THE TECHNICAL SECTION OF THE BRITISH PAPER AND BOARD MAKERS' ASSOCIATION (INCORPORATED)

The Prediction of Dye Formulæ and the Blueing of White Papers

Dr. H. J. SELLING

PROCEEDINGS OF THE TECHNICAL SECTION OF
THE BRITISH PAPER & BOARD MAKERS' ASSOCIATION
(INCORPORATED)

1950, Vol. 31, PART 2

Mr. S. F. SMITH in the Chair

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INTRODUCTION

In reality, the white light coming from the sun or from an incandescent lamp is composed of a great number of colours (the spectrum). Monochromatic red, orange, yellow, green, blue and violet radiations give the impression of white light when mixed approximately in the proportions occurring in daylight.

· The non-luminous objects in our surroundings reflect or transmit the radiations coming from a source of light. After this reflection or transmission these radiations enter our eye and the object becomes visible. If an object absorbs no light whatever or, in other words, if the light is reflected or transmitted for about 100 per cent., the object gives the impression of being *white*.

If by this reflection or transmission light is absorbed without, however, causing a considerable change in the relative amounts of the monochromatic coloured radiations in the white light, the colour of the object in question will be a grey or, in the case of total absorption, black. If the reflection or transmission considerably changes the original composition of the white light, due to a selective absorption of one special colour, the object gives a coloured impression. Dependent on the kind of light absorbed, the colour impressions of the objects will be different—for example, if the object absorbs the blue and violet radiations, it will have a yellow colour ; if the yellow and red radiations are absorbed, the colour of the object will be blue.

The spectrophotometer enables us to measure the absorption

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properties. The result of a measurement of this kind is the so-called reflection (transmission) curve (*see* Fig. 1). In this graph the reflection (transmission) values (100 minus absorption) of the surface for different colours of the light have been plotted against these colours (wavelengths).

In this way it is possible to lay down objectively the differences between the dyes with which a given paper or textile fabric has been dyed and to determine the relation between the reflection and the concentration of the dyes present in the material, etc.[1]
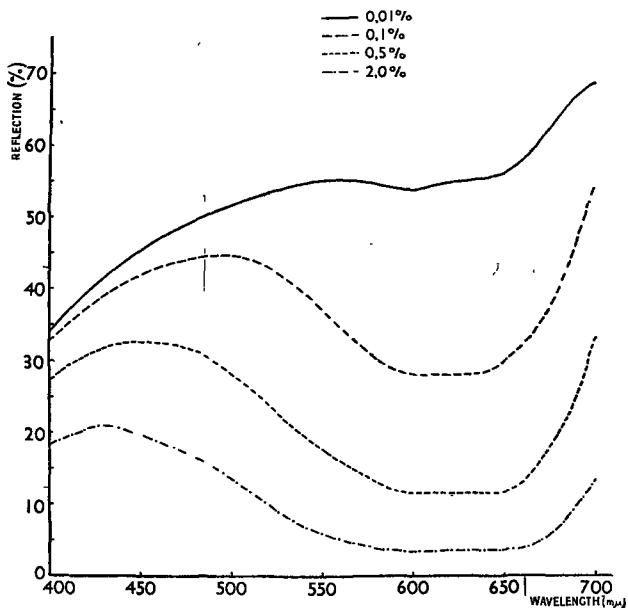
Reflection curves of woollen samples dyed with different amounts of Alizarine Blue BG

Fig. 1

It is a well known fact that the colour impression of every visible radiation reaching the eye can be imitated by a mixture of three other given radiations. If a unit is defined and if it is possible to measure the number of units needed of each of the three given radiations to imitate any desired radiation, the colour impression caused by this radiation can be expressed in the unit amounts of the three given *primary* radiations. In principle any three arbitrary independent radiations can be used as primary radiations. For

practical reasons, however, it is advisable to make a careful choice.

In 1931 the *Commission Internationale de l'Eclairage* recommended three primary radiations now generally used and indicated as X, Y, Z stimuli.[2]

The values of the stimuli X, Y, Z—that is, the colour impression of a radiation reaching the eye after reflection against an opaque surface—are determined by three factors.

First of all the composition of the incident light (E) is important. If the composition of two sources of light are different, the radiations reflected by the same surface will generally also be different. Although normal daylight and the light originating from a normal incandescent lamp are both called white light, there is a considerable difference in their composition. Besides, the composition of daylight changes continually during the day and the seasons and among incandescent lamps there are also considerable variations. In order to exclude all misunderstanding the c.i.e. defined a standard lamp and a standard daylight.

The second important factor of the colour impression is the sensitivity of the observer's eye for colour. Even among people with normal colour sense the colour sensitivity curves can be slightly different from person to person. Based on the research results of Guild and Wright the c.i.e. standardised curves for the average sensitivity of the eye ($\bar{x}$, $\bar{y}$, $\bar{z}$), that is, a standard observer.[2]

The third influence on the colour perception of a reflecting surface is caused by its absorption properties. The reflection curve (r_λ) is characteristic for these absorption properties.

With a source of light with a spectral composition E_λ, for an observer with colour sensitivity curves $\bar{x}$, $\bar{y}$, $\bar{z}$, the colour impression (X, Y, Z) of a reflecting surface (reflection curve r_λ) is composed of these three factors in the following way—

$$X = \int_0^\infty E_\lambda \bar{x}_\lambda r_\lambda d\lambda \qquad Y = \int_0^\infty E_\lambda \bar{y}_\lambda r_\lambda d\lambda \qquad Z = \int_0^\infty E_\lambda \bar{z}_\lambda r_\lambda d\lambda$$

According to the present methods of measurement, the X, Y, Z values of a given surface can be determined in three manners, namely—

(a) *With the aid of the spectrophotometer*—By means of tables containing the values of $E_\lambda \bar{x}_\lambda \triangle \lambda$, $E_\lambda \bar{y}_\lambda \triangle \lambda$ and $E_\lambda \bar{z}_\lambda \triangle \lambda$, the values of the integrals can be approximated by summations calculated from the reflection curve measured with this apparatus. This method has the advantage that, besides an exact determination of X, Y and Z, one has the disposition of the reflection curve, which is indispensable for analytical and scientific purposes. It

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may be called a disadvantage that this method of determining X, Y and Z requires considerable time or very expensive automatic apparatus.

(*b*) *By means of the visual colorimeter*—The three arbitrary primary radiations present in the apparatus are mixed in such a way that, visually, the colour of the mixture is equal to that from the reflecting surface with a given source of light. The specification obtained in this way can be converted into the international stimuli X, Y and Z.

A skilled observer can carry out the measurement in a reasonable time, but the accuracy of the results depends entirely upon the observer.

(*c*) *By means of the photo-electric colorimeter*—An appropriate combination of a source of light, filters and a photo-electric cell makes it possible, in principle, to determine immediately the X-Y-Z specification of a reflecting surface. In practice, however, the theoretical conditions which the transmission of the respective filters would have to satisfy are only approximately realised. When using an instrument of this kind, inexactness in the X-Y-Z determination can therefore be expected, especially for deeply coloured surfaces (reflection curves with steep absorption maxima). Notwithstanding this disadvantage these instruments will in practice be a useful aid in many cases. The measurements can be carried out in a short time and the cost of the instrument is relatively very low.

For studying colour problems in the paper and textile industry it is desirable that the research worker has a spectrophotometer available. In elaborating his problems he has to take into account, however, that most instruments used in industry will be of type (*b*) or (*c*).

THE PREDICTION OF DYE FORMULAE

By analogy with the analysis of dyes in solution, the possibility of analysing dyeings of mixtures of acid dyes on wool was discussed at the Symposium of the Society of Dyers and Colourists held at Blackpool, September 1947.[1]

Furthermore, a calculating method was given with which an approximate dye recipe can be obtained starting from the reflection curve of a given sample. This method is based on measurements which can only be carried out with a spectrophotometer. The elaboration of the results requires calculations which take at least $1\frac{1}{2}$ hr. time even for a skilled worker. Finally, the recipe obtained

in this way is only an approximate one; its correctness cannot always be ascertained in advance.

Although, in principle, these studies showed the prediction of dye recipes to be possible, this method was not yet suitable for practical use, but further investigations have removed these objections.

Suppose the colour of the original sample be given by the specification X, Y, Z. In order to fulfil the condition for the equality of colour of the sample and its imitation it is sufficient that the specification X', Y', Z' of the imitation is the same as that of the sample under the given source of light. This involves[1] that the sums of the reflections at selected wavelengths have to be the same—

$$\sum_x r_\lambda = \sum_x r'_\lambda \qquad \sum_y r_\lambda = \sum_y r'_\lambda \qquad \sum_z r_\lambda = \sum_z r'_\lambda$$

For most textile fabrics the law of Kubelka and Munk can be applied as a first approximation, so that for one wavelength the following relation exists—

$$r'_\lambda = 1 + (a_1c_1 + a_2c_2 + a_3c_3) - \sqrt{(a_1c_1 + a_2c_2 + a_3c_3)^2 + 2(a_1c_1 + a_2c_2 + a_3c_3)}$$

In these equations the scattering coefficient is assumed to be constant and is calculated in the absorption coefficient a_λ. The sum $\sum_x r'_\lambda$ is, therefore—

$$\sum_x r'_\lambda = \sum_x \left\{ 1 + (a_1c_1 + a_2c_2 + a_3c_3) - \sqrt{(a_1c_1 + a_2c_2 + a_3c_3)^2 + 2(a_1c_1 + a_2c_2 + a_3c_3)} \right\}_\lambda$$

Also

$$\sum_y r'_\lambda = \sum_y \left\{ 1 + (a'_1c_1 + a'_2c_2 + a'_3c_3) - \sqrt{(a'_1c_1 + a'_2c_2 + a'_3c_3)^2 + 2(a'_1c_1 + a'_2c_2 + a'_3c_3)} \right\}_\lambda$$

and

$$\sum_z r'_\lambda = \sum_z \left\{ 1 + (a''_1c_1 + a''_2c_2 + a''_3c_3) - \sqrt{(a''_1c_1 + a''_2c_2 + a''_3c_3)^2 + 2(a''_1c_1 + a''_2c_2 + a''_3c_3)} \right\}_\lambda$$

where $\quad a_\lambda$ = the absorption coefficient of the dyes at wavelength λ and

$\quad c_1, c_2, c_3$ = the concentrations of the dyes present in the material.

