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A PHOTOMETRIC METHOD FOR MEASURING THE HIDING POWER OF PAINTS

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Bureau of Standards

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A PHOTOMETRIC METHOD FOR MEASURING THE HIDING POWER OF PAINTS

By H. D. Bruce

ABSTRACT

This paper presents the results of an investigation carried out at the Bureau of Standards to develop a method for measuring from dry films the hiding power of paints. A photometric method was evolved in which the contrast is measured between the two shades of a black and white plate showing through a thin overlying coating of paint. The degree of this contrast is a function of the film thickness and the hiding power of the paint. The relationship between the film thickness and its effected contrast is worked out, whereby, with the formulas and tables presented, the hiding power in square feet per gallon can be readily calculated.

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I. INTRODUCTION

View in diffused light a thin coat of paint spread over black lettering upon a pure white wall. The important optical effect of that paint coating is a reduction in contrast. Because of the coating the black will appear less black and the white will appear to have decreased in brightness. The greater the hiding power of the paint the greater will this contrast be reduced, film thicknesses being the same.

The method developed for the measurement of hiding power of paints depends upon the measurement of this reduction of contrast by means of a suitable photometer. In principle and in the optical arrangement for measurements, the method and apparatus adopted are essentially the same as previously developed by the colorimetry section of the Bureau of Standards for the measurement of the "transparency of paper."¹ The background for the paint film is a

¹ Priest, "The Bureau of Standards Contrast Method for Measuring Transparency," Trans. Am. Ceramic Soc., **17**, February, 1915; B. S. Circular, No. 63, May, 1917. The apparatus with spherical illumination chamber, as used in the present work, was subsequently designed by Priest as an improvement on the apparatus described in the above references, but no description of it has been published heretofore.

glass disk, half black and half white. The paint is not brushed, but spread mechanically by pouring it upon the disk while the latter is being rotated. The film is allowed to dry and the contrast between the two halves at any point and the thickness of the dry film at this point are measured. From these two measurements the hiding power of the paint is calculated. In the following are presented the details of our apparatus, its manipulation, certain pertinent mathematical deductions, the method of computing the hiding power from experimental observations, and typical data obtained by this method.

II. APPARATUS AND EXPERIMENT

The plate used in this work as a background for the paint film is circular, 10 inches in diameter, and made of opaque glass. One half of the plate is white, the other half is black, the shades being as true a white and black as possible. The halves were cemented rigidly together upon a glass backing with litharge-glycerin cement and then ground to a very flat, semipolished surface with No. 303 optical emery.

The whirling-disk method of Walker and Thompson was adopted for the preparation of the paint films.² Briefly, the plate is clamped to a vertical spindle capable of rotation. Twenty or thirty cubic centimeters of paint, previously passed through a 200-mesh sieve to remove coarse particles and skins, is poured upon the center of the plate and the spindle is set into motion. The plate thus spins about an axis through its center and all excess paint is quickly thrown off by centrifugal force leaving a film of very fine appearance with a surface nearly free from imperfections. A paint film made in this way tapers from a small peak in the center to a minimum at the outer edge. Thus, upon a single whirled plate a dozen or more measurements can be made, each upon a different film thickness.

A Martens photometer is used to measure the relative brightnesses of the two halves of the plate. For the construction and theory of this instrument, the original paper by Martens should be consulted.³

On looking into the photometer eyepiece, a divided field is seen. These two fields are brought to equal brightnesses by rotating a Nicol prism. The angles of rotation are read off and the relative brightnesses of the test surfaces are calculated as a function of these angles.

For proper use of the photometer a lighting box is necessary for uniform illumination. In Figures 1 and 2 is shown the diffusion lighting sphere used in this investigation. It is made of steel and the interior glazed with white porcelain enamel.⁴ Within the sphere and

² Proc. A. S. T. M., 22, Pt. II, p. 465; 1922.

³ Physikal. Ztsch. (Leipzig), 1, p. 299; 1900.

⁴ Better photometric practice would be to have the enamel surface coated with matte white magnesium oxide, deposited as "smoke" from burning magnesium ribbon. The data presented in part IV were not obtained with a magnesia reflecting surface. Later experiments, however, have proven that, with the particular set-up used, the results would have been the same under either condition.

