Whiteness and Fluorescence of Fabrics

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Abstract

A method was devised for measuring the whiteness of fabrics containing optical brighteners. It is simple in operation and gives excellent agreement with the visual appraisal by 27 observers of the whiteness for fabrics with different values for their fluorescence, lightness, yellowness or blueness, and redness or greenness. The fabrics contained different quantities of various blues and optical brighteners.

Apart from duplicates it requires only four measurements for each surface, viz., lightness, tristimulus amber and blue reflectance, and the tristimulus blue part of the fluorescent light. Yellowness or blueness, redness or greenness, fluorescence effect on the whiteness, whiteness without fluorescence, and whiteness including fluorescence are calculated from the measurements.

The method also indicates which fabrics cannot be called "near white" because they are too gray or too strongly colored. It can be adapted to different compositions of the incident light with regard to the relative intensity of the ultraviolet and visible portions.

Visual Whiteness Without Fluorescence

An ideally white surface has a reflectance of 100% for all visible light rays. If white light falls on such a surface, the re-emitted light has the same composition as the original light rays with regard to its spectral composition, i.e., the intensity of the light rays of different wavelengths.

When the surface re-emits rays of all wavelengths to the same degree but not completely, it appears to be more or less gray and still uncolored. Its lightness is less than 100%, and its redness, greenness, yellowness, blueness, etc., is = 0.

When light-rays of different wavelengths are re-emitted to different degrees, the lightness again is less than 100% and the surface appears to be colored. For paper and textiles violet and blue light is usually re-emitted to a smaller degree than light rays of other, longer wavelengths: green, yellow, orange, and red. Then they appear to be yellowish.

The yellowish tinge can be taken away by the addition of a bluing. This re-emits yellow light to a smaller degree than the light of other wavelengths. In general, the lightness of the bluing is smaller than that of a yellowish textile. Therefore the lightness of the surface is decreased further, i.e., its graying is increased; nevertheless the surface may appear to be "whiter" than in the absence of bluing. One could say that, in the re-emitted light, the balance of yellow and blue light rays is restored so that it does not make a colored impression. Therefore yellow and blue are called complementary colors. Likewise red and green are complementary.

Surfaces which are nearly "ideally white" can be put visually into an order of decreasing whiteness. In doing so, the system (eye-nerves-brains) of the observer weighs the importance of differences in lightness and in color one against the other.

Visual Whiteness Including Fluorescence

Whiteness can also be increased by the presence of an "optical brightener" (OB) or "optical white" (OW) on or in the substrate (paper, textile, plastic). Such compounds transform incident ultraviolet rays partly into visible light. The change of electromagnetic rays of one wavelength into rays of another wavelength is called fluorescence; the emitted light should be nearly white and should have a slightly bluish tinge; the blue may be on the greenish or the violet (reddish) side. This is more or less complementary to the yellowish color of the visible light re-emitted by the substrate itself. The small excess of blue in the fluorescent light compensates for the lack of blue in the latter. In the combination of the two kinds of visible light all colors or wavelengths can be in a balance corresponding to white. Moreover the total quantity of light coming from the surface is increased, i.e., its lightness appears to be higher.

The sensitivity of the human eye for blue light with very short wavelengths, between 400 and 420 nm, is very small. Most optical whites convert such blue light into light containing rays of longer wavelengths to which the eye is more sensitive. Sunlight, daylight, and the light from fluorescent lamps contain the visible light of all wavelengths and ultraviolet rays so that the above-mentioned effects are obtained. Light from incandescent bulbs, surrounded by a lamp shade, contains few, if any, ultraviolet rays or blue light of short wavelengths. In such light, linen in a cupboard and on beds is viewed in the evening and at night.

Therefore it is useful to assess or to measure the whiteness of fabrics in two kinds of light: in visible light only and in visible light + U.V. rays.

This is also desirable because one often wishes to know the effects of detergent composition and washing process on graying, yellowing, and whiteness apart from the effect of the optical brightener.

In these investigations, the ranking orders for increasing the whiteness of a large series of fabrics containing different quantities of various bluings and optical whites are determined by panels of 10 to 27 observers. All fabrics of one series are compared in pairs. The ranking orders assigned by individual observers agree very well, e.g., for a series of 12 fabrics assessed by 27 observers (women and men between 16 and 60 years of age) the level of significance for the agreement was $<<0.001$ ($x^2 = 215$) according to the statistical method of m rankings (13).