Because $\Sigma r'_\lambda = \Sigma r_\lambda = \dfrac{X}{K_1}$ $\Sigma r'_\lambda = \Sigma r_\lambda = \dfrac{Y}{K_2}$ $\Sigma r'_\lambda = \Sigma r_\lambda = \dfrac{Z}{K_3}$
$\;\;x\;\;\;\;\;\;\;x$ $\;y\;\;\;\;\;\;y.$ $\;z\;\;\;\;\;z$

and X, Y and Z of the sample are known, three equations in the three unknown concentrations are now given.

It is difficult to solve these' equations algebraically, though with the aid of graphs this is very easy to do.

For a given set of three dyes (for example, red, yellow and blue), three series of graphs can be made; the first series has the values of X as a parameter, the second the values of Y and the third the values of Z.

The prediction of the dye recipe in three given dyes for the imitation of a given sample has now been reduced to the following simple series of manipulations—

1—Determine the specifications of the given sample with a simple photo-electric colorimeter—for example, $X=14500$, $Y=14100$, $Z=15500$ (time needed about 5 min.).
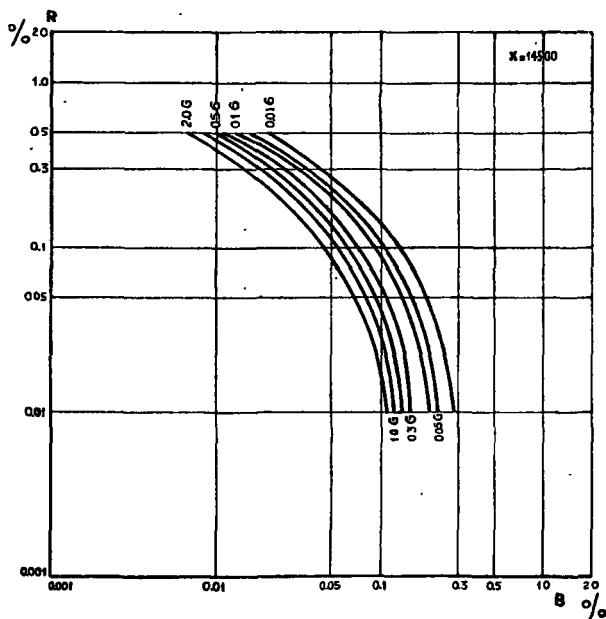
R=red   B=blue   G=yellow

The relation between the concentrations of red and blue for constant amounts of yellow for a given value of X (14,500)

Fig. 2

2—Select the graphs drawn on transparent paper for the measured *X*, *Y* and *Z* values (*see* Fig. 2, 3 and 4).

3—Arrange the graphs (on transparent paper) in such a way that the squares cover each other. Draw a line through points of corresponding yellow concentration in the *X-Y* combination and do the same in the *X-Z* combination (*see* Fig. 5). (The time needed is about 5 min.)

4—Read the recipe determined by the point of intersection of the two lines.

<div align="center">'WHITENESS'</div>

Among the colours of reflecting surfaces the 'near-whites' have a special position.

Physically it is easy to define an ideal white. A surface will be ideally white if it reflects the incident radiations of every colour (wavelength) for 100 per cent. In practice, however, it is impossible to realise these surfaces. None of the raw materials from which papers
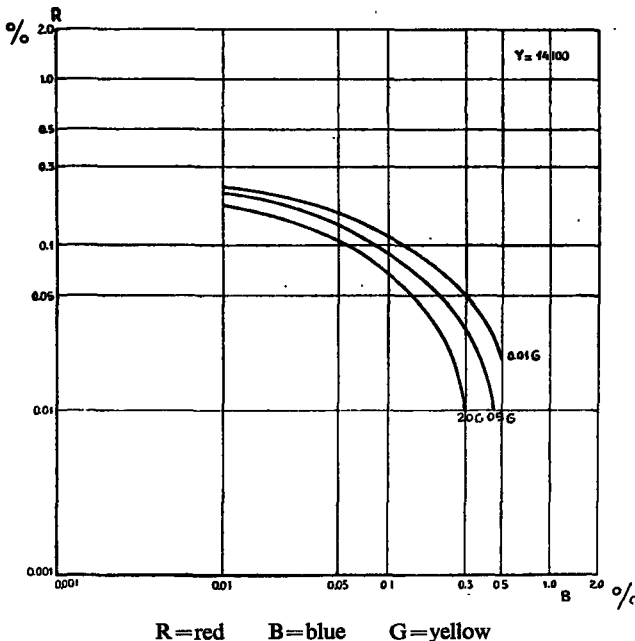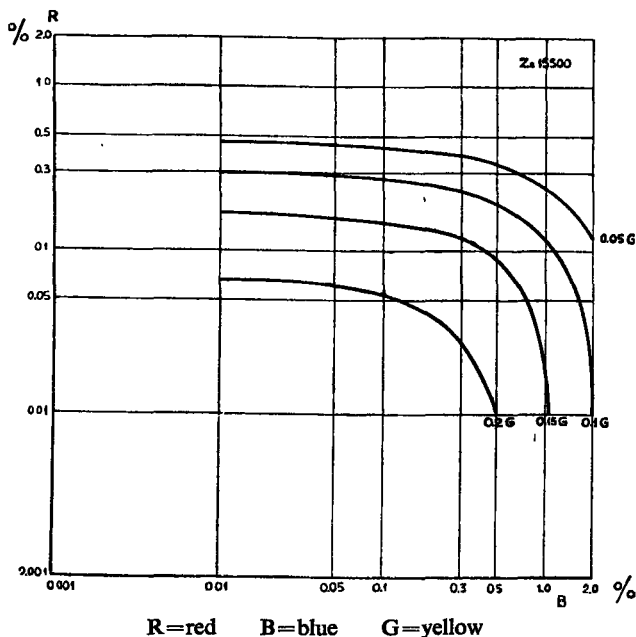

R = red   B = blue   G = yellow

The relation between the concentrations of red and blue for constant amounts of yellow for a given value of *Y* (14,100)

<div align="center">Fig. 3</div>

and textiles have to be made are pure white. The papermaker and the textile manufacturer now have to solve the problem of making a product as 'white' as possible from these imperfect raw materials.

In principle, the raw materials can deviate only in two ways from white. First of all, the raw material might reflect all colours of the white light in an equal measure, though not 100 per cent., in which case the deviation is neutral and the material is grey.

The second possible deviation is of a selective kind. For part of the wavelength range of the light the reflection is 100 per cent., but

R=red   B=blue   G=yellow

The relation between the concentrations of red and blue for constant amounts of yellow for a given value of Z (15,500)

Fig. 4

for the rest it is less. Practically, there are only 'white' materials for which a combination of deviations occurs. The 'near-white' materials of natural origin usually have a yellowish grey colour. This means that with the neutral deviation a selective absorption in the blue-violet part of the spectrum takes place.

By bleaching the raw materials the neutral deviation is decreased as much as possible; however, the material will usually remain somewhat yellowish. In order to neutralise the yellow colour the

material is blued.* For the blueing process a dye has to be used, the maximum absorption of which coincides with the dominating colour (wavelength) of the material to be neutralised. The neutralisation is attained by absorption, that is, by loss of light. Even if an ideal blue dye is applied—namely, a dye which only absorbs light at those wavelengths where this is required—the lightness will decrease.

Dyes available in practice, which have a maximum absorption in the required wavelength range, absorb also at wavelengths where
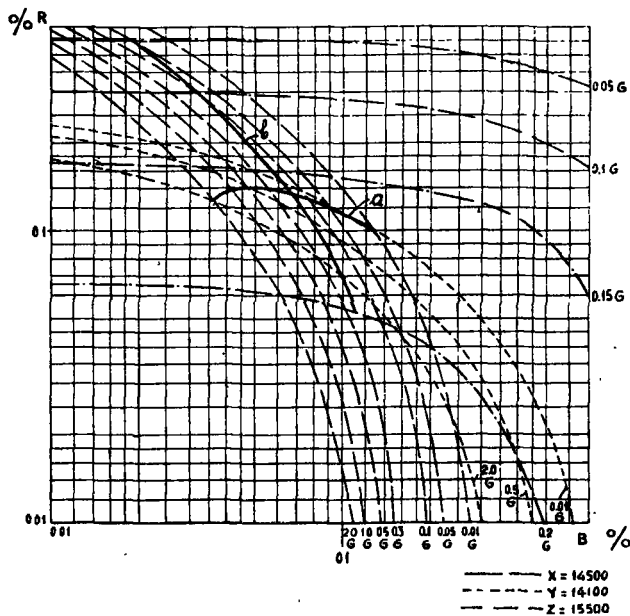
R=red   B=blue   G=yellow

Combination of the graphs Fig. 2, 3 and 4 in order to determine the dye recipe for the colour $X=14{,}500$, $Y=14{,}100$ and $Z=15{,}500$

Fig. 5

no absorption should take place; this results in an extra loss of lightness. When using blue dyes it is important, therefore, to examine the relation between the loss of lightness and the neutralising capacity of these dyes.

A second practical problem is—to what extent has the material to be blued ? What quantity of 'blue' dye yields the maximum

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* The method of increasing the whiteness by chemicals fluorescing in the blue part of the spectrum will not be discussed here.

whiteness for the mean observer ? Both these problems can be solved only if it is possible to evaluate the 'whiteness' impression.

