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THE COLOUR OF PIGMENT MIXTURES

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ABSTRACT. It is shown that the colours produced by mixing pigments in any given medium may be deduced from formulae involving two constants for each pigment. These constants, which vary with the wave-length of the incident light, measure respectively the absorbing power of the pigment for light and its scattering power. Relative values of these constants for a series of pigments may be deduced from their reflectivities at different wave-lengths and the reflectivities of one mixture of each pigment with one standard pigment. The relative values so obtained enable the reflexion curves, and hence, if desired, the colours, of any mixture of two or more of the pigments investigated to be predicted correctly.

§ 1. INTRODUCTION

I T is a well-known fact that the colours produced by mixing coloured pigments are different from those produced by mixing lights of the same colours. Whereas in the latter case the colours produced follow known laws, no method has hitherto been known for predicting quantitatively the colours produced by mixing pigments. In the present paper, however, it will be shown that the colours of such mixtures are dependent in a relatively simple way on the optical constants of the pigments and may be accurately predicted if these are known.

The nature of the colours produced by the mixture of coloured lights was examined by a series of workers and led to the modern methods of colorimetry and systems of colour specification typified by the C.I.E. system [1]. It is now possible to predict with certainty the colour which will be produced on mixing any number of lights of known colour in any given proportions. Hence, it is possible to deduce the colour of any light, given its spectral composition. The problem of the prediction of the colours of pigment mixtures therefore reduces to the purely physical one of determining the relationship between the reflexion spectrum of the pigment mixture and the composition of the mixture. Since the different wave-lengths may be considered independently and the effect of each wave-length on the colour finally integrated over the range of the visible spectrum, it is sufficient to discover the general law relating the reflectivity of a pigment mixture for any one wave-length to the optical constants of the component pigments and the proportions in which they are mixed. In the present paper, such a relationship will be evolved and shown to apply to a series of pigment mixtures.

§ 2. THEORETICAL

It is commonly stated that when coloured lights are mixed the effect is one of additive mixture, but that when coloured pigments are mixed the effect is subtractive, i.e., that the absorptions produced by the separate pigments are added together to produce the colour of the mixed pigment. Thus, the green colour observed in many cases when a blue pigment and a yellow pigment are mixed is attributed to the fact that green is the only colour reflected by both pigments; light of any other colour is absorbed either by the blue pigment or by the yellow pigment, and is therefore absorbed by the mixture. This generalization, however, is only an approximation to the truth, and lacks the quantitative precision necessary for the prediction of the exact shade of colour which will be produced when the pigments are mixed in varying proportions.

In the case where two substances in solution are mixed (in the absence of chemical reaction), the colour of the mixture may be deduced from the extended form of Beer's law

$$I/I_0 = e^{-(\varepsilon_A c_A + \varepsilon_B c_B + \cdot)h} \qquad \ldots\ldots(1),$$

where I is the intensity of the transmitted light, I_0 that of the incident light, h is the thickness of solution traversed by the light, and $\varepsilon_A, \varepsilon_B, \ldots$ are the extinction coefficients and $c_A, c_B, \ldots$ the concentrations of the substances A, B, etc. A similar relationship holds when light is passed through a series of coloured, transparent filters. When, however, the coloured substances are mixed as dry powders or as powders in suspension in a medium, as in the mixing of artists' colours, the manufacture of paints, and the colouring of cement, rubber, paper, etc. by means of pigments, this law no longer applies.

Various formulae have been evolved for the reflecting (more accurately, remitting) and transmitting powers of suspensions of solid particles, and those recently put forward by Amy, Sannié and Sarraf [2] are now found to form a basis from which, making certain assumptions, it is possible to deduce an equation by means of which the colours of paints containing a mixture of different pigments may be predicted correctly.

