Measurement and Assessment of Substrates Containing Fluorescent Whitening Agents

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ABSTRACT

White, as a color sensation, can be determined by colorimetric methods of measurement. With other than colorimetric methods, no satisfactory correlation between measured value and visual assessment can be expected. The contribution of hue, saturation and luminosity to the degree of whiteness as found by six formulas widely used in industry was analyzed and the results were plotted in the form of a graph. An easy-to-use nomogram for whiteness determination was developed, based on the CIE 1931 2°-color system. Another nomogram is presented which provides an easy means to determine the hue of a sample treated with fluorescent whiteining agents (FWAs). The new whiteness determination is based on the measurement of true tristimulus values for fluorescent samples using the new International Commission on Illumination standard illuminant D 65. The magnitude of the just perceptible difference in whiteness was determined in a panel test using 11 samples and 22 observers. The results were evaluated statistically. Pending standardization of an illuminant, not only for colorimetric measurements, but also for visual assessment of white samples containing FWAs, it would scarcely seem possible to arrive at a more accurate determination of degrees of whiteness. All visual rankings of fluorescent white substrates are widely scattered around a mean value for the different phases of natural daylight. The relative energy emitted by artificial daylight lamps in the near UV region is insufficient in many cases. Xenon lamps are quite satisfactory for instrumental evaluation. In an internationally approved system, with a known hue preference, it would be possible to compare an objective measured value with each subjective result obtained by visual evaluation.

INTRODUCTION

It is very important for all industries using fluorescent whitening agents (FWA) to determine the degree of whiteness of materials. This is particularly true of the soap and detergent industry which consumes more than 50% of all FWAs.

There are two distinct, but closely related approaches to the assessment of whiteness of fluorescent white surfaces: visual perception on the one hand and instrumental determination the other (Fig. 1).

The physiological response to white depends upon whether the observer has normal color vision or not. It is not known how observers with faulty color vision evaluate white. A psychological factor is reflected in the observer's qualitative assessment of white. The less white a substrate, the poorer its quality is judged to be and, conversely, the whiter a substrate, the better its quality is judged to be, although for practical purposes there is no difference between the two substrates. A further psychological factor is the assessment of substrates of different shades. As yet, there is no agreed explanation for hue preference among the various authors (4,10-16,19).

The problems of instrumental determination are of a different order. In the first place fluorescence is physically a totally different phenomenon from, say, the simple reflection of light by nonfluorescent substrates. Fluorescent substrates hence call for different or at least more comprehensive measuring methods. This applies with particular force to the colorimetric determination of the color white. In this connection illumination is particularly important. Until recently there was no suitable standard illuminant for the colorimetric measurement of fluorescent substrates. The CIE (International Commission on Illumination) has now recommended the spectral energy distribution of mean daylight as standard illuminant D 65.

If this spectral energy distribution can be duplicated with artificial light sources it will be possible, with tristimulus filter photometers, to obtain true tristimulus values for fluorescent substrates. The Elrepho tristimulus filter photometer (Zeiss) essentially meets the requirements. On the basis of tristimulus values it should be possible to standardize measurement of whiteness. Before this can be done, the relative contributions of hue, saturation and lightness must be established to whiteness.

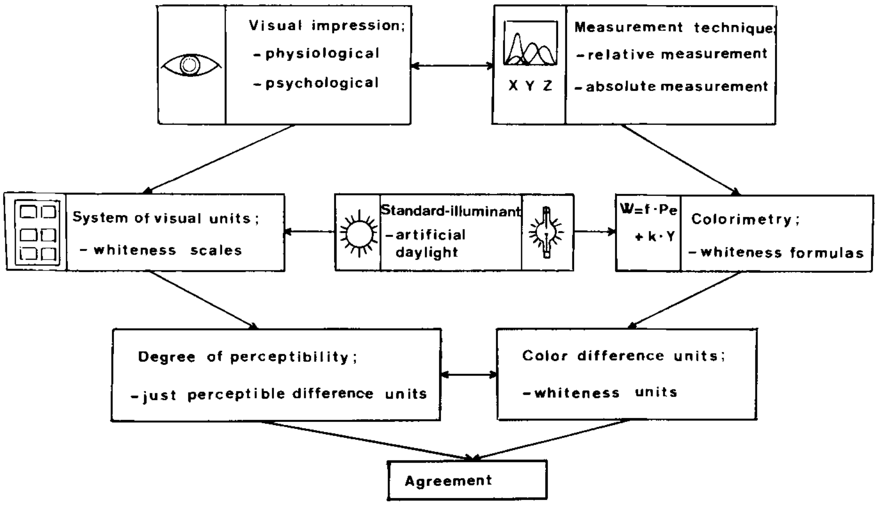

FIG. 1. Evaluation of whiteness of fluorescent speciments (problematic).