The measurement of whiteness

From the measurement of colours it is known that the radiation reflected by a surface can be defined by *three* magnitudes. For the radiations reflected by nearly white surfaces practice requires a qualification in *one* magnitude. One value expressing the 'whiteness' is required—but can this be achieved ?
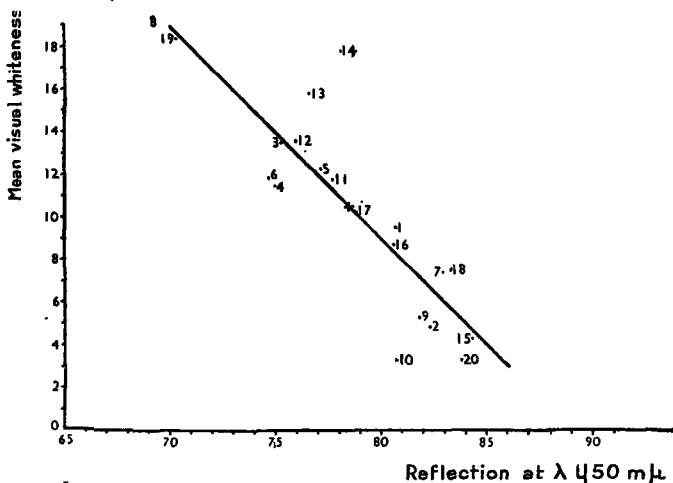
The correlation between the mean visual whiteness and the reflection at wavelength $\lambda = 450 \, m\mu$ ("brightness")

Fig. 6

Two series of very faintly dyed and of undyed 'white' paper samples were given to about 35 observers. Series *A* contained 31 samples, and series *B* 20 samples. The observers were requested to grade the samples of each series in order of decreasing 'whiteness'. The results of the gradings were correlated according to the Kendall method.[3, 4] A distinct agreement amongst the gradings of the observers became evident. The experiment was repeated after one month, thus testing the reproducibility of the first gradings. These results were favourable, too.

As a result of these experiments the following conclusion was drawn—

The subjective whiteness impressions harmonise sufficiently from person to person and prove to remain sufficiently constant in the

course of time to enable the 'whiteness' to be expressed in a value based on the mean visual impression.

Various methods and formulae exist already for expressing 'whiteness' in one value. In Fig. 6-10 the 'whiteness' values determined according to the best known of these methods are compared with the average visual 'whiteness' gradings. Fig. 6 gives the relation between the mean visual whiteness value and the whiteness values determined according to the 'brightness' method. (Paper brightness is defined as the reflection at wavelength $\lambda = 450$ mμ.) From the spreading of points about the line the correlation coefficient,
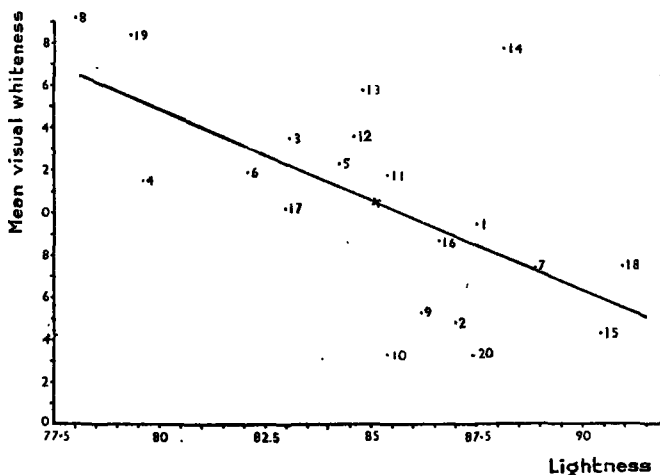
The correlation between the mean visual whiteness and the lightness

Fig. 7

$r = 0.86$, was calculated. This shows that the use of this method is very appropriate for faintly blued papers.

The wide spreading of the points about the line in Fig. 7 shows that the 'lightness' is a bad measure for the 'whiteness'. The correlation coefficient r is 0.73.

The results of the first whiteness formula of Judd's are given in Fig. 8.

$$W(\text{hiteness}) = \sqrt{Y - k \triangle (s)^2}$$

where $Y =$ the lightness,

        $s =$ the distance between the neutral point and the colour point of the sample in the uniform chromaticity scale.

In this formula the lightness is weighted against the colour saturation. The whiteness values resulting from this formula are in good agreement with the visually estimated whiteness values (correlation coefficient $r=0.83$). In those cases, when $k(\triangle s)^2$ becomes greater than Y—which is quite well possible for the 'nearly white' surfaces (samples 14, 19 and 8)—the whiteness value becomes imaginary.

The 'whiteness' formula developed by Stephansen[6] at the
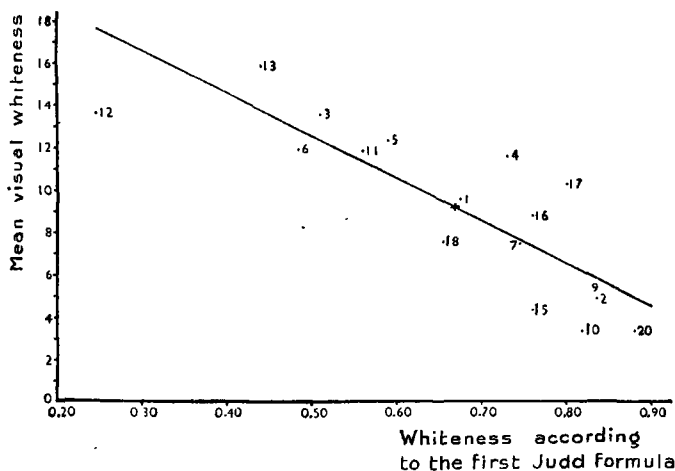
The correlation between the mean visual whiteness and the whiteness according to the first Judd formula

Fig. 8

Norwegian Institute for Paper Research is frequently used in the Scandinavian countries.
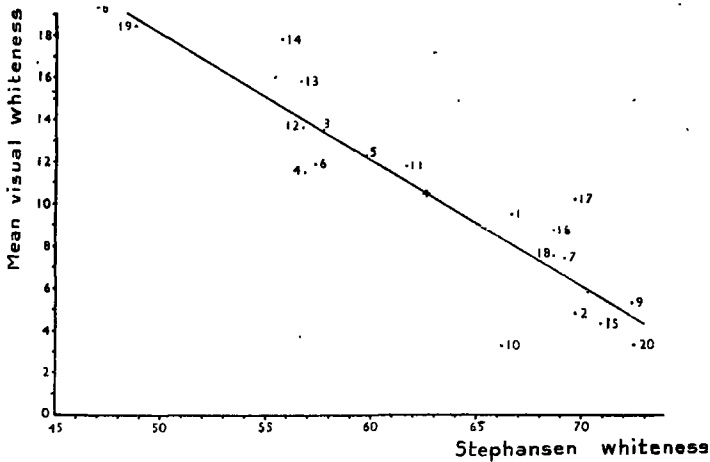
$$W\text{(hiteness)} = 2B - R$$

where R and B are the reflections measured at the wavelengths 670 and 430 mμ.

The whiteness formula given by Harrison[7] strongly resembles the Stephansen formula. Harrison uses—

$$W\text{(hiteness)} = 100 - R + B$$

For these formulae, too, the given paper samples show a good correlation coefficient, namely, 0.91 and 0.81, respectively.

The correlation between the mean visual whiteness and the whiteness according to Stephansen

Fig. 9

Even on theoretical grounds it must be expected that the brightness method and the lightness method, as well as the formulae of Stephansen and Harrison, are unsuitable for measuring the whiteness of actually blued papers.

During the war a new whiteness formula was developed at the Vezelinstituut T.N.O., namely—

$$W\text{(hiteness)} = 100 - \sqrt{(10\Delta\sqrt{Y})^2 + k(\Delta s)^2}$$

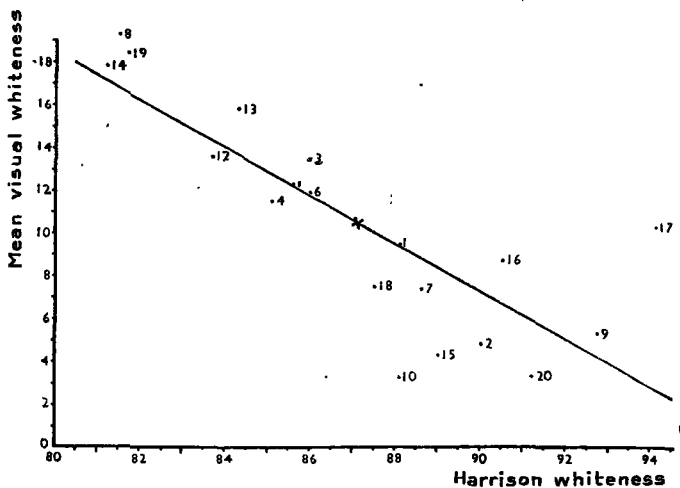where $\Delta\sqrt{Y}$ = the difference between the square roots of the lightness of the samples and of magnesium oxide (value 100),

Δs = the colour saturation of the sample, measured on the uniform chromaticity scale diagram of McAdam,[8]

k = a constant.

A simplification of this formula was tried for practical purposes[9]—

$$W\text{(hiteness)} = 100 - \sqrt{(\Delta Y)^2 + k'(\Delta s)^2}$$

The correlation between the mean visual whiteness and the whiteness
according to Harrison

Fig. 10

The values of the constants k and k' were determined experi-
mentally as $k=0.8\times10^6$ and $k'=3.0\times10^6$.

Both formulae have a good correlation with the mean visual
whiteness impression (*see* Fig. 11). The correlation coefficients are
for the original formula, $r=0.95$; for the simplified formula,
$r=0.94$.

When the American wartime publications became available, Judd
was found to have developed a whiteness formula[10]—

$$W = 1-\frac{\Delta E_{\text{MgO—sample}}}{\Delta E_{\text{MgO—black}}}$$

In this equation

$$\Delta E = \sqrt{(c\Delta\sqrt{\bar{Y}})^2+49\times10^4\sqrt{\bar{Y}}(\alpha^2+\beta^2)}$$

where $\sqrt{\alpha^2+\beta^2}$ = the chromaticity difference measured on the
uniform chromaticity scale of Hunter,[11]

c = a constant=20.