Existing Instrumental Methods

The appraisal of whiteness by means of the human eye is laborious and time-consuming. It can only be done by means of comparisons. Several authors have tried to avoid these disadvantages by the use of measuring instruments (1,2,5,9,10). A survey of the field with many literature references has recently been made by Stensby (15). Some methods relate explicitly or implicitly to the whiteness of paper or plastics, others to that of textiles.

Investigations in the author's Institute showed that the proposed methods lacked either agreement with the visual appraisal of fabrics or necessitated rather complicated calculations, e.g., the formulae proposed by Berger (3) and by Friele (5) gave correlation

TABLE I

Whiteness Including Fluorescence of Washed, Originally Clean, White Bleached Cotton Test Pieces Measured Values Compared with Visual Estimations[a]

Sample	8	K	1	M	7	3	S	C	2	9	6	0
For visible light only with filters between light source and fabric												
Lightness	88.10	86.72	87.14	84.36	87.95	87.41	88.90	84.10	85.99	82.08	82.72	90.26
Tristimulus blue reflectance	83.75	83.09	82.85	81.72	83.35	82.98	85.51	79.28	81.36	77.48	78.22	86.70
Yellowness	4.3	3.6	4.3	2.6	4.6	4.4	3.4	4.8	4.6	4.6	4.5	3.6
Whiteness, W_v	78.6	78.8	77.4	78.0	78.1	77.8	81.7	73.7	76.0	72.3	73.0	82.8
Blue reflectance for all visible light + ultraviolet rays from a xenon lamp, B_x	91.5	89.3	91.5	85.5	87.7	87.1	87.7	81.9	83.7	79.3	79.8	85.8
Whiteness according to Berger $W_{Bx} = G + 3(B-A)$ for all visible light + UV rays from a xenon lamp	96.8	96.4	92.3	87.7	85.3	84.8	87.1	79.0	80.3	75.5	76.2	77.1
Whiteness, W_d, including the tristimulus blue part of the fluorescence, the latter having been measured with ultraviolet rays from a												
xenon lamp, W_{dx}	111	107	106	98	98	97	95	90	90	86	86	83
Tungsten over-voltage lamp, W_{db}	108.7	106.5	104.8	99.5	97.0	97.3	96.6	91.4	93.0	88.9	87.8	84.2
Mercury arc W_{dk}	108.8	106.2	105.5	99.2	96.9	97.3	96.3	91.0	91.9	88.3	87.3	83.4
Average ranking order according to visual comparisons for whiteness in daylight by 27 observers	1.7	2.7	3.0	4.2	5.2	5.9	6.1	8.5	9.2	9.8	10.4	11.3

[a] The 27 ranking orders of the 27 observers agreed with each other significantly: $p \ll 0{,}001$. ($X^2 = 245{,}6$) according to the method of m rankings (11).

All differences in average ranking number between pairs of samples were significant, $p \ll 0{,}05$, with only the following exceptions: 8-K; K-1; 7-3; 3-S; C-2; 2-9; 6-0.

The blue reflectance for all visible light + ultraviolet rays from a xenon lamp B_x shows no correlation at all with the visual whiteness in daylight; correlation coefficient 0.61.

The whiteness calculated according to the equation by Berger from measurements will all visible light + ultraviolet rays from a xenon lamp has a correlation coefficient = 0.82 with visual appraisal.

The correlation of W_d with the visual observation is very good; correlation coefficients 0.94–0.97.

Correlation coefficients were calculated by means of Kendall's rank correlation method (12).

coefficients with visual appraisal equal to 0.82 and 0.61 only for the samples of Table I and Figure 5.

The formula proposed by Taube (16), which was recommended by Hunter (8), has the disadvantage of having a low precision; its experimental error amounts to seven times the experimental error of one single reflectance measurement. This precludes the use of relatively simple and inexpensive measuring instruments.

The method by Vaeck and van Lierde (17) gives good agreement with visual appraisal; however it necessitates rather complicated calculations in order to transform the measured reflectance values into coordinates of the MacAdam uniform chromatic scale.

Therefore a need exists for a simple method which gives a good correlation with the visual appraisal of whiteness, including fluorescence.

Principles of Measurement

For the normal human eye each light impression of moderate intensity depends on three different quantities. In light of low intensity, e.g., moonlight colors are not seen, only lightness; by light of high intensity the eye is blinded.

