Colorant Formulation and Color Control in the Textile Industry

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The development of instrumental color measurement and its application to color problems in the textile industry are reviewed. The areas considered are: color formulation, color control, color tolerances, standards, and color faults and their evaluation. In each of these areas a fairly detailed account is given of the capabilities of modern instrumentation and theory to deal with the problems. Many practical problems in the coloring of textiles lend themselves to instrumental solution. To realize the potential of these methods, we do not need an abundance of new theories but rather more precise and reliable instrumentation. Perhaps, more importantly, we need colorists thoroughly trained in the theory and practice of spectrophotometry, color measurement, and color science.

Color is often one of the most important feaures of a textile material. While many other physical, chemical, and mechanical properties are important in textile design, style and fashion dictate a major role for color. This article is concerned with textile color and the application of instrumental color measurement to some textile color problems.

A. C. Hardy's research at MIT from 1928 to 1935 resulted in the development of a recording spectrophotometer. This instrument, commercially developed by the General Electric Co., is used to measure the reflectance of a material rapidly and precisely. Hardy was so confident of the future for this type device that he stated in 1932 (*15*):

The utilization of color measurement is in its infancy . . . it seems inevitable that the control of color processes will be eventually taken over by men possessed of an accurate knowledge of the subject of color and equipped with suitable instruments.

During the decade 1935–1945 considerable research was devoted to the industrial development of Hardy's thesis. It is impossible to credit adequately those concerned since much of the significant work was not published, but Pineo and Stearns (American Cyanamid Laboratories), I. H. Godlove (General Aniline), Simon (Sidney Blumenthal), O'Neill (Pacific Mills), Hanlon (Mohawk Carpet Mills), and Ingle (Monsanto) come immediately to mind. In addition to their industrial experiments, basic studies were in progress at the National Bureau of Standards by Judd and Keegan, at the Department of Agriculture by Nickerson, and by Hardy and his outstanding staff at the MIT Color Measurement Laboratory. This latter group provided the nucleus for many contributors to the early efforts in this field. The classic "Handbook of Colorimetry" prepared under their direction was first published in 1936. Its concise, clear presentation of the essential facts has maintained the importance of this publication for over 30 years (4th printing, 1966).

Despite this substantial effort, which undoubtedly provided a better basic understanding of our problems, as late as 1954 the author could state (*12*):

Within the last ten years, progress has been made in instrumentation and techniques which should encourage the wide use of instrumental color control of textiles. That the practical realization of such programs is not widespread is evidenced by the fact that, to the author's knowledge, no more than ten spectrophotometers are actively engaged in such work in the United States. This is partly due to the high cost of the instrumentation and partly to the general feeling that such methods are complicated and of dubious practical value.

While reflectance or transmittance could be measured with considerable precision in a few minutes using the Hardy instrument, the resultant curve, plotting R (or T) as a function of wavelength was not interpreted readily in terms of visual results, particularly for small color differences. To relate two reflectance curves to the visual difference, one had to resort to the psychophysical theory of color measurement formalized by the CIE in 1931. This procedure has been well documented (*14*). Unfortunately, a fairly complicated integration is required. Although a few instruments were provided with mechanical or electrical integrators—the early MIT instrument had a prototype of a modern digital readout—most work had to be done by hand using a desk calculator. The results were slow, tedious, and often inaccurate. They were not suited to the routine use of statistical analysis since one rarely could afford two integrations. Thus, when Davidson and Imm produced their mechanical integrator in 1949 based on the Librascope "ball and disc" integrator, the way was open for much more widespread use of colorimetry as opposed to spectrophotometry. Note should be made here of R. S. Hunter's early work in carrying out the integration by carefully

matching filter transmissions and photocell sensitivities. This early work provided the basis for all modern filter colorimeters.

In our laboratory, upon acquiring a Librascope, we became aware of the greater precision associated with continuous integration. In addition, multiple measurements within and between samples became commonplace. The application of simple statistical techniques to the data paid great dividends. In my opinion, we have not advanced greatly in the last 20 years over the basic instrumentation and techniques at our command in the late 1940's. The major gain has been in the area of more rapid data acquisition and the use of digital readout devices, which enable us to evaluate rapidly virtually any functional relation between the variables involved by high speed computers. These are conveniences and, in many cases, economic necessities, but they do not solve basic problems.

The major problems associated with textile color are:

(1) Color Formulation. The production of a formulation of colorants having the desired physical and chemical properties, which in addition produces the desired color (or shade) on the consumers' textile material.

(2) Color Control. Once the customer has accepted the above formulation and production is started, it is necessary to control the process variables to maintain and deliver the desired color.

(3) Color Tolerances. Inherent in the decision as to whether the process is in or out of control is the necessity for establishing tolerances.

(4) Standards. In many instances it is desirable to maintain "standard colors—*e.g.*, colors of military uniforms, insignia and flags, and historic emblems. Since physical samples may fade or change color with time, a method of specifying the color without retaining a sample is desirable.

(5) Color Faults and Their Evaluation. If, for any reason, a problem arises in producing the desired shade, formulation, fastness, etc., spectrophotometry and colorimetry (particularly the former) are useful tools in solving the problem.

We shall consider each of these problems in turn, confining most of our remarks to the problem of formulation.

Color Formulation

In the textile industry, color formulation generally implies "color matching." The color of an object poses no great difficulty to the average observer [for simplicity, we will restrict our discussion to object color (5, 17)]. Man's visual sense has developed to such a degree that color as an element of appearance is determined readily with considerable discrimination. As with many other phenomena in nature, a detailed quantitative comprehension of the entire process is not easily gained.

The study of atomic and molecular structure is a well known example of this type problem. Complex organic molecules contort, react, interchange atoms, etc., with little concern for those versed in the intricate mathematics of quantum mechanims to follow and explain their behavior; so it is with color and the eye.

Simply stated, color matching implies

$$\text{Color A} = \text{Color B} \qquad (1)$$

The difficulty arises with the meaning of equals ($=$). It seems that what is implied is that the sensation of color is equal, or that

$$\text{Color Sensation A} = \text{Color Sensation B}$$

[In general, the statement should be Appearance A $=$ Appearance B where terms such as size, shape, location, texture, and gloss are considered. For this paper we will consider only the color aspect.]

The problem in color matching is: given Color A (Sensation A), how are the available variables adjusted to reproduce this visual response—on fabric, plastic, paper, or leather, for example. This is a very complicated problem for which no universally accepted solution can be given. Studies carried out over the last 200 years resulted in an important advance—i.e., three suitably chosen variables are necessary generally to describe a color.