If the whiteness is expressed in percentages, Judd's whiteness
formula can be written as—

$$W\text{(hiteness)} = 100-\sqrt{(10\sqrt{\bar{Y}})^2+\frac{49\times10^7}{c^2}\sqrt{\bar{Y}}(\alpha^2+\beta^2)}$$
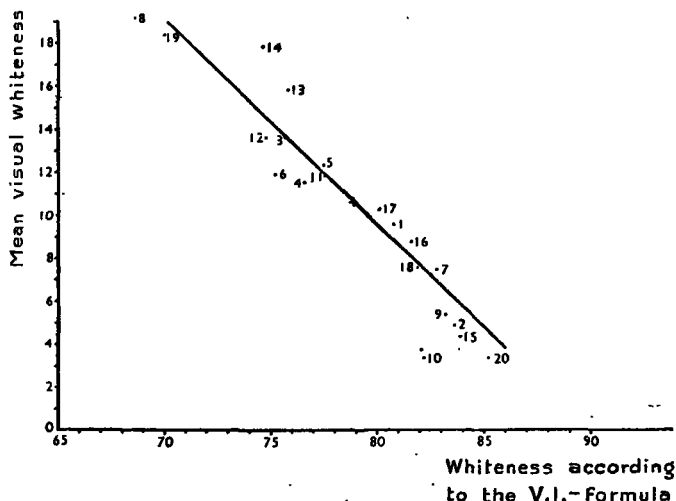
The correlation between the mean visual whiteness and the whiteness according to the second V.I. formula

Fig. 11

Correlation of whiteness values according to this formula and the mean visual whiteness values gave a rather disappointing result. The correlation coefficient r is 0.84.

At the Vezelinstituut the value of c was determined experimentally, and, instead of 20, a value of 70 was found. This value also agrees better with the value of c used by Judd for calculating other colour differences.[12] The whiteness values of the modified Judd formula give a correlation coefficient $r = 0.95$.

The measurement of the whiteness of blued papers

A problem arising in practice is what amount of blue dye must be added to the given material to attain the optimum 'whiteness'. To solve this it is necessary to measure the whiteness of blued papers. Accordingly, three new series of papers were made, one of esparto, one of aspen and one of a 1 : 1 mixture of esparto and woodpulp. In each series the papers were identical but for the content of blue dye. The whiteness values of all samples were determined by the aforementioned formulae and methods. Thirty three observers took part in estimating the visual whiteness. Every observer was asked to choose from each series the sample giving him the best whiteness impression.

Table I gives a list of whiteness values for the blued esparto paper samples, computed by means of the lightness, brightness, Stephansen and Harrison methods. The dye percentage has little influence on the whiteness value according to the 'brightness' method. The whiteness values according to the lightness method decrease gradually as the dye content increases. By increasing the dye percentages, the
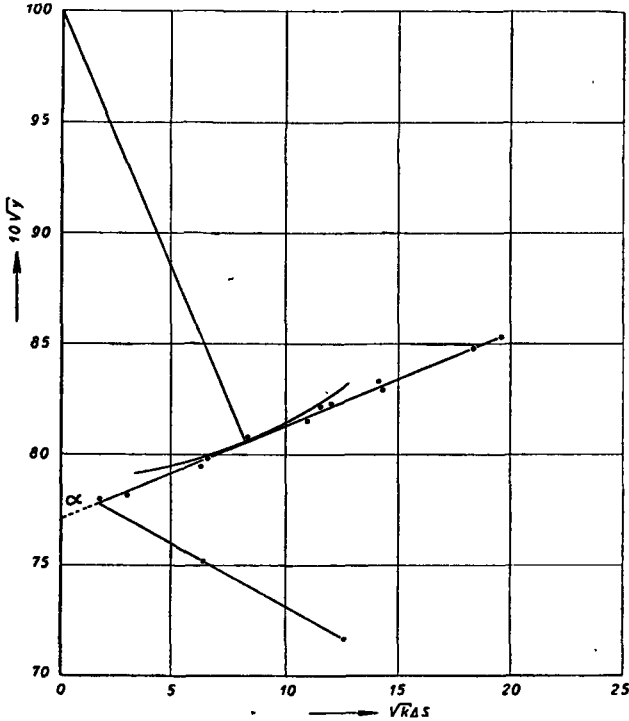
Determination of the optimum dye concentration and the effectiveness
of the dye for esparto dyed with Alizarine Irisol

Fig. 12

whiteness values according to the Stephansen and Harrison formulae rise continually.

From experiments it is obvious (*see* the visual choice frequency in Table II) that these methods are not suitable to qualify the whiteness of blued papers.

In Tables II, III and IV the whiteness values, calculated according to the other formulae, have been compared with the visual choice

frequencies. Each of the columns of whiteness values shows an optimum. For the first Judd formula the optimum lies at a much too high dye percentage. According to the frequency of choice the optimum of the whiteness values calculated with the second Judd formula (with a value $c=20$) lies at too low a dye content.

APPLICATION OF THE WHITENESS FORMULÆ

An easy way to estimate the dye concentration, yielding optimum whiteness for a given raw stock and blue dye, is to plot the lightness against the colour saturation according to the equation used. In Fig. 12 this is done for esparto dyed with Alizarine Irisol in various concentrations. The ordinate measures $\sqrt{Y}$, the abscissa $\sqrt{k\triangle s}$ (that is, the first v.i. formula was used). The points representing the samples with increasing dye content are indicated. The graphic relation consists of two straight lines. The tangential circle indicates in the common point the sample of optimum whiteness. The dye concentration needed to give this optimum value can be interpolated between the nearest available points.

A comparison between two dyes used for blueing paper can be made in the same diagram. The aim of the addition of a blueing agent being a decrease of the yellowness of the paper, with as little decrease of lightness as possible, the angle between the straight sample line and the lightness axis can be taken as a measure for the effectiveness of a dye. The smaller the angle, the less effective the dye.

TABLE I

Esparto paper blued with Alizarine Irisol

Dye concentration (%)	Whiteness values according to			
	Brightness	*Lightness*	*Stephansen*	*Harrison*
0	59.8	72.7	29.3	72.8
0.01	60.1	71.9	34.6	76.3
0.03	59.7	68.9	32.7	75.9
0.07	60.3	69.5	34.7	77.0
0.09	60.2	67.8	35.2	77.9
0.10	60.2	67.6	35.7	78.1
0.11	59.5	66.6	35.3	78.0
0.14	59.6	65.1	36.7	79.4
0.17	59.1	63.7	38.1	81.1
0.18	58.9	63.2	37.7	80.4
0.24	59.1	61.1	39.9	82.4
0.26	60.2	60.8	40.5	83.4
0.40	59.8	56.6	42.7	86.6
0.60	57.2	51.4	47.0	93.3

TABLE II

Esparto paper blued with Alizarine Irisol

Dye concentration (%)	Whiteness values according to					
	Judd I	*V.I. formula I*	*V.I. formula II*	*Judd II constant 20*	*Judd II constant 70*	*Choice frequency*
0	imaginary	75.6	53.4	79.7	75.2	
0.01	imaginary	76.2	54.8	80.5	75.7	
0.03	imaginary	77.8	58.4	80.7	77.7	
0.07	imaginary	78.1	59.1	81.0	78.1	2
0.09	imaginary	78.6	60.3	80.7	78.6	
0.10	imaginary	78.8	60.6	80.7	78.7	
0.11	imaginary	78.6	60.6	80.4	78.6	6
0.14	0.368	79.0	61.6	80.1	79.0	9
0.17	0.593	78.8	61.6	79.5	78.9	11
0.18	0.605	78.6	61.3	79.2	78.7	3
0.24	0.748	78.0	60.7	78.1	78.0	
0.26	0.763	77.9	60.7	78.0	77.9	
0.40	0.361	74.4	54.9	74.8	74.3	
0.60	imaginary	69.0	45.6	70.3	68.7	

TABLE III

1 : 1 *mixture esparto+woodpulp with Alizarine Irisol*

Dye concentrations (%)	Whiteness values according to					
	Judd I	V.I. formula I	V.I. formula II	Judd II constant 20	Judd II constant 70	Choice frequency
0	imaginary	77.4	56.9	81.5	77.0	
0.03	imaginary	79.9	62.5	81.9	79.9	7
0.05	0.170	79.8	62.7	81.0	79.8	9
0.07	0.600	80.1	63.7	80.7	80.1	16
0.09	0.680	79.4	62.7	79.8	79.4	1
0.11	0.755	79.3	62.8	79.5	79.4	
0.17	0.756	77.8	60.5	77.9	77.8	
0.25	imaginary	73.4	53.1	74.0	73.3	
0.50	imaginary	64.8	37.6	67.8	64.6	

TABLE IV

Aspen with Alizarine Irisol

Dye concentrations (%)	Whiteness values according to					
	Judd I	V.I. formula I	V.I. formula II	Judd II constant 20	Judd II constant 70	Choice frequency
0.	0.346	87.1	75.2	88.9	86.8	
0.010	0.649	87.7	76.6	88.7	87.6	11
0.020	0.770	87.9	76.8	88.5	87.8	16
0.030	0.839	87.2	76.1	87.5	87.3	4
0.035	0.840	87.1	75.9	87.3	87.1	
0.040	0.857	86.8	75.3	86.9	86.8	2
0.060	0.842	84.9	72.1	85.0	84.9	
0.1	0.494	81.2	65.4	81.8	81.0	
0.3	imaginary	67.6	55.3	72.1	67.5	

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DISCUSSION

THE CHAIRMAN: Gentlemen, we have heard Dr. Selling's paper this morning and some of us, practical papermakers especially, may feel somewhat surprised to find that it is, possible to use the applications of theoretical physics to this extent in colour matching; we may even feel that we must have fallen behind the march of progress to know so little of these methods. I do not think we really need feel any concern in this respect, since I would say—subject to correction—that we are witnessing a new development and it is a question whether any mill anywhere is yet using these methods in regular operation.

I suppose it has been known for about 80 years that the trichromatic theory of colour vision accounts fairly well for human response to colours: that is, the eye behaves as though it has three—and only three—different responses, each sensitive to a different band of the visible spectrum. Confidence in the ability of this theory to account quantitatively for human colour vision gradually became established and the next step, to put the theory on a footing from which it could be developed, was for the response curves of the three receptors of the human eye to be established. This was done by the C.I.E. commission in about 1931 and, with that work as a basis, developments like those we have heard about today have gone forward.