Lightness is always zero for absolute black. It is equal to 100 for an absolutely white, nonfluorescent surface, e.g., for magnesium oxide, freshly deposited from the vapor phase. Such a surface re-emits diffusely all visible light which falls on it. Near-white surfaces have lightness values between 80 and 100, e.g., bleached white cotton has values between 80 and 92. The lightness of gray surfaces has values between 0 and 80; the latter limit is rather arbitrary. Colored surfaces also have lightness values between 0 and 100, usually between 0 and 85; these values are higher for surfaces which, according to the human eye, are "lighter" under the same illumination. The lightness impression is one of the three stimuli ("sensitivities") of the human eye, as defined by the Commission Internationale d'Eclairage (International Committee on Illumination, CIE or ICI) (14).

As the two other quantities by which color is defined, one may choose yellowness and redness or their complementaries, blueness and greenness. This choice is made because the most common discolorations of undyed textiles are yellowness and its opposite, blueness. The third quantity should be independent of the first two; this is true for redness and its opposite, greenness.

The color of a surface with regard to yellowness and redness can be represented by a point in a mathematical plane containing a system of coordinates.

Positive values of one coordinate may indicate the degree of yellowness; negative values of the same coordinate indicate the degree of blueness. In a Cartesian or rectangular system positive values of the other coordinate may indicate the degree of redness; negative values of that coordinate indicate the degree of greenness. The origin of the system corresponds to neutral or colorless, i.e., gray, between the extremes of absolute black and white.

Another line may be erected perpendicular to the plane in the origin of the coordinate system. The coordinate along this line may indicate the lightness. Then it is possible to characterize each color wholly by means of a point in space. The points representing all colors are situated in a solid, three-dimensional figure, called a color solid. For more details about color solids the interested reader is referred to the standard books on the subject, e.g. by Judd and Wyszecky (10).

Surfaces with the same whiteness may have different values for lightness, yellowness or blueness, and redness or greenness. The points in the color solid representing their "colors" will be situated on a plane. Points representing the "colors" of other surfaces with a constant value of whiteness which is different from the first mentioned are situated on another plane.

In space the distances between two points can be calculated from their coordinates by means of equations which contain square powers and roots. However when the distances are small, linear approximation equations can be used. This simplifies calculations greatly. Likewise it will be shown in this paper that, for near-white fabrics, whiteness can be calculated by means of a simple, linear equation from lightness, yellowness (or blueness), and redness (or greenness), provided that these quantities are measured in the right manner.

It is relatively easy to measure lightness, but for measuring yellowness and redness more complicated instruments are necessary. However these two quantities can be calculated easily, by simple subtraction, from measurements made by simple and inexpensive instruments. The quantities to be measured are tristimulus blue and tristimulus amber reflectances or remissions. The names are derived from the fact that there exists a close relationship with the other two sensitivities of the human standard observer besides lightness, as defined by the Commission Internationale d'Eclairage (14).

A system for measuring lightness and tristimulus blue and amber reflectances was published by Hunter 6,7). When buying an instrument one should make sure that the combinations of light source (color temperature), filter transmittance, and photocell sensitivity are in accordance with the specifications for tristimulus measurements (6,7,14).

The lightness, G, of a surface is expressed as a percentage of the lightness of the whitest substance known, magnesium oxide, freshly deposited from the vapor phase. A decrease of the lightness is equivalent to graying. Hence graying is also expressed as a percentage of the lightness of magnesium oxide, which is about 7% higher than that of the whitest textiles without fluorescent brighteners.

Likewise the tristimulus blue and amber reflectance or remittance values, B and A, are expressed as percentages of the corresponding values of magnesium oxide. In practice, secondary standards, which are gauged against this primary standard, are used.

Yellowness can be calculated by the formula

$$J' = \frac{G - B}{G} 100$$

and redness by

$$K' = \frac{A - G}{G} 100$$

The lightness G of a white cotton standard test fabric varies very little. Therefore yellowness J and redness K can be calculated by means of the simpler equations

$$J = G - B \qquad \text{and} \qquad K = A - G$$

A negative value of J indicates blueness, a negative value of K, greeness.

As a rule graying and yellowness have different causes. Therefore separate figures for these entities are useful in a search for causes and remedies.