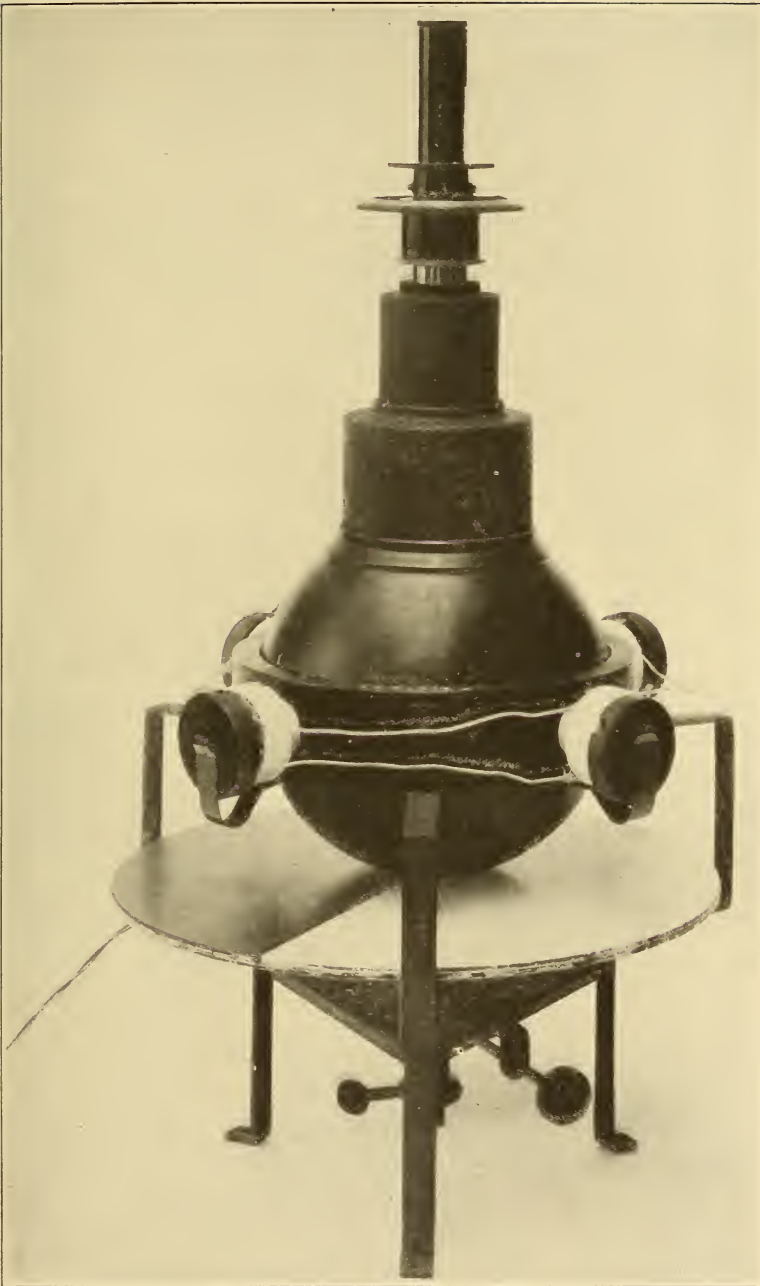


FIG. 1.—*Apparatus for measuring the hiding power of paints*

symmetrically arranged are four small 9-volt lamps. At the bottom of the sphere an opening of 3 cm diameter is cut, against which the test surface is held. The photometer is so set that practically no specularly reflected light can enter it.

When a photometric reading is to be made, the plate, covered with the dry paint film, is clamped against the opening in the bottom of the

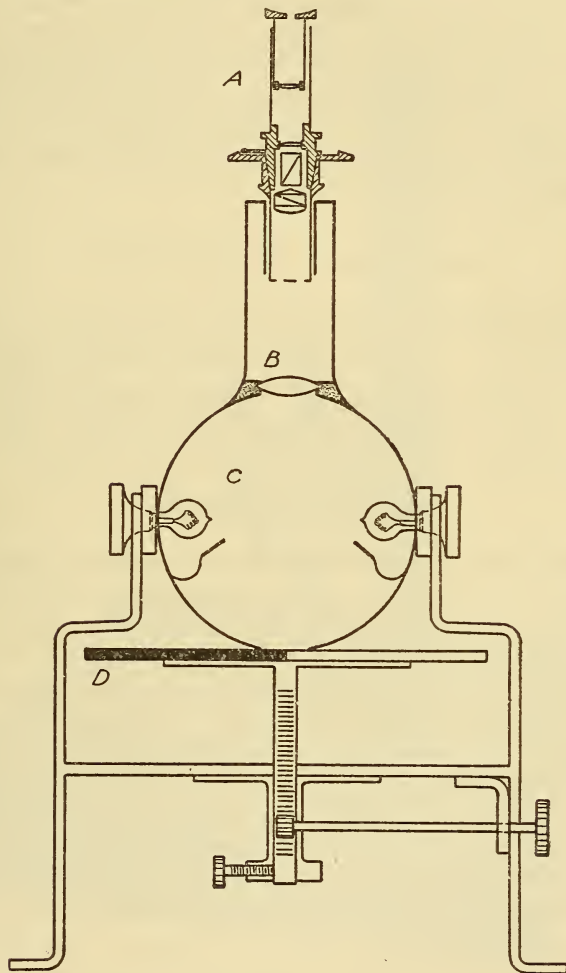


FIG. 2.—A, Photometer; B, converging lens; C, lighting sphere; and D, black and white plate

sphere so that the desired spot along the diameter separating the two halves of the plate will be under observation and so that the two photometer fields are illuminated, one by light from the black side, the other by light from the white side. The light is adjusted to a moderate degree of intensity as the sensitiveness of the eye for small

variations in brightness is highest for moderate brightnesses. This done, the two halves of the field of view are matched and the angle read to 0.1° . The optical system of the photometer is then rotated 180° and the fields again matched. (Only values falling in the first quadrant should be used in order to simplify calculations.) When the photometer is so set that the light from the black side is completely extinguished with the index turned to 0° , let the measured angle be θ_1 . Rotated 180° from this position, the light from the black side is extinguished at the reading 90° and the measured angle in this position is θ_2 . Then the degree of hiding of the particular thickness of paint film examined is measured in terms of the ratio of B , the brightness of the black side, to W , the brightness of the white side, and is calculated from the angles as follows:

$$\text{Contrast ratio}^5 = \frac{B}{W} = \cot \theta_1 \cdot \tan \theta_2$$

The dry film thicknesses were measured directly by an Ames' dial, shown in Figure 3. A reading is taken upon the paint film, the film then removed with a penknife and a second reading taken upon the bare plate. The difference is the film thickness. Readings are made directly to 0.01 mm and estimated to 0.001 mm.

III. COMPUTATIONS

The hiding power of a paint as ordinarily defined is that property which enables it to obscure any background upon which it may be spread. From a consideration of the absorption and scattering of light during its passage through successive layers of a translucent material, it seems certain that total hiding by a paint film could theoretically be possible only at infinite thickness. Accordingly, in expressing hiding power as a reciprocal function of the minimum thickness of film which will hide "completely," that is, as effectively as an infinitely thick layer, the sensitivity of the eye for brightness variations is brought into question. In photometry it is considered that under favorable conditions a normal human eye observing two fields in proper juxtaposition, one 99 per cent as bright as the other, can just distinguish that two fields are present. This assumes that the attention of the eye is not diverted by details, that the two fields are of sufficient size, and that the light intensity is moderate. Practically, the smallest visible intensity difference may be somewhat greater, the ratio being only 98 to 95 per cent, and for objects obscured by detail or shadow as low as 75 per cent. For white paint to obscure black letters on a white wall is a severe test, but quite

⁵ This term "contrast ratio" has been used before in this sense by Nutting, of the Eastman Kodak Co., as well as by the Bureau of Standards. For a previous application of the term see B. S. Circular No. 63.