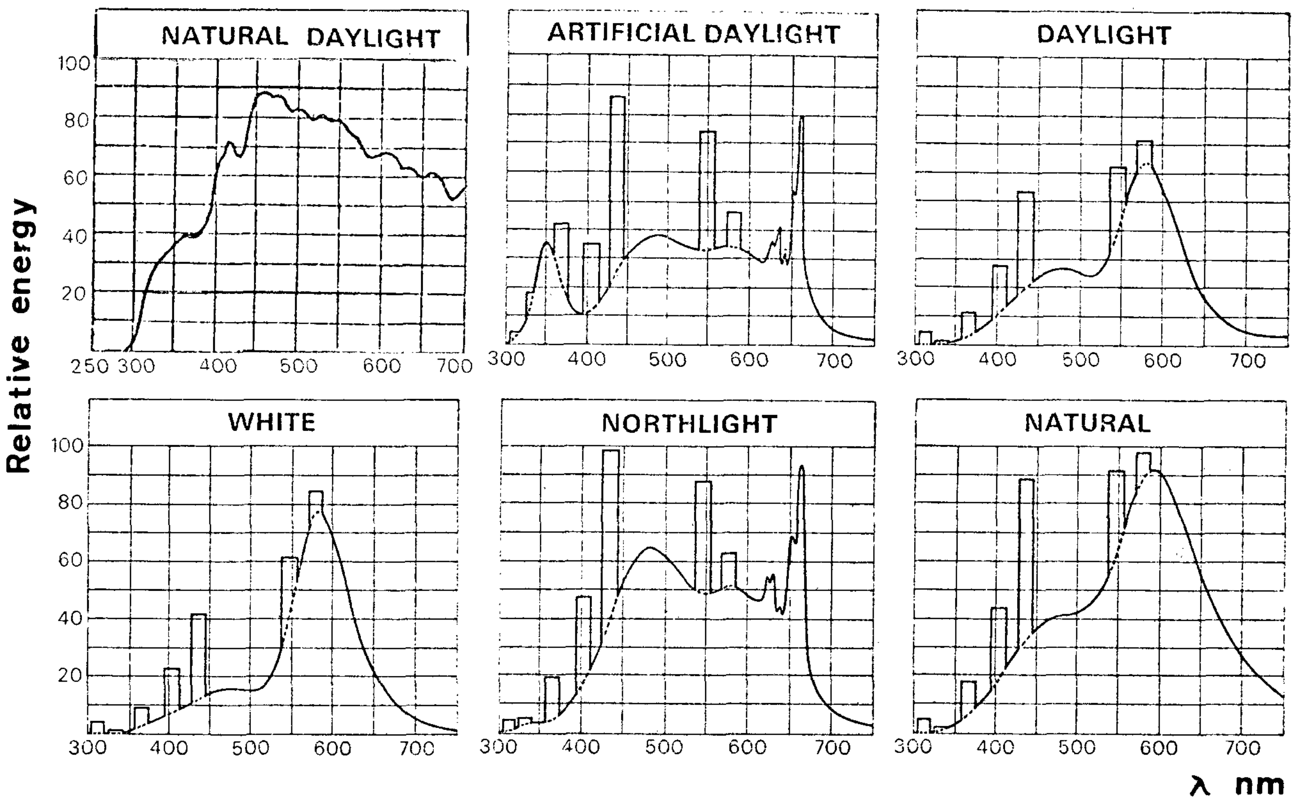

FIG. 2. Spectral energy distribution of different light sources.

The relations between these three parameters should be expressed in a simple formula to permit measurement of whiteness of substrates encountered in industry. To accomplish this, a basis had to be established on which a correlation between visual whiteness assessment and colorimetric measurements could be made. With this in mind, CIBA recently manufactured a lightfast washable whiteness scale of Cibanoid plastic (1). The scale was issued to institutes and industries concerned with visual assessing or processing goods treated with FWAs (6). For instrumental determination of whiteness a useful technique is described.

CHOICE OF ILLUMINANT

Whiteness measured instrumentally on fluorescent white samples illuminated by incandescent lamps will not give a good correlation with results determined visually in daylight. Unfortunately this is frequently overlooked in industry. For visual assessment, no less than for colorimetric measurement using tristimulus filter photometers, an artificial light source is required which has the same spectral energy distribution as daylight, including the UV region. In our experience combinations of fluorescent lamps are unsuitable for the assessment of whitened materials because they emit relative little energy in the UV region (Fig. 2).