We can see that the time scale has been such that it is too early yet for these developments to have reached our own or, indeed, any industry—from 1931 to 1950 is 19 years, out of which we must take the war years, which were hardly available for research of this kind. Then quite a long period has been required to develop the particular kinds of measuring instruments which can be useful in this connection and which had to wait for the recent development of electronics to become practicable. I refer to the Hardy and similar type of recording spectrophotometers and to the filter and other photometers discussed by Dr. Selling this morning which are not on the same absolute basis. It is probably true to say that this is the start of a movement which has not been in the least retarded by the slowness of industry to take it up and it is, in fact, an early stage in the application of physical principles to the matching of colours. At the present time, of course, colour matching in the paper industry is done entirely by practical methods, using trial and error and the subjective knowledge of what happens when colours are mixed—which have been the only methods available.

What I am trying to suggest is that this being one of the first attempts at applying physics to colour matching, I do not think we

should be too ready to criticise it adversely, although a number of difficulties which still have to be overcome will undoubtedly occur to us; one of these, which I will put to the speaker presently, seems to me to be something of a stumbling block at the moment. We should rather greet this paper as an early step in something which will surely come to fruition in a few years' time and put colour matching on a scientifically sound basis to our great advantage.

I propose to start the discussion by asking Dr. V. G. W. Harrison, who has worked a good deal in this field and who has been in touch with Dr. Selling and his work for some time, to address the meeting.

My own question to Dr. Selling, which I referred to a moment ago, is as follows—I gather that the calculated matching recipe is the proportion of the three dyes present in the dyed paper. Surely there is a big difference between adding the dyes to the beater and getting them into the paper. From the work of various people—I will mention Mr. North as one—the proportion of dye retained on the fibre, especially for a deeply dyed paper, is only a fraction of the whole and my recollection is that to have only 50 per cent. retained would not be at all unusual. This apparently means that the adsorption behaviour of each of the three dyes in the conditions of use must also be known quantitatively to convert the dye concentrations in the coloured sheet into a beater furnish.

Dr. Harrison, I will now call upon you to address the meeting.

DR. V. G. W. HARRISON: Mr. Chairman and gentlemen, as I think I was responsible for suggesting that Dr. Selling should be invited to give this paper, perhaps I may say one or two words on the set-up over in Holland. Dr. Selling will probably be too modest to say so, but he is employed in a research organisation in Holland which is comparable in every way with our own research associations in this country. The Fibre Research Institute does not cover quite the same ground as PATRA or the British Paper and Board Industry Research Association. It is not concerned with printing problems: it is wise! It *is* concerned with all fibres including textiles and not just paper fibres; therefore, their work does not quite coincide with ours. Nevertheless, our problems are very similar indeed and I think we have a lot to learn from each other. I have had the privilege of going over twice to visit the Vezelinstituut at Delft and it is an extremely fine organisation. It is well worth anybody's while to pay it a visit and I am quite sure you will get a good welcome—I certainly did.

Naturally, we at PATRA are interested in the work which Dr. Selling has done, because it is very closely connected with the appearance of paper. Two parts of the work are described. One is the prediction of the amounts of dyes necessary to match a given colour—I think that is important in textile dyeing, but of less importance to papermakers. The second half is the prediction of the optimum whiteness of a sheet of paper—which is a practical problem of the greatest importance. I know that for the last two or three months several people have been concerned over this question of whiteness or brightness of paper and the subject is always coming up for discussion.

As Dr. Selling said this morning, you start off with a yellowish pulp with a not very great reflection factor. You bleach it to produce a yellow which reflects more light, but it is still yellow. Then, if you want to get an acceptable paper, you have to neutralise the yellow by putting in pigments or dyes. The principle is exactly the same as that of the blue bag used in domestic washing. You do not add light—in fact, you subtract it—but you do repress the yellowness of the paper and it looks whiter. If you put too much blue in, you can overdo the whitening factor and, then suddenly, instead of getting something which looks white, it looks blue. So the question of the optimum quantity of dye or pigment to add is something of considerable practical importance. You want to get the best effect, but you do not want to overdo it.

There are two ways of deciding that. One is to try to do it the hard way by trial and error and notice what your customers think of the paper. The other is to try to get some method of scientific control. Up to the present, there have been several formulæ suggested to define the whiteness of papers. I am responsible for one, which gives, I think, about the worst results that Dr. Selling has discovered. I never intended it very seriously; but Judd and Stephansen have suggested methods of measuring whiteness in terms of a percentage figure. There is a brightness meter used widely over in the United States, which measures the reflection factor and, in rather carefully specified conditions, it does correlate moderately well with papermakers' judgment of whiteness. But you cannot decide which formula is the best simply from the point of view of physics, because it is not a purely physical effect; whiteness is a psychological effect as well. In fact, Dr. Selling has shown quite well that what one would consider to be the whitest paper is really a very faint yellow and, if you get a truly neutral white paper, it seems a definite blue white to most people. It is a most curious effect and I do not quite know what the explanation is.

I have read the original report of Dr. Selling which is quite a voluminous document and it seems to me to be thoroughly sound. I have only one criticism to make, namely, that the work has been done with a comparatively small number of observers (about 35) and it should be checked with a much larger number—say, 200 or so—if we can get a sufficient range of papers for testing. I hope that PATRA and our friends at Kenley will be able to combine with the Vezelinstituut to do a more extended range of tests.

There are one or two other points that arise. There is the question of instruments suitable for colour measurement. Assuming we are going to use the whiteness formula and use it for predicting the amount of dyes to be added to the fibres, obviously, we have to have some sort of instrument, but there is considerable difficulty in the availability of instruments in this country. We at PATRA are expecting to get a spectrophotometer which is not much different from the one Dr. Selling is using. The trouble is that every time we ask about it, the delivery date is pushed forward another two months. It is non-recording, but it should be as accurate as the Hardy instrument of America. As for less accurate but cheaper instruments, there are one or two being developed. One recently brought out enables you to get X—Y—Z values approximately. I have not tried it out myself, so I cannot vouch for it, but one is being delivered for tests fairly soon and I hope we shall be able to give some report on its capabilities shortly. It costs about £70 and I think it should be suitable for this kind of work. We ourselves have developed, in conjunction with an instrument maker, a form of approximate spectrometer in which the curves are determined through a set of eight narrow-band filters. It costs somewhere about £100 altogether. It is quite suitable for a lot of control work and is undergoing some tests now. Thus some instruments are gradually becoming available and I think we should hear of more shortly.

There are points in connection with Dr. Selling's paper that may have occurred to you. One is that the experiments were done on laboratory sheets made in the sheetmaking apparatus, in which the question of making a series of papers of known composition is comparatively easy. On that basis it is possible to calculate definitely the percentage of dye that should be added to give the optimum whiteness for the sheets; but it is rather a different matter to apply that result to actual mill papers, because there are various disturbing factors. That is another step that will have to be investigated fairly soon.

I do think this work needs a lot of encouragement. Though rather highbrow and scientific, it is of great practical importance

and, ultimately, I think it will lead to a reduction in the time required to make matches and will also cut down the wastage of materials.

THE CHAIRMAN: Before we throw the meeting open for discussion, would Dr. Selling care to answer the point about the adsorption of dyestuffs on fibres?

DR. H. J. SELLING: I will try to do so. When I spoke to you this morning perhaps it seemed as though I knew everything, but that is not the case. We know nothing and we know that we know nothing —and that's a lot! In the prediction of dye formulæ with acid dyes on wool, we had to conquer some theoretical difficulties and did not introduce practical problems in order to attack only the theoretical troubles. On paper, I know that only part of the dyestuff will be retained on the fibres; however, if the man in practice has a sample he wants to imitate, he goes to his sample book, looks out his recipes and says, "Well, it's in between those two colours." He can only do so, if the colours he makes are reproducible. But, if there is a reproducibility, there must be a law. I believe that the law for paper will be different from the one I used for the prediction of dye formulæ on wool. If you cannot calculate a law that makes the retention of your dye fit the formula, try to do it experimentally.

In this way, you can also get the curves and you can then make the graph. I believe the prediction of dye formulæ cannot be made as accurate and effective in the manufacture of paper as in the dyeing of wool. There will be far more difficulties than in the case of textiles. In the first place, you must know the quantity of dye retained on the fibre. If you know this relation, you can substitute it in the relation between the reflection and the quantity of dye used in the beater. Secondly, the relation must be converted into mathematical equations or empirical graphs.

It is easy to give these rules, but I know it will cause a lot of trouble to practise them; nevertheless, I believe that it must be possible to predict dye formulæ in papermaking, too.

MR. F. NORTH: Mr. Chairman and gentlemen, I should like first to congratulate Dr. Selling on his paper and particularly on his command of the English language. I wonder how many of us could go to Holland and give a similar paper—or indeed any paper—in Dutch! I should like, however, to discuss certain points that he has made as one who has to match samples commercially day by day, week in and week out. There are many snags about this physical

prediction of colour. One of these has been pointed out by our Chairman. I could not hope to list all the others; but one that occurs to me is the enormous time required to collect all the necessary data on which to base your predictions. As a dyestuff manufacturer, you not only have to know the characteristics of your own dyestuffs though, unfortunately, you do occasionally receive samples dyed with other people's dyestuffs—and you have to know all about them. The absorption characteristics vary from furnish to furnish and, in the case of mixed furnishes, it is not known that the coefficients are additive.

Another thing that occurs to me is that you get an approximate recipe by means of prediction formulæ, but an approximate recipe is less than a quarter of the battle, because it is always that last bit of shading to get the exact match that takes up the time. Therefore you still have to carry on, by means of practical dye trials from your approximate recipe, to get the exact mixture required and that is the part of the process which consumes the time.

The last factor which comes to mind is the relative cost of doing this job in the ordinary practical way and doing it on the basis that Dr. Selling has suggested. Think of the enormous capital outlay for equipment and instruments required and the cost of physicists to look after them and so on. As a matter of interest, we have calculated that every curve that we turn out on a Hardy recording spectrophotometer costs us 8s., which is quite a lot of money if you go on turning them out at the rate of one every $2\frac{1}{2}$ min.