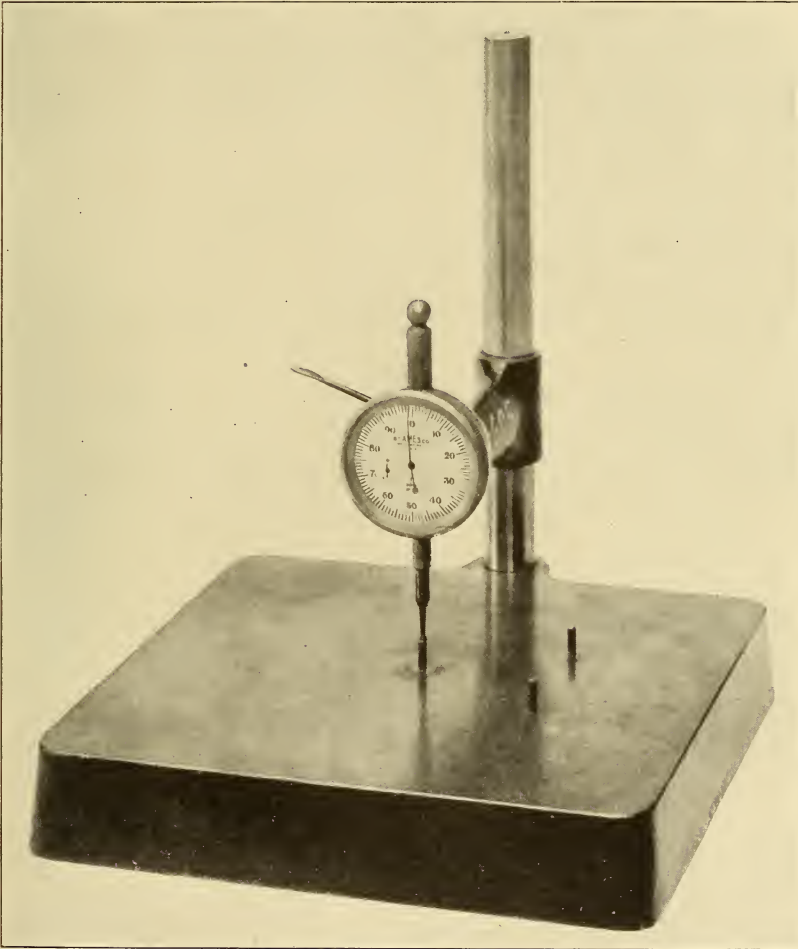


FIG. 3.—Ames' dial used for measuring thickness of paint films

practical, and the figure representing the sharpness of vision should be high. As a good practical figure for moderate illumination and natural visibility conditions, 98 per cent was chosen for this work. Accordingly, the hiding power of a paint is derived from that thickness of dry film at which the black side of the plate is 98 per cent as bright as the white side of the plate. This is our meaning of the term *hiding thickness* as it is hereinafter employed.

Experimentally, the contrast ratio is usually measured upon a thinner film than the hiding thickness. Inasmuch as the thickness that would effect a contrast of 98 per cent is the value that we wish to know, the relationship between the film thickness and the contrast ratio must be understood. If we plot values experimentally derived

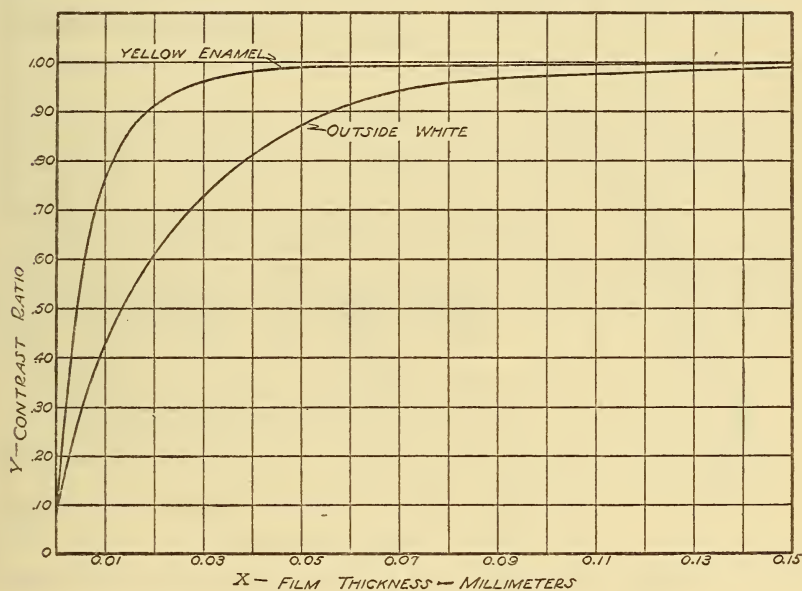


FIG. 4.—Typical contrast ratio-film thickness curves

from some one paint, we obtain a rounded curve of an apparently hyperbolic or logarithmic type as shown in Figure 4. Our problem lies in formulating a mathematical equation to express the relationship represented by this graph.

From a consideration of the physical absorption and reflection of light during its passage through a paint film, a formula has been derived for the functional relationship between the contrast ratio and the film thickness. The development of this formula will be offered in an appendix. It probably represents the actual natural law with considerable truth, and very accurately fits the experimental data as shown in Figure 5, where the continuous line is the graph of the formula, using constants ($a=0.705$ and $b=0.90$) derived

from two observations (at 0.036 and 0.072 mm), and the encircled dots are laboratory observations.