Proposed Equation Without Fluorescence

Sometimes it is necessary to "compare" the whiteness of fabrics, which have different values for graying (or lightness), yellowness, and redness. This comparsion can be made by eye, preferably by a number of observers. Extensive investigations which the author has made showed that the whiteness in visible light only, W_v, can be calculated according to the equation:

$$W_v = 2B - A = G - (A - G) - 2(G - B)$$

or in words: whiteness is equal to lightness minus the sum of the redness and twice the yellowness.

Comparison of the results of this equation with the visual estimation of the whiteness in light from incandescent bulbs (tungsten) by 27 observers were carried out with large series of fabrics, for which

$$5{,}5 \geqslant G - B \geqslant 1; \quad 1{,}0 \geqslant A - G \geqslant -0{,}3; \quad G < 82$$

This means that in visible light only, without fluorescence, the fabrics were not too yellowish, too bluish, too reddish, too greenish, or too gray to be called "near white." Perhaps some of the above limits can be drawn even somewhat wider without making the expression for W_v invalid.[1]

The equation for W_v should not be mixed up with the whiteness formula by Stephansen:

$$W_s = 2R_{430} - R_{670}$$

in which R = reflectance for monochromatic light with wavelengths 430 or 670 nm respectively.

Stephansen invented his formula for the calculation of the whiteness of paper. The requirements for a paper to be called visually "white" however are different from those which the housewife applies to near-white fabrics. Stephansen's formula gives a less effective correlation with the appraisal of the whiteness of fabrics by the human eye than the above formula for W_v. In the latter equation A, B, and G are reflectances for whole bands of wavelengths in the visible spectrum; these bands are chosen in accordance with the three sensitivities of the human eye. Therefore they are called tristimulus values.

It is desirable that, in the tristimulus measuring instrument, the tristimulus filters shall be placed be-

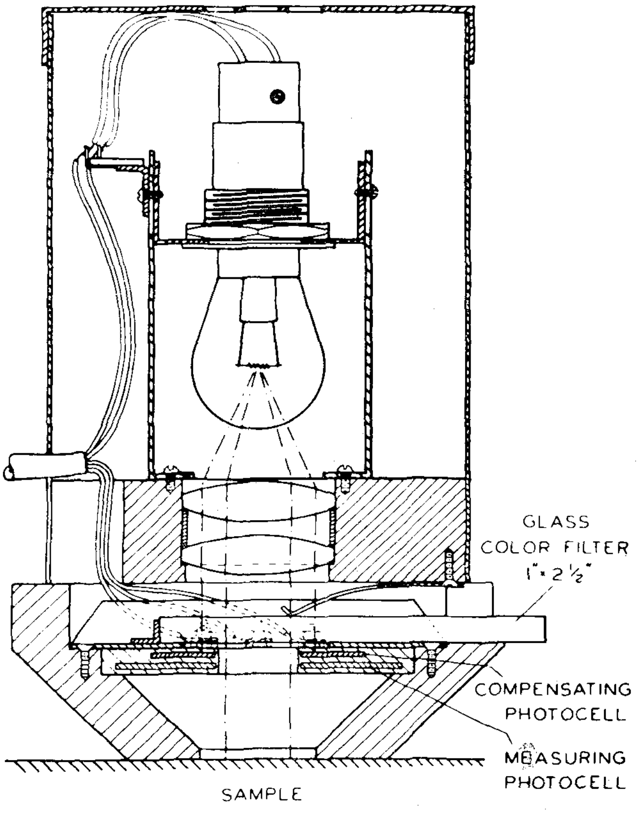

Fig. 1. Longitudinal section of a convenient arrangement for measuring reflectance values of textiles for visible light only: light source—tristimulus filter—sample—measuring photocell. In this way the presence of optical brighteners on the sample has hardly any effect on the measured reflectance values.

The color temperature of the light source (a.o. voltage), the transmittance of the filter for a part of the visible spectrum, and the sensitivity curve of the cell have to be such that, by their combination, the three sensitivities of the human eye in visible light of standard composition are easily matched.

The photo-electric cells have an annular shape. Therefore the average reflectances in warp and weft direction of the fabric are automatically obtained.

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[1] At any rate, it is useless to calculate a "whiteness" figure for yellow, blue, red, green, or gray fabrics.