According to these investigators, for a layer of translucent material,

$$\frac{I}{I_0} = \frac{2\sqrt{\alpha(\alpha+2\delta)}e^{-h\sqrt{\alpha(\alpha+2\delta)}}}{\alpha+\delta+\sqrt{\alpha(\alpha+2\delta)}-[\alpha+\delta-\sqrt{\alpha(\alpha+2\delta)}]e^{-2h\sqrt{\alpha(\alpha+2\delta)}}} \qquad \ldots\ldots(2)$$

and

$$R = \frac{\delta[1-e^{2h\sqrt{\alpha(\alpha+2\delta)}}]}{\alpha+\delta+\sqrt{\alpha(\alpha+2\delta)}-[\alpha+\delta-\sqrt{\alpha(\alpha+2\delta)}]e^{-2h\sqrt{\alpha(\alpha+2\delta)}}} \qquad \ldots\ldots(3),$$

where R is the ratio of the intensity of remitted (so-called reflected) light to that of the incident light, h is the thickness of the layer of material, and α and δ are constants for the material for any given wave-length, but, in general, vary with the wave-length of the incident light, α being the extinction coefficient as defined by the relationship: light absorbed by an element of the film of thickness $dh = I_0\alpha\,dh$, while δ is the coefficient of scatter, similarly defined by the relationship: light remitted by the element due to scattering $= I_0\delta\,dh$. Similar expressions have been proposed by Neugebauer [3].

When the thickness is such that any further increase therein produces no further change in colour by reflected light (i.e., in R), a condition which is fulfilled when $e^{-2h\sqrt{\alpha(\alpha+2\delta)}}$ becomes negligible compared to 1, these expressions reduce to

$$\frac{I}{I_0} = \frac{2\sqrt{\alpha(\alpha+2\delta)}e^{-h\sqrt{\alpha(\alpha+2\delta)}}}{\alpha+\delta+\sqrt{\alpha(\alpha+2\delta)}} \qquad \ldots\ldots(4)$$

and

$$R = \frac{\delta}{\alpha+\delta+\sqrt{\alpha(\alpha+2\delta)}} \qquad \ldots\ldots(5).$$

In the present paper attention will be confined mainly to the application of equation (5) to paint films. Amy and collaborators confirmed the truth of various simplified expressions deduced from (4) and (5) for cases in which δ^2 is negligible compared with α^2. In particular, they studied the change in R on adding (to paper or white paint) a small proportion of an intensely coloured substance, which was assumed to cause an increase in α and to have no appreciable effect on the value of δ. In the present paper, the general case is considered, in which α and δ may have any values and the proportion and nature of the pigments added may be such as to cause considerable variation in both α and δ.

Attention is confined initially to the case where the medium is clear and colourless.

For the present purpose, equation (5) may be more conveniently written in the form

$$\delta/\alpha = 2R/(1-R)^2 \qquad \ldots\ldots(6),$$

which is obtained by solving (5) as a quadratic in δ, the other root being $\delta=0$.

δ can have the value zero only in certain special cases, viz., when the film is unpigmented, when the pigment dissolves completely in the medium (in which case it is more suitably described as a dye or stain), and when the refractive index of the pigment is identical with that of the medium. In these cases, δ being zero, equation (4) reduces to $I/I_0 = e^{-h\alpha}$ (Beer's law) and (5) becomes $R=0$.

Since the expression $2R/(1-R)^2$ will occur frequently throughout the work, it is convenient to refer to it as the " reflectivity function " of the paint and to denote it by the letter Φ:

$$\Phi = 2R/(1-R)^2 \qquad \ldots\ldots(7).$$

If it is assumed that for a paint containing a mixture of pigments, viz., c_A parts of pigment A, c_B parts of pigment B, etc., the values of α and δ each follow a simple additive law, i.e.,

$$\alpha_M = c_A\alpha_A + c_B\alpha_B + c_C\alpha_C + \ldots$$

and

$$\delta_M = c_A\delta_A + c_B\delta_B + c_C\delta_C + \ldots$$

where α_M and δ_M are the values of α and δ for the mixed paint, α_A and δ_A are the values for a paint containing only A, and so on, then

$$\Phi_M = \frac{c_A\delta_A + c_B\delta_B + c_C\delta_C + \ldots}{c_A\alpha_A + c_B\alpha_B + c_C\alpha_C + \ldots} \qquad \ldots\ldots(8).$$

In the practical application of this expression, c_A, c_B, etc. may conveniently be taken as the percentages of each pigment in the pigment mixture, ignoring the medium, since variation of the proportion of medium, except when excessive, has no influence on the value of Φ.