This equation is quite complex, as should be expected, and is not serviceable for practical use. For this reason, the complex equation and any simpler approximate modification of it were abandoned in favor of a purely empirical formula.

If we let $y' = \frac{1}{y}$ and $x' = \frac{1}{x^2}$ (where y = contrast ratio and x = film thickness, as in fig. 4) and plot y' against x' , a graph is obtained which very closely approximates a straight line, except for very

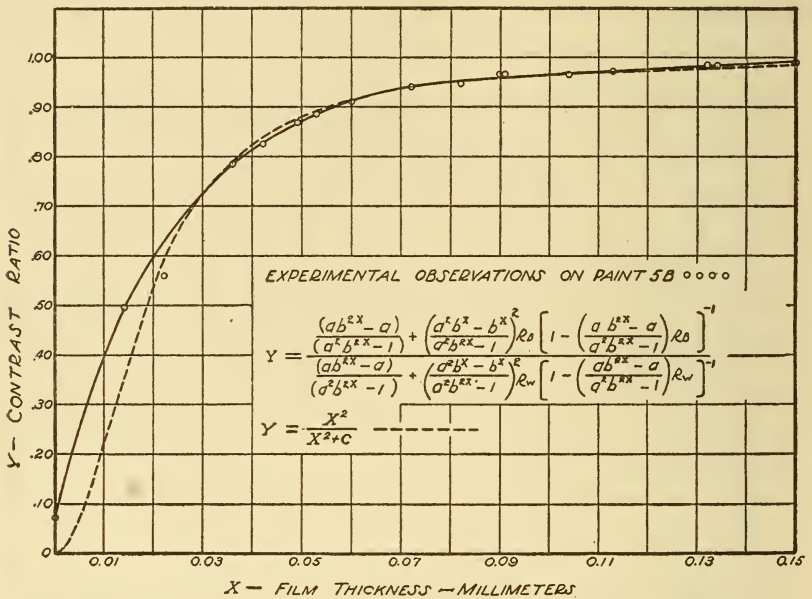


FIG. 5.—Graphical comparison between the rational and the empirical formulas

high values of $\frac{1}{y}$ where the experimentally derived points seem to fall slightly but consistently low. The straight line always passes through the point (0, 1) and, therefore, has the formula $y' = cx' + 1$. The constant c is strictly empirical and the ordinate intercept, 1, has the important significance of designating $y = 1$, as the asymptote of the contrast ratio-thickness curve, which, accordingly, can be approximately defined by the formula:

$$\frac{1}{y} = \frac{c}{x^2} + 1 \quad \text{or} \quad y = \frac{x^2}{x^2 + c}$$

Compare the complex formula with this empirical one in Figure 5 where the former is shown by the continuous line, and the latter by the broken line calculated from one observation at 0.072 mm.

The new formula, $y = \frac{x^2}{x^2 + c}$, has the disadvantage of expressing no definitely known physical relationship and of being off the true course at its extreme lower end. But, at low thicknesses, measurements by our present methods are quite impracticable and the lower portion of the curve is quite unimportant. However, for ordinary paint films, this empirical formula represents the observed relationship with remarkable accuracy, certainly within our experimental error, for no very evident orderly deviation of the constant, c , has been detected. It should serve quite satisfactorily until much finer methods of measurement are devised for this purpose.

The use of a simple formula with one constant has its obvious advantages in that the hiding power of a paint can be calculated from a single observation on any thickness of paint film. The contrast ratio, y , and the thickness, x , are measured and their values substituted in the equation $y = \frac{x^2}{x^2 + c}$. The constant, c , is thus evaluated and x is then calculated when $y = 98$ per cent. This value of x (when $y = 0.98$) is by our definition the hiding thickness of the paint; that is, the thickness of the dried film that will be required to hide "completely."

Now that a usable formula for the relationship between thickness of film and degree of contrast has been evolved, the hiding thickness can be incorporated as the unknown into the equation for direct use. Let

- a = the measured film thickness,
- b = the measured contrast ratio,
- X = the hiding thickness of the paint,

then

$$b = \frac{a^2}{a^2 + c} \quad \text{or} \quad c = \frac{a^2}{b} - a^2$$

and

$$0.98 = \frac{X^2}{X^2 + c} = \frac{X^2}{X^2 + \frac{a^2}{b} - a^2}$$

Simplifying,

$$X = 7a\sqrt{\frac{1}{b} - 1}$$

The hiding thickness can be calculated by means of this last formula or can be read directly from Figure 6, a graphical representation of this formula, which is useful not only because it simplifies the calculations but also for the reason that the effects of the limits of accuracy in making these physical measurements can be more readily appreciated. For instance, it is evident from the table at 0.70 contrast an error of 0.002 mm in the thickness reading would cause an error in the final result of 0.009 mm, while at 0.96 the same error would introduce a change into the hiding thickness of only

0.003 mm. An error of 0.005 in the contrast ratio would change the final result about 0.001 mm at 0.70 contrast, but 0.004 mm at 0.96.

In accordance with the practice of previous investigators the hiding power is expressed in terms of the area in square feet that 1 gallon of paint will cover and hide. Table 1 is herewith submitted, by means of which the dry film value can readily be converted into square feet per gallon of wet paint.

