single vitreosil plate, assuming that it absorbs no light. If we define the

following as:

a = the fraction of light reflected from the vitreosil-air interface,

b = the fraction of light reflected from the vitreosil-liquid interface,

n_V = the refractive index of vitreosil,

n_L = the refractive index of material in cell,

then

$$x = a + (1-a)^2 b + (1-a)^2 ab^2 + \ldots = a + \frac{b(1-a)^2}{1 - ab}$$

and

$$x - abx = a + b - 2ab$$

whence:

$$b = \frac{x - a}{1 - 2a + ax} \qquad (5)$$

a can be calculated from Fresnel's Law:

$$a = \left(\frac{n_V - 1}{n_V + 1}\right)^2$$

x can be calculated from R and T by equations (3) and (4). Hence b can be calculated from equation (5). Also, from Fresnel's Law:

$$b = \left(\frac{n_V - n_L}{n_V + n_L}\right)^2 ,$$

so that n_L can be calculated:

$$n_L = \frac{n_V(1 \mp \sqrt{b})}{\pm \sqrt{b} - 1} \qquad (6)$$

Thus the refractive index of the material being tested can be determined approximately from (6) if it is known whether it is larger or smaller than that of the vitreosil in the ultra-violet.

Appendix C.

Calculation of Pigment Absorption.

Figure 9 shows the decrease in ultra-violet reflection factor with increase in the volume ratio of vehicle to pigment, for two pigments. It is seen that, for small volume ratios, the decrease in the logarithm of the reflection factor is proportional to the volume ratio. Since a reflection factor less than one represents absorption by the reflecting material, it is reasonable to ascribe this decrease in reflection to absorption by the vehicle. If this is so, one should be able to calculate, from the rate of decrease and the absorption coefficient of the vehicle, the length of a mean light path through the paint, and therefrom the absorption coefficient of the pigment. One must make several assumptions, however, which render the results only approximate.

Let V = ratio of volume of vehicle to volume of pigment,

R = reflection factor at a volume ratio V,

R_0 = reflection factor of dry pigment ($V=0$),

k = absorption coefficient of paint,

k_v = absorption coefficient of vehicle,

k_p = absorption coefficient of pigment,

L = length of the mean light path through the paint, not including distance traveled through air between particles, defined by the equation $R=e^{-kL}$. Thus reflection

is here represented as the result of absorption, according to Lambert's Law, and so this equation is also a definition of k. In other words, of all the light paths possible through the paint, the mean light path, L, is that one which, if traveled by all the light, would give the observed reflection factor, R.

L_v = that portion of L contained in vehicle.

L_p = that portion of L contained in pigment.

L_o = length of the mean light path through the dry pigment (V=0).

n = the number of pigment particles along the mean path L.

For small values of V, each curve of Figure 9 can be represented by a straight line whose equation is:

$$\ln R = \ln R_o - wV \qquad (1)$$

where w is a constant expressing the slope of the curve at V=0. Equation (1) can be rewritten:

$$R = R_o e^{-wV} \qquad (2)$$

Consider a cubical particle of edge length d, covered by a very thin uniform coating of vehicle of thickness b. Then, for this particle:

$$V = \frac{6d^2b}{d^3} = \frac{6b}{d} \qquad (3)$$

Equation (3) also holds for a spherical particle.

Assume that the following approximations hold:

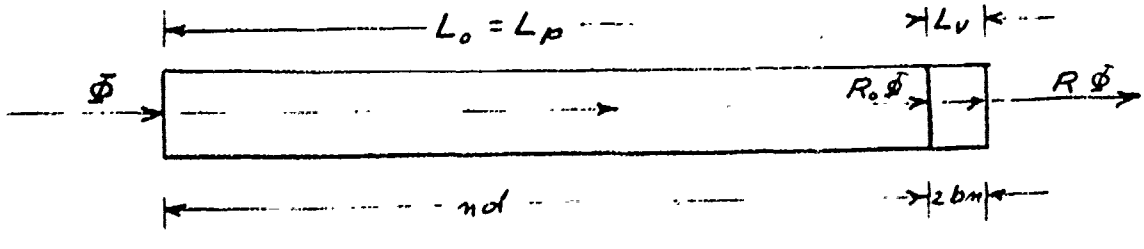
1. L approaches L_0 as V approaches 0. This is strongly suggested by the smooth transition from paint to dry pigment for magnesium carbonate. The type of packing of the particles will not affect this assumption materially, since L and L_0 do not include the distance traveled through air between particles.