In contrast the spectral energy distribution of xenon radiation is very similar to that of daylight (3,4). A close match to natural daylight can be obtained by the use of suitable filters (Loof, private communication). The whiteness scale of Cibanoid plastic is also suitable for testing whether or not the relative UV radiation of a given source is sufficient for assessing the whiteness of fluorescent materials (5).

Measuring Technique

An Elrepho tristimulus filter photometer (Zeiss) (Fig. 3) equipped with a xenon light source was used to measure the whitened materials. New tristimulus filters were developed for this instrument (7).

The xenon radiation in the Elrepho was matched to the new standard illuminant D 65 with a conversion filter. This set-up allowed colorimetric measurements of fluorescent substrates to be carried out with the instrument under close to standard conditions (Fig. 4).

D. Eitle and E. Ganz of CIBA's Physical Department have developed and described a method for determining the true tristimulus values of fluorescent substrates (8). Comparative measurements showed satisfactory agreement between the two methods in the area of white colors.

The features which characterize a color are: hue, saturation and lightness. The corresponding terms in colorimetry are: dominant wavelength, excitation purity and luminosity. These three terms can be obtained by calculation of the tristimulus values, and the chromaticity coordinates for the CIE-1931 2°-color system (9).

For standard illuminant D 65, using a tristimulus filter photometer, the calculation is as follows: (a) $X = RX \cdot 0.770 + RZ \cdot 0.180$; $Y = RY$; $Z = RZ \cdot 1.088$, where RX, RY, RZ are the readings; X, Y, Z, the tristimulus values; and x, y, z, the chromaticity coordinates. The calculation of the chromaticity coordinates is as follows: (b) $x = X / (X + Y + Z)$; $Y = Y / (X + Y + Z)$; $z = z / (X + Y + Z)$.

The chromaticity coordinates x, y, are the ordinates for the CIE 1931 2°-color system. Figure 5 shows the scheme of a color space. The position of nomogram 1 to determine the degree of whiteness is plotted in this color space. Nomogram 1 is described later.

The dominant wavelength $\lambda_d 470$ nm is a mean of a large number of colorimetric measurements on substrates containing FWAs and can therefore be considered as the preferred yellow-blue axis. It was clear that the white substrates had the highest excitation purity along with high luminosity. The bluer and brighter the substrates are, the whiter they appear to be. In the extreme case the highest degree of whiteness would be achieved with a monochromatic light source of about $\lambda_d 470$ nm, i.e., a color on the spectrum locus of the CIE-1931 2°-color system. To enable

FIG. 3. Elrepho tristimulus filter photometer and xenon lamp 150 W1 + conversion filter for standard illuminant D 6500.

this color to be approximately attained, the fluorescence spectrum of a substrate containing FWAs would have to be as monochromatic as possible. Organic substances can scarcely be expected to have this type of fluorescence spectrum, so that the theoretically optimum white will never be reached. Unfortunately it is not sufficient to know these qualitative relationships between whiteness and color characteristics.

Besides knowing the quality of the visual impression of whiteness, we also should be able to express the effect quantitatively, i.e., the degree of whiteness. We thus require a unit of measurement which should be based on a visually perceptible threshold value. The magnitude of this just perceptible difference unit (JPDU) as the smallest visual unit for whiteness must first be visually determined by a panel test, statistically verified and fixed instrumentally (10).

DETERMINATION OF THE JUST PERCEPTIBLE DIFFERENCE UNIT IN WHITENESS

To determine the magnitude of the just perceptible difference unit, we prepared 11 whitened plates of Cibanoid plastic. The plate-to-plate difference in degree of whiteness was very small, the largest difference between the extremes among the 11 plates being about 6-7 JPDU. The plates differed scarcely in lightness and in hue, differing only in saturation. The choice of these 11 plates is such that the relative spectral energy of the illuminant is uncritical (UV filtration by windows). These plates were then assessed in pairs, behind window glass in natural north daylight between 10 AM and 3 PM by 22 experienced observers.

Eleven plates give 55 test pairs which, when examined by 22 observers, give 1210 individual results. These results were statistically evaluated. Experienced observers were chosen because as a rule they also have to assess fastness ratings. Untrained observers are generally not able to assess such small differences in whiteness. These same plates were measured repeatedly on the Elrepho. The whiteness was determined from the mean of the values RX, RY, RZ which in no case diverge more than 0.1%. Evaluation of the observer's results was intended to determine the difference in degree of whiteness still just perceptible, with a statistical certainty of 90%, 95% or 99%, to an experienced observer (Fig. 6).

The statistical evaluation is based on a binomial distribution, the parameter β being evaluated from:

$$\beta = (n_a - n_b)/(n_a + n_b)^{0.5}$$

where: n_a is the number of observers with a preference for sample a, as the whiter of two samples (a and b), and n_b is the number of observers preferring sample b.