Now, I should like to discuss the Kubelka and Munk equations in the light of the work we have been doing over the last few years. These equations are derived for diffuse incident light though, in practice, there is no spectrophotometer I know of which does illuminate with diffuse light. Most instruments use collimated incident light and this complicates the theoretical treatment, giving equations which contain two absorption coefficients and four scattering coefficients. These are of academic interest only and are not suited to routine use; nevertheless, we can do as Dr. Selling has done, take these equations as an approximate step and see how it goes. We have done this for dyed paper, which, as Dr. Selling has pointed out, is a very different case from woollen or cotton fabrics. We have reached the conclusion that the absorption coefficient is only linearly related to dyestuff concentration over a very small range. When the concentration rises above 0.05 per cent., that linear relationship breaks down; however, if you plot K over S against dye concentration, the linear relationship holds up to about 0.5 per cent. The reason for that is that on increasing the dye concentration, the scattering co-

efficient decreases and it decreases very markedly after about 0.1 per cent. I am not very clear why it should do that—one presumes that the dyestuff is precipiated on the fibre in a different form and therefore scatters in a different sort of way.

Recognising those limitations, the Kubelka and Munk theory has a very definite application in research on the dyeing of paper rather than on the practical aspect of matching colours—for example, we have used it in a number of ways, including studying the effect of pH on the dyeing of paper. Thus, with Metanil Yellow YKS the retention is at a peak between pH 5 and 6; however, if you work out the absorption coefficients of the dye deposited in the range pH 5—6, it is found that it has considerably less visual colour value than when the dyestuff is applied outside this range. Therefore, it is not sufficient to determine the dyestuff retention in any particular set of conditions by examining the amount of dye remaining in the backwater, since this would give misleading figures for the optimum dyeing pH value. Again, acid dyestuffs have a greater visual effect when applied to paper by surface colouring than when applied, together with rosin and alum, to the stock in the beater. Direct dyestuffs may be dyed with or without the use of rosin and alum and here it is found that, for a given quantity of dyestuff, the sized dyeings have a greater visual effect than the unsized ones. Thus by recognising the limitations of the theory and working within its limits, you can get quite a lot of interesting information.

Finally, if anyone here is interested in applying this theory to their own particular problems, I would say that the mathematical labour involved in using the equations is very great. If anyone does want to use the equations, we have produced graphs covering the relations between the values of R_o, R_∞ and S_x for all values between 80 per cent. and 0 per cent. reflectivity and we shall be only too glad to allow anybody to use those graphs if they wish to do so.

MR. N. C. UNDERWOOD: I should like to ask Dr. Selling one or two questions. First of all, I should like him to give us some idea of the accuracy which he expects to obtain and the steps which he would take to obtain accuracy from any of his instruments. Last night I did a little mental arithmetic. I do not guarantee it, but I assumed that we had a uniform reflection curve at 90 per cent. reflection with magnesium oxide. I further assumed that over half the range 400—550 I went wrong so that instead of reporting from my instrument 90 per cent. reflection, I returned only 89 per cent. I do not think that is overmuch for an instrument of this type. From

that, I then derived three functions: x, y and z, which are slightly different, but quite closely related to Dr. Selling's X, Y and Z. I found that they differed from the correct value by one part in the third decimal place. That is not much but, when you consider that with some similar estimates which I made with clays, the total difference between a very good clay and a very bad clay was only one part in the second decimal place—two parts at the very most—I could quite easily have returned through a very small error in my instrument quite a large error in the figure which I was returning for the colour.

The point I want to make is that we must have very accurate instruments to measure these colours if we are going to make measurements at more than one mill or in more than one laboratory. If I may ask a second question—Dr. Selling, in applying his formula, uses the Macadam method, the idea being that uniform distances measured on the graph which represents the colours represent equal changes in sensations. The c.i.e. system does not do that. I should like to ask Dr. Selling which, in his opinion, is the best method—the Macadam or the c.i.e.

Thirdly, I wonder if I dare ask him if he could tell us something about the measurement of colours incorporating fluorescent materials?

DR. SELLING: Mr. North told us about the difficulties of applying the law of Kubelka and Munk to paper. I cannot say very much about this. I have been using the law of Kubelka and Munk in its general form on undyed paper with different backgrounds and have found that the relation between the thickness, the scattering and the absorption holds good. For the prediction of dye formulæ you need the assumption of Nolan, namely, that in the first place the absorption increases linearly with the quantity of dye on the fibre and that, secondly, the scattering coefficient is independent of the quantity of dye on the fibre. From the literature, we know that the second assumption is certainly not true.

As I said, we have not studied the prediction of dye formulæ on paper up to now; therefore, I cannot give you a positive answer for all of the practical problems. But again I ask you: is the dyeing of paper reproducible or not ? I believe it is, for if there is no reproducibility the dyemaster cannot make a good recipe. If the dyeing of paper is reproducible and the mathematical equations are too complicated then try to obtain your graphs empirically.

I would like to make the following remarks about the costs involved. For the preparing of the graphs needed for the prediction,

you require the absorption properties of three given dyestuffs. If the absorption coefficients are different from furnish to furnish, you may only say that you have the absorption coefficients for the given furnish.

With the help of the absorption coefficient of the given furnish you prepare your graphs for the values X, Y and Z. If there is a given shade you want to imitate you do not need to know the absorption coefficient of the foreign dyes used in the given sample, but you only have to measure the X-Y-Z of the given sample. After that you can find with the help of the graphs, a recipe in the dyes related to the graphs. Dyeing out the given recipe on the used furnish gives you a paper, the colour of which gives a rather good approximation to the given sample.

The difference caused by the variations in furnish cannot be avoided. Therefore the dyemaster must see the determined recipe as a starting point for the match he has to make.

If the graphs for a given set of dyes are made by the dyestuff manufacturer the papermaker only needs a fairly cheap instrument— for example, a photoelectric colorimeter. With this, an unskilled man can measure the X-Y-Z in a very short time (about 5 min.) and predict the recipe with the help of the graphs within 3 min. The costs of the obtained approximate recipe in this way must be very low and of great help to the dyemaster. Another point is that you must be very careful when buying a cheap colorimeter, for the following happened to me. I bought an American instrument with one set of three filters and it gave me good results. At one time I said to one of my collaborators, "I think it is very dangerous that we have only one filter for X, one for Y and one for Z, because should one break we cannot do the work. Therefore order three new filters so that we shall have a double set." He did and, when they came in, we tried the new set. What happened? The value of X measured with the other set of filters was quite different. The first set was, I should say, in rather good agreement with the real values of X, Y and Z. But the amber filter of the second set was quite different and with some red colours you had discrepancies of 10 per cent., which is very high. We measured the curve of the filter and, indeed, there were great differences in the absorption curves of the two delivered filters. If we go on working in this way, I believe the reputation of the photoelectric instruments will become very bad.

The second speaker asked me about the accuracy of instruments. I must say that, so far as I know, all instruments will find it difficult to compete with the sensitivity of the eye.

The C.I.E. system is internationally accepted and therefore I always use it to specify colours. For certain things I must use a U.C.S. system and for this reason we used the Macadam scale. I know there are more U.C.S. systems and none of them is ideal, however, you must realise that the measurement of colour is a rather young science which we have to take up and work with as it is. I am sure we will meet with many difficulties that must be conquered, but in its present form it is already of great value to different kinds of problems.

The last point is the hardest nut to crack, namely, fluorescent dyes. I can only say a few things about that. All spectrophotometers —so far as I know, even the Hardy instrument—are at present incapable of measuring the characteristics of the fluorescent dyes. Yet there are possibilities; if the light sources for daylight, etc. are standardised not only for the visible part but for the ultraviolet part too and the spectrophotometers are changed in such a way that the reflected light is monochromaticised, then it will be possible to measure the characteristics of fluorescent dyes and specify the colours.

This problem figures on the programme of my laboratory, too— but there are so many points on the programme and so few men to do them. Perhaps I shall come to it in the future, but at this moment I must agree with you that nothing can be done with fluorescent dyes.

MR. E. ATHERTON: I wonder if I could comment upon one of the points raised by Mr. North concerning the Kubelka and Munk equation.

As Dr. Selling is no doubt aware, the Kubelka and Munk equation is derived for conditions of diffuse incident illumination. It seems to me rather surprising and, to some extent, gratifying that the equation can be applied to the prediction of dyeing recipes on the basis of experimental methods using spectrophotometers which employ parallel incident light. General considerations might lead one to expect a significant difference between the reflectance figures obtained with parallel and diffuse incident light.

Thinking on these lines, I was reminded of a paper by Kubelka, in 1948, in which he took into consideration the fact that, with diffuse lighting, the average light path through the paper was not equal to the normal thickness of the paper but involved a trigonometrical function. As a result, I believe he was able to calculate that by illuminating his surface at 60° he could duplicate the conditions obtaining for diffuse incident light.

I wonder if Dr. Selling has had any experience of this matter, if it would make any difference to his prediction formulæ and whether the accuracy could be increased by such considerations.

DR. SELLING: In our spectrophotometer the specimen is illuminated at 45° with a nearly parallel beam and observed by the photocell perpendicularly. The condition of diffusely lighting the specimen is not fulfilled with the geometry of our spectrophotometer, nevertheless, we found that for textiles, dyed and undyed and for undyed paper, the law of Kubelka and Munk in its general form fairly well fixed the relation between the values of R_{R^1}, R_1 and R_∞ for different backgrounds and different values of X (thickness). Looking for an explanation for this we found some articles in the literature dealing with light going through diffusing media.* Spijkerboer and Dreosti observed that the direction distribution of a radiation, after passing through an optically "sufficiently thick layer" of a scattering medium has become independent of the original energy distribution of the incident light. I therefore believe that, in the case of the woollen samples, the thickness was optically thick enough to diffuse the incident light totally.

I have read the publication of Kubelka of 1948 but I have no experience with an illumination of the specimen at 60°. To Mr. North I should like to remark that the condition of independent absorption of the dyes and the fibres is not always fulfilled in applying the law of Kubelka and Munk (in Nolan's modification) on mixtures of dyes. This may be why the linear relationship between the value of K and the concentration is not true.

MR. D. TOUGH: I should like to ask, first of all, a question about Dr. Selling's graphs and how he produced them, because, if they were obtained as a result of a large number of experimental dyeings by varying the ratios of the three dyes, then it would appear that he already has an album of shades at hand for future predictions. A time factor is also involved for, even if he obtains sets of graphs for his three dyes, for one particular fibre, weave and fabric, then the whole process has to be gone through again when you consider different fibres, different weaves, different fabrics and different dyes. In that case, the time involved would be much longer than that required to obtain a match by practical dyeing tests.