2. The particles are of uniform size, and the number of particles, n, in the mean light path remains the same as V approaches 0, so that $L_p = L_0$. This can only be true for very small values of V when the vehicle surrounds each particle with a thin coat and air still fills the spaces between particles.

3. When V is small, the vehicle surrounds each particle with a uniform coat.

4. The thicknesses of the paint films tested for reflection are great enough so that all light paths are included in reflection measurements, and the films may be considered as effectively infinite in thickness.

The accompanying diagram represents the mean light path straightened out, with the pigment and vehicle paths separated. From this diagram, it is evident that, with the



assumptions above,

$$R = R_o e^{-k_v(2bn)} \tag{4}$$

and

$$R_o = e^{-k_p L_o} \tag{5}$$

Equating R from equations (3) and (4),

$$wV = k_v(2bn)$$

or

$$w = \frac{k_v n}{V} \cdot 2b \tag{6}$$

Substituting for b from equation (3),

$$w = \frac{k_v n}{V} \cdot \frac{Vd}{S} = \frac{k_v}{S} nd = \frac{k_v L_o}{S} \tag{7}$$

Substituting for L_o from equation (5),

$$w = \frac{k_v}{S} \left(\frac{-\ln R_o}{k_p}\right) \tag{8}$$

or

$$k_p = -\frac{k_v \ln R_o}{Sw} \tag{9}$$

Equation (7) can be rewritten:

$$L_o = \frac{Sw}{k_v} \tag{10}$$

Equations (9) and (10) are the desired results. It must be remembered that they are only approximate due to the assumptions involved, and can probably give only order of magnitude results. For the curves of Figure 9, k_v=50. For magnesium carbonate, w=0.127 and $-\ln R_o$=0.223, from which L_o=0.01 inches and k_p=20 in^{-1}. For white lead, w=0.024 and $-\ln R_o$=0.481, from which L_o=0.002 inches and k_p=200 in^{-1}.

Appendix D.

Derivation on Rhodes and Fonda's Assumptions.

Making the same assumptions as Rhodes and Fonda, consider the paint film as a series of superimposed layers each reflecting a fraction R and transmitting a fraction T of the incident light. Consider now the multiple reflections between the n^{th} layer and the n-1 layers beneath it, much as in Appendix B:

$$B_n = R + TB_{n-1}T + TB_{n-1}RB_{n-1}T + \cdots$$
$$= R + B_{n-1}T^2 (1 + RB_{n-1} + R^2B_{n-1}^2 + \cdots) \qquad (1)$$

where B_n and B_{n-1} denote the reflection from n and n-1 layers respectively. Since RB_{n-1} is less than one, (1) can be rewritten as:

$$B_n = R + \frac{B_{n-1}T^2}{1-RB_{n-1}} = \frac{R + (T^2-R^2)B_{n-1}}{1 - RB_{n-1}} \qquad (2)$$

Let

$$B_n = \frac{a + C_n}{1 + aC_n} \qquad (3)$$

where a is a constant and C_n is a function of n, related to B_n as shown in (3). Substitute (3) in (2):

$$\frac{a + C_n}{1 + aC_n} = \frac{R(1+aC_{n-1}) + (T^2-R^2)(a+C_{n-1})}{(1+aC_{n-1}) - R(a+C_{n-1})} \qquad (4)$$

Solve for C_n:

$$C_n = \frac{(Ra^2-a+R+a(T^2-R^2)) + (Ra-a^2+Ra+T^2-R^2)C_{n-1}}{(1-Ra-Ra-a^2(T^2-R^2)) + (a-R-a^2R-a(T^2-R^2))C_{n-1}} \qquad (5)$$