Recent important studies by Evans (13) on the variables of perceived color indicate that three variables may not be sufficient to describe color in the natural view—i.e., surrounded by other colors.

It is not essential to our arguments that we commit ourselves as to the number of variables involved since the conclusions will be the same regardless of the choice of variables.

If for the sake of argument and simplicity we confine ourselves to the three variables—hue, saturation, and brightness (5)—a color may be related to the eye, brain, and related response systems.

$$\text{Color A} = (H, S, B)_a \qquad (2)$$

This resultant visual sensation may, in turn, be related to many variables in the observer's environment or within his responsive system. Thus, the three variables may be related as follows (5):

$$(H, S, B) = f (E, R, r, g, b, M, S, A, O, T \ldots . u, v, w) \qquad (3)$$

Where the product of E and R represent the spectral composition of the light striking the eye, r, g, b the particular observer's spectral sensitivity, M his memory, (S) the nature of the surrounding, A a state of adaptation of the observer, (O) the nature of surrounding objects, (T), the observer's attitute and u, v, w, other unspecified variables. Thus, the

color matcher's problem is to manipulate the variables at hand (dyes, concentrations, finishes, etc.) so that

$$\text{Color A} = (H, S, B)_A = \text{Color B} = (H, S, B)_A \qquad (4)$$

Substituting the functional Equation 3 into this equality, one obtains a reasonably concise statement of the problem. Thus,

$$f(E, R, r, g, b, M, S, O, T \ldots u, v, w)_a \quad \text{must equal}$$

$$f(E, R, r, g, b, M, S, O, T \ldots u, v, w)_b$$

Since the color matcher is restricted in the number of variables he can control or manipulate, his dilemma under many practical situations is apparent.

Some basic facts need to be summarized at this point.

(1) Since the color of an object is a visual sensation, it is always related to the eye, brain, and related response systems.

(2) The general functional relationship in terms of the psychological scales, hue, saturation, and brightness is related in a fairly complicated and generally unknown way to the measurable variables.

Obviously, color cannot really be measured by any means other than the eye. However, by placing certain restrictions on the functional variables involved, it is possible to relate instrumental measurements to visual experience and, consequently, to obtain many useful results. That such a procedure is possible has been experimentally verified hundreds of thousands of times in the last few decades. How is this simplification carried out?

First, one eliminates all variables in Equation 3 except $E, R, r, g, b,$ either by keeping them constant or by arranging conditions so they are zero. Next, recognize that under these restrictions only the reflectance (R) can affect the comparison of samples A and B by any one observer. Acknowledging this point, (E) and $r, g, b,$ were standardized or defined in 1931. The result was the CIE system of color measurement, described in great detail elsewhere (6, 14).

In this system,

$$\text{Color} = (X, Y, Z) = \int (E_{std} R, x, y, z) \qquad (5)$$

or, keeping E_{std} and $x, y, z,$ constant, we have:

$$\text{Color} = F(R) \qquad (6)$$

Under the assumptions and restrictions imposed, we now have:

$$\text{Color A} = (X, Y, Z)_a = \text{Color B} = (X, Y, Z)_b \qquad (7)$$

as the basic instrumental color measurement equation.

These results are implicitly related to the eye since

$f(x, y, z)$ (standard observer) = average of $f(r, g, b,)$ for n observers

With these fundamental considerations of instrumental color measurement in mind, we are prepared to consider the color matcher's request, "what dyes do I add and how much of each to match the customer's shade?" Since R (reflectance) is the only variable, for one observer examining the two samples under one light source—e.g., the standard observer in standard illuminant (C), it is clear that if $R_a = R_b$ then Color A will equal Color B (under the restrictions imposed above).

Part of the answer to the matching question then is to add dyes in the proper amount which have the spectral characteristics to produce identical reflectance for the standard and the match. One method of doing this (probably the only method guaranteeing success) has been detailed by Saltzman (26) as color matching by colorant identification. Often it is possible to obtain closely similar reflectances without resorting to identical colorants. The elegance of this approach is that the match will be independent of observer and illumination conditions provided the restrictions above are complied with.

How does one know that $R_a = R_b$? One determines $R_a = R_b$ by measuring the two samples on a spectrophotometer. Such a procedure may not be completely satisfactory since R in the preceding equations refers to the observer's illuminating and viewing conditions. These may be far different from those used in any particular instrument. The problems inherent in measuring R reliably have been treated in detail elsewhere (3, 16); hence, we shall not discuss them further here.

In using a spectrophotometer to measure the reflectance difference between two samples, it is usually hoped that since both samples were measured on the same instrument, the results will at least be comparative and proportional to the visual results. If there is any appreciable difference in texture between A and B, the experience is apt to be poor.

To proceed with the practical possibilities, let us assume that instrumentation is available that permits a reliable measure of R (actually, modern instruments produce satisfactory results in most cases if proper care is taken in sample preparation and presentation). A reliable reflectance measurement is defined as one which, when substituted in our functional relation for object color, produces results in agreement with the average observer under standard viewing conditions. A common method used by visual color matchers that approximates the use of a spectrophotometer is to examine the two samples under as many light sources as possible (north light, artificial daylight, tungsten light, fluorescent light, "overhand," etc.). If the samples match under all these conditions, the chances of the reflectances being significantly different are remote.

Often, owing to technical requirements other than color (*e.g.*, chemical stability, and cost), colorants must be used which cannot result in $R_a = R_b$. Under these circumstances, life becomes more difficult, but not impossible. Since the color, as seen by the observer, is an integrated result of the interaction of the light sources, reflectance and observer sensitivity (in the simple case), there are many combinations which fulfill the basic equation.