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* J. Spijkerboer, *Verstrooiing van Licht*—Dissertation, Utrecht, 1917; G. M. Dreosti, *Absorptie en Verstrooiing van Licht in Melkglas*—Dissertation, Utrecht, 1930.

On the question of the measurement of whiteness, I should like to ask him why he uses the Macadam uniform chromaticity system, because I believe that that system is most accurate between Munsell values of 4—6 and becomes inaccurate at values above 8. Assuming that such a system can be applied, then from the appearance of Dr. Selling's formulæ, he measures whiteness by the colour difference between pure magnesium oxide and the pattern. It is a moot point whether magnesium oxide is the best visual white which we would expect if we compared it, say, with something slightly tinged with blue but only of slightly lesser lightness.

In his formulæ he introduces a K factor which serves to equate differences in the colour plane with differences in the lightness scale and Dr. Selling says that the value of K has been obtained experimentally. I feel that this value of K may only give the best results for this particular problem. Can he tell us if he has attempted to apply his formula to any other type of whiteness measurement—in particular, to one where the patterns have low colorimetric purity and high lightness? Quite recently, I have been doing some work on the measurement of the whiteness of off-white painted panels of very low purity, of different hues and of high lightness. I applied Judd's formula, Harrison's formula and so on, as Dr. Selling has done—also Dr. Selling's formula—and discovered that the best correlation between the visual estimations and the calculated whiteness was obtained by the application of Harrison's formula.

DR. SELLING: In the first place, you ask me how many dyeings I needed for preparing graphs for the prediction of dye formulæ with three dyestuffs. In the main, I only required three dyeings of a given concentration, namely, one for each of the three components. However, you will have to make more than these because there are always mistakes in the dyeings and the measurements and, besides, we have to verify whether the law used holds for the mixture. In the case of acid dyes on wool I made 216 dyeings. If you can find no law for the mixing of the dyes used and you have to make the graphs empirically, I think you will need about 800 dyeings. The graphs obtained are, to be exact, only right for the fabric on which you made the dyeings. By dyeing out the found recipes on fabrics of other weaves or made from yarns with a different twine you will find discrepancies. We experienced this and found that in these cases, too, the predicted recipes are of considerable value.

An album of about 200 or 800 dyeings is not sufficient to cover the whole range of colours which can be formed by admixture of three dyes. About 100,000 different colours can be made with three

dyes. The time and costs required to make the graphs is rather great for one textile factory or papermill but, if the dyestuff manufacturers were to make the graphs and distribute them to the paper and textile industries, then the cost would be very low and the time saved in those industries very great.

Concerning the measurement of whiteness, you are wondering why I took magnesium oxide as white standard and not a surface that was slightly tinged with blue and of almost the same lightness as magnesium oxide. The reason for this was the following. Judd made some experiments as to what is the favourite white surface for the paperman. He did the work with very few (15) observers. From these experiments he concluded that there should be three standards, namely, natural paper white, magnesium oxide and something in between those two. In his further work he decided to use magnesium oxide as the only standard.

The K value used in the whiteness equation has been obtained experimentally by using neutral plates and a new series of papers. Afterwards the found K value was applied to other papers and also on nearly white textiles. In both cases the whiteness equations held good.

Determining the value of K we found that it is not quite a constant. For surfaces which we call near white, the discrepancies are relatively small. Without data at hand I cannot explain why you found a better agreement with Harrison's formula to the visual estimation of whiteness than with Judd's or mine.

Finally, I would remark that if you need estimations and visible observations of near white or coloured surfaces I found that women are far better in their observations than men. I will not go into details now, as this is only an experimental conclusion.

DR. A. H. NISSAN: Before our laboratories are flooded with female assistants (on the basis that they are excellent estimators), is it in order to put a question to the meeting rather than to the lecturer? The paper is dealing with the estimation of matching colour and the lecturer has given us, in my view, an extremely practical, although based on theoretical and scientific bases, way of attacking the problem and he has come within measurable distance of the target. Several of us have spoken to the effect, "Yes, that is all right, but it is not practical. Instruments are costly and methods are complicated." As I am neither a practical nor theoretical man, particularly of this kind, I should like to ask the practical people to tell us how they do estimate colour matching so that we, in our

innocence, can compare the two methods and see which one to follow.

I am afraid this is a point that arises at every discussion in which a new scientific principle is involved. Most of us stand up to say, "Why do not the scientists study practical problems instead of dealing with such abstruse subjects?" Then the poor scientist goes and tackles the practical problem. (Of course, the practical problem has been in the hands of practical men for 2,000 years and they have come to a certain stage.) The scientist began in 1926; he now presents his results in 1950—this is his widow's mite. It may be very little, but this is all he has to offer. Having told him he has to tackle practical problems, practical men simply throw it back in his face. "This is not right; we can do it much more simply."

The practical knowledge we have, we have gathered over a period of immeasurable time ever since man started to observe phenomena, to classify them and pass the results to his sons and daughters. Therefore, I should like to make the point that it is not really fair to compare the results of practical work over the centuries with a few years' work by the scientist. Faraday was asked when he produced his electro-magnetic induction coil—"What is it? What is it good for?" He said: "You never know; one day you may want to tax it." I believe he said that to a Prime Minister. We do know that he was right—not only do they tax electricity, but they cut it! So one day we may be able to tax this form of light studies, perhaps even to nationalise it and use it as an instrument of politics.

Coming back, as an innocent man in these matters, in all seriousness, I would very much like to hear contributions from the practical people as to how they match their colours. How near are first shots obtained; how many shots does one have to fire before getting to the target and how many people would agree that those men are hitting the target afterwards?

THE CHAIRMAN: I have had it in my mind to take some course to broaden the discussion and Dr. Nissan has amply provided the means. It seems a very good proposition at this stage in the discussion to ask practical colour matchers—if there are any here (and I very much hope there are)—to give an outline of their methods.

MR. A. H. RUTT: Mr. Chairman, Dr. Nissan has suggested that the discussion should be brought to a practical level and, whilst one naturally hesitates to join in a discussion at this high technical level, it is so unique in the history of the Technical Section that a man of such technical attainments as Dr. Nissan should appeal for

practical assistance, that I feel the challenge should not go un-answered.

The dyeing of papers with three primary colours is not new. I myself put forward the idea about 15 years ago and have since used my ideas on this matter extensively with some considerable measure of success. It must be appreciated that whilst the difficulties of dyeing paper in the mill can be helped and overcome to some extent by chemical and physical research and experiment, the final word is always with the practical man whose skill and experience dictate whether it should be half an ounce or an ounce of a particular colour to bring it to the right shade.

The first essential for the papermaker, if he is to make a success of dyeing paper, is that he should be fully conversant with the characteristics of the dyes which he is using—not only their tinctorial value, but also the way they react to the pH value of the stuff. This latter is most important and was admirably stressed in a paper given before the Northern Division by Mr. North.* We must, however, assume—if one is to discuss the practical way in which the papermaker dyes his paper—that he is conversant with the dyes he is going to use and proceed to the practical application.

The first essential is that a laboratory matching should be made and, if the chemist making this match is fully conversant with mill operation, his experience should dictate the right proportions to get a reasonable initial match. This information is then passed to the beater house and it is here that one meets the first troubles because of the variables with which a colourman has to contend.

If one is boiling one's own raw materials, such as esparto or straw, there may be a variation in the boiling, in the bleaching and in the washing. Technicians may say that such variables should not be present, but this is an ideal which has yet to be achieved, particularly with straw.

The next variable is the amount of fibre that each beater contains, which suggests a very close watch on beater consistency—closer than is accepted as necessary by the majority of papermills.

And then, the variability of the beating. Whatever method you may employ, be it the touch of the beaterman or some form of freeness tester, the fact remains that every beater in the mill varies due to the wear of the roll and plate or plates and this must inevitably produce a beaten stuff which varies from beater to beater.

All the variables which I have mentioned must upset any rigid scientific control. The lecturer wisely states that he gets satisfactory

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* *Proc. Tech. Sect. P.M.A.*, 1948, **29** (1), 127

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results on wool but he is not quite so certain about paper and it is easily understood why when one considers the variables which, I might add, are by no means finished with yet. The consistency of the machine chests, the drainage rate of the machine wire which varies almost from day to day, the pressure applied at the presses, the rate of drying—all play their part in varying colour and it is here that the practical man finds his skill and experience of such inestimable benefit in being able immediately to assess what a paper needs to get it to the right colour.

Dyestuffs should be added to the beater in as dilute a form as possible. They should be added in plenty of time to enable them to be well beaten into the stuff and everything should be done, if possible, to avoid adding dyestuffs to the mixing chest or the machine chests. If it is added at this stage (and most colour mills have to do this from time to time), then it should be added as dilute as possible after very carefully straining to avoid undissolved dye specks appearing in the paper.

I may not have given exactly what Dr. Nissan requires, but if I endeavoured to tell you all about the practical addition of dyes then I fear that I would be keeping you for a long time, but I hope I have told you sufficient to indicate that whilst scientists have helped in the past and are helping now to solve our problems, they have by no means presented to the papermaker all the answers.

MR. T. TREVOR POTTS: I agree with Dr. Nissan that this very important matter should be referred back to the practical mill man. It is on his experience that commercial colour matching is based.

Unfortunately, so much production of coloured papers is based on repetition of former errors. There is a strong tendency when repeating a making, to put in, first of all, the dyestuffs used for the previous making, find that this does not reproduce the shade, add more dyestuffs, until eventually the recipe is very complicated and, probably, most unsuitable anyway. This empirical method also produces appreciable quantities of 'off-shade' papers which progressively swell the standard range.

Dr. Selling, in his admirable paper today, has at least pointed the way to a means of closer co-operation between the mill laboratory and the papermaker. If he does no more than prove that, for a certain coloured paper, certain dyestuffs are called for and that the addition of other less suitable dyestuffs is wrong, then he will have done a great deal. There is no need for disappointment if it takes some time before the exact quantities of dyestuffs required can be accurately predicted.