In order to make the relationship between C_n and C_{n-1} simple,

set:

$$a^2 - \frac{1-T^2-R^2}{R}a + 1 = 0 \tag{6}$$

Then:

$$G_n = \frac{2Ra - a^2 + T^2 - R^2}{1-2Ra - a^2(T^2-R^2)} G_{n-1} \tag{7}$$

Since a, T, and R are constants, this can be rewritten,

$$G_n = KG_{n-1} \tag{8}$$

where K is a constant. The solution of (8) is

$$G_n = CK^n \tag{9}$$

where C is an arbitrary constant. Equation (3) then becomes:

$$B_n = \frac{a + CK^n}{1 + aCK^n} \tag{10}$$

In order to evaluate K, substitute for a^2 from equation (6):

$$K = \frac{T^2-R^2+1+a\left(\frac{T^2-1+R^2}{R}\right)}{T^2-R^2+1+a\left(\frac{(T^2-R^2)(T^2-R^2-1)-2R^2}{R}\right)} \tag{11}$$

K will be less than one if

$$T^2-1+R^2 \geq (T^2-R^2)(T^2-R^2-1) - 2R^2 \tag{12}$$

or if

$$4R^2 \geq (T^2-R^2)(T^2-R^2-1) - T^2 + R^2 + 1$$

or if

$$4R^2 \geq (T^2-R^2-1)^2 \tag{13}$$

This inequality, (13), can be shown to be true, for, since there is always some absorption,

$$T \leq 1 - R \tag{14}$$

and $$T^2 / 1 - 2R + R^2$$

or $$2R / 1 + R^2 - T^2$$

and $$4R^2 / (1+R^2-T^2)^2 = (T^2-1-R^2)^2 \qquad (15)$$

Hence K is less than one, provided the film has some absorption, and one can then write:

$$K^n = e^{-kn}$$

where k is a positive constant. Then

$$B_n = \frac{a+Ce^{-kn}}{1+aCe^{-kn}} \qquad (16)$$

B_n must approach B_u, the ultimate or maximum reflection, as n approaches infinity, so that

$$B_u = a \qquad (17)$$

B_n must equal 0 when n=0, so that

$$0 = B_u + C$$

or $$C = -B_u \qquad (18)$$

The final result, after substituting for a and C, is then:

$$B_n = \frac{B_u (1 - e^{-kn})}{1 - B_u^2 e^{-kn}} \qquad (19)$$

Appendix E.

Film Thickness and Hiding Power.

1. Reflection-Thickness Curve Derivation.

In order to derive the functional relation between the reflection factor of a film and its thickness, one need make only two assumptions. They are:

I. The material composing the film is of uniform composition throughout.

II. Either the angular distribution of the penetrating light is the same at any depth in the film; or the reflection of light by the film at any depth is independent of the angular distribution.

Let $R(t)$ be the fraction of light reflected from a film of thickness t,

$T(t)$ be the fraction of light transmitted by a film of thickness t.

Consider a film of thickness t divided by an imaginary plane into two layers of thicknesses t_1 and t_2. Because of the assumptions above, the reflection and transmission of the lower layer can be expressed by the same functions R and T, where the light incident on the lower layer is that transmitted through the upper layer. For brevity, denote $R(t_1)$ by R_1, $T(t_1)$ by T_1, $R(t)=R(t_1+t_2)$ by R_{12}, and so forth. Taking account of multiple reflections in a manner analogous to that used for the transmission cell (Appendix D),

one obtains for R_{12} the infinite series:

$$R_{12} = R_1 + T_1R_2T_1 + T_1R_2R_1R_2T_1 + \ldots = R_1 + T_1^2R_2(1 + R_1R_2 + R_1^2R_2^2 + \ldots)$$

The series can be summed, since $R_1R_2 < 1$:

$$R_{12} = R_1 + \frac{T_1^2R_2}{1 - R_1R_2} = \frac{R_1 + (T_1^2 - R_1^2)R_2}{1 - R_1R_2} \qquad (1)$$