The basic theory of Table 1 assumes that all the volatile thinner evaporates away, that the drier undergoes no change in density, and that the specific volume of the oil remains unchanged during the drying process. This is not strictly true, but is a sufficiently close

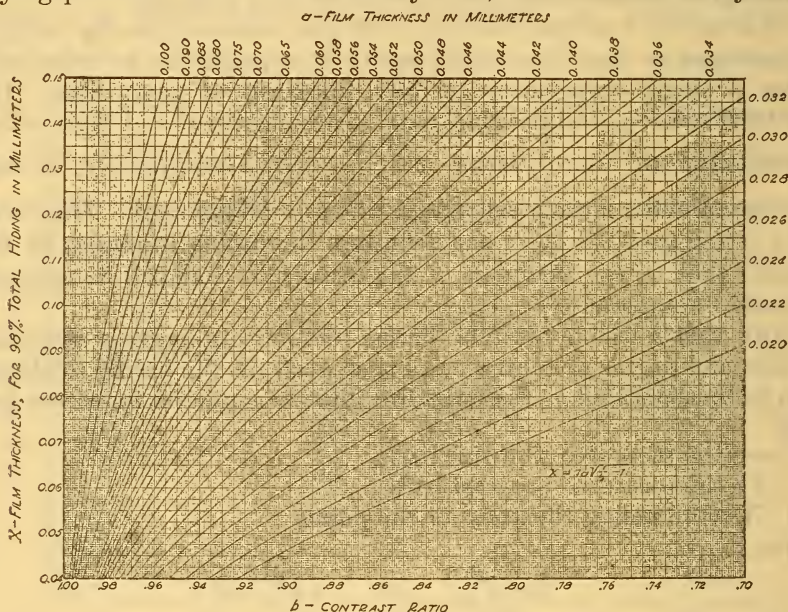


FIG. 6.—Hiding thickness chart

an approximation that, in the absence of definite information, this table will meet all but the most exacting requirements.

A knowledge of the volume percentage of volatile thinner in the material is essential in order that allowance may be made for diminution in volume by evaporation. Analyses usually give percentages by weight. From these the percentages by volume can be calculated as follows:

Let

- a = specific gravity of the paint or varnish,
- b = specific gravity of the volatile constituent,
- c = weight percentage of volatile constituent,
- x = volume percentage of volatile constituent,

Then

$$x = \frac{ac}{b}$$

TABLE 1.—Square feet per gallon when material contains volume percentage volatile matter given at head of columns

Thickness of dry film in millimeters	0 per cent	5 per cent	10 per cent	15 per cent	20 per cent	25 per cent	30 per cent	35 per cent	40 per cent	45 per cent	50 per cent	55 per cent	60 per cent	65 per cent	70 per cent	75 per cent	80 per cent	85 per cent	90 per cent
0.01	4,075	3,871	3,667	3,464	3,260	3,056	2,852	2,649	2,445	2,241	2,037	1,834	1,630	1,426	1,222	1,019	815	611	407
0.02	2,037	1,935	1,834	1,732	1,630	1,528	1,426	1,324	1,222	1,121	1,019	917	815	713	611	509	407	306	204
0.03	1,358	1,290	1,222	1,154	1,087	1,019	951	883	815	747	679	611	543	475	407	340	272	204	136
0.04	1,019	967	917	866	815	764	713	662	611	560	509	458	407	357	306	255	204	153	102
0.05	815	774	733	693	652	611	570	530	489	448	407	367	326	285	244	204	163	122	81
0.06	679	645	611	577	543	509	475	441	407	374	340	306	272	238	204	170	136	102	68
0.07	582	553	524	495	466	437	407	378	349	320	291	262	233	204	175	146	116	87	58
0.08	509	484	458	433	407	382	357	331	306	280	255	229	204	178	153	127	102	76	51
0.09	453	430	407	385	362	340	317	294	272	249	226	204	181	158	136	113	91	68	45
0.10	407	387	367	346	326	306	285	265	244	224	204	183	163	143	122	102	81	61	41
0.11	370	352	333	315	296	278	260	241	222	204	185	167	148	130	111	93	74	56	37
0.12	340	323	306	289	272	255	238	221	204	187	170	153	136	119	102	85	68	51	34
0.13	313	298	282	266	251	235	219	204	188	172	157	141	125	110	94	78	63	47	31
0.14	291	276	262	247	233	218	204	189	175	160	146	130	116	101	87	72	58	43	29
0.15	272	258	244	231	217	204	190	177	163	149	136	122	109	95	81	68	54	41	27
0.16	255	242	229	216	204	191	178	165	153	140	127	115	102	89	76	64	51	38	25
0.17	240	228	216	204	192	180	168	156	144	132	120	108	96	84	72	60	48	36	24
0.18	226	215	204	192	181	170	158	147	136	124	113	102	91	79	68	57	45	34	23
0.19	214	204	193	182	172	161	150	139	129	118	107	96	86	75	64	54	43	32	21
0.20	204	194	183	173	163	153	143	132	122	112	102	92	81	71	61	51	41	31	20

IV. DATA

In Table 2 are presented data, observed during the course of our investigation, typical of results that may be accomplished by this method.

TABLE 2.—Showing the agreement in calculations made from observations upon different film thicknesses

Paint	δ^1 contrast ratio	a^2 film thickness in milli- meters	x^3 hiding thickness in milli- meters	Deviation of hiding thickness from average
5B.....	0.494	0.014	0.099	-0.026
	.559	.022	.137	.010
	.782	.036	.133	.006
	.822	.042	.137	.010
	.868	.049	.134	.007
	.886	.053	.133	.006
	.908	.060	.133	.006
	.942	.072	.125	-.002
	.947	.082	.135	.008
	.967	.090	.115	-.012
	.967	.091	.118	-.009
	.965	.104	.134	.007
	.971	.113	.137	.010
	.985	.132	.115	-.012
	.985	.134	.117	-.010
	.986	.153	.128	.001
	.986	.153	.128	.001
	.992	.202	.127	.000
Average.....			.127	.008
2D.....	.850	.034	.100	-.001
	.858	.035	.099	-.002
	.874	.040	.107	.006
	.952	.062	.098	-.003
	.959	.070	.101	.000
	.966	.077	.101	.000
	.979	.098	.099	-.002
	.986	.122	.100	-.001
Average.....			.101	.002
3D, gray.....	.959	.039	.057	.002
	.960	.041	.059	.004
	.969	.045	.055	.000
	.972	.045	.052	-.003
	.975	.047	.052	-.003
	.977	.053	.057	.002
	.982	.055	.052	-.003
	.987	.065	.054	-.001
Average.....			.055	.002
Red enamel.....	.621	.029	.159	-.003
	.631	.030	.161	-.001
	.658	.031	.156	-.006
	.849	.056	.165	.003
	.904	.071	.162	.000
	.942	.092	.160	-.002
	.966	.128	.168	.006
Average.....			.162	.003
Yellow enamel.....	.922	.021	.042	-.001
	.925	.023	.046	.003
	.936	.023	.042	-.001
	.962	.034	.047	.004
	.966	.032	.042	-.001
	.980	.040	.040	-.003
	.982	.042	.040	-.003
Average.....			.043	.002

¹ Measured by Martens photometer.