$$(X, Y, Z)_A = (X, Y, Z)_B \qquad (8)$$

An example taken from practice is shown in Figure 1. This represents a compromise on the part of the color matcher necessitated by the fact that the available dyes for fiber B cannot possibly duplicate R_a. In general, these combinations are apt to be quite sensitive to the nature of the light source and to the observer. Such matches are called metameric or perhaps preferably conditional. They are a general source of complaints by customers regarding the quality of the match. The basic requirements for object color matches under the simplified color measurement conditions are summarized in Table I.
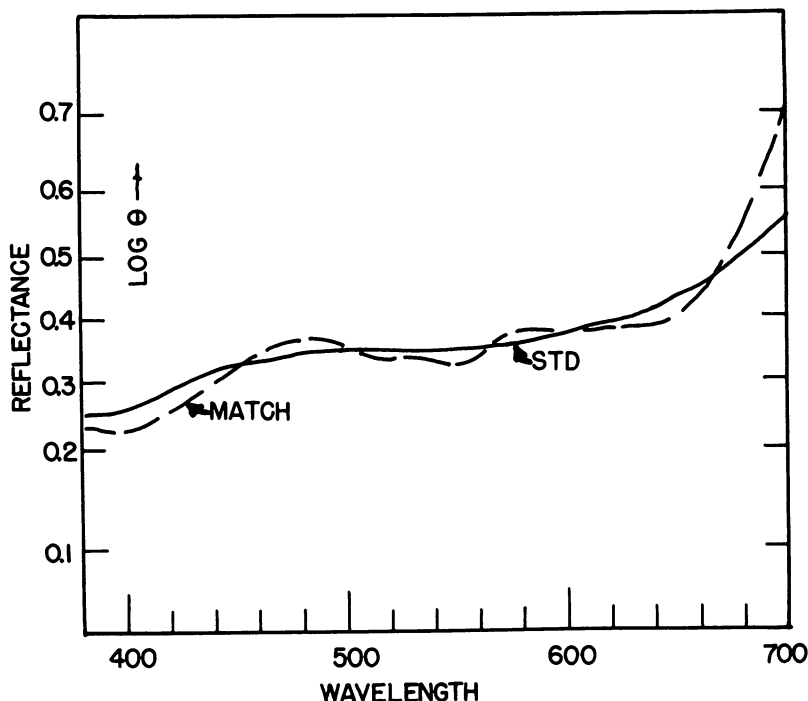

Figure 1.   A commercial metameric match prepared by visual color matching. Available colorants cannot match standard reflectance curve

Table I. Summary of Basic Color Matching Relations

(1) Color A = Color B when,

$$\int (E, R, r, g, b)_a = \int (E, R, r, g, b)$$

or, for instrumental color measurement purposes when,

$$(2)\ (X, Y, Z)_a = (X, Y, Z)_b\quad \text{or,}$$

$$\int (E_{std}.\ R, \bar{x}, \bar{y}, \bar{z})_a = \int (E_{std}.\ R, \bar{x}, \bar{y}, \bar{z})_b$$

(3) A special case occurs when
$R_a = R_b$ (throughout the spectral range of visual sensitivity)
This match is independent of observer and illuminant.

(4) Generally, if

$$X_a = \int_{400\ nm}^{700\ nm} E_{std}.\ R_a\ \bar{x}\ d\lambda = \int_{400\ nm}^{700\ nm} E_{std}.\ R_b\ \bar{x}\ d\lambda = X_b$$

(similar expressions for Y, Z)

then, Color A = Color B under illuminant E_{std}, and to the observer x, y, z these may not correspond to any available light source or observer. This is a metameric or conditional match.

   With hundreds of dyes at his disposal, how does the textile color matcher select the particular dyes and concentrations to satisfy the functional relations in Table I? Although extremely important technically, we shall not concern ourselves here with the methods of evaluating dyes for chemical and physical properties or fiber affinities. It is assumed that a range (20–30 dyes) is available displaying the requisite properties of chemical stability, cost, and ease of application. This assumption may be difficult to justify for a new synthetic fiber—e.g., polypropylene. Since little or no progress can be made unless we accept the availability of a suitable range of colorants, we will make this assumption. The question remains—how do we determine the quantity of the selected dyes necessary to obtain the desired values of R at different wavelengths?

   This becomes complicated since the reflectance of a textile material, owing to scattering and surface reflection, is not a simple function of the molecular absorption characteristics of the applied dyes. In addition, the fiber has its own characteristic absorptions.

   Much research during the last 50 years has produced a number of analytical and empirical relations of the form

$$C = f\ (R) \text{ or conversely} \tag{9}$$

$$R = F(C) \tag{10}$$

It is not sufficient merely to find a relationship that satisfies Equation 9. To be useful, it must be an additive function for each dye and substrate over the concentration range of interest, thus

$$f(R)_{total} = f(R)_{dye\,1} + f(R)_{dye\,2} + f(R)_f + \ldots \ldots \tag{11}$$

This important point was made by Parks and Stearns in a paper published in 1943 detailing the principles of instrumental color matching (*23*).

Illustrating such a function is the simple relationship that exists for solutions which follow Beer's Law, where the additive function relating concentration is

$$A = \log \frac{1}{T} = KC \tag{12}$$

Thus, for three dyes, one has the simple expression

$$A_{total} = A_1 + A_2 + A_3 \tag{13}$$

The mathematical details, assumptions, and boundary value solutions for the reflectance of turbid media have been extensively reviewed elsewhere (*17, 18, 19*).

With respect to colorant formulation on textiles, it is my opinion that sufficiently precise relationships are available to suit most needs, and little gain would be obtained in refining the present functional relations further, and generally increasing their complexity. This observation is not intended to discourage research work in this area for it is always better to understand the underlying reasons for physical observations.

It has been shown by several methods (*2, 18, 22*) that the function

$$\theta = \frac{(1-R)^2}{2R} = KC \tag{14}$$

is a useful additive function for textile color formulation. This expression is equivalent to the Kubelka-Munk analysis for the reflection of turbid media having zero transmission. In their two constant theory, $\theta = K/S$ where K is an absorption coefficient and S is a scattering coefficient. Pineo (*25*) derived an identical expression independently without the necessary restrictions placed on the Kubelka-Munk analysis. For low values of R the surface reflection of the material R_s should be subtracted before applying Equation 14. R_s is generally less than 1%. In most textile applications K/S is taken as a ratio, with absolute values for either constant unknown, hence is more conveniently designated θ.

Since $\theta = KC$, this is an additive function, and we have

$$\theta_T = \theta_f + \theta_{D1} + \theta_{D2} + \theta_{D3} \tag{15}$$

for a three-dye (D_1, D_2, D_3) system plus substrate (θ_f).

Since Equation 14 relates concentration to reflectance, the condition $R_A = R_B$ will be satisfied if $\theta_A = \theta_B$.

In stating that $R_A = R_B$ we are referring to the complete visible spectrum (approximately 400–700 nm). Thus, when we indicate a match is obtained for $\theta_A = \theta_B$, the same range is indicated.

The "matching equations" in terms of dye concentrations, are then

$$\theta_A = \theta_B = C_1\,\theta_{D1}' + C_2\theta_{D2}' + C_3\,\theta_{D3}' \qquad (16)$$

where θ_{D1}' is the value of $(1 - R)^2/2R$ for a known concentration of Dye$_{D1}$.