By symmetry,

$$R_{21} = R_{12} = \frac{R_2 + (T_2^2 - R_2^2)R_1}{1 - R_1R_2} \qquad (2)$$

Equating these two values of R_{12},

$$R_2 + R_1T_2^2 - R_1R_2^2 = R_1 + R_2T_1^2 - R_1^2R_2$$

Dividing by R_1R_2, and rearranging,

$$\frac{1 - T_1^2 + R_1^2}{R_1} = \frac{1 - T_2^2 + R_2^2}{R_2} \qquad (3)$$

Equation (3) states that a function of layer 1 alone is equal to a function of layer 2 alone. Since the thicknesses t_1 and t_2 are arbitrary, this function must be a constant, K, characteristic of the material composing the film, so that

$$1 - T^2 + R^2 = KR \qquad (4)$$

When $t = \infty$, $T_\infty = 0$, R approaches a maximum value r, and then

$$K = r + \frac{1}{r} \qquad (5)$$

Substituting for T_1^2 in equation (1) by equation (4),

$$R_{12} = \frac{R_1 + R_2 - KR_1R_2}{1 - R_1R_2} \qquad (6)$$

In order to solve the functional relation (6), let

$$R(t) = \frac{r - S(t)}{1 - rS(t)} \qquad (7)$$

where S(t) is a function of t to be determined. Equation (6) becomes, on substituting (7);

$$\frac{r-S_{12}}{1-rS_{12}} = \frac{(r-S_1)(1-rS_2)+(r-S_2)(1-rS_1)-K(r-S_1)(r-S_2)}{(1-rS_1)(1-rS_2)-(r-S_1)(r-S_2)}$$

Solving for S_{12},

$$S_{12} = \frac{(r-S_1)(1-rS_2)+(r-S_2)(1-rS_1)-K(r-S_1)(r-S_2)-r(1-rS_1)(1-rS_2)+r(r-S_1)(r-S_2)}{-(1-rS_1)(1-rS_2)+(r-S_1)(r-S_2)+r(r-S_1)(1-rS_2)+r(r-S_2)(1-rS_1)-rK(r-S_1)(r-S_2)}$$

Collecting terms,

$$S_{12} = \frac{(r+r-Kr^2-r+r^3)-(1+r^2-Kr-r^2+r^3)(S_1+S_2)+(r+r-K-r^3+r)S_1S_2}{(-1+r^2+r^2+r^2-Kr^3)+(r-r-r-r^3+Kr^2)(S_1+S_2)+(-r^2+1+r^2+r^2-Kr)S_1S_2}$$

or,

$$S_{12} = \frac{r(1-Kr+r^2)-(1-Kr+r^2)(S_1+S_2)+(3r-K-r^3)S_1S_2}{(-1+3r^2-Kr^3)-r(1-Kr+r^2)(S_1+S_2)+(1-Kr+r^2)S_1S_2} \qquad (8)$$

From equation (5),

$$1 - Kr + r^2 = 0 \qquad (9)$$

Substituting equation (9) in equation (8),

$$S_{12} = \frac{(3r-r-1/r-r^3)S_1S_2}{-1+3r^2-r^4-r^2} = \frac{1}{r} S_1S_2 \qquad (10)$$

Except for the trivial solution S=0, equation (10) can be satisfied only by an exponential relation of the form

$$S(t) = re^{-at} \qquad (11)$$

where a is a constant, characteristic of the material of the film. Equation (7) now becomes:

$$R_p = \frac{r(1-e^{-at})}{1-r^2e^{-at}} \tag{12}$$

where the subscript p refers to the paint film of thickness t, with no correction for surface reflection. In order that R_p may approach r as t becomes infinite, a must be a positive constant, thus justifying the negative sign in the exponent.