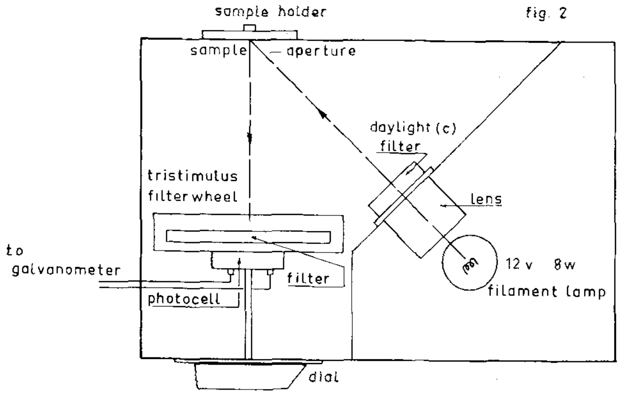

FIG. 2. Diagrammatic representation of a less convenient arrangement for measuring reflectance values of textiles for visible light only: interchangeable tristimulus filter between sample and photo-electric cell.

An extra filter between lamp and sample is necessary in order to cut off the UV rays and nearly all blue light of short wavelengths. The color temperature of the light source (a.o. voltage), the transmission curves of all filters as a function of the wavelength, and the sensitivity curve of the cell have to be such that, by their combination, the three sensitivities of the human eye in visible light of a standard composition are easily matched.

The incident light comes from one direction. Therefore the reflectances in warp and weft direction of the fabric have to be measured separately.

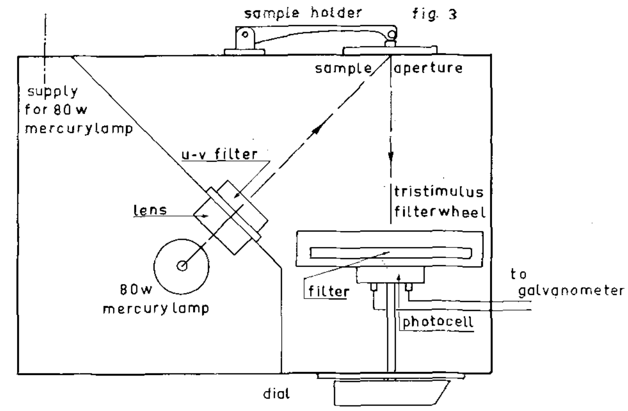

FIG. 3. Arrangement for measuring the tristimulus components of the fluorescent light emitted by a fabric containing an optical brightener and irradiated by UV rays only. As a source of UV rays an incandescent lamp or a xenon lamp can also be used.

The transmittance curve of the tristimulus filters and the spectral sensitivity of the photocell have to be such that, by their combination, the three sensitivities of the human eye for visible light are matched.

The combination of the measurements with visible light only of Figures 1 or 2, and those with UV rays only of Figure 3, to whiteness values for light containing rays both of the visible and the UV regions has been described in the paper.

tween the light source and the fabric to be measured (Figure 1). This position of the tristimulus filters is important. It makes the quantity of blue light rays with short wavelengths (shorter than 420 mm), which fall on the fabric, very small. Otherwise these rays would cause some fluorescence if optical white were present on the fibers, and this would cause arbitrary increases of the tristimulus value A, B, and G. In the arrangement of Figure 2 the filter between light source and photo-electric cell should cut off all UV rays and nearly all blue light of short wavelengths.

Simple Equation Including Fluorescence

The fluorescence can be measured separately and in the right way by illuminating the fabrics with ultraviolet rays and filtering the re-emitted visible light rays through a tristimulus blue filter. This again is important. When the whole fluorescence (all visible light) is measured, no good values for the whiteness, including fluorescence, are obtained. Behind the filter is a photoelectric cell which sends its weak electric current to a sensitive galvanometer, which indicates the value F_B. The product of the transmission curve of the filter and the sensitivity curve of the photo-electric cell must have the right tristimulus blue shape (part of the CIE Z-curve) (Figure 3).

The contribution of the fluorescence to the whiteness is calculated to be $n.F_B$ so that the whiteness in daylight containing ultraviolet rays W_d is:

$$W_d = W_v + n.F_B$$

The factor n depends on the sensitivity of the apparatus and on the wavelength-composition of the ultraviolet rays. When these are given, n has been shown to be a constant. Its magnitude was found by comparison with a large series of fabrics containing different quantities of different blue pigments and dyestuffs and different whites.