Colorants must be found whose spectral absorption characteristics are such that concentrations can be found to satisfy Equation 16 at all wavelengths. It is obvious that without a high speed computer or some special technique such a solution would be difficult to find. Some hint as to the solution may be obtained by noting that to match a blue we should not choose a brown dye: thus, by this logical procedure, the number of random trials can be reduced drastically.

An ingenious method of solving Equation 16 was patented in 1938 by Pineo (American Cyanamid Co.). It involves devising a system wherein a spectrophotometer plots the function $\log \theta$ as an ordinate instead of reflectance. By this method, curves as a function of wavelength are produced, whose shape (ratio of absorption to scattering as a function of wavelength) is independent of concentration. Changes in concentration merely displace the curves vertically as shown in Figure 2. For a solution to the matching equation at all wavelengths to be possible, it is necessary that some vertical displacement of the curves for individual dyes ($\log \theta_{dye\,1}$, etc.) permit superposition on the $\log \theta_a$ curve. If this appears possible, the concentrations may be obtained by solving three simultaneous equations or by the nomographical method developed by Stearns (27).

Figure 3 shows this procedure for a simple three-dye combination. The procedure has been discussed in considerable detail by Derby (10). While this method has existed for some time, it still has considerable utility in solving problems involving textile colorants.

For the last 20 years nearly all reflectance curves recorded in our laboratories have been drawn with $\log \theta$ as the ordinate. The utility of this type of presentation arises from its speed (55 sec), flexibility, and simplicity of interpretation. Simple formulations, containing two to three dyes, with clearly separated absorption maxima can be prepared in a few minutes. More complicated ones, using five or six colors with badly overlapping absorption bands, take somewhat longer.

Colorants are selected readily by inspection since the curve shape is constant regardless of concentration (as long as $\theta = KC$). In most
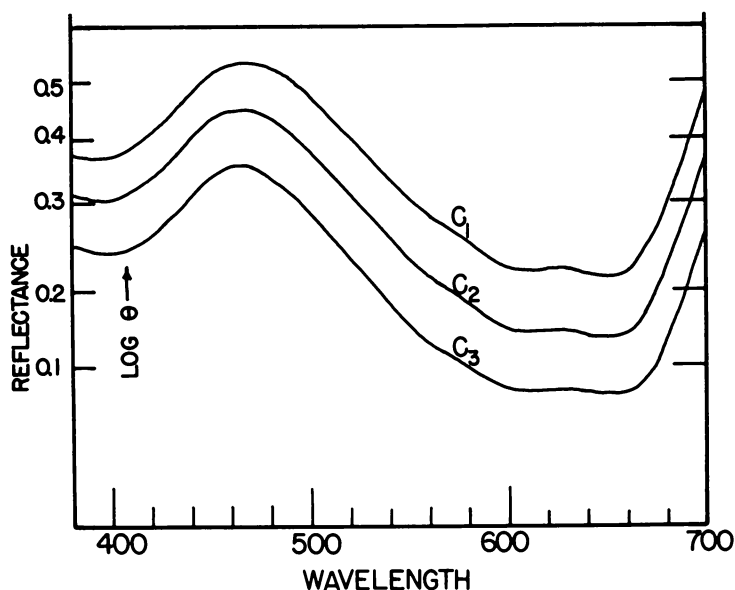
Figure 2. Log $\theta = \log (1 - R)^2/2R$. Plot vs. wavelength (nanometers) showing constancy of curve shape at different concentrations C_1, C_3, C_2

instances, colorants for other methods of computation are selected by this method in our laboratory. The curve shape will also be independent of concentration for several other additive functions of the form $\theta = KC^n$.

A number of "improved" forms of the basic θ function can be put into such form; consequently even if the system does not obey the simple Kubelka-Munk equation, equally useful results are obtained. Under these conditions, a correction factor equal to n must be applied to the vertical displacement to obtain the true concentration differences.

The details of other methods (*1, 4, 8*) for solving the required equations will not be considered here, but any physical quantity proportional to θ can be used to obtain solution. This may be distance, as in the graphical solutions above, or voltage, as in electrical solutions. Since methods are widely available for accurately controlling and proportioning voltages, the electrical approach is appealing. The electrical analog approach has been developed extensively by Davidson in experiments with analog simultaneous equation solving starting in the early 1950's. These experiments culminated in the commercial production of an ingenious device called COMIC (COlorant MIxture Computer) which permits the solution of 16 simultaneous equations to be observed on an oscilloscope (*8*). While this device is being superseded to some extent by digital computers, some of its features are novel and worthy of mention.
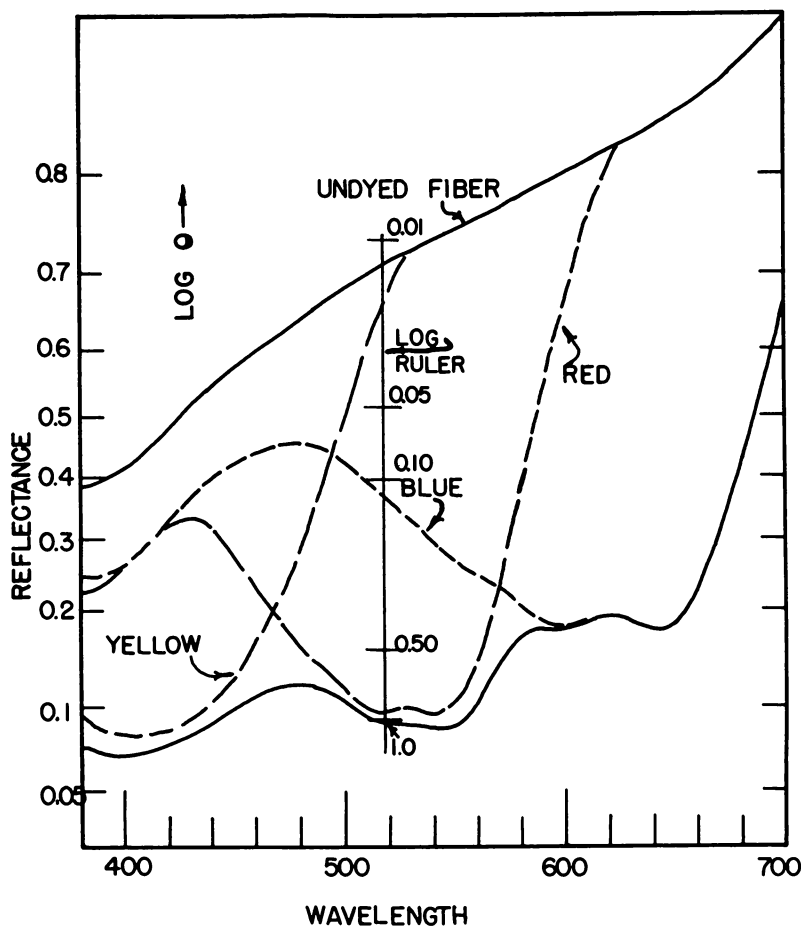
Figure 3. The Pineo method of colorant formulation. Since $\theta = (1 - R)^2/2R$ is an additive function, the combination of yellow, red, and blue necessary to match the standard (solid line) is readily determined. The relative concentrations of each dye are read directly from the transparent logarithmic nomographic scale. In principle, this is the same method used in the D & H COMIC and in digital computer methods where the solution $R_A = R_B$ non-metameric match is desired.