The transmission of the film is obtained by substituting equations (12) and (5) in equation (4):

$$T_p = \sqrt{1-(r+\frac{r}{p})\frac{r(1-e^{-at})}{(1-r^2e^{-at})}+\frac{r^2(1-e^{-at})^2}{(1-r^2e^{-at})^2}}$$

$$= \frac{\sqrt{(1-2r^2+r^4)e^{-at}}}{1-r^2e^{-at}}$$

or,

$$T_p = \frac{e^{-at/2}(1-r^2)}{1-r^2e^{-at}} \tag{13}$$

Equations (12) and (13) can be expressed very concisely by making the substitution, where s is a constant:

$$r=e^{-s} \tag{14}$$

They then become:

$$R_p = \frac{e^{-s}(1-e^{-at})}{1-e^{-2s-at}} = \frac{e^{+at/2}-e^{-at/2}}{e^{s+at/2}-e^{-s-at/2}}$$

and

$$T_p = \frac{e^{-at/2}(1-e^{-2s})}{1-e^{-2s}e^{-at}} = \frac{e^{s}-e^{-s}}{e^{s+at/2}-e^{-s-at/2}}$$

These can now be expressed in terms of the hyperbolic functions as follows:

$$R_p = \frac{\sinh(at/2)}{\sinh(s+at/2)} \tag{15}$$

and

$$T_p = \frac{\sinh (s)}{\sinh (s+at/2)} \qquad (16)$$

2. Correction for Surface Effects.

Up to this point, the reflection at the surface of the film and the reflection at the interface between the film and its supporting surface have been neglected. Multiple reflections will of course take place between these surfaces and the body of the film, and must be considered. The reflection at the interface is important when considering the ability of a film of finite thickness to hide a background of varying reflection factor. In the experiments here conducted on film thickness, the films were sprayed on a background of baked black enamel whose vehicle has a refractive index so close to that of the paints being tested that the reflection factor of the interface is negligible. Hence only the surface reflection need be considered.

The multiple reflections between surface and film can be summed exactly as for the case of two layers of the film. Equation (1) then becomes:

$$R = \frac{R_o + (T_o^2 - R_o^2)R_p}{1 - R_o R_p} = \frac{R_o + (1 - 2R_o)R_p}{1 - R_o R_p} \qquad (17)$$

where now

R_p = reflection of paint film, neglecting surface effect, equation (15),

R_0 = reflection factor of surface,

$T_0 = 1-R_0$ = transmission factor of surface.

For a film of infinite thickness:

$$R_\infty = \frac{R_0 + r(1-2R_0)}{1 - rR_0} \tag{18}$$

For a film of thickness approaching zero, R will approach R_0. This is a definite value for each experimental curve which can be easily determined since the reflection-thickness curve is linear at very small thicknesses and can be extrapolated to zero thickness.

By substituting equation (18) in (17), one obtains:

$$R = \frac{(R_0-2rR_0+r) + r(2R_0-1-rR_0)e^{-at}}{(1-rR_0) + r(R_0-r)e^{-at}} \tag{19}$$

Eliminating r between equations (18) and (19), one obtains:

$$R = \frac{\frac{R_\infty(1-R_0)^2}{1-2R_0+R_0R_\infty} + \left[\frac{(R_\infty-R_0)(1-R_0)(3R_0-2R_0R_\infty-1)}{(1-2R_0+R_0R_\infty)^2}\right]e^{-at}}{\frac{(1-R_0)^2}{1-2R_0+R_0R_\infty} + \frac{(R_\infty-R_0)\left[R_0(1-2R_0+R_0R_\infty)-(R_\infty-R_0)\right]}{(1-2R_0+R_0R_\infty)^2}e^{-at}} \tag{20}$$

Rearranging,

$$R = \frac{R_\infty - \frac{C_2}{C_1}e^{-at}}{1 + \frac{1}{C_1}e^{-at}} \tag{21}$$

where

$$C_1 = \frac{(1-R_0)(1-R_0)-R_0(1-R_\infty)}{(R_\infty-R_0)(2R_0-R_\infty-R_0R_\infty)} \tag{22}$$

and

$$C_2 = \frac{1-3R_0+2R_0R}{2R_0-R_\infty-R_0R_\infty} \tag{23}$$

The usual problem is to fit equation (21) to the experimental data and determine the constants a and R_∞. For this purpose, it can be rewritten:

$$e^{-at} = \frac{C_1(R_\infty - R)}{C_2 + R} \qquad (24)$$

As was pointed out above, R_0 is readily determined. R_∞ can be estimated quite closely if the data include points at large film thickness. Knowing R_0 and a trial value of R_∞, one calculates C_1 and C_2. Then one calculates, for each value of R, the expression on the right side of equation (24). If this expression is then plotted on semi-log paper against t, a straight line will result if R_∞ has been correctly chosen. The slope of this line will be the constant, a.