Figure 6 shows that approximately 95-99% of the observers were able to distinguish significantly between steps of 5 CIBA whiteness scale units. A few results with more than 99% statistical certainty and higher whiteness than 30 CIBA whiteness units are not mentioned. With smaller differences in degree of whiteness visual assessment becomes so erratic that they can no longer be distinguished significantly with the same statistical certainty. For clarity's sake, we have based our white scales on steps of five units.

The origin of the CIBA method for determining whiteness is discussed below in some detail, and this method compared with the numerous formulas used in industry to calculate whiteness.

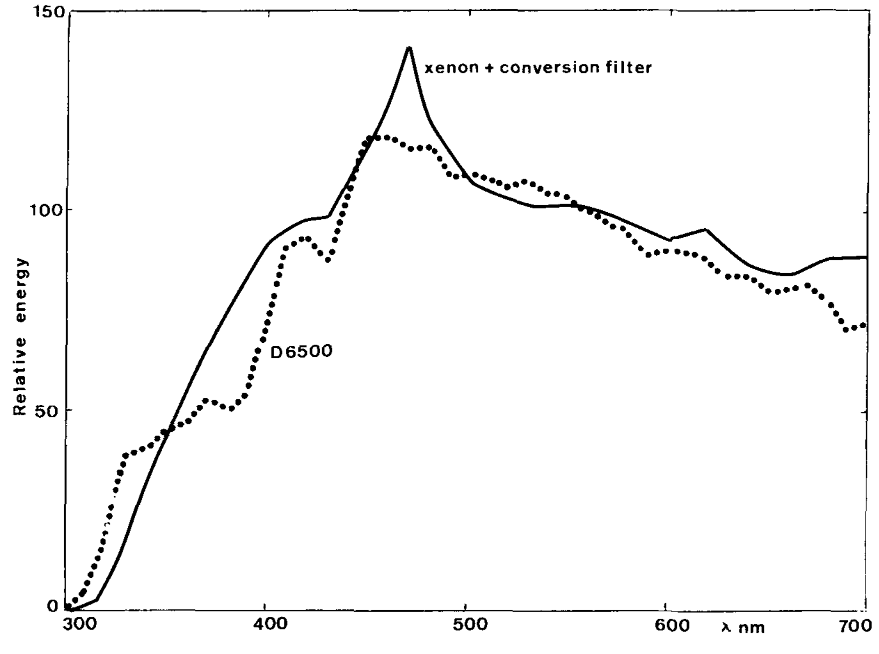

FIG. 4. Relative spectral energy distribution Elrepho + Xenonlamp XBO 150 W-1.

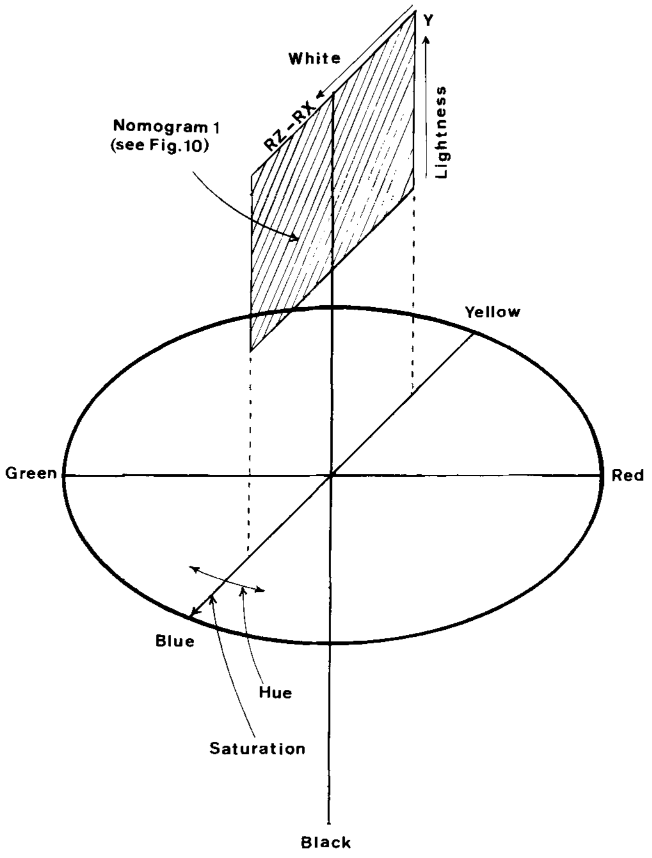

FIG. 5. Organization of a color-perception space (scheme).