The 16 points displayed are redundant by 11. All that is needed to solve for the concentrations of five colorants are five simultaneous equations with θ_T of V_T at five selected wavelengths. The redundance is necessary to determine whether the correct colorants have been selected by checking the solution at the other 11 points.

The oscilloscope display permits the simple determination of the almost unheard of concept (before high-speed computers)—namely, the best possible solution to 16 simultaneous equations when there is no exact

solution. By using auxiliary equipment this "solution" can be made the best possible in a colorimetric sense.

At this point, if all of the assumptions are correct and sufficient precision is maintained throughout, we will have answered the question, "what dyes and how much"? The techniques discussed above and other similar methods permit the entire process (including measurement) to be carried out in 15–20 minutes. At this point we have a trial formulation, not a match on the material at hand.

Until now we have developed a solution only for the special case where $R_a = R_b$ (or only slightly disagrees). If such a solution is impossible because of other requirements such as fastness, price, dyeing process, etc., we must produce a metameric or conditional match. In this case the values of R_b must be adjusted by varying dye concentration and selection so that equality exists for a set of at least six integrals of the form (for X).

$$\int_{400\ nm}^{700\ nm} E_c R_a \bar{x} d \lambda = \int_{400\ nm}^{700\ nm} E_c R_b \bar{x} d \lambda$$

Similar equations exist for the tristimulus values Y and Z. If more than one illuminant is of interest, six integrals will be required for each light source.

The reason for the importance of the solution $R_a = R_b$ should be apparent. Since in practice we never really know the value of E or the observer's spectral sensitivity, the only simple general solution possible is where $R_a = R_b$.

Assuming a standard light source and a standard observer, it is possible by various methods to express the difference in tristimulus values ΔX, ΔY, ΔZ in terms of ΔR (8, 23). The fairly complicated mathematical operation of reducing ΔX, ΔY, ΔZ to a sufficiently small number by varying ΔR through the functional relation $\theta = f(R) = KC$, can be carried out by modern analog or digital computers by iteration methods. An elegant exposition of the mathematics involved in these methods has been given by Allen (1). Several computer programs have been developed along these lines.

By combining the various approaches outlined above, it is possible, within a few minutes after obtaining the spectral reflectance data on a sample, to obtain a formulation which mathematically satisfies the equations of a simple color match, as outlined in Table I.

Almost any variety of modifications to the basic procedure can be introduced into this system. ΔX, ΔY, ΔZ can be calculated in a few illuminants, a "metameric index" (17) obtained, and the formulation

altered to obtain the optimum value. A minimum cost formula can also be calculated. Fastness properties, compatibility with the system, affinity, etc. can also be built into the combined computer and information retrieval system. The complexity of the calculations for four or more dyes transcends simple comprehension, but apparently it is within the capability of modern high speed computers.

In favorable cases, the results using any of these methods are straightforward. First trials of computed formulations produce matches within at least three or four color difference units of the standard.

What are the limitations that prevent, at this time, 100% instrumental match formulation using the simple methods outlined above? Unfortunately, they are fairly numerous and constitute a difficult, if not, insurmountable barrier to realizing the goal of color matching solely by reference to instrumental measurements and computation. Some common causes of difficulty are outlined below.

Failure to obtain a reliable measure of reflectance is one difficulty. It is caused by lack of correspondence of instrument geometry, with visual viewing conditions, lack of sensitivity or accuracy of instrument, and nature of sample with respect to size or texture. Another problem
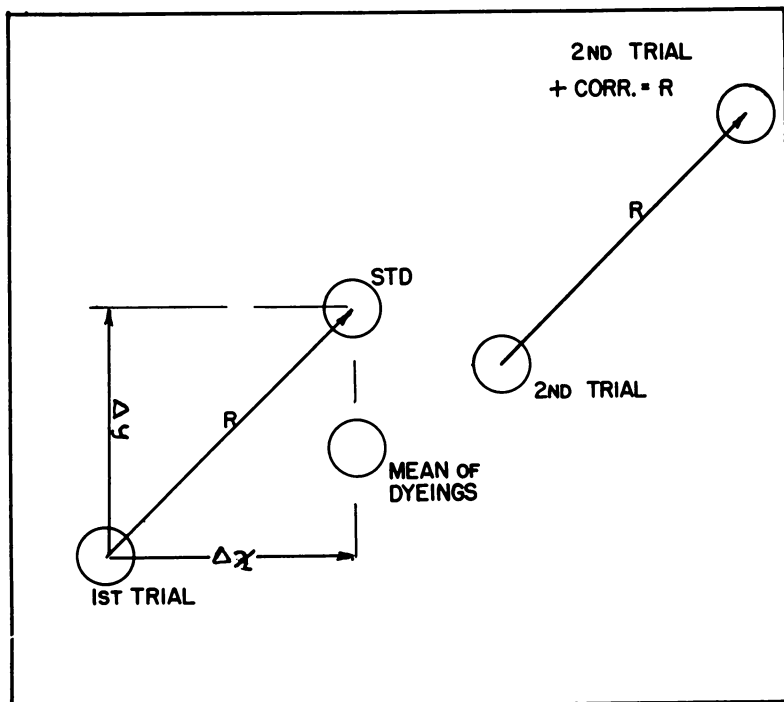

Figure 4.   Effect of reproducibility of dyeing and measurement process on predicted match

is the failure of (ΔX, ΔY, ΔZ) equal to zero by computation to be equal to zero visually. This is related to the reflectance problem, to metamerism, and to a number of less common problems.