3. Hiding Power.

Hiding thickness, of a paint is here defined as that film thickness ~~of a given paint,~~ and hiding power, is here defined as the area covered by unit volume of the paint at hiding thickness, which is necessary to make insensible to the eye the difference between two contrasting surfaces beneath the film. That is, the difference in reflection factor of the paint film over a low reflectance and a high reflectance background must be just less than the "least perceptible contrast" or "photometric sensibility" of the eye. Thus, no matter what rela-

tionships are used, any determination of hiding power is arbitrary to the extent of the value used for the least perceptible contrast. Lowry[E1] measured the photometric sensibility $\Delta B/B$, where B is the brightness, of a number of observers at different field brightnesses. He found that it varied with the field brightness, with a minimum value of 1.37 per cent at 25 millilamberts. Previously, the accepted value was 2 per cent, as determined by Konig and Brodhun[E2].

As a first approximation, the surface reflection from the film will be neglected in calculating hiding power. This is reasonable, since R_0 will be the same for the same paint over different backgrounds. Let

R_L be the reflectance of the paint film over a background of reflectance L,

R_D be the reflectance of the paint film over a background of reflectance D $\angle$ L,

k be the least perceptible contrast.

Then, adopting equation (1) to this case,

$$R_L = \frac{R + L(T^2-R^2)}{1 - RL} \qquad (25)$$

and

$$R_D = \frac{R + D(T^2-R^2)}{1 - RD} \qquad (26)$$

E1. E. M. Lowry - The Photometric Sensibility of the Eye and the Precision of Photometric Observations. J.O.S.A. 21, 132 (1931).

E2. P. G. Nutting - Outline of Applied Optics, p.126 (1912).

The condition for the hiding thickness is then:

$$k = \frac{R_L - R_D}{R_L} = 1 - \left(\frac{1-RL}{1-RD}\right)\left(\frac{R+D(T^2-R^2)}{R+L(T^2-R^2)}\right) \qquad (27)$$

The most extreme case of hiding is when L=1 and D=0. Equation (27) then becomes:

$$k = 1 - \frac{(1-R)R}{R+T^2-R^2} = \frac{T^2}{R-R^2+T^2} \qquad (28)$$

Substituting for R and T from equations (12) and (13),

$$k = \frac{e^{-at}(1-r^2)^2}{r(1-e^{-at})(1-r^2e^{-at}) + e^{-at}(1-r^2)^2 - r^2(1-e^{-at})^2}$$

or

$$k = \frac{(1-r)(1+r)^2e^{-at}}{r + (1-r^3)e^{-at} - r^3e^{-2at}} \qquad (29)$$

This is a quadratic equation in e^{-at}, and, since r and a are known from the reflection-thickness curve, can be solved numerically for e^{-at} and t. If the characteristics of the background to be hidden are known, that is if L and D are known, substitution from equations (12) and (13) is made directly into equation (27). The result will in general be a cubic equation in e^{-at}, from which the hiding thickness can be determined.

It is evident from equation (29) that, if the value of k has been decided on, the hiding thickness depends on both r and a. For two paints having the same maximum reflectance, r, the hiding thicknesses will vary inversely ~~proportional to~~ as their a constants. For curves having the same curvature

constant a, the hiding thickness decreases as r increases from almost zero to nearly one. This can be seen most easily by using equation (12), choosing a value of e^{-at} nearly 0 (say, 0.05) and computing $\frac{r-R}{r} \cdot 100$, the percentage decrease below the maximum.