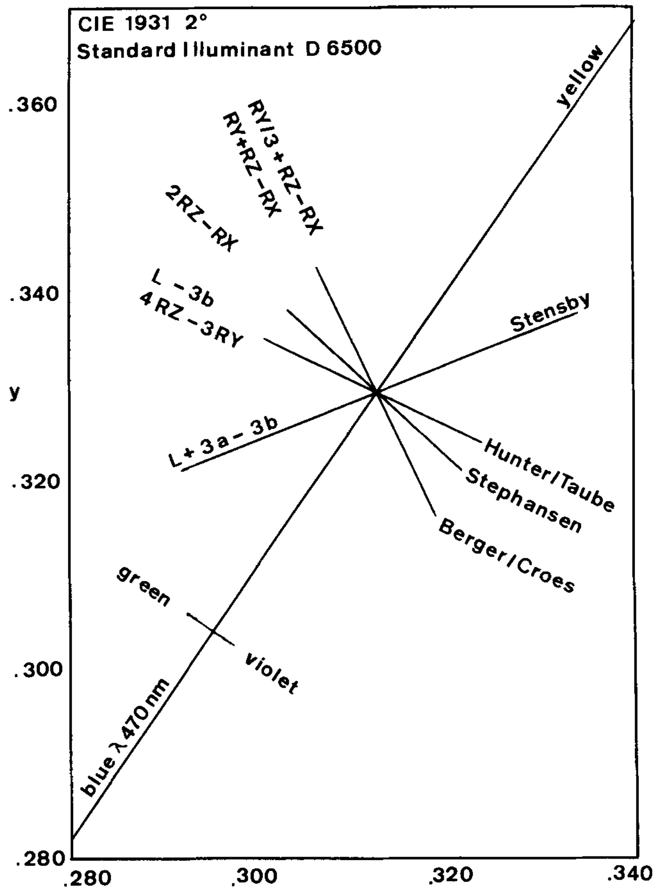

FIG. 7. Equal white by different formulas.

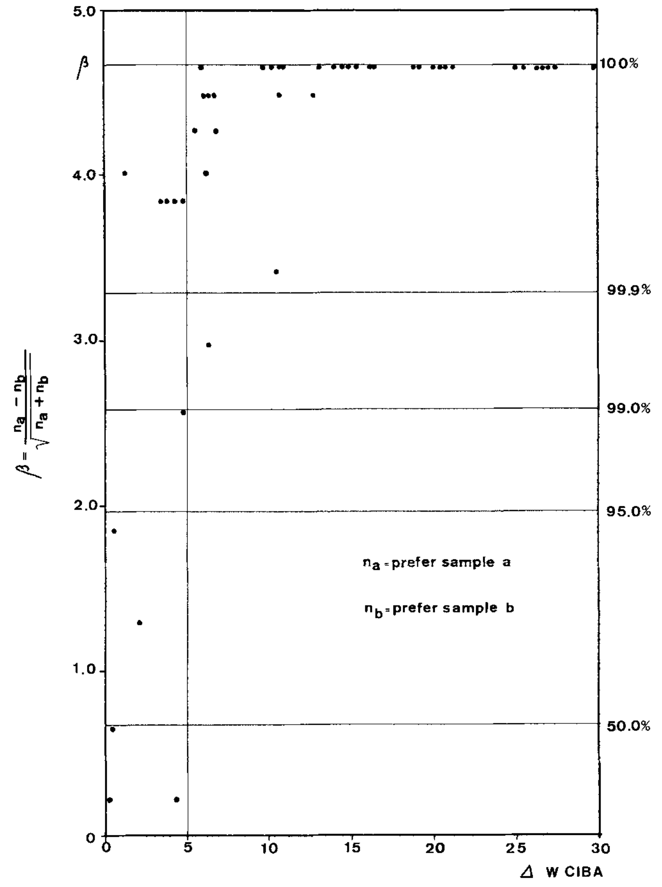

FIG. 6. Statistical evaluation of the just perceptible difference in whiteness.