Variation in the dyeing process causes other problems. For a number of reasons, such as concentration errors, fiber variation, and control of the dyebath pH and temperature duplicate dyeings often vary by an amount which exceeds the matching tolerance. This leads to the problems illustrated in Figures 4, 5, 6. When the first trial formulation is dyed, it usually does not match the standard; therefore, a correction must be applied. Since the measured ΔX, ΔY, ΔZ is not the true value owing to the variability of the process, the correction, no matter how mathematically precise, will only produce a match by chance. The probabilities associated with this chance are readily determined once the variances are known.
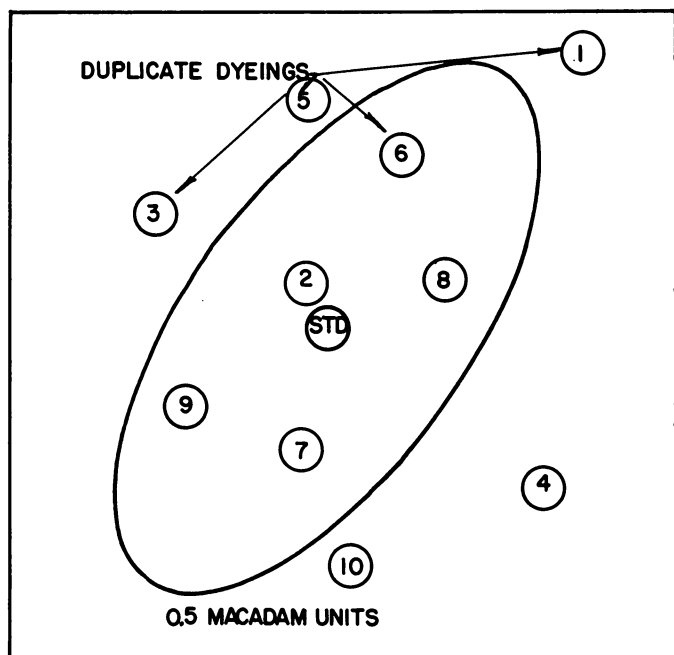
Figure 5.   Variation in dyeings. Dyeings 1–10 were made simultaneously using the standard formula under carefully controlled conditions.

In addition to the variation of the dyeing process one must consider the variance of the measuring process. Depending on the nature of the sample and the precision of the instrument, this may be smaller or larger than the dyeing variation. On a good instrument with a simple homogeneous sample, this variance can be expected to be about 10% of the
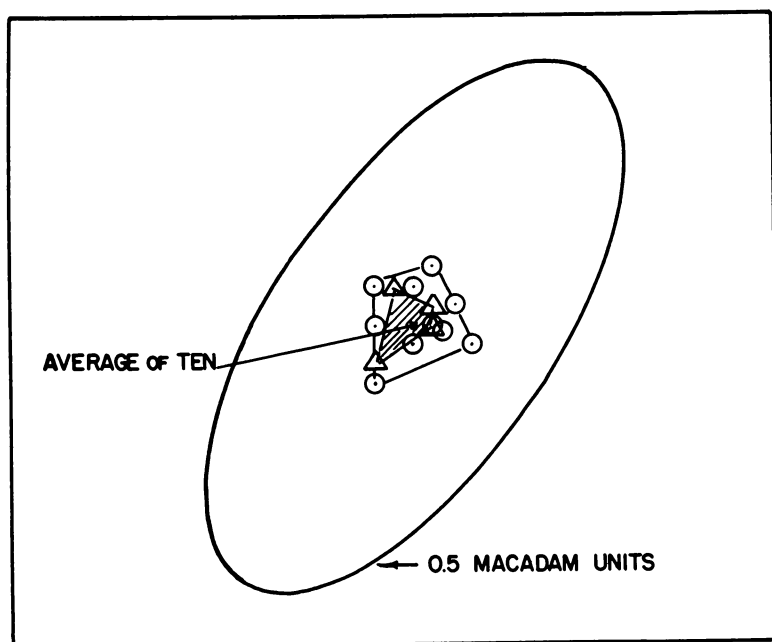
*Figure 6. Variation in repeat measurements on same sample removed
and remounted. Comparison of single with means of two measurements.*

○ = *Single measurement*
△ = *Mean of two*

variance associated with the dyeing process. Some interesting observations on these matters have been made recently by Marshall and Tough (22). The importance of statistical considerations in all aspects of instrumental color measurement cannot be overemphasized. Figure 6 shows the variation in repeat measurements on a piece of wool flannel. The improvement in variation from the mean, obtained by the simple expedient of comparing the averages of two readings is clearly demonstrated and is close to the theoretical improvement.

In actual practice it is rarely worth making more than four readings on the same sample. The gain in precision is not sufficient to justify the extra time involved. Attempts to produce matches within a smaller tolerance than the sum of the variances is not logical from a statistical viewpoint; however, it is necessary in practice. The color matcher must, by some means, obtain a match that suits the customer no matter how small his tolerance; therefore, he must know that such a match can actually be attained. Experience indicates that a certain formulation may produce a near, but unacceptable, match, but it is not possible to correct the formulation further to attain a better match.

Metamerism is the greatest single cause of disagreement between customer and supplier, regarding the quality of the match. The difficulty a visual color matcher encounters in attempting to produce a metameric match that satisfies the customer (whose spectral sensitivity function is unknown) in several light sources is evident by considering Equation 5.

Figure 7 shows the results of a color matchers' attempt to produce a metameric match as compared with the non-metameric match of the same color. The difficulty with the metameric match is that he is attempting to compromise several illuminants—not just the illuminant C illustrated. In fact, he is not even matching in standard illuminant C, but rather in an artificial daylight lamp (MacBeth), whose spectral energy distribution differs considerably from illuminant C. This is not a factor in the non-metameric case, but it may be critical for the metameric match. Instrumental color matching in the metameric case will produce more consistent results since the instruments experience no such conflict of goals. However, comparison between the instrumental match and a visual match will frequently be poor.
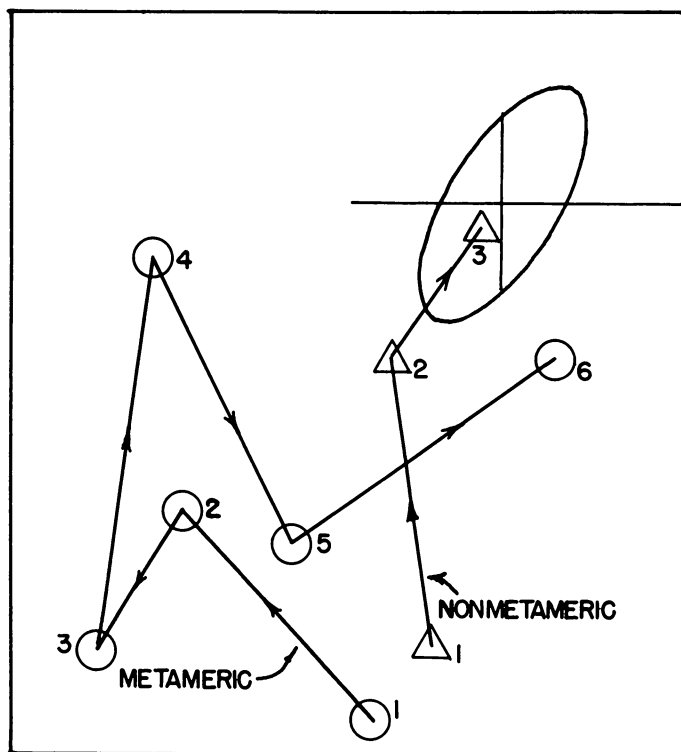

Figure 7. Comparison of metameric and non-metameric matching with respect to trials and difficulty of attaining match. Ellipse represents "target" match.