In evaluating a paint for brightness and hiding power from the experimental constants a and r, therefor, r may be taken as a direct measure of brightness, and the larger the constants a and r the better the hiding power. This does not contradict the known fact that addition of a black or colored pigment to a white paint decreases the brightness and increases the hiding power (see, for example, the work of Rhodes and Starr[59]), for such an addition will increase a faster than it decreases r, so that the hiding thickness will decrease.

T. R. 436
6th Supp.
9 - 8 - 39

REVIEW OF "SOME FACTORS INFLUENCING THE REFLECTION OF ULTRA-VIOLET LIGHT BY PAINTS".

R. H. Kewish

"Some Factors Influencing the Reflection of Ultra-violet Light by Paints" is a report by D. F. Wilcock covering the excellent work that he has carried out in the problem of developing a paint having high reflection in the near ultraviolet. In reviewing this report, a tabulated statement of the things that Wilcock has accomplished will first be given, then a discussion of these accomplishments, and finally a criticism of the report.

List of Things Accomplished

1. The development of a precision method for measuring reflection and transmission of ultraviolet light.
2. The improvement of the precision of the integrating sphere by the use of a smaller window for the sample.
3. The derivation of equations by means of which correction can be made for the effect of holes in the sphere.
4. The derivation of equations essential to the accuracy of transmission cell measurements.
5. The measurement of reflectances of a large number of pigments, and absorption coefficients of a large number of thinners, oils, resins, driers, and plasticizers.
6. The measurement of the effect of additions of aluminum bronze to white pigments and the working out of an explanation for the unusual results.
7. The discovery that larger aggregate size leads to greater reflection, and that the creation of an aggregate structure with inerts improves their ability to reflect light and their hiding power.
8. The development of pigment combinations for one or two pleasing tints of high ultraviolet reflectance.
9. The development of several paints which have satisfactory reflectance and film characteristics and which retain their reflectance properties after prolonged exposure to ultraviolet light.
10. The derivation of equations for determining from transmission cell measurements on liquids their refractive indices for ultraviolet light.
11. The derivation of equations for determining mean light path through and absorption coefficients of pigments.
12. The derivation of equations relating reflectance to thickness of paint films.

Discussion

Undoubtedly the greatest contribution which Wilcock has made is the precision method which he has developed for measuring reflection and transmission. By using two photocells, the effects of variation in the intensity of the light source are eliminated, and by a direct balancing of potential

in the phototube circuits before amplification, the effect of variations in amplification are eliminated. Other methods either do not eliminate variations in the source, or also require a complicated system of rotating prisms to split the light into two beams of equal intensity. In Silcock's method the precision is attained with relatively inexpensive equipment. The importance of this contribution is not centered solely in the measurement of ultraviolet. By the use of other photocells the method can be easily extended to the measurement of visible light. Here a great range of use becomes apparent, for example: measurement of gloss by measuring the intensity of reflection at various angles, accurate comparison of the effectiveness of flatting agents, accurate measurements of hiding power and opacity, color comparisons by the use of filters or monochromatic light sources - in other words a whole range of properties that we have no facilities for measuring at the present time. The practical value of such measurements in research, production control, and technical development is obvious.

The development of the accurate equations for cell transmission, although essential to the development of an ultraviolet-reflecting paint, may be of somewhat less practical value to us. They are essential to the accuracy of any transmission cell measurements.

The other equations which have been derived are at present of a rather more theoretical than practical interest. The equations on mean light path, absorption coefficient of pigments and reflectance vs. film thickness form a working basis for any fundamental investigation of hiding power.

The discoveries as to the effects of aggregate size are of great practical value and open up a wide field for investigation.

Zirconium oxide is interesting as a new pigment possibility.