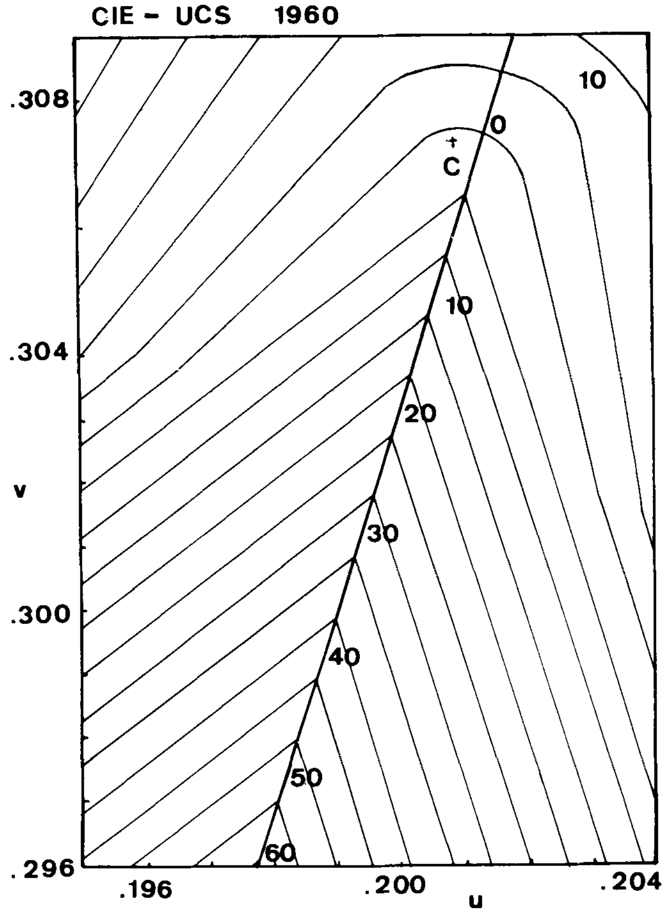

FIG. 8. Equal-white by Vaeck kY + Equ.

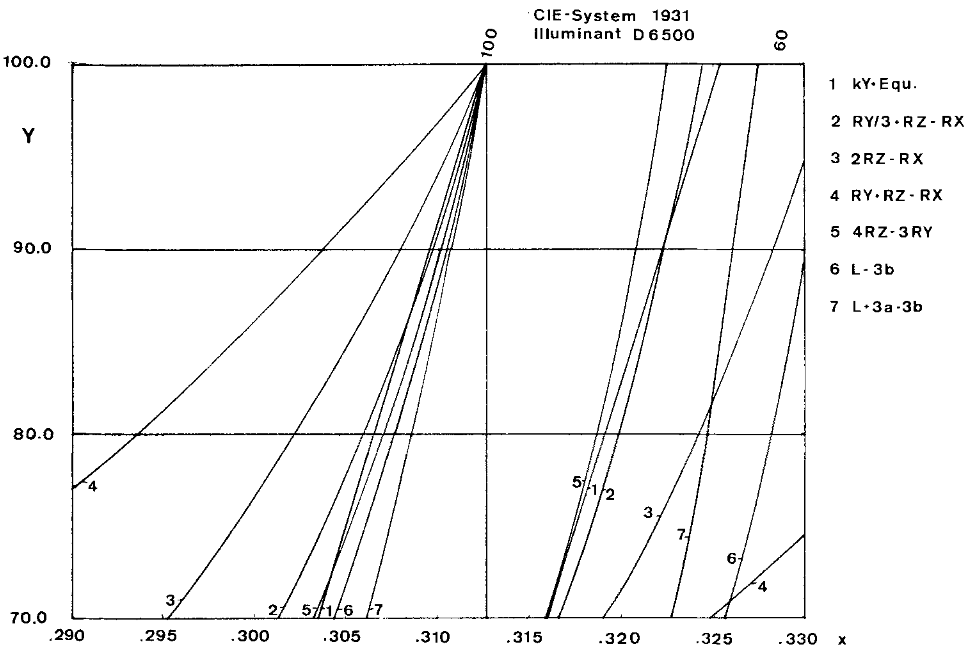

FIG. 9. Comparison of different formulas.

COMPARISON OF DIFFERENT WHITENESS FORMULAS

The formulas selected for comparison are those of Vaeck (11), Berger (12), Stephansen (13), Hunter (14), Taube (unpublished results), Croes (15), and Stensby (16). All these formulas are based on tristimulus values. In our opinion other formulas based only on reflectance values at selected wavelengths without a colorimetric evaluation are basically unsuitable for the precise determination of degrees of whiteness. This group includes fluorescence measurements with simple fluorimeters or photometers. Instruments of this nature are very often used for whiteness measurements.

Figure 7 shows the lines of equal white in the CIE color system calculated from different formulas. It is apparent that the choice of a particular formula automatically imposes a certain hue preference. Starting from the neutral point and an equal luminosity Y of, say, 100%, Stensby's formula clearly prefers violet white materials and rejects whites with a greenish cast. The formulas of Berger and Croes on the other hand seem to prefer whites with a greenish cast. The remaining formulas occupy an intermediate position.