The preceding argument is not to be construed as indicating that metamerism should be avoided at all costs; however, it is a major source of rejected material and customer complaints. One should be fully aware of the dangers involved when deliberately producing such matches. It is often noted in the literature that the easiest method to ensure non-metameric matches is to formulate with the same dyes or colorants as in the standard. If more than three dyes are used in the formulation, no insurance against metamerism is provided by this method. It can only be stated that under these conditions, it is possible to produce a non-metameric match. It is also possible to produce a large number of metameric ones. This possibility increases rapidly with the number of colors involved.

Samples which are difficult or impossible to measure are another source of difficulty. Intimate blends containing many colored fibers produce interesting style effects, but matching such a mixture, where the spectral and colorimetric nature of the components is unknown, is extremely difficult. Usually, one has to resort to "microscope matching." Very small samples—portions of prints, mixed yarns, or very small colored areas within a larger sample—are difficult to measure with reliability.

Both instrumental and visual matching of fluorescent materials can be difficult since in this case R is a generally unknown function of E. Thus, it is not possible to measure reflectance under one light source and calculate the results for another, as in the simple color measurement equations where E and R are independent variables. Hence, one cannot expect the precision we have come to expect of non-fluorescent colorimetry. A new variable is introduced, and we have the possibility of a fluorescent metamerism where two samples match under a source which has little effect on R but do not match under a more active source.

Many fabrics contain two, three, or more different fibers. Each of these may be dyed with several different dyes. The ideal circumstance would exist if each set dyed only one fiber or one set dyed them all. Unfortunately, this is rarely the case, and each fiber displays its own relative affinity. This affinity depends on many things and is not independent of the quantity and type of other fibers present. Many practical cases become unbelievably complicated, and again one must resort to the microscope.

Visual effects outside the limits of the simple color measurement equations cause additional difficulties. These problems will not be discussed in detail, but common examples may be found in textile color and design of virtually every color phenomenon or illusion (5, 17). Some of the more common are: simultaneous contrast, spreading effects, area effects, surround and diffuse edge effects. These are all cases where

although $(X, Y, Z)_A$ may be equal to $(X, Y, Z)_B$, the samples or areas do not match.

To produce the desired match (or mismatch), it is necessary to produce an ΔX, ΔY, ΔZ different from zero. Unfortunately, the functional relations are not generally available which would permit instrumental formulation of the proper difference to produce the desired color effect.

Present Capabilities. The functional relations and instrumentation are sufficiently developed at present to enable rapid calculation of formulations from basic data where one is given either reflectance or colorimetric data on the material to be matched. Thousands of calculations of this type have been made during the last 20 years, which indicate the validity of the underlying assumptions. The formulations produced by these methods can be expected to produce initial matches within a few color-difference units of the standard in many instances. For the variety of reasons, detailed above, but mainly because of variances inherent in the measurements and the basic data, it is unlikely that much greater precision can be expected. In addition, certain fundamental errors are involved in relating instrumental color measurements to visual results. In the future, one can expect further gains in data acquisition, presentation, and convenience. The complexity of any calculation will provide no deterrent to its usage. The facts and basic data on various colorants will be stored in an easily retrievable state. Thus, the colorist of the future will have available improved instrumentation and computational techniques based on the principles already proved. These will enable him to produce the proper color match more readily and intelligently. It appears, however, that the final arbiter will always be the color sensation produced in the eye and brain of the customer.

In considering the complexity of color-matching, it is not considered likely in the foreseeable future that the entire problem will be handled instrumentally. Rather, the color matcher will be trained in the use of spectrophotometry, colorimetry, and computer methods. These aids will relieve him of much of the routine, sample-matching tasks and enable him to cope more intelligently with the complex. To this extent, it would appear we are on the verge of realizing the vision of the future expressed by Hardy nearly 40 years ago.

Color Control

If color can be measured or quantified, its control becomes a matter of applying the already well-developed methods of statistical quality control. Some sort of a control chart or color map (similar to that shown in Figure 8) is usually employed. A number of ingenious and convenient plotting methods have been devised. Hundreds of thousands of instru-
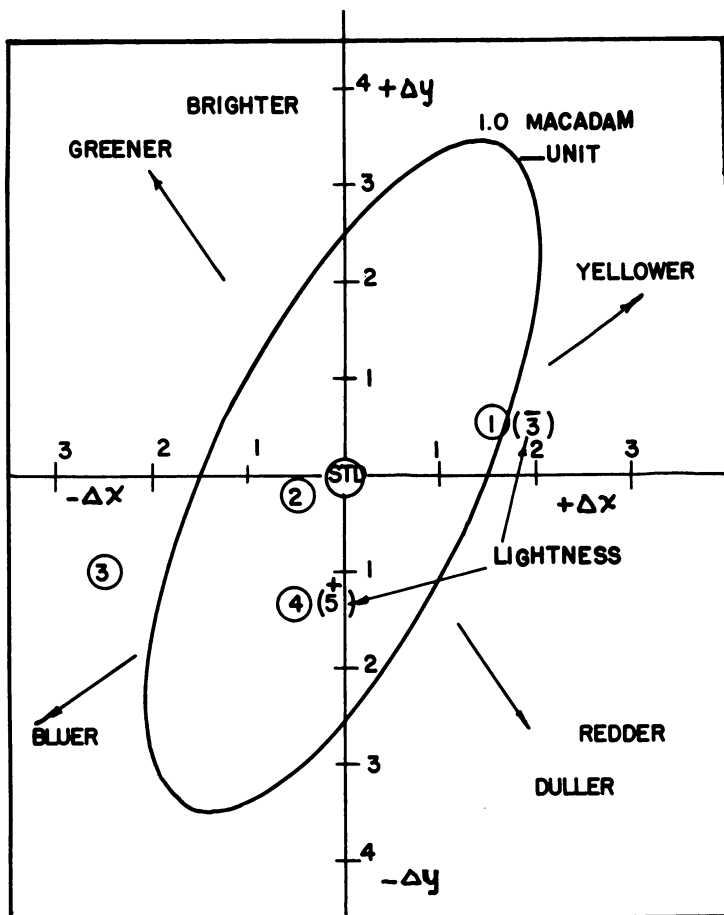
Figure 8. Color quality control chart of the four production samples shown. No. 3 is unacceptable for chromaticity (outside ellipse), No. 4 for lightness (+5 in parenthesis), and No. 1 is borderline. The units are Δx, Δy, ΔY × 1000.

mental color measurements are made each year for this purpose. Their success provides some confidence in the theory of color measurement.