The comparisons were made with ultraviolet rays from a xenon arc (continuous and discontinuous line spectrum), a mercury vapor arc (discontinuous line spectrum), a tungsten filament over-voltage bulb (continuous spectrum).

Three factors n_x, n_k, and n_b were obtained respectively, which assigned to all fabrics such values for W_d that their order of increasing W_d was the same as the order of increasing visual whiteness in daylight according to 27 observers.

After the right values of n_x, n_k, and n_b had been found in this way, the most encouraging thing was that the calculated values for

$$W_{dx} = W_v + n_x.F_{Bx}$$
$$W_{dk} = W_v + n_k.F_{Bk}$$
$$W_{db} = W_v + n_b.F_{Bb}$$

agree within experimental error. Some examples are given in Table I and Figures 4, 5, 6, and 7.

The values for W_{dx} are the least accurate because

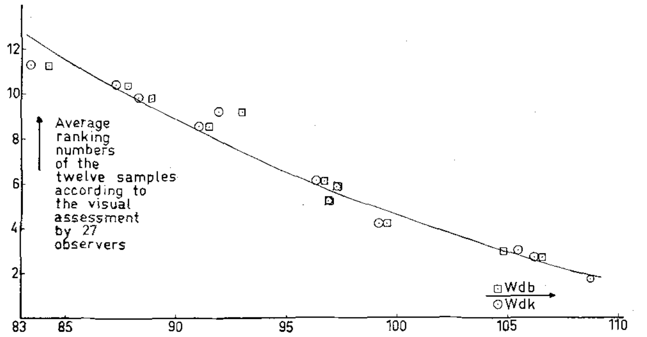

FIG. 4. Excellent agreement between whiteness of 12 samples in daylight containing UV rays, assessed by 27 observers, and whiteness calculated from a combination of measurements according to Figures 1 and 3.

W_{db} = whiteness in daylight; an incandescent over-voltage projector lamp with continuous spectrum was used as a source of UV rays only, for measuring the tristimulus blue part of the visible fluorescent light, emitted by the optical brightener on the fabric (Figure 3).

W_{dk} = whiteness in daylight; a mercury lamp with discontinuous spectrum (line 366 nm) was used as a source of UV rays for these measurements (Figure 3).

The whiteness in visible light only was measured according to Figure 1.

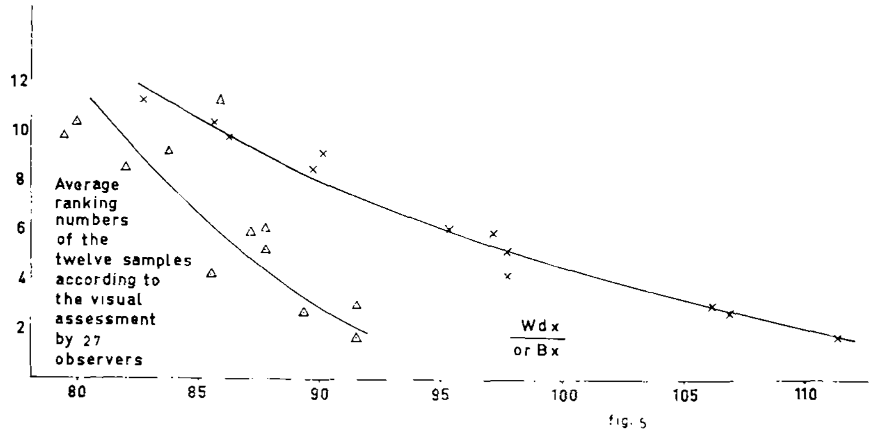

FIG. 5. No agreement between whiteness of 12 samples in daylight containing UV rays, assessed by 27 observers, and $B_x = \triangle$, the total tristimulus blue reflectance when the samples are irradiated by all visible light + UV rays from a xenon lamp. Excellent agreement again for W_{dx} = whiteness in daylight; a xenon lamp with semidiscontinuous spectrum was used as a source of UV rays only, for measuring the tristimulus blue part of the visible fluorescent light emitted by the optical brightener on the fabric.

The whiteness in visible light only, W_v, was measured according to Figure 2.

F_{Bx} had to be calculated as the difference of two measurements: one with all the rays from the xenon arc, visible + ultraviolet rays, and the second one with only the visible light rays. On the other hand the measurement of F_{Bk} or F_{Bh} is direct and straightforward with only the ultraviolet rays from either of these two sources. Theoretically the formula should be:

$$W_d = W_v + m(2F_B - F_A)$$

Here F_A = tristimulus amber-part of the fluorescence light.