Vaeck has described a method for determining whites of different shades. Unfortunately Vaeck's method of calculating the degree of whiteness is too involved (Fig. 8). Vaeck uses the CIE uniform chromaticity chart (UCS 1960)

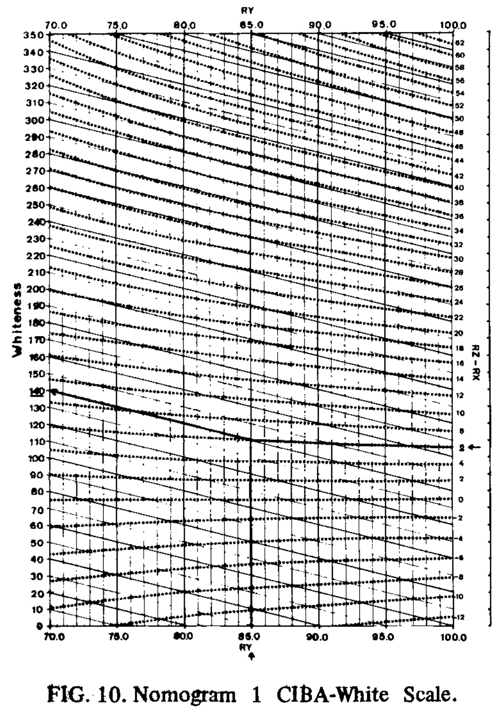

FIG. 10. Nomogram 1 CIBA-White Scale.

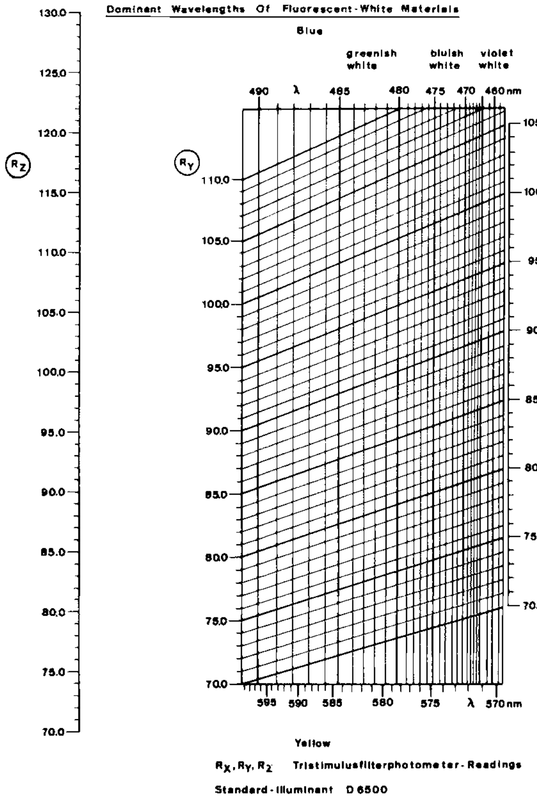

FIG. 11. Nomogram 2 Dominant Wavelengths of Fluorescent-White Materials.

instead of the CIE 1931 2°-system. In Figure 9 these same formulas, as in Figure 7 and 8, are set out again but allowing for luminosity in three dimensions.

Figure 9 shows a vertical section through the color space in the region of white materials through the neutral point. The projection of the optimum yellow-blue axis on the x-axis forms the abscissa, lightness the ordinate. Here again, the plots are of equal white but this time they relate to materials of different lightness with unequal excitation purity. Differences are also found here between formulas which gave the same assessment of shade. On comparison it will be found that lightness as a component of whiteness is differently weighted in each formula. It would also be true to say that for equal lightness, purity is weighted differently from one formula to another. This inconsistency is evidently tolerated by the respective authors, probably for the sake of easier calculation.

The following formulas are arranged in descending order of the contribution of lightness to whiteness: (1) RY + RZ - RX (Croes); (b) 2RZ - RX (modified Stephansen); (c) RY/3 + RZ - RX (RY + 3RZ - RX) (Berger); (d) kY + Equi. (Vaeck); (e) 4RZ - 3RY (Taube); (f) L - 3b (Hunter); (g) L + 3a - 3b (Stensby).

Furthermore all formulas except Vaeck's assess the lightness of yellowish materials differently from that of bluish white materials.

Possibility of an Ideal Whiteness Formula

The main requirements for an ideal whiteness formula are the following:

There should be no exaggerated preference for whites with a greenish or violet cast. There would hence seem to be no justification for preferring a particular hue differing from the preferred mean yellow-blue axis. We therefore propose a method of determining degrees of white which rates as equally white substrates with the same excitation purity and luminosity, irrespective of hue differences (λ_d 460 - λ_d 480 nm).

A certain ratio must be maintained between the contributions of lightness and purity to the degree of whiteness. As previously mentioned, only Vaeck's method meets this requirement. The nonlinearity of the other equi-white lines in Figure 9 is caused by the simple constitution of the formulas. The contribution of luminosity and saturation to the degree of whiteness was visually assessed on substrates of equal saturation and different luminosity and samples of equal luminosity and different saturation. Our results confirmed Vaeck's findings.