The ability to record, transmit, and statistically evaluate the control data is a major advantage of instrumental methods over visual methods. The limitations on instrumental color control are inherent in the theory of. color measurements as discussed earlier. A further complication is difficulty of obtaining meaningful instrumental results on many colored materials of commercial importance.

The future in this area is well defined. One can expect a steady advance in the ease of data acquisition, storage, and display. An increased awareness of the power of statistical methods coupled with the ease of computation will prove rewarding.

Color Tolerances

The problems in this area are not unique to textiles. Fundamentally, the difficulty lies in that there is no universally satisfactory method of specifying, by a single number, the difference in color between two samples. Some equations have been proposed (4) to combine variations in the three dimensions of color to produce a single number which hopefully is proportional to the perceived difference. For small color differences (five units or less) these methods work reasonably well. Our experience indicates that calculations based on MacAdam's data (20) or the Adams-Nickerson Equation (17) are suitable for expressing small color differences. Based on extensive use of MacAdam's data for the last 20 years, we feel that it provides a reliable guide to the relative importance of chromaticity differences. The major problem seems to arise when one attempts to incorporate the lightness term. No simple constant ratio between the lightness difference and the chromaticity seems to produce generally saisfactory results.

The success of the "Grey Scale" method of evaluating color differences would seem to indicate the feasibility of equating a lightness difference to a chromaticity difference. Based on visual experience and examining the data on thousands of samples, it is our feeling that there exists a fundamental problem in that the relation is not constant. Again, for small differences (the smaller the better) this is not a major problem, and consistent results are obtained. Believing that chromaticity differences (ΔC) and lightness differences (ΔL) are fundamentally visually distinct, it is our practice to record these differences separately as well as combined in a "total" color difference (ΔE).

Owing to the fact that the numerical results are not adequately normalized—*i.e.*, the same value of color difference in the yellow and blue regions does not appear visually equal—it is difficult to generalize with respect to tolerances. The following represents an approximate guide based on examining thousands of results in our laboratory:

Close tolerance chromaticity: 0.5–1.0 MacAdam's units lightness 5%

Commercial tolerance chromaticity: 2.0 MacAdam's units lightness 10%

One of the most sensitive areas of color discrimination occurs when the eye is adapted to the color being judged. In practice this occurs when examining large areas of cloth for area shade variations. Such differences produce a condition referred to as "shady," "cloudy," or "streaky" material. Some years ago we demonstrated an excellent correlation between the judgment of inspectors at the mill level and color difference measurements on samples of this type (11). This work was based on the Adams-Nickerson color difference equation, but owing to the small size of the differences, other equations will undoubtedly give satisfactory results.

The tolerances found were (using $f = 100$ in the equation):

ΔE less than 1.0 (blues 0.80) acceptable
ΔE greater than 1.0 less than 2.0 slightly shaded
ΔE greater than 2.0 badly shaded

Another difficulty with color-tolerance specification is that they may not represent a uniform relation to perception differences. Thus, because of preference, knowledge of the end use, etc., certain directions in color space may be tolerated to a greater extent than one would predict, based on perception data. For example, it is almost certain that the green tolerance in the case of meat, borders on the limits of perceptibility, whereas almost any saturation or lightness variation would be tolerated.

When used with care and knowledge, the reduction of colorimetric data to a single number "color difference" can be most useful. However, indiscriminate application of these methods will eventually produce results which are not consistent with visual examination. The ease of evaluating these rather complex equations with modern computers will have a tendency to amplify this problem.

The only important advance to be realized in this area would be improved color-difference equations. Owing to the complexities involved (primarily the weighing between lightness and chromaticity differences) only slow progress, if any, can be expected. In the meantime, considerable utility can be obtained by discrete use of the existing equations, particularly those based on MacAdam's work (21).

Standards

Maintaining standards without recourse to physical samples has always been of interest. If one wishes to specify a homogeneous colored textile by colorimetric data, in order that its shade may be reproduced in the future, great care must be taken in the measurements. We believe it is possible to specify a color on such a basis to within about 3 color difference units. However, this requires careful, well calibrated measurements. Using permanent standards as reference points, the samples should be reproducible within two color difference units. Again, the need for special care and reliable measurement is emphasized if these goals are to be attained.

Color Faults and Their Evaluation

In the daily production of large quantities of colored textiles often consisting of several fibers, each dyed with several dyes, faulty results inevitably arise. The colorist must determine the nature and cause of the problem as rapidly as possible. Spectrophotometry is an indispensable

tool in many óf these problems. Colorimetry, on the other hand, is of little value since it adds nothing beyond what the eye can readily see. Space is not available to recount the many problems where spectrophotometric analysis, particularly with the aid of the log θ ordinate plot has been the key to a correct and expeditious solution. It suffices to say that we would be handicapped in our daily work without this instrumentation.

In 1900 Paterson stated: "Theoretical knowledge alone cannot make a successful color mixer, but it certainly proves of great value in explaining the true causes of failure and in directing the conditions which lead to success" (*24*). This statement is as true today as it was then. While our sophistication in colorimetry, spectrophotometry, and color science has increased greatly, so have the problems.

The modern colorist must cope with an ever increasing number of new fibers, new dyes, and new finishes. The number of combinations of shade, fiber, and finish becomes large quite rapidly. New demands on chemical stability or fastness places further restrictions on the available solutions. The increasing search by designers for styling and properties with new market appeal leads to evaluation of every conceivable combination. Without the aid of instrumental color measurement, computer color formulation and computer information retrieval, the task facing the colorist or "color mixer" of the future would be formidable if not impossible. To realize the potential of instrumental methods we need more precise and reliable instrumentation, but more important, we need colorists thoroughly trained in the theory and practice of spectrophotometry, color measurement, and color science as applied to the color of textiles.

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