However, for all optical brighteners tested, F_A is so small that the experimental errors of its measurement are more important than its variations with regard to F_B for different optical brighteners or, in other words,

Δ F_A caused by experimental inaccuracy >

Δ $\frac{F_B}{F_A}$ caused by changing the optical brightener

and $n = m(2 - \frac{F_A}{F_B})$ is constant

for different optical brighteners within experimental error.

Another advantage of the above formula for W_d is that the value of n can be chosen in accordance with lighting conditions which prevail in the visual assessments of the whiteness.

The institute samples were compared in pairs, one meter behind a window on the north, when the sun was shining outside the building. When the incident light contains relatively more or less ultraviolet rays,

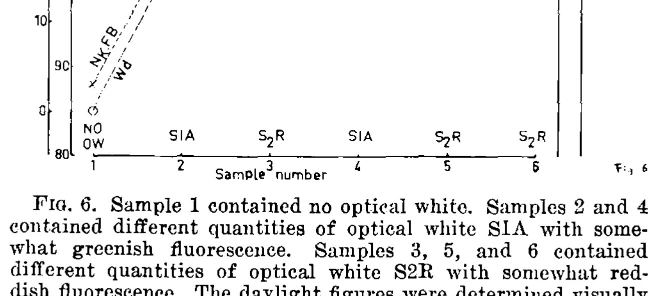

FIG. 6. Sample 1 contained no optical white. Samples 2 and 4 contained different quantities of optical white SIA with somewhat greenish fluorescence. Samples 3, 5, and 6 contained different quantities of optical white S2R with somewhat reddish fluorescence. The daylight figures were determined visually in the laboratory of the producer of the optical whites.

Excellent agreement between these daylight figures on one hand, and $N_k.F_B$, the tristimulus blue part of the fluorescent light emitted by the optical white on the fabrics, on the other hand. The measured whiteness in daylight, W_d, runs almost parallel to $N_k.F_B$ because the whiteness in visible light only, W_v, was also the same for all samples; and $W_d = W_v + N_k.F_B$. There was no agreement at all between the visual daylight figures and the total fluorescence (total amount of visible light emitted by the optical whites on the fabrics when irradiated by UV rays).

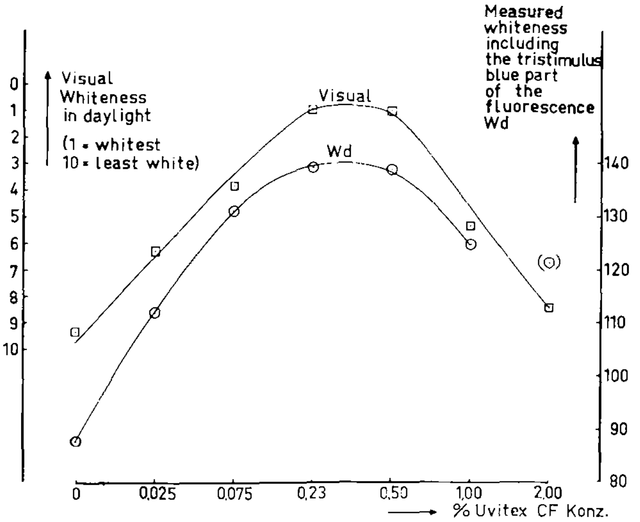

FIG. 7. Seven samples containing different quantities of the same optical white. There was excellent agreement between the measured values of W_d and the visual appraisal of their whiteness in daylight. For the sample containing 2.0% optical white, the yellowness J was too large (= 6,3) so that no value for W_d could be calculated. Both curves show clearly the optimum concentration of the optical brightener with regard to whiteness in daylight containing UV rays. Measurement of W_d is more rapid and convenient than visual assessment.

higher or lower values of n would result from the comparison of the visual order of whiteness with the measured values of W_v and F_B.

Measurements of W_v (A, B, and G) were carried out with light as from source C, defined by the Commission Internationale d'Eclairage (4). This is now accepted as a standard light source in most countries.

The values of n for different instruments can be ascertained by means of measurements of one or more standard fluorescent surfaces, e.g., fabrics containing optical whites, or standard fluorescent plates.

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