On the optimum yellow-blue axis, the lightness of yellowish and bluish white surfaces must provide a defined contribution to the degree of whiteness.

Calculation should be as simple as possible.

If these requirements are considered closely it will be clear that a formula satisfying the first three cannot comply with the fourth. We have therefore developed a nomogram which dispenses with the need for calculation and which still satisfies requirements 1-3.

This nomogram (Fig. 10) represents a section of the color space and spans the region appropriate to materials treated with FWAs. To determine the degree of whiteness the values RX, RY and RZ are measured in the usual way with a suitable tristimulus filter photometer. Only RZ-RX is calculated. The function RZ-RX was chosen because it avoids an extreme hue preference.

Surfaces of equal luminosity and having approximately the same excitation purity are measured as being equally white. In the light of our practical experience of visual assessment this arrangement is perfectly justified. Incidentally, without an agreed standard light source not only for color measurement but also for visual assessment, it seems futile to embark on a systematic study of hue preference. The relationship between luminosity and CIBA whiteness scale units is such that a 5% change in the former corresponds to a 10 units change on the latter scale.

The relationship between whiteness on the one hand and purity and luminosity on the other can approximately be expressed by the formula: W = Pe + Y.

The whiteness is calculated using the formula: W = f Pe + 2Y - 65, where W is the whiteness and Pe the excitation purity given by: $100 (x_w - x_s) / (x_w - x_d)$. [$x_s$, chromaticity coordinate of the sample; x_d, chromaticity coordinate of the spectrum color (λ d) which has the same dominant wavelength as the sample; x_w, chromaticity coordinate of the adopted illuminant D 65; Y, luminosity.] The factor f = 12.3 (2) can be determined from $\Delta W_{CIBA} / \Delta Pe$ and was derived from the steps of the CIBA white scale.

In addition to the very simple and fairly accurate determination of whiteness using nomogram 1, we have also tried to find a simple means of determining the hue of a white surface from the tristimulus values RX, RY and RZ in form of the dominant wavelength λ_d (Fig. 11).

In a second nomogram the dominant wavelength, which serves as a measure for the hue of a material treated with FWAs, can be determined by purely graphical means. To determine the dominant wavelength, a line is drawn between the RX and RZ values on the respective ordinates. The point of intersection between this line and the proper RY line will give the dominant wavelength. Upward extension of the point of intersection gives the dominant wavelength for bluish whites, downward extension the dominant wavelength for yellowish white surfaces. As a rule of thumb, if the straight line connecting RZ to RX is intersected by RY from below, the test specimen has a bluish cast. If RY intersects from above, the test specimen has a yellowish cast.

If the straight line from RZ to RX coincides with the RY value the specimen is achromatic. The accuracy of determination of the dominant wavelength increases with increasing saturation. The two nomograms can be used for any tristimulus filter photometer, provided that the illumination is matched as closely as possible to the new standard illuminant D 65.

REFERENCES

1. Anders, G., J. Soc. Dyers Color. 84:116 (1968).
2. Anonymous, Text. Mfr. 5:211 (1965); D.B. Judd, D.L. MacAdam and G. Wyszecki, J. Opt. Soc. Amer. 54:1031 (1964).
3. Fruhling, H., W. Munch and M. Richter, Die Farbe 5:2 (1965).
4. Grum, F., "Proceedings of the Symposium on Colour Measurement in Industry," Imperial College, Great Britain, April 1967.
5. Anders, G., Fette, Seifen, Anstrichm. 11:881 (1968).
6. Heuberger, H., Textilveredlung 4:101 (1969).
7. Loof, H., Das Papier 6:297 (1967).
8. Eitle, D., and E. Ganz, Textilveredlung 8:389 (1968).
9. Judd, D.B., and G. Wyszecki, "Color in Business, Science and Industry."
10. Vaeck, S.V., Ibid. 5:275 (1967).
11. Vaeck, S.V., Ann. Sci. Text. Belg. 1:(2966).
12. Berger, A., Die Farbe 8:4-6,187 (1959).
13. Stephansen, A., "Norwegian Paper Research Institute Report," 1933.
14. Hunter, S., J. Opt. Soc. Amer. 48:597 (1958).
15. Croes, A.W., J. Opt. Soc. Amer. 49:830 (1959).
16. Stensby, P.S., Soap Chem. Spec. 43:80 (1967).
17. Atlas Lighting Ltd, Reprint: "Fluorescent Tubes and Discharge Lamps."
18. Schultz, U., R. Lehmann, "Zur technischen Realisierung von kunstlichem Tageslicht," Paper presented at the AIC-Congress, Stockholm, June, 1969.
19. Goldwasser, S., Soap Chem. Spec. 9:62 (1962).

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