As several white and tinted paints of high ultraviolet reflectance and satisfactory film properties have been developed, the original purpose of the work has been accomplished. The work which remains to be carried out is the adjustment of solvent balance so that the paints will have satisfactory working characteristics. The tendency toward excessive settling also much be corrected. The working out of the first of these problems depends almost entirely on the uses to which the paints are put, and on the methods of application. The preliminary problem here, then, is one of sales investigation. Various possible uses which have been suggested for ultraviolet-reflecting paints are:

1. In homes or office buildings in connection with illumination containing ultraviolet light. Walls may be painted with an ultraviolet-reflecting paint, or papered with a paper coated with an ultraviolet-reflecting paint.
2. In hospitals which maintain rooms in which the air has been sterilized by means of ultraviolet light.
3. In meat packing houses which are using ultraviolet light for the rapid curing of meat.
4. Westinghouse is manufacturing a "Sterilamp" for use in preventing mold and bacterial growth in refrigerators. A coating of high ultraviolet reflection would be essential to the efficient use of such lamps.

5. White paints having high ultraviolet reflectance have nearly perfect reflectance in the visible. The paints may find some use in cases where high illuminating efficiency is desired.

Criticism

There are no unfavorable criticisms to be made other than to point out a few minor corrections in terminology and mathematics.

p. 132. It would seem that the terminology here could be considerably improved by using the term "illumination" instead of "intensity normal to the surface".

p. 134. In the second paragraph the statement is made that " - the intensity at any point C on the sphere surface will be $\frac{\mathfrak{F}r}{2\pi a^2}$, where $\mathfrak{F}$ is the intensity of incident light, - . . . very narrow incident beam of light of a given intensity would not illuminate the point C to the same extent as a larger beam of the same intensity. Hence incorrect terms are being used. A better statement would be " - the illumination at any point C on the sphere surface will be $\frac{Fr}{2\pi a^2}$ where F is the flux of incident light, - ". Flux is a power factor and represents the total quantity of incident light per second (intensity times cross sectional area).

p. 136. It might be a little another approach to consider the effect of a single hole in the sphere and then point out that the effect of the sample would be that of a hole of area $\frac{(r-R)b}{r}$.

p. 137. The equation for a single hole is -

$$\frac{\mathfrak{F}'_b}{\mathfrak{F}_p} = \left(1 - \frac{C}{4\pi a^2}\right)R.$$

If the diameter of the sphere is 25.4 cm. (10 in.) then the error in determining R by simply taking the ratio of $\mathfrak{F}'_p$ to $\mathfrak{F}_p$ will be C/2030. In order for the error of measurement to be less than 0.1% the area C must be less than 2.03 sq. cm. However, it would not be necessary to hold the area of C to this value, since the correct value of R can be obtained by means of the above equation. To do this the area of the hole through which the beam enters, as well as the effect of the phototube opening would have to be known. Since it is the ratio of $\mathfrak{F}'_p$ to $\mathfrak{F}_p$ that is actually measured, neglect of these corrections leads to slightly lower values of R, so that it may be said that the reflectances that Wilcock has obtained are slightly low, rather than slightly high as he has indicated on page 138.

p. 143, - line 4. - should read "- the decrease in the logarithm of the reflection factor is proportional to the volume ratio".

p. 145. The assumptions given are reasonable, and within these assumptions the derivation is correct.

p. 148. Equation (11) should read -

$$K = \frac{T^2-R^2+1+a\left(\frac{T^2-1+R^2}{R}\right)}{T^2-R^2+1+a\left(\frac{(T^2-R^2)(T^2-R^2-1)-2R^2}{R}\right)}$$

(Note that the first two terms in the denominator are squared.)

This correct statement of the equation removes any doubt as to the validity of inequalities (12) and (13) and the question marks are unnecessary.

p. 157 Hiding power

A better statement of the first sentence in the paragraph is: "Hiding thickness of a paint is here defined as that film thickness which is necessary to make inscrible to the eye the difference between two contrasting surfaces beneath the film, and hiding power is here defined as the area covered by unit volume of the paint at hiding thickness.

p. 158 Equation (28) should read

$$K = 1 - \frac{(1-R)R}{R+T^2-R^2} = \frac{T^2}{R-R^2+T^2}$$

(Note the negative sign in the denominator of the first fraction.)

p. 158. Next to last line. " - the hiding thicknesses will be inversely proportional to their a constants." This statement is not true in a strict sense, but is approximately true.

L. . Kovich

COPIES:

EMP
DAK
JMP
SEL
File
Extra