In the special case of the binary mixture of a white pigment (or other white substance, such as paper pulp, cement, etc.) A, with a coloured pigment, B, the value of α_A may be taken as zero to a close approximation, when (8) simplifies to

$$\Phi_M = (c_A\delta_A + c_B\delta_B)/c_B\alpha_B,$$

whence

$$\Phi_M = \frac{c_A}{c_B} \cdot \frac{\delta_A}{\alpha_B} + \frac{\delta_B}{\alpha_B} \qquad \dots \dots (9),$$

or

$$\Phi_M = \frac{c_A}{c_B} \cdot \frac{\delta_A}{\alpha_B} + \Phi_B \qquad \dots \dots (10).$$

Hence the reflectivity function for a series of paints containing different ratios of A to B is a linear function of that ratio, a relationship which has been confirmed experimentally for numerous mixtures. The gradient of this line gives the value of the ratio δ_A/α_B and the reflectivity function of the paint containing the undiluted pigment B gives the value of the ratio δ_B/α_B. Hence, α_B and δ_B may be evaluated in terms of δ_A. Similarly, the relative values of α and δ for a series of pigments may be deduced from the reflectivities of each pigment and of one mixture of each pigment with the standard white pigment. Instead of mixing the pigment with the standard white pigment, it may be mixed with any pigment which has already been compared with the white pigment in this way, equation (8) being then used for deducing the values of α and δ for the pigment under test. In order to obtain reasonable accuracy, the two pigments must differ considerably in reflectivity.

From the relative values of α and δ so obtained, it is possible to calculate the reflectivity function of a paint containing a mixture of any number of these pigments in any proportions, by means of equation (8). The reflectivity follows from equation (7), and having calculated the reflectivity for different wavelengths, the colour of the paint may be calculated therefrom [1].

The values for the reflectivities of paints containing different pigment mixtures deduced in this way agree within the limits of experimental error with those found by direct measurement.

§ 3. EXPERIMENTAL METHOD

The paints for examination were made up by grinding the required weights of each pigment together with a concentrated aqueous solution of gum arabic by hand in a mortar until complete homogeneity, as indicated by the absence of change in colour on further grinding, was obtained. The resultant paste was spread thickly and evenly on cardboard and allowed to dry. A disc was then cut out of this coated cardboard and mounted concentrically on top of a pair of larger

discs, one black and one white, which were interlocked so that the proportions of black and white exposed could be varied at will (Maxwell's discs). The discs were illuminated by light incident at 45° and were viewed normally through a system of filters transmitting a narrow band of the spectrum. The angle of the black and white sectors was varied until a match was obtained on revolving the discs, the mean of a number of readings being taken.

The black and white discs used were coated respectively with lampblack and with white lead in gum arabic. The relative reflectances of these discs were determined photometrically, i.e., by measuring the relative intensities of illumination on the two discs necessary to produce a match when viewed through the different combinations of filters.

The results were calculated relative to the reflectivity of the white lead as standard, this substance having, in the gum-arabic medium, the highest reflectivity at all wave-lengths of all the pigments examined. The same sample of white lead was employed throughout the work and was shown by analysis to consist of pure basic lead carbonate of the formula $Pb(OH)_2, 2PbCO_3$. This pigment was used as the standard white pigment A referred to in the theoretical section.

It was found that a series of filters transmitting suitable bands could be obtained by combining Ilford Micro filters in pairs. The transmittances were determined by means of a Nutting photometer and the mean wave-lengths for the transmission bands calculated according to the formula:

$$\lambda_{mean} = \Sigma\left(\frac{I}{I_0}L\lambda\right)\Big/\Sigma\left(\frac{I}{I_0}L\right),$$

where L is the visual luminosity at wave-length λ of the light used. The values of λ_{mean} are accurate only for the particular source of light used. This source was too poor in violet for accurate measurements to be taken in this region. The combinations of filters used are shown in table 1.

Table 1

Series of filter combinations used for isolating different bands of the spectrum

Ilford micro filter nos.	Colour	Mean wave-length (mμ.)
1+6	Blue	460
1+9	Blue	483
2+4	Green	530
3+5	Yellow	578
5+7	Orange-red	616
5+6	Red	675

§ 4. EXPERIMENTAL RESULTS

In illustration of the results obtained, the data for mixtures of zinc oxide and lampblack in yellow light will be considered in detail, and the results with other mixtures will then be reported rather more briefly.

For mixtures of this type (one white and one coloured pigment), equation (10) would be expected to apply. This may be written

$$\frac{c_A/c_B}{\Phi_M - \Phi_B} = k,$$

where k is a constant.

The data obtained are given in table 2. It will be seen that there is a close agreement between the observed and calculated values of R. Since a small error in R introduces a relatively large error in Φ and hence in k (e.g., an error of 0·01 in R corresponds to a 6 per cent error in Φ and k when $R=0.50$), it will be seen that the value of k is constant within the limits of accuracy attainable experimentally. If c_A/c_B is plotted against $\Phi_M - \Phi_B$, it will be found that a close approximation to a straight line is obtained.

Table 2. Reflectivity data for mixtures of zinc oxide and lampblack in a gum-arabic medium for yellow light of mean wave-length 578 mμ.

c_A	c_B	c_A/c_B	R_{obs}	Φ_M	$\Phi_M - \Phi_B$	k	R_{calc}
100	0	∞	1·00	∞	∞	—	1·00
98·8	1·2	82·3	0·60	7·50	7·47	11 0	0·60
97·0	3·0	32·3	0·43	2 65	2·62	12·3	0·45
95·0	5·0	19·0	0·36	1·76	1·73	11·0	0·36
93·1	6·9	13·5	0·31	1·30	1·27	10·6	0·31
90·0	10·0	9·0	0·25	0·89	0·86	10·5	0·24
87·0	13·0	6·7	0·21	0·674	0·642	10·4	0·20
80·0	20·0	4·00	0·14	0·379	0·347	11 5	0·14
73·0	27·0	2·70	0·11	0·278	0·246	11·0	0·11
60·0	40·0	1·50	0·075	0·174	0·142	10·6	0·072
0	100	0	0·016	0·032	0·000	—	0·016
Mean value of k (used in calculating R)						11·0	

According to the theory, $k = \alpha_B/\delta_A$ and $\Phi_B = \delta_B/\alpha_B$. Hence, α for lampblack is 11 0δ_{ZnO} and δ is 0·35δ_{ZnO} for yellow light ($\lambda = 578$ mμ.). Corresponding values for lampblack relative to $\delta_{white\ lead}$ are similarly found to be $\alpha = 4·3\delta_{white\ lead}$ and $\delta = 0·14\delta_{white\ lead}$. The observed values of R for mixtures of lampblack and white lead, and the values calculated assuming the above figures, are given in table 3.

Table 3. Reflectivity data for mixtures of lampblack **and white lead in** yellow light ($\lambda = 578$ mμ.)

Per cent lampblack	$R_{observed}$	$R_{calculated}$
0	1·00	1·00
5	0 49	0·48
10	0·34	0·35
20	0·24	0·23
30	0 18	0·16
50	0·10	0·10
100	0·015	0·015

Hence we have $\delta_{\text{lampblack}} = 0.35\delta_{\text{ZnO}} = 0.14\delta_{\text{white lead}}$, whence $\delta_{\text{ZnO}} = 0.40\delta_{\text{white lead}}$. The observed ratio of the reflectivities of the zinc oxide and white lead used is as 0.96 to 1 00 at $\lambda = 578$ mμ. Hence, if the white lead is taken as the standard of whiteness ($R = 1$, whence $a = 0$), then Φ_{ZnO} is 1200. Hence, $\delta_{\text{ZnO}}/a_{\text{ZnO}} = 1200$, and therefore

$$a_{\text{ZnO}} = \delta_{\text{ZnO}}/1200 = 0.40\delta_{\text{white lead}}/1200 = 3 \times 10^{-4} \cdot \delta_{\text{white lead}}.$$

Whilst absolute values of a and δ could be obtained from opacity measurements of thin films, these relative figures are all that is required for the calculation of the colours of pigment mixtures by reflected light. Relative values on this basis ($a_{\text{white lead}} = 0$, $\delta_{\text{white lead}} = 1$) will be written $[a]$ and $[\delta]$ for purposes of distinction from the absolute figures. Since $a_{\text{white lead}}$ is very small in comparison with $\delta_{\text{white lead}}$, $[a] = a/\delta_{\text{white lead}}$ and $[\delta] = \delta/\delta_{\text{white lead}}$ to a close approximation.

The values of $[a]$ and $[\delta]$ obtained in this way for several pigments at a number of wave-lengths are given in table 4. It should be noted that the value of $\delta_{\text{white lead}}$ probably varies somewhat with the wave-length, so that the unit of measurement is not exactly the same at all wave-lengths, but this does not affect the accuracy with which the colours of mixtures may be predicted. It should also be stressed that these figures refer only to the particular samples of pigment used, in the gum-arabic medium employed. In particular, $[\delta]$ would be expected to vary with the particle size of the pigment and with the refractive index of the medium.

Table 4

Values of $[a]$ and $[\delta]$ for a series of pigments.
Standard: white lead, $[a] = 0$, $[\delta] = 1$, for all wave-lengths

		Blue 460 mμ.	Blue 483 mμ.	Green 530 mμ.	Yellow 578 mμ.	Orange-red 616 mμ.	Red 675 mμ.
Red lead	$[a]$	0.54	0.64	0.61	0.08	3×10^{-3}	3×10^{-5}
	$[\delta]$	0.034	0.070	0.115	0.32	0.44	0.56
Lampblack	$[a]$	4.5	4.5	4.7	4.3	5.0	5.9
	$[\delta]$	0.17	0.17	0.16	0.14	0.14	0.14
Zinc oxide	$[a]$	4×10^{-3}	2×10^{-3}	6×10^{-4}	3×10^{-4}	2×10^{-4}	2×10^{-4}
	$[\delta]$	0.42	0.40	0.39	0.40	0.43	0.44
Lead chromate	$[a]$	5.3	4.3	0.76	0.022	0.0092	0.0064
	$[\delta]$	1.00	0.93	1.27	2.07	2.06	1.84
Chromium oxide	$[a]$	10.6	9.8	2.82	5.55	7.4	4.3
	$[\delta]$	3.3	2.9	3.2	2.11	2.5	2.6

In illustration of the accuracy with which the reflectivities of pigment mixtures may be predicted by means of these data, all the observed values of R for a series of binary mixtures of chromium oxide and lead chromate with one another and with white lead, two ternary mixtures of these three pigments, and one quaternary mixture with lampblack as the fourth pigment are compared in table 5 with the

figures calculated by means of equations (7), (8) and (10) using the values of $[\alpha]$ and $[\delta]$ given in table 4.

Table 5. Observed and calculated values of R for various pigment mixtures. The calculated values are given in parentheses

Pigments	% second pigment*	Blue 460 mμ.	Blue 483 mμ.	Green 530 mμ.	Yellow 578 mμ.	Orange-red 616 mμ.	Red 675 mμ.
Lead chromate +chromium oxide	0	0·10 (0·10)	0·09 (0·09)	0·35 (0·35)	0·87 (0·87)	0·91 (0·91)	0·92 (0·92)
	5	0·10 (0·10)	0·09 (0·09)	0·34 (0·34)	0·58 (0·59)	0·56 (0·55)	0·63 (0·62)
	20	0·10 (0·10)	0·10 (0·10)	0·30 (0·32)	0·37 (0·37)	0·32 (0·33)	0·40 (0·40)
	50	0·10 (0·11)	0·11 (0·11)	0·29 (0·30)	0·22 (0·22)	0·20 (0·20)	0·27 (0·27)
	80	0·12 (0·12)	0·12 (0·11)	0·29 (0·29)	0·19 (0·17)	0·16 (0·16)	0·23 (0·22)
	100	0·12 (0·12)	0·12 (0·12)	0·29 (0·29)	0·14 (0·14)	0·13 (0·13)	0·19 (0·19)
White lead + lead chromate	5	0·52 (0·50)	0·52 (0·52)	0·76 (0·76)	0·97 (0·96)	0·97 (0·97)	0·97 (0·97)
	10	0·37 (0·37)	0·40 (0·40)	0·69 (0·68)	0·95 (0·95)	0·96 (0·96)	0·97 (0·97)
	20	0·26 (0·27)	0·26 (0·28)	0·57 (0·58)	0·92 (0·93)	0·95 (0·94)	0·96 (0·96)
	30	0·19 (0·20)	0·19 (0·21)	0·52 (0·53)	0·89 (0·90)	0·92 (0·94)	0·94 (0·94)
	40	0·16 (0·17)	0·17 (0·17)	0·48 (0·48)	0·88 (0·89)	0·92 (0·93)	0·93 (0·94)
	50	0·16 (0·16)	0·15 (0·14)	0·45 (0·45)	0·88 (0·89)	0·91 (0·92)	0·92 (0·93)
White lead +chromium oxide	10	0·32 (0·29)	0·32 (0·32)	0·51 (0·50)	0·38 (0·38)	0·36 (0·34)	0·44 (0·43)
	20	0·21 (0·21)	0·23 (0·23)	0·39 (0·40)	0·27 (0·27)	0·25 (0·25)	0·33 (0·34)
	30	0·19 (0·18)	0·18 (0·18)	0·34 (0·37)	0·23 (0·23)	0·22 (0·21)	0·29 (0·29)
	50	0·15 (0·14)	0·14 (0·14)	0·30 (0·33)	0·18 (0·18)	0·16 (0·16)	0·24 (0·24)
White lead Lead chromate Chromium oxide	12·5 75·0 12·5	0·11 (0·10)	0·11 (0·13)	0·34 (0·38)	0·40 (0·44)	0·37 (0·39)	0·46 (0·47)
White lead Lead chromate Chromium oxide	80·0 10·0 10·0	0·24 (0·23)	0·26 (0·26)	0·47 (0·47)	0·43 (0·40)	0·39 (0·36)	0·47 (0·45)
White lead Lead chromate Chromium oxide Lampblack	50·0 25·0 12·5 12·5	0·14 (0·14)	0·14 (0·14)	0·26 (0·28)	0·27 (0·28)	0·23 (0·25)	0·26 (0·27)

* Percentage composition in the last three entries.

In calculating the theoretical value of R, it is necessary to solve the quadratic equation (7); of the two solutions obtained, the value to be accepted is the one lying between 0 and 1, the other root, which is greater than unity, representing a purely imaginary case, since the reflectivity cannot lie outside this range. In order to avoid the solution of numerous quadratic equations, the corresponding values of Φ and R are tabulated in table 6.

§ 5. DISCUSSION OF RESULTS

It will be seen that the experimental results confirm the theoretical reasoning advanced in § 2 and indicate that the colour-mixing properties of a pigment may be expressed in terms of two constants which are respectively measures of the light-absorbing and light-scattering properties of the pigment. These constants vary with the wave-length of the incident light, but are otherwise invariant in any one medium.

Whilst no attempt has been made in this paper to study quantitatively the effect of variation of the medium, it is to be expected that, whilst α is probably independent of the medium, δ will vary considerably with the refractive index of the medium and may also be affected by its pigment-dispersing properties, since if the pigment is present as large flocculates its scattering power will be less than if it is well dispersed. The use of a medium of high refractive index may also involve the introduction of a correction for reflexion at the air-medium interface. This reflexion is of two types: (1) external reflexion (specular reflexion), which is constant for all paints made up in the same medium, provided the proportion of pigment is not too high; and (2) internal reflexion, which would have the effect of increasing the apparent thickness but would probably have no effect on the colour at infinite thickness.

In the event of the medium being coloured, allowance could be made for this by considering it as an additional pigment with $\delta = 0$ and α having a value depending on its colour (equal to its extinction coefficient if suitable units are employed throughout). Dissolved dyes could be treated similarly.

Owing to the additive nature of α and δ, materials known to be mixtures, such as Brunswick green, lithopone, and dyes laked on substrates, may be treated as single substances, for which values of $[\alpha]$ and $[\delta]$ may be deduced. Even pigment pastes may be so treated, provided that they are made up in the same medium as the paint to which they are added.

Although the experimental work quoted relates to water paints, the principles evolved may be expected to be applicable to other types of paints and to other pigmented systems, such as coloured cements, pigmented paper, plastics, rubber, etc. The data of Amy and collaborators [2] show, indeed, that simplified equations which are based on the same fundamental assumptions as the present accurate formulae are applicable to pigmented papers and lacquers.

In the present investigation attention has been confined to the reflexion of light. Expressions are, however, quoted (viz., (2) and (4)), in which the opacity of films

Table 6. Values of $\Phi[=2R/(1-R)^2]$ corresponding to values of R from 0 to 1

R	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
0·0	0·000	0·020	0·042	0·064	0·087	0·111	0·136	0·162	0·189	0·217
0·1	0·247	0·278	0·310	0·343	0·379	0·414	0·453	0·493	0·535	0·578
0·2	0·63	0·67	0·72	0·78	0·83	0·89	0·95	1·01	1·08	1·15
0·3	1·23	1·30	1·38	1·47	1·56	1·66	1·76	1·86	1·98	2·10
0·4	2·22	2·36	2·50	2·65	2·81	2·97	3·16	3·35	3·55	3·77
0·5	4·00	4·25	4·51	4·80	5·10	5·44	5·79	6·2	6·6	7·0
0·6	7·5	8·0	8·6	9·2	9·9	10·6	11·4	12·3	13·3	14·4
0·7	15·5	16·7	18·4	20·0	21·9	24·0	26·4	29·1	32·3	35·8
0·8	40·0	44·8	50·7	57·5	66	76	88	103	122	147
0·9	180	224	287	379	522	760	1200	2160	4900	19800
1·0	∞									

is expressed in terms of the same constants. It should, therefore, be possible to utilize the data for predicting the relative hiding powers of paints. No attempt has been made to do this, but there is little doubt that reliable predictions could be made, since opacity measurements by Amy and collaborators on coloured paper gave results in accord with this theory. It can, moreover, be shown mathematically that the present theory leads to the same values for the reflectance of a thin translucent film over a dark background as the Kubelka-Munk theory[4], which has been shown[5] to be applicable to cold-water paints similar to those employed in the present investigation.

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DISCUSSION

Dr. R. F. HANSTOCK. Equation (3) can be identified with one developed by T. Smith (*Trans. Opt. Soc.* **33**, 155 (1931–2)), and both equations can be reduced to the following form:

$$kh = \tfrac{1}{2} \log_e \frac{r(1 - Rr)}{r - R}.$$

Amy's constants (a, δ) are related to Smith's constants (k, r) by the equations

$$a = k \left[\frac{1 - r}{1 + r} \right] \quad \text{and} \quad \delta = k \left[\frac{2r}{1 - r^2} \right].$$

Mr. T. SMITH. I am particularly pleased to read Dr. Duncan's account of his experiments and to find that he has obtained good agreement between observation and theory. The theory to which he refers partially covers the ground of some work I carried out more than eight years ago. Since then I have attempted on more than one occasion to interest workers in the dyeing and other colour industries in the theoretical results, but without much success. I only recall coming across one worker who appreciated the value of theory in dyeing, and I think he was too engrossed with a theory which I could not accept to be interested in another. The workers to whom Dr. Duncan is indebted for the formulae he uses have established their results by a line of argument entirely different from those I employed; the applications which form the subject of this paper are illustrations only of the simplest set of conditions which may be found. My purpose in drawing attention to this is to state emphatically that the general

structure of the expressions found is imposed by considerations of a very general kind, so that we can claim confidently that they are generally applicable to problems of this type. It happens, however, that in this paper they are not expressed in the form most convenient for numerical use. As tables of hyperbolic functions of suitable accuracy are readily obtainable it is best to use them. The essential formulae are

$$I_0/I = \cosh h\theta + \sinh h\theta \cosh \phi$$

and

$$R/I = \sinh h\theta \sinh \phi.$$

It at once follows, in the author's notation, that for a thin section

$$\alpha + \delta = h_0\theta \cosh \phi, \qquad \delta = h_0\theta \sinh \phi,$$

or

$$\coth \phi = 1 + \alpha/\delta, \qquad h_0\theta = [\alpha(\alpha + 2\delta)]^{\frac{1}{2}}.$$

Since the author only deals with reflected light, it should be noted that he has checked only part of the predictable results.

I might add that the effects of the air-paint surface can be taken into account as a correction to $1/(1 - R)$, constant for a given medium.

AUTHOR'S REPLY. It is very satisfactory that the two lines of argument should lead to expressions which are equivalent to one another. The relative convenience of the different expressions depends upon the use to which they are to be put. For a general theoretical treatment, particularly when the transmission of light has to be considered, Mr. Smith's formulae undoubtedly have the advantage, but for the particular problem in which I was interested I feel that the use of [α] and [δ] is simpler and more likely to be acceptable to the technical worker.

It may be added that the experimental work was not undertaken with the object of testing Amy's theory. It was carried out over ten years ago in testing certain theoretical views of my own, which, however, did not agree well with the experimental results, and I was therefore particularly pleased to find, on the publication of Amy's theoretical views, that they lead to expressions which gave results agreeing so well with my previously determined experimental data.