² Measured by Ames' dial.

³ Calculated by formula, $x = 7a\sqrt{(1/b)-1}$.

In the data presented in Table 2, the contrast ratio, b , was calculated by the formula $b = \cot \theta_1 \tan \theta_2$, as previously explained. Each angle, θ_1 and θ_2 , was the average of 5 to 10 unprejudiced readings. They were read to 0.1° by means of a vernier, and the extreme variations in the different readings were rarely more than 0.2° . For test surfaces of so nearly the same hue and saturation as we have to deal with, a Martens photometer can be used with considerable precision and the contrast ratio figures are probably exact to four-thousandths of a unit or less. The thickness measurements are accurate to about two-thousandths of a millimeter.

Eighteen paints varying widely in character and hiding power were examined in this work. Their compositions are presented in Table 3 and their hiding power data summarized in Table 4.

TABLE 3.—Percentage composition by weight

Paint	White lead	Zinc oxide	Lithopone	Titanox	Barytes	Lampblack	Toluidine red toner	Chrome yellow	Nonvolatile vehicle	Volatile thinner
5B	68.3								30.6	1.1
Outside white, A	70.0								29.3	.7
Outside white, B	63.0				7.0				29.3	.7
Outside white, C	56.0				14.0				29.3	.7
2D		31.8	31.8						32.1	4.3
2D+10 per cent turpentine		28.6	28.6						28.9	13.9
2D+20 per cent turpentine		25.4	25.4						25.7	23.5
2D+50 per cent turpentine		15.9	15.9						16.0	52.2
2B		29.8	29.8						31.2	9.2
3B		17.8		41.5					31.4	9.3
3D		19.0		44.3					32.4	4.3
3D, light gray		18.9		44.1		0.4			32.3	4.3
3D, gray		18.8		44.0		.8			32.1	4.3
3D+10 per cent oil		17.1		39.9					39.2	3.8
3D+20 per cent oil		15.2		35.5					45.9	3.4
3D+10 per cent oil+10 per cent dark drier		15.2		35.5					38.9	10.4
Red enamel							6.0		53.2	40.8
Yellow enamel								33.3	41.6	25.1

TABLE 4.—Hiding power data

Paint	Number of determinations	Average hiding thickness		Hiding power
		mm	Average deviation of hiding thickness from the average ¹	
5B	18	0.127	0.008	Sq. ft./gal. 315
Outside white, A	5	.124	.002	323
Outside white, B	5	.137	.001	292
Outside white, C	5	.152	.003	263
2D	8	.101	.002	366
2D+10 per cent turpentine	12	.102	.003	291
2D+20 per cent turpentine	14	.099	.004	240
2D+50 per cent turpentine	12	.095	.004	123
2B	6	.120	.003	286
3B	10	.090	.006	371
3D	8	.085	.003	437
3D, light gray	8	.065	.002	572
3D, gray	8	.055	.002	676
3D+10 per cent oil	8	.091	.003	414
3D+20 per cent oil	8	.097	.002	395
3D+10 per cent oil+10 per cent dark drier	8	.087	.002	380
Red enamel	7	.162	.003	146
Yellow enamel	7	.043	.002	678

¹ That is, the average deviation of the hiding thickness values, calculated for each individual determination, from their average.

The deviations of the individual readings from their average in the 18 cases herein set forth average less than 0.004 mm. Accordingly, it can be expected that a single reading taken on an unknown paint would give a figure for the hiding thickness within about 0.004 mm of its true value.

In 2D+50 per cent of turpentine, we have the case of very thin films. The film of this paint varied from 0.018 to 0.032 mm and the calculated hiding thickness tended to increase with increasing film thickness, ranging in this case from 0.092 to 0.102 mm with an average value of 0.095. The empirical formula does not hold closely for extremely thin films.

The hiding thickness of a paint as given by this method depends upon the pigment-oil ratio and not upon the percentage of volatile thinner. Paint 2D gave an average figure of 0.101 mm; thinned with 10 per cent of turpentine, the same paint gave an average value of 0.102 mm; with 20 per cent of turpentine, 2D showed a measured value of 0.099 mm. As a conclusion from this, a thick paint that produces upon whirling a heavy coating that dries slowly or wrinkled can advantageously be thinned with volatile solvent before coating the glass plate without materially affecting the hiding thickness.

When the coated plate is set aside to dry it should be protected as much as possible from dust, but should also be kept in diffused daylight to prevent any material yellowing of the oil. The effect of yellowing is to aid in reducing the contrast, as may be seen with white 3D after adding 10 per cent linseed oil and 10 per cent dark japan drier. The japan drier contained about 27 per cent nonvolatile vehicle. Hence the paint had 12.7 per cent more fixed vehicle than the original, and if it retained its original whiteness should have a hiding thickness somewhat greater than 3D+10 per cent oil. Despite the thinning the hiding thickness is nearer 3D than 3D+10 per cent oil. (See Table 4.)

Substitution of extenders for the more opaque pigments materially reduces the hiding power, although the eye may often have difficulty in making a qualitative distinction. This was the case of the outside whites (Table 4) where the photometer readily showed a decrease in hiding power caused by the substitution of barium sulphate for 10 per cent of white lead.

From Table 4 it may be noted that dilution with oil decreases the hiding power, but that slight tinting is very effective in increasing the hiding power. The photometer method readily detects these changes.

This method is not applicable to very opaque paints inasmuch as such paints must be spread to such extremely thin films to effect an appreciable contrast in the black and white background that the

normal character of the film is changed and thickness measurements by a direct-reading dial are impracticable.

The method can be used upon enamel paints. Most enamels, however, possess so low a yield value that surface tension and the force of gravity are sufficient to level off the center peak leaving the disk coated with a nearly uniform film. Check measurements made upon a single spun enamel film are thus at nearly the same thicknesses. The data of Table 2 on the yellow and red enamels were obtained from several successive coatings to show that calculation of the hiding power by the empirical formula is allowable in the case of enamels.

The use of a plate of perfectly black and white shades would, of course, be ideal. The question quite properly arises as to how the results are affected by the use of a plate in which there is not a maximum contrast even before the application of any coating. Of the plate we have used, the white was 75 per cent as bright as a magnesium carbonate block and the black 5.3 per cent as bright. Thus, without any paint film upon the plate, the photometer would give a reading of $\frac{5.3}{75.0} = 0.071$. From the shape of the curve as shown in Figure 4, it may be seen that the first increment of film thickness has a tremendous obscuring effect and the relative effects of the successive layers upon the reduction of contrast very rapidly diminish. Accordingly, the thickness of a normal paint that would be spread upon a perfectly black and white plate to reduce the contrast to 0.071 would be minute and would add an inappreciable amount to the hiding power values as now calculated.

V. CONCLUSIONS

In this paper is outlined a photometric method which can be utilized to obtain hiding power measurements upon light-colored paints. The process of the method may be summarized in the following steps:

- (1) A black and white plate is coated with paint.
- (2) The paint coating is allowed to dry.
- (3) The contrast ratio is measured with a photometer.
- (4) The film thickness is measured with a gauge.
- (5) The hiding thickness is computed from the formula $x = 7a\sqrt{\frac{1}{b} - 1}$ or is read directly from Figure 6.
- (6) The hiding power in square feet per gallon is then read from Table 1 or calculated from the formula

$$H. P. = \frac{0.4075 (100 - \text{per cent of volatile})}{\text{hiding thickness in mm}}$$

The method is adapted for use upon dry paint films and gives results close to those experienced in actual painting practice. The ac-

curacy is good for a physical measurement of this sort, and, with the probable error of the order of one-seventh the thickness of a thinly brushed film, is quite sufficient for practical use.

VI. APPENDIX

Most formulas in engineering are empirical, and, although often discovered more or less blindly, are of extreme practical usefulness. They are, however, admittedly artificial and tell little or nothing of the true kinship of the involved phenomena. On the other hand, true, rational formulas—formulas; that is, deduced through processes of mathematical reasoning from a knowledge of the exact conditions of the physical question or from elementary and established physical laws—invariably enhance the value of scientific and technical investigations. A rational formula for the contrast ratio-film thickness relationship, if one be possible, would permit us to mark those limits wherein only does the empirical formula closely apply, or to evaluate the magnitude of errors introduced by its use as an approximation.

The transmission of light through photographic emulsions has been carefully studied,⁶ and the relationship has been conclusively determined that the density, defined as the negative logarithm of the transmission, is directly proportional to the mass of silver per unit area. The pigment particles of light-colored paints, on the other hand, reflect most of the light incident upon them as contrasted with the almost totally nonreflecting black silver grains. This reflection and the consequent multiple reflection of light between particles within the film complicates very much for paints the simple exponential density law despite the apparent analogy between films of paint and photographic emulsions.

Sir George G. Stokes published in 1862 a mathematical discussion⁷ "On the Intensity of the Light Reflected from or Transmitted Through a Pile of Glass Plates," in which he takes into consideration absorption of light due to imperfect transparency and multiple reflection between plates and develops the following formulas

$$\phi(m) = \frac{b^m - b^{-m}}{ab^m - a^{-1}b^{-m}} \quad (1)$$

$$\psi(m) = \frac{a - a^{-1}}{ab^m - a^{-1}b^{-m}} \quad (2)$$

$\phi(m)$ and $\psi(m)$ are, respectively, the light reflected from and transmitted through a pile of parallel glass plates m in number. a and b are constants which bear a functional relationship to the fraction of light reflected from and transmitted through each plate.

⁶ Hurter and Driffield, Jour. Soc. Chem. Ind., May, 1890. Davis and Walters, B. S. Sci. Paper No. 439.

⁷ G. G. Stokes, Math. and Phys. Papers, 4, p. 145.

We might consider a paint film as divided into layers, each layer of finite thickness and corresponding to a single plate in Stokes' derivation. The surface reflection from a plate is replaced by the body reflection from the layer. The number of plates (and hence layers) is taken proportional to the film thickness. Complete diffusion of the light incident on the film, and reflected and transmitted by each layer and the base plate is assumed. On these assumptions Stokes' law may thus be applied to our case. Of the light incident upon the paint film, ϕ is the light reflected from the surface and from within the interior of the film, and ψ is the light transmitted through the film to the base plate where a portion is absorbed. Let R be the reflection factor of the glass plate, then ψR is reflected from the glass and of this quantity, $\psi^2 R$ emerges from the upper surface. A portion of the light ψR initially reflected from the base plate is internally reflected and returned to the plate. This portion amounts to $\psi R \phi$, and, of this, $\psi R^2 \phi$ is again reflected outwards and $\psi^2 R^2 \phi$ emerges. In this way there results the following geometric sequence, where Σ is the summation of all the light emerging from the film after reflection from the base plate.

$$\Sigma = \psi^2 R + \psi^2 R^2 \phi + \psi^2 R^3 \phi^2 + \psi^2 R^4 \phi^3 + \dots + \psi^2 R^{n+1} \phi^n$$

Summing this up, $\Sigma = \frac{\psi^2 R}{1 - R\phi}$, and the total emergent light from the film is $\phi + \frac{\psi^2 R}{1 - R\phi}$. Let Y be the ratio of the observed light from the black side of the plate to the observed light from the white side of the plate, X be the film thickness, and R_b and R_w be the respective reflection factors of the black and white sides. Then

$$Y = \frac{\phi + \frac{\psi^2 R_b}{1 - \phi R_b}}{\phi + \frac{\psi^2 R_w}{1 - \phi R_w}}$$

or

$$Y = \frac{\left[\frac{ab^{2x} - a}{a^2 b^{2x} - 1} + \frac{\left(\frac{a^2 b^x - b^x}{a^2 b^{2x} - 1} \right)^2 R_b}{1 - \left(\frac{ab^{2x} - a}{a^2 b^{2x} - 1} \right) R_b} \right]}{\left[\frac{ab^{2x} - a}{a^2 b^{2x} - 1} + \frac{\left(\frac{a^2 b^x - b^x}{a^2 b^{2x} - 1} \right)^2 R_w}{1 - \left(\frac{ab^{2x} - a}{a^2 b^{2x} - 1} \right) R_w} \right]} \tag{3}$$

This equation should be the true formula for the contrast ratio-film thickness curve, provided our assumptions and application of Stokes' laws are permissible and without fault.

Transmission measurements were made upon various thicknesses of paints in an endeavor to secure experimental justification for applying Stokes' laws derived for glass plates to paint films. To obtain these data two hollow wedges were made up of plane glass surfaces each 12.2 cm long and 1904 μ as the maximum width. The paints used in the wedges consisted of zinc oxide ground in oil. A somewhat smaller percentage of pigment than in a commercial paint was incorporated in order that the transmission measurements might extend over a longer thickness range than is possible with a more opaque normal paint. Castor oil rather than the less viscous

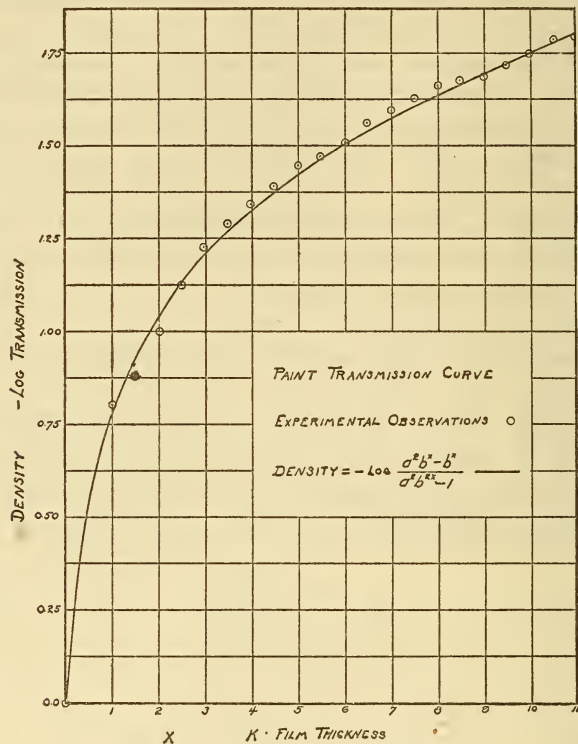


FIG. 7.—Paint transmission curve

linseed was used to diminish the possibility of settling out of the pigment particles.

To obtain the data of Figure 7, one wedge was filled with the paint and measurement of the transmission of light through various parts of the wedge were made with a Martens photometer using, as a standard, a beam of light coming from the same source and passing through the second unfilled wedge. In Figure 7 is plotted for one paint laboratory observations of the density ($-\log$ transmission) against a value proportional to the film thickness. The continuous line was calculated from Stokes' equation (2) using constants derived

from two observations ($a=0.9833$ and $b=0.92$). It is evident that the general forms of the observed and calculated curves are quite nearly the same.

For Figure 8, one wedge was filled with white paint and cemented to the black side of the black and white disk. The other wedge was left unfilled and placed upon the white side of the plate as a comparison standard. Light from a source above fell upon the wedges, each of which diffusely reflected light to one field of the Martens photometer. In this way it was possible to measure the intensity of light emergent from one side only of the plate; that is, to evaluate experimentally either the numerator or denominator of equation (3). In Figure 8, it is shown for one paint how closely

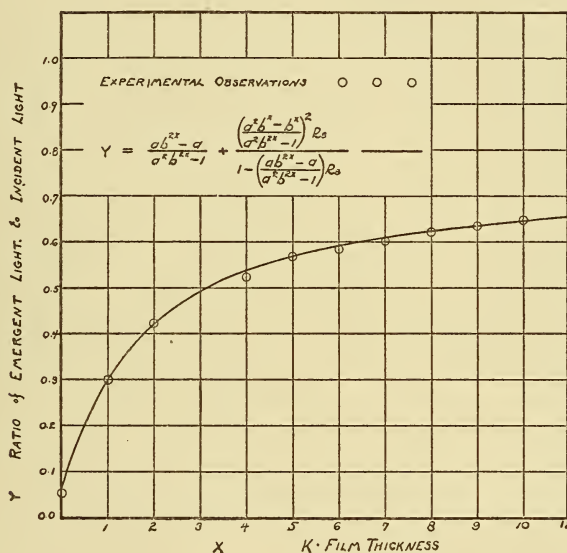


FIG. 8.—Light emergent from paint film upon black opaque glass

the experimental observations fall upon the curve demanded by theory.

How closely the rationally derived equation in its final form as equation (3) comes to coinciding with the experimentally derived data has been indicated in Figure 5. A colloidal suspensoid of the type of which paint is an illustration is an exceedingly complex system optically as well as otherwise, and it would indeed be rash to claim that any mentally evolved mathematical formula describes completely and perfectly its properties. From the evidence at hand, however, it does seem permissible to infer that equation (3) is a close approximation to the natural transmission law for pigment in oil suspensions.

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