THE CHAIRMAN: Dr. Nissan's suggestion has certainly enlivened our discussion and, since I have had to do with colour matching on paper- and boardmachines for many years, I would like to make a contribution of my own before Dr. Selling comments on the practical colour matcher's practice.

Little has been said so far about the choice of dyes; I think Mr. Rutt is unorthodox in making the whole range of dyeings from three primary colours only and I believe it is by far the commonest practice to do something like the following.

A particular shade has to be matched: two dyes are selected, one of which will give dyed hues on one side of the sample and the other on the other side. Thus, if the sample is a middle green, a bluish green dye and a yellow (or yellowish green) dye, in suitable quantities, will give the correct hue and depth of shade. The result may be too bright, however and will then need dulling or saddening; for this a third dye or colouring matter will be needed. The dulling colour may be a black such as nigrosine or carbon black or it may be a colour near to or containing the hue complementary to the main hue (red being used to dull or sadden green, for example). In this way, a recipe of three dyes is arranged which will match the sample. The choice of dyes or colouring materials will be made from those with which the mill is familiar or from dyemakers' trial dyeings (of individual dyes).

A corollary of this practice is that only three dyes are needed in any dyeing recipe and, if no dulling is required, two dyes are sufficient. Unlike Mr. Potts, I believe there has been progress in practical colour matching in this respect. I remember being shown the colour recipe book of a well known mill about 25 years ago—a mill renowned for its coloured papers and for keeping to a close match—and the number of colours used in each recipe was anything up to six. That, I believe to be a thing of the past, so that it is rare for any mill to use more than three colours nowadays. Even so, very occasionally, there may be a good reason for using a fourth. For instance, if a very deep yellow is being matched with Chrysophenine it is often found that if the quantity of Chrysophenine is increased above a certain amount, a dull orange or buff shade is produced instead of the proper bright yellow. If, however, the amount of Chrysophenine is kept below that amount and another yellow dye or colouring matter used to build up the depth required, the deep yellow can be matched quite successfully.

A practical point in selecting the dyes for a particular recipe is concerned with the ease with which adjustments may be made during the run on the machine so as to maintain a match. It is very

much better to have one of the main dyes quite close to the hue required and the second dye some distance on the other side, rather than to have the dyes more or less equally spaced in hue on each side of the colour required. As an illustration—if a middle green is being matched, a bluish green dye and a yellowish green dye might be used in more or less equal proportion. If now during the run the make is a little on the blue side, but correct in depth, the bluish green dye must be reduced in amount and the yellowish green increased —a double adjustment calling for a fairly exact knowledge of the relative colouring strengths of the two dyes. If, however, a bluish green dye and a *yellow* dye are used, a small addition of the yellow dye corrects the blue cast with a negligible effect on depth. In practice, colour correction always seems easier with mixtures of the second type. For similar reasons, the third component—the dulling colouring matter—should preferably be neutral (that is, black) and, failing this, should be quite close to the complementary of the main hue, otherwise additions for dulling purposes change the hue and a double adjustment is needed in this case also.

To my mind, until what is probably the fairly distant time when colour matching based on physical principles is established, it is well worthwhile teaching beater and machine foremen and others concerned in the matching of colours the well established rules of subjective colour mixture, using the Ostwald colour circle or something equivalent, together with rules of convenience and good practice like those just mentioned.

As Mr. Rutt has said, laboratory matches are usually no more than a reasonable guide, mainly I believe, because of the difficulty in arranging to have the same loss of colour in the backwater on the experimental and making machines. If the laboratory recipe is passed to the beater house, the colouring of the first beater being started well on the underside and gradually worked up, making hand trials of the beater either on a hand-mould or on the machine, it is almost always possible to get reasonably near with the first beater so that the shade is rapidly settled down with the second and following beaters.

DR. SELLING: Mr. Chairman, I followed, as far as I could, your practical difficulties and your efforts to solve those problems. I must say there are many difficulties which cannot as yet be solved in a theoretical way. I can understand the question about the use of only three colours. With three given dyestuffs you can fill up a range of colours which can be made with those three dyes. If there is a colour you want to imitate which lies outside the colour

range determined by the three given dyestuffs, you cannot make it. Theoretically, you would have to add a negative quantity of one or two of the three used dyestuffs. In practice this is impossible. In order to make this colour you will have to use other dyestuffs: the choice must therefore be made in such a way as to cover a colour range which is as large as possible and which suits the usual colours as well as possible.

From a commercial and technical point of view, I do not think that one set of three dyes can suffice; for instance, if you have to make a very dull shade, it cannot be made commercially with bright colours. There are more practical difficulties. If you make a match in your laboratory you cannot use the same recipe on the paper machine; nevertheless, if you know the laboratory recipe you have a valuable starting point. There may be still more practical applications I have not experienced. Thus, it is possible to put a colour measurement apparatus on the web of paper on the machine and measure X, Y and Z continuously. With the help of the measured values of X, Y and Z and the diagram for the prediction of dye formulæ, you can see directly what is wrong with the colour of the paper on the machine.

THE CHAIRMAN: I should like to ask Dr. Selling one more question. Does he consider that it is commercially satisfactory to base matchings on tri-stimulus values alone? Is there any danger of finding that what will apparently be a satisfactory match is in fact not satisfactory because of a different appearance of the sample and the match in different quality illumination?

DR. SELLING: If you are making a match and you are using in your imitation other dyestuffs than those with which the sample has been dyed out, there will always be the possibility that the two dyed fabrics which are the same in colour, for example, in daylight, will differ when observed under other sources of light, such as, incandescent light. If you measure the X-Y-Z of a sample you measure them for one of the three standard light sources A, B or C. In general, if the X-Y-Z values of two fabrics are the same for a given source of light then the colour impression under this source of light of those two fabrics will also be the same. In answer to your question whether the tri-stimulus values are for commercial purposes sufficient for matchings, I can therefore say, generally, yes. But the accuracy with which the X-Y-Z values can be measured with some of the commercially available equipment will, in some cases, be insufficient to compete with the colour sensitivity of the eye.

THE CHAIRMAN: If there are no further questions, I will bring the discussion to an end by calling upon our Vice-Chairman to propose a vote of thanks to Dr. Selling.

MR. I. G. BURNS: After listening to Dr. Selling this morning, I had it in mind to say that I rose from the depths of ignorance, but after listening to Mr. Potts this afternoon, I feel it would be much more appropriate to say—seeing that I claim to be a practical paper-maker—that I rise from the depths of abysmal ignorance! I was very glad, in these circumstances, to hear our Chairman put the practical papermaker's case in this matter in what I regard as a much more appropriate light. I think there has been a very considerable advance in day-to-day dyeing technique in papermills in the last few years and I am sure that that advance will continue in the future.

I hold inordinate admiration for anyone who can deliver a paper on a subject such as we have been dealing with today—after all, an extremely complicated and, in some ways, abstruse subject; not only to deliver the paper, but to answer, effectively and extemporan-eously, questions which are posed from many different points of view. I am positively consumed with envy when all this is done in a language foreign to the speaker. For that reason alone, if for no other, I think our very sincere thanks are due to Dr. Selling.

At two successive Annual Conferences of this Section we have had papers on subjects which are essentially scientific, as opposed to the severely practical, in character. On both occasions I have been struck by one thing in particular, which both Dr. Selling today and Dr. Nissan last year, stressed strongly—that is, that these in-vestigations in which they are concerned represent the beginning only of new lines of thought, which may in due course, exert a consider-able influence on practical methods. It, therefore, seems to me to be of the greatest importance that we are fortunate enough to have people like Dr. Selling who are prepared to carry out work of this kind and to commit their investigations to a paper such as we have enjoyed today. In affording the opportunity for these papers to be presented publicly and discussed, it does seem to me that we are fulfilling an important part of the aims and functions of this Tech-nical Section.

I am sure I speak for you all, when I say that we ought to give a most cordial vote of thanks to Dr. Selling for his most excellent and interesting paper and especially for the way in which he has dealt with our many enquiries.

DR. SELLING: Gentlemen, I have listened to all you have had to

say and, of course, I admit I feel honoured by your words. I know that this is wrong, for one must always see that what one has done is but part of a small thing.

I believe theoretical work alone is sterile. Technical practice suffers if there is not a good relation between the laboratory and the mill. In the laboratory we do not know anything about your practical problems and in the mill it is very difficult, I realise, to do theoretical work. If in the laboratory the research workers succeed in solving a problem there will still always be the difficulty of applying the results on the machine. The manager of the mill has to keep up production and the risk he takes if he makes changes in his process is very great. Therefore, I believe we must find a way of developing research work on a technical scale. In Holland, we are not yet so far, though in America, they are and accordingly we see high production. There they produce the most beautiful things and spend a great amount of money on their research. In one factory I know of, there are 10 Hardy instruments which is a capital outlay of about £30,000. They do not do these things for pleasure. America is commercially minded and I believe we have to follow their example. If the laboratories in your country and in mine work independently of each other, I do not think we will ever be able to compete with them.

We made a start at co-operation on problems of gloss and whiteness with Dr. Harrison of PATRA who has been to our country to tell us something about gloss. We were surprised at the work done and I said, "Well, I need not do anything on this subject, because you are doing it and very well, too. I was doing something on whiteness, but nothing that you have done." That as I see it, is the way for laboratories to co-operate. We have divided the various problems on the optical properties of paper between us to avoid duplicating the work. In this way, I believe we can bring something forward and compete with the larger countries.

I thank you very much for the opportunity to tell you something about the work we are doing at the Fibre Research Institute, also for the very kind things you have said. I hope to continue with my work and, if I have new results, to bring them to you once more.

MR. L. G. COTTRALL: Might I just crave your indulgence for one moment? I would like to ask the meeting to pass a vote of thanks to you, Sir, for the excellent way in which you have conducted the proceedings today. I think the meeting will agree that the way in which you have conducted the proceedings today shows that we have made an excellent choice in our Chairman. I should like to congratulate you on your introductory speech to Dr. Selling's paper,

which I think summed up the situation admirably. Gentlemen, I am sure you would like to pass a hearty vote of thanks for the excellent way in which the Chairman has sustained the meeting to-day (*prolonged applause*).

THE CHAIRMAN: Thank you very much indeed, gentlemen. I do not think I should reply to that. I will just declare the